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Is My Sun Protection Fading Away?

The Impact of Photostability on Beach Goers, SPF Claims and the Environment

J. Vollhardt

abstract

Sunscreens are widely used to protect against damaging effects of sun exposure. Avoiding the pain of sunburn is a key motivator for applying sunscreen, however, these products offer much broader protection because when applied correctly and balanced with informed and managed exposure, they can also protect against skin cancer and minimize skin ageing effects. A product category that has such widespread use needs to be very safe in all foreseeable ways. It also needs to be compatible with the environment, in particular marine flora and fauna as it will often be used in coastal areas such as the beach. Due to the general popularity of sunscreens, concerns of any kind tend to spread rapidly, even if an adversity claim has only been formulated as a potential hazard without proper investigation or evaluation of the likelihood and impact of the risk. Even for scientists, risk evaluations are labor-intensive processes that require a solid scientific education, so unsurprisingly, consumers who cannot make such evaluations on their own, often adopt an avoidance strategy towards potential hazards. In the case of sunscreens though, this increases the risk further, and not just in terms of sunburn, because the skin cancer incidence rate also increases. In view of this, it is of utmost importance to stick to the facts, to perform a risk analysis on hazard claims, and to provide clear information to consumers before they consider avoidance actions which may entail not so obvious downsides.

Another concern that has materialized around sunscreen centers on the fact that some UV filters – or combinations of UV filters – are not photostable and degrade, leading to a loss of performance. It sounds like a contradiction in terms that sun radiation itself could reduce the efficacy of a product designed to protect against such radiation. We have therefore revisited this topic and investigated state of the art formulas to assess how much performance is lost after a full day at the beach or on a sunny winter's day skiing outdoors. We have also looked at the impact of photostability and claim making. What strategy should be followed – especially when creating high protection formulas? Finally, we have considered what photo-stability could mean in terms of the environment.

What is photo-instability?

Molecules that absorb light are transferred into excited states. The energy absorbed can be lost through several mechanisms with different rate constants, ranging from extremely short to minutes and hours. UV light contains considerable energy, enough to potentially trigger bond breakage, configurational molecular changes, and new molecule formations. Generally, there are four possible types of reaction that do not result in the molecule returning to its relaxed ground state and could also destroy the molecule's absorptive properties:

1. Photo-destruction

Compound A → Break down compounds with no UV absorption

Example: Avobenzone, which at a certain yield can enter the long-lived triplet stage, from which bond breakage is possible which then leads to smaller non-absorbent compounds.

2. Photo-isomerization

Compound B1 → Compound B2 (Isomer)

Examples: Octyl methoxycinnamate (OMC) in its excited state has a very much weakened double bond which in turn leads to isomerization forming a larger proportion of the Z-configurated isomer. This reaction is reversible and leads quickly to an equilibrium mixture of E- and Z-isomer. Note that this does not destroy the chromophore, however, the Z-isomer has a lower extinction. Performance thus stabilizes at the equilibrium mix. Additionally, Avobenzone undergoes isomerization from the enol to keto-form. The keto-form only has some UVB absorption properties and no UVA absorption, however, protonation-deprotonation reactions quickly regenerate the enol back, which is why, generally, this process cannot be observed within sunscreens using regular spectroscopic methodology. Nevertheless, working with diluted HPLC samples in solvents requires attention in sunscreen analysis and the samples need to be protected from daylight.

3. Photo-reactions

Compound A + Compound B → Adduct with no UV absorption

Examples: different reactions are possible here. An important type of reaction is the [2+2] cycloaddition, where

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two molecules with a double bond fuse together to form a cyclobutane derivative. That is not very stable in light and reacts further to other products that all show no effective absorption. Molecular partners that are well known for this reaction type are OMC+OMC and Avobenzone + OMC. There is currently no technology to prevent [2+2] cycloaddition. Furthermore, the combination of Diethylamino hydroxybenzoyl hexyl benzoate (DHHB) and Avobenzone is not photostable and leads to the destruction of both compounds [1].

4. Oxidative processes

Oxidative processes can also occur, but they require the presence of oxygen and enabling chromophores for activation, e.g.: by formation of singlet oxygen. Sunscreen chromophores in general should not be good activators at all, because potent activators belong to the category of photo-toxic compounds and would not make it through registration. Nevertheless, with very low quantum yields this process might happen in sunscreen, also triggered by other materials. Therefore, adding small amounts of anti-oxidants to sunscreens is advised.

The "photo-destruction" mechanism plays a pivotal role in sunscreen photostability. This is easy to characterize through laboratory experiments on templates covered with sunscreens as it is a feature of a single compound. HPLC supported methods are also available to quantify loss of material, e.g. [2]. Most concerns centered around this topic therefore arise when discussing sunscreen photostability, particularly in relation to Avobenzone.

The impact of photostability on consumers using sunscreens

To approach this question, it is important to understand what kind of radiation burden consumers are exposed to. This seems to be an easy question and easy to measure with photometric devices. However, collecting the exposure dose human skin receives is rather tricky. Solar light intensity depends on so many factors, e.g.: global location, calendar day, cloud cover, dust particles in the air, time of day, and the angle at which the sun hits the skin's surface [3] and reflective objects like snow or water, adding further burden to direct sun exposure. For these reasons, measuring sun intensity with a fixed device somewhere, or sporadically measuring sun intensity, are not accurate approaches. The dosimeter needs to be worn by a subject all day long. Fortunately, a couple of studies have already dealt with this topic under realistic and intense exposure conditions. Test subjects have been sent on beach holidays in the Canary Islands and Egypt or on skiing holidays in Austria [4,5] wearing such dosimeters. Outdoor workers who are exposed to intensive periods of sunlight in their professional routines have also been followed with wrist dosimeters [6,7]. The total energy of sun light to skin was not the focus in these studies, only the erythemal energy was registered, utilizing the sensitivity function of human skin towards erythema (e.g.: ISO/CIE 17166:2019). That way, dosages could be compared with daylight radiation devices used in laboratories to test sunscreens for photo-stability and the solar simulated radiation (UVA and UVB light 10:1) used to test subjects when measuring and testing Sun Protection Factor (SPF).

The unit of measurement proposed to measure this dosage is the Standard Erythemal Dose (SED) [8,9]. In comparison to the Minimal Erythemal Dose (MED), the SED is not skin type dependent and allows easy and well-defined comparison of light sources towards erythemal action. One SED is set to 100 J/m^2. For example, a skin type 2 person would require between 2.4 and 4 SED to receive an erythema (1 MED). According to a study by Peterson [4], beach goers received about 10 SED daily during their holidays. For a skin type 2 person (the study recruited mainly Danish subjects who are likely to be skin type 2) this is considered to be about 2.5 to 4.2 MED – enough to cause serious sunburn and to make sunscreen use advisable. Skiers also received 7.5 SED daily, just a little more than outdoor workers with a maximum of 6.4 SED. All situations call for sunscreen use to protect against serious erythema. However, in the laboratory it is common practice to challenge sunscreen with much higher doses – not to predict their behavior at the beach, but to estimate whether a desired claim can be achieved. Typically, doses of 25 MED (62.5 SED) or even 40 MED (100 SED) are used. The endpoint of such radiation experiments could lead to concerns, were they to be performed under realistic use conditions. But to what degree do sunscreens deteriorate when radiated "only" with environmental doses, e.g.: 10 SED? Keeping in mind that while this is a typical value for a sunseeker's beach holiday, consumers in Japan, concerned about their complexion, would probably be unlikely to expose themselves to more than 0.1 MED (0.5 SED for a skin type 4 person). To answer this question, we performed radiation experiments with commercial sunscreens and exposed them to various doses (see example in **Figure 1**) up to the 25 MED typical for laboratory challenging. Concentrations of Avobenzone, as a key ingredient of concern, were followed using HPLC. At consumer relevant levels of radiation, it barely decayed and remained stable to 95%, moreover, this represents the value at sunset, after a long beach day. Loss of performance due to photostability therefore poses no concern to consumers due to their relatively low exposure levels compared to artificial challenges in laboratories.

Another concern related to loss of performance is the potential for toxic byproducts to form due to photo-instability. Of course, if a radiation dose is only at environmental exposure levels, a formula's stability remains rather unchallenged and the amount of photo-products is relatively small. Moreover, for registration approval UV filters have to pass through sev-

eral photo-toxicity setups to be used in sunscreens, and there is also a requirement to provide skin related safety data under the radiation conditions in which such products will develop. In the case of Avobenzone several large human cohort studies exist which specifically recruited subjects with sunscreen or sun related sensitivity. A recent multi-center study [10] involving 1031 selected subjects utilized photo-patch testing and measured just 1.7% reactions. This result indicates a very low incidence in the random population and we can assume it will be even lower in reality, because in this patch test setup Avobenzone was not stabilized and rather prone to photo-destruction, whereas in sunscreens this process is inhibited by specific UV filters. Such human cohort studies suggest that the impact of potential harmful photo-destruction products is rather limited for Avobenzone.

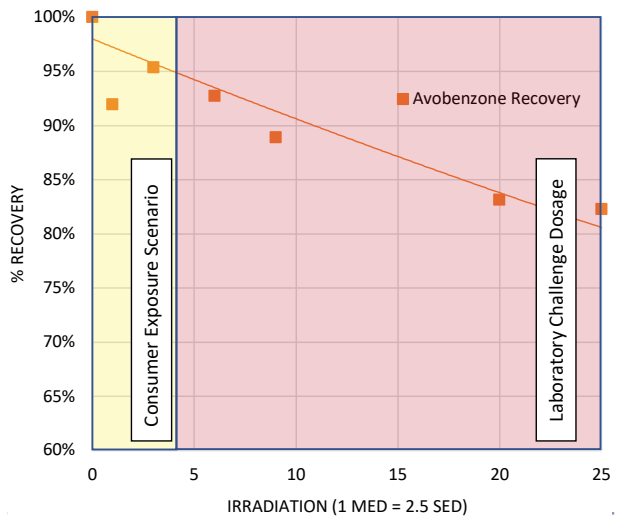

Fig. 1 Stability of Avobenzone in a commercial sunscreen lotion SPF 50+. The yellow area marks the typical dosage measured for beach goers according to the study [5], while the red area is a typical laboratory challenge.

Photostability and its impact on achieving a very high SPF claim

Should we now stop testing sunscreens artificially in laboratories, using dosages that are almost impossible to get on this planet? No! For formulators aiming for high protection SPF claims this is still an essential piece of information. SPF claims are currently substantiated through *in vivo* testing in accordance with standards such as ISO 24444. Under these conditions, the protective sunscreen film is exposed to very high dosages indeed. For example, to pass for the SPF 50 claim, a formulation on human skin is exposed to 50 MED (between 125 and 300 SED depending on the subject's skin type). The film needs to let just 1/50th of the applied radiation burden through, which then causes a radiation burden of 1 MED on skin. By the end of the radiation period, the UV filter composition has been taken to the limit, keeping in mind that such a dosage can hardly be collected on the Earth's surface [11]. The radiation source is a mix of UVB and UVA light at a ratio of 1:10, UVB being more erythemal than UVA light by a magnitude of about one, and UVA light contributing to about 10% of erythema in the SPF testing setup. Significant losses on the UVB side would be detrimental, but even though losses on the UVA side are 10 times less important, they should also be limited, e.g.: through stabilization or by avoiding unstable UV filter combinations. For example, to achieve high SPF numbers, Avobenzone should always be formulated with a triplet quencher such as Bis-Ethylhexyloxyphenol methoxyphenyl triazin (BEMT) and not combined with OMC. Many commercial examples, such as the one shown in **Figure 1**, illustrate that by stabilizing Avonbenzone with BEMT it is easy to achieve the 50+ claim. SPF testing in regard to photo-stability is an "integrative" measurement, meaning a photo-unstable sunscreen starts with high protection and ends up lower. One the basis of reaction kinetics one can calculate an quasi stable average of Avobenzone considering the whole period. Ironically, photo-unstable formulas offer consumers more protection during the short period in which they are exposed to radiation, e.g. on the beach, than their labels indicate, as they need to compensate for the loss in the later phase of SPF testing. However, that radiation dosage phase is never reached on Earth as the day of exposure is terminated in the afternoon by sundown.

Photostability in the environment

Sunscreens, and their UV filters in particular, are also a concern in terms of their impact on the environment, especially marine fauna and flora. Recently, the Hawaiian government banned two UV filters due to concerns raised in laboratory experiments [12] that they may damage corals around the Hawaiian islands. Although most recreational sunscreens are formulated water resistant, it cannot be ruled out that a fraction is rinsed off by water. The impact that a material released into the environment has depends on its toxicity, which in turn is species dependent, and on the length and intensity of exposure. Fortunately, most compounds are degraded by micro-organisms, but the speed of destruction can differ greatly. Ideally, compounds should be broken down quickly, which is the case if they had been tested to be "readily biodegradable". Interestingly, although OMC has this feature it is still one of the compounds banned in Hawaii. Metabolic destruction by micro-organisms is not the only way by which a compound can be eliminated from the environment. Abiotic pathways can also destroy molecules, especially with the help of sun radiation. Although photo-instability presents sunscreen formulators with challenges, the same feature is appreciated in the environment. We recently conducted exposure experiments with Avobenzone in quartz cuvettes in water at typical environmental concentrations just below its solubility

level and found that even after two days at a window (UVA light only!) it was broken down by 60-70%, indicating fast elimination from exposed water streams. When reviewing the literature on water analysis studies of UV filters in lakes, rivers and the sea [13,14] Avobenzone is seldom found, and only in low concentrations, giving a further indication that a fast abiotic elimination process may indeed take place through sun light, at least in layers of water that are close to the surface. And it is these layers which harbor the species a compound may be exposed to. In that sense, photo-instability becomes an interesting design feature in UV filters and could make a product more environmentally compatible. Of course, sunscreen formulators need solutions to overcome photostability challenges, as they have with Avobenzone by combining it with triplet quenchers. But when released into the environment the liaison with stabilizers is broken by dilution enabling deterioration to take place. In this sense, although they were not aware of this when they designed the molecule, the inventors of Avobenzone built in an environmental exit switch.

Conclusion

Photostability is a hot topic for sunscreens, however, in some ways its impact is overrated or wrongly interpreted. It plays a significant role in formulating sunscreens, especially for high performance products at SPF 50 and 50+ level. Here, formulators need to be aware of stabilization techniques and problematic combinations they should avoid. For consumers however, if a sunscreen has been assessed at SPF 50 level or higher, it is indeed sufficiently photo-stable, otherwise such a claim would not manifest. Furthermore, with the radiation doses sunseekers at the beach are exposed to, components barely break down. There is no particular reason for concern about losing protection performance after a short period of exposure. When it comes to the environment, photo-degradation by sunlight is a positive feature because it can help eliminate the compound faster than biodegradation through micro-organisms alone. However, a temporary solution during its application in sunscreens and on human skin is required.

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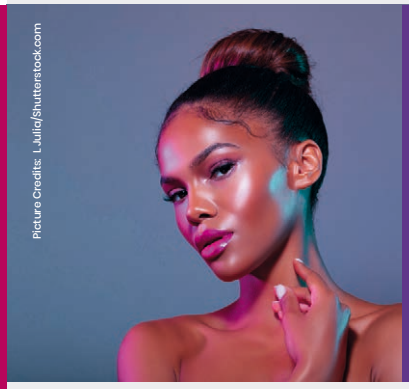

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Performance, Safety and Sustainability – All in Tris-Biphenyl Triazine

M. Sohn, S. Krus, M. Schnyder, S. Acker

abstract

Disrupting changes in the suncare field that signal the avoidance of Octocrylene (OCR) and Ethylhexyl Methoxycinnamate (EHMC) in newer sunscreen developments express a real challenge in terms of performance achievement. Ethylhexyl Triazone (EHT) and Bis-ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT) are often used as replacements but the achievement of higher Sun Protection Factors (SPF) requires additional UVB filters. This paper aims to evaluate the benefits of using Tris-Biphenyl Triazine (TBPT) as additional UV filter in comparison to Phenylbenzimidazole Sulfonic Acid (PBSA) and Titanium Dioxide (TiO2) seeing that TBPT is organic like PBSA and particulate like TiO2. We measured the UV absorbance and photostability as product specific performance criteria, and evaluated the risk of the production of free radicals under UV exposure since this is closely linked to photostability and can impact the irritation potential of sunscreens. Their effect in market relevant UV filter combinations was further assessed in view of their contribution to SPF, UVA-PF, blue light protection, and water resistance. We evaluated the ocular acceptability of a sunscreen containing TBPT and proposed solutions for environmentally friendly sunscreens. In this contribution, we show the broadness of the benefits gained in using TBPT in the future production of sunscreens. As a whole, this work reveals the huge potential of TBPT in modern sunscreens.

Introduction

Disrupting changes in the suncare field include the avoidance of Octocrylene (OCR) and Ethylhexyl Methoxycinnamate (EHMC) in new sunscreen developments due to rising concerns regarding their safety profile for humans and for the environment. The number of products without OCR and without EHMC rose from 15% in 2015 to 39% in 2020 in Europe [1]. These new UV filter systems express a real challenge in terms of performance achievement and a real split with the UV filter systems of past decades where sunscreens contained either EHMC or OCR. Ethylhexyl Triazone (EHT), Diethylhexyl Butamido Triazone (DBT) and Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT) are very often used as replacement of OCR and EHMC, and create the core of the UVB and broad-spectrum protection. The three belong to the efficient 1,3,5-Triazine filter type, and they are supplied as a powder and require appropriate solubilization. Salicylate-based UV filters including Ethylhexyl Salicylate (EHS) and Homosalate (HMS) are efficient solubilizers and rather used for this feature than for their mere absorbing performance. Recently, the SCCS (Scientific Committee on Consumer Safety) published a new final opinion on the UVB filter HMS after a revaluation in view of its endocrine disrupting potential. Earlier, HMS was evaluated twice in 2001 and 2007 (SCCP/1086/07) and was considered as safe for the consumer up to a concentration of 10%. The final opinion of June 2021 regards the use of HMS as safe for the consumer up to a maximum concentration of only 0.5% in the final product [2]. HMS was used in approximately 30% of sunscreens launched in Europe in 2020. Formulating out salicylate-based filters might become an effect of this new final opinion. Other available filters are more effective in absorbing UV rays than salicylate-based UV filters and comprise essentially Phenylbenzimidazole Sulfonic Acid (PBSA), Titanium dioxide (TiO2), and Tris-Biphenyl Triazine (TBPT). The purpose of the present study is to evaluate the benefits and effects of using TBPT in comparison to PBSA and TiO2 in sunscreens seeing that TBPT is a water dispersion of organic particles, thereby combining the properties of both the organic-like PBSA and particulate-like TiO2 filters. We measured the UV absorbance spectrum and photostability profile which consisted of product specific performance features. We evaluated the potential to produce free radicals under UV exposure, which is closely linked to the photostability profile and can impact the irritation potential of sunscreens [3]. We further investigated the effect of studied UV filters in market-relevant UV filter combinations in terms of SPF, UVA PF, blue light protection, and water resistance. We evaluated the benefit of using TBPT for the sensitive eye area and for eco-friendly sunscreens.

Materials and methods

UV filters

We analyzed the benefits of using TBPT in sunscreens by comparing the efficacy and effects of TBPT to PBSA and to TiO2, since TBPT is added to the water phase like PBSA and is in particulate form like TiO2. **Table 1** provides the properties of the three UV filters.

UV absorbance

To evaluate the UV performance of Tris-Biphenyl Triazine (TBPT), we measured the extinction from 290 to 400 nm of a 1% (active amount w/v) dispersion at an optical thickness of 1 cm using a UV/Vis spectrophotometer Perkin Elmer Lambda 25. These conditions provide the so-called E1,1 value for each wavelength which allows a direct performance comparison between different UV filters. We compared the spectrum of TBPT with the spectra of PBSA and TiO2.

Abbreviation	TBPT	TiO2 with coating	PBSA
INCI	Tris-Biphenyl Triazine (nano)	Titanium Dioxide (nano)	Phenylbenzimidazole sulfonic acid
Nature	Water dispersion of particles	Particles (powder or dispersion)	Water soluble
pH in formulation	No limitation	No limitation	> 7
Molecular weight (g/mol) [1]	538 / molecule $1.7 \cdot 10^9$ / particle	80 / molecule $2.3 \cdot 10^8 – 4.5 \cdot 10^9$ / particle	274
Median particle size (D50) as given in SCCS dossiers	81 nm (FOQELS) [2]	28 to 75 nm (disc centrifuge)	< 1nm

[1] [4]
[2] Fiber-optic quasi-elastic light scattering.

Table 1: Properties of TBPT, PBSA and TiO2

Photostability

The recovery (%) after UV irradiation of 1% TBPT and 1% PBSA without or with 5% Butyl Methoxydibenzoylmethane (BMDBM) or 5% Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB) was determined with HPLC measurements (Agilent 1100 Series, Agilent Technologies, Santa Clara, CA, USA). In this methodology, the studied UV filter/UV filter combination was formulated in an oil-in-water (O/W) base which was spread on a sand-blasted quartz plate at an amount of 5.6 mg (thickness layer of 2 mg/cm²) followed by 30 minutes of equilibration time. The plates were irradiated with UV light (Suntest CPS+ irradiation chamber, Atlas, Illinois, USA) with increasing exposure times of 0h, 1h, 2h, 4h and 10h corresponding to 0, 5, 10, 20 and 50 MED (Minimal Erythemal Dose respectively), 1 MED equaling 59.8 kJ/m². After irradi-

ation, the formulation was washed off the quartz plate with a solvent (in a 5 ml volumetric flask) and the remaining parent UV filter concentration evaluated via HPLC. The averaged peak area of the probe without irradiation was set to 100% and the ones after irradiation related to the one without irradiation. Analysis wavelengths were chosen as 314 nm for TBPT, 300 nm for PBSA, 357 nm for BMDBM and DHHB.

Measurement of free radicals

The formulations were the same as for the evaluation of the photostability. Photostability of a UV filter is a key factor for its potential to generate free radicals under UV exposure. We evaluated the percentage of UV-induced free radicals in the O/W emulsion containing 1% TBPT or 1% PBSA, either alone or combined with 5% BMDBM or 5% DHHB via electron spin resonance (ESR) spectroscopy (MiniScope MS300, Magnettech GmbH Berlin, Germany). The measurement was performed following the method described earlier, referred to as study 1 in Sohn et al. [5]. In this methodology, the spin probe PCA, (2,2,5,5-tetramethyl pyrrolidine N-oxyl, Sigma-Aldrich, Munich, Germany) is added to the probe (0.01 mM).

It is stable over time but reacts with free radicals produced in the formulation under UV irradiation (UV solar simulator 300 W Oriel, Newport) to be reduced to the ESR-silent hydroxylamine. The integrated irradiances values were 23.5 W/m² for the range 280 to 320 nm and 180 W/m² for the range 320 to 400 nm. The signal intensity decay of PCA was measured as a function of UV exposure doses, and the samples were exposed up to 10 minutes of UV irradiation (= 13.9 J/cm²). The amount of reduced PCA can be measured and the percentage of UV-generated free radicals deduced.

SPF and UVA protection

To assess the benefits of TBPT in a product without OCR and EHMC, we measured the SPF *in vivo* [6] and the UVA protection of an O/W formulation containing a core UV filter system of 3.0% EHT, 4.0% DHHB, and 1.0% BEMT. In addition, we added either 3% TBPT or 3% PBSA or 3% TiO2. For the UVA protection, the ratio UVA-PF/SPF expressed as superior or inferior to the value of 1/3 was given. The criterium of 1/3 is recommended by the European Commission so that the minimum UVA protection factor afforded by a sunscreen should be at least equal to or higher than 1/3 of the SPF [7].

Trade Name	INCI abbreviation	% in product PBSA based	% in product TBPT based
Eumulgin Prisma	Disodium Cetearyl Sulfosuccinate	0.5	0.5
Eumulgin Sucro Plus	Sucrose Polystearate (and) Cetyl Palmitate	3.0	3.0
Cutina GMS SE	Glyceryl Stearate SE	2.0	2.0
Cutina HVG	Hydrogenated Vegetable Glycerides	2.5	2.5
Cetiol OE	Dicaprylyl Ether	2.0	2.0
Cetiol CC	Dicyprylyl Carbonate	10.0	10.0
Cetiol RLF	Caprylyl-Caprylate/Caprate	5.0	5.0
Hydagen CAT	Triethyl Citrate	5.0	5.0
Dermosoft Octiol	Caprylyl Glycol	0.4	0.4
Sensiva SC50	Ethylhexylglycerin	0.2	0.2
Spherilex 10PC	Hydrated Silica	2.0	2.0
Uvinul A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate	4.0	4.0
Uvinul T 150	Ethylhexyl Triazone	2.5	2.5
Tinosorb S	Bis-ethylhexyloxyphenol Methoxyphenyl Triazine	1.0	1.0
Water	Aqua	Qsp 100%	Qsp 100%
Glycerin	Glycerin	5.0	5.0
Rheocare XGN	Xanthan Gum	0.3	0.3
	Phenylbenzimidazole Sulfonic Acid	3.0	----
Tinosorb A2B*	Tris-Biphenyl Triazine (nano), Aqua, Decyl Glucoside, Butylene Glycol, Disodium Phosphate, Xanthan Gum	----	5.0

* 50% dispersion, 5.0% Tinosorb A2B corresponds to 2.5% active amount of Tris-Biphenyl Triazine

Table 2: Composition of the products in the water resistance test

Water resistance

Water resistance became a standard performance claim; 65% of sunscreens launched in Europe in 2020 claimed water resistance [8]. We measured the *in vitro* water resistance of two sunscreens based either on TBPT or on PBSA as additional UVB filters according to a method described earlier referred to as the "solution method" [9]. In this methodology, 2 mg/cm² of the tested sunscreen was applied on four plates made from Ethylene Methacrylate Acid Copolymer named M14 EMA in [9]. Two of them were immersed in a water bath, and, after immersion, each of the four plates (immersed and not immersed) was rinsed off with a solvent mixture (THF/Ethanol/Neutrol TE (50:48:2)). The solvent/formulation solution was diluted (1:40) and measurements of the UV absorbance were performed from 290 to 400 nm using a Lambda 20 device. The static SPF *in silico* value was deduced from the UV absorbance spectra of the non-immersed plates and the wet SPF *in silico* from the UV absorbance spectra of the immersed plates using a computational method developed for this purpose. The percentage of water resistance is calculated from the ratio between the average wet and average static *in silico* SPF.

The composition of tested formulations is given in **Table 2**. The SPF *in silico* was 16 for the UV filter composition without PBSA and without TBPT, and increased to 30 with an additional 3% PBSA or 2.5% TBPT [10].

Blue light protection

Blue light protection was measured with the same formulations as for the water resistance test **(Table 2)**. The blue light transmittance of the probe applied on PMMA plates (SB6 from HelioScreen Labs, FR) with an amount of 1.2 mg/cm² was measured using a Labsphere UV-2000S device (Labsphere Inc, USA) between 400 and 450 nm. Three plates were prepared per probe and 5 transmittance measurements were performed per plate. The average transmittance value was used to calculate the blue light protection. The blue light protection factor given in percentage corresponds to the reduced transmitted light between 400 and 450 nm.

Trade Name	INCI abbreviation	% in product
Cetiol B	Dibutyl Adipate	8.0
Cetiol OE	Dicaprylyl Ether	7.0
Cetiol Sensoft	Propylheptyl Caprylate	6.0
Cetiol Ultimate	Undecane, Tridecane	4.0
Euxyl PE 9010	Phenoxyethanol and Ethylhexylglycerin	1.0
Uvinul A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB)	5.0
Uvinul T 150	Ethylhexyl Triazone (EHT)	3.0
Tinosorb S	Bis-ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT)	1.5
Water	Aqua	Qsp 100%
Glycerin	Glycerin	3.0
Avicel PC 611	Microcrystalline Cellulose, Cellulose Gum	1.0
Rheocare XGN	Xanthan Gum	0.2
Tinovis GTC UP	Acrylates/Beheneth-25 Methacrylate Copolymer	1.5
Sodium Hydroxide	Sodium Hydroxide	Qs
Tinosorb A2B	Tris-Biphenyl Triazine (nano), Aqua, Decyl Glucoside, Butylene Glycol, Disodium Phosphate, Xanthan Gum	6.5
Tinosorb M	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (nano), Aqua, Decyl Glucoside, Propylene Glycol, Xanthan Gum	4.0

Table 3: Composition of the product assessed for ocular acceptability

Sensitive eye area

The stinging potential on eyes of a formulation containing TBPT was evaluated in a clinical test (Eurofins, Dermscan, Gdansk, Poland) performed in accordance with the Helsinki declaration and successive updates. The methodology consisted in a single-blind and intra-individual test involving 20 subjects with a phototype I to IV and an average age of 43 ± 4. An amount of 0.5 ml of the tested probe was applied by the subject on the contour of one of its eyes as in normal conditions of use, under the control of the technician. A saline solution used as a comparison product was applied on the other eye contour by the technician using a soaked cotton pad and by wiping 3 times. The panelists were asked to blink several times. A clinical examination of the eyes and contours was performed by an ophthalmologist before and after a single application of the probe. The observation included the examination of the state of the cornea, bulbar and palpebral conjunctiva and eyelids using a slit lamp. After product application, the same examination was performed by the same ophthalmologist to detect any modification and to assess ocular acceptability. In parallel, the subjects made a self-evaluation of the stinging and watering sensation. The tested product shows a SPF *in silico* of 50 [10], and its composition is given in **Table 3**.

Eco-friendly sunscreens

Concerns of the damaging effects of UV filters on ecosystems gained a high level of awareness in public debates, since they are likely to be directly released into the environment. To meet the demand of eco-conscious consumers, some manufacturers focus their promotion on the biodegradability of their product with a protocol which was developed for the testing of the biodegradability of raw materials and not of finished formulations [11]. Besides, describing the eco-friendliness of a UV filter combination with the isolated biodegradability factor is inadequate; it should encompass all ecological relevant compartments. We used the EcoSun Pass value to characterize the eco-friendliness of UV filter combinations with Tris-Biphenyl Triazine [12,13]. The EcoSun Pass value considers the individual environmental hazard profile of the UV filters plus the efficacy of the composition using the SPF and UVA-PF in relation to the total UV filter concentration. The environmental hazard profile of a UV filter is determined individually using representative criteria of the environmental fate and ecotoxicological profile of the corresponding UV filter. These criteria encompass the biodegradation, bioaccumulation, acute and chronic aquatic toxicity, chronic terrestrial toxicity, and sediment toxicity. The EcoSun Pass aims to facilitate the selection of the most appropriate UV filter combination in respect of eco-friendliness.

Results

UV absorbance

Figure 1 displays the E(1,1) absorbance profile of TBPT, PBSA and TiO2 (coating; Aluminum Hydroxide (and) Dimethicone (and) Dimethicone/Methicone Copolymer).

From the absorbance curves, we can deduce that the maximum E(1,1) value is 1110, 875, 945 for TBPT, PBSA, TiO2 at the wavelength of 310, 305, and 290 nm, respectively. Also, the area under the curve (AUC) is used as an indicator factor of the efficacy of the UV filter since it provides information on the UV coverage effectiveness obtained with 1% active of UV

filter. The AUC obtained from the absorbance data equals 580 for TBPT, 245 for PBSA and 450 for TiO2 over the UV range 290-400 nm. The E (1,1) and the AUC values express the efficacy and anticipate the impact of the UV filter on the SPF. The higher the values, the higher the impact on the SPF is expected to be. **Figure 1** also reveals that the shape of the absorbance curves varies between the UV filters; the profile of TBPT is unique since it shows a shoulder in the UVAII range extending up to 340 nm with a value of E(1,1) of 825. Sayre et al. showed that a UVB-loaded sunscreen blocking exclusively radiation from 290 to 320 nm would assumably reach a maximum SPF of 11 because a continuous amount of UVAII radiation, which is likewise erythemally active, is transmitted [14]. From its absorbance profile, TBPT should positively impact the SPF and UVA protection versus PBSA and TiO2 whose efficacy is lower in the UVB range and lacking the UVAII shield.

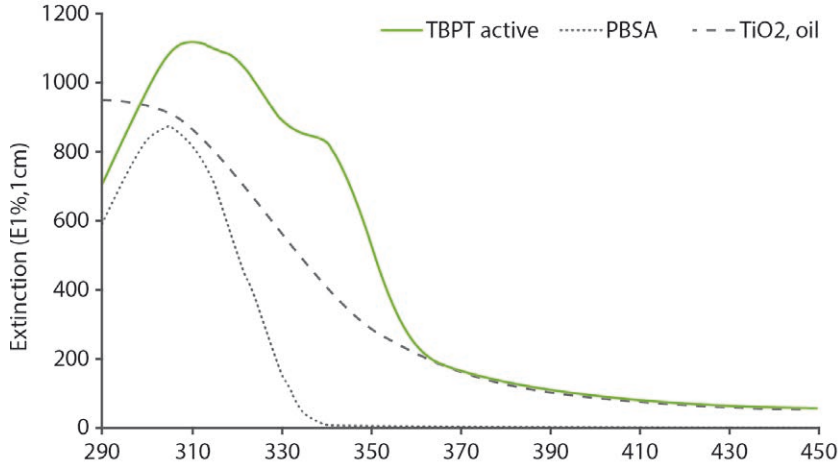

Fig. 1 E(1,1) absorbance profile of TBPT, PBSA and TiO2

Photostability

The recovery (in %) of PBSA and TBPT, alone and in combination with either 5% BMDBM or 5% DHHB, after increasing irradiation doses is shown in **Figure 2** and **Figure 3**.

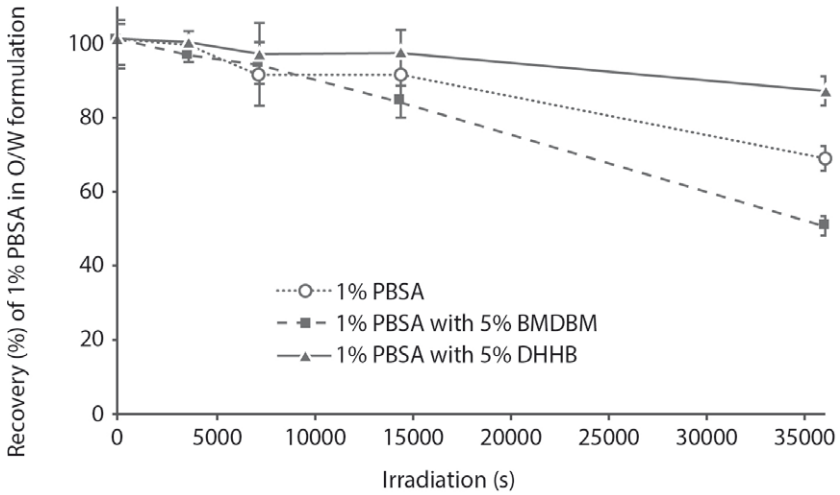

Fig. 2 Recovery (%) of 1% PBSA without and with 5% of BMDBM or 5% DHHB

TBPT is sensibly more photostable than PBSA, with 100% of the parent molecule that is recovered for TBPT versus 91% for PBSA after an irradiation of 14400 s (corresponding to 20 MED) and 85% for TBPT versus 68% for PBSA after an irradiation of 36000 s (corresponding to 50 MED). The photostability profiles of TBPT and PBSA highly differ when combined with BMDBM. Whereas TBPT remains photostable in combination with BMDBM, PBSA is photodegraded when combined with BMDBM **(Figure 2)**. By contrast, PBSA is photostabilized in combination with DHHB with a recovery of 97% after 14400 s UV irradiation. DHHB remains fully photostable (data not shown).

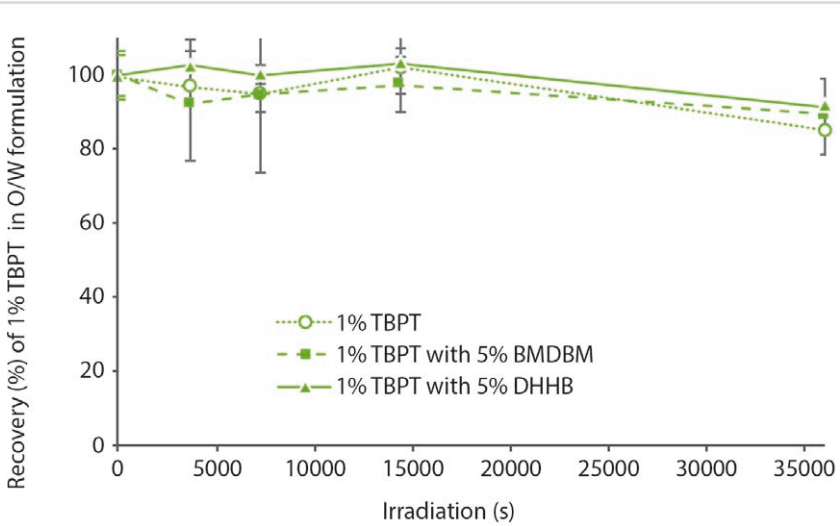

Fig. 3 Recovery (%) of 1% TBPT without and with 5% of BMDBM or 5% DHHB

Measurement of free radicals

The percentage of free radicals generated in an O/W formulation after UV irradiation was determined by electron spin resonance (ESR) spectroscopy. The formulations were the same as for the photostability test and differed only with the filter composition. The results are given in **Table 4**. A value of 0% would signify that the spin probe PCA remained as is in the

formulation and no free radicals are generated with UV irradiation; by contrast, a value of 100% would signify that the spin probe PCA is immediately and totally reduced into ESR silent hydroxylamine because it reacted with the free radicals generated intensively and immediately after starting the irradiation of the formulation with UV light.

Table 4 indicates that PBSA actively initiates the production of free radicals upon UV irradiation. This is in line with the investigations of *Inbaraj et. al* and *Bastein et al*. who studied the photophysical and photochemical properties of PBSA and showed its ability to photogenerate reactive oxygen species and free radicals capable of damaging DNA [15,16]. In combination with DHHB, the number of UV-generated free radicals produced in the formulation is decreased by 40%, which is most probably related to the improved photostability of PBSA in combination with DHHB **(Figure 2)**. Compared to PBSA, the number of free radicals produced in the formulation containing TBPT is approximately 80% lower, which is further reduced to a very small number when TBPT is combined with DHHB. Free radicals might also be generated by some of the formulation excipients, but it is not possible here to specifically distinguish the effect of each excipient.

UV filter combination	Free radicals (%)
1% PBSA	75.7% (+/-0.05)
1% PBSA + 5% DHHB	45.3% (+/-0.35)
1% TBPT	12.7% (+/-0.54)
1% TBPT + 5% DHHB	3.7% (+/-0.18)

Table 4: Free radicals (%) generated in the formulation after UV irradiation, n=2

SPF and UVA protection

To substantiate the observations regarding the absorbance spectra, we investigated the impact of TBPT in comparison to PBSA and TiO2 on the UV efficacy in a realistic UV filter combination. **Table 5** provides the SPF *in vivo* value [6] and the ratio UVA-PF/SPF expressed as superior or inferior to the value of 1/3 of a UV filter combination containing EHT, DHHB, BEMT plus PBSA, or TiO2, or TBPT.

As expected, the SPF *in vivo* of the base was increased by the addition of a further UVB filter, but the level of increase differed highly between investigated UV filters. An SPF increase of 70% and 47% was achieved by adding PBSA and TiO2 to the base, respectively. In comparison, the addition of TBPT resulted in a SPF push of 150%. Looking at the UVA protection, only TBPT was able to maintain the ratio UVA-PF/SPF superior to 1/3 like for the base. This overall and strong boosting can be explained by three of its features. The SPF is directly and positively impacted by the higher UVB absorbance seen for TBPT versus PBSA and TiO2. The extended absorbance in the UVAII benefits both to the SPF and UVA-PF, which explains the safeguarding of the UVA protection. Furthermore, the presence of TBPT in the water phase of the emulsion is an additional advantage to avoid the formation of unprotected areas of the non-volatile water part, remaining after spreading of the product [17]. Finally, its particulate nature accounts a lot in the boosting properties of TBPT. When UV light hits a TBPT particle, one part is absorbed and another part is scattered; the pathlength of the scattered light is increased and the likelihood that it is absorbed by a surrounding UV filter molecule is increased. This mechanism was described in detail by Herzog et al [18].

UV combination	SPF *in vivo*	UVA-PF / SPF
Base (3% EHT + 4% DHHB + 1% BEMT)	17	> 1/3
Base + 3% PBSA	29	< 1/3
Base + 3% TiO2 (Aluminum Hydroxide (and) Stearic Acid)	25	< 1/3
Base + 3% TBPT	43	> 1/3

Table 5: SPF *in vivo* and UVA-PF/SPF criterium

However, nano particulate UV filters currently suffer from a downgrade in the media and by digital consumer apps using a biased evaluation that reaches the end consumer and provokes worries with respect to the human safety of UV filters in nano form. The concern relates to their percutaneous absorption potential, yet all registered UV filters including nano UV filters needed to go through an extensive safety evaluation to obtain a positive SCCS opinion to be marketed [19]. TBPT exhibits a logarithmic octanol/water partition coefficient (log Pow) much higher than 4, a negligible water solubility in the ng/L range, a melting point of 281°C, and a molecular weight over 500 g/mol, not to mention the molecular weight of the particles. Each single of these properties has been determined to decrease the potential for dermal penetration. In combination, they explain the unlikeliness of TBPT to penetrate skin. Taking solely the particle size criterium, implying that several molecules connected to each other to form a particle, comparing TBPT (particle) to the size of a soluble UV filter molecule, basically "Nano means Big". This enlightens us why there is no scientific rationale to downgrade nano UV filters in sunscreens due to their solely particulate nature.

Water resistance and blue light protection

The water resistance *in vitro* and blue light protection were evaluated with the same formulations **(Table 2)**, and the results are given in **Table 6**. The formulations differed by the addition of either PBSA or TBPT to achieve an SPF of 30.

The water resistance of the sunscreen containing TBPT is much higher than of the one with PBSA. This is presumably due to the washing off of the water-soluble filter during

water contact. The SPF *in silico* of the filter system equaled 16 and 30 without and with PBSA respectively. Since the water resistance is 51%, we may assume that a large portion of PBSA was rinsed off of the plate during water immersion. By contrast, TBPT consists of hydrodispersed but hydrophobic particles and is not dissolved in the water phase which explains the significantly greater water resistance of 71% achieved when adding TBPT in comparison to PBSA. Another advantage of the particulate nature of TBPT versus soluble PBSA is its scattering properties, which leads to the extension of the protection into the blue waveband even as an UVB filter. The transmission in the short visible range could be reduced by 35% with the combination containing TBPT, in comparison to 7% with the combination containing PBSA, the latter being ascribed mostly to the absorption tail of the present UVA filter DHHB.

	PBSA-based sunscreen	TBPT-based sunscreen
In vitro water resistance (%)	51%	72%
Blue light protection (%)	7%	35%

Table 6: Water resistance and blue light protection of PBSA versus TBPT containing sunscreens with SPF 30

UV combination	SPF 20	SPF 30	SPF 50	SPF 50+
Ethylhexyl Triazone	2.00	2.50	3.00	3.50
Tris-Biphenyl Triazine	1.25	2.50	3.50	4.00
Bis-ethylhexyloxyphenol Methoxyphenyl Triazine	1.00	1.00	2.50	3.00
Diethylamino Hydroxybenzoyl Hexyl Benzoate	3.00	4.00	5.00	6.00
EcoSun Pass value	228	246	259	261
				

Table 7: UV filter combinations (in % in finished formulation) fulfilling EcoSun Pass of at least 200 for SPF 20 to 50+ with UVA-PF/SPF > 1/3

Sensitive eye area

The clinical ocular assessment of tested cream-gel containing a mixture of 5% DHHB, 3% EHT, 1.5% BEMT, 3.25% TBPT and 2% MBBT did not reveal any modification of the state of the cornea, bulbar and palpebral conjunctiva or eyelids. No undesirable or adverse effects, such as stinging or watering, could be felt by the subjects. The formulation fulfilled the criterium for claiming "does not sting the eyes" and "tear free".

Eco-friendly sunscreens

Table 7 provides UV filter combinations fulfilling the EcoSun Pass criterium optimized with respect to minimal impact on the environment for SPF values of 20 to 50+. The threshold for satisfying the EcoSun Pass criterium was set to 200, which can be reached with UV filters currently on the market. This criterium, however, also shows that there is room for improvement in the development of optimized eco-friendly sunscreens that respect the environment and nature.

Conclusions

In this contribution, we showed the broadness of the benefits gained in using TBPT in the future production of sunscreens. Compared to the soluble UVB filter PBSA and particulate filter TiO2, TBPT offers unique absorbance coverage; it highly contributes to an increase in SPF without unbalancing the UVA protection thanks to its unique UVAII shield. Compared to PBSA, its particulate nature allows the upholding of the water resistance and the extension of the protection up to the blue waveband. TBPT is also photostable with both commonly used UVA filters BMDBM and DHHB, which is essential not to generate free radicals under UV exposure. TBPT has not led to any undesirable skin reaction in an acceptability test around the sensitive eye area. Finally, TBPT allows the development of eco-conscious sunscreens up to SPF 50+. As a whole, this work reveals the huge potential of TBPT in modern sunscreens.

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Blue-Light Reimaged – Delighting Ingredients for Skin Protection

Beyond Personal Care: Nutricosmetics

U. Wollenweber, C. G. Suárez Rizzo

in a nutshell

Consumer behaviour is shifting during the COVID-19 pandemic, we are on screens even more than we usually are because we are working from home and doing business via video conferencing. This situation raises awareness of blue light exposure and digital detox emerges as a growing need. Personal Care considers the influence of artificial visible light emitted by the screens, which is a good opportunity to position products that promote blue light protection.

In this article, we summarise several ways to combat blue light and to reduce premature skin aging. Approaches related to UV filters, restoring cells' energy metabolism and antioxidants are considered. Besides skin protection with conventional approaches like topical applications, we include the positive impact of using nutricosmetics giving holistic solutions to the consumers.

Introduction:
Screen-based lifestyles are bringing new needs

Next to the chronological aging, photoaging has become a huge issue in Personal Care. If one seriously wants to prevent premature ageing, protection from UVA and UVB rays is no longer enough, as evolving research confirms that blue light is also bad for our skin.

The spectral distribution of the solar energy at the sea level comprises up to 7% of UV irradiation (290–400nm), 44% of visible light (400–700 nm), and 53% of infrared (IR) radiation (700–1440 nm) [1]. The effects of UV irradiation are well documented. Because we thought in the past that visible light and IR only produce heat, only few studies have looked at their effects on skin. Actually new data show that wavelengths of visible light and especially the high-energy spectrum of blue light (400 – 500 nm) penetrate deep into the dermis and cause damage leading firstly to photoaging.

Moreover, taking into account that the spectrum of artificial light is also involved in the emission of blue light, researchers have warned consumers about the health impact of excessive smartphone/laptop usage. Following this and since a couple of years, Personal Care Industry also considers the influence of electronic devices all over the day in the skin.

The development of electronic devices like laptops, tablets and smartphones revolutionized our daily life during the last years. In its 2014 Digital Consumer Report of the USA, NIELSEN analysed that in average every American owns 4 digital devices [2] – as a result, consumption habits are changing and being online all the time also effects our health.

Now, since more than one year staying in the Covid-19 pandemic, suffering lockdown and restrictions, we stay at home during work and leisure time and digital updates are replacing human touch and face-to-face interactions. These led to a drastic increase of the usage of electronic devices and therefore to even a more intensive exposure to artificial visual light (AVL) [3].

As quarantine measures continue, there will be opportunities to raise awareness of blue light exposure and to position products that promote blue light protection [4,5]

Exposure of the skin to high energy light and its consequences

Already in 2008 the damage of the skin through its exposure to visible light had been published [6] but in general, the attention of artificial light limited its effect to the eye's health and a decreased sleep quality [7]. Since about five years, Personal Care considers the influence of artificial visible light emitted by the screens of our smartphones, tablets and laptops and its effect.

Visible light, both natural and artificial, penetrates deeply into the dermis **(Figure 1)** [8]. It is known that the irradiation induces the formation of Reactive Oxygen Species ROS and matrix degrading enzymes [9]. Therefore, the exposure to High-Energy visible (HEV) Light effects especially the dermal cells by DNA damage, rapid cell death and cells' shrinkage. It results also in a slowed down proliferation of the fibroblasts and decreased production of procollagen I and ATP leading to photoaged and fatigue skin **(Figure 2)**. Therefore, it is

taken into account that blue light emissions are more and more becoming a cause of extrinsic skin aging [10].

As a result, the cosmetics industry has responded to this challenge by innovation and development of blue light protection products.

Approaches to combat blue light for topical applications

In general, for anti-blue light ingredients we delight several approaches in Personal Care to fight high energy visible light. Additionally, we like to point out an important trend coming from botanicals and bringing nutritional aspects to combat photoaging.

1. Blue light filters

UV filters only cover the spectrum of UV B and A from 280 – 400 nm and therefore do not prevent the penetration of high energy light into the skin.

Therefore, one approach is to provide the skin with a shielding film, which absorbs scatters and reflects the light to avoid a penetration into the skin.

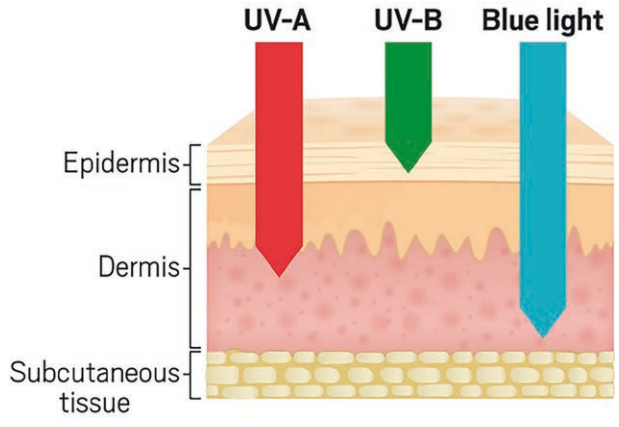

Fig. 1 Blue light penetration modified from Reisch MS. [8]

Here, especially inorganic sun filters like titanium dioxide (TiO_2) and Zinc oxide (ZnO) may be modified to "broaden" the absorption spectrum up to a wavelength of 500 nm. One possibility to obtain an enlarged absorption profile is the right selection of the coating material for inorganic filters that expands the absorption spectrum into the blue light range [11].\

It could be also shown that iron oxides provide enhanced protection against blue light, especially when combined with zinc oxide [12].

In the same direction goes the combination of inorganic UV filters with functional fillers like mica, which results in an improved defense against HEV. As an added benefit, functional fillers may correct the skin tone [13].
One natural source of filters is red algae, because they live in deeper parts of the ocean where only blue and UV light can reach them. As such, they adapted a mechanism that allows them to absorb blue light in order to survive at these depths. A pigment called phycoerythrin gives the red color, which absorb the blue light and reflect the red light.
Next to photoprotection, red algae are also interesting for cosmetics related to skin damage, skin structure restoring, etc. [14]

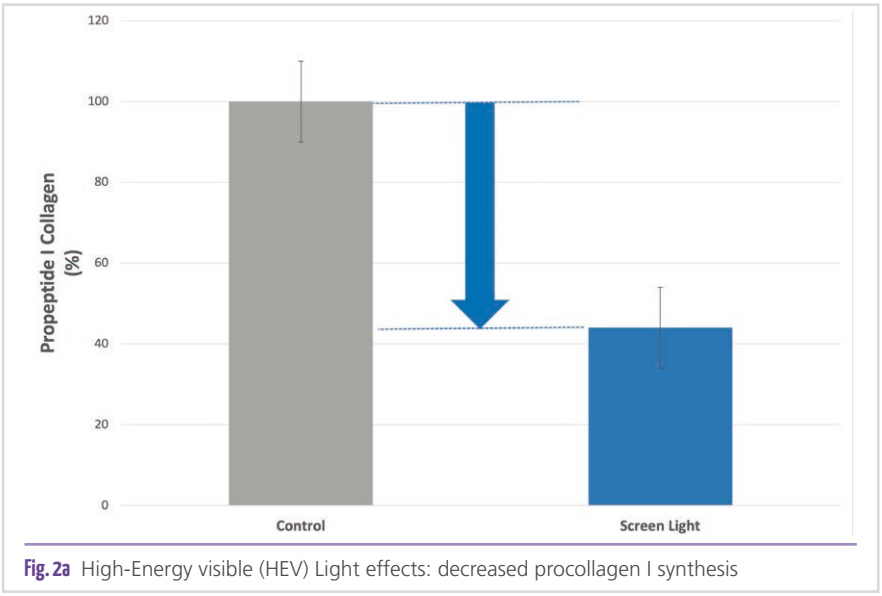

Fig. 2a High-Energy visible (HEV) Light effects: decreased procollagen I synthesis

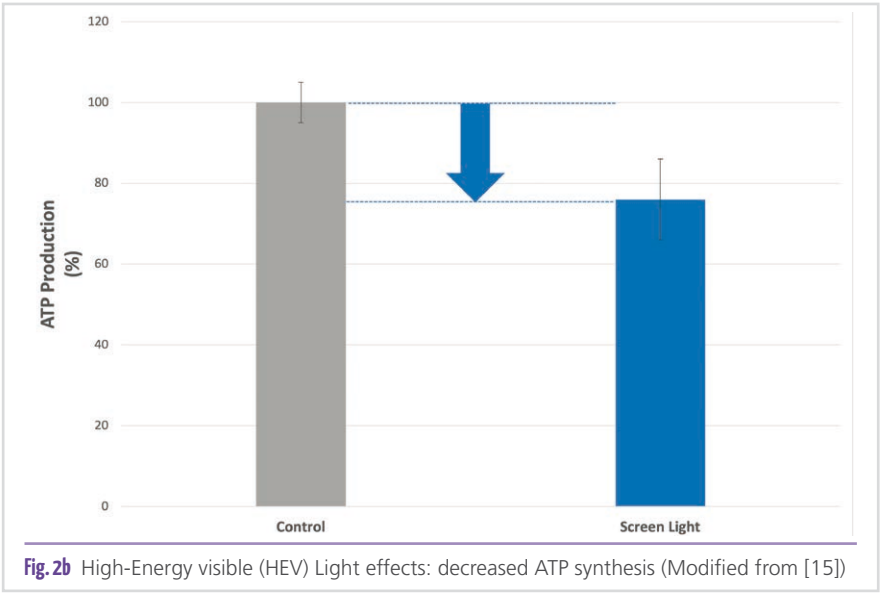

Fig. 2b High-Energy visible (HEV) Light effects: decreased ATP synthesis (Modified from [15])

2. Restore cells' energy metabolism

To protect skin cells from screen-emitted artificial visible light, several ingredients were developed to support or restore the cellular metabolism and defense system. These ingredients are very often plant-based extracts e.g. of licorice, Indian Ginseng, marigold etc.

The extract of Indian Ginseng is able to regulate genes involved in energy metabolism of fibroblasts and therefore maintains cellular activity and improves the synthesis of procollagen I and ATP. It contains amino acids and withanolids; the synergetic action of these two phytochemical families supports its high level of efficacy. As a result, the skin is visibly revived [15,16].

Other extracts with anti-aging effects comes from the *Panax ginseng plant*. Ginseng is absorbed into the skin and helps skin keep its original shape. It has also been found to promote the growth of collagen. Studies have shown ginseng's ability to preserve skin against UVB ray damage [17].

3. Antioxidants

As if plants have to defense often harsh environmental conditions, they contain active ingredients to protect and/or to repair themselves.
In general, these plants are rich in flavonoids which are a class of secondary phenolics with significant antioxidant and chelating properties. The protective effects of flavonoids in biological systems are ascribed to their capacity to transfer electrons to quench free radicals, chelate metal catalysts, activate antioxidant enzymes, reduce alpha-tocopherol radicals, and inhibit oxidases [18]

The efficacy of flavonoids therefore is directly connected to their capability to quench reactive oxygen species (ROS) which are formed through the effects of blue light irradiation [19].
ROS lead to further side effects such as DNA damage, loss of cell viability, activation of inflammation pathways and decreases in cell function [20,21]
Natural flavonoids have the potential to act as direct and indirect antioxidants as well as anti-inflammatory and immunomodulatory agents.

During the examination of physiological response of skin to visible light (400-700 nm) the importance of antioxidant activity to restore the cellular balance between anti- and prooxidants was already studied in 2012. For that a combination of UV A/B-sunscreen containing an extract of feverfew was used which was rich in the antioxidant and flavonoid Apigenin (5,7,4'-trihydroxyflavone) [9,18].

The efficacy of antioxidants is shown in **Figures 3a and 3b.**

Popular extracts or botanicals like green tea, ginger, cocoa, carrot and marigold are sources for antioxidants like carotenoids used as protection from blue-light in topical applications. Other ingredients that gained popularity in this sector are vitamins like B3 (niacinamide) and C and E [22,23].

Approaches to combat blue light:
A complementary nutrition

Skin's maintenance requires appropriate topical cosmetic care that protects the most external layers of the skin from pollutants. It is well-known that internal structures of the skin can also be affected, which means that when using topical products, such as moisturizing creams, serums, and lotions, their impact is limited. This is where the positive impact of using nutricosmetics comes into play. As if Blue Light is penetrating deep into the dermis, a nutrition strategy can reach deeper skin layers resulting in long-lasting effects.

Botanical-based photoprotection is likely to increase in popularity as consumer trends worldwide continue to place an emphasis on naturally occurring compounds used solely or in conjunction with synthetic products [24].

Data on botanical oral preparations have demonstrated photoprotective potential in *in vitro*, animal, and human studies.

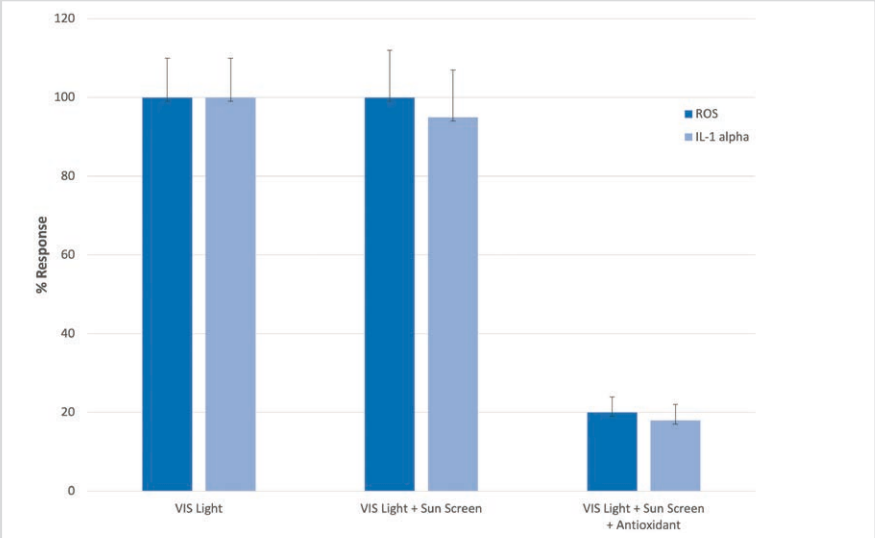

Fig. 3a The effect of visible light on skin cells: Exposure to visible light significantly increases ROS, and IL-1a (*in vitro*, human epidermal equivalents)

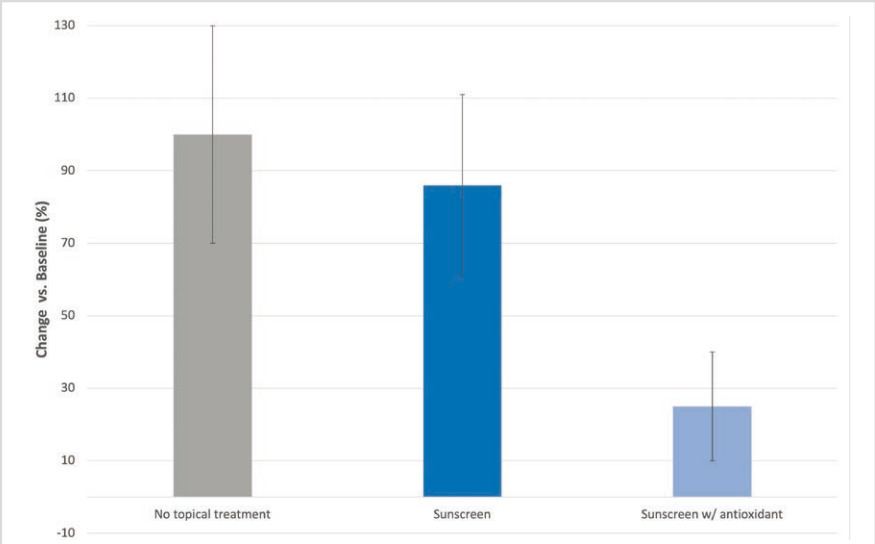

Fig. 3b The effect of visible light on skin cells: Free-radical production on the skin of human subjects after a defined dose of visible light (N = 40). ROS formation was tested by chemiluminescence. (Modified from Liebel et al. [9])

1. Tea and Flowers as sources of blue light fighters

One of the most extensively studied is green tea, produced from the leaves of *Camelia sinensis*, which is a widely consumed beverage in the world.

Catechins from green tea is a group of very active flavonoids representing 60–80% of all polyphenols. The primary and the most bioactive constituent of green tea is (–)-epigallocatechin-3-gallate (EGCG) [25].

These epicatechin derivatives all possess antioxidant, anti-inflammatory, antimicrobial, and anticarcinogenic properties.

In humans, studies have reported that topical Catechins from green tea reduce photodamage [26,27]. However, they have poor skin penetration when topically applied due to their poor lipid solubility [28]. They are also subject to photodegradation [27]. In contrast, orally administered Catechin has been shown to have good skin bioavailability. This was noted after supplementation of green tea Catechins daily for 12 weeks [29,30].

Chamomile also known as German chamomile has an extended traditional use as tea and in herbal medicine. Evidence-based information *in vitro* confirmed that Chamomile can be used in skincare as an anti-inflammatory and soothing ingredient [31].

The main constituents of the flowers include several phenolic compounds,

primarily the flavonoids apigenin, quercetin, patuletin, luteolin and their glucosides. The principal component of the essential oil extracted from the flowers is a terpenoid called bisabolol. The chamomile oil can be processed into pills, and the flower head can be taken as an herbal tea- two teaspoons of dried flower per cup of tea [31].

In green plants, xanthophylls act to modulate light energy and serve as non-photochemical quenching agents. One of the most well know xanthophylls is Lutein; it is concentrated in a small area of the human eye called retina and it is responsible for three color vision. Therefore, in the last couple of years many nutraceutical products were launched in the eyes health category with the claim: "protects from screen pollution or blue light" and some are also especially designed for e-gamers [32].

Currently, the primary source of lutein is the marigold flower. Two factors are influencing the Market of Lutein: its cost of production and its bioavailability. The cost associated with lutein production is high since it is only extracted during bloom season. A critical factor that significantly influences the bioavailability of lutein is its uptake rate. If a good absorption is carried out in the body, a lower dose will be required and, therefore, the formulation will be more cost-effective [33]. Consequently, emulsion-based delivery systems for lipophilic bioactive agents have been developed, which include O/W emulsions, nano-emulsions, microencapsulation, and liposomes [34].
On the other hand, potential sources of lutein from microalgae species are already marketed and the trend will growth as they produce about 5 g/kg biomass mainly in free lutein form.

Fig. 4 **Examples of botanicals for skin care**
4a. Red algae; 4b. Polypodium leucotomos; 4c. Ginger root; 4d. Elderberry; 4e. Licorice root; 4f. Pomegranate; 4g. Rose hip; 4h. Chamomile flower; 4i. Green tea

2. Fruits

Elderberry is a medicinal plant used throughout history: Scientifically called Sambucus berries or elderberries have been used from treating pain to decreasing inflammation and swelling and for immune response [35; 36].

Elderberries are nutrient & antioxidant-rich, making them ideal for use in skincare. Some of the skin-boosting nutrients found in elderberries include bioflavonoids, choline, omega-3 fatty acids, omega-6 fatty acids, pectin, and tannins. These give the elderberry its anti-inflammatory and antiviral properties [35; 36].

The extract from *Punica granatum* or pomegranate is rich in phenolic compounds, specifically, anthocyanins, catechins, and tannins [28]. Significant amounts of these compounds are most concentrated in the peel and juice [37]. At present, pomegranate extract is widely available as an over-the-counter oral supplement or topical formulation.

Pomegranate extract has anti-inflammatory properties and a very potent antioxidant activity - even greater than that of green tea or red wine [18; 28]. It confers photoprotection through inhibition of UV-induced production of free radicals, erythema and burning, DNA damage, cell proliferation, and apoptosis [18; 38] It can also decrease collagen breakdown [39]

Rose hip *(Rosa canina)* is rich in antioxidants, that helps to fight against inflammation and to protect cells from free radicals. As certain phytochemicals (e.g. flavonoids, ascorbic acid) are able to scavenge reactive oxygen species produced by UV-radiation and so reduce skin damage, increase moisture content of forehead, improve skin elasticity, and support skin

cell regeneration [40]. Moreover, in some studies surprisingly were found, that a synergistic effect occurs between Collagen hydrolysates and one special Rosehip extract when both are simultaneously given. The synthesis of Collagen hydrolysates tested *in vitro* was twice higher for the combination than for collagen hydrolysate alone [41]

3. Leaves

Another extract which interest has spiked is *Polypodium leucotomos*, mainly focusing on its antioxidant properties. *Polypodium leucotomos* (PL) is a fern native to America. It has been traditionally used for treating skin diseases (e.g., psoriasis and atopic dermatitis).

It displays anti-inflammatory effects and it also accelerates the removal of UV-induced photoproducts, which contributes to its photoprotective effects. PL supplementation acts at a molecular and cellular level to enhance endogenous antioxidant systems and inhibit generation of reactive oxygen species, thus decreasing light-mediated oxidative DNA mutations [42,43].

3. Roots

Roots like licorice and ginger have experienced massive interest in the past years.

The root of the licorice plant comprises phytochemical constituents that help protect and brighten the skin. Its extract contains nearly 300 compounds that have antiviral, anti-bacterial, and anti-inflammatory properties [44].

Ginger (*Zingiber officinale* Roscoe) is a **medicinal plant** used both in Chinese and Ayurvedic medicine.

Many bioactive compounds in ginger have been identified, such as phenolic and terpene compounds.

As for ginger and skincare, the root extract contains *gingerol* that has potent antioxidant and anti-inflammatory properties. The antioxidant activity of different gingers showed high Trolox-equivalent antioxidant capacity and ferric-reducing ability, and an aqueous extract of ginger exhibited strong free radical scavenging activity and chelating ability. Ginger can be used as fresh or dried, as oleoresin, extracts, or powders [45,46].

At a glance

The trend in Cosmetics and Nutricosmetics related to blue light protection is fast accelerating in popularity and seems to stay. Even after the pandemic, people will keep some habits like digital connections, streaming and e-gaming. Multiple ingredients are available on the market to fight against blue

light-induced skin damage. Some approaches like combinations of UV filters with antioxidants or the support of the skin cells keeping or increasing cellular activity have been shown good effects for skin protection against blue light.

Many antioxidants, flavonoids or xanthophylls used as active ingredients have poor skin penetration when topically applied due to their poor solubility. Therefore, nutraceuticals including plant-based ingredients can reach deeper skin layers resulting in long-lasting effects.

The importance of skin protection with conventional approaches like topical applications should include the positive impact of using nutricosmetics giving consumers a solution when they are looking for a holistic approach.

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Microbiological Requirements for Cosmetic Raw Materials

U. Eigener

abstract

The microbiological quality of raw materials has an important impact on the microbiological quality and safety of cosmetic products. The raw materials producer has to guarantee a consistent quality and to ensure adequate hygiene and preservation measures during manufacture, storage and transport of the materials. For each raw material microbial limit values have to be defined. The cosmetics producer has to avoid additional microbial contamination of the raw materials as well as microbial growth in the production site and in the finished product. This needs hygiene measures, a suitable processing of raw materials and an adequate preservation of the product. Microbiological controls have to be established to safeguard the entire raw material process. Valid microbial examinations, risk-assessment and expert-decisions need adequate personal qualification. To fulfil all the microbiological tasks a quality management-system (MQM) should be employed.

Microbiological quality and safety of cosmetic products are significantly influenced by the used raw material. Different aspects have to be observed to avoid microbiological risks resulting from a raw material contamination, the growth of such microorganisms or a loss of preservation-efficacy due to raw material influences (see **Figure 1**). Consequently, various microbiological measures are needed, which lie in the responsibility of the raw materials producer and also of the cosmetics producer, who is liable for the quality and safety when marketing the products. This paper covers chemical raw materials, which are purchased by the cosmetics producer from a raw material producer (or via a trader) and which are delivered into the cosmetic production site. Water as important raw material is not subject of this paper.

Fig. 1 Microbiologically relevant aspects of cosmetic raw materials

There are microbiological requirements for cosmetic raw materials given in the EC-Cosmetics Regulation (2009) and in the cosmetic-GMP (DIN EN ISO 22716) [IKW, 2020]. The EC-Cosmetics Regulation demands microbiological specifications for raw materials, which must be understood as end-point targets. To reliably reach these target values, effective measures must be taken, like contamination-protection for the material, prevention of microbial growth and process controls. But also correct processing and use of raw materials and maintenance of adequate raw material quality must be observed.

1. Microbial counts in cosmetic raw materials

The bioburden of cosmetic raw materials is caused through the origin of the material and though the manufacturing process. Various types of microorganisms are found as contaminants [Eigener, 1995; Ochs, 1999], which are then transported with the raw material into the cosmetic plant where they can lead to a contamination of the cosmetic products. Therefore, the EC Cosmetics Regulation (Annex I, 3. Microbiological Quality) demands a microbiological specification for raw materials. Since no limit values are given in the Regulation, these values must be defined for each single raw material basing upon a risk assessment. According to the cosmetics GMP (DIN EN ISO 22716, Chap. 6.5) [IKW, 2020] the raw material quality must be defined in such way that it does not impair the cosmetic products quality. This, of course, also includes the microbiological quality requirements.

As microbiological limit values for cosmetic products, usually the requirements of the DIN EN ISO 17516 are used. When defining the according microbial limit values for raw materials, the following aspects have to be taken into account:

- the amount of raw material used in the cosmetic product,
- the microbiologically relevant conditions of the cosmetic manufacturing method,

- the preservation of the cosmetic product, and
- the conditions of use of the cosmetic product (kind of application, application area, user group).

The limit values of the raw material should consist of the total count (TVC) and also of the limit for specified microorganisms, corresponding to the norm. The group of specified microorganisms should not be restricted to the four species mentioned in the norm. In each case, further specified microorganisms should be included, which might be of relevance for raw material/product damages as well as health hazards for the user of the cosmetic product [Eigener, 2021]. It is generally important that the cosmetics producer knows about all microorganisms found in the raw material in order to make a risk assessment possible and to install an effective control system.

Actual information about type and counts of microorganisms found in raw materials is very limited. Information given in literature is in most cases outdated, often from the 1970ies/1980ies. However, the quality awareness of raw materials producers has definitely increased in the meantime, due to legal requirements but also to own initiatives, as can be seen in the development of GMP-guidelines by the EFfCI [EFfCI, 2017] (s. 2.1). For raw materials, limit values (TVC) are used in most cases in the range of 100 cfu/g or ml to 1000 cfu/g or ml, which can be judged as adequate for the cosmetics area. In some cases, however, information about specific microorganisms is not sufficient. "Sterile" raw materials are only offered for selected materials and specialities, where the sterilisation is necessary due to a high contamination or if a high contamination risk is expected. A general demand of this kind of microbiological quality, however, would neither be realistic nor really necessary.

2. Responsibilities of the raw materials producer

2.1 Production / quality of raw material

Raw material quality has an impact on characteristics of the cosmetic product, for instance regarding chemical-physical parameters, cosmetic efficacy, compatibility and toxicology aspects. But there are also influences on the microbiological product quality. Microbial contamination depends upon the origin of the material, the manufacturing process and the transport conditions. Additionally, all aspects of microbiological stability/preservation efficacy of the cosmetic product strongly depend upon a reliable raw material quality, because this stability is closely connected with certain chemical-physical parameters (e.g. pH-value, water-content), the efficacy of antimicrobial agents and further supportive ingredients.

Even though the cosmetic GMP (DIN EN ISO 22716) [IKW, 2020] is directed to the manufacture of cosmetic products as mentioned in the introduction, the GPM ideas can also be used as valuable system for the manufacture of raw materials. Accordingly, raw materials producers as members of the EFfCI (European Federation for Cosmetic Ingredients) have developed a GMP-guideline [EFfCI, 2017], which is even more progressive and has a wider scope than the ISO-norm. Even though this guideline is not a legal requirement, it can be used when asking for a reliable raw material quality (Quality Management System).

The manufacturing process of raw materials needs to define hygiene requirements and to apply respective measures [DGK, 2019], and microbiological controls and approvals must be installed. Besides these requirements, which shall mainly avoid contamination problems and sustain the target counts, an effective preservation has to be ensured. Chemical-physical material-parameters, which are used as preservative system, have to be adequately tested and should be part of the specifications. When using preservative agents, appropriate analyses should be available and the efficacy must be proven in challenge tests [DGK, 2015]. In the case of sterilised raw materials, adequate information must be available about the sterilizing process and control tests. Whenever additives for preservation are changed, this has to be communicated to the cosmetics producer, since this may have an impact on the quality and safety of the cosmetic product (s. 3.1).

2.2. Storage, transport and delivery

Microbiological risks may also appear during the process following the raw material production (storage, packing, transport). Therefore, hygiene measures and controls must be applied here to avoid contamination risks and microbial growth [Müller et al., 2019]. Respective activities are needed to keep pipes, valves and containers clean for intermediate storage and filling of raw materials into containers/sacks and to protect the material. This is of special importance if tank lorries are used for the transport. With external partners engaged for the transport respective hygiene measures and controls must be included in the contracts. Microbiological controls and testing must be defined according to the process-risks to obtain meaningful results.

During the transport, damage to packaging and containers must be avoided. It also has to be observed that depending upon raw material and type of packaging, critical temperatures/temperature changes might lead to problems (e.g. regarding temperature stability of preservative raw materials) or condensed water may appear in containers, which leads to microbial problems.

3. Responsibilities of the cosmetics producer

3.1 Contractual arrangements

The selection of a raw material and of its producer calls for a check of various preconditions according to the cosmetic GMP (DIN EN ISO 22716, Chap. 6) [IKW, 2020], and the delivery conditions should be fixed in written. Part of these activities should be audits/inspections by a qualified person. Microbiological specifications and suitable test methods should be defined in these fixed conditions (s. a. 4.1). Information about the production method should be available as well as the corresponding hygiene measures. Agreements about packaging and transport should be made due to a possible impact on the microbiological quality.

The agreements should bind the raw material producer to inform the cosmetic producer about all relevant changes (e.g. regarding components, production method, preservation, and controls). On the other hand, the cosmetics producers' organisation must ensure that such information is communicated to the relevant expert units in time, to initiate changes of procedures and instructions, to perform new evaluations, to define new instructions, tests and controls (e.g. changing from materials in barrels to tank lorry delivery).

A special situation is given if the raw material is delivered via a trading company. In such case, it is essential as well that above-mentioned conditions are defined and information about respective changes are communicated.

3.2 Income control and approval

Upon delivery of the raw material, the cosmetics producer has to approve the material for the manufacturing process (cosmetic GMP (Chap. 6.5)). Besides the physical/visual inspection (GMP, Chap. 6.3) the approval must be based upon tests which show that the raw material is in conformity with the defined acceptance criteria (GMP, Chap. 9.2 – 9.5). This covers microbiological tests which are part of the quality specifications.

Depending upon the process-reliability and the kind of material/microbiological sensitivity a test-dynamization may be applied for the microbiological controls ("skip lot" method). In any case, such proceeding needs an expert reasoning and written process procedures. It may also be acceptable to use test results of delivery certificates for the approval by the cosmetics producer if certain preconditions are fulfilled (e.g. greed test methods) (GMP, Chap. 6.5.3) [Eigener, 2021].

3.3 Storage and handling of raw materials

The cosmetics producer should establish rules for the storage and use of accepted raw materials. The materials must be protected in an adequate way and the contamination, growth and spreading of present microorganisms must be avoided. From a microbiological point of view, requirements for temperature and duration of stability should be observed as well as the installation of hygiene measures (Müller et al., 2019). The duration of stability, for instance, may be limited for selected preservative raw materials. According GMP requirements for controlling the durability during storage, for retesting and new evaluation (GMP, Chap. 6.7) include microbiological controls if applicable. Hygiene measures must be applied for pipes-systems/flexible pipes, technical installations and equipment and all types of containers, but also material removal, weighing activities and a safe re-sealing of packaging and containers.

Kind and frequency of hygiene measures must be adapted to the type of raw material. Accordingly, microbiologically sensitive materials need a more extensive protection. But even in the case of water-free materials (e.g. oils) that are stored in tanks which are refilled on the residues of the former lot, the storage tank equipment should be cleaned and disinfected in defined intervals.

Additionally, adequate microbiological controls should must be installed during all relevant processes (e.g. checking pipes and tanks, re-tests of materials with respect to the durability of storage, conditions during tank lorry delivery).

It must be observed that sterilized raw materials are only sterile when delivered as intact package. Whenever the packaging material has been opened and parts of the material have been removed, a contamination is possible. Therefore, used packages should not be kept for further use – exceptions are only possible if a limited re-contamination is acceptable (e.g. sterilized colour powder).

3.4 Production process

The ingredients of the cosmetics formula define the product character and mutually influence each other. A defined raw material quality is therefore a fundamental prerequisite for the consistent quality of the cosmetic product. The impact of raw material quality, but also of the production processes/production method on the microbiological product quality and safety has already been underlined [Eigener et al., 2015, Eigener, 2021]. In this context, the focus is, of course, on influences on the preservation of the cosmetic product (additives according to Annex V of the EC-Cosmetics Regulation), but also other antimicrobials and raw materials, which influence the microbiological stability. However, production parameters (e.g. temperature, phase-distribution, pH-values, and the sequence of material addition) are also of importance in this respect, since for instance the bioavailability of preservative additives may dependent upon such criteria.

The manufacturing process of cosmetics is not an aseptic system. Even though higher contamination should be avoided (e.g. through hygiene measures, limit values for raw materials), it is essential that process steps are defined in such way that they do not allow a multiplication of present microorganisms (e.g. heating, preservation). Critical process steps must be avoided resp. be kept under control. Such critical process steps, for instance, result from watery pre-solutions of raw materials (e.g. colours), which are kept for a longer time. Even if the number of microorganisms is low at the beginning a microbial growth may take place during time. Similar problems may appear in connection with raw materials, which contain very few acceptable numbers of microorganisms (e.g. spore formers in thickeners). If these raw materials are part of an unpreserved phase, which is then kept for a critical time period, microbial growth and resulting problems may be found. For such cases, standing times should usually be restricted to maximum 3 hrs. When in doubt, respective control tests have to be applied to define the acceptable standing time.

The importance of the up scaling-phase should be expressly noted here. This phase is used to define the production method for the industrial production, which usually differs from the development phase regarding the process steps and also the raw materials, and accordingly demands for new evaluations and even new testing. In the same way, changing of the production plant must lead to respective alterations (regarding tests, controls, hygiene measures) since usually neither identical raw materials nor processual procedures are employed in such cases [Eigener et al., 2015, Eigener, 2020a].

4. Safeguarding the processes

4.1 Microbiological examinations / controls

Wherever microbiological examinations are employed, adequate methods must be used. This is the case when testing for microbial counts, but also for preservative efficacy testing with raw materials or for hygiene monitoring. Since there are various material types of raw materials (e.g. powders, watery solutions, solid/liquid fatty materials), it is essential to select an appropriate testing method. The tests should enable the total viable count result as well as the exclusion of specific microorganisms, which demands tests with the respective exclusion volume of material. Generally, for raw material testing, the same methods can be used as applied for the cosmetic products (surface method, pour plate method, filtration, enrichment) [Eigener, 2021, Ochs, 1999]. For each raw material a microbiological specification should be available as well as the appropriate examination method. In case of positive results, the microorganisms should be identified in order to

enable the exclusion of specific microorganism and also the root cause analysis of the contamination.

For the microbiological examination of raw materials, an adequate neutralization is essential. Otherwise, false-negative results can be expected because undiluted raw materials as well as preserved raw material-dilutions may cause a growth inhibition effect. Accordingly, also in case of raw material-examinations a pre-dilution (1:10) for the examination is recommended, if possible, to better exclude inhibiting effects. The suitability of the test methods should be proven in respective tests. Microbiological examinations by means of the "dip-slide method" or of direct streaking on solid media must be deemed unsuitable. In both cases false-negative results due to inhibiting effects through undiluted raw material cannot be ruled out.

Irrespective of the selected examination method and target values, the extent of control tests must be defined according to the process risks. Microbiological controls start with the raw materials producer who has to ensure the quality of his products, and are essential in the processes on the side of the cosmetics producer. Controls have to be defined according to the type and the microbiological sensitivity of the material. In the case of microbiologically robust raw materials (e.g. alcohols, fats), regular, frequent microbiological controls can be skipped if a negative test history is available. Raw materials which usually show positive microbiological results, which are preserved or are well known to be sensitive must regularly undergo microbiological control testing. Additionally, controls are essential during processes with well-known microbiological risks (contamination, microbial growth, reduced preservative efficacy).

4.2 Quality management-system (MQM)

Microbiological aspects of cosmetic raw materials are of concern for different processes and make demands on various responsible personnel. This regards the cosmetics producers' organization as well as the raw materials producer. With respect to the fulfilment of microbiological quality and safety requirements, it is essential to enable an information exchange about data, results and knowledge to assess risks in an adequate way and to define effective measures. This way of handling of raw material aspects contributes to avoiding microbiological risks connected with raw materials, which also have to be observed in the microbiological safety assessment resp. the safety report which has to be prepared for the cosmetic product. A sufficient safeguarding of the processes can only be reached through a quality management system. For the microbiological working area, this system is presented in the MQM-system, which includes the GMP-system [Eigener, 2020b]. An MQM-system should therefore be established by the cosmetics as well as the raw materials producer, and this system must, of course, take into account interfaces with used external partners. Thanks to the secured cooperation between the raw material manufacturer and the cosmetics manufacturer, raw material-related failure costs in the area of microbiology can be avoided.

The MQM system includes the definition of all necessary specifications and procedures and also ensures that there is sufficient professionally qualified staff available in the organisation for the microbiological tasks. Not only does this qualification concern the microbiological technical requirements, but also sufficient knowledge of the processes to be able to determine examination methods and effective control points, to enable meaningful examinations, to adequately assess results and risks and to make robust decisions.

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How Can the Right Choice of Packaging Materials Prevent a Loss of Quality in Sun Care Products?

A. Springer, M. Reinelt, M. Jesdinszki, J. Wunderlich

abstract

Sun Care products contain active ingredients protect the skin before, during and after sun exposure. However, these active ingredients can lose their effect due to the influence of light and temperature during storage. To prevent this, packaging can be specifically adapted to the requirements of these products in terms of light protection. In addition, the packaging also protects the products from oxidative influences. An adapted oxygen and water vapor barrier can guarantee high product quality over the storage period. Currently, there is a great demand for sustainable packaging. However, these often lead to compromises in terms of barrier properties and product quality. Current research is determining how the product's requirement for packaging can be reconciled with sustainability. With the help of so-called digital modeling tools, product quality can be predicted over the storage period, thus facilitating sustainable packaging selection.

How sunlight, skin damage and Sun Care products are connected

Sun Care products protect the skin from sunburn, skin cancer and premature aging.

Sunlight has some positive effects on humans. For example, it has a mood-lifting effect by inhibiting melatonin synthesis, can promote blood circulation through infrared radiation and stimulates the skin to produce the essential vitamin D3 (calcitriol).

However, too much sunlight can cause skin damage. The high-energy UV-B radiation in the light spectrum can penetrate into the dermis of the skin. Damage to keratinocytes in the epidermis causes inflammation (sunburn), which reaches its maximum after 12-24 hours. The lowest dose to achieve a perceptible reddening of the skin when irradiated with light of wavelength 297 nm (UV-B radiation) at 21 mJ/cm² is called the minimum erythema dose (MED). However, DNA damage due to strand breaks, photoadducts, or base dimerization due to the formation of free radicals (reactive oxygen species, ROS) is possible from 60% of MED. This damage can lead to skin cancer. Activation of matrix metallo-proteases by UV-A radiation degrades collagen and elastin in the skin, causing it to lose elasticity. This leads to the formation of wrinkles and a thickening of the *stratum corneum* and thus to light-induced skin aging. In addition, UV radiation inhibits sebum production and can thus dry out the skin [1]. The human skin has its own UV protection through the formation of the brown pigment melanin. This pigment is polymerized from the amino acid tyrosine to form eumelanin and pheomelanin. However, it only protects the skin with a sun protection factor (SPF) of 3-10 and lasts for a few months. This protection is not sufficient to spend a long time in the sun in case of sensitive skin types and weather with a higher UV index [2].

Sun Care products with a high sun protection factor (SPF) are therefore ideal for protecting and caring for the skin. Organic or mineral UV filters are contained in the products. Organic UV filters are often derivatives of camphor, salicylic acid or cinnamic acid. They absorb high-energy UV radiation and re-emit it as lower-energy, longer-wave radiation. The concentrations used for the individual substances range from 4% (4-methylbenzylidene camphor) to 10% (e.g. homosalates, benzophenone-3, octocriles) [3].

Although UV filters protect well against sunburn by absorbing the light energy, the molecules themselves can also be damaged as a result. While the natural skin pigment melanin converts nearly 100% of UV radiation into heat, organic filters are far less effective. In the case of octyl methoxycinnamate (4-methoxycinnamic acid 2-ethylhexyl ester), the efficiency level is still 80%, while in some others it is less than 50%. The remaining energy leads to chemical degradation of the active ingredients. On the one hand, this can reduce the effectiveness of the product, and on the other hand, it can lead to allergic reactions and hormone-like effects [4,5,6].

Special requirements of Sun Care products for packaging

The absorption of UV radiation takes place not only on the skin, but often already in the packaging. UV rays can penetrate the packaging and damage the UV filters for example in retail lighting on the sales rack, through the window in the bathroom or in direct sunlight on the beach. The high temperatures that develop in the packaging in the process also accelerate the

chemical degradation reactions. Therefore, photoprotective barriers are very important for Sun Care products to protect the active ingredients and the consumers.

Oxidation reactions can take place faster under the influence of light than in the dark. In particular, autoxidative processes can be initialized by high-energy light such as UV radiation. The exclusion of UV light, e.g. by using effective UV filters in transparent packaging, can provide product protection and increase quality retention.

Many plastics already have reduced light transmission in the UV-C and UV-B range (see **Figure 1**). Transmittance is a measure of the light transmission of a material at a given wavelength. It can be used to compare the ability of different plastics to absorb UV radiation. For example, polymethyl methacrylate (PMMA, acrylic glass) absorbs UV radiation completely up to 235 nm, while polyethylene terephthalate (PET) still shows complete absorption at 310 nm [7].

PET and polypropylene (PP) are commonly used for bottles and tubes of cosmetic products. Acrylic glass (PMMA) is often used for transparent packaging such as jars, powder compacts and lipgloss tubes. However, oxidation reactions and active ingredient degradation can occur because these materials are transparent to most of the UV-A radiation between 280 to 400 nm.

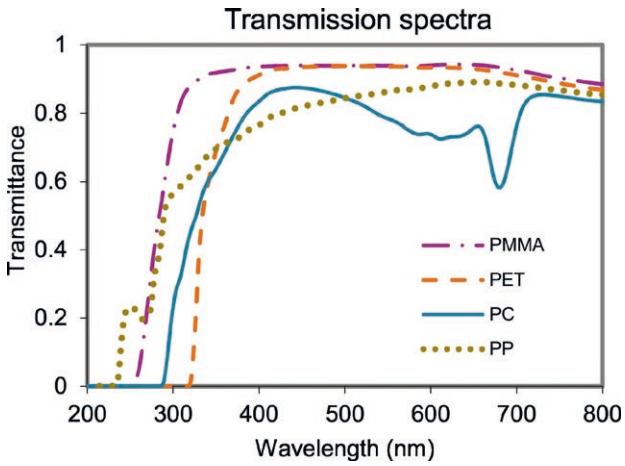

Fig. 1 Transmission spectrum of the plastics PMMA, PET, PC and PP [7]

Mineral or organic UV absorbers, similar to sunscreen products, can also be incorporated into packaging to increase light protection. Inorganic substances are used, for example, as nanoparticles of titanium dioxide, zinc oxide and iron oxide. Benzotriazole or benzophenone absorbers, for example, can be used as organic additives for plastics. Since sunlight primarily emits UV radiation from 290 nm to 400 nm, UV filters must absorb the radiation almost completely across the entire wavelength spectrum. Although Sun Care products are preferably purchased in the summer, they are available in stores

throughout the year. To ensure effective product protection even under retail lighting, UV filters for plastic packaging should maximize absorption of UV light, especially at 365 nm, the main UV emission peak of fluorescent lamps. Although these agents can be incorporated into the plastic, this often leads to disadvantages during recycling. Applying a coating layer containing UV filters to the surface of the packaging can ensure product protection and sustainability [8,9].

To determine the effect of different UV filter coatings, UV filter active ingredients were incorporated into a coating and doctored onto a plastic film. A barrier film was used for the coating (PET 12 µm with 5 µm EVOH). Polyvinyl lactate Vinnapas 4fs (Wacker Specialities) was used as coating base. The following procedure was used to prepare the coating solutions: 5 g of coating base was dissolved in 50 ml of solvent (ethyl acetate). The UV filter substances were added to the varnish solution in the amounts of 15% w/w - based on the dry masses - and also dissolved. The film was coated in DIN A3 format on the Coating Unit CUF5 coating machine from Sumet-Messtechnik at the Fraunhofer IVV. The coatings with the different UV filter substances were applied in defined layer thicknesses to the barrier film with a blade and then dried in the coating machine [10].

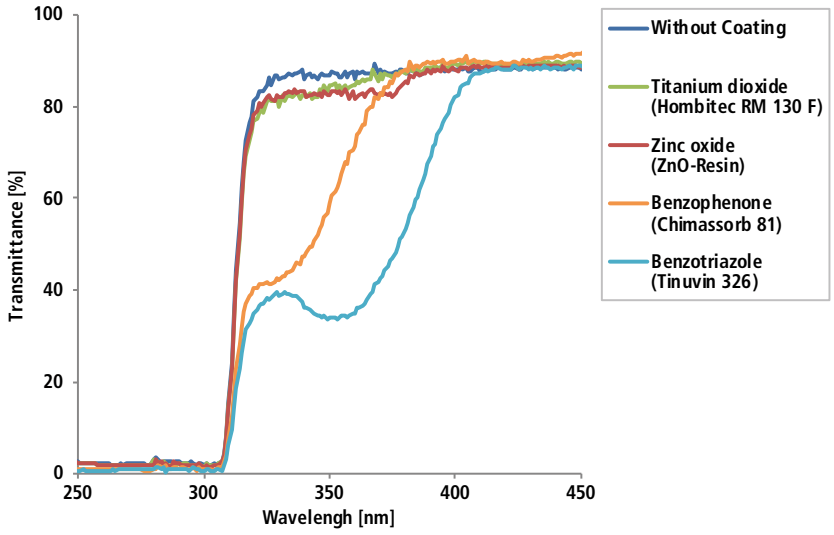

Fig. 2 Transmission spectra of various UV filter films (UV filter coating with 15% active ingredient content coated with a film thickness of 0.12 mm on carrier film); measured using a spectrometer with integrating sphere device.

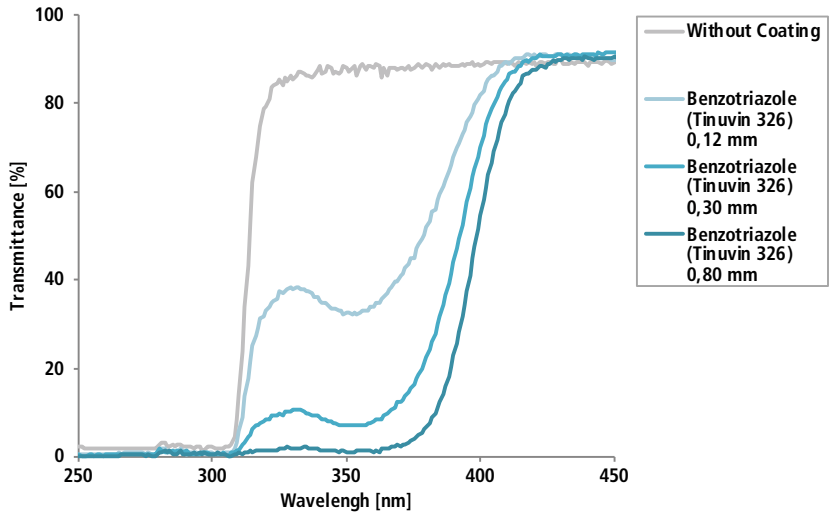

Fig. 3 Transmission spectra of UV filter films with benzotriazole coating (Tinuvin 326) in different film thicknesses (UV filter coating with 15% active ingredient content coated on carrier film in film thicknesses from 0.12 mm to 0.80 mm); measured using a spectrometer with integrating sphere device.

The light transmission was investigated spectroscopically by means of transmission measurements. The materials were placed in the beam path of a spectrophotometer with integrating sphere (Ulbricht sphere) and examined in the wavelength range of 200 - 800 nm at intervals of 1 nm. With the aid of the integrating sphere, not only the directly transmitted radiation component but also the scattered light was focused and detected.

Figure 2 shows that Tinuvin 326 exhibited the best UV filter effect compared to the other UV filter substances and absorbed a large proportion of the light up to 400 nm over a wide wavelength range.

Subsequently, the resist film thickness was increased in several steps and thus more UV filters were applied per area in order to increase the absorption of the UV filters. It can be seen, that with increasing film thickness, the light transmission in the UV range decreased (Figure 3).

To analyze the light transmission spectrum under trade illumination, a DAD sensor was inserted into the package and the difference spectrum between the trade illumination inside and outside the package in the range of 200 - 800 nm was evaluated (Figure 4). The analysis of the light transmission spectrum of the films with the benzotriazole varnish coating (Tinuvin 326) in concentrations from 0 to 15% was carried out with exposure to daylight fluorescent tubes with an irradiance of 4 W/m2 and an additional UV tube with a film thickness of 0.8 mm. Compared to the film without coating, the UV filter film transmitted only 3.7% of the irradiance [W/m²] between 300 and 380 nm.

The light barrier in packaging is an important aspect for product protection, as it protects the product from photooxidation

and light-induced active ingredient degradation and can thus extend shelf life.

Oxygen and water vapor permeability of cosmetic packaging

In addition to the light barrier, oxygen and water vapor barriers are also essential for maintaining the quality of cosmetic products [11,12].

A suitable oxygen barrier can protect products from oxidation. To preserve the moisture and regenerative capacity of the skin, unsaturated fatty acids, such as γ-linolenic acid [13,14] and antioxidants, such as carotinoids [15] are essential. These can neutralize free radicals and build up the skin's protective barrier. However, atmospheric oxygen can damage the sensitive ingredients, which in the case of unsaturated fatty acids can lead to rancid, fishy, bitter or pungent off-flavors. Antioxidants lose their regenerative effect through oxidation. The simultaneous presence of light leads to photooxidation, which significantly accelerates the oxidation rate. Photosensitizing substances can accelerate this reaction furthermore, for example chlorophyll. Due to its lipophilic properties, chlorophyll can pass into the cosmetic ingredients during oil extraction from plants or during the production of plant extracts from herbs. Many other factors, such as the large interface in emulsions, increase the oxidative susceptibility of the cosmetic product [16,17].

Water vapor entering an anhydrous product through the packaging can lead to hydrolysis of the triglycerides to free fatty acids. Free fatty acids exhibit a pungent, rancid, musty or soapy aroma. Diffusion of water vapor from water-containing products through the packaging into the atmosphere can lead to weight loss, which may result in non-compliance with the weight or volume declaration on the product or in instability of emulsions due to a change in the ratio of water to oil phase.

By providing an adequate oxygen and water vapor barrier, the ingredients and formulation can be protected with the help of the packaging.

Typical barrier materials for tubes, bottles and jars contain EVOH interlayers. In addition, ultrathin metallizations, ceramic layers of ultrathin silicon oxide, and barrier coatings with nanomaterials are also possible. The high density of the polymer, low mobility of the molecular network and intermolecular interactions, such as hydrogen bonding, reduce gas movement and provide a high barrier. It should be noted that different barrier materials may also have different permeabilities for oxygen, water vapor, or even aromatic substances. Due to the different affinity of the gas molecules to the polymer network, they can dissolve in the packaging in different strengths and migrate through it.

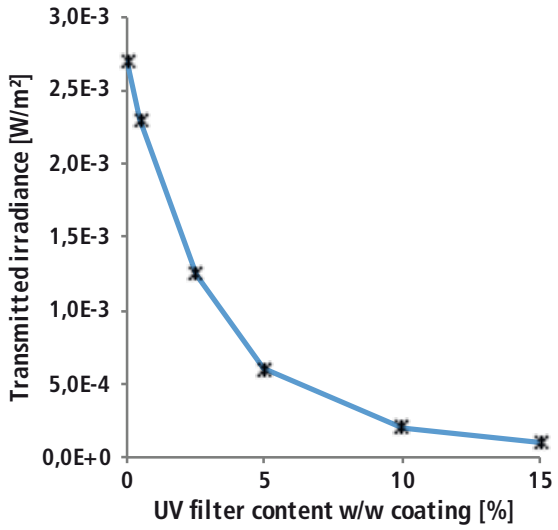

Fig. 4 Transmission energy of wavelengths between 300 and 380 nm of daylight fluorescent tubes and UV tubes with an irradiance of 4 W/m2 through UV filter films with 0%, 2.5%, 5%, 10% and 15% Tinuvin 326 with a coating thickness of 0.8 mm

Barrier properties in terms of oxygen, carbon dioxide and water vapor permeation are important criteria for product protection, as they can protect the product from loss of inert gas or oxygen penetration and extend microbiological and oxidative shelf life. Plastics commonly used in packaging are shown in Figure 5 with their respective normalised water and oxygen permeabilities. Depending on the sensitivity of the packaged products, the packaging material should be selected to provide the products with the protection required in each case [18].

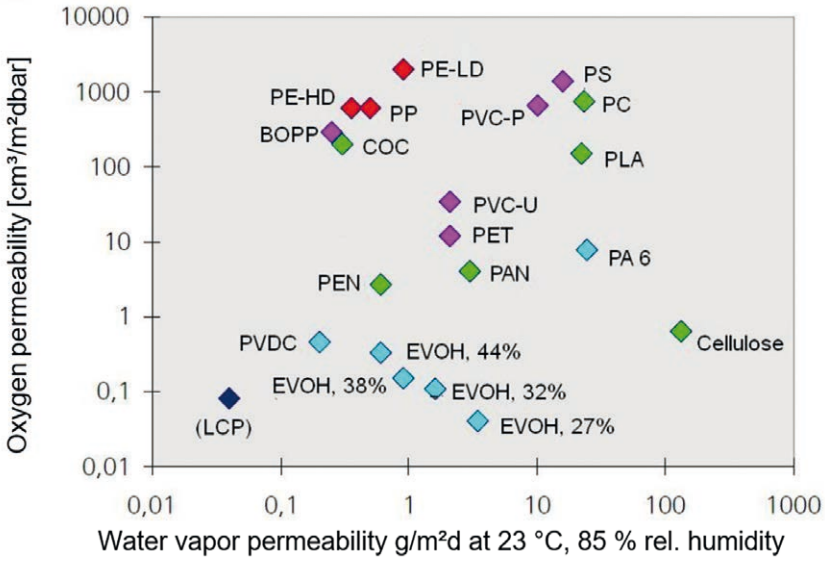

Fig. 5 Water vapor and oxygen permeabilities at 23 °C and 100 µm film thickness for bulk plastics (red, magenta) and special packaging plastics [18]

The investigation of the permeability of flat as well as formed packaging materials can be carried out in various ways. Oxygen permeability measurements are often carried out in accordance with DIN 53 380-3 using an oxygen-specific carrier gas method. Here, the amount of oxygen that has passed through the sample is detected by an electrochemical sensor. The measurements are typically carried out at 23 °C and 50% relative humidity. To determine the CO_2 permeability of the packages, the gas composition in the packages is tested after storage in a 100% CO_2 atmosphere. Since the packages are filled with air (21% O_2 and 79% N_2) before storage, CO2 permeates into the package due to the partial pressure gradient, and N_2 and O_2 permeate out of the package in the opposite direction. With the aid of mathematical calculations (gas permeation kinetics), the gas permeabilities can be calculated from the measured values. The measurements are taken at 23 °C and 0% relative humidity. The water vapor permeability test is carried out in accordance with DIN 53 122-1 (gravimetric method) at a temperature of 23 °C and a relative humidity gradient of 85% to 0%.

Product shelf life when using sustainable packaging

To protect sensitive products from oxygen, they are often packaged in multilayer film packaging under vacuum or inert gas. These multilayer plastics are made of at least two materials and do offer higher barrier properties against oxygen, water vapor, light, organic substances and other environmental influences. However, multilayer packaging made of different materials often also has poorer recyclability.

With greater environmental awareness, recyclable, biodegradable and sustainable packaging is being demanded by consumers. Glass containers offer good recyclability, but due to their weight they increase CO_2 emissions during transport and pose a risk to the consumer due to possible breakage. Therefore, plastic remains the material of choice.

However, recyclable monomaterials such as PE, PP and PET offer lower barrier properties than multilayer packaging. The product's quality can be compromised by the influence of light and oxygen. Therefore, special consideration must be given to the oxidation sensitivity of the bulk, the light and gas permeability of the packaging material, and the wall thickness of the packaging when selecting a packaging material for the desired shelf life. Further research is needed to develop suitable packaging that fully meets the requirements of sustainability, recyclability and product quality preservation.

In order to constantly gain new insights, scientists at the Fraunhofer Institute IVV are constantly ongoing research in the areas of process engineering, packaging, product impact, recycling and product shelf life. Digital methods, such as chemical/physical shelf life models (so-called "shelf life modeling"), can be accelerate development cycles. Thereby, the shelf life of products can be modeled as a function of the packaging and storage conditions.

In summary, the wrong choice of packaging materials can deteriorate product quality. If light protection and oxygen barrier are insufficient, chemical degradation and (photo-) oxidation of active ingredients may occur. Inadequate water vapor barrier may result in product weight and stability change. However, proper selection of packaging materials can contribute to longer shelf life and improved quality of the product.

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VINCENTZ

The History of Sun Protection: New Findings and Old Myths

K. Stanzl

abstract

The history of sun protection is a recurring theme and publications are being written about it. The most recent publication on this topic is by two English physicians and is entitled: The History of Sunscreen: An updated view [1]. So this is about the history of sunscreen. Unfortunately, many of the authors fall for old myths again and again and simply copy information that was once wrongly put into the world. This article is an excerpt from my dissertation on the history of sunscreen, which I am working on under PD Dr. rer. nat. Beate Ceranski at the Department of History of Science and Technology at the University of Stuttgart.

It is indeed gratifying that natural scientists repeatedly take up the task of recounting the genesis of sun protection. Unfortunately, a completely false picture emerges when the context in which a particular event takes place is disregarded and the past is not embedded in the social and cultural situation of that era. It becomes particularly bad when only digital databases are searched with English keywords and it is left to the computer's algorithm to identify the relevant publications. The narrative of the emergence of light protection is more than just a string of facts and figures.

Unfortunately, once data has been put into the world, it is rarely challenged but accepted as fact. Yet, as we have seen in the Corona pandemic, it is essential that experts communicate the knowledge generated to laymen. This is necessary so that the know-how available at the time becomes comprehensible to all and is substantiated. But if knowledge is deliberately put into the world wrongly or unconsciously wrongly by these authorities, the incorrect knowledge solidifies and becomes part of a general, misconceived view. One can see this very clearly when the emergence of the first commercial sunscreen brands is reported. Depending on which country the report comes from, the order of the products entering the market varies [2].

In the German edition of Wikipedia, for example, there are a number of contradictory statements in succession. Moreover, the appearance of modern sunscreen is placed in 1933, whereas in the above-mentioned article by the two doctors, the first UV-B filters were produced in 1928, their efficacy and toxicological safety were established in 1956 and the development of the sunscreen factor was started in 1974. They go on to write that the first commercial sunscreen product came on the market in 1933, contained para-aminobenzoic acid and was marketed by Eugene Schueller under the name Ambre Solaire.

All these statements are false and could have been prevented by accurate work, as taught by the science of history.

I would like to set the record straight about some of the myths and misinformation and explore the question of why and under what conditions sunscreen products became established on the market.

If we look back into the past, we find that the history of sun protection goes back several thousand years. On papyrus rolls we find references to substances that contained extracts of rice and jasmine [3]. Modern analysis has shown that rice contains γ-Oryzanol, an UV-absorbing substance. In the 19th century, physicians had discovered that sunlight can trigger skin diseases. Moriz Kaposi (1837-1902) described xeroderma pigmentosum in 1870, but did not conclude that light was responsible, which was done by the German dermatologist Paul Gerson Unna (1850-1929) in 1894. Jonathan Hutchinson (1828-1913) discovered prurigo aestivalis in 1878 and the Stuttgart physician Theodor Veiel (1848-1923) discovered polymorphous light eruption in 1887. As a preventive measure against these diseases, doctors prescribed coloured pastes to their patients to protect them from the dangerous rays of the sun. Veiel found out through experiments that red cloth best kept the damaging rays away and therefore recommended to a woman who had fallen ill that she should wear a red scarf when leaving the house. Both approaches were unpleasant for the people affected. Therefore, for the first time at the end of the 19th century, a systematic search was conducted to replace the pastes with transparent products. This is when the story of commercial sun protection begins.

Sun protection to prevent sunburn and to achieve a tanned skin only plays a role in the western world. The reason for this is genetically determined. Light-skinned people need to protect themselves more from the sun's rays than dark-skinned people. Moreover, from the mid-1920s onwards, the ideal of beauty for these people changed and the seamless brown replaced the distinguished pallor. But in order to understand the historiographical development, we first need to look at the basics.

Basics

A new understanding of light began in 1671, when Isaac Newton (1643-1726) established his ideas about light and colour [4]. He had broken down visible light into its individual components with the help of a prism and discovered that colours are not formed in the prism. He had thus revolutionised the concept of light. It would take another 100 years before it was recognised that there were other rays outside the visible range that had comparable properties to visible light but could not be perceived by the human eye. William Herschel (1738-1822) discovered infrared radiation in 1800 and Wilhelm Ritter (1776-1810) discovered UV radiation in 1801 based on analogy considerations.

In the beginning, the study of the rays found by Ritter focused on their stimulation of chemical reactions. Joseph Louis Gay Lussac (1778-1850) and Louis Jacques Thénard (1777-1857) showed in 1809 that sunlight converts hydrogen and chlorine into hydrochloric acid gas. In the early 19th century, the British pioneer of photographic technology Thomas Wedgewood (1771-1805) and the chemist Humphry Davy (1778-1829) exposed silver salts to light and discovered the sensitivity of silver iodide, which was later used for photography.

In addition to various chemicals, the skin also reacts sensitively to light, and an excess of light causes sunburn, which the English physician Robert Willan (1757-1812) called 'eczema solare' in his book 'On Cutaneous Diseases' published in 1808 [5]. Everard Home (1756-1832) showed in 1821 that sunburn is not caused by the heat and that the term sunburn is therefore incorrect, as it is not a burn [6].

Until the 1920s, the ideal of beauty was radiant skin that was not tanned by the sun. To achieve and maintain this condition, the upper classes mostly stayed indoors towards the end of the 19th century. Skin tanned by the weather was the characteristic of people who had to work outdoors, like farmers and sailors, and was the distinguishing feature of the lower classes. Negative attitudes in the USA against dark-skinned contemporaries contributed to the preference for light skin colour, which was also associated with physical and social comfort. Swimming costumes and sportswear covered more than 80% of the body. Light skin was considered a sign of beauty and wealth. Up until that point, sunbathing was a medicine prescribed by doctors to cure tuberculosis and rickets.

The industrial revolution had driven many people from the fields to the factories in the course of the 19th and at the beginning of the 20th century. Working people who had previously been outdoors and were tanned suddenly had a fair complexion. The upper classes restored social distinction by exposing their skin to the sun and acquiring a tanned complexion. The ideal of beauty was reversed. Now, tanned skin was recognised by those who were able to maintain a healthy and active lifestyle with plenty of free time.

In a 1936 cartoon, a white-skinned newcomer on the beach is told that it will take a few days before she looks like her friends. The caption reads:

"Don't worry, Darling, you'll look quite respectable in a day or two"

A deeply tanned woman in a white bikini and, to emphasise the contrast, a light-skinned woman with a bathing cap in a black swimming costume are standing opposite each other. The well-known fashion magazine Vogue, whose readers belonged to the upper classes, wrote:

"The 1929 girl must be tanned".

In order to avoid sunburn and still come home with a tan, cosmetic products were developed that block the rays that cause sunburn and allow the tanning rays to pass through. The knowledge of which range of the sun's rays causes skin redness goes back to the German physicist Karl Wilhelm Haußer (1887-1933). Haußer, a student of the Nobel Prize winner Philipp Lenard (1862-1947), took over the physical-medical laboratory of the company Siemens & Halske in Berlin in 1919. Shortly after joining, he fell ill with pulmonary tuberculosis and went to a heliotherapeutic sanatorium in Davos for almost a year. Tuberculosis was a frequently fatal disease at that time, whose pathogen Mycobacterium tuberculosis was discovered by Robert Koch (1843-1910) in 1882. Niels Rydberg Finsen (1860-1940) used the effect discovered in 1877 that sunlight kills bacteria to cure skin tuberculosis.

The curative findings of light were exuberantly celebrated at the beginning of the 20th century and attempts were made to cure other diseases, such as pulmonary tuberculosis, with sunlight. During his time in the Swiss Alps, Haußer observed with interest that: "*long glacier walks of several hours in the afternoon hours with the sun burning [remained] without consequences, while a few days later a short stay in the snow at midday caused a violent sunburn to develop*" [7].

The crucial point of this story was that Haußer was a natural scientist who had observed a problem but was dissatisfied with the existing knowledge about the origin of sunburn. He therefore wanted to investigate the phenomenon with the help of scientific research. As an experienced radiation physicist, Haußer knew that the radiation intensity of UV-B light changes during the day and decreases significantly towards the afternoon, while the power of UV-A remains the same throughout the day. As a trained physicist, he defined two parameters, namely erythema formation and pigmentation, which needed to be investigated, and he asked himself which radiation range was responsible for sunburn. Back in Berlin, he undertook the first study that showed the dependence of erythema and pigmentation on the wavelength of the exciting radiation. Here, too, chance helped. Only at Siemens & Halske it was possible to build such a powerful device with which Haußer and his colleague Wilhelm Vahle could carry out their measurements.

They obtained a maximum at 297 nm and a second one at 254 nm for the erythema-forming wave range. (Graph) They found out that there is a difference when erythema is produced with relatively long waves - about 297 nm - or shorter wavelengths - about 254 nm. In the first case, it takes longer for the redness to develop and it slowly subsides and is replaced by 'significant pigment deposition', whereas in the second case the reaction takes place in a short time and the effect is reduced or absent. They showed that UV light with a wavelength around 297 nm is more effective in pigmenting the skin, while the shorter wavelengths cause reddening and possible blistering [8] **(Figure 1)**. The peak at 254 nm is irrelevant for life on Earth, as rays with a wavelength of less than 280 nm are blocked by the ozone layer in the atmosphere. In the long-wave range, only the lines of 334 nm and 366 nm were available to them through the spectrum of the mercury vapor lamp, as the Hg-vapour lamp did not emit a continuous spectrum. At 334 nm, no success was achieved even after hours of irradiation. However, at 366 nm they found a clear erythema in a worker with sensitive skin after 5 hours of irradiation, after all previous attempts in people with normal skin colour had been unsuccessful. In their opinion, the irradiation energies of 297 nm to 366 nm are in a ratio of 1:1000 and an erythema with long-wave UV radiation can only be produced in people with sensitive skin. With the lines in the visible range of 405 nm and 436 nm available to them, no reddening could be achieved even with high energy. Haußer and Vahle noticed that the redness produced at 366 nm quickly changes to a brown colour.

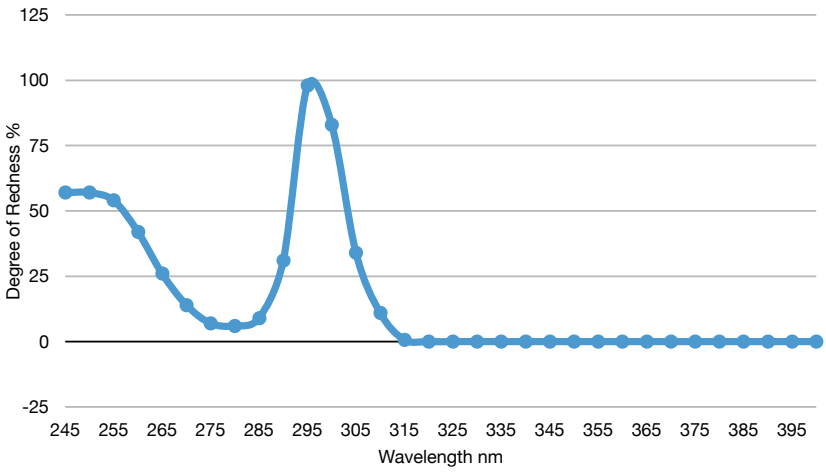

Fig. 1 Dependence of Lighterythema of the wavelength of emitted radiation

With this knowledge, it was now possible to search specifically for substances that absorb radiation in the 297 nm range. However, the first sun protection products suitable for practical use had already been successfully developed without this knowledge.

The first transparent sun protection products

Towards the end of the 19th century, the Stuttgart dermatologist Friedrich Hammer (1860-1943) was surprised to find that sunburn had not yet received much attention from a dermatological point of view. He searched the literature and came to the conclusion that the little he found was based on the erroneous idea that heat rays were responsible for its development. In 1891, Hammer described the difference between eczema caused by chemical rays and eczema caused by heat rays. Heat rays cause reddening of the skin that disappears within minutes, while sunburn forms on a spot of skin that has been hit by light with an abundant content of ultraviolet rays. After a few hours, an intense reddening of the skin develops at this exact spot. The erythema is always followed by pigmentation. He concluded that it must be the chemical rays that cause the skin inflammation [9]. He tried to find out if there were any transparent substances that could prevent the erythema when applied to the skin. He experimented with quinine dissolved in sulphuric acid, which he worked into glycerine at a rate of 10%. In his own experiments, he found that the quinine ointment he had made worked better than cold cream, glycerine or paraffin, both in sunlight and with artificial light [10]. However, his suggestion had the disadvantage that the sulphuric acid used to dissolve the quinine led to an undesirable skin reaction. Therefore, the Hamburg dermatologist Paul Gerson Unna (1850-1929) enthusiastically took up the idea of the pharmacist Carl Mannich (1877-1947), who suggested to him easily water-soluble, colourless coumarin derivatives for sun protection. Shortly after his habilitation in 1907, Mannich had begun to systematically search for substances impermeable to UV rays. His work was successful, and together with Franz Zernik (1876-1941) he applied for a patent in the USA with the simple title "Light Filter". The substances protected by the patent were particularly suitable for protecting textiles, paper and oil paintings, but also protected human skin from sunburn. (US Patent 1,099,710 granted on 9 June 1914). A comparable patent was granted in Germany to the Berlin company of Kopp & Joseph. (DRP 253 334). Kopp & Joseph used the compounds in their products Zeozon and Ultrazeozon, as Unna confirmed in a publication of 1911 [11].

Zeozon and Ultrazeozon are probably the first commercial sunscreen products that contain a substance that blocks UV rays and can be applied transparently to the skin.

After the First World War, Josef Maria Eder (1855-1944) and Leopold Freund (1868-1943) succeeded in developing alkaline naphtholsulfonic acid salts, which have a very strong protective effect over the entire ultraviolet range up to the visible light. A preparation containing this substance in 2-4% in lanolin was Antilux [12]. Eder was granted a patent in 1923 (DRP 379 699)

for a: "*Process for the preparation of light protection preparations to prevent the harmful effect of ultraviolet rays, characterised in that neutral or alkaline reacting salts of naphthol sulphonic acid, or naphthylamine sulphonic acid or its salts or other blue fluorescent naphthalene derivatives, or the analogously composed derivatives of anthracene with or without the addition of alkaline acting substances are mixed with a base or the said bodies are dissolved in the latter.*"

The development of filters continued, and three years later P. S. Meyer and Siegfried Amster confirmed the light-protective effect of tannin [13].

Sun protection products in the 1920s and 1930s

When tanned skin had established itself as a beauty symbol in the USA, the first sun protection product appeared on the market there in 1928. After Haußer and Vahle had determined the wavelength responsible for sunburn of the skin, it was now only necessary to find substances that absorb in this wavelength range. Emil Klarfeld (1900-1963), as head of research at the company Lehn & Fink, used salicylic acid benzyl esters and benzyl cinnamic acid esters in a product that the company marketed under the brand name Dorothy Gray **(Figure 2)**. The advertising for Dorothy Gray Sunburn Cream explicitly states [14] that:

"The creamy lotion actually prevents sunburn by absorbing the part of ultraviolet ray which is responsible for the burning."

During the period of the Weimar Republic (Germany's government from 1919 to 1933, the period after World War I until the rise of Nazi Germany), the rise of sunscreen began in Germany. One of the reasons was that there was a need to spend free time in the fresh air cycling or hiking, mountain climbing or swimming. Since the constraint of the Wilhelmine dress code had disappeared, these activities could take place in a more relaxed outfit and therefore protection was needed for the now uncovered parts of the skin. Freund said in 1925 that one could speak of a 'general hygienic light fanaticism' and that the fashion was a tanned complexion. Therefore, from his point of view, it was necessary for doctors to deal with this topic [15]. At the beginning of the 1930s, more than 29 brands were on the market in Germany and their effectiveness was examined by Richard Hahn of the Dermatological Clinic of the University of Gießen. In his opinion, products were thrown on the market and advertised with great propaganda, whose performance in practice was judged very differently. Therefore, he set himself the goal of getting a clear picture of the most common light protection ointments [16]. He applied the products to the back of his test subjects and irradiated them with a mercury quartz lamp for half, one, one and a half, two and two and a half minutes. Hahn then assessed the degree of redness of the skin compared to the untreated area. The mean value of all measurements provided the erythema index, which was 50.3 for the untreated skin area. As the best product, he determined Ultrazeozon with a value of 0.3.

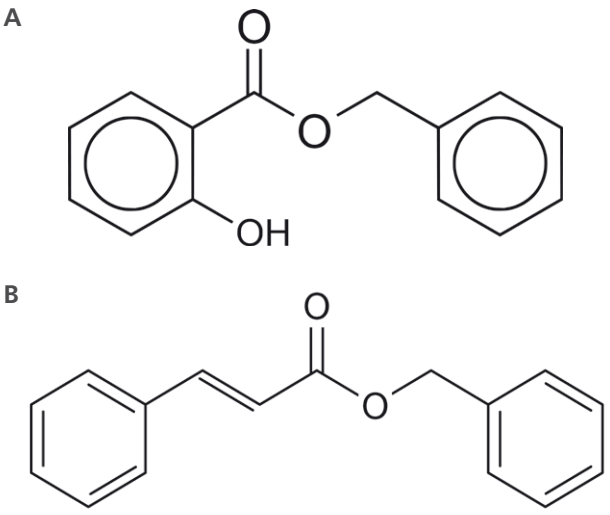

Fig. 2 **A** Salicylic acid benzyl ester total formula: $C_{14}H_{12}O_3$
B Benzyl cinnamic acid ester total formula: $C_{16}H_{14}O_2$

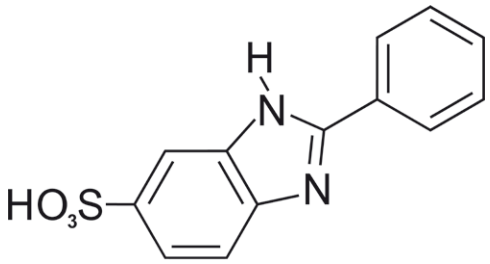

Fig. 3 Phenylbenzimidazolesulfonic acid (Novantisolsäure)

Research into new light filter substances continued unabated and the physicist Erich Merkel (1886-1974) and the chemist Christian Wiegand (1901-1978), who worked for IG Farben in the physical laboratory at the Elberfeld plant, found Phenylbenzimidazolesulfonic acid **(Figure 3)** as an effective filter substance, for which a patent application was filed. (DRP 676 103; US Patent 2,104,492). IG Farben founded a subsidiary called Drugofa to market a product with the active ingredient under the name Delial. The product was intensively promoted and a novel campaign consisting of television commercials' and an open air concert was created. The so-called 'Delial truck' was to bring the uniqueness of the new product closer to the sun-seekers. A film projector with two large loudspeakers, which had a range of 1 km, were mounted on a truck, which also carried its own power generator. In sound and vision, consumers were convinced that now really no one needed to fear the sun. The events were held on the beaches of the North and Baltic Sea. In advertisements the slogan was advertised as follows [17]:

"Pale faces become rare
Delial
Tanning sunscreen ointment. No sunburn and still tan"

The development in France differed from that in Germany. There, after only a few months in office, the socialist government under Léon Blum introduced a two-week statutory holiday entitlement in July 1936. August 1936 was thus the starting point of the annual holiday season and is referred to in French historiography as the beginning of mass tourism [18].
Although Eugène Schueller, the owner of the company 'Société Française des Teintures Inoffensives pour Cheveux', which he renamed L'Oréal in 1939, was opposed to paid holidays, he knew how to capitalise on them. There is a myth that Schueller, a chemist who was a keen sailor and always got sunburn, developed a cure for it himself. The fact is, however, that he failed and therefore commissioned his laboratory to work on the subject. It took several months for their technical director to find an effective substance that blocked the ultraviolet rays. It was the same substance that Klarfeld had already used in Dorothy Gray's Sunburn Cream - salicylic acid benzyl ester. To ensure its effectiveness, the company tested the product on five volunteers on the Côte d'Azur. He called the sunscreen oil Ambre Solaire, which was meant to evoke the amber hue of a tan, and the scent of rose and jasmine meant holidays for the French from 1937 on. The bottle with its recessed grip was easy to grasp and did not escape from fingers slippery with suntan oil. The first slogan sums up the promise of the product:

"Brunir sans brûler" - "Get brown without burning".
"Le hâle c'est de la santé accumulée pour l'hiver.
Je brunis cinq fois plus vite et sans brûlures avec Ambre Solaire."
"A tan is healthy for the winter.
With Ambre solaire I tan five times faster without burning"

said the brand's first advertisement in 1937, and the first jingle, "Ta-TiTa-Ta", rang out on the airwaves of Radio Cité. But it was not until the "Trente Glorieuses", the thirty glorious post-war years, that the French began to flock the beaches. The amber-coloured sunglasses, popularised in the fifties by the famous pin-up Suzy and her bikini, which every outlet had to present in a life-size cardboard box, became synonymous with holidays, seduction and pleasure.

"Soyez insolée, mais non rissolée.
Be suntanned, but not burnt"

the ad proclaimed. The ad showed a young woman in a bikini that had just come into fashion. The advertising slogan was similar to that of Delial.

On the other side of the world, in Australia, the young chemist Milton Blake started working on protective products because of the sunny climate **(Figure 4)**. He had read the 1925 work of Meyer and Amster on the UV-absorbing effect of tannin and subsequently spent four years developing a product containing 10% tannic acid. The work was tested and found to be good by Kerr Grant, a professor of physics at the University of Adelaide. Hamilton's Sun-burn Cream was born.

Fig. 4 Milton Blake (left) in picture

Towards the end of the 1930s, companies in Europe, the United States and Australia had taken into account the change in consumer and leisure behaviour and developed a market for sun protection products. The effective filters were substances that absorbed in the UV-B range. Klarfeld took the first step in the USA with salicylic acid and cinnamic acid ester compounds, which are still used today. L'Oréal copied this approach and IG Farben developed a new water-soluble substance, which is also still in use today. Cut off from what was happening in Europe and the USA, Blake went his own way and used tannic acid, which was difficult to process.

The next step in the development of sun protection in the USA was taken during the Second World War by the US Army, which was looking for a product with which life rafts in aircraft had to be equipped. It was to protect pilots who were shot down over the Pacific and survived the crash from the scorching sun. In December 1942, the American Air Force commissioned the Council on Pharmacy and Chemistry to find a remedy for sunburn. The US Army Air Forces submitted the criteria for the product and a collaboration was agreed with General Electric's Lighting Research Laboratory in Cleveland, Ohio. The laboratory, under the supervision of the physicist Matthew Luckiesh (1883-1967), was ideally equipped to carry out quantitative spectral measurements and to clarify all physical problems in connection with the compounds to be investigated. Despite the high time pressure, the development at GE was carried out systematically. The desired protection could be achieved by using a red petroleum jelly, which did not cause any reddening even after 20 minutes of irradiation. The scientists also found on this occasion that phenyl salicylate 10% incorporated in a cream showed excellent effects.

Many publications on the history of sunscreen say that, as a member of the Air Force, Benjamin Green (1896-1982) developed the greasy ointment for his fellow soldiers. This beautiful anecdote must be contradicted. Green, who worked as a phar-

macist for GE, left the company in 1943 and moved to Miami Beach to take over a pharmacy. Green saw a market opportunity, when he watched people in southern Florida exposing themselves to the sun without protection, and improved his former employer's formula by adding cocoa butter and other ingredients. He tested each new batch on his bald head. After many attempts, he was finally satisfied with the formulation and searched for a suitable name. He found it in the word for the skin tone he wanted to achieve Coppertone **(Figure 5)**. He created the labels himself and the first Coppertone product was sold to a trader on the beach. The label was decorated with an Indian head and the text read:

"Don't be a paleface".

The sun protection factor - a concept is born

In almost all publications on the subject of light protection of the skin, either the German physicist and meteorologist Rudolf Schulze (1906-1974) or the Austrian chemist Franz Greiter (1919-1985) are referred to as the inventors of the sun protection factor. Before these two, however, Americans had already introduced a definition for the protective effect of sun products. Harold Franics Blum (1888-1957) and his colleagues at the National Medical Research Institute in Bethesda, Maryland, were also approached by the US Army to find a sunscreen product that could be packed with life rafts. In order to speed up implementation, the US Army had opted for parallel development. An approach that is very common for the military sector. Their search for an existing method to determine effectiveness was unsuccessful. They therefore developed a method that gave them the ability to compare products. In order to be able to do this, they needed an endpoint for testing that could be easily determined. For them, this marker was a just visible redness caused by UV radiation. Other researchers before them had already called this value the minimum erythema dose (MED). For monochromatic radiation, the energy Q_λ required for this is the product of the intensity $I_{0\lambda}$ irradiated onto the surface per unit time.

$$Q_\lambda = I_{o\lambda} t_\lambda \quad (\lambda = \text{Wavelength})$$

As a measure of the effect of a product, they defined the quotient of the energy required to produce a comparable erythema from protected (Qp) to unprotected skin (Q). This ratio, or the time tp and t required for this, is identical, as can be seen from the above formula, since the intensities are the same, and was defined by them as

$$P = Q_p / Q = t_p / t$$

and described in formula form. The unspecified letter 'P' probably stands for 'Protection'. Blum et al. also described a method of determining the value of P. They applied 90 mg of substance to an area of 36 sq. cm, which results in 2.5 mg per sq. cm

Fig. 4 Original Coppertone product portfolio with the logo of the head of an Indian chief.

and, at a density of 1 g/cm^3, leads to a layer thickness of 25 µ The concept of the light protection factor was born and the basic idea for its determination was described [19].

On the other side of the American continent, a photobiologist from Stanford University, Professor Arthur Giese (1905-1994) and the pharmacist Julian Wells (1902-1948) from the University of California San Francisco also worked on the problem and defined the quality of a sunscreen product: "*A convenient method of grading would be the ratio of the MED values with and without ointment.*" [20].

In Germany, the director of the University Dermatological Clinic in Hamburg, Josef Kimmig (1909-1976), introduced the term ‚Schutzfaktor' (protection factor) at the first scientific meeting of the German Dermatological Society in Frankfurt/Main in 1953. He said: "*The measure of the quality of a light protection agent is the quotient of the irradiation time with light protection agent and the irradiation time without light protection agent.*" [21].

Schulze took up the idea and, inspired by the Beiersdorf company with which he had been working since 1946, resumed his medical-biological research from the pre-war period. In 1951 and 1952, Schulze examined the effectiveness of sunscreens. He tested the products on the backs of test persons in comparison to untreated skin. He defined the protection factor as the ratio of the time until the just visible redness with light protection product occur to the time without light protection product. Schulze adopted the definition of the quotient P proposed by Blum and Giese and called it the ‚Lichtschutzfaktor' (light protection factor) for the first time in 1956. For a better understanding he gave the following numerical example: "*[...] if, during sunbathing in summer, the first weak sunburn occurs after one hour on the skin areas coated with sunscreen, but after three hours, then one speaks of a sun protection factor of 3.*" [22].

According to Schulze, the biological experiment in the sun had proven successful for determining the light protection factor. At the same time, he suggested using the Osram Ultra Vitalux lamp instead of natural sunlight to shorten the process. In his opinion, the sunbather wants to get a tan and not a sunburn. Therefore, he demanded that a sunscreen should absorb only UV-B, so that a direct pigmentation by UV-A light would be possible, which requires about 1500 times more energy than the UV-B light needs to produce an erythema.

The rapid development of the effectiveness of sunscreen products surprised dermatologists. In 1959, Arthur Wiskemann (1922-2015) stated that the sun protection factor, which had reached a maximum of three in his first series of tests, had now risen three years later to six with Delial sun milk. His verdict on this preparation was that it would meet the highest demands, even when used in the high mountains or on extremely sensitive skin. In his opinion, it would replace the pigment-added pastes that have been common up to now [23].

Stiftung Warentest, a non-profit German consumer organisation, tested sunscreens for the first time in 1966 and also determined the protection factor of the 46 products tested. For the measurement, the skin was rubbed with the sunscreens and irradiated with ultraviolet light until the redness was as strong as on an unprotected and also irradiated skin area. The sun protection factor was calculated from the time difference that the protected skin could stay longer under the quartz lamp [24].

The Tyrolean Greiter intervened on the interpretative sovereignty of the inventor of the term light protection factor. Greiter had founded the Piz Buin company in 1946 and marketed sun protection products. In 1974, he published for the first time about the origin and methodology of the sun protection factor [25]. Greiter claimed the invention of the method for determining the sun protection factor in a 1982 publication in 'Principles of Cosmetics for the Dermatologist' [26]. Schulze could no longer defend himself against this claim as he had already died in 1974. Beiersdorf AG, in the person of its head of light protection research, Wolfgang Henne, stepped in his place and claimed a year later that Schulze's contractual co-operation with Beiersdorf created the then recognised term 'light protection factor' as a result of many joint studies [27]. Greiter replied: "*Originally, nobody wanted to have it [...]. Now everyone wants to have developed it themselves [...].* " [28].

While scientists in Germany were working intensively on the method for determining the effectiveness of sunscreen products, consumer protection organisations in the USA took up the issue. In the 1930s, the women's magazine 'Good Housekeeping' reviewed all advertising claims made by advertisers in its issues. In 1936, under the headline 'Sun-stripes', a report appeared on how 'sunburn preventives' were tested."*[...] No guesswork or theory - real skin, measured sunlight, accurate control. To be acceptable, a sunburn preventive must at least double the period of safe exposure to the sun, compared to the period for untreated skin. [...] Good Housekeeping does for you what you cannot do for yourself. And always Good Housekeeping's scientific methods are characterised by their plain common sense.*" [29].

The statement was accompanied by a picture of a woman lying on her stomach with dark stripes on her back to indicate how she had been tested. In the United States, products to protect against sunburn were introduced in the 1930s, as they were in Germany.

Elizabeth Arden launched her 'Sun Pruf Cream' in the summer of 1933 and promoted the article in an advertisement describing the benefits of the product. Under the headline: "*A picture of Loveliness under the Sun*", the advertisement [30] declares that:

"burning and peeling have become unnecessary evil".

Dorothy Gray advertised her products as controlling tanning and preventing painful sunburn, and Lentheric sold a 'Sunplexion cream' to protect against sunburn [30].

By the late 1940s, there were so many items on the market in the US that it was worthwhile for a magazine to compare the products. In the 1949 June issue of the Consumers' Research Bulletin, it presented the results of eight substances that had been tested by absorption measurements. The article identified the 296.7 nm wavelength as the one that causes sunburn and should be protected against. Seven of the eight products tested blocked this wavelength. To achieve a good skin tan, wavelengths greater than 334 nm should be allowed through, according to the magazine's experts [31].

Summary

Many myths have been created in connection with the history of sun protection that need to be rectified. For example, the first commercial sunscreen products were not launched in 1928 and the inventors of the method for determining the sun protection factor were not Schulze or Greiter. It is the task of historiography to show the background for the emergence of these myths. For this purpose, methods derived from historical science were used and the sources were subjected to critical analysis. The interpretation of these sources made it possible to trace the history.

The history of scientific sun protection began towards the end of the 19th century, when doctors were interested in finding products that protected against sunlight. They had discovered that sunlight could cause skin diseases. In order to prevent these skin diseases, they looked for suitable measures and came up with the idea of using coloured pastes or completely covering the corresponding parts of the body. However, both means were not very popular with the patients. Another option

would be to incorporate substances into creams that absorbed UV light and remain invisible when applied to the skin. The search for these light filters was successful at the beginning of the 20th century and the first transparent sun protection products came on the market. The products Zeozon and Ultrazeozon contained Coumarin derivatives and were marketed by the company Kopp & Joseph.

During the Weimar Republic, the rise of sunscreen began in Germany. There was what Freund called a 'general hygienic fanaticism about light' and the fashion demanded a tanned complexion [32].

In the early 1930s, an industry emerged to develop and manufacture sunscreen products, and there were so many sunburn prevention products in Germany that it made sense for medical professionals to compare their effectiveness. Their motivation was to 'protect customers from the promotion of worthless preparations' [33]. For this purpose, *in vivo* and *in vitro* test methods were developed, from which the method valid today for determining the sun protection factor emerged. Comparative studies of sunscreen products were also carried out in the USA, but only in the late 1940s and initiated by consumer protection organisations. Medical scientists in the USA dealt with this topic years later.

The definition of the protection factor with which the effectiveness of sun protection products can be compared, goes back to work by Blum and Giese. In the mid-1940s, they independently proposed taking as a measure the quotient of the time a person can stay protected in the sun longer than unprotected. This work had been initiated by the US Army, which had to protect pilots shot down over the Pacific and who had survived the crash from the scorching sun. Ten years later, Schulze took up this definition and called the quotient light protection factor. He did not cite Blum or Giese in any of his publications, and so Schulze had become established in the scientific community and likewise in the popular press as the inventor of the sun protection factor. Greiter tried to usurp the interpretative sovereignty, but also the supremacy and the material advantage over the term light protection factor by renaming it sun protection factor.

The term 'Sun Protection Factor' is currently found on every sunscreen product package and today, as it was 75 years ago, indicates the amount of time you can stay in the sun before your skin turns red.

Picture credits

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Preservative Compositions for Moist Cleaning Wipes

K. Henning

abstract

Moist cleaning wipes may be protected against microbial infestation with a preservative composition comprising a gluconolactone, a benzoic acid or a salt thereof, and a preservative-enhancing product. The preservative-enhancing product causes the gluconolactone and benzoic acid composition to inhibit or kill microorganisms such as *Burkholderia cepacia*. The preservative enhancer may be, for example, a phenol ether, an organic acid, or a salt of an organic acid.

Protection against contamination of pre-saturated cleaning wipes

Moist cleaning wipes for cleaning surfaces, such as those used for removing cosmetics, wiping hands, for use with infants during diaper changes, for disinfecting surfaces and the like contain cleaning compositions which, when applied, are each intended to provide effective cleaning. To apply these cleaning compositions to the respective surface, the cleaning wipe is saturated with them to saturation.

These pre-saturated cleaning wipes are particularly useful for use while traveling, such as in a car or in public areas where conventional cleaning methods such as soap and water are not available.

One problem more commonly encountered with the use of presaturated wipes and other similar substrates is adequate protection against microbial contamination. Although the substrate is saturated with the cleaning composition, many commonly used wiping solutions, including antimicrobial compositions, are not effective against various microorganisms known to attack wiping substrates. This is particularly true of wiping substrates containing cellulose.

For example, the *Burkholderia cepacia* group may include complex bacteria that may be composed of at least 18 different bacterial species found in soil and water. These contaminate natural substrates, especially cellulosic substrates. The gram-negative bacterium *B. cepacia* is extremely resistant to many antiseptic and antibacterial compositions. Other microorganisms that can contaminate and/or attack wipe substrates include *Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Candida albicans*, and *Aspergillus brasiliensis*.

The problem of preservative protection of wipe substrates has been exacerbated by the trend toward using naturally occurring antimicrobials in preservatives.

Preservation against *Burkholderia cepacia*

The wet wipe with the applied cleaning solution and/or impregnated therewith not only facilitates wiping of the surface or an adjacent object, but also protects the substrate itself from microbial contamination. The cleaning solution is formulated to effectively protect the substrate from microorganisms, particularly *Burkholderia cepacia*.

The wet cleaning wipe consists of a nonwoven web of cellulose fibers that contains the cleaning composition as a liquid-absorbent substrate. This contains a preservative composition comprising a gluconolactone, a benzoic acid or a salt thereof, and a preservative-enhancing product.

The preservative-enhancing product causes the gluconolactone and benzoic acid composition to inhibit or kill microorganisms such as *Burkholderia cepacia*. The preservative enhancer may be, for example, a phenol ether, an organic acid, or a salt of an organic acid.

When an organic acid or salt of an organic acid is used, the preservative enhancer may have a carbon chain length of 6 to 8 carbon atoms. This may comprise a cyclic compound or an acyclic compound. Particularly suitable examples include phenoxyethanol, sodium dehydroacetate, potassium sorbate and the like, and mixtures thereof.

The amount of preservative enhancer in the cleaning composition may be <0.5% by weight. Gluconolactone may be present in an amount of 0.75% to 0.2% by weight and benzoic acid or the salt thereof may be present in an amount of 0.5% to 0.05% by weight. The combination of gluconolactone with the preservative enhancer and benzoic acid or the salt thereof provides effective efficacy against microorganisms such as *Burkholderia cepacia*.

The ratio of preservative enhancer to gluconolactone may be in the cleaning composition in a weight ratio of 5:1 to 1:5, for example 2:1 to 1:2, 1.5:1 or 1:1.5. The cleaning composition may contain other ingredients, for example a solvent such as water and/or an organic solvent. The antimicrobial composition may further contain one or more surfactants, chelating agents, builder substances, dyes or fragrances.

Example	Preservative compositions (Units wt.-%)
1	0.75% Gluconolactone/sodium benzoate (3:1)
2	0.75% Gluconolactone/sodium benzoate (3:1) and 0.25% Potassium sorbate
3	0,75% Gluconolactone/sodium benzoate (3:1) and 0.1% Sodium dehydroacetate
4	0,75% Gluconolactone/Sodium benzoate (3:1) and 0.1% Sodium benzoate
5	1.0% Gluconolactone/Sodium benzoate (3:1)
6	Inspection

Tab. 1 Preservative compositions (Example 1 to 6)

The combination of gluconolactone, benzoic acid or a salt thereof, and a preservative enhancer provides an effective preservative for moist cleaning wipes.

Examples

Example 1

A 28-day preservative efficacy test was performed with wet wipes soaked in cleaning solutions. The ratio of cleaning solution to cleaning wipe was 3:1. The cleaner formulations contained surfactants, emulsifiers, pH-adjusting agents, buffers, solvents and a preservative conforming to the compositions described above. The preservative compositions used are shown in **Table 1**.

In each case, 3 series of experiments were inoculated with the following 6 groups of microorganisms using wet cleaning wipes impregnated with these preservative compositions: *Staphylococcus aureus* (ATCC 6538), *Escherichia coli* (ATCC 8739), and *Pseudomonas aeruginosa* (ATCC 9027); *Burkholderia cepacia* (ATCC 25416); and *Candida albicans* (ATCC 10231) and *Aspergillus brasiliensis* (ATCC 16404).

Microbial load and percentage of reduction in microbial load were measured in each cleaning cloth sample. Germ counts were taken after 0, 1, 2, 7, and 14 days. Samples were re-inoculated with the appropriate germs on day 14 and germ counts were performed on days 14, 15, 16, 21 and 28. Standard preservation test procedures were followed here.

Samples 1 to 6 were inoculated with microorganisms to recover 1.5 × 10^6 colony-forming units (CFU) of microorganisms on day 0, and then inoculated again to recover 1.2 × 10^6 CFU/clean cloth on day 14. The results are shown in **Table 2**.

Sample (cfu per wipe) % reduction	Residual microbial content/Microbial reduction (%)								
	Day 0	Day 1	Day 7	Day 14	Day 14 (Post inoculation)	Day 15	Day 16	Day 21	Day 28
1	6.4u+05 55.9%	< 100 100.0%	< 100 100.0%	< 100 100.0%	1.1u+06 8.3%	< 100 100.0%	< 100 100.0%	< 100 100.0%	< 100 100.0%
2	7.2u+05 50.3%	< 100 100.0%	< 100 100.0%	< 100 100.0%	2.1u+06 no reduction	< 100 100.0%	< 100 100.0%	< 100 100.0%	< 100 100.0%
3	9.1u+05 37.2%	< 100 100.0%	< 100 100.0%	< 100 100.0%	1.6u+06 no reduction	< 100 100.0%	< 100 100.0%	< 100 100.0%	< 100 100.0%
4	1.1u+06 26.9%	< 100 100.0%	< 100 100.0%	< 100 100.0%	9.0u+05 25.0%	< 100 100.0%	< 100 100.0%	< 100 100.0%	< 100 100.0%
5	5.0u+05 65.5%	2,0u+02 100.0%	< 100 100.0%	< 100 100.0%	8.5u+05 29.2%	1.2u+04 99.0%	< 100 100.0%	< 100 100.0%	< 100 100.0%
6	1.1u+06 26.2%	9.3u+06	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07
		no reduction							

Tab. 2 Residual microbial determination in the microbial load test of moist cleaning cloths.

Sample (cfu per wipe) % reduction	Residual microbial content/Microbial reduction (%)								
	Day 0	Day 1	Day 7	Day 14	Day 14 (Post inoculation)	Day 15	Day 16	Day 21	Day 28
1	1.4u+06 17.7%	< 100 100.0%	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07
			no reduction						
2	8.2u+05 53.1%	< 100 100.0%	< 100 100.0%	< 100 100.0%	1.5u+06 no reduction	3.0u+04 97.5%	1.3u+03 99.9%	< 100 100.0%	< 100 100.0%
3	7.4u+05 57.7%	< 100 100.0%	< 100 100.0%	< 100 100.0%	9.5u+05 20.8%	3.0u+04 97.5%	< 100 100.0%	< 100 100.0%	< 100 100.0%
4	9.4u+05 46.3%	< 100 100.0%	< 100 100.0%	< 100 100.0%	9.3u+05 22.5%	1.0u+02 100.0%	< 100 100.0%	< 100 100.0%	< 100 100.0%
5	1.1u+06 39.4%	1.2u+03 99.9%	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07	> 3.0u+07
			no reduction						
6	1.6u+06 8.6%	2.5u+07	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07	>3.0u+07
		no reduction							

Tab. 3 Residual microbial count in the microbial load test of moist cleaning cloths.

Example 2

In another test series, samples 1 to 6 were inoculated with microorganisms, the cleaning cloth was exposed to 1.8×10^6 cfu/cleaning cloth of microorganisms on day 0, and then inoculated again on day 14 to obtain 1.2×10^6 cfu/cleaning cloth.

Table 3 shows the percentage germ reduction for samples with the second test series.

References:

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Die mikrobiologische Produktsicherheit ist eine unabdingbare Voraussetzung für den Verbraucherschutz. Grundlagen hierfür sind sowohl die Kenntnis der Faktoren für die mikrobiologische Stabilität und damit der Konservierung im umfassenden Sinne, als auch die Absicherung und der Nachweis der Konservierungsmittelwirkung. Der Konservierungsbelastungstest (Preservation Efficacy Test, Microbiological Challenge Test) ist hierbei von zentraler Bedeutung.

Das von der Fachgruppe „Mikrobiologie und Betriebshygiene" der DGK e.V. jetzt veröffentlichte Buch behandelt alle Aspekte zum aktuellen Stand der mikrobiologischen Stabilität und des Konservierungsbelastungstests.

Das Buch liefert Fakten und Beurteilungen in einer umfangreichen Zusammenstellung von Autorinnen und Autoren, aus allen relevanten Bereichen. Es bietet grundlegende Information und dient als Nachschlagewerk für spezielle Fragestellungen.

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Several traditionally used organic UV filters, such as Octocrylene, are faced with rising concerns regarding their environmental and health safety profiles. Emollients directly influence the possibility to formulate with safe, highly efficient alternatives. In their function as solubilisers of solid organic UV filters, emollients determine the maximum applicable UV filter concentration and resulting SPF. Emollients also have an impact on dispersion stability of inorganic UV filters such as Zinc Oxide and Titanium Dioxide. Furthermore, they strongly influence skin feel and homogeneous product application, thus supporting efficient skin protection and consumer acceptance.

Jungbunzlauer offers two emollients specifically suited for sunscreen formulation. **CITROFOL® AI** (Triethyl Citrate) and **CITROFOL® BI** (Tributyl Citrate) are clear, odourless, oily liquids and have a long history of safe use in personal care products. Highlighting their applicability in sun protection, important parameters comprising solvent power, influence on sun protection factor (SPF) and UVA protection factor (UVA-PF), dispersability of inorganic filters and sensory attributes were investigated.

Our solubility tests revealed the exceptional solvent power of **CITROFOL® BI** for the UV filter Ethylhexyl Triazone (EHT) of up to 35%. Both **CITROFOL® BI** and **CITROFOL® AI** showed excellent solvent power of 29% for Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB). Greater solvent power of the emollient allows for higher filter loading and thus higher SPF. It also increases formulators' flexibility regarding the exact composition of the oil phase: the overall amount of oil can be lowered and co-emollients can be chosen based on their sensory performance.

A sensory profiling of Jungbunzlauer's **CITROFOL®** citrate esters in test emulsions showed that **CITROFOL® BI** was rated similar to the reference with C12-15 Alkyl Benzoate and can thus be an economic 1:1 replacement. **CITROFOL® AI** outperformed the reference emollient in a range of attributes, offering a better gliding effect, lighter consistency, better spreadability and a smoother after feel.

To investigate the potential influence of the solvent matrix on UV absorbance and SPF/UVA-PF, *in vitro* tests were performed. Neither **CITROFOL® AI** nor **BI** interfered with the SPF. Moreover, **CITROFOL® AI** boosted the UVA-PF by almost 40% compared to the calculated value.

Focusing on certified-natural sunscreen, **CITROFOL® AI** proved suitable to achieve stable dispersions of inorganic UV filters. The beneficial sensory of **CITROFOL® AI** was confirmed in a test formulation with inorganic UV filters only. Specifically, consistency was lighter, gliding effect and distributability were more pronounced and the skin feel was much more pleasant than in commercially available benchmarks.

Overall, **CITROFOL® AI** and **CITROFOL® BI** showcase remarkable advantages for sunscreen formulations. The excellent solvent power of **CITROFOL® BI** enables cost-efficient, high-SPF formulation with flexibility regarding co-emollients. **CITROFOL® AI** is a COSMOS-approved alternative distinguished by a pleasant sensory profile in both formulations based on organic UV filters and those with inorganic UV filters. In addition, it can potentially boost UVA-PF and thus crucially contribute to product labelling with a UVA claim. Both **CITROFOL®** grades represent outstanding values in the formulator's palette of emollients for use in sunscreens, optimising performance, costs and consumer experience.

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SOFW eVENTS

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Challenges and new insights in the field of sun protection

On **June 17, 2021**, the third **eVENT** from the new **SOFW eVENT** series took place. More than **375 experts** registered for the sun care **eVENT "Here comes the SUN – takeCARE"** and listened to eight presentations around the topic of "sun care". New scientific insights as well as product presentations of well-known companies like **BASF, DSM**, **Jungbunzlauer** and **Symrise** were examined.

In one of the four **keynote** lectures, **Prof. Dr. Dr. Jürgen Lademann** discussed the *need for sunscreens* not only to protect against UV radiation alone, but also to provide additional protection against the visible and invisible infrared spectral range. To achieve this, pigments and antioxidants with a high radical protection factor are needed in sunscreens.

In his presentation, **Uli Osterwalder** explained the *meaning and differences of SPF, UVA protection and UVA indicator*, as well as the various legal requirements, which vary from country to country and must be considered in a formulation for sunscreen products. Several SPF measurement methods were looked at in detail. Also part of the presentation were the question of an environmentally friendly product and the high consumer expectations.

The *historical background of sunscreens* was explained by **Dr. Klaus Stanzl**: In the 19th century, doctors recognized skin diseases caused by sun exposure and tried to help their patients with colored ointments, which, however, did not enjoy great popularity. The dermatologists' search for transparent filters that could be easily incorporated into creams or lotions picked up speed, and the importance of sun protection has become indispensable today.

Prof. Dr. Leonhard Zastrow spoke about a *universal body constant – the so-called FRTV (Free Radical Threshold Value)*. The stability of redox homeostasis is maintained by a complex antioxidant system. Intense sun exposure produces excess free radicals that permanently destroy this balance: The total number of excess free radicals and the ratio of ROS to LOS reach a point where this "instability" is no longer balanced by the antioxidant system. According to calculations and experiments, this happens at a value of about 3.5 *1012 radicals/mg of skin tissue. This range is the border between "essential/beneficial" and "damaging/hostile to life" and is called FRTV.

In her **exhibitor presentation**, **Dr. Myriam Sohn (BASF)** addressed the *challenge of developing environmentally friendly and safe high SPF sunscreens*. She showed that triazine UV filters, including oil-soluble triazines and water-dispersed tris-biphenyl triazines (TBPT), offer a real alternative to EHMC and OCR, which have come under scrutiny.

Consumer demands for a comfortable, lightweight sunscreen texture that is also easy to use, practical, travel-friendly and, not to forget, environmentally friendly was highlighted by **Laetitia Marlier (DSM)**. There is a trend towards multifunctional or hybrid sunscreen products, which fulfill several functions in one product. Formulators face the difficult task of achieving high aesthetic properties with very high SPF and UVA protection with less UV filters, while being safe for people and the environment.

The presentation by **Dr. Teresa Berninger (Jungbunzlauer)** focused on *citrate esters*. These are used, for example, as emollients and solubilizers of organic UV filters in sunscreens, and have a significant influence on the type and amount of UV filters and the sun protection factor achieved during formulation. The 100% bio-based *CITROFOL® AI* contributes to an improvement in the protection effect of sunscreens, a pleasant skin feel and a reduction in production costs.

Nadine Krug and **Ev Süß (Symrise)** presented their ingredients *SymEffect™ Varytex* and *NeoHeliopan® Flat*. These feature a wide range of applications, easy handling and dosing. Both ingredients can also be combined with each other and help to optimize costs, production time and energy.

Formulations for sun care and sun protection products are very complex and require extensive knowledge on a wide range of levels and areas. Consumer demands also continue to increase, especially in terms of environmental friendliness. In this sense, we are very pleased with the numerous, interested participants, which came for the most part from the business field "raw material manufacturers and suppliers" **(28.5%)** and "manufacturers of end products" **(26.5%)**. Experts from laboratory and analytical facilities were represented with **15%**.

On **September 09, 2021**, our next **eVENT "SkinNEWvation"** will take place, quite surprisingly, around the topic "skin care". Here we will cover *microbiome-friendly & probiotic cosmetics, facial care, skin cleansing, soaps & hand sanitizing, moisturizing and skin analysis*. **Registration** for this opens on **August 05, 2021**.

BE PART OF IT AS A SPONSOR OR VISITOR!

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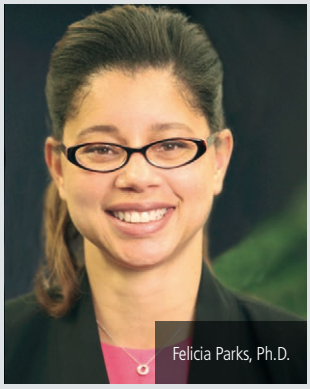
Hallstar Innovation in Clean, Elegant and Safe Sun Care

Interview with Felicia Parks, Ph.D., Technical Director, Hallstar Beauty


Felicia Parks, Ph.D.

HALLSTAR BEAUTY

It is increasingly challenging to develop globally acceptable sun protection products that work within regional limitations on allowable UV filters, levels and combinations. How does Hallstar assist formulators with this challenge?

The first challenge for any ingredient supplier is tracking all the ever-changing global restrictions for sun care products. **Hallstar** maintains a strong understanding of current and anticipated global regulations and regional legislation so it can quickly produce customer solutions that address any proposed changes.

There are two common themes in regulatory: restricted and open markets. A 'regulatory restricted' designation generally applies to organic UV filter packages, as the global regulations for inorganic filters are more similar across regions when it comes to maximum usage levels. The United States is an example of a regulatory and regionally restricted market since the US government permits only a handful of organic UV filters – making it nearly impossible to obtain SPF 30 and above in a sun care formulation without critical performance aids. These performance aids are used to photostabilize the formula, provide solvency for crystalline organic UV filters, promote uniform distribution of actives on skin, improve water resistance of the formulation, optimize skin feel to promote use of the appropriate quantity of sunscreen, and impart physical stability.

Hallstar has a suite of materials that, individually or in combination, provide this type of support to sunscreen development, enabling higher performing global sunscreen product development that meets regulatory restricted market requirements. For example, **Hallstar**'s photostabilizers – triplet and singlet excited state quenchers and solvent polarity optimizers – reduce the photodegradation from any combination of UV filters and other actives, which effectively increases finished products' SPF and PFA.

With your Micah® photoprotection technology, you won the Innovation Zone Silver Award at in- cosmetics some years ago. Why do you call Micah® an 'ante-oxidant?'

Even now, four years after we took home the in-cosmetics Global Silver for **Micah®** [INCI: Bis(Cyano Butylacetate) Anthracenediylidene], it is still an ingredient ahead of its time. By focusing research on light-induced oxidative stress – specifically, how to stop the generation of reactive oxygen species (ROS) – **Hallstar** chemists developed a new technology that, rather than repair already-damaged DNA or block some of skin's exposure to ultraviolet or visible light, protects by quenching excitation of skin's [endogenous] photosensitizers. Photo-induced aging damage is thus avoided because the formation of singlet oxygen and other ROS is stopped before it starts. For this reason, we refer to **Micah®** as an 'ante-oxidant.'

You have made further studies on this molecule. What did you find out?

Singlet oxygen is an extraordinarily reactive molecule. When singlet oxygen attacks cell membranes, it can create leakage, cell death, and most visibly, peroxidation. You'll see this when you leave a book out in the sun: the book cover becomes photobleached (i.e., color molecules are destroyed) in a matter of days.

But it is singlet oxygen's impact on cell DNA that is especially catastrophic for skin. There is a cause and effect relationship between DNA damage and the onset of inflammation. We also know that the inflammatory response is the single most effective mechanism for accelerating skin aging. One singlet oxygen molecule can introduce one single 8-OH-dG (or lesion) in one DNA molecule and that alone will trigger what is called the NFkB cascade – the onset of inflammation that entails a chain reaction of thousands of molecular modifications in the cell membrane, as well as the over-expression of MMP-1 which destroys collagen and other elastic fibers.

Given this reality, **Micah®**'s ability to prevent virtually 100% of UVA-induced 8-OH-dG lesions is the most significant finding of the new in vivo tests – and it puts **Micah®** in a category all its own.

Consumers want natural ingredients in their products. What new natural ingredients do you offer for sun care products?

While beauty customers who strongly prefer natural ingredients are historically known to make concessions for effective anti-photoaging chemistry like **Micah®**, interest in nature-derived beauty has continued to increase rapidly. Add to that the recent proliferation of sun care regulations limiting permissible UV filters and the accelerating popularity of mineral sunscreens, and you can understand why we're so excited about introducing several all-natural sun care ingredients this year.

We're beginning our naturals expansion with multifunctional **SolaPure™ Glo** [INCI: Vegetable Oil, Simmondsia Chinensis (Jojoba) Seed Oil, Curcuma Longa (Turmeric) Root Extract]. **SolaPure™ Glo** is inspired and guided by nature – and more specifically by the inherent culinary, beauty and wellness benefits of turmeric. The curcuminoids found in turmeric plants boast anti-inflammatory, antioxidant and anti-microbial properties, and have even been known to reduce the ROS production that leads to oxidative skin damage. **SolaPure™ Glo** leverages curcumin's benefits to improve sun protection's SPF and PFA performance, control hyperpigmentation and promote overall skin wellbeing.

Emulsifiers play an important role in sun care formulation. Do you have solutions for the formulators?

Hallstar has always recognized the impact that performant emulsifiers can have on successful sun care formulations. Functional bases form fluid (even sprayable) sun care lotions, enhancing the texture and viscosity of formulation and improving emulsion stability, sensorial profile and dermatological compatibility.

Over the years, **Hallstar Beauty** has launched some of the world's most successful emulsifiers, emollients and surfactants. The fatty acid composition of these products and their ability to generate liquid crystal structures that biomimic the strateum corneum organization of human skin allow for light, nourishing ingredients with exceptional sensoriality.

Our newest cold process emulsifier, **Olivem® 2090** [INCI: Polyglyceryl-4 Olivate/Polyricinoleate], is a water-in-oil, nature-derived ingredient that is especially well-suited to sun care. In addition to improving spreadability and enabling an excellent after-feel, **Olivem® 2090** allows a reduction in solvent quantity and makes it easier to formulate with inorganic UV filters and powders as well as organic sun filters because of its all-natural powder dispersion properties. Its simple emulsification process can be achieved with either cold or hot process, making **Olivem® 2090** very versatile.

For organic UV filter based systems, another Hallstar cold-process emulsifier, **Olivem® 2020** [INCI: Ethylhexyl Olivate, Sodium Acrylates Copolymer, Polyglyceryl-4 Olivate] provides the ability to stabilize high oil phases with 0.5 – 2.0% with no additional emulsifiers or thickeners, enabling a wide variety of viscosities from a lotion spray to a gel or cream. In addition to the sensory contribution, this reduction in emulsifiers and thickeners provides improved skin feel.

The positive impact of our **Olivem** products on sensoriality and spreadability is critical to successful sun care formulations. After all, the safest and most effective sunscreen is the one you are willing to use regularly!

Hallstar
BeautyCS@hallstar.com I **www.hallstarbeauty.com**

EASY AS WINKING SPF 50+

symrise

Environmentally-Friendly | 30/CCSUN20073/02

Phase	Material Name	EU INCI	% Material
A	**SymEffect™ Varytex (342911)**	PROPANEDIOL DICAPRYLATE/CAPRATE TRIISONONANOIN DIISOPROPYL ADIPATE CAPRYLIC/CAPRIC TRIGLYCERIDE STEARYL HEPTANOATE GLYCERYL OLEATE CITRATE CETEARYL NONANOATE STEARYL CAPRYLATE	10.00
	Neo Heliopan® Flat (294843)	HOMOSALATE, OCTOCRYLENE, BIS-ETHYLHEXYLOXYPHENOL, METHOXYPHENYL TRIAZINE, BUTYL METHOXYDIBENZOYLMETHANE, ETHYLHEXYL SALICYLATE	30.00
	SymDecanox™ HA (972276)	CAPRYLIC/CAPRIC TRIGLYCERIDE HYDROXYMETHOXYPHENYL DECANONE	1.00
	Edeta® BD	DISODIUM EDTA	0.10
	Fragrance	PARFUM	0.50
	Sensocel® 10	CELLULOSE	2.00
	Cosphaderm® X Soft	XANTHAN GUM	0.30
B	Aqua/Water	AQUA	49.45
	Bentone™ Hydroclay 2000	HECTORITE	0.80
	Avicel® PC 611	MICROCRYSTALLINE CELLULOSE CELLULOSE GUM	0.80
	Glycerin 99.5%	GLYCERIN, AQUA	1.00
	SymReboot™ L19 (846066)	MALTODEXTRIN LACTOBACILLUS FERMENT	0.50
	Hydrolite® 5 green (996442)	PENTYLENE GLYCOL	1.50
	SymOcide® PH (973949)	PHENOXYETHANOL HYDROXYACETOPHENONE CAPRYLYL GLYCOL, AQUA	3.00
	Dragosine (844033)	CARNOSINE	2.00
C	Citric Acid 10% Sol.	AQUA, CITRIC ACID	0.50
			100.00

Processing

Phase A: Premix phase A
Phase B: Disperse Avicel PC 611 and Bentone EW in water with an Ultra-Turrax stirrer at 6.000 rpm for 7 minutes. Add all remain ingredients Add all remian ingredients to the water phase. Add phase B to phase A and start to homogenize. The pH value of the finished product should be approx. 6.0 and has to be checked.
Reference: 24344 C

In vivo SPF: Measured according to the ISO 24444:2010 "Determination of Sun Protection factor SPF " on a five-subject panel test, the formula has an *in-vivo* SPF 61.5.

MICROBIO ME SPF 50+ and water resistant

symrise

Sun Balance | 40/CLSUN21000/02

Phase	Material Name	EU INCI	% Material
A	**Emulsiphos® (677660)**	POTASSIUM CETYL PHOSPHATE HYDROGENATED PALM GLYCERIDES	1.5
	SymEffect™ Sun (105604)	CERA ALBA SODIUM STEAROYL LACTYLATE	3.0
	Neo Heliopan® 357 (622501)	BUTYL METHOXYDIBENZOYLMETHANE	5.0
	Neo Heliopan® OS (131494)	ETHYLHEXYL SALICYLATE	5.0
	Ethylhexyltriazone	ETHYLHEXYL TRIAZONE	5.0
	Neo Heliopan® BMT(102814)	BIS-ETHYLHEXYLOXYPHENOL METHOXYPHENYL TRIAZINE	8.0
	SymMollient® PDCC (102119)	PROPANEDIOL DICAPRYLATE/CAPRATE	10.0
	Isoadipate (660014)	DIISOPROPYL ADIPATE	10.0
	Caprylic/Capric Triglyceride	CAPRYLIC/CAPRIC TRIGLYCERIDE	10.0
	Edeta® BD	DISODIUM EDTA	0.1
	Keltrol® CG-BT	XANTHAN GUM	0.1
	Carbopol® Ultrez 10 Polymer	CARBOMER	0.4
B	Aqua/Water	AQUA	30.7
	Neo Heliopan® Hydro (103089)	PHENYLBENZIMIDAZOLE SULFONIC ACID	2.0
	Neo Heliopan® AP (106796)	DISODIUM PHENYL DIBENZIMIDAZOLE TETRASULFONATE	2.0
	Biotive® L-Arginine (621277)	ARGININE	1.0
	Sodium Hydroxide 10% solution	AQUA SODIUM HYDROXIDE	5.0
	Hydrolite® CG (199602)	CAPRYLYL GLYCOL	0.5
	SymSave® H (979940)	HYDROXYACETOPHENONE	0.7
			100.0

Processing

Phase A: Heat up phase A to approx. 85 C without Keltrol CG-BT and Carbopol Ultrez 10 Polymer. Disperse Keltrol CG-BT and Carbopol Ultrez 10 Polymer into the hot Oil phase.
Phase B: Mix Phase B at ambient temperature . Add phase B to phase A and start to homogenise with an Ultra-Turrax T 25 (3min / 13000 RPM). Cool down phase A/B while stirring to ambient temperature. The pH value of the finished product should be approx. 6.5 and has to be checked.

Reference: 54239 C

Measured according to the ISO 24443:2012 „Determination of UVA photoprotection *in vitro*" the emulsion has an in-vitro SPF >100 and an UVA-PF 32. (Used plates : PMMA WW5 from Schönberg). Measured according to the ISO 24444:2010 „*In vivo* determination of Sun Protection factor (SPF)" on a four-subject panel test, the formula has an *in-vivo* SPF mean 84.

PRODUCT LAUNCH

Lubrizol Announces PemuPur™ START Polymer

Polymeric emulsifier for skin and sun care formulations

CLEVELAND, USA | 15 JULY 2021

Lubrizol Life Science – Beauty (LLS Beauty) introduces PemuPur™ START polymer – naturally sensational, simply refreshing.

Consumer priorities on health and sustainability are challenging formulators to develop stable skin and sun care formulations that are naturally derived without sacrificing the refreshing sensory experience.

PemuPur™ START polymer meets consumers' expectations as a high-performing, natural-derived polymeric emulsifier. Its name promises excellent STA-bility and R-efreshing T-exture, making it a grounded solution to START building oil-in-water emulsions.

PemuPur™ START polymer provides excellent emulsion stabilization at low use levels (0.5-1.0 wt%) and up to 50% oil content, limiting the need for co-emulsifiers. These characteristics, coupled with its limited surface activity, make it ideal for creating mild, fluid and sprayable emulsions suitable for all skin types, including sensitive skin.

PemuPur™ START polymer has a Renewable Carbon Index of 0.96, according to ISO 16128, and it is readily biodegradable (OECD 301F).

For more information, visit:
Lubrizol.com

COMPANY NEWS

BASF

Publishes Fifth Palm Progress Report

LUDWIGSHAFEN, GERMANY | 15 JULY 2021

BASF launched the fifth edition of its Palm Progress Report featuring figures for 2020. One of BASF's key renewable raw materials is palm kernel oil and its primary derivatives which are mainly used to produce ingredients for the cosmetics, detergent and cleaner industries, as well as in human nutrition.

In the past year, BASF has reached an important milestone on the road to sustainable palm oil. The company has committed to source palm (kernel) oils exclusively from RSPO-certified sustainable sources since then. In 2020, BASF purchased 227,213 metric tons of RSPO-certified sustainable palm (kernel) oil. This corresponds to 100 percent of the total volume purchased. In addition, BASF made further progress in developing transparent supply chains: almost 95 percent of the global oil palm footprint – a total of 441,107 metric tons – could be traced back to the oil mill.

BASF is now fully focused on the other part of its 2015 commitment: to also include the commitment of certified sourcing to those significant intermediates which are based on palm oil and palm kernel oil by 2025, e.g. fatty alcohols and fatty acids.

The BASF Home Care, I&I and Industrial Formulators Europe business is expanding its portfolio of palm-based surfactants with RSPO certifications. It now offers around 150 surfactants certified according to the RSPO standard 'Mass Balance', in line with the company's efforts to work towards a sustainable future along the entire value chain. In addition, it is helping its European customers to meet consumer demand for environment-friendly products both in the detergents and cleaners industry and amongst users of industrial applications. As one of the first RSPO members, BASF is thus underlining its continued commitment to support the production of sustainable palm (kernel) oil in the future.

www.basf.com

Lilybelle® by Symrise:
Lily of the Valley Fragrance Ingredient from Renewable Sources

HOLZMINDEN, GERMANY | 15 JULY 2021

Symrise has developed a special fragrance raw material from renewable sources: Lilybelle®, a lily of the valley fragrance ingredient with a refreshingly flowery note. It will provide perfumers with novel possibilities for the creation of scents for personal care products, cleaning products and laundry care products. Symrise manufactures Lilybelle® using byproducts from the orange juice industry, so that 83 percent of it is composed from renewable raw materials. The product is also readily biodegradable.

With Lilybelle®, Symrise is expanding its portfolio of special fragrance ingredients to include a sustainable, readily biodegradable fragrance ingredient. It emphasizes the flowery scent of lily of the valley in perfumes, providing ozonic green facets and lightly aqueous transparent accents.. All in all, Lilybelle®brings freshness and a certain lightness to fragrance creations. The scent of lily of the valley flowers has long played an important role in perfumery and is considered timeless due to its transparency, freshness and naturalness. It is used particularly often in men's fragrances in combination with citrus notes.

"*With Lilybelle®, we have once again demonstrated our innovative strength*," says Susanne Borchert, Senior Marketing Manager at Symrise. "The versatile fragrance offers perfumers novel possibilities for creating fascinating scent compositions."

Symrise uses byproducts from the orange juice industry

Lilybelle® impresses in two ways due to its scent and its sustainable qualities. In manufacturing it, Symrise uses D-limonene from renewable raw materials, which stems from byproducts of orange juice production. This means 83 percent of Lilybelle® comes from renewable sources, and it is readily biodegradable.

"*We have integrated sustainability as a major component of our corporate strategy,*" says Borchert. "*With its high proportion of renewable raw materials, Lilybelle® provides an excellent example of the application of the 12 Principles of Green Chemistry. The increasing consumer demand for products that are manufactured in an environmentally friendly manner shows that we are on the right path*".

www.symrise.com

Givaudan Active Beauty Unveils Zanthalene®
the Scalable Active Able to Mimic Botox Properties to Combat Wrinkles and Skin Discomfort

ARGENTEUIL, FRANCE | 12 JULY 2021

Givaudan Active Beauty presents Zanthalene®, a scalable natural active ingredient crafted by green fractionation with botox-like efficacy and skin sensitivity modulation benefits. Created from commonly known as Sichuan pepper, Zanthalene® is a cosmetic ingredient derived from spice and able to act on neuromuscular communication within the skin structure, providing well-ageing effects and soothing benefits depending on its concentration in formulas.

All consumers eventually experience the effects of ageing on the skin, such as wrinkles and sensitivity. However, a large number will not be motivated to reverse these effects through invasive treatments. According to our CMI study1, 86% of consumers are currently interested in beauty products containing natural ingredients that help soothe skin discomfort while smoothing for a botox-like effect.

Giada Maramaldi, Personal Care Category Manager, Givaudan said: "*Each facial expression activates a large number of muscles. With time and the decrease of collagen production, these expressions become even more marked and embedded on the skin, leading to the formation of wrinkles. In order to fight against these effects, Zanthalene® offers a neurocosmetic strategy, enabling facial muscle relaxation in a safe, reversible and natural way, adding a sensation of comfort while removing skin discomfort.*"

Crafted from Sichuan pepper, a plant widely used as a spice in Asian cuisine, Zanthalene® is extracted from its fruit husks using super critical CO_2. Its efficacy has been proven during several clinical studies.

www.givaudan.com/activebeauty.

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