論文 EyesOn

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Terephthalylidene Dicamphor Sulfonic Acid: Tackling Contemporary Challenges in Suncare Solutions

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The formulation of sunscreens that are effective, safe, and environmentally considerate presents increasing challenges. Regulatory restrictions on certain UV filters, growing consumer demand for eco-conscious products, and the need for balanced protection with photostable formulations add further complexity. Balancing efficacy, skin compatibility, and sustainability remains a key hurdle for formulators. The article examines Terephthalylidene Dicamphor Sulfonic Acid (TDSA), a hydrophilic, UVA filter, as a versatile solution. Comparative data are presented on its broad photoprotective efficacy, photostability, low dermal penetration potential, and compatibility with aqueous phases. TDSA could be shown to demonstrate synergistic effects when used in combination with other UV filters. The combination of its technical and performance attributes along with its recently expanded market availability offers formulators new opportunities for the development of modern sunscreen formulations.

1. Introduction

The number of UV filters currently considered safe for use is dwindling, largely due to increased regulatory scrutiny and emerging concerns about their potential effects on human health and the environment. In particular, commonly used organic filters such as Octocrylene (OCR) and Ethylhexyl Methoxycinnamate (EHMC) have come under debate, even leading to their restriction in several regions. As a result, the search for safer and more sustainable alternatives has become urgent.

Furthermore, public concerns about the penetration of nanoparticulate UV filters through the skin barrier persist despite considerable evidence indicating that nano UV filters remain on the skin's surface and are much bigger in size than soluble UV filter molecules and pose no risk of systemic absorption. The EU Regulation on cosmetic products (EC No.1223/2009) [1] requires additional approval for nanoscale ingredients. In order to become authorized, scientific data on the safety of raw materials must be provided.

Adding to these complexities is the need to meet consumer expectations in terms of formulation formats and sensory attributes. Consumers are increasingly demanding sunscreens that not only provide high SPF and UVA protection but also offer a pleasant application experience, whether in the form of a water-resistant cream for beach activities, a light non-sticky spray, or a daily-use photoprotection. The formulation must also fulfill different skin type preferences and be suitable for different skin tones, avoiding, for example, whitening effects on darker skin.

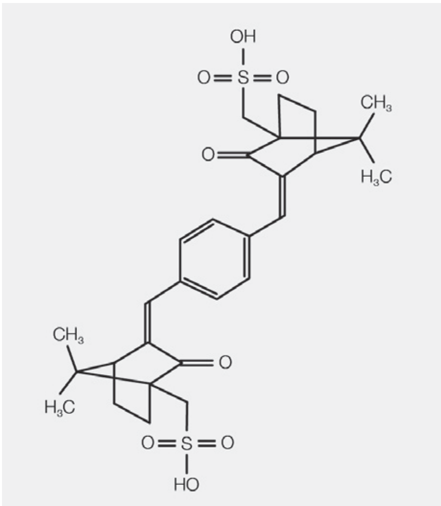
Balancing these multiple requirements—effectiveness, regulatory compliance, safety, environmental sustainability, and consumer satisfaction – makes the development of modern sunscreens a challenging endeavor: it involves selecting the right combination of UV filters and formulation technologies to create products that are both effective and desirable.

Given the reduced choices of UV filters, there is an increasing demand for photoprotective agents that can meet these complex criteria. The aim of this article is to examine Terephthalylidene Dicamphor Sulfonic Acid (TDSA) (Trade name: Uvinul® TS Hydro), a broad-spectrum UV filter whose recent expanded market availability provides additional options for sunscreen formulations.

2. Terephthalylidene Dicamphor Sulfonic Acid (TDSA) Meets Complex Criteria

TDSA is an organic UV filter originally developed to provide robust protection against UVA radiation, with demonstrated stability and compatibility in a wide range of sunscreen applications. Chemically, TDSA consists of a central terephthalylidene group flanked by two camphor-derived moieties, which contribute to its efficient absorption of UV radiation. In addition, the molecule is functionalized with two sulfonic acid groups, which confer hydrophilicity and make TDSA highly soluble in water. This characteristic makes it particularly advantageous for formulations containing water and thus for achieving UV protection in both phases of emulsions (Figure 1).

A noteworthy aspect of TDSA is its relatively high molecular weight of approximately 563 Dalton (Da), exceeding the value of 500 Da that is frequently referenced as a threshold. Compounds with molecular weights below 500 Da are more likely to permeate the skin, while those above this value typically exhibit limited dermal absorption. Neutralized TDSA will even exceed this value. Accordingly, unlike many other older UV filters with a molecular weight ranging around 300 Da, TDSA's molec-



■Fig. 1 The molecular structure of Terephthalylidene Dicamphor Sulfonic Acid (TDSA).

ular weight suggests a low potential for systemic absorption, addressing common safety concerns related to transdermal delivery of UV filters.

Uvinul® TS Hydro is supplied as an aqueous solution of 33% acive TDSA material. This format facilitates ease of handling and incorporation into cosmetic emulsions without the need for additional solubilization steps. The UV filter is introduced into the water phase of formulations and requires pH adjustment due to its intrinsic acidity.

It is recommended to neutralize TDSA with organic bases, such as tromethamine or L-arginine, to avoid the risk of recrystallization that can occur with inorganic neutralizers (e.g. sodium hydroxide or potassium hydroxide), thus reducing its water solubility. There is no need to neutralize to pH 7. Maintaining the pH around 5.5 is sufficient to ensure the solubility and stability of TDSA in the formulation for maintaining better skin compatibility.

3. Technical Features of TDSA

3.1 Photoprotective Performance

TDSA is primarily categorized as a UVA filter due to its maximum absorption peak at 345 nm. However, its absorption spectrum extends into the UVB region, enabling it to contribute to both UVA protection and sun protection factor (SPF) enhancement through additional UVB attenuation. This broad-spectrum absorption profile makes TDSA a versatile component in the formulation of comprehensive photoprotective systems.

Figure 2 illustrates the absorption spectrum of TDSA compared with the UVA filter Diethyl-

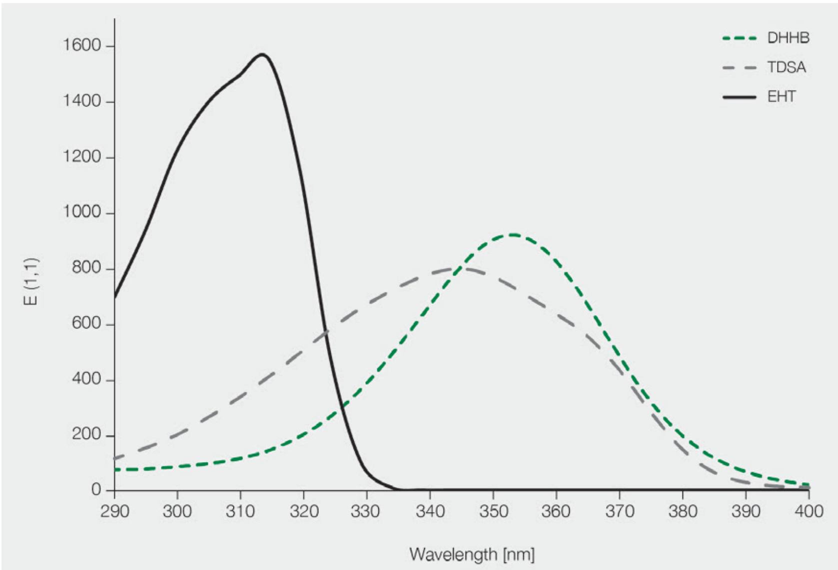


Fig. 2 The absorption spectrum of TDSA in comparison to DHHB and EHT.

amino Hydroxybenzoyl Hexyl Benzoate (DHHB) and the UVB filter Ethylhexyl Triazone (EHT). As shown below, TDSA provides significant absorption throughout the UVA range, with an extension into the shorter UVB wavelengths. This spectral coverage supports its role as a key UV filter in the aqueous phase of emulsions.

The extinction, expressed as E(1,1), represents the absorbance of a 1% (w/v) solution measured at an optical path length of 1 cm. This parameter enables a direct comparison of the absorption efficiency between UV filters. TDSA demonstrates a high E(1,1) value across its absorption spectrum, confirming its effectiveness as a UV absorber. Its strong UVA absorbance, combined with appreciable UVB coverage, contributes to both long-wave UVA protection – which is critical for mitigating photoaging and deep dermal damage – and the enhancement of SPF, which is predominantly influenced by UVB attenuation.

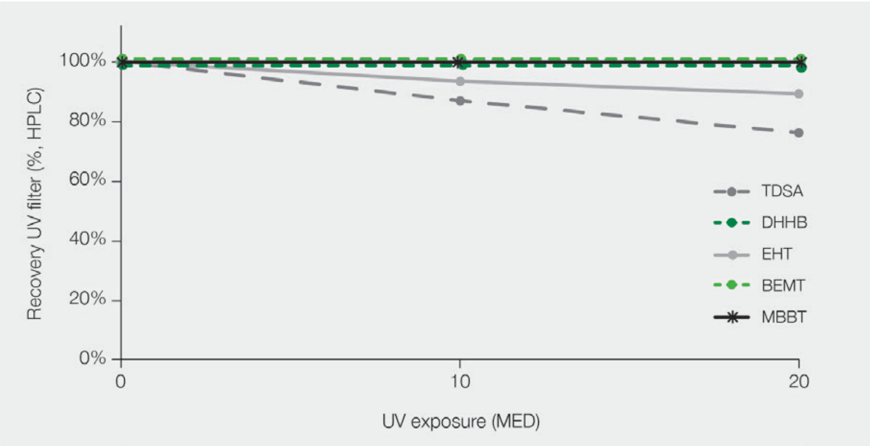
TDSA's compatibility with water phases allows formulators to combine it effectively with oil-phase UV filters, enabling the development of balanced, high-performance sunscreens. This flexibility supports the creation of formulations with favorable sensory characteristics, such as non-greasy, lightweight textures.

3.2 Photostability Profile

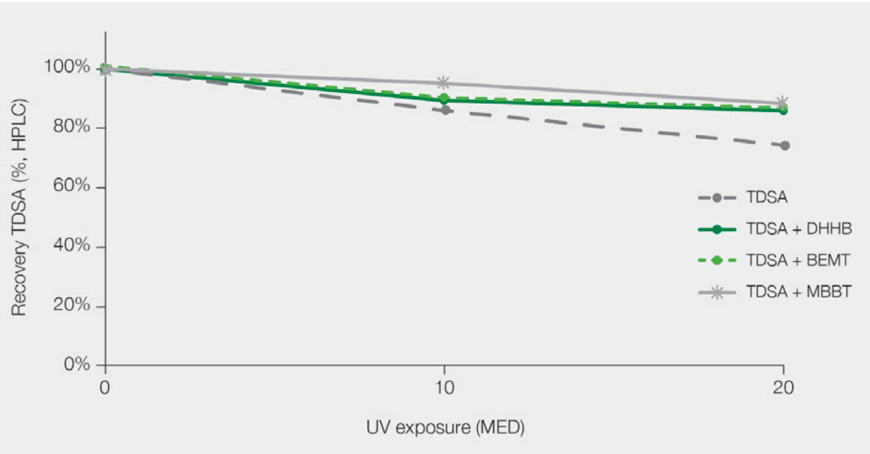
In addition to its broad-spectrum absorption and formulation versatility, TDSA demonstrates high photostability, an essential characteristic for ensuring the sustained performance and safety of sunscreen formulations during UV exposure. Photostability refers to the ability of a UV filter to retain its chemical structure and functional integrity following exposure to ultraviolet radiation. The degradation of UV filters upon exposure to sunlight not only diminishes their potential protective performance but can also result in the formation of free radicals, i.e. reactive or potentially harmful breakdown products, raising safety concerns and complicating formulation strategies.

Figure 3 presents the photostability profile of TDSA when incorporated into a standard oil-in-water emulsion and subjected to controlled UV irradiation. After exposure to a dose equivalent to 20 minimal erythema doses (MED) (calibrating for a skin phototype II), TDSA exhibited a recovery rate of 80% as determined by high-performance liquid chromatography (HPLC). The loss might be partly due to a reversible trans-cis photo-isomerization, followed by photo excitation [2). Recovery at this level is generally considered indicative of acceptable photostability in sunscreen formulations, supporting continued UV protection under normal usage conditions.

The combination of TDSA with UV filters such as Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT), Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (MBBT), and Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB) was positive (Figure 4). In these combinations, TDSA exhibited recovery rates of up to 100% post-irradiation, indicating no mea-



■Fig. 3 Recovery of TDSA (in %) by HPLC measurements after UV irradiation compared to BEMT (Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine), DHHB (Diethylamino Hydroxybenzoyl Hexyl Benzoate), EHT (Ethylhexyl Triazone), and MBBT (Methylene Bis-Benzotriazolyl Tetramethylbutylphenol).



■Fig. 4 Recovery of TDSA (in %) by HPLC measurements after UV irradiation alone and in binary filter combination.

surable degradation under specified test conditions, as determined by HPLC analysis. L'Alloret et al. also described the beneficial effect of combining TDSA with BEMT in terms of protection factors and protection against UVA-induced oxidative stress [3].

4. Performance in Formulation

TDSA, as a hydrophilic UV filter, provides strategic flexibility by delivering broad-spectrum photoprotection within the water phase of emulsions. Its photostable profile, in combination with complementary lipophilic filters, such as BEMT, supports the development of balanced, high-performance sunscreen formulations. While BEMT offers oil-phase photostable protection across the UVA and UVB spectrum, TDSA broadens this protection by reinforcing the water phase, leading to enhanced film homogeneity and comprehensive coverage.

4.1. Synergistic Effect in Multi-Filter Systems

An illustrative formulation as shown in Table 1 demonstrates the synergistic benefits of incorporating TDSA. The base formulation consists

■Table 1 Illustrative formulation without and with increased amount of TDSA. Uvinul® TS Hydro is a 33% active solution of TDSA; 3% and 9% of Uvinul® TS Hydro therefore corresponds to 1% and 3% TDSA, respectively.

Phase	Trade name	INCI	% by weight		
			UV-22-009-11-1	UV-22-009-11-2	UV-22-009-11-4
A	Eumulgin® Prisma	Disodium Cetearyl Sulfosuccinate	1.00	1.00	1.00
	Emulgade® PL 68/50	Cetearyl Glucoside (and) Cetearyl Alcohol	3.00	3.00	3.00
	Lanette® O	Cetearyl Alcohol	0.80	0.80	0.80
	Cetiol® ABV	C12-15 Alkyl Benzoate	7.00	7.00	7.00
	Cetiol® B	Dibutyl Adipate	15.00	15.00	15.00
	Cetiol® Sensoft	Propylheptyl Caprylate	5.00	5.00	5.00
	Euxyl PE9010	Phenoxyethanol (and) Ethylhexylglycerin	1.00	1.00	1.00
	Uvinul® T 150	Ethylhexyl Triazone	3.00	3.00	3.00
	Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	3.50	3.50	3.50
	Uvinul® A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate	4.50	4.50	4.50
B	Water	Aqua	47.90	44.30	37.10
	Glycerin	Glycerin	5.00	5.00	5.00
	Verdessence® Xanthan	Xanthan Gum	0.30	0.30	0.30
C	**Uvinul® TS Hydro**	**Aqua (and) Terephthalylidene Dicamphor Sulfonic Acid**	**-**	**3.00**	**9.00**
	L-Arginine	Arginine	-	0.60	1.80
D	Cetiol® Ultimate	Undecane (and) Tridecane	3.00	3.00	3.00

of three oil-soluble UV filters: EHT (UVB protection), DHHB (UVA protection), and BEMT (broad-spectrum protection). This combination provides a balanced UV spectrum coverage in the oil phase and achieves an *in vivo* SPF of 28.

Upon inclusion of TDSA at 1% active concentration in the base formulation, the SPF value increased from 28 to 33 – a 20% enhancement – while representing an increase of less than 10% of the total filter content. A similar positive trend was observed in UVA protection factors (UVA-PF), as illustrated in Figure 5. Further addition of TDSA up to 3% yielded similar improvements, confirming its efficacy in elevating both SPF and UVA-PF values through a synergistic effect with existing oil-phase filters.

4.2. Enhancing Film Homogeneity

The addition of TDSA addresses a key vulnerability inherent in emulsions that rely solely on lipophilic UV filters. After application and water evaporation, areas of the film consisting primarily of the water phase can remain insufficiently protected, presenting potential pathways for UV radiation transmission. Light microscopy images (Figure 6) illustrate the microstructure of an applied sunscreen film post water evaporation, with the water and oil phase stained with blue and red pigments, respectively. Figure 6 highlights the presence of distinct clusters of water phase (blue-green) in the oil-phase film (red). In the absence of a hydrophilic UV filter like TDSA in the blue-green area, the aqueous regions may lack adequate UV protection, allowing UV rays to penetrate. By fortifying the water phase, TDSA enhances the overall film uniformity and in-

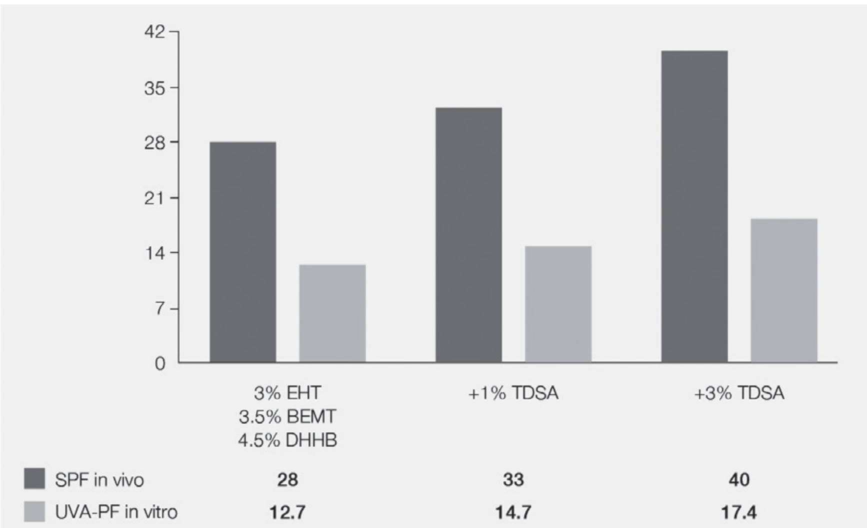
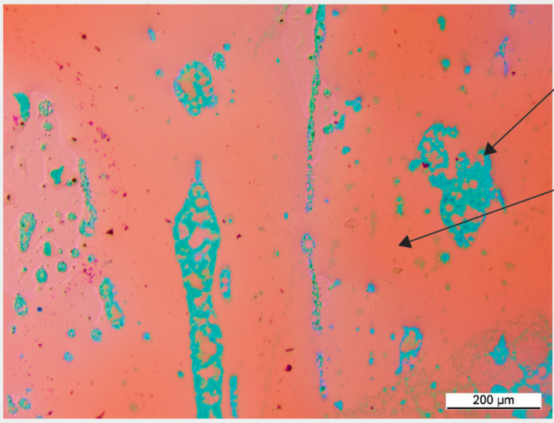


Fig. 5 Sun protection factor *in vivo* and UVA-PF in vitro by addition of TDSA.



■Fig. 6 Light microscopy of a sunscreen applied on a glass substrate after water evaporation, with the water and oil phase stained with blue and red pigments, respectively.

tegrity, leading to a more consistent protective barrier across the skin's surface.

4.3. Versatility of TDSA in Sunscreen Formulations

The incorporation of TDSA in the aqueous phase enables a reduction in the concentration of oil-soluble UV filters for achieving a same SPF. Consequently, this reduces the need for high levels of emollients, which are necessary to dissolve the commonly used solid lipophilic filters. Lowering the total oil-phase content contributes to more flexibility, and lighter and less greasy formulations with improved sensory characteristics – an important consideration not only for daily facial photoprotective care but also for the classical beach care products designed for enhanced cosmetic acceptability.

For example, a comparative evaluation using a standard formulation (Table 2) demonstrated that exclusive use of oil-soluble UV filters necessitated a total content of filters plus emollients of 56% to achieve the desired SPF and UVA-PF (Table 3). In contrast, substituting a portion of the oil-phase filters with TDSA enabled a significant reduction of the sum filters plus emollients to 36%, without compromising sun protection efficacy. The further addition of a particulate UV filter, such as Tris-Biphenyl Triazine (TBPT), which offers both UVB and UVAII protection, allowed the total oil phase required to dissolve the remaining solid lipophilic filters to be reduced further to 26%. This organic particulate filter, added post-emulsification, does not require solubilization in emollients and contributes additional light scattering, further boosting performance. Notably, formulations incorporating TDSA and a reduced oil phase demonstrated excellent physi-

■Table 2　Example for standard formulation.

Phase	Trade name	INCI	UV-DE-24-LB-153-0045-4-11
A	Emulgade® Verde 10 OL	Polyglyceryl-10 Oleate	3.00
	Eumulgin® Prisma	Disodium Cetearyl Sulfosuccinate	0.50
	Cetiol® ABV	C12-15 Alkyl Benzoate	x%
	Cetiol® B	Dibutyl Adipate	x%
	Cetiol® CC	Dicaprylyl Carbonate	x%
	Myritol® PGDC	Propylene Glycol Caprylate / Caprate	x%
	Lanette® 22	Behenyl Alcohol	1.00
	Protectol® PE	Phenoxyethanol	1.00
	Sensiva SC 50	Ethylhexylglycerin	0.20
	Uvinul® A Plus	Diethylamino Hydroxybenzoyl Hexyl Benzoate	x%
	Uvinul® T 150	Ethylhexyl Triazone	x%
	Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	x%
B	Water	Aqua	Qsp 100%
	Glycerin	Glycerin	5.00
	Verdessence® Xanthan	Xanthan Gum	0.30
	Hydrolite-5 Green	Pentandiol	3.00
	Uvinul® TS Hydro	Aqua, Terephthalylidene Dicamphor Sulfonic Acid	x%
	Tris amino ultra PC	Tromethamine	Qs
C	Tinosorb® A2B	Tris-Biphenyl Triazine (nano), Aqua, Decyl Glucoside, Disodium Phosphate, Butylene Glycol, Xanthan Gum	x%
	Verdessence® RiceTouch	Oryza Sativa (Rice) Starch	2.00
	Cetiol® Ultimate	Undecane, Tridecane	4.00

cal stability, whereas equivalent formulations with higher amount of emollients lacking TDSA were less stable under identical test conditions.

4.4. Sunscreen Formulations Guide containing TDSA

The ability to minimize emollient content makes TDSA particularly advantageous for products where sensory attributes are critical, like facial care. Additionally, TDSA's broad formulation compatibility supports the development of sunscreens that align with evolving environmental standards and regulatory expectations.

Two formulation examples highlight the versa-

Table 3 Filter systems based either on solely oil-soluble filters or on mixture with filters for the water phase and their corresponding required emollient concentration for achieving the same desired SPF and UVA-PF.

		Oil-Soluble only	Oil- + Water-Soluble	Oil- + Water-Soluble + Particulate
UV filters	Uvinul® T 150	5.0%	4.0%	2.50%
	Uvinul® A Plus	10.0%	7.5%	6.0%
	Uvinul® TS Hydro	-	**10.0% (3% active)**	**3.0% (1% active)**
	Tinosorb® S	5.0%	3.5%	2.2%
	Tinosorb® A2B	-	-	**5.0% (2.5% active)**
Emollients	Cetiol® ABV	10.0%	4.0%	5.0%
	Cetiol® B	11.0%	11.0%	8.0%
	Cetiol® CC	10.0%	3.0%	2.0%
	Myritol® PGDC	5.0%	3.0%	
Oil phase (filters + emollients)		**56%**	**36%**	**26%**

tility of TDSA in modern sunscreen systems:

- **Lotion SPF 30** (Figure 7): Incorporation of TDSA enables a light lotion texture. For increased viscosity and a richer sensory experience, Cosmedia® SP (INCI: Sodium Polyacrylate) can be added, resulting in a cream-gel structure ideal for daily skincare applications.
- **Spray Sunscreen** (Figure 8): TDSA can be used in the development of fluid formulations, such as for sprays that exclude nanoscale particulate filters. Such formulations are increasingly demanded by consumers seeking products that are easy to apply while maintaining high SPF and broad-spectrum protection.

5. Conclusion

Terephthalylidene Dicamphor Sulfonic Acid (TDSA) addresses several key challenges in modern sunscreen formulations. As a hydrophilic, broad-spectrum UVA filter with additional UVB attenuation, TDSA enables the development of photostable and effective sunscreens that meet current regulatory and consumer requirements. Its solubility in the aqueous phase allows for a reduction in solid oil-soluble UV filters and subsequently associated emollients, facilitating the development of lighter formulations with improved sensory properties.

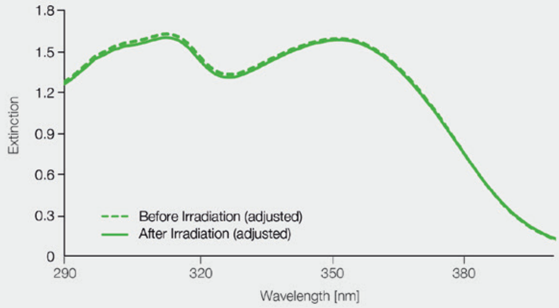
Acknowledgments:

Thank you to the technical service team BASF Grenzach GmbH.

Water Power Shield SPF 30
UV-DE-22-009-11-2

Phase	Ingredients	INCI	% by weight
A	Emulgade® PL68/50	Cetearyl Glucoside (and) Cetearyl Alcohol	3.00
	Eumulgin® Prisma	Disodium Cetearyl Sulfosuccinate	1.00
	Lanette® O	Cetearyl Alcohol	0.80
	Cetiol® Sensoft	Propylheptyl Caprylate	5.00
	Cetiol® ABV	C12-15 Alkyl Benzoate	7.00
	Cetiol® B	Dibutyl Adipate	15.00
	Preservative	[Preservative]	qs
	Uvinul® T 150	Ethylhexyl Triazone	3.00
	Uvinul® A Plus	Diethylamino Hydroxy-benzoyl Hexyl Benzoate	4.50
	Tinosorb® S		3.50
B	Water, demin.	Aqua	45.90
	Glycerin	Glycerin	5.00
	Verdessence® Xanthan	Xanthan Gum	0.30
C	Uvinul® TS Hydro	Aqua, Terephthalylidene Dicamphor Sulfonic Acid	3.00
	L-Arginine	Arginine	qs
D	Cetiol® Ultimate	Undecane, Tridecane	3.00

Specifications	
pH value (25°C)	6.2 - 6.4
Viscosity (Brookfield; RVNext; spindle RV04; 10 rpm; 25°C)	7200 - 7800 mPa s



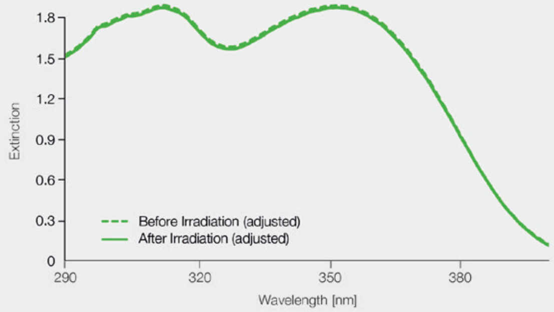
SPF in silico	29
SPF in vivo	33 | 38
UVA-PF in vitro	14.7
EcoSun Pass	213

■Fig. 7　Formulation example for lotion SPF 30 with a light texture.

Balanced Protection Sun Care Fluid SPF 50
UV-DE-23-TD-153-033-1-1

Phase	Ingredients	INCI	% by weight
A	Emulgade® Verde 10 MS	Polyglyceryl-10 Stearate	3.00
	Cetiol® B	Dibutyl Adipate	10.00
	Cetiol® CC	Dicaprylyl Carbonate	10.00
	Myritol® PGDC	Propylene Glycol Dicaprylate / Dicaprate	6.00
	Uvinul® A Plus	Diethylamino Hydroxy-benzoyl Hexyl Benzoate	8.00
	Uvinul® T 150	Ethylhexyl Triazone	4.00
	Tinosorb® S	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	3.50
	Preservative	[Preservative]	qs
B	Water, demin.	Aqua	40.20
	Hydrasensyl® Glucan Green	Water, Pentylene Glycol, Beta-Glucan, Caprylyl Glycol	3.00
	Avicel PC 611 (FMC BioPolymer)	Cellulose, Cellulose Gum	1.00
	BergaSom Sun 75 (Berg+Schmidt)	Lecithin	0.10
C	Water, demin.	Aqua	5.00
	Eusolex 232 (Merck)	Phenylbenzimidazole Sulfonic Acid	1.70
	Uvinul® TS Hydro	Aqua, Terephthalylidene Dicamphor Sulfonic Acid	4.50
	Tris Amino Ultra PC (Angus Chemie)	Tromethamine	qs

Specifications	
pH value (25°C)	7.0 - 7.2



SPF in vivo	66
SPF in silico	50
UVA-PF in vitro	23.2
EcoSun Pass	228

■Fig. 8　Formulation example for lotion/spray where no nano filters are possible.

References:

1) Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products

2) *Abid et al.* Photo-stability and photo-sensitizing characterization of selected sunscreen's ingredients. J Photochem Photobiol A (2017): 241-250

3) *L'Alloret et al.* New combination of ultraviolet absorbers in an oily emollient increases sunscreens efficacy and photostability. Dermatol Ther (2012)

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