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From nature to ingredients®

# facts

CITROFOL® citrate esters
in sunscreen formulation

## Introduction

In sunscreen formulations, several components act synergistically to provide effective protection to the exposed skin. Alongside the UV filters themselves, emollients are particularly relevant to both effectiveness and consumer acceptance of the product. This is due to their influence on the solubility of solid organic UV filters, dispersibility of inorganic UV filters and skin feel of sunscreen products.

With the specific challenges posed by sunscreen formulation in mind, we will take a closer look at the use of citrate esters as emollients in this context. Citrate esters are clear, odourless, oily liquids and have a long history of safe use as emollients in various personal care products. Jungbunzlauer's CITROFOL® citrate esters are obtained by acidic esterification of citric acid, which is produced by fermentation of carbohydrate raw materials like corn. Among Jungbunzlauer's portfolio of citrate esters, Triethyl Citrate (CITROFOL® AI) and Tributyl Citrate (CITROFOL® BI) are the most relevant derivatives for use in sunscreen formulation. Both come with a guaranteed non-GMO status. As shown in table 1, both are regarded as medium spreading emollients, but differ as regards other physico-chemical properties.

**Table 1: Overview of properties of citrate esters.**

| | **CITROFOL® AI** | **CITROFOL® BI** |
|---|---|---|
| INCI | Triethyl Citrate | Tributyl Citrate |
| CAS registry number | 77-93-0 | 77-94-1 |
| ISO 16128[a] | NOI = 1 | NOI = 0.39 |
| COSMOS | Yes | No |
| Interfacial tension [mN/m][b] | 32.0 | 28.5 |
| Spreading value [mm²/10 min][b] | 660 | 531 |
| Solubility in water at 25°C [g/100 ml][b] | 5.8 | Insoluble |
| Viscosity at 20°C [mPas][b] | 37 | 43 |

[a]Natural Origin Index; [b]own data

The fundamental parameter for our investigations was the solvent power of Triethyl Citrate and Tributyl Citrate in relation to selected standard organic UV filters. We also assessed the influence of both citrate esters on sun protection factor (SPF) and UVA protection factor (UVA-PF) in vitro. Their sensory profile was evaluated and compared to a benchmark emollient in a sunscreen matrix. The dispersibility of TiO2 and ZnO in Triethyl Citrate was investigated with a specific focus on certified natural formulations. Based on the results, we outline the benefits of using citrate esters as emollients with regard to cost-in-use and formulation flexibility.

## Formulating sunscreens with organic UV filters

Emollients function as solubilizers of solid organic UV filters such as the widely used Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT), Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB) and Ethylhexyl Triazone (EHT), but their solvent power differs significantly for the various UV filters. The choice of emollient and its usage rate therefore correlate directly to maximum applicable UV filter concentration and resulting SPF.

In addition to emollients, oily-liquid UV filters such as Ethylhexyl Salicylate (EHS) and Octocrylene are often incorporated into sunscreens to improve solvent power. However, this approach is not always feasible. Restrictions may arise from regulatory constraints. For example, in the EU, EHS is allowed only up to 5% in formulations according to Annex VI of the Regulation (EC) No 1223/2009 on Cosmetic Products. Octocrylene, in contrast, may be incorporated up to 10%, but has come under scrutiny as an endocrine disruptor with potentially negative effects on human health and the environment.[1,2] Furthermore, the absorbance spectrum of the oily-liquid filter with the best solvent power may not be the most suitable fit to provide efficient broad spectrum coverage, resulting in a loss of filter efficiency and increased costs. Last but not least, oily-liquid UV filters do not optimise product haptics. They frequently leave a greasy skin feel, hamper spreadability and absorption and thus limit consumer acceptance.

When using emollients as solvents it is important to consider their potential effect on the SPF. While a potential increase in absorbance can be exploited to improve the performance of sunscreens at the same usage rate of UV filter, resulting in an attractive cost benefit, this must be weighed against any potential reduction in the UV light absorbance.
The choice of solvents is therefore influenced by considerations affecting targeted SPF, regulatory and certification aspects, costs and skin feel.

**Solubility and efficient use of organic UV filters**

Ethylhexyl Triazone (UVINUL® T150 – EHT), Diethylamino Hydroxybenzoyl Hexyl Benzoate (UVINUL® A plus – DHHB) and Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (Tinosorb® S – BEMT) were selected as representatives of solid organic UV filters. Their solubility at 25°C in Triethyl Citrate and Tributyl Citrate was determined according to the method described by Herzog et al.[3] For *in silico* analysis, examples of UV filter combinations based on two different solvent systems were defined. The solvent systems consisted of a combination of 5% EHS and either 15% Dibutyl Adipate (reference) or 15% Tributyl Citrate. Consequently the maximum usage rate of EHT differed depending on solubility and/or regulatory limits. SPF, SPF rating and filter efficiency (i.e. SPF divided by total filter concentration) were determined *in silico* (http://www.sunscreensimulator.basf.com).

Table 2 gives an overview of the solubility values of BEMT, EHT and DHHB in standard emollients and citrate esters. The table reveals the exceptional solvent power of Tributyl Citrate for EHT of up to 35%. This is more than twice as high as that of Dibutyl Adipate, the standard emollient ranked second in solvent power at 16%. A formulation with Tributyl Citrate thus allows for a higher loading with EHT and thus a higher SPF. Both Tributyl and Triethyl Citrate showed excellent solvent power of 29% for DHHB, which is in line with the solvent power of the widely used emollient Dibutyl Adipate.

**Table 2: Maximum solubility of UV filters BEMT, EHT and DHHB in different solvents.**

| Solvent INCI | Solubility BEMT [%] | Solubility EHT [%] | Solubility DHHB [%] |
|---|---|---|---|
| Caprylic/Capric Triglyceride | 5[a] | 6[a] | 14[a] |
| Dibutyl Adipate | 10[a] | 16[a] | 31[a] |
| Tributyl Citrate | 3[b] | 35[b] | 29[b] |
| Triethyl Citrate | 1[b] | 11[b] | 29[b] |
| Dicaprylyl Carbonate | 9[a] | 6[a] | 18[a] |
| C12-15 Alkyl Benzoate | 12[a] | 4[a] | 22[a] |
| EHS (UV filter, max. usage rate 5%) | 20[b] | 4[b] | 34[b] |

[a]Sohn et al., 2020; [b]own data

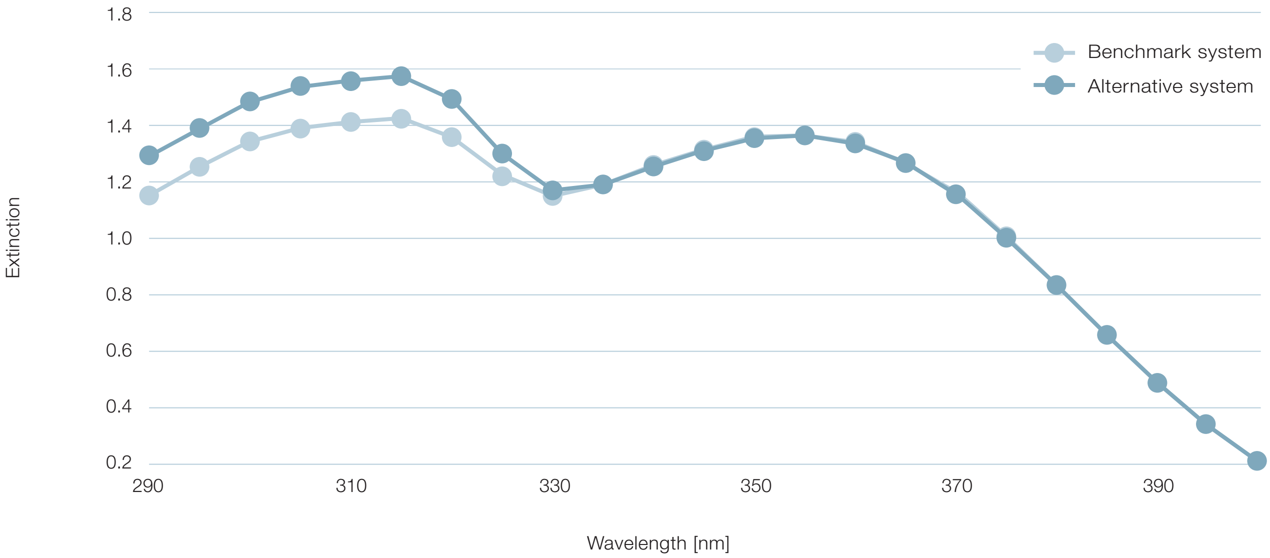
The example calculation illustrates that the increased solvent power for EHT positively affects SPF efficiency: table 3 shows the maximum solubility values of BEMT, EHT and DHHB in a formulation with 5% EHS and 15% emollient (benchmark system with Dibutyl Adipate vs. alternative system with Tributyl Citrate). In the benchmark system, the use of EHT is limited to 3% due to solubility. In the alternative system, the use of EHT can be increased to the limit of 5% imposed by regulatory restrictions. The other components of the UV filter combination were kept equal between the two systems. The use of Tributyl Citrate enables a slightly higher amount of EHT, a UVB filter with exceptionally high absorption efficiency,[4] which results in a significant increase in extinction in the UVB range (figure 1). Consequently, the SPF increases from 23.7 to 31.9, leading to an increase in the SPF rating from 20 to 30. The increase in filter efficiency (i.e. SPF/filter concentration) from 1.73 to 2.03 is of direct economic benefit.

**Table 3: Maximum solubility and regulatory limit of different UV filters in benchmark system (15% Dibutyl Adipate + 5% EHS) versus alternative system (15% Tributyl Citrate + 5% EHS). Usage rate refers to UV filter combination used to determine performance *in silico*. Solubility was calculated according to the following formula: amount solvent A* filter solubility in solvent A/(100-filter solubility in solvent A) + amount solvent B* filter solubility in solvent B/(100-filter solubility in solvent B).**

| UV filter | Max. solubility [%] in benchmark system | Max. solubility [%] in alternative system | Max. [%] permitted* | Usage rate [%] in benchmark system | Usage rate [%] in alternative system |
|---|---|---|---|---|---|
| BEMT | 3.0 | 1.7 | 10.0 | 1.3 | 1.3 |
| EHT | 3.0 | 8.2 | 5.0 | 3.0 | 5.0 |
| DHHB | 9.3 | 8.8 | 10.0 | 5.4 | 5.4 |
| EHS | - | - | 5.0 | 4.0 | 4.0 |

*according to Annex VI of the Regulation (EC) No 1223/2009 on Cosmetic Products

**Figure 1: Comparison of extinction between benchmark system and alternative system. An increased extinction in the UVB range is observed in the alternative system with higher EHT content.**



In addition, greater solvent power of the emollient gives the formulator flexibility regarding the exact composition of the oil phase to optimise skin feel and product aesthetics. When using Tributyl Citrate, the oil phase can be lowered overall and still offer sufficient solvent power for UV filters, thus achieving a lighter, less greasy skin feel. Furthermore, co-emollients can be chosen based on their sensory properties instead of having to focus on good solvent power.

**Influence of emollients on SPF and UVA-PF**

Another important aspect is the influence of the solvent matrix on UV absorbance and SPF. This has been described in the scientific literature both for technical solvents[5] and for emollients widely used for sunscreen formulations.[6] It was demonstrated that emollients can shift the wavelength of maximum absorbance ($\lambda_{max}$) and the specific extinction at the maximum absorbance $E\,(1,1)_{max}$.[6]

To investigate a possible influence of the emollient on the SPF, three o/w test emulsions with a calculated SPF of 25 and UVA-PF of 16 were prepared (table 4). They differed only in the emollient system. To ensure full solubility of the filter platform, 10% Dibutyl Adipate was used in all test formulations, combined with either 15% C12-15 Alkyl Benzoate (reference), Tributyl Citrate or Triethyl Citrate.

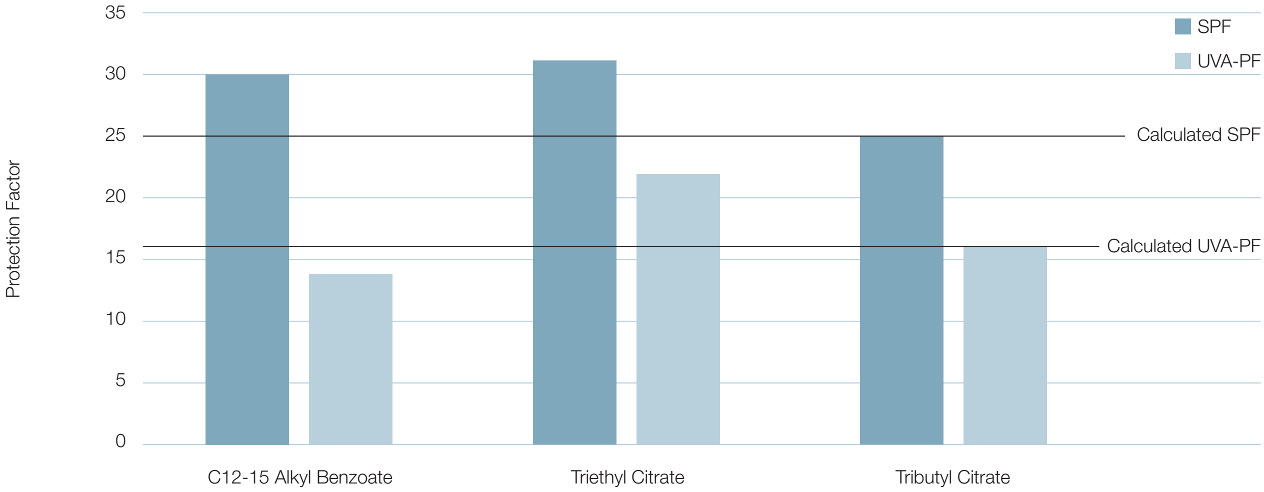
SPF and UVA-PF were determined *in vitro* based on ISO 24443:2012 with slight adaptations. An amount of 27.6 mg of sunscreen formulation was applied to roughened PMMA plates (4.8 cm x 4.8 cm, Type SB 6, Helioscreen, Paris, France). The sunscreen formulation was rubbed with a saturated latex gloved finger so that it was distributed evenly on the PMMA plate. After an equilibration time of 30 minutes, 5 transmittance measurements per plate were performed using a UV Transmittance Analyzer UV 2000S (Labsphere, North Sutton, USA). *In vitro* SPF and UVA-PF before irradiation (UVA-PF0) were calculated from the transmission data. The plates were then irradiated with a dose calculated using the ISO 24443 spreadsheet by means of an Atlas Suntest CPS+ (Atlas MTT, Linsengericht, Germany). Transmission measurements were taken again and post-irradiation UVA-PF calculated. The SPF and UVA-PF values given in figure 2 represent the mean results from three plates (5 measurements per plate).

Table 4: **Composition of test formulations used for SPF and UVA-PF *in vitro* determination and sensory profiling.**

| Phase | INCI/Name | Reference formula [%] | Formula with Triethyl Citrate [%] | Formula with Tributyl Citrate [%] |
|---|---|---|---|---|
| A | Aqua | q.s. to 100 | q.s. to 100 | q.s. to 100 |
| | Glycerine | 3.0 | 3.0 | 3.0 |
| | Sodium Gluconate | 0.2 | 0.2 | 0.2 |
| | Xanthan Gum | 0.4 | 0.4 | 0.4 |
| B | Cetyl Alcohol, Glyceryl Stearate, PEG-75 Stearate, Ceteth-20, Steareth-20 (Emulium® Delta MB) | 4.0 | 4.0 | 4.0 |
| | Dibutyl Adipate (Cetiol® B) | 10.0 | 10.0 | 10.0 |
| | C12-15 Alkyl Benzoate (Cetiol® AB) | 15.0 | | |
| | Triethyl Citrate (CITROFOL® AI) | | 15.0 | |
| | Tributyl Citrate (CITROFOL® BI) | | | 15.0 |
| | Diethylamino Hydroxybenzoyl Hexyl Benzoate (Uvinul® A Plus) | 6.0 | 6.0 | 6.0 |
| | Ethylhexyl Triazone (Uvinul® T 150) | 2.5 | 2.5 | 2.5 |
| | Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (Tinosorb® S) | 2.0 | 2.0 | 2.0 |
| | Ethylhexyl Salicylate (Eusolex® OS) | 5.0 | 5.0 | 5.0 |
| C | Preservative | q.s. | q.s. | q.s. |

Analysing the test emulsions, all of the combinations achieved an SPF of ≥ 25 (figure 2). No negative deviation from the previously calculated SPF was observed when formulating with citrate esters. Looking at the UVA-PF, only the formulation with C12-15 Alkyl Benzoate showed a slightly negative deviation from the calculated value of 16.1. The formulation with Tributyl Citrate matches the calculated UVA-PF exactly. Interestingly, when using Triethyl Citrate, an increase in UVA-PF by almost 40% compared to the calculated value was obtained. This may be explained by a higher polarity of Triethyl Citrate compared to C12-15 Alkyl Benzoate. The use of emollients with higher polarity has previously been described as resulting in higher UVA protection.[6]

**Figure 2: SPF and UVA-PF determined *in vitro* in different test formulations.**

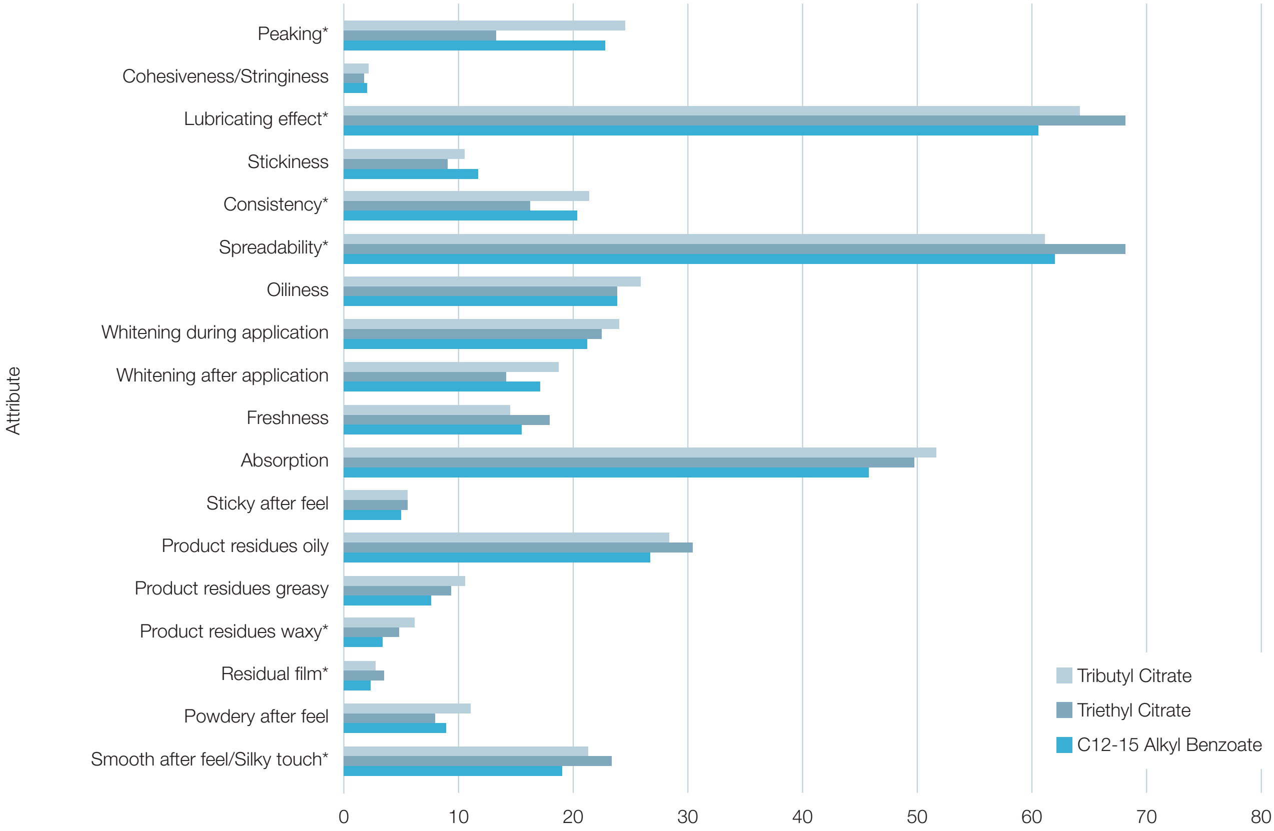



**Sensory profiling of sunscreen with organic UV filters**

To evaluate the sensory performance of Tributyl Citrate and Triethyl Citrate compared to C12-15 Alkyl Benzoate as a reference, the test formulations as described in table 4 were presented to a sensory panel trained for personal care leave-on products. The samples were anonymised and evaluated by the panel in two replicate sessions under standardised conditions (sensory booths, 20.6–21.5°C, 51–52% relative humidity). Descriptive profiling was based on a method adapted from ASTM Standards E 1490-92.[7,8] Data collection and analysis was performed using FIZZ Network/SENPAQ software. The samples were ranked on a scale from 0 (attribute not pronounced) to 100 (attribute strongly pronounced).

The detailed sensory profiling of citrate esters in the test emulsions showed that Tributyl Citrate was rated similar to C12-15 Alkyl Benzoate, whereas Triethyl Citrate actually outperformed it in a range of attributes (figure 3). Based on these data, Tributyl Citrate can be regarded as an economic 1:1 replacement for C12-15 Alkyl Benzoate. The formulation with Triethyl Citrate came with further sensory benefits, including reduced peaking, better gliding effect, lighter consistency, better spreadability and a smoother after feel. Tributyl and Triethyl Citrate fell behind slightly in only one attribute, which was related to residues in after feel. Overall, these results highlight the potential of both types of citrate ester to improve product functionality and aesthetics simultaneously.

**Figure 3: Sensory profiling of test formulations with different emollients (Tributyl Citrate vs. Triethyl Citrate vs. C12-15 Alkyl Benzoate). Values are means of n = 8 panelists. Asterices denote attributes which were evaluated as differing significantly between test formulations.**




## Formulating with inorganic UV filters for certified-natural sunscreens

In view of rising concerns regarding the environmental and health safety profiles of many organic UV filters, the demand for products containing exclusively inorganic UV filters is increasing. This is caused by a stricter regulatory framework especially in the US, where the FDA lists only the inorganic filters titanium dioxide ($TiO_2$) and zinc oxide (ZnO) as GRASE (generally recognised as safe and effective) for use in over-the-counter sun protection products.[9] Moreover, consumers increasingly prefer natural sun protection products. To date, $TiO_2$ and ZnO are the only UV filters which are COSMOS approved by Ecocert for use in COSMOS-certified natural cosmetic products. Although inorganic UV filters do not require the presence of specific solvents, the choice of emollients does have a profound influence on dispersion stability. For the formulation to be considered natural, the emollient itself must, of course, satisfy the relevant criteria.

**Dispersion of inorganic UV filters**

When preparing dispersions of inorganic, particulate UV filters in emollients, the physico-chemical characteristics of each phase play an important role in product appearance, stability and performance. Generally, molecular weight, structure and especially polarity of an emollient influence the dispersion. For example, in the case of uncoated ZnO higher emollient polarity promotes better dispersion.[10]

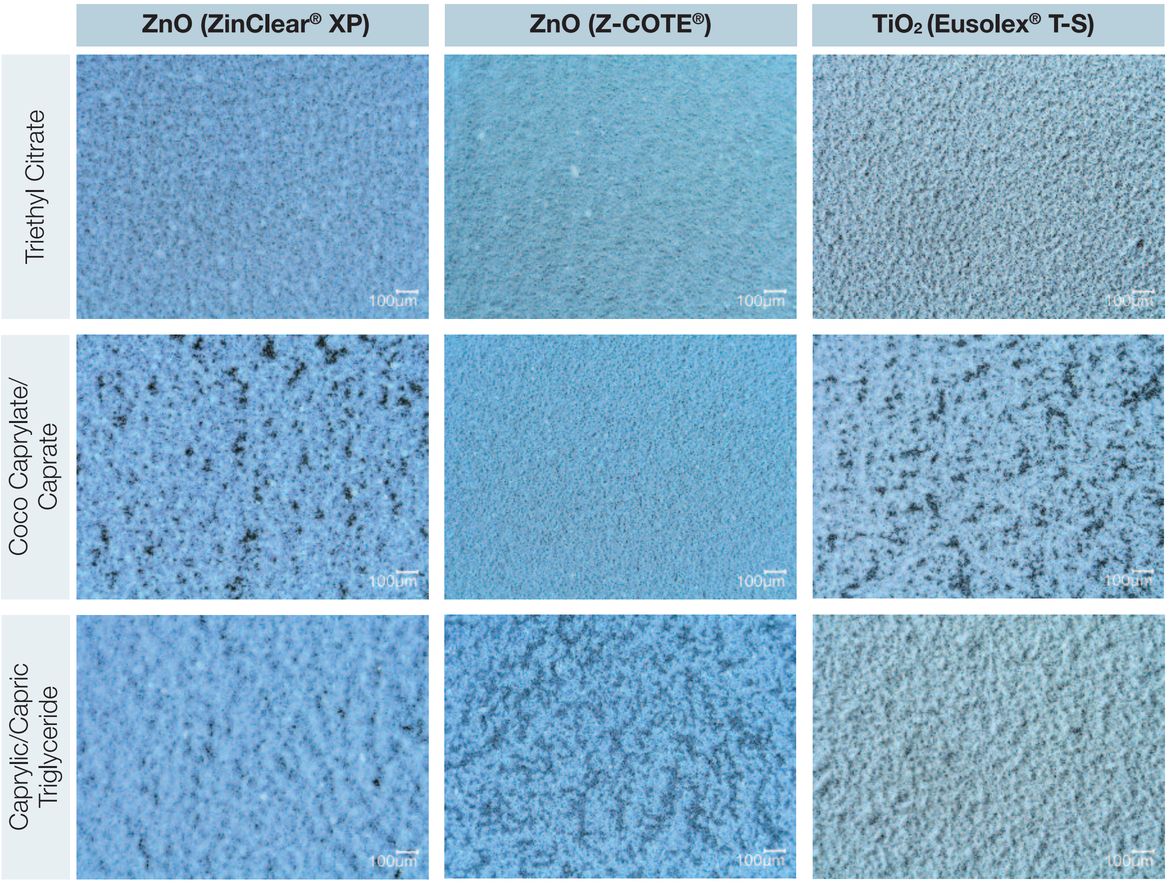
Focusing on UV filters suitable for natural formulations, two grades of uncoated ZnO (Z-COTE® and COSMOS-approved ZinClear® XP) and one COSMOS-approved $TiO_2$ (Eusolex® T-S) were investigated for their dispersibility in COSMOS-approved emollients. Coco-Caprylate/Caprate and Caprylic/Capric Triglyceride served as benchmarks for comparison with Triethyl Citrate. The particulate filters were dispersed in the emollient at a ratio of 1:9 using an ULTRA-TURRAX® homogeniser at a high shear rate (13,000 rpm) for 5 min. The dispersion was monitored by microscopy.

The microscopic evaluation of uncoated ZnO revealed profound differences between the tested emollients (figure 4). Triethyl Citrate proved to be a suitable matrix in which to uniformly disperse both ZnO products, resulting in images showing an adequate dispersion as described in the literature.[11] The use of Coco-Caprylate/Caprate and Caprylic/Capric Triglyceride led to the formation of particle aggregates depending on ZnO types.

Certain surface modifications, such as the vegetable-derived surface coating on the tested filter, are permitted for $TiO_2$ even in certified natural products. Triethyl Citrate provided the most uniform dispersion for $TiO_2$ among the tested emollients, with no particle aggregation.

These results provided proof of principle of the applicability of Triethyl Citrate in achieving uniform dispersions of commercially available test material.

**Figure 4: Dispersibility of inorganic UV filters in different emollients. Scale bars denote 100 µm.**



**Sensory profiling of formulation with inorganic filters**

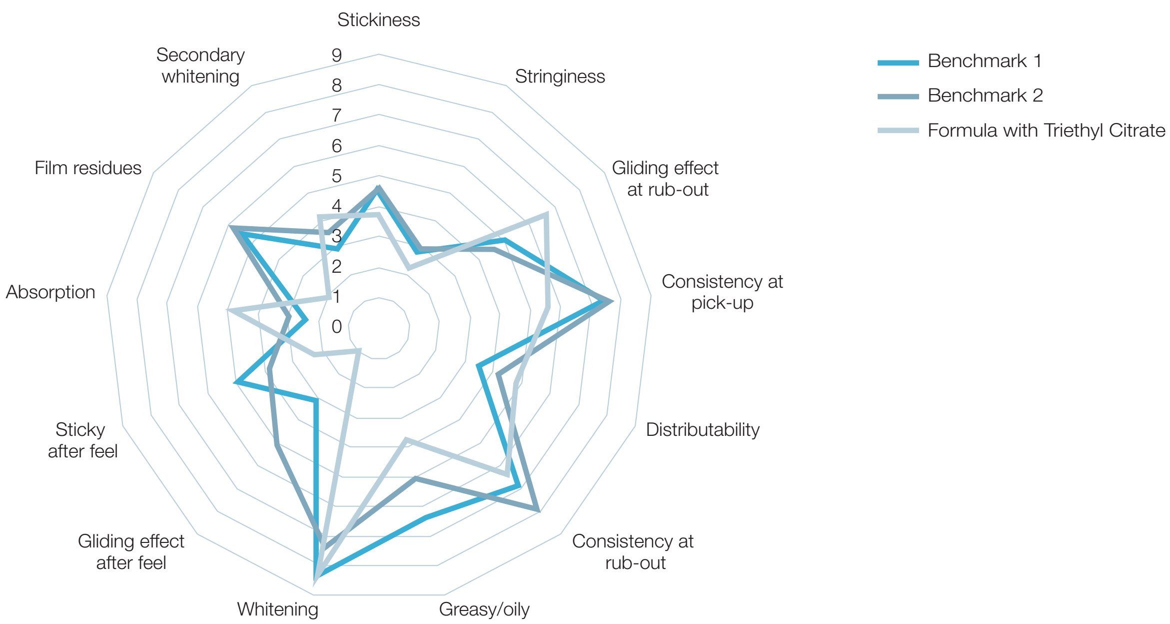
Particle dispersion is also reflected in distributability on the skin, which is an important requirement for effective protection from sun. Furthermore, emollients influence attributes related to pick up of the product, rub out and after feel on the skin, and thus consumer acceptance. To evaluate the applicability of Triethyl Citrate, a full formulation comprising only inorganic UV filters with a calculated SPF of 30 and a UVA-PF > 10 was prepared as shown in table 5. The sensory attributes of this formulation were compared with those of two commercially available, certified natural benchmark formulations with SPF 30 and UVA protection claims. This was done by presenting the anonymised formulations to a trained sensory panel consisting of 10 panellists. The samples were ranked on a scale from 0 (attribute not pronounced) to 10 (attribute strongly pronounced).

**Table 5: Composition of example sunscreen formulation with inorganic filters and Triethyl Citrate.**

| Phase | INCI/Name | Amount [%] |
|---|---|---|
| A | Aqua | q.s. to 100 |
| | Glycerine | 3.0 |
| | Sodium Gluconate | 0.2 |
| | Xanthan Gum | 0.4 |
| B | Zinc Oxide (Z-Cote®) | 13.1 |
| C | Cetyl Alcohol, Glyceryl Stearate, PEG-75 Stearate, Ceteth-20, Steareth -20 (Emulium® Delta MB) | 4.0 |
| | Triethyl Citrate (CITROFOL® AI) | 20.0 |
| D | Titanium Dioxide (Eusolex® T-S) | 9.0 |
| | Preservative | q.s. |

In the sensory profiling, the sunscreen formulation with inorganic UV filters and Triethyl Citrate showed beneficial characteristics compared to benchmarks from the market. Specifically, consistency was lighter and gliding effect and distributability were more pronounced while at the same time the skin feel conferred was less greasy/oily. This resulted in faster absorption and less film residues after product application. Triethyl Citrate is therefore a promising ingredient for formulations of certified-natural sunscreen products.

**Figure 5: Sensory profiling of sunscreen with Triethyl Citrate compared to commercially available natural-certified benchmarks. Values are means of n = 10.**



## Conclusion

The emollients Triethyl Citrate and Tributyl Citrate showcase remarkable advantages for sunscreen formulations. The excellent solvent power of Tributyl Citrate enables cost-efficient, high-SPF formulation with extraordinary flexibility regarding co-emollients, especially when relying on EHT as an organic UV filter. Triethyl Citrate is a COSMOS-approved alternative emollient 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 citrate esters represent outstanding value in the formulator's palette of emollients for use in sunscreens, optimising performance, costs and consumer experience.

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## About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Thanks to continuous investment, state-of-the-art manufacturing processes and comprehensive quality management, we are able to provide outstanding product quality.

Our mission "From nature to ingredients®" commits us to protecting people and their environment.

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