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The Easy Way to Make a Sunscreen

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The Easy Way to Make a Sunscreen

Introduction

This article presents easy ways to develop sun care formulations with the best UV filters and key ingredients while using innovative tools to develop innovative products that meet the latest regulatory requirements as well as consumer wishes. Designing and manufacturing a sunscreen has become more and more complex (1, 2). Over the decades the purpose of a sunscreen has shifted from just **»tanning without sunburn«** to prevention of premature skin-aging and skin cancer in addition. Technology has thus improved to cover UVA protection and also performance standards have become more stringent over the years. The Sun Protection Factors (SPF) are much higher and there are also UVA protection criteria that must be fulfilled, e.g. the European Recommendation which requires the UVA Protection Factor to be at least 1/3 of the SPF value or greater (UVA-PF ≥ 1/3 SPF). Measuring the SPF and the UVA-PF are expensive and sometimes, the expected result after an elaborate development of a sunscreen is not achieved. Furthermore a sunscreen has to please its user. For a sunscreen to be successful in the market place, using it has to be a pleasant experience. This means it must have a pleasant skin feel during and after application, as well as being optically acceptable (no whitening) and diffusing a nice scent. For designers and manufacturers of sunscreens the requirements can be summarized in the following 4 Basic Requirements (3): **1. Efficacy**, choosing the right UV filters combination and other key ingredients to achieve the desired performance, **2. Safety**, be it objective or just perception by the media and the consumer, **3. Registration**, which is most important if the sunscreen is to be distributed in different regions or even globally, and **4. Patent Freedom**, i.e. **»freedom to operate«** while respecting 3rd party intellectual property (IP) rights.

Abstract

This article presents easy ways to develop sun care formulations with the best UV filters and key ingredients. Designing and manufacturing a sunscreen has become more and more complex. Technology has improved to cover UVA protection and also performance standards have become more stringent over the years. The first step to overcome the complexity of designing a sunscreen is using an easy tool such as, the BASF Sunscreen Simulator, available at www.basf.com/sunscreen-simulator. *In silico* design is the easiest way to get an overview of the performance of various UV filter combinations. Easy-handling UV filters, as aqueous dispersions or solutions in oil, can be used to increase the SPF of sunscreens while maintaining sufficient UVA protection, or to make sunscreens via cold process. The easiest way to make a sunscreen we can imagine, would be by using a sunscreen concentrate that turns into a sunscreen by just adding water. BASF has indeed developed such a concentrate, called Uvinul® Easy. Any sunscreen between SPF 6 and SPF 50 can be readily manufactured; for a desired SPF X one simply has to dilute the Uvinul® Easy concentrate to X %.

BASF Sunscreen Simulator for basic design of a sunscreen

The first step to overcome the complexity of designing a sunscreen is using an easy tool such as the BASF Sunscreen Simulator, available at www.basf.com/sunscreen-simulator (4). **Fig.1** shows a typical calculation on the Sunscreen Simulator. First the region has to be chosen; only UV filters approved in a certain region will be available for simulation. The region setting **»Global«** will thus only allow the UV filters that are globally approved and only at concentrations below the lowest limit worldwide, i.e. a very limited selection of UV filters. On

the other hand, the region setting **»All Filters«** allows the use of all UV filters that are available in the Sunscreen Simulator at the maximum concentration limit worldwide. In this setting also new UV filters such as Tinosorb® A2B which are not yet approved in all regions, but nonetheless commercially available can be tested *in silico*. **Fig. 1** shows such an example. Thanks to the new very efficient UV filter Tris-Biphenyl Triazine (TBPT, Tinosorb® A2B) an *in silico* SPF 54 can be achieved with only 14.5 % UV (Filter Efficacy displayed: SPF/ % Filter = 3.7).

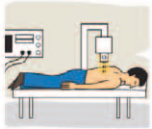
The Sunscreen Simulator takes into account the photo stability of each UV absorbers and also of certain UV filter combinations that are known to either destabilize or stabilize each other (example EHMC/BMBM and OCR/BMBM respectively). *In silico* results correlate well with *in vivo* SPF results. Detailed descriptions can be found in the literature (5, 6). The Sunscreen Simulator is continuously being updated and adapted to the latest regulations. The latest metric introduced is the **»Normalized Transmitted UV Dose at 1 MED«**. This metric measure shows how close a certain UV filter combination reaches the profile of **»the ideal sunscreen«**, which is a flat profile through-

INPUT

Region: All filters **Date:** 2014/06/27 17:14:12
Application amount: 2.0 mg/cm²

UV Filter composition INCI name	USAN name	Abbreviation	Amount
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (Tinosorb S)	Bemotrizinol	BEMT	2.5 %
Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (Tinosorb M, active)	Bisoctrizole	MBBT	6 %
Ethylhexyl Triazone (Uvinul T150)	Octyltriazone	EHT	2 %
Tris Biphenyl Triazine (Tinosorb A2B, active)	-	TBPT	4 %
		Total:	14.5 %

SPF



SPF (ISO 24444): 54.5

Rating: 50

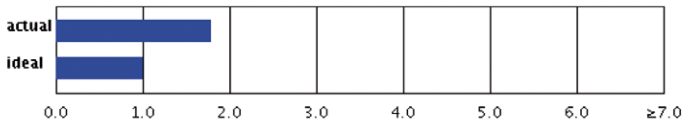
Simulation of the sun protection factor in vivo (SPF,ISO 24444) is performed. A description of the calculations is given in:
„*In silico* Determination of Topical Sun Protection", *Bernd Herzog* and *Uli Osterwalder*, Cosmetic Science Technology 2011, 62 - 70

UVA-Metrics

Country	in vivo	in vitro	Rating
EU, CH	**Simulated PPD** UVA-PF (ISO 24442): 18.0 UVA-PF/SPF: 0.33	**EC Recommendation** (UVA-PF/SPF > 0.33) UVA-PF (ISO 24443): 18.4 UVA-PF/SPF: 0.34 Critical wavelength: 378.0 nm	UVA
AUS, MERCOSUR	**UVA-PF and ratio calculation with labeled SPF** Labeled SPF: -	**(Method: Cosmetics Europe)** UVA-PF (ISO 24443): - UVA-PF/SPF: -	
GB		**Boots Star-Rating UVA/UVB ratio** w/o irradiation: 0.79 with irradiation: 0.79	UVA ★★★
JP	**JCIA Rating** UVA-PF (ISO 24442): 18.0		PA++++
USA		**FDA Final Rule** Critical wavelength: 379.0 nm	**Broad Spectrum** decreases the risk of skin cancer and early skin aging caused by the sun
Global		**No global standard has been defined**	

Fig. 1 BASF Sunscreen Simulator, Input and Results (4). INPUT: The simulated sunscreen is based on 4 UV filters and a total amount of 14.5 %. SPF: The sunscreen simulator calculates the SPF following ISO 24444, i.e. using the COLIPA lamp that is used in *in vivo* testing. It also gives the SPF category (= Rating) according to the European Recommendation.
UVA-Metrics: All relevant UVA protection performance metrics are calculated and displayed.

Normalized Transmitted UV Dose at 1MED



An "ideal sunscreen" would perform like a neutral density filter with the same protection at any wavelength. In such a case the Transmitted UV Dose at 1 MED has a value of 7.9 J/cm². This value is used to normalize the Transmitted UV Dose @ 1 MED. The closer the normalized value comes to 1, the more ideal is the spectral profile of the respective sunscreen.

Fig. 2 Normalized Transmitted UV Dose at 1 MED (4).The recently introduced metric **»Normalized Transmitted UV Dose at 1 MED«** (NTUVD) shows the distance of a sunscreen from the performance of the ideal sunscreen.

out the relevant UVB/UVAII and UVAI range from 290 to 400 nm. **Fig. 2** shows the NTU-VD of the composition in **Fig. 1**. The value of 1.8 is a very good value. Most sunscreen today are still quite UVB biased in their protection profile and have thus NTUVD values between 2 and 3. The old completely UVB biased sunscreen had values > 7.

Easy-handling UV filter to increase the SPF of a sunscreen

In sunscreen development it is a common task to increase the SPF of an existing sunscreen, say from SPF 20 to 30, ideally without changing all the other characteristics of the formulation. Common practice is to just add more UVB filter; but than in order to keep the 1/3 UVA ratio, this means also adding more UVA filter, which in turn may mean adapting the oil phase to avoid crystallization of UVA filter, which leads to adjustment of the emulsifier concentration and possibly the sensory characteristic has also to be corrected. **Fig. 3** shows the typical ingredients in a sunscreen. The whole new formulation will of course have to be tested for stability. This scenario shows that a **»simple«** SPF increase from 20 to 30 can quickly turn into complicated laboratory and testing work.

The easy way to increase SPF 20 to SPF 30 can be achieved by adding 2 % (**»as active«**) of Tinosorb® S Aqua (BEMT). Because BEMT is a broad-spectrum UV filter the whole absorbance curve of the SPF20 formulation will shift to higher level and thus keeping the UVA-PF/SPF ratio above 1/3 (**Fig. 4**). Since this is Tinosorb® S in an aqueous form, there is no danger to overload the oil phase of the formulation.

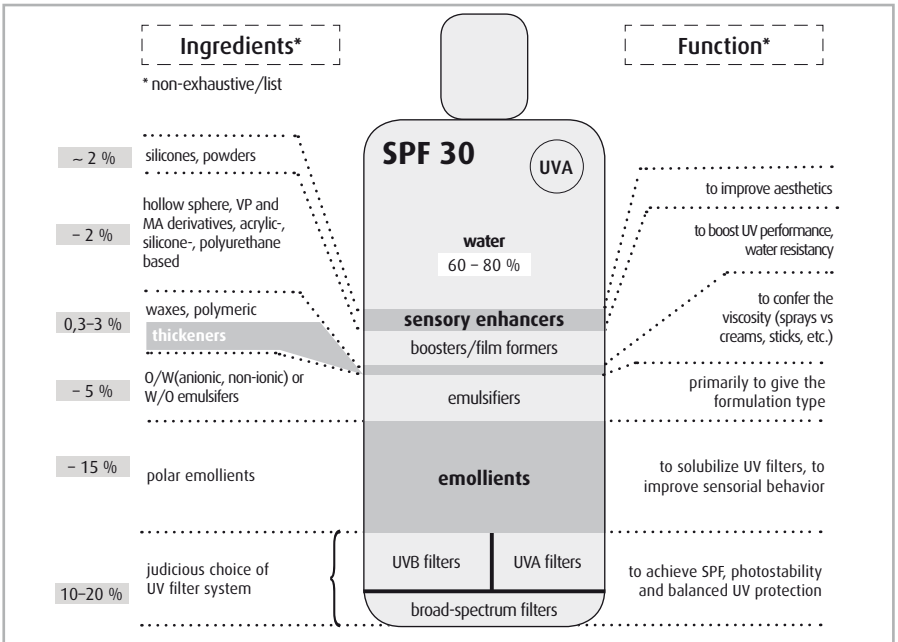


Fig. 3 Ingredients of a typical sunscreen and its functions (1). SPF, sun protection factor; O/W, oil-in-water; W/O, water-in-oil; UV, ultraviolet.

Cold Process thanks to easy-handling UV filters

The next example shows the easy way to make an SPF 50 sunscreen. The high SPF and efficient UVA protection comes from the aqueous particulate, broad-spectrum UV filter Tinosorb® M and the liquid oil-soluble UV filter system Uvinul® A plus B. The use of these UV filters makes a cold process possible. It means also fewer raw materials and easier processing with reduced manufacturing time and energy consumption. Only a low concentration of Eumulgin® SML 20 emulsifier is required, helped by Tinovis® ADE as thickener. Cetiol® B and Cetiol® C5 provide a nice skin feeling (**Table 1**). This example shows that it is possible to achieve high performance with a simple formulation.

Claimed SPF	20	30
Uvinul® MC80 Tinosorb® S Uvinul® A Plus Tinosorb® S Aqua	5% 1.5% 5%	5% 1.5% 5% + 10% (2% active)
SPF calc.	20	30
UVA-PF calc.	12.5	19.2
Critical Wavelenght [nm]	374nm	376nm

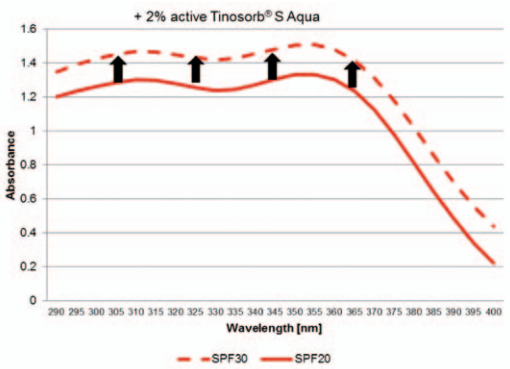


Fig. 4 Use of Tinosorb S Aqua to increase SPF from 20 to SPF 30. The advantage of using Tinosorb S Aqua while maintaining the EU recommendation on UVA protection (UVA-PF/SPF ≥ 1/3)

Ingredients	INCI	% by weight	Function
Eumulgin® SML 20	Polysorbate 20	1.00	Emulsifier (O/W)
Cetiol® B	Dibutyl Adipate	10.00	Emollient
Cetiol® C 5	Coco-Caprylate	5.00	Emollient
Cosmedia® DC	Hydrogenated Dimer Dilinoleyl/Dimethylcarbonate Copolymer	2.00	Water resistance agent
Uvinul® A Plus B	Ethylhexyl Methoxycinnamate, Diethylamino Hydroxybenzoyl Hexyl Benzoate	15.00	Broad spectrum UV filter
Water, demin.	Aqua	49.80	
Edeta® BD	Disodium EDTA	0.20	Complexing agent
Tinovis® ADE	Sodium Acrylates Copolymer, Hydrogenated Polydecene, PPG-1 Trideceth-6	1.00	Rheology modifier
Tinosorb® M	Methylene Bis-Benzotriazolyl Tetramethylbutylphenol (nano), Aqua, Decyl Glucoside, Propylene Glycol, Xanthan Gum	15.00	Broad spectrum UV filter
Protectol® PE	Phenoxyethanol	1.00	Preservative
Perfume	Parfum	qs	Fragrance

Table 1 Frame Formulation SPF 50, using easy-handling UV filters.

The ultimate easy way: making a sunscreen with Uvinul® Easy

Combining the use of the sunscreen simulator and the easy handling UV absorbers simplifies developing suncare formulations already tremendously. As the even easier way to make a sunscreen we can imagine using a sunscreen concentrate that turns into a sunscreen by just adding water. BASF has developed such a concentrate. It is called Uvinul® Easy.

Phase inversion of emulsions

The technology of Uvinul® Easy is based on phase inversion processes, which can be used for the low-energy formation of fine emulsions. The most common emulsion structures for personal care applications are either oil-in-water emulsions (O/W), which consist of oil droplets in a continuous water phase, or water-in-oil emulsions (W/O), where water droplets are present in a continuous oil phase. The emulsion type depends on many parameters such as emulsifier type, temperature T, salt concentration and also the oil-to-water-plus-oil ratio α. A first approximation for the preferred emulsion structure is given by the Bancroft rule, which states that the solubility of the emulsifier sets preference for the continuous phase of an emulsion. This rule explains the principle influence of the emulsifier structure, salt concentration and temperature. Phase inversions of emulsions, from O/W to W/O or vice versa, can be enforced by a variation of these parameters.

As an example a schematic phase diagram for ethoxylated surfactants is shown in **Fig. 5**. The emulsion type is given in dependence of α and T. The grey areas indicate inversion regimes, where micro emulsions, lamellar phases or multiple emulsions are present. Two possible routes for phase inversions from W/O to O/W are shown. First, cooling a mixture with a fixed composition from A to B leads to a phase inversion from W/O to O/W. The use of a temperature induced phase inversion is called Phase Inversion Temperature process (PIT). It is utilized for the preparation of fine emulsions in a low energy process, where high shear stress is not necessary. The PIT process and its use have been described in many publications, e.g. (7). Second, an alternative route is to keep the temperature fixed and to change the

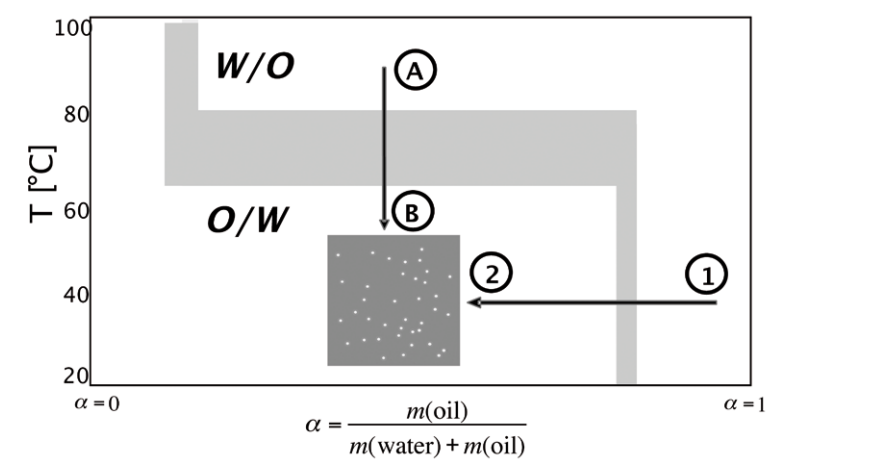


Fig. 5 Phase Inversion Emulsion. Example for the phase behavior of emulsions with ethoxylated surfactants. Inversion processes are possible via temperature shift (from A to B) or concentration shift (from 1 to 2).

composition. As an example this can be achieved by reducing α, which is indicated in **Fig. 5** as the route from 1 to 2. This method is called phase inversion by concentration shift. This approach has been studied and described for example by the research group of Solans (8).

In **Fig. 6** the effect of water addition (horizontal axis) to an oil concentrate with emulsifiers is shown. The starting point is indicated by a star on the lower left hand side of the graph. The oil concentrate contains about one percent of water, which is present in inverse micelles. The addition of water leads first to a formation of intermediate phases and finally to an O/W emulsion. Microscope pictures are shown in the graph. From the left to the right: First a liquid two phase system is formed, where water droplets are surrounded by oil. On further addition of water, a multiple emulsion structure is formed and finally a fine O/W emulsion is obtained. The viscosity passes through a maximum on dilution with water. A possible reason is the formation of liquid crystalline phases. The conductivity increases and later also decreases on dilution with water. Here two opposite effects are present: in the beginning the change from an oil continuous structure to water continues structure and also the dilution with deionized water.

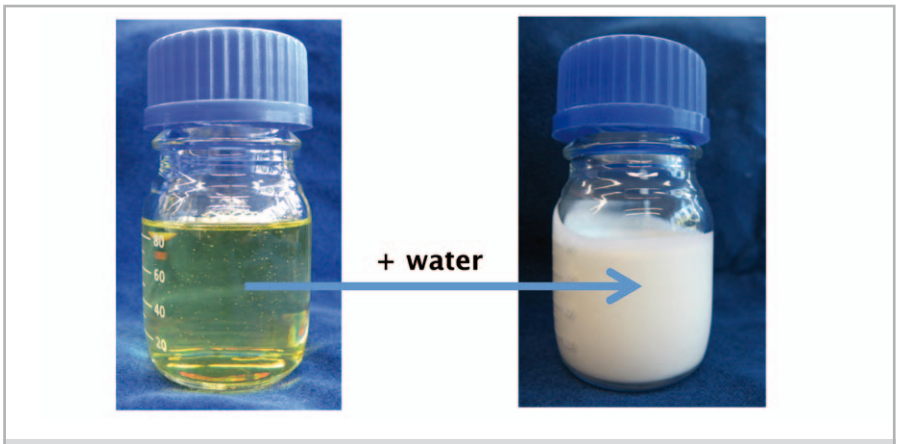


Fig. 7 Formation of O/W Emulsion with UV Filters by Dilution of Uvinul® Easy. On the left side an oil based concentrate with UV filters is shown. It contains small amounts of water, which is present in inverse micelles (L2 Phase). The addition of water leads to a spontaneous formation of an oil-in-water emulsion (O/W).

How to use Uvinul® Easy

Uvinul Easy and its dilution are shown in **Fig. 7**. On the left-hand side, Uvinul® Easy is shown. It is an oil based concentrate with UV filters and emulsifiers. It is transparent and the small amounts of water are present in inverse micelles. On the right, the addition of water at constant temperature with moderate stirring leads to a spontaneous formation of fine white O/W emulsion. This emulsion will show creaming on standing due to its low viscosity. Therefore it is necessary to adjust the rheological profile by the addition of a thickener.

With Uvinul Easy any sunscreen between SPF 6 and SPF 50, i.e. the range of SPF categories recommended in Europe (9), can be readily manufactured. For a desired SPF X one has to dilute the Uvinul Easy concentrate to X %. For example, if for making an SPF 30 sunscreen, the concentrate has to be diluted down to 30 %. The SPF values have been confirmed at different test institutes according to ISO 24444 (10) with 5 subjects with frame formulations with SPF´s between SPF 6 and 50.

The right amount of UVA protection is automatically achieved (ISO 24443). Thickener can be added to achieve the desired rheological properties, e.g. to make various sun protection formats, such as lotion, cream, spray etc.

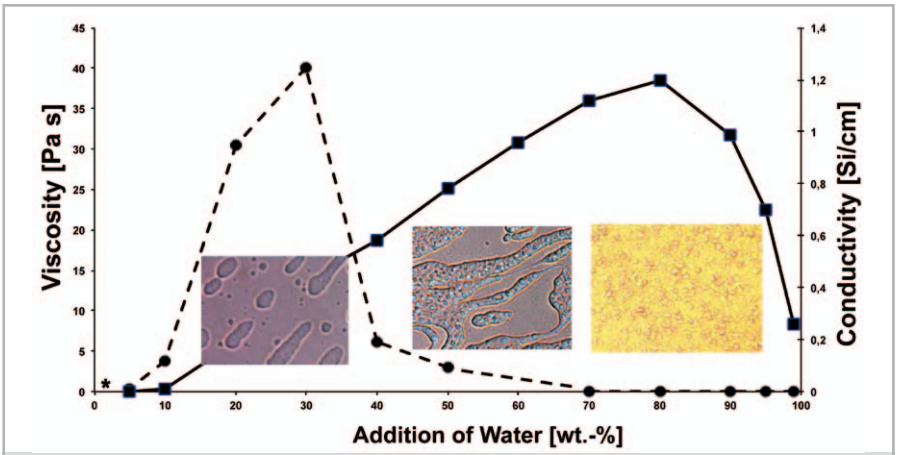


Fig. 6 Phase Inversion of Emulsions – Viscosity and Conductivity. Addition of water to an oil based concentrate (star) leads to changes in conductivity (squares), viscosity (spheres) and structure.

Composition of Uvinul® Easy

INCI
Dibutyl Adipate, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Ethylhexyl Methoxycinnamate, Laureth-7 Citrate, Polyglyceryl-2 Dipolyhydroxystearate, Ethylhexyl Triazone, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Lauryl Glucoside, Triethanolamine

UV Filters	Concentration
Uvinul A Plus	20 %
Uvinul MC 80	20 %
Uvinul T 150	6 %
Tinosorb S	5 %

Thickener, Preservatives and Fragrances etc. to be added individually in order to make the product unique.

	Daily Care SPF15 UVA	Suncare SPF30 UVA	Lip Stick SPF50 UVA
A: UV absorbers	15 % Uvinul® Easy	30 % Uvinul® Easy	50 % Uvinul® Easy
B: Emollients	10 % Cetiol® Sensoft		5 % Cetiol® MM 3 % Cetiol® SB45
C: Emulsifiers			9.5 % Lameform® TGI
D: Thickeners	0.4 % Cosmedia® SP 1.5 % Tinovis® ADE	3.2 % Tinovis® ADE	10 % Candelilla Cera 2.5 % Cera Microcristallina (Paramelt) 3.5 % Polyethylene (Honeywell)
E: Sensory enhancers	2 % Polymethyl Methacrylate (Sekisui Plastic) 2 % Cyclopentasiloxane (Dow Corning)		
F: Film formers			8 % Cosmedia® DC
G: Preservatives, actives, perfume	0.5 % Dermiscan® SPB LS 9337		0.5 % Covi-ox® T90
H: Others	0.2 % Edta® BD 3 % Glycerin	0.2 % Edta® BD q.s NaOH	2 % Chione® HD Crisp Gold S230V 2 % Chione® Snowfall White S130D 2 % Chione® Super Red 434Z
I: Water	q.s	q.s	-

Table 2 Frame Formulations with Uvinul® Easy.

Customized Products

Customization of the formulation is possible by addition of other emollients and sensory enhancing products (silicones, powders...) to adapt the aesthetics of the formulation to that desired. Furthermore preservatives and fragrances are added to increase the possibilities to make a unique product. It is possible to make other cosmetic formats such as skin care formulations (Daily cream with SPF) and make-up formulation (BB Cream or Lipstick). Frame formulations demonstrate the broad application of Uvinul® Easy (**Table 2**).

Limitations (of the easy way to make sunscreen)

Whereas the BASF sunscreen simulator can very accurately predict the average potential performance of a sunscreen (5,6), it cannot make any prediction about possible interactions between that sunscreen and the skin, e.g. especially the spreading behavior which is crucial for film-building and thus what actual SPF can finally be achieved. Since it is absolutely crucial for good compliance that the skin feel of the sunscreen is acceptable to its user in order to assure sustainable sun protection (11), these properties have to be designed and tested by physical laboratory work.

Although the sunscreen concentrate Uvinul® Easy leaves a lot of room to make a product unique, the variability is of course never as large as by starting sunscreen manufacturing from scratch. The latter requires however much more know-how and experience in formulating.

As always in making a sunscreen or in fact any other goods, one has to respect the intellectual property (IP) of third parties. Knowledge of the IP landscape can be especially challenging in the manufacturing of sunscreens. There are hundreds of application patents that may have to be considered. In the case of Uvinul Easy BASF has already analyzed relevant 3rd party patent rights. The following disclaimer applies to a patent application that covers the combinations of the UV filter Tinosorb® S and the emollient Cetiol® B (12):

The combination of Tinosorb® S and Cetiol® B is subject to a pending patent application of third parties in Germany, especially DE 10038713. Therefore, BASF does not offer or sell this product combination in Germany, nor for the use in Germany. Furthermore, BASF excludes any liability towards its customers if they interfere with said IP right.

Conclusions

Although making sunscreens can be very complex there are now easier ways to achieve this. This starts by using the BASF sunscreen simulator in the design or to just to gain more understanding of how the performance of sunscreens can be influenced by varying the composition and the concentrations of the UV filters.

Easy-handling UV filters, Tinosorb® M, Tinosorb® A2B, Tinosorb® S Aqua and Uvinul® A Plus B allow the preparation of sunscreens by cold process, which makes manufacturing easier and energy efficient. Broad-spectrum UV filters can be used to increase the SPF of a sunscreen while maintaining the UVA-PF/SPF ratio. Uvinul® Easy has been created to rapidly incorporate an SPF claim into different application formats without specific knowledge in sun care area. This is ideal for cosmetics manufacturer with limited know-how and resources in sun care. The launch of Uvinul® Easy is planned at the IFSCC 2014 in Paris in October 2014.

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