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abstract

Cosmetic products are exposed to oxygen during their life cycle. This can cause several challenges. The formation of allergens, formation of sensitizers like peroxides, building of smell, rancidity, reduction of active ingredients by oxidation, changes of olfactory fragrance and inducing pathogen skin disorders like acne aestivalis. So, there is a need to use the right antioxidant system to protect the finished product in order to minimize these issues. In this study we demonstrate that StoppOx®, a new natural synergistic antioxidant blend, performs well or even better compared to the benchmark BHT. We measured the antioxidative potential and the radical potential in an exposition scenario to UV rays, oxygen and thermal energy.

Introduction

Ensuring the oxidative stability of perfumes, oils and cosmetic actives is a must for cosmetic players. If that is done successfully the result is a longer product shelf life and improved brand perception among consumers. Another challenge for production companies is the formation of irritants and allergens from oxidized fragrance compounds. (**Fig. 1**)

Fragrance allergens – which trigger an immune response in the individual – can be structural allergens from the plant of origin. But there are also allergens that occur during the lifecycle of the product because of oxidation. Preventing oxidation-formed allergens and irritants like peroxide, which, in contrast to allergens, elicit a negative but not immune-related

reaction from skin upon contact, was the primary aim behind the creation of StoppOx®, a new natural antioxidant supplied by Germany's All Organic Treasures. A secondary effect, however, has proven to be of particular interest to the beauty industry: namely StoppOx's® ability to extend finished products' best before dates. It consists of a combination of vitamin E – not isolated α-tocopherol, but a mixture of tocopherols – and ethyl ferulate, deriving from rice shells. As well hop extract. (INCI: Helianthus annuus seed oil, Humulus lupulus, tocopherol, ethyl ferulate).

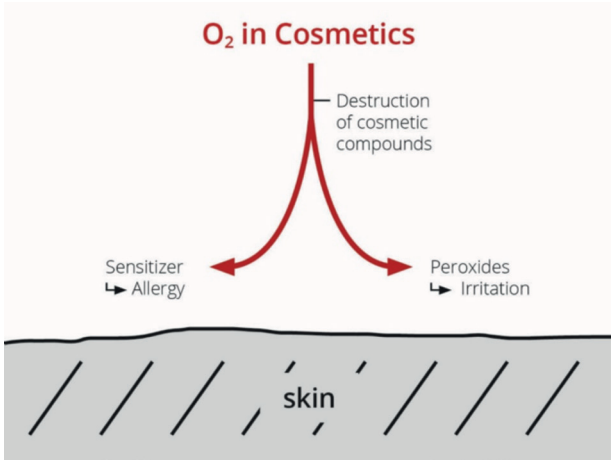

Fig. 1 Oxygen in cosmetics

The SCCS OPINION [1] on Fragrance allergens in cosmetic products 2012 says: "Experimental and clinical studies have shown that there are fragrance substances that act as prehaptens, i.e. their sensitization potency is markedly increased by air exposure due to oxidation (autoxidation). The clinical studies show that the exposure to allergens formed due to autoxidation causes significant contact allergy in consumers."

"Air oxidation of prehaptens can be prevented to a certain extent by measures during handling and storage of the ingredients and final products to avoid air exposure, and/or by addition of suitable antioxidants."

Another challenge when it comes to the formation of Peroxides in (Suncare) Products is that they can induce Acne Aestivalis [2]. Here the Peroxides react with lipids from the suncare product or sometimes with skin lipids through energy by light.

It is very well reported that the fragrance compound Tea tree oil forms sensitizers like the endoperoxide Ascaridol under oxidation [3,4]. This was the reason why in this investigation Tea Tree oil was used. When it comes to controlling free radicals in materials across many industries, butylated hydroxytoluene (BHT) stand tall as the benchmarks with regards to efficacy. This was the reason to include BHT in the testing scenario. We measured the antioxidative potential and the radical potential in an exposition scenario to UV rays, oxygen and thermal energy.

Material and Methods

The Antioxidative Power (AP) [5,6]

The new antioxidative power (AP) method offers determination of the overall antioxidative power of active ingredients, i.e. plant extracts, vitamins etc., by monitoring the reducing activity against a stable test radical – diphenyl-picryl-hydrazyl (DPPH) with ESR spectroscopy. The AP method utilizes the well-known DPPH method with the major difference that both the antioxidative capacity and the antioxidative activity are used to characterize the antioxidant being tested. For this purpose, different concentrations of the active ingredients are assayed in real time by ESR spectroscopy and the decrease of the test radical spins is tracked accordingly for each set. With this innovative technique important kinetic information is additionally obtained that is completely neglected by most other test systems. Therefore, both the reaction time and the reduction potential of the antioxidants contribute to the calculation of the AP.

AP = n° free radicals / mg*min

The resulting AP is expressed in antioxidative units (AU), where 1 AU corresponds to the activity of a 1 ppm solution of pure vitamin C (ascorbic acid) as a benchmark.
This method allows a rapid and generally applicable technique for the measurement of the AP across a range of very different classes of substances.
The AP method provides:

(1) a standardized analytical method with benchmarked results,

(2) a meaningful comparison of active ingredients regarding their capability to scavenge free radicals and/or to terminate radical chain reactions,

(3) a framework for controlling the variation within or between products, and providing quality standards that are benchmarked for quality control and efficacy claims.

The AP method permits functional Quality Control during the whole production process. It enables selection of raw materials with the highest antioxidant activity and is essential for the quality control during long term stability testing and stockage conditions and represents an important new tool for the creation of new products with high antioxidant activity.

Radical Potential (RP)

The method is based on the reaction between peroxide and lipid radicals and UV-radiation. Radical chain reactions occur when lipidic radicals are exposed to UV light. These radicals can be determined by using Electron Spin Resonance (ESR) probing techniques.
Fats, oils, emulsions, flavors, among others, can be analyzed by the RP method.

To be able to compare different raw materials and to detect different radical species, it is necessary to dilute the test substances in an emulsion. The emulsion itself shall not contain any chemicals that influence the radical generation or that react with UV light (unsaturated lipids, PEG-emulsifiers, metal ions). A cosmetic inert cream basis was chosen (Physiogel hypoallergic moisturizing cream). This emulsion is able to absorb hydrophilic and lipophilic raw materials.

Measurement of Antioxidative Potential
The measurements of the antioxidant capacity and reactivity were performed by using Electron Spin Resonance (ESR) spectroscopy. Since this spectroscopic technique is able to quantify free radicals and since it is applicable to opaque, viscous, and colored samples, it is particular suitable for the analysis of antioxidants in cosmetic products. The measurements discussed in this article were performed with the X-band ESR spectrometer Miniscope MS 300 (Magnettech, Germany) and the following technical parameters: 60 G sweep width, 100 Gain, 1 G modulation amplitude, 7 mW attenuation, 3365 G central field, 0.14 sec time constant. The Antioxidative Power (AP) is a parameter able to quantify both the reaction capacity and velocity of antioxidants. The test radical DPPH (2,2-diphenyl-1-picryl-hydrazyl, Sigma-Aldrich, Munich, Germany) is used as a detector molecule. At least 3 concentrations of the test sample were prepared in EtOH (99 %) and added to DPPH to obtain an initial radical concentration of 0.1 mM. The signal intensity decay of each concentration of the test samples is recorded at different time intervals during the reaction until saturation is reached and all antioxidant active molecules had reacted with the test radical.
From these intensities a first order kinetic is obtained for each concentration set. The kinetic parameters are used to calculate the reaction time tr and the static parameters are used to calculate the characteristic weight wc. Both parameters are used to calculate the AP by means of the following equation:

AP = RA x N (DPPH) / tr x wc

For a direct comparison of different antioxidants, the AP method is standardized to the activity of vitamin C (ascorbic acid, supplied by Sigma-Aldrich, Munich, Germany at the highest grade of purity). The antioxidative activity of a solution of 1 ppm vitamin C is defined as an antioxidative unit (AU).

Measurement of Radical Potential

Sample Preparation
The tea tree oils are incorporated into the neutral emulsion (Physiogel Hypoallergenic cream) to an end concentration of 10 % (w/w).
The obtained formulations were then diluted 1:10 with distilled water.

To the samples a semistable spin probe PCA (2,2,5,5-tetramethyl pyrrolidine N-oxyl) 0.01 mM final concentration was added, the samples are inserted in capillary quartz tubes, the concentration of the spin marker is monitored by ESR spectroscopy before and after defined UV radiation doses. The PCA spin probe is photostable and resistant to antioxidants, but it promptly reacts with the UV generated free radicals inside the samples (mainly lipid peroxides and lipidic radicals). The amount of UV generated free radicals can be quantitatively detected from a calibration curve. HC-AP-RP-01-2017 5 .

UV Irradiation

The UV irradiation of the samples was performed with a UV solar simulator 300 W Oriel (Newport). The irradiances as integrated value over the spectral ranges were E (UVB=280-320) = 23,5 W/m² and E (UVA = 320-400nm) = 180 W/m². To test the effect of different UV doses the irradiation time was varied. The emitting Intensity is controlled before each measurement.

Instrumentation

The measurements were performed with a commercial high sensitive X-band bench top Electron Spin Resonance Spectrometer MiniScope MS300, supplied from Magnettech GmbH Berlin, Germany.

The UV radiation time and the corresponding UV dose and the middle erythema dose (MED) is reported in **Tab. 1**.

The oils were incorporated at 10 % (w/w) into the base emulsion (Physiogel), measured directly after the incorporation, and stored at 40 °C. Once a week the vials were opened and mixed). After 3 weeks, and 6 weeks the RP value was re-determined.

Irradiation time	UV dose (J/cm²)
30 s	0.696
60 s	1.392
120 s	2.784
180 s	4.176
300 s	6.960

Tab. 1 UV dose and irradiation time

Results and Discussion

Antioxidative Power (Tab. 2)

All data are means affected by a standard deviation < 5 %.

The Antioxidant Power determines the activity of antioxidants and radical scavengers. The higher the capacity of a test substance to neutralize free radicals is and the higher the reaction velocity is, the higher is the AP:

$$AP = n° \text{ free radicals} / wc*tr \quad [1]$$

Therefore, low wc values and low tr values will result in high AP values.

Both parameters can be used as indicators for a given antioxidative system.

The AP values are benchmarked against ascorbic acid (vitamin C) and expressed in Antioxidative Units (AU).

T = 0

The tea tree oil (TTO) showed no antioxidant activity, although the test radical is unstable in the pure oil due to peroxide reactions.

The addition of 1 % of the BHT solution showed only a very low antioxidant activity. BHT can be considered as a weak and low reactive antioxidant.

The addition of 2 % of the StoppOx® solution showed a high antioxidant performance. The reaction time of Ethylferulate was found.

T = 3 weeks

No antioxidative activity in the pure TTO.

A very low capacity and reactivity in the TTO + BHT sample.

A lower AP value in the TTO+StoppOx® sample (49 % of the initial value). Lower reactivity was observed.

Time	Product	Antioxidative Power	
		AP (AU)	t_r (min)
T = 0 24.02.17	Tea tree oil	0	–
	Tea tree oil + 1 % BHT Lsg.	3	13.77
	Tea tree oil + 2 % StoppOx® Lsg.	278	0.70
T = 3 weeks 17.03.17	Tea tree oil	0	–
	Tea tree oil + 1 % BHT Lsg.	2	17.90
	Tea tree oil + 2 % StoppOx® Lsg.	136	1.27
T = 6 weeks 13.04.17	Tea tree oil	0	–
	Tea tree oil + 1 % BHT Lsg.	0	–
	Tea tree oil + 2 % StoppOx® Lsg.	95	1.99

Tab. 2 Results of the Antioxidative Power testing

T = 6 weeks
No antioxidative activity in the pure TTO and in the TTO + BHT sample.
A lower AP value in the TTO+StoppOx® sample (34 % of the initial value). Capacity values remained unaltered. Lower reactivity was observed. The addition of 2 % of the StoppOx® solution showed a high antioxidant performance.

Radical Potential

The amount of UV-induced free radicals inside the diluted samples was measured. The results are reported in **Tab. 3**.
Knowing the concentration of the spin trap PCA within the sample (0,01 mM), the amount of reduced PCA can be calculated. Since one electron is needed to reduce 1 molecule of PCA, the radical concentration inside the sample can be calculated using a calibration curve.
From the Area under the Curve (AUC) analysis the following radical concentrations have been calculated.

T = 0
The placebo sample did not show any increase in UV-inducible free radicals.
The addition of 10 % of the oils showed the generation of higher amounts of UV-inducible free radicals.
The addition of the antioxidant solutions (BHT and StoppOx®) reduced the amount of inducible free radicals to 57 % and 58 % of the pure TTO, respectively. The samples were stored at 40 °C and will be analyzed after several weeks of storage.

T = 3 weeks
The pure TTO showed an increase in inducible free radicals from 29.4 to 55.5 %.
The addition of the antioxidants (BHT and StoppOx®) showed the same low values of free radicals as at the t=0 timepoint. Only 35 %-36 % of the free radicals in the pure TTO were detected.

T = 6 weeks
The pure TTO showed an increase in inducible free radicals from 29.4 to 41.3 %.
The addition of the antioxidants (BHT and StoppOx®) showed a significant reduction in the amount of inducible free radicals. The differences between the two antioxidant additions are clearly visible: with BHT an RP value of 27.9 % was found, whereas the addition of StoppOx® showed a very low RP value of only 11.3 %.
The radical amounts are depicted as a function of the UV-irradiation doses (**Fig. 2**).

Time	Product	Abbreviation	% of induced free radicals	induced free radicals (mM)	± sd
	Placebo (Physiogel)		**0**	0	–
T = 0 24.02.17	Tea tree oil	TTO	**29.4**	2.94×10^{-3}	0.18×10^{-3}
	Tea tree oil + 1 % BHT Lsg.	TTO + BHT	**16.8**	1.68×10^{-3}	0.18×10^{-3}
	Tea tree oil + 2 % StoppOx® Lsg.	TTO + StoppOx®	**17.2**	1.72×10^{-3}	0.22×10^{-3}
T = 3 weeks 17.03.17	Tea tree oil	TTO	**41.3**	4.13×10^{-3}	0.40×10^{-3}
	Tea tree oil + 1 % BHT Lsg.	TTO + BHT	**14.6**	1.46×10^{-3}	0.02×10^{-3}
	Tea tree oil + 2 % StoppOx® Lsg.	TTO + StoppOx®	**15.1**	1.51×10^{-3}	0.25×10^{-3}
T = 6 weeks 13.04.17	Tea tree oil	TTO	**55.5**	5.55×10^{-3}	0.14×10^{-3}
	Tea tree oil + 1 % BHT Lsg.	TTO + BHT	**27.9**	2.79×10^{-3}	0.16×10^{-3}
	Tea tree oil + 2 % StoppOx® Lsg.	TTO + StoppOx®	**11.3**	1.13×10^{-3}	0.17×10^{-3}

Tab. 3 Results of the Radical potential testing

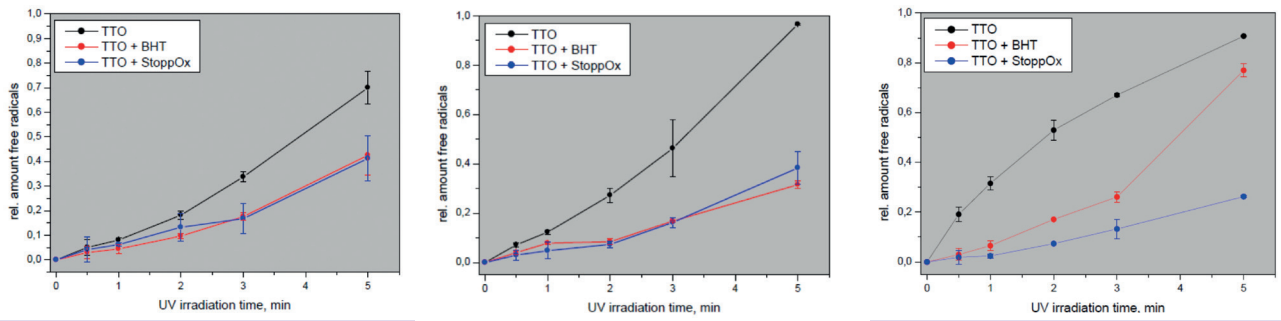

Fig. 2 Stability Testing of oxidation under UV Rays

Summary

The results demonstrate that under long term exposure of? thermal energy, oxygen and UV Rays the StoppOx® system is able to protect sensitive compounds like fragrances or lipids from short and long term oxidation. As it is natural the performance of synthetic BHT is given or even beaten.

Thanks

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contact

Corresponding Author:
Dr.rer.medic. David Hauck
Dipl.-Ing.(FH) Pharm. Chemie
E-Mail: RD@aot.de

Distribution in North Amerika:
Gary Bartl
Austrade Inc
3309 Northlake Boulevard, Suite 201
Palm Beach Gardens, Florida 33403
www.austradeinc.com

Manufacturing:
All Organic Treasures GmbH
Am Mühlbach 38
87487 Wiggensbach | Germany
www.cosmetic-oils.com