

## Novel findings for a long established product that enhance versatility and stability of sunscreens

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### Abstract

According to the gel network theory of emulsion stability, the aqueous phase consists of a gel-network generated by hydrophilic emulsifiers (HLB > 7) and lipophilic co-emulsifier (HLB < 6) forming an envelope around emulsified droplets and membrane-like structures throughout the aqueous phase. The oil phase ideally consists mainly of liquid crystalline lipid structures.

Latest research revealed a unique emulsifier that is able to form mainly lamellar structures with very dense packed layers of water phase and liquid crystalline lipid phases. Additionally the rarely seen micro-domains which are known to be responsible for stabilizing emulsions could be identified by freeze-fracture Transmission-Electron-Microscopy. Comparative science will show formulators how to overcome current challenges, such as high load of UV filters and pigments over a broad viscosity range, and illustrate possibilities to develop a new generation of high sophisticated sunscreens and day care products with a high protection factor whilst also respecting sensorial needs.

### Introduction

Emulsions are thermodynamically unstable systems formed by a mixture of two immiscible liquid phases and a third phase, the emulsifier (Baby et al. 2008). These emulsifiers can be classified according to their predominant chemical charge as non-ionic, anionic, cationic and amphoteric. Independently on the molecule charge in water dispersion each emulsifier has particular mechanism to stabilize emulsion systems (Korhonen 2004). The main reason for using emulsified systems for sunscreens over e.g. single oil phase formulas is to enable easy non-oily skin application and to build non-tacky, smooth films on skin. Emulsion bear a variety of parameters for optimization of those features and a good emulsion system can significantly improve the consumers compliance. (Ansel 2000, Lachmann 2001)

According to the gel-network theory of emulsion stability, the aqueous phase consists of a liquid crystalline (LC) gel-network generated by hydrophilic emulsifiers (HLB > 7) and lipophilic co-emulsifier (HLB < 6) forming an envelope around emulsified droplets and membrane-like structures throughout the aqueous phase (Dahms 2010). The oil phase ideally consists mainly of liquid crystalline lipid structures. The membrane-like structures are responsible for the viscosity of the emulsion as well as for the stabilization of the water-oil interphase. These membrane-like gel-network structures behave similar in an aqueous medium like polymers as with increasing concentration the viscosity increases in an exponential way (Dahms 2010).

The objective of this study was to get a deep understanding what kind of emulsion structures are formed in complex sunscreen emulsions and how do they look different depending on the type of emulsifier. As a second step the emulsification power of different emulsifiers has been investigated.

## 1. Assessment by Transmission Electron Microscopy

For understanding on how emulsifiers work DSM investigated emulsions on a 'close to the molecular structure'-level. Emulsions can be complex mixtures and sometimes can contain 30 different ingredients. All of them may have an influence on the structure of the emulsion and on its thermal stability. To understand those structures in more detail it is important to first visualize them. Freeze-fracture Transmission Electron Microscopy (TEM) is a technique delivering deep insights of such emulsion structures.

For sample preparation the emulsion was applied on a grid in a very thin layer and then frozen by jet-freezing technique. This layer was first freeze fractured and then further freeze etched to enhance visibility of liquid crystalline domains and a replica is taken from the frozen emulsion template. The replica imprint were mounted onto copper grids, dried and those samples finally analyzed by TEM pictures.

### *Comparison of PEG-100 Stearate and Potassium Cetyl Phosphate in a model emulsion base system*

Two different emulsifiers from the group of non-ionic polymeric emulsifiers and anionic emulsifiers, often used in sunscreens, have been chosen: PEG-100 Stearate and Potassium Cetyl Phosphate (PCP). The model system based on a simple gel-network has been prepared consisting of only the emulsifier, Glyceryl Stearate as co-emulsifier in a ratio of 1:4 and water. We chose a relatively long (3 weeks) settling phase after preparation of the emulsion to allow full and stable development of the network before freeze-fracture TEM has been performed and pictures were taken with a CCD camera ( $\mu$ -Eye).

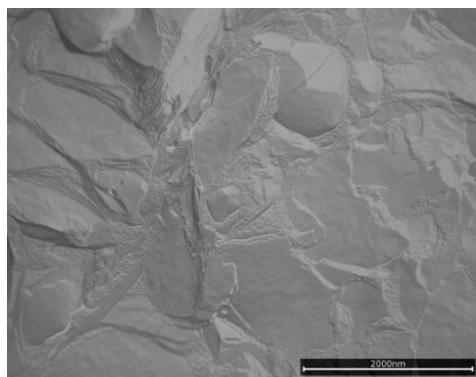


Fig. 1: PEG-100-Stearate

PEG-100 Stearate leads to a lot of smaller smooth areas of LC structures with uneven edges.

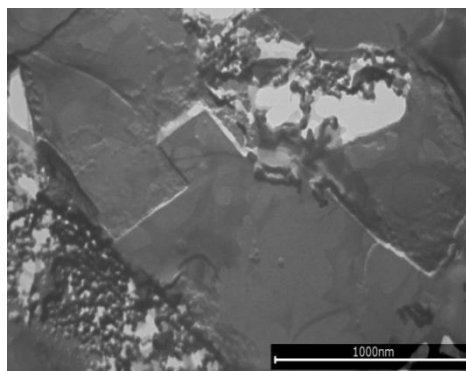


Fig. 2: Potassium Cetyl Phosphate

PCP shows large smooth LC areas with smooth edges and sharp corners.

Smooth surfaces in the TEM pictures indicate liquid crystalline emulsifier layers (LC), rough surfaces indicate a water phase. Both emulsifiers form lamellar liquid crystalline structures creating a gel-network throughout the aqueous phase (Fig. 1 and 2). The lamellar structures are very dense packed with water between the layers of emulsifier. Our simple model emulsion consisting of 3 ingredients: emulsifier, co-emulsifier and water showed some remarkable differences in the liquid crystalline network. Freeze-fracture treatment revealed that PEG-100 Stearate leads to a lot of smaller smooth areas of LC structures with uneven edges whereas Potassium Cetyl Phosphate showed rather large smooth LC areas with smooth edges and sharp corners. Additionally small round micro-domains became visible on top of the lamellar structures which seem to be very specific for PCP (Fig. 3-4).

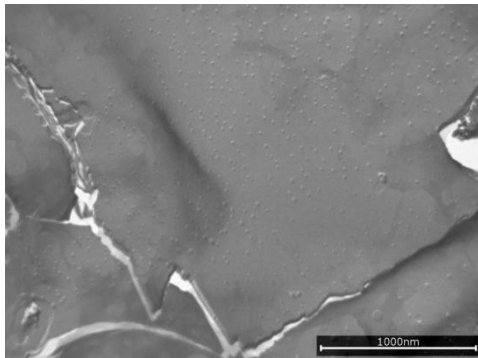


Fig. 3: Micro-domains in PCP gel-network

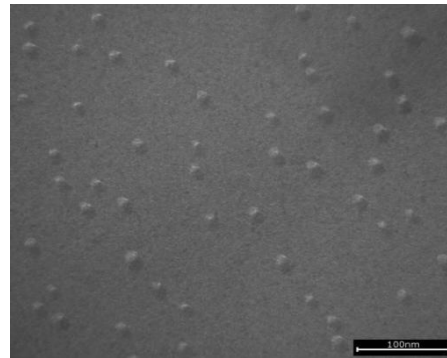


Fig. 4: Micro-domains in PCP gel-network

These micro-domains are most likely self-organized Potassium Cetyl Phosphate molecules on the surface of liquid crystalline lamella and vesicles charging the network negatively by the polar head groups. This charge distribution leads to a repulsion of vesicles when they would converge (Fig. 5). Such repulsion of vesicles is the main reason for an ultimate stabilization of an emulsion.

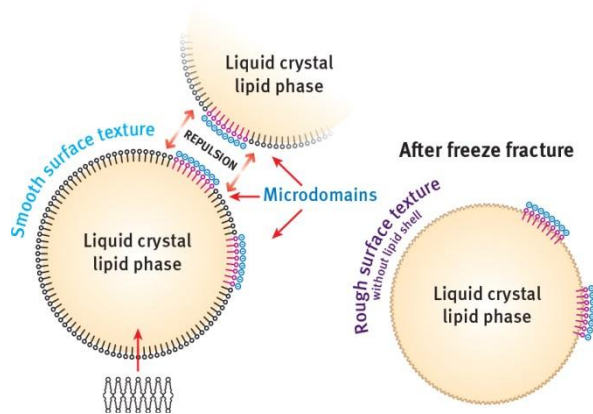


Fig. 5: Schematic representation of the micro-domains found in emulsions based on Potassium Cetyl Phosphate as emulsifier: Formation of micro-domains lead to repulsion of vesicles and a stabilization of the emulsion.

## 2. Assessment of the stabilization power of different emulsifiers

As indicated already before sunscreens are very complex systems. The challenge is to stabilize a high amount of oils including UV filters also during elevated temperature testing. Beside the emulsifier the choice of co-emulsifiers and the used ratio of emulsifier and co-emulsifiers is critical and plays a significant role when developing a high SPF sunscreen.

### *Stabilization of challenging cosmetic ingredients*

After working out the optimal ratio of different emulsifiers (PEG-100 Stearate, Glyceryl Stearate Citrate, Cetearyl Glucoside, Potassium Cetyl Phosphate, and the mixture of Dicethyl Phosphate and Ceteth-10 Phosphate) with the co-emulsifier Cetearyl Alcohol we examined the stabilization power of each emulsifier for oil, inorganic particles and salt.

### *Oil stabilization*

As commonly used emollients we have picked a) Ethylhexyl Benzoate and b) a 1:1 mixture of Diisopropyl Sebacate and Caprylic/Capric Triglyceride. These materials representing polar, hydrophobic solvents, necessary to properly dissolve UV filters and also to provide a reasonably good skin feel. The formulations have been done with 1% emulsifier and increasing concentrations of oil. After 48 hours storage the formulations have been evaluated with regard to oil separation.

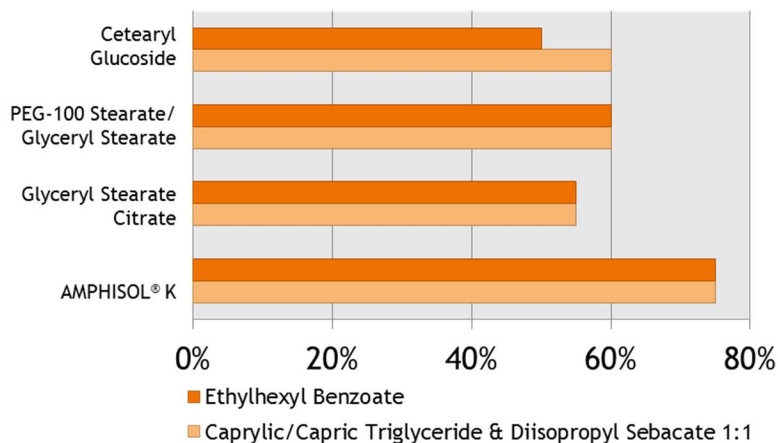


Fig. 6: Lipid stabilization potential of different emulsifiers: PCP stabilized the highest amount of oil.

Potassium Cetyl Phosphate revealed the highest potential to stabilize polar and medium polar emollients. 1% use concentration of Potassium Cetyl Phosphate is capable to stabilize up to 75% of oil (Fig. 6).

### *Stabilization of inorganic nano-pigments*

A second challenge beside a high oil load is represented by inorganic nano-pigments like TiO<sub>2</sub> or ZnO. These materials can, depending on the coating, also adversely interact with the emulsifier system and can lead to significant viscosity and stability changes. As pigmentary UV filter we have chosen Titanium

Dioxide, coated with Silica and Dimethicone (PARSOL® TX). The oil phase contained 30% of a 1:1 mixture of Diisopropyl Sebacate and Caprylic/Capric Triglyceride. Increasing amounts of Titanium Dioxide have been formulated with 1%, 2% and 3% emulsifier respectively. After 48 hours and 2 months storage the formulations have been evaluated with regard to separation.

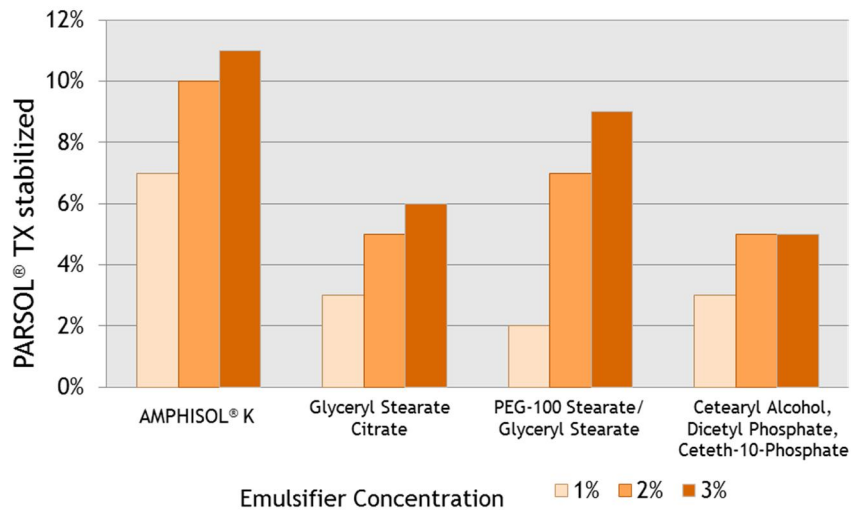


Fig. 7: Stabilization of Titanium Dioxide comparing different emulsifiers: PCP stabilized the highest amount of Titanium Dioxide at each emulsifier concentration.

Potassium Cetyl Phosphate revealed the highest potential to stabilize Titanium Dioxide. E.g. with 1 % use concentration Potassium Cetyl Phosphate could stabilize up to 7 % of Titanium Dioxide, with the other tested emulsifiers only 2% and 3% Titanium Dioxide could be stable formulated (Fig. 7).

### *Salt stabilization*

A third class of challenging ingredients for an emulsifier system is represented by ionic materials, e.g. water soluble UV filters. They consist usually of sulfonated aromatic systems and are utilized in form of salts or zwitterions.

We have chosen Phenyl Benzimidazole Sulfonic Acid, a water soluble UVB filter (PARSOL® HS). The oil phase contained again 30% of a 1:1 mixture of Diisopropyl Sebacate and Caprylic/Capric Triglyceride. Increasing amounts of Phenyl Benzimidazole Sulfonic Acid have been formulated with 1%, 2% and 3% emulsifier respectively. After 48 hours storage the formulations have been evaluated with regard to separation.

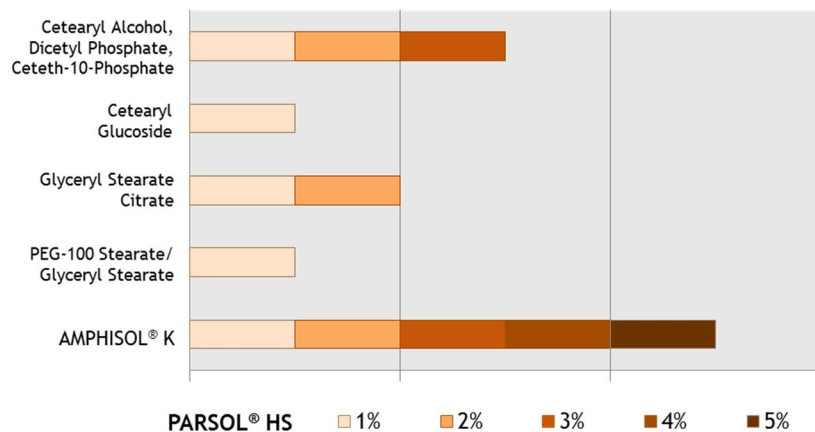


Fig. 8: Stabilization of PBSA comparing different emulsifiers at a use level of 1%: PCP stabilized the highest amount of PBSA.

Potassium Cetyl Phosphate revealed the highest potential to stabilize Phenyl Benzimidazole Sulfonic Acid. Already 1% use concentration of Potassium Cetyl Phosphate is stabilizing 5% of Phenyl Benzimidazole Sulfonic Acid, whereas the other tested emulsifiers can only stabilize between 1% and 3% Phenyl Benzimidazole Sulfonic Acid (Fig. 8).

## Summary

Developing sunscreens or day care with UV protection is in terms of reaching the performance goals already quite challenging and ends up into often relatively complex compositions. These mixtures require robust emulsifying systems in order not to constantly also adapt emulsifier use levels. In particular the high oil load, the use of pigments, e.g. also in BB creams and also ionically charged UV filters represent significant challenges for creating stable emulsion systems with pleasing sensory features. Latest research at DSM revealed that Potassium Cetyl Phosphate (known under the tradename AMPHISOL® K) is a unique emulsifier that is able to form lamellar structures with very dense packed layers of water phase and liquid crystalline lipid phases as well as vesicles containing oil stabilized by liquid crystalline structures as well. Furthermore, the in principle rarely seen micro-domains which are known to stabilize emulsions could be frequently identified by freeze-fracture Scanning-Electron-Microscopy. Comparative formulation trials with different emulsifiers can be used globally by formulators how to overcome current challenges, such as high load of UV filters, pigments and salts and illustrate a way to ultimately stabilize critical emulsions with DSM Potassium Cetyl Phosphate.

## Literature

Baby A. R., Santoro D. M., Robles Velasco M. V., dos Reis Serra C. H.; Emulsified systems based on glyceryl monostearate and potassium cetyl phosphate: Scale-up and characterization of physical properties; *Int. J. Pharm.*, 361, pp. 99-103; 2008

Ansel H.C., Popovich N.G., Allen Jr., L.V.; Farmacotécnica: formas farmaceuticas e sistemas der liberacao de farmacos; 6<sup>th</sup> Ed. Premier, Sao Paulo, pp. 299-311; 2000

Lachmann I., Libermann H.A., Kanig J.L.; Teoria e pratica na industria farmaceutica; Fundacao Calouste Gulbenkian, Lisbon, pp. 855-904; 2001

Korhonen M., Niskanen H., Kiesvaara J., Yliruusi J.; Determination of optimal combination of surfactants in creams using rheology measurements; Int. J. Pharm., 197, pp. 143-151; 2000

Dahms G.; Workshop; 2010