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LIGHT SKIN FEELING & FLUID TEXTURE

Interview | Dr Holger Seidel presents the latest developments and advantages in Pickering emulsions. This type of emulsion is named after Persival Spencer Umfreville Pickering, who published his work in 1907. Seidel explains the ways in which the production of a Pickering emulsion is different from that of other emulsions.

Interview

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COSSMA: What is a Pickering emulsion and what are its advantages in comparison to other emulsions?

Dr Holger Seidel: Pickering emulsions are particle-stabilised emulsions. They are not an invention of modern times; Walter Ramsden, British physiologist and biochemist, described the phenomenon of an emulsion stabilised by boundary layer adsorbed solid particles as early as 1903. This type of emulsion is named after Percival Spencer Umfreville Pickering, who published his work in 1907.
Advantages of o/w-Pickering emulsions are their light skin feeling and fluid texture which are particularly preferred for men's cosmetic products. Furthermore, particle-stabilised interfaces are extremely stable against coalescence. Because there are less emulsifiers in Pickering emulsions, they also have a higher water resistance. This makes them particularly suitable for sun protection products.

In what way is the production of a Pickering emulsion different?

In principle, o/w-Pickering emulsions can be produced by cold/cold manufacturing. The particles are not able to develop significant spreading pressures at oil/water interfaces. This makes it difficult to obtain smaller emulsion droplets. Therefore, the production process must be adapted in such a way that the smallest possible emulsion droplets are formed during the emulsification process. The inverse production method, in which the particles are pre-dispersed into the oil phase, has proved to be successful. During emulsification, the particles migrate from the oil phase to the interface to be adsorbed there. In addition, a higher viscosity

of the outer phase compared to the inner oil phase is essential to improve emulsification efficiency.

Are there any advantages in the production or is it more complicated?

Neither. Pickering emulsions can be produced in a cold/cold manufacturing process, but this applies generally to the production of o/w-emulsion gels.

What are the major challenges involved when formulating Pickering emulsions?

One challenge is the identification of potentially suitable particles for the production of stable Pickering emulsions. Simple wetting tests can be used to measure the time required for the particles to completely penetrate the water surface. O/w-emulsion-stabilising particles are immersed in water extremely quickly, or at least with a short time delay. Particles that are not wettable with water stabilise emulsions of the w/o-type.
O/w-Pickering emulsions based on coated titanium dioxides, starches, silicas or even mica usually have bigger emulsion droplet sizes, up to 30 µm diameter. The bigger the emulsion droplet, the higher the risk of emulsion instability. Suitable hydrocolloids such as Dehydroxanthan gum (Amaze XT, Nouryon) have to fulfil important protective functionalities to prevent the emulsion droplets from creaming or coalescening.

What effect does the wettability of particles have on the stability of a Pickering emulsion?

The wettability of the particles determines how strongly the particles are adsorbed at the oil/water-interface. If the particles are too hydrophilic, they will remain in the aqueous phase instead of migrating to the interface. If the particles are too hydrophobic, they will prefer to remain in the oil phase. Interface-stabilising particles must be partially wettable by both the water and the oil phase. The particles that are just half immersed in the oil phase have a wetting angle of 90°. These are most strongly adsorbed and irreversibly trapped at oil/water-interface. With contact angles greater or smaller than 90°, the adsorption energy of the particles de-creases exponentially.

What types of emulsions can be produced with a Pickering emulsion? What factors have an impact on the different types of emulsion?

The most important determining factor is the particle wettability. According to Bancroft's theory, the phase that wets the solid better is the external phase. Thus, solids that are better wetted by water form o/w-emulsions, those that are more wetted by the oil phase stabilise w/o-emulsions. It is well known that for the stabilsation of w/o-emulsions extremely small water emulsion droplets (usually well below 1 µm) and high internal phase volumes are required. Cosmetic solid particles that develop almost no spreading pressure at the interface and in view of their relatively large particle diameters, w/o Pickering emulsions are extremely difficult to stabilise.

What factors have an impact on the formation of a Pickering emulsion?

Besides wettability, the particle size and the particle geometry have an impact on the formation of a Pickering emulsion. For those particles which are small enough not to be

Advantages of o/w-emulsions are their light skin feeling and fluid texture.

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under the influence of gravity (< < 1 µm) an exponential increase of the adsorption energy with increasing particle size is calculated. For bigger particles, above 500 nm, however, the mentioned correlation between particle size and adsorption energy is no longer valid. Investigations on adsorption energies of particles with different particle geometries have shown that the adsorption energy of particles with disk or platelet structure is highest, followed by particles of cylindrical and spherical shapes. This can be explained by the fact that interface-adsorbed disc-shaped particles have much higher and more effective capillary forces, which makes them more tightly packed in the interface.

What role do coated particles play in the formation of a Pickering emulsion?

The coating of the particles determines the wettability of the particle surface which, in turn, determines whether the particles are adsorbable at oil/water-interfaces and, if so, what kind of emulsion is formed.

The formation of Pickering emulsions is based on the use of particles. As sun care formulations are based on a high content of particles, in what way are they special?

Special grades of hydrophobic coated titanium dioxides are able to stabilise Pickering emulsions very efficiently. O/w-surface-stabilising titanium dioxide types remain in the oil droplets after the emulsification process and do not migrate into the external water phase. This allows the pigments to participate in the final oil film formation on the skin to achieve high SPF efficiency. The particles content used is therefore linked to its oil phase pigment loading capacity.

Are there any interesting examples for Pickering emulsions in sun care?

Pigment loaded sun protection emulsion gels are very popular because of their high efficiency and light texture. Based on our results, Pickering effects are also relevant for all polymer-based sun gels containing amphiphilic titanium dioxides. Highly hydrophobic coated pigments such as stearic acid-coated titanium dioxide tend to form w/o-Pickering emulsions. Acrylate-based emulsion gels with added amounts of extreme hydrophobic coated pigments leads to the formation of in situ w/o/w emulsions.

What are the advantages of using starch in Pickering emulsions?

Modified starch particles are extremely powerful here. The o/w-Pickering emulsions show droplet sizes between 5 and 10 µm. Similar to synthetic polymers, they provide an extremely rich and velvety skin feeling. Their sebum absorption capacity can be used in many different cosmetic formulations.

What is the role of mica in Pickering emulsions and what experience is there in this field?

Mica is also able to stabilise o/w-emulsions. Only bigger emulsion droplets between 30 to 50 µm can be achieved. A special feature of these formulations is their pearlescent effect.

What effect does silica play when formulating Pickering emulsions?

In addition to surface stabilising properties, silica particles create a mattifying effect on the skin and reduce the stickiness of o/w-formulations. The delayed dry skin feeling can be exploited especially in After Shave formulations.

What are the options for optimising Pickering emulsions?

We have concentrated our investigations on particles that are commonly used in cosmetic products. Lithium sodium magnesium silicate particles gave the best results because of their extremely small particle size of approx. 25 nm. Cosmetic emulsions whose stability is exclusively based on the Pickering mechanism are rather rare. Interfacial stabilising solids compete with conventional emulsifiers, which fulfil many different functionalities such as skin feel, stability improvement, and viscosity enhancement.

The first aim was not to develop Pickering emulsions that were as stable as possible, rather to uncover Pickering effects in particle-loaded cosmetic emulsions. Nevertheless, it is amazing how many commonly used cosmetic solids are able to stabilse Pickering emulsions.

A new research approach for the production of stable Pickering emulsions consists of the application of so-called Janus particles. Janus particles are specifically designed nanoparticles or microparticles, whose surfaces are half hydrophilic and half hydrophobic. This allows the production of small emulsion droplets stabilised by close packed and strongly adsorbed particles. □

During emulsification, the particles migrate from the oil phase to the interface to be adsorbed there.

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