A new emulsion technology from Evonik’s Care & Surface Specialties Business Unit allows easy manufacturing and processing of low-viscosity oil-in-water nanoemulsions that are free from emulsifiers based on polyethylene glycol (PEG). Such blends are highly attractive for the growing market for impregnating emulsions for moisturized tissue. Evonik scientists have transferred the advantage of easy processing to classic emulsions.
Il-in-water emulsions (O/W emulsions) play an important role in cosmetics: They are fundamental to the formulation of such products as body lotions, skin creams, and sunscreens. Another relatively recent but fast-growing field of application is emulsion-based wet wipes for such applications as baby care and make-up removal. The key components in these products are low-viscosity O/W emulsions with good storage stability. Classic emulsions have typical particle radii of between 0.5 and 10 micrometers which causes their typical white appearance, and usually show viscosities of over 1,000 mPas. They are kinetically stable, and can be manufactured with the help of a homogenizer. Because their particles are relatively large, however, comparable low-viscosity systems are unstable and cream up.

Alternatively, O/W microemulsions are easy to produce because of their thermodynamic stability. They are translucent, and their typical particle radii range between ten and 40 nanometers. Microemulsions form spontaneously upon mixing, and the order in which the components are added makes no difference. However, microemulsion formation usually requires large quantities of emulsifiers and surfactants.

In terms of their properties, nanoemulsions are positioned between microemulsions and traditional emulsions. Their typical particle radii range between 30 and 100 nanometers which causes their typical blue-shining appearance. At these small particle sizes, the Brownian motion prevents creaming, and as a result nanoemulsions often have a long-term good stability. Like classic emulsions, nanoemulsions are kinetically stable. They are typically not easy to produce as they require either high-pressure homogenizers or very specific manufacturing processes.

The scientists from Evonik’s Care & Surface Specialties Business Unit have now overcome this disadvantage with the development of a low-energy emulsion process for the manufacturing of nanoemulsions. In this process, a phase with extremely low surface tension is passed. In this phase, the transitional phase inversion occurs as the affinity of the emulsifier towards the oil and water phase changes continuously. To put it in graphic terms, the curvature of the surface changes from W/O (concave) to O/W (convex) in this process. As it changes, the emulsion goes through a microemulsion-like phase in which the surface is not curved.

The conventional process for manufacturing finely dispersed O/W emulsions with a transitional phase inversion is the PIT method (Phase Inversion Temperature method), in which the phase transition is obtained by cooling. O/W nanoemulsions manufactured by this method are long-term stable and are used for a number of cosmetic applications (e.g. wet wipes, sprayable emulsions). PIT emulsions utilize the temperature-dependent hydrophilicity of the ethoxylated emulsifiers.

With the PIT method, the phase inversion temperature method, the affinity of the emulsifier for the two phases changes at the oil and water interface, depending on the temperature. When a W/O emulsion is cooled, a transitional phase inversion occurs that results in low-viscosity, finely-dispersed O/W nanoemulsions with good storage stability.

Wanted: PEG-free alternatives to PIT emulsions

The use of ethoxylated emulsifiers, however, is seen more and more as a disadvantage. Because consumers increasingly prefer natural ingredients in cosmetics, the industry is extremely interested in PEG-free emulsions. And this is just what Evonik has now made possible: the manufacture of nanoemulsions without homogenizers, without energy input for heating/cooling steps, and without ethoxylates. An oil phase based on this new technology platform typically consists of three components: PEG-free emulsifiers (ten to 30 percent), cosmetic oils (50 to 90 percent), and cosurfactants (one to 20 percent). Cosurfactants are surface-active. However, unlike surfactants, they do not form micelles in water, and therefore do not tend to self-aggregate.

With Water

Dr. Jürgen Meyer
sume that the water-solubility of the phenoxyethanol is decisive for the occurrence of a microemulsion-like phase: With increasing water concentration, the cosurfactant increasingly migrates out of the surface film and into the water phase, which assists the phase inversion. The phase inversion is also promoted by a co-emulsifier, such as dilauryl citrate, that becomes more hydrophilic with increasing water concentration.

Following the successful development of such O/W nanoemulsions, Evonik's scientists wondered what they could transfer to the formulation of classic emulsions. In the end, they were able to develop a PEG-free emulsifier that requires no heating or homogenizer. For this emulsifier they used a mixture of polyglyceryl-4-laurate and dilauryl citrate, which had been developed for PIC emulsion systems and has self-emulsifying properties. This mixture is pasty, however, and too expensive for typical applications. Consequently, they combined this highly active mixture with the liquid basic emulsifier sorbitan laurate. Marketed as TEGO® Care LTP, this new O/W emulsifier mixture can be cold-processed, and allows simple and cost-effective production of cosmetic products in the form of sprays, lotions, and creams.

If water is added to this kind of liquid and clear oil phase, a microemulsion-like phase is passed and a low-viscosity O/W nanoemulsion with good long-term stability is obtained. The first of Evonik's products based on this technology are TEGO® Wipe DE and TEGO® Wipe DE PF, which are for the simple manufacture of impregnating emulsions for cosmetic wet wipes.

In their tests, Evonik’s scientists were able to determine that the viscosity of the TEGO® Wipe DE system depends heavily on the water content. In the microemulsion-like phase, there is a significant reduction in viscosity, which indicates extremely low interfacial tension at this point. Similar to the PIT emulsion system, this kind of minimum viscosity is typical for the point of phase inversion from W/O to O/W. Because this inversion point occurs at a certain water concentration, the Care & Surface Specialties Business Unit calls the new process a phase inversion concentration technology. These PIC emulsion systems require no stirring or heating. Even the order in which the oil and water are added has no impact on the result. The emulsion mixture and cosurfactant content, however, must be precisely adjusted with the oil phase to be emulsified.

In the TEGO® Wipe DE system, the surface-active phenoxyethanol, which is often used as a preservative in the cosmetics industry, plays the role of the cosurfactant. The researchers had been developed for PIC emulsion systems and has self-emulsifying properties. This mixture is pasty, however, and too expensive for typical applications. Consequently, they combined this highly active mixture with the liquid basic emulsifier sorbitan laurate. Marketed as TEGO® Care LTP, this new O/W emulsifier mixture can be cold-processed, and allows simple and cost-effective production of cosmetic products in the form of sprays, lotions, and creams.

The role of the cosurfactant in PIC emulsions: The solubility of the cosurfactant presumably ensures that, with increasing water concentration, the cosurfactant increasingly migrates from the surface film into the aqueous phase, thereby assisting the phase inversion.

Phase behavior of the TEGO® Wipe DE system, depending on the water content, at 20 °C (68 °F). At a water content between 35 and 70 percent, the phase transition from a W/O emulsion to an O/W emulsion occurs. The pronounced viscosity minimum indicates that a phase with extremely low interfacial tension is passed.

Simple manufacture of nanoemulsions – for example, for moisturized tissues: Add water to the clear oil phase of the TEGO® Wipe DE system (left), and following a microemulsion-like phase (middle), a low-viscosity O/W nanoemulsion with long-term stability forms (right).