Emulsifiers 2018 1<sup>st</sup> appeared in SPC 2018 John Woodruff Emulsifiers are essential for th

Emulsifiers are essential for the preparation and stability of most creams and lotions used in skin care and this feature will discuss some of the latest introductions for cosmetic compositions.

The obvious trend in emulsifiers is towards natural-based materials that are PEG-free but supplying light, non-greasy textures is also important. Sucramulse 163 from **Alchemy Ingredients** meets both requirements. It is a PEG-free COSMOS approved emulsifier based on sugar chemistry, [INCI: Glyceryl stearate, cetyl alcohol, sucrose stearate, sucrose tristearate], and is described as a non-ionic, oil-in-water (O/W) emulsifier that forms a stable liquid crystal structure. Sucramulse creates emulsions with an excellent skin feel, no creaming effect on the skin and improved moisturising independent of the oil phase. By varying the level of Sucramulse, different emulsions can be made from light lotions to rich body butters, all with a characteristic luxurious texture.

Sugar chemistry is responsible for Emulgade Sucro Plus from **BASF.** It is a mixture of sucrose polystearate and cetyl palmitate available in pellet form and it is an O/W emulsifier claimed to show good electrolyte compatibility, to provide lamellar structures and to be suitable for providing creamy textures to lotions, gels and sprays. **BASF** also markets a material trade named Power of 3. This is a mixture of sodium polyacrylate, sodium stearoyl glutamate and pentaerythrityl distearate, which work together to provide strong emulsifying properties with a good sensorial profile and long-term emulsion stability. It may be used to provide lotions, creams and body butters and can be used to emulsify polar and non-polar oils and silicones in O/W emulsions.

Driven by the need for PEG-free emulsifiers and the benefits of lamella structures, the industry has seen a significant increase in the use of polyglyceryl-ester emulsifiers. Polyglyceryl esters are used extensively within the food industry because of their amphiphilic nature and excellent toxicity profile. The corresponding polyglyceryl esters are produced from polyglycerol and fatty acids in direct esterification of triglycerides and polyglycerol. The emulsifiers are non-ionic and exhibit HLB values from 6 to 11 and are used to prepare O/W and W/O emulsions. The amphiphilic properties of the polyglycerol ester in water promotes the formation of liquid crystalline structures to form stable emulsions with effective moisturising properties.

Polyglyceryl esters are widely available from cosmetic ingredient suppliers, either singly or in combination to form propriety mixtures with optimum properties. An investigation into the production and emulsifying effect of polyglycerol and fatty acid esters determined that maximum emulsifying effect was found for tri- and tetra- esters of capric, lauric, and caprylic acids. Regardless of the HLB value of the polyglycerol ester a 4:1 ratio of sunflower oil to water formed a W/O type emulsion. When mixing oil and water in a 1:1 ratio, mono- and di- esters of polyglycerol formed an O/W type emulsion, hepta- esters formed a W/O type emulsion, and tri- and tetra- esters formed both of types of emulsions, depending on the length of the acid hydrocarbon radicals [Ref 1].

Emulium Mellifera MB, [INCI: Polyglyceryl-6 distearate, jojoba esters, polyglyceryl-3 beeswax, cetyl alcohol] from **Gattefossé** is an example of an optimised mixture of emulsifier and stabilising and texturizing additives. It is a non-ionic emulsifier that allows the formulation of a wide range of textures suitable for all skin types and climates. Emulsions have a white and luxurious appearance, a light and smooth consistency and form a flexible film on the skin, providing significant moisturising properties and protecting it from external aggressions. It was the gold medal winner in the innovation zone at In-Cosmetics 2014.

**Medolla Ltd.** produces olive oil--based polyglyceryl esters: Olivatis 18 [INCI: Olive oil polyglyceryl-6 esters, sodium stearoyl lactylate, cetearyl alcohol] is an O/W emulsifier with excellent emulsifying power and low inherent odour and colour that is stable at acidic and alkaline pH. Olive oil is rich in

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fatty acids like those found in human sebum and lactic acid is an essential component of the natural moisturising factor or NMF. The combination of these two ingredients makes Olivatis 18 a superior emulsifier with skin moisturising and protecting properties. Olivatis 19 [INCI: Olive polyglyceryl-6 esters, phospholipids] is a combination of olive oil derivatives and phospholipids. The olive oil esters restore the natural hydrolipidic film of skin while phospholipids enhance the penetration of actives in skin and improves its water balance. Trans-esterification that allows the substitution of part of the glyceric fraction of olive oil with ethoxylated vegetal glycerol results in a water-soluble olive oil derived O/W emulsifier, marketed as Olivatis 15 [INCI: Olive oil glycereth-8 esters].

In a similar manner, **Gale & Cosm. Sri.** provide water-soluble versions of argan oil and avocado oil. GaleArgan WS is argan oil polyglyceryl-6 esters and GaleAvocado WS is avocado oil polyglyceryl-6 esters. Both are recommended as emollients for shower gel, shampoo, micellar water and make-up remover. For imparting a gloss to lip glosses and eyeshadows Gale & Cosm. suggest Galegloss, a W/O emulsifier and emollient that is a mix of polyglyceryl-3 triolivate and sorbitan isostearate.

EcoDropGel [INCI: Coco-caprylate/caprate, polyglyceryl-4 isostearate, disteardimonium, hectorite] from **Sunjin** is a silicone-free emulsifying system that provides a 'quick break' texture and a water drop effect. It allows the formulation of W/O products with an improved feel. The release of water droplets from emulsions when applied to the skin creates a significant cooling and refreshing feeling and is a characteristic of high internal phase (HIP) emulsions.

An emulsifier that enables the formulator to create a high internal phase emulsion is HIPEgel Aqua from **Alchemy Ingredients.** It is a mixture of isopropyl palmitate, polyglyceryl-3 oleate, coco-caprylate/caprate and sorbitan sesquioleate and it can be used to create a W/O emulsion with a water phase of more than 90%. Despite this, because of the nature of the polygonal packing of water droplets in the structure, stable viscous systems are made without the use of added thickeners. The finished emulsion can form a barrier on the skin but, due to the high-water content, it's also very light and has a 'quick break' effect. **Alchemy** suggest it is ideal for use in anti-pollution cleansers, which require the delivery of actives into the skin to neutralise free radicals and deactivate toxins. Water soluble actives are naturally encapsulated by the thin film of oil that surrounds them, leading to extra protection, and a fine layer of oil forms a physical barrier on the skin to prevent entry of particulates.

Patent WO2015054135 A1 filed in 2014 by **Presperse** addresses the problem of preparing stable HIP emulsions while avoiding high levels of surfactant. The patent described how a stabilising compound may be produced comprising a Gemini surfactant, a sugar-derived compound and a hydrophobically modified polymer at a very low concentration. This stabilising compound is then used to prepare HIP emulsions that exhibit high emulsion stability, require low energy input to produce and are extremely versatile when used as a formulating tool. Gemini surfactants have two hydrophilic head groups and two hydrophobic groups in the molecule and are considerably more surface-active than conventional surfactants. Examples of suitable Gemini surfactants include sodium dilauramidoglutamide lysine and sodium cocoyl ethylene diamine PEG-15. The patent claims a high internal phase emulsion composition comprising 0.2 to 5% of the stabilising compound, 15 to 35 % continuous phase, and 65 to 80% internal phase.

Although out of favour with COSMOS, silicone chemistry provides many interesting emulsifier systems. **ShinEtsu** combines polyglyceryl chemistry with silicones to create polyglyceryl emulsifying elastomers. KSG-710 is dimethicone/polyglycerin-3 crosspolymer with dimethicone for forming W/Si emulsions. The KSG-800 series of emulsifiers is lauryl dimethicone/polyglycerin-3 crosspolymer in a

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variety of solvents and the KSG-800Z series is polyglyceryl-3/lauryl polydimethylsiloxyethyl dimethicone crosspolymer with either isodecane or cyclopentasiloxane. ShinEtsu publishes an informative leaflet on the compatibility and emulsifying properties of these W/Si emulsifiers.

Gransurf 2106, [INCI: Dimethicone, PEG-10 dimethicone crosspolymer] from **Grant Industries** is a self-emulsifying elastomer with an HLB of 4.5. It can absorb up to 90% water to form a HIP-type W/O emulsion that discharges water droplets onto the skin on application. HIP emulsions may be used as a basis for pre-emulsified concentrates of emollients, moisturisers and sunscreens. The emulsion concentrates allow simple cold mixing, and, because of their excellent stability, formulators can easily adjust emollient levels to obtain the desired skin feel. WaterDropSil from **Sunjin** is a mixture of dimethicone, cyclopentasiloxane, dimethicone/vinyl dimethicone crosspolymer and PEG-10 dimethicone that is used to prepare emulsions that release droplets of water when topically applied to give a unique feel of moisturising. WaterDropSil-D is a non-cyclopentasiloxane version that can be used to form stable W/Si emulsions, which break quickly upon rubbing on the skin to release water droplets.

HIP emulsions using silicone emulsifiers are a speciality from **Dow Corning** that produces many variants. An example is DC 7-3101 Elastomer Blend that is a HIP emulsion of dimethicone crosspolymer in cyclopentasiloxane and dimethicone. In common with other Dow silicone-based HIP emulsions it has been prepared using a proprietary process to give a particle size similar to the silicone elastomer gels in the emulsion. It is stabilised with non-ionic surfactants to provide maximum compatibility in formulations that contain other surfactants. Other examples are DC 7-3100 Gum Blend of ultra-high viscosity dimethiconol in cyclopentasiloxane and DC 7-3101 Elastomer Blend comprising cyclopentasiloxane, dimethicone crosspolymer, dimethicone and laureth-23 and laureth-4.

A presentation from **Symrise**, "Cosmetic Emulsions Made Easy" discusses the importance of skin feel and texture when creating cosmetic emulsions. Emollients provide parameters like spreadability, polarity, viscosity and volatility and play a key role in providing the sensorial profile of an emulsion. However, emulsifiers also contribute significantly to the sensorial profile and emulsifier attributes like texture, appearance and pick-up have an impact on the initial skin feel. The presentation describes four **Symrise** emulsifiers and how they can be used to give the desired end-product. Emulsiphos [INCI: Potassium cetyl phosphate, hydrogenated palm glycerides] is an O/W emulsifier based on the potassium salt of an anionic phosphate ester in a plant-derived lipid matrix. Its molecular structure promotes the ability to form liquid crystalline structures similar to skin lipids and its clinically proven skin compatibility makes it particularly suitable for sensitive skin. The other emulsifiers from **Symrise** are Dracorin CVE [INCI: Glyceryl stearate citrate] and Dracorin GOC [INCI: Glyceryl oleate citrate, caprylic/capric tri-glyceride].

Preparing emulsions that are stable under challenging conditions is a frequent problem for the cosmetic formulator. As already discussed, polyglyceryl esters may be used to avoid the use of ethoxylates and to prepare emulsions with high internal phases. The patent by **Presperse** addresses the problem of stabilising HIP emulsions. An alternative stabiliser is Inutec SLI from **Gova**, which is prepared from inulin extracted from the root of Cichorium (chicory) intybus, and lauric acid derived from Cocos (coconut) nucifera oil. Inulin is a linear polysaccharide that intensively adsorbs water. This is grafted with lipophilic lauryl chains to form an emulsifier. When introduced to an emulsion the lauryl chains become firmly anchored into the oil, while the long inulin polymers encapsulate tightly the oil droplet. In this way an unbreakable film of strongly hydrated inulin stabilises the oil droplets and greatly improves the stability performances of all other O/W-emulsifiers. Inutec SLI is

Emulsifiers 2018 1<sup>st</sup> appeared in SPC 2018 John Woodruff effective from pH 4 – 11, is unaffected by electrolytes and can be used to prepare a sprayable emulsion with 50% internal oil phase.

Preparing stable HIP emulsions at low pH can also be achieved using **Global Seven** Hest PGFA [INCI: Polyalkoxylene polyester copolymer]. It is described as a highly effective polymeric emulsifier for making W/O emulsions. It is suitable for hot or cold processing and Global Seven provides illustrative formulations to demonstrate its effectiveness, as in the example shown.

Ingredient	%w/w
Aqua/water	78.30
Lactic acid	6.50
Sodium sulfate	1.00
Hest PGFA	1.00
C12-15 alkyl benzoate	13.20
Potassium hydroxide to adjust pH to 3.7	
Mix water with lactic acid and adjust pH to 3.7	
with KOH. Add Sodium Sulfate. Combine Hest	
25B is with C12-15 alkyl benzoate and with	
adequate mixing, slowly add oils to water phase.	

Another emulsifier effective over a broad pH range and electrolyte tolerant is Emulium Delta [INCI: Cetyl alcohol, glyceryl stearate, PEG-75 stearate, ceteth-20, steareth-20] from **Gattefossé**. It is described as is an O/W sensory emulsifier that is characterised by its soft and velvet skin feel, allowing the creation of rich and luxurious textures. It is said to be compatible with most cosmetic ingredients including AHAs and hydrogen peroxide in acidic formulations and ammonium thioglycolate and sodium hydroxide in high pH compositions. It is also recommended for use with sensitive actives such as DHA, vitamins, urea, sodium polycarboxylate and aluminium salts.

Finally, an ingredient for combining oils and water that is not a surfactant is Emulfree from **Gattefossé**, which forms a bi-gel with oils and water. This is described as a dispersion of an oily network within an aqueous gel, stabilised by synergistic association of ethyl cellulose with emollients. The ethyl cellulose locates both in the oil droplets and at the oil-water interface and stabilises the droplets via steric repulsion, preventing flocculation and coalescence. On application to the skin the bi-gel structure breaks, releasing water droplets and providing a refreshing and long-lasting sensation of coolness. Two variants are available Emulfree P, [INCI: Propylene glycol laurate, ethylcellulose, propylene glycol isostearate] and Emulfree CBG, [INCI: Isostearyl alcohol, butylene glycol cocoate, ethylcellulose].

REF 1. S. Shikhaliev et al. (2016). Production and Emulsifying Effect of Polyglycerol and Fatty Acid Esters with Varying Degrees of Esterification. Journal of the American Oil Chemists' Society 10.1007/s11746-016-2894-6.

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