Emulsifiers & Surfactants
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An emulsion is a colloid of two or more immiscible liquids where one liquid contains a dispersion of the other and an emulsifier is a substance that stabilises an emulsion. Emulsification takes place by reduction of interfacial tension between two phases or by repulsion, whereby the emulsifying agent creates a film over the dispersed droplets, which repel each other and so remain suspended in the dispersion medium.

Until the mid-1970s the commonly used emulsifying systems for cosmetics were beeswax/borax, sodium lauryl sulfate, triethanolamine stearate and sorbitan esters and their ethoxylated counterparts. More recently the trend has been away from ethoxylated compounds and towards materials of natural origin and those that create liquid crystal formations and they are the focus of this feature.

Lecithins appeal to the formulator of “natural” cosmetics. Human cells are separated into compartments by bio membranes of phospholipids, which form the double layer surface of all cells. They have one water-soluble end formed by a polar phosphate group and a lipid-soluble end formed by a non-polar fatty acid tail. Within membranes polar ends point outwards, whereas non-polar ends point inwards. Lecithins can provide similar structures when used to formulate cosmetic emulsions; the lamellar emulsion mimics the lipid structure of the stratum corneum and helps restore the cutaneous barrier of damaged skin, forming a restructuring film which reduces trans epidermal water loss (TEWL).

Cosphatec GmbH produce a number of lecithin-based emulsifiers from Helianthus (sunflower) annuus seed oil that is non-GMO and has a low allergenic potential. Standard lecithins, represented by Cosphaderm SF-S, have a characteristic odour and a typical brown colour and are used to form rich water-in-oil (W/O) emulsions. Cosphaderm SF-D is a de-oiled lecithin of almost pure phospholipids and, because nearly all of the accompanied substances are removed, there is a decrease in odour and colour and an increase in water solubility. Lysolecithins are the result of enzymatic treatment with phospholipase, which separates one of the fatty acids, decreasing the non-polar part so the overall polarity increases, and they may be used to form either W/O or O/W emulsions depending on the concentration of the lipid phase. Examples are Cosphaderms E NGM, E NGM 50 and E 100 E IP, which are characterised by high water solubility and best suited for cosmetic formulations with high water content.

Fractionated lecithins are de-oiled to increase the phospholipids content then enriched with phosphatidylcholine by fractionation with ethanol. Depending on the number of fractionating steps different phosphatidylcholine enriched lecithins can be produced, as represented by Cosphaderm SF-50, SF-70 and SF-90. These may be used to form W/O emulsions and, because they form

liposomes, skin penetrating powers are increased. Cosphaderm SF-75H; SF-90H are similar to the fractionated lecithins but are additionally hydrogenated and carefully bleached, resulting in a white powder best suited for brilliant white formulations characterised by high temperature stability.

When combined with other fatty acids and fatty alcohols the emulsifying properties of phospholipids are improved. They first form monolayers around oil droplets and a bilayer network is formed in the aqueous phase to create a lamellar structure. Fatty acids and alcohols may form part of the lipid phase or may be combined by ingredient suppliers to provide a balanced emulsifying system.

Biophilic from **Lucas Meyer** is a patented natural lamellar O/W system based on the emulsifying properties of phospholipids combined with other vegetable lipids. Two grades are available: Biophilic H [INCI: Hydrogenated lecithin, C12-16 alcohols, palmitic acid] and Biophilic S [INCI: Lecithin, C12-16 alcohols, palmitic acid]. The hydrogenated lecithin in Biophilic H provides very important thickening properties and allows the formulation of white and odourless emulsions from cream to butter. Biophilic S contains unsaturated lecithin, creating softer and more fluid off-white textures from lotion to cream. The emulsion melts on the skin for a sophisticated skin feel during application and forms a restructuring film which reduces TEWL.

Lecithins are considered multi-functional emulsifiers because they also have skin-smoothing properties and enhance skin penetration of cosmetic compositions, however they have little effect on product viscosity. Polyaldo Polyglyceryl Esters from **Lonza** are described as naturally-derived emulsifiers with viscosity enhancement properties. They are made via esterification of a polyglycerol and a fatty acid to form a molecule containing a hydrophilic head group and hydrophobic tail group, are non-ionic in character and create stable O/W emulsions. There are four polyglyceryl esters available from Lonza: Polyaldo 6-2-S [INCI: Polyglyceryl-6 distearate]; Polyaldo10-1-S [INCI: Polyglyceryl-10 stearate]; Polyaldo 10-1-O [INCI: Polyglyceryl-10 oleate] and Polyaldo 10-2-P [INCI: Polyglyceryl-10 dipalmitate].

Lonza suggests that optimum results are obtained by using two esters together. Because of their molecular structures this results in closer packing at the interface; an increase in viscosity and a tendency to form lamellar structures. Lonza has produced a brochure with extensive information on the use of Polyaldo emulsifiers and the different ways to affect emulsion attributes when using them. For those preferring an on-line resource Lonza has just launched FormulaCreate.com, which describes how to build a variety of stable leave-on emulsions. Designed with formulators in mind, it provides detailed guidance on which Polyaldo polyglyceryl esters to use and at what ratio to create a specific emulsion base.

For preparing O/W emulsions **Dr Straetmans** has a number of polyglyceryl esters available under its Dermofeel trade name including Dermofeel PP [INCI: Polyglyceryl-3 palmitate]; Dermofeel PS [INCI: Polyglyceryl-stearate] and Dermofeel DGMC [INCI: Polyglyceryl-2 caprate]. This latter material is a co-emulsifier that can also be used as a deodorant active ingredient due to its activity against gram-positive bacteria. For preparing O/W emulsions **Dr Straetmans** suggests Dermofeel GO soft [INCI: Polyglyceryl-2 sesquioleate], which is a versatile W/O emulsifier with a unique skin feel. It converts W/O creams into soft and pleasant formulations that are easily applied on the skin. Dermofeel PGPR (INCI: Polyglyceryl-3 polyricinoleate] is an emulsifier for W/O emulsions that may contain up to 80% water.

Polyglyceryl esters also feature in Imwitor liteMULS [INCI: Glyceryl citrate/lactate/linoleate/oleate, polyglyceryl-4 cocoate, polyglyceryl-3 caprate, glyceryl caprylate] from **IOI Oleo GmbH**. It is liquid at room temperature and is easily manageable for cold production process, readily forming totally liquid emulsions at room temperature. At a typical use concentration of 1-3%, it forms a liquid milk suitable for sprayable hair conditioner and milks for body and face care and for wet wipes.

The ability to produce cold-process low viscosity emulsions that are suitable for spray applications is the claim made for Dermofeel Easymuls Plus [INCI: Glyceryl oleate citrate] from **Dr Straetmans**. It is based on sunflower seed oil and can be used as the sole emulsifier for low viscosity O/W emulsions or as a co-emulsifier for improving skin feel or stabilising O/W-emulsions without increasing their viscosity. Also from **Dr Straetmans** is Dermofeel GSC [INCI: Glyceryl stearate citrate]; a PEG-free emulsifier based on Brassica (rape) napus seed oil. It has a high melting point and confers good high temperature stability to emulsions, making them ideal for sun care compositions.

Stephenson Personal Care recently launched its Durasoft naturally derived polyglycerol esters to produce creams, lotions and foaming oil-based formulations that offer specific value to producers of cold process products from sustainable raw materials. Stephenson utilises patent-pending technology to provide each emulsifier with a wide HLB range of 4-14 for a greater stability profile. Durosoft PK-SG is an O/W polyglyceryl-4 laurate emulsifier derived from RSPO certified palm oil to produce water-thin lotions, deodorant roll-ons and wet wipes. Durosoft SF is a W/O polyglyceryl-4 oleate emulsifier derived from sunflower seed oil for creating self-emulsifying oils such as foaming bath and shower oils, hair and beard oils and cleansing oils.

Providing improved sensorial experience is a common claim for emulsions created using emulsifiers that promote lamellar structures. Emulium Mellifera [INCI: Polyglyceryl-6 distearate, jojoba esters, polyglyceryl-3 beeswax, cetyl alcohol] from **Gattefosse** is claimed to do so and to adjust results according to climate. It is created from natural ingredients using green chemistry: beeswax and

jojoba wax are reacted with vegetable polyglycerol to change the texture into a soft homogeneous butter that is then combined with polyglyceryl-6 distearate and cetyl alcohol to optimise emulsification and texturizing capacity. Its key features are that it allows the formulation of a wide range of textures suitable for all skin types, having significant moisturising properties and visibly improving skin texture.

Monoglyceryl esters are also featured in recent launches of innovative emulsifiers: from **Kalichem Italia** are three emulsifiers based on glyceryl esters in combination with cetearyl alcohol and Olea (olive) europea oil derivatives. Olive Oil Avenate and Olive Oil FOKDNaB have the same INCI combination of cetearyl alcohol, glyceryl oleate, glyceryl stearate and potassium olivoyl hydrolysed wheat protein. According to the makers olivoyl hydrolysed wheat protein is a lipo-protein with a fatty amide structure, showing high inter-facial activity. It is obtained by condensation of one amino group of proteins and the carboxyl group of fatty acids of olive oil. In order to achieve an amphiphilic system suitable for the stabilisation of O/W emulsions this structure is combined with olive oil wax, promoting liquid crystal structures in which the oil droplets are surrounded by bi-layers of amphiphilic molecules, which strengthen the interface stability.

The third emulsifier from **Kalichem** is Olivoil Glutamate Emulsifier [INCI: Cetearyl alcohol, glyceryl stearate, sodium olivoyl glutamate]. Olivoyl glutamate, a lipo-amino acid with a fatty acid amine structure, shows high interfacial activity and is obtained by condensation between the amino group of glutamic acid and the carboxyl groups of the fatty acid. The result of this combination is a new emulsifier structure with high skin compatibility and maximum biodegradability. Cetearyl alcohol and glyceryl stearate are present as co-emulsifiers and to add structure to the final emulsion. Like many emulsifier systems that result in liquid crystal structures the method of preparation is important. **Kalichem** recommend the addition of the emulsifier to the oil phase and heating to about 70C followed by the addition of about 20% of the total water phase heated to 70-75C for the emulsification process then slow addition of the remaining part of the water phase to cool the system.

Amisol Soft from **Lucas Meyer** is a combination of glyceryl stearate with lecithin. behenyl alcohol and Glycine soja (soybean) sterols. According to the supplier, lamellar O/W creams and lotions formulated with Amisol Soft are organised in phospholipidic bilayers with interspersed phytosterols and fatty alcohols. The combination of phospholipids with phytosterols allows the formation of a stable, supple, lamellar network, leading to fluid emulsions and this biomimetic structure is particularly suitable for sensitive or stressed skins. In addition, the phytosterols soothe and calm irritated skin due to their anti-inflammatory properties.

Montanov 68 from **Seppic** has been in use for many years but now a new version is available; Montanov 68MB uses Elaeis (palm) guineensis oil certified mass balance by Roundtable on Sustainable Palm Oil (RSPO). Montanov 68MB [INCI: Cetearyl alcohol, cetearyl glucoside] allows the formulation of cream textures in skin care or hair care. It was one of the first emulsifier systems known to promote liquid crystal formation and *In-Vivo* trials prove it delivers up to 5 hours moisturising and skin restructuring performance through TEWL reduction.

Emulsifiers based on sugar chemistry are natural alternatives to glyceryl esters: **Alfa Chemicals** has produced a number of emulsifiers, emulsion stabilisers and emulsion thickening agents based on sugar chemistry under its Alfacos trade name. Sucrose laurate is the principal emulsifying agent in four Sucragel emulsifying systems that are also useful for thickening cosmetic oils. As well as sucrose laurate, water and glycerin common to all Sucragels the CF variant contains caprylic/capric triglyceride; AOF contains Prunus Amygdalus dulcis (sweet almond) oil and AOF Bio contains Prunus amygdalus dulcis (sweet almond) oil and Citrus aurantium dulcis (orange) fruit water triglyceride. A little different is Sucragel AP, which is an oil-free version containing alcohol and sucrose myristate. Sucrose laurate is also the principal emulsifier in Sucrabase ready to use bases for creating cosmetic products by simple additions of water, active ingredients and fragrance.

Also promoted as a ready-to-use cosmetic base Emulfeel SGP CHI [INCI: Helianthus annuus (sunflower) seed oil, sodium polyacrylate, xylitol, caprylic acid, glyceryl stearate] from **Chemyunion** does not need pre-dispersion or neutralisation and can tolerate ethanol up to 30%. It forms a double gel network combining liquid crystal formation with a polymer gel structure and is claimed to provide enhanced sensorial attributes to emulsions while substantially reducing the number of ingredients required. Trisatin [INCI: Glyceryl stearate, cetearyl alcohol, sodium stearoyl lactylate] from **Tri-K Industries** is also claimed to create a lamellar crystalline gel network providing a complete emulsification system with barrier protection and moisturising properties.

A new type of emulsion SWOP (Switch-Oil-Phase) based on formulation of O/W emulsions that invert into W/O emulsions during application on the skin were described in a paper appearing in the International Journal of Cosmetic Science, June 2016 [Ref 1]. The SWOP emulsion described was stabilised with a combination of the non-ionic emulsifier polyglyceryl-2 dipolyhydroxystearate (Dehymuls PGPH, **BASF**), an anionic surfactant that is a mixture of lauryl glucoside and sodium lauryl glucose carboxylate (Plantapon LGC Sorb, **BASF**) and the polymeric stabiliser, sodium polyacrylate (Cosmedia SP, **BASF**). SWOP emulsions form a lipophilic, water-resistant layer on the skin and are generally considered as stable under normal storage conditions and are especially suitable as a carrier in sun-protection products.

Korać, R., Krajišnik, D. and Milić, J. (2016), Sensory and instrumental characterization of fast inverting oil-in-water emulsions for cosmetic application. International Journal of Cosmetic Science, 38: 246–256. doi: 10.1111/ics.12282

Please Note: the majority of materials described are certified natural and/or organic by recognised certification organisations but those interested are urged to contact the suppliers for more information.

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