Emulsifiers are a group of materials that have expanded in type and functionality in recent years as suppliers endeavour to fill the various niches created for cosmetic products. At one time it seemed that triethanolamine stearate, self-emulsifying glyceryl monostearate and sorbitan esters and their ethoxylated counterparts were going to dominate emulsion formulation forever but then came a realisation of the benefits of liquid crystal structures; a demand for emulsifying high silicone-content products, for cold-processing and for non-ethoxylated materials, preferably of natural origin.

Silicones are one of the most popular groups of materials used in cosmetic formulation [See SPC January 2013] but bring their own problems of compatibility with other ingredients and difficulties in emulsification. Designed to overcome these difficulties are silicone-based emulsifiers such as **Dow Corning's** Formulation Aids. This company has published a quick guide to silicone emulsifier selection based on inputting answers to various criteria. First is that of the viscosity of the emulsion required and then the emulsion type. This leads to a selection of possible emulsifiers with which to experiment and then a simple flow diagram asks was the emulsion a success and if not it gives useful tips on what to do next.

Altogether **Dow Corning** has nine possible silicone-based emulsifiers; all contain polyethylene glycol with varying degrees of ethoxylation the simplest of which is DC 5612, PEG-10 dimethicone. It is recommended for preparing water-in silicone (W/Si) or water in silicone in oil (W/Si/O) emulsions and is suitable for cold-processing. The most recent introductions from **Dow Corning** are ES-5226 DM and ES-5227 DM. Both contain the silicone polyether PEG/PPG-18/18 dimethicone and are recommended for preparing low to medium viscosity W/Si emulsions. ES-5226 DM is a 37.5% dispersion of PEG/PPG-18/18 dimethicone in a low viscosity, volatile dimethicone fluid and ES-5227 DM is a 25% dispersion in a low viscosity, non-volatile dimethicone fluid.

Shin-Etsu Chemical Company is a Japanese supplier of silicones of every description. For preparing W/O emulsions it recommends KF-6005, which is a 100% active polyether modified silicone fluid [INCI: PEG-9 dimethicone]. Its low molecular weight is beneficial in that it can stabilise high internal phase emulsions of low viscosity without sacrificing stability. It has excellent aesthetics with light and silky skin feel and ambient processing is possible if all ingredients are liquid. Also from Shin-Etsu is KF-6050L, a linear W/Si emulsifier [INCI: Dimethicone, PEG/PPG-18/18 dimethicone] that shows good compatibility with cyclomethicone and dimethicone of low viscosity and with KSG-210. This latter material is a crosslinked elastomer emulsifier [INCI: Dimethicone/PEG-10/15 crosspolymer, dimethicone] that enables the formulation of unique textures of W/Si emulsions containing up to 90% water.

Kodasil 451 S from **Koda** is described as a new and unique silicone that incorporates a dimethicone copolyol into its crosspolymer network [INCI: Dimethicone, phenyl trimethicone, cyclopentasiloxane, dimethicone/vinyl dimethicone crosspolymer, PEG/PPG 20-15 dimethicone]. Due to the immediate availability of the copolyol low temperature emulsification is possible and the copolyol/crosspolymer network allows the use of a high water load in W/Si emulsions.

Chemsil Silicones simplifies the use of silicones by providing product bases such as Gelaid CPE to which formulators are encouraged to add water and water-soluble actives to formulate stable, elegant emulsions. Its properties can be further modified by the addition of esters, natural oils and mineral oil. Gelaid CPE is a mixture of cyclopentasiloxane, dimethicone/vinyl dimethicone crosspolymer and hydroxyethyl acrylate/sodium acryloyldimethyl taurate copolymer and it is suitable for cold-processing. Gelaid CPE-CF is similar but without cyclomethicone.

Polymeric emulsifiers have been slowly establishing themselves with formulators; they do not form true emulsions in that the dispersed oil droplets are stabilised by the polymer matrix. They have the advantage that emulsions prepared using them are almost immune to temperature fluctuation. Also they can be added at any stage of the processing operation, they thicken as well as emulsify and are suitable for cold processing. To satisfy this trend **Croda Europe** is re-launching its acrylic-based emulsifiers under its ViscOptima.brand name.

Viscoptima LV [INCI: Sodium polyacrylate, isotridecyl isononanoate, trideceth-6] gives instant and efficient thickening at low inclusion levels and emulsifies up to 20% oil and silicone. When a higher oil or silicone content is required ViscOptima SE [INCI: Sodium polyacrylate, ethylhexyl cocoate, PPG-3 benzyl ether myristate, polysorbate 20] is recommended. Up to 30% oil or silicone can be included in the formulation without the need for additional emulsifiers. ViscOptima SE and ViscOptima LV can also be used as aqueous phase rheology modifiers and emulsion stabilisers in traditional emulsions containing conventional emulsifiers. They will create a higher viscosity, a higher yield point, a different texture on the skin and improve the stability of the emulsion.

Rockwood Additives Ltd. has developed a cold process method to produce surfactant-free Pickering emulsions, stabilised using low concentrations of colloidal sized particles of Laponite ED. This was described by Pauline Ayres, **Azelis**, at Formulate 2012, who said that this novel "one-pot" process can result in a significant reduction in the time required to make stable emulsion systems. O/W and W/O systems can be prepared with emulsion droplet particle sizes ranging from a few microns to a few millimetres using a variety of oil types of different polarity, from silicone oils and non-polar hydrocarbons through to polar alcohols. Laponite ED [INCI: Lithium magnesium sodium silicate] is a high specification Laponite grade that is dispersed in the oil phase and the water phase then added with high shear mixing, creating a thickened emulsion.

Water-in-oil (W/O) emulsions often appear heavy and less easy to spread than the more popular O/W type. A co-emulsifier from **Seppic** trade named Fluidanov 20X [INCI: Octyldodecanol, octyldocecyl xyloside] is claimed to improve the texture and appearance of W/O emulsions by reducing particle size. It also helps to disperse pigments and has moisturising and emollient properties. **Dr Straetmans** makes similar claims for its Dermofeel GO Soft [INCI: Polyglyceryl-2 sesquioleate] that is said to improve W/O emulsions by imparting a very soft touch, similar to that of whipped cream.

A non-ionic W/O emulsifier from **AarhusKarlshamn** (**AAK**) is Akoline PGPR [INCI: Polyglyceryl-3 polyricinoleate]. The emulsifying and stabilising properties of Akoline PGPR are a combination of the large hydrophilic polyglyceryl group combined with a large hydrophobic polyricinoleic acid chain. It can also be used in anhydrous systems as a pigment-dispersing agent.

Providing ready-to-use bases for preparing cosmetics is not a new idea but modern emulsifiers and formulating techniques are encouraging their use. **Prodotti Gianni** has recently introduced its EmulFreddo System based on an extremely stable concentrated emulsion that can be used for the production of any type of cosmetic product using a cold manufacturing process. The basic emulsion is a mixture of water, C12-15 alkyl benzoate, triisostearin, ceteareth-22, palmeth-2, diglycerin, glyceryl stearate, cetyl palmitate, cetearyl alcohol, palmeth-2 phosphate and dimethicone and depending on the degree of dilution and the possible addition of other ingredients a wide range of cosmetic emulsions is possible.

Also from **Prodotti Gianni** Emulprogress 57 is a mixed system of emulsifiers [INCI: Polyglyceryl-10 stearate, polyglyceryl-6 tristearate, cetearyl alcohol, hydroxypropyl guar] for the production of O/W emulsions. It can emulsify any kind of oil regardless of polarity and it does not require the use of a rheology modifier. Beautyderm WW from **B.T Cosmetic & Food** is a cold-process emulsifier derived from skin-compatible raw materials of natural origin: olive oil, castor oil and vegetable glycerine. Being a liquid emulsifier, an O/W emulsion with emollient and softening activity is easily produced by agitation alone [INCI: Olive oil PEG -7 ester, ethyhexylstearate, polyglyceryl-3 polyricinoleate, sorbitan oleate].

B.T. also supplies Beautyderm HP [INCI: Glyceryl stearate; cetearyl alcohol; stearic acid; sodium lauroyl glutamate]. It is able to emulsify oils and fats of different polarity and viscosity to prepare emulsions from milk to creams by varying only the composition of the fat phase. Emulsions formed using Beautyderm HP have very small droplet size and liquid-crystalline structure. They also provide a strong moisturising action, thanks to the presence of sodium lauroyl glutamate, which is broken down by skin enzymes to form sodium PCA, one of the ingredients naturally present in the skin's natural moisturising factor (NMF).

Multifunctional materials are always of interest; From **BSC Skincare** Bimiol BSC 033 is a ready to use mixture of triglycerides, fatty acids, cholesterol and ceramides, all of which are present in the skins natural barrier. It is a lamellar system that rapidly regenerates the lipid barrier of the skin and is recommended for dry, atopic, mature and sensitive skins as it imitates the skins own barrier function.

Supplying carefully formulated blends of ingredients with multi-functional properties enables suppliers to escape the necessity of competing in the supply of commodities while simplifying the formulating process for new development laboratories. **Dr Straetmans** leads this trend with its Symbio emulsifiers. Symbio Muls GC [INCI: Glyceryl stearate citrate, cetearyl alcohol, glyceryl caprylate] is described as a 100% natural, PEG-free ready to use emulsifier blend with a soft skin feel. Symbio Muls WO is a multi-component mixture of Ecocert approved materials for producing cold-process W/O emulsions.

The phosphate ester, Crodafos BES-70 from **Croda Europe** is similar in structure to the phospholipids found in the skin and is therefore substantive and compatible with the skin's natural lipids. Like phospholipids, di-alkyl phosphate esters have surfactant characteristics that promote the formation of bilayers or lamellar structures. Such behaviour is thought to be the primary mechanism responsible for enhanced oil deposition and delivery of actives onto the skin. Crodafos BES-70 [INCI: Beheneth-30 phosphate, cetearyl alcohol, dicetyl phosphate, cetyl phosphate] is said to be pH tolerant, naturally substantive to skin and to provide a unique sensory profile. Normally it requires neutralisation in-situ when formulating emulsions but for self-tanning products and those containing AHAs this may not be necessary.

Croda also produce the NatraGem range of natural emulsifiers; NatraGem E145 [INCI: Polyglyceryl-4 laurate/succinate] is a versatile high HLB, O/W emulsifier effective in the creation of sprayable to pourable lotions. NatraGem EW [INCI: Glyceryl stearate, polyglyceryl-4 laurate/succinate] is an efficient emulsifying wax with stabilising and thickening properties capable of creating formulations ranging from lotions to high viscosity creams, which are non-whitening on the skin and have excellent sensory benefits. Both these materials may be used for cold-processing and **Croda** has published its Blue Book as a guide to cold-process emulsification.

Natural emulsifiers that may be suitable for cold-processing are growing in popularity. **Kemin Industries** has introduced Lysofix; a natural emulsifier extracted from soybeans [INCI: Glycerin, glycine max (soybean) seed extract]. It is described as a single chain phospholipid that forms stable O/W emulsions and it can stabilise high oil content formulas. Lysofix also has moisturising benefits to skin upon application.

Avogelia from **Variati** is a product entirely of plant origin that contains no ethoxylated compounds or petroleum derivatives. It comprises approximately 70% avocado oil plus lipo-amino acids and lipoproteins from coconut oil and rice proteins and amino acids. It is described as a multifunctional product that can be used as an emulsifier, moisturising emollient and carrier of active ingredients. Published data from **Variati** shows the effect of using different lipids and rheological modifiers in products emulsified with Avogelia.

As a forward to its brochure about BergaMuls ET1 **Berg and Schmidt** write that in addition to a host of physical and chemical properties, modern emulsifiers must also meet other demands like biodegradability, be of natural origin and from environmently-friendly manufacture. Its BergaMuls ET1 is based on natural fruit and cereal fibres and is said to meet these criteria and to provide excellent emulsifying and thickening properties. It is a mixture of beta-glucan and pectin and is compatible with vegetable oils, silicone oils, esters, electrolytes and UV filters and is suitable for cold-process emulsification.

Sisterna is well known for its sucrose-based emulsifiers that satisfy Ecocert for natural certification. **Sisterna SP70-C** [INCI: Sucrose stearate] is an extremely mild non-ionic surfactant that can be used in to prepare cold process O/W emulsions. It also claims antimicrobial activity against bacteria and fungi responsible for body odour; nappy rash and thrush, dental plaque and fungal infections of the feet. SP70-C should

Emulsifiers & Surfactants 1st Published in SPC – 2013 John Woodruff always be added to the water phase and will impart a moisturising, smoothing and cooling effect on the formulation.

Sisterna SP30-C [INCI: Sucrose distearate] is a natural emulsifier for hot process O/W emulsions and provides a cooling effect, excellent skin feel, smoothness, emolliancy and moisturising properties. Its makers suggest a combination of SP30-C and SP70-C at a ratio of 3:1 to promote the formation of lamellar liquid crystals. The same ingredients can be used to create mousses and soufflés at 2% on a 1:1 ratio when used in conjunction with a thickener such as xanthan gum or microcrystalline cellulose. Using a combination of Sisterna PS750-C [INCI: Aqua, sucrose laurate, alcohol] and Sisterna L70-C a novel idea from **Sisterna** is a gel-to-milk composition in which an anhydrous oil in glycerine formulation turns into a milky emulsion upon contact with water. This has applications in areas such as make-up removal, shave gels and even sugar scrubs as there is no water to dissolve the sugar.

A company that makes use of olive oil for its ingredients is **B**& **T**, now part of **Hallstar**. B&T Olivem 1000 Crystal Skin is described as a complex combination of olive-oil derived fatty acids that is chemically similar to skin surface lipid composition. It has the ability to self-emulsify in hydrophilic or lipophilic conditions to generate liquid crystal structures. These liquid crystals are formed of alternating layers of fatty acids and water thereby mimicking the stratum corneum intercellular lipid matrix structure. A technical booklet by B&T describes this material in detail with many tests to demonstrate its emulsifying and skin compatible properties.

AAK produces two emulsifiers based on citric acid esters. Akoline GC is a mixture of citric acid esters of monoglycerides, mainly glycerol stearate, made from edible fully hydrogenated vegetable fat. Akoline LC is an anionic emulsifier, which is partially neutralised citric acid ester of mono/diglycerides, making it dispersible in water and suitable for cold processing applications. Both materials release citric acid by hydrolysis on skin contact, supplementing the natural moisturising factor (NMF).

Both Akoline GC [INCI: Hydrogenated vegetable glycerides citrate] and Akoline LC [INCI: Glyceryl stearate citrate] are capable of forming liquid crystals if combined with non-ionic emulsifiers such as mono/diglycerides, polyglycerol esters or ethoxylated fatty alcohols, making them good emulsion stabilisers and consistency improvers. They can also be combined with a high-HLB anionic emulsifier such as Akoline SL [INCI: Sodium stearoyl lactylate] to further stabilise the liquid crystals formed.

Finally comes some suggestions from **Lucas Meyer** for much improved body butters. According to Lucas Meyer Vegetable butters are widely used worldwide for their nourishing and softening properties combined with the sensation of unctuousness and comfort they provide during application. Unfortunately butters can leave an unpleasant greasy sensation and tacky after-feel on the skin. However, by using phospholipid-based emulsifiers, **Lucas Meyer Cosmetics Laboratories** has developed four formulations containing up to 18% butter without greasy or tacky after feel. These formulations are available from Lucas Meyer and its agents and include a body scrub with a yogurt texture provided by Lecigel [INCI: Sodium acrylates copolymer, lecithin] and 15% shea butter. Mellow butter has a cushion effect Emulsifiers & Surfactants 1st Published in SPC – 2013 John Woodruff provided by an emulsion of 15% pistachio butter and an after sun butter has a high content of oil phase comprising 18% of shea butter and 2% of cotton oil.

All of the materials mentioned in this feature are backed by technical information and toxicity data from the suppliers,. To save space some INCI listings are incomplete and those interested are advised to seek further details of this and of Ecocert approval from the suppliers.

John Woodruff

www.creative-developments.co.uk