Green Chemistry

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What is “Green Chemistry?” Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances [Ref 1]. Green chemistry seeks to reduce the impact of chemistry on the environment by preventing pollution at its source and using fewer natural resources.

A monthly journal entitled Green Chemistry is published by the Royal Society of Chemistry and it covers subjects related to reducing the environmental impact of chemical substances and fuels by developing alternative and sustainable technologies that are non-toxic to living things and the environment, including:

- Improved production methods, formulations, and delivery systems including solvents
- The use of sustainable resources
- Biotechnology alternatives
- Environmentally-friendly process engineering

Many cosmetic manufacturers and their ingredient suppliers now subscribe to this philosophy and “green” claims were very much in evidence at In-Cosmetics 2014. This feature aims to describe materials and processes of production that appear to fit the definitions given above.

Traditionally plant extracts have been obtained using boiling with water or by solvent extraction with alcohol, glycols or volatile solvents. Alcoholic or glycolic extracts had the advantage of recovering more active components without the need for heat and reducing or eliminating the need for preservative. However such extraction techniques resulted in only partial and often non-specific extraction of the plant active constituents. This did not matter if the extract was only being added as label dressing but now the emphasis is on identifying the active molecules within the plant and extracting them unaltered after which they may be concentrated in order to supply sufficient material to support a claim for effect.

Plant extraction by improved process engineering is therefore an area that has received a lot of attention by ingredient suppliers of natural materials. An example is that used by **Alban Muller** in the production of some of its extracts. It is called Zeodration and is carried out under vacuum at a maximum temperature of 45°C. The zeolite contained in the drum absorbs water and creates an exothermic reaction, which helps to reduce the energy needed during the process while preserving the original characteristics of the plant.

Phenbiox has patented a process of plant extraction that it has named molecular bioliquefaction. This enzyme-based technology enables Phenbiox to recover 100% of the bioactive plant compounds as water-based liquid ingredients in a completely bio-available and active form. Phenbiox claims that there are also relevant environmental advantages to using this technology including a reduction in the use of non-renewable resources like solvents and a reduction of waste production.

Liquid molecular bioliquefaction utilises plant enzymes to hydrolyse all the plant structures that contain the molecules that constitute the active phyto-complex. Once the bio-catalysers are selected the optimum strategy to hydrolyse the plant molecules is employed in order to ensure the efficiency of the treatment. Using more enzymes in sequence and/or together can allow both to overcome the inhibition effects that some enzymes suffer and that can compromise the process yield. It is also possible to create synergistic hydrolytic effects

improving the quality of the product. Phenbiox claims that bio-catalytic treatments specifically hydrolyse the features of the target plant in order to recover, in a bio-available form, all the active principle contained in it, including those linked to the solid structure of the plant such as ferulic acid or the arabinoxylans in wheat bran

Examples of extracts produced by Phenbiox using this strategy are Oleox [hydrolysed olive fruit] with anti-free radical activity; Hydropom [hydrolysed tomato skin] and Cruox [hydrolysed wheat bran] with anti-wrinkle properties. Phenbiox has also patented a method using vegetal stem cells to culture specific parts of the plant. This innovative process forces plant stem cells to overproduce bioactive compounds to further boost the efficacy of the active ingredients. Examples are G-Cell, which is an anti-ageing material cultured from unripe red grape and P-Cell with skin firming properties that is cultured from the stem cells of red pepper.

Aloe is Life is an Italian company involved in the technological innovation and transformation of natural products and it has filed a number of European patents to protect a novel process for combining the active components of plants into oils such as olive oil and jojoba without the use of emulsifiers, solvents or maceration. Patent EP 2110122A2 describes how aloe leaves are centrifuged to extract the liquid fraction, which is then mixed under pressure with the carrier oil. The speed of addition and pressure exerted is precisely controlled such that the aloe extract disperses homogeneously and irreversibly into the oil to yield a clear solution that will not separate. Working in association with **Arterra Bioscience**, a biotech research company focused on the discovery of new active products for different applications, the increase in concentration of bio-available active components in the aloe/oil mixtures has been identified and quantified.

Avoiding the use of solvents is encouraged by green chemistry. **Green Line Botanicals** uses a process described as low heat percolation to produce a very extensive line of botanical extracts available in a variety of carriers with minimum order quantities as low as 5kg. **Oleos** uses vegetable oils to extract the active ingredients from plants using a patented process it calls Oleo-Eco-Extraction. It is a combined multi-step process that only lasts for a few minutes and is carried out under nitrogen to avoid oxidation to ensure maximum recovery of bio-active material. Examples of plants treated in this way are water hyacinth, barley, banana and pomegranate. Using its Oleo-Eco-Extraction process Oleos also creates a naturally-derived antioxidant by combining gallic acid of vegetable origin with green tea polyphenols. It is named AntiOx GT; it is oil-soluble at its effective level and shows antioxidant properties that are superior to mixed tocopherols.

The use of fermentation and biocatalysis are two areas that fully comply with the rules of Green chemistry. Fermentation to produce cosmetic ingredients is a well-known process but biocatalysis is a recently developed method to provide new, safe and green molecules. Biocatalysis refers to a synthesis process that relies on an enzyme to catalyse a specific reaction. An example is the synthesis of Inoveol by **Induchem,** which is the result of using an enzymatic method to graft glucose onto a large variety of polyphenols that are more soluble, stable and biologically active than the original polyphenols. This enzymatic reaction tales place in water at 37°C, and uses only plant extracts, saccharose and an enzyme to produce the new glycosylated-polyphenols. Induchem states that by using this new green chemistry process skincare companies have access to improved derivatives of caffeic acid, gallic acid,

epigallocatechin gallate, phloridzin, resveratrol, rosmarinic acid and oleuropein with further ingredients in development.

Palm oil and its derivatives appeared to be an easy answer to the trend to replace animal fats and petrochemicals in the last quarter of the 20th Century. It needs less than half the land required by other crops such as sunflower, soybean or rapeseed oil to produce the same amount of oil and it is the least expensive vegetable oil in the world. It was then realised just how much environmental damage was being caused to sensitive areas of Asia, Central and Southern America, Indonesia and the Solomon Islands, which were being deforested in order to plant palm trees.

This led to the setting up of the Round Table for Sustainable Palm Oil [RSPO]. The first line of its mission statement is "To advance the production, procurement, finance and use of sustainable palm oil products" Its code of conduct states that "It is fundamental to the integrity, credibility and continued progress of the RSPO that every member supports, promotes and works towards the production, procurement and use of Sustainable Palm Oil" The RSPO defines sustainable palm oil as that obtained from plantations where no new primary forests or high conservation value areas have been cleared for palm oil production since November 2005. Currently output certified by the RSPO is 9.7 million metric tons, which represents 16% of the world market in palm oil. For full details of this organisation, its aims and achievements refer to http://www.rspo.org/.

There are various levels of conformance: Identity Preserved (IP) means that certified product is uniquely identifiable to the certified plantation through the whole supply chain. Segregation (SG) ensures that certified palm oil is kept physically separated from non-certified palm oil but allows blending with other batches of CSPO from different plantations and guarantees that the end product contains only CSPO. Mass Balance (MB) allows product of certified and non-certified sources to be mixed at any stage in the supply chain. Each company handling Mass Balance CSPO is only allowed to sell the same amount of certified palm oil drawn from the "mixed" oils that it originally bought as certified. Finally Book & Claim (B&C), also known as GreenPalm, is a certificate trading system that ensures payment for each certificate goes directly to the producer of CSPO.

Ingredient suppliers are very supportive of the RSPO. **Cremer Care** joined the RSPO in 2007 and was granted the RSPO SCCS supply chain certificate in 2011. It has produced a presentation explaining the environmental and economic benefits of using RSPO certified palm oil over other vegetable oils and now lists fourteen palm oil derivatives with RSPO certification. It is important that the whole supply chain be identified; **KemCare** is the exclusive distributor for Cremer Care in the UK & Ireland and has recently registered under RSPO SCCS to ensure its customers have a full RSPO SCCS supply chain.

BASF also subscribes to RSPO and markets a range of palm oil derivatives including emulsifiers and surfactants meeting RSPO requirements using either MB or SG systems. BASF states that it is an important step to support more sustainable production of oil palm products and towards fulfilling its commitment to purchase all its palm and palm kernel oil from certified sustainable sources by 2015.

Croda is a significant user of palm oil and supporter of the RSPO and it sponsored the annual RSPO Conference held in London in June 2014. By 2015, all of Croda's manufacturing sites

handling palm oil and derivatives will have RSPO Supply Chain Certification and the company is working towards all of their supply chains being certified by 2017.

AAK is one of the founders of the RSPO and also founded and operates the GreenPalm certification program. The GreenPalm programme allows trading by small producers direct to the palm oil users. Through these activities, AAK continuously contributes to the production of sustainable palm oil. It is also a founding member of the Global Shea Alliance, which is a multi-stakeholder association promoting quality and sustainability in the shea industry. It supports rural African communities and promotes women's empowerment by strengthening the shea industry and value chain.

When sourcing shea kernels in West Africa **AAK** introduces fair trade principles and educates rural women in quality improvement. The sourcing of shea kernels includes cooperation with governments and NGOs and AAK believes that proactive work with its supply chains is behind the development of sustainable solutions.

Sustainability and Fairtrade were very much keywords at In-Cosmetics and they often went together. Fairtrade generally brings to mind poor farmers in South America, Africa and the Indian subcontinent however they also exist in Switzerland. **DSM** produces its Alpaflor range of bioactives extracted from rare Alpine plants and actively encourages their planting and sustainable harvesting through Fairtrade agreements with hill farmers' cooperatives. In this way it ensures traceability from the seed to the extract and secures its supply and quality.

Premier Specialities is a supplier of fragrances and botanicals and reports that since its inception and incorporation in 1999 it has been committed to a holistic approach to the sourcing and creation of its products. Its botanicals can be traced to the tree or plant whence they came and it can certify those sustainable products originating from Nicaragua and Honduras with the FSC and Rainforest Alliance. It has an extensive list of extracts, oils and butters but Premier also realises that "Going Green" applies to more operations than careful sourcing of ingredients. In a continuing effort to reduce its impact on the environment it constantly documents water, electrical, and gas usage, and uses this information to set new goals for the reduction of waste and more efficient water and energy usage in its facilities.

Laboratoires Expanscience is a member of the Union for Ethical Biotrade, an international non-profit organisation that works to promote ethical practices in the supply of ingredients sourced from native biodiversity. One of the central aims of this approach is to reduce the social, economic and environmental challenges raised by the plant supply chains in question. An example is its procurement of *Acacia macrostachya* seeds from Burkina Faso where they are traditionally used in cooking, medicine and religious ceremonies. In the past they were harvested by women for little reward. Expanscience organised them into local cooperatives, guaranteeing a fair return for properly harvested seeds, which it then uses to prepare its skin hydrating material, Aqualicia by enzyme hydrolysis.

The bark of Quillaja saponaria trees has long been used as a source of natural surfactant but until relatively recently only the bark was used and the tree left to rot. Over 50,000 trees per annum were being lost in this way until **Desert King** became involved. Desert King International and its Chilean affiliate, Natural Response, utilise the entire Quillaja tree biomass in the production of Quillaja extracts and powders. The biomass is obtained by pruning native forests and plantations, utilising branches, bark and limbs and the number of

trees being felled has dropped to 10,000 per year. By removing aged trees, and implementing selective branch pruning to improve and promote tree growth, Desert King is stimulating the growth and rejuvenation of native Quillaja tree forests.

Desert King also harvests yucca in a sustainable manner, following all the rules and regulations set forth by the Mexican Forestry Department, to ensure that the Yucca extraction rate is not more than the plant's natural recovery rate. All current raw material is obtained from wild harvest, however, Desert King has developed experimental Yucca plantations to assure a continued renewable supply for years to come.

Environmentally friendly engineering includes the use of cold process emulsification, which saves energy in both the heating and cooling cycles of cosmetic production. **Sisterna** produces emulsifiers based on sucrose esters that are suitable for this and the company has produced a useful guide to their use. It took a simple basic emulsion and compared the effect of using three different sucrose esters on droplet size, viscosity, method of production and skin feel. The effect of using different oils and at different concentrations was also measured.

It was concluded that all Sisterna sucrose esters with higher mono ester values can be used in cold production to obtain stable emulsions. Sisterna L70-C [INCI: Aqua, sucrose laurate, alcohol] forms emulsions with the smallest droplet size and the lowest viscosity. When a higher viscosity is needed the best solution is Sisterna SP70-C [.INCI: Sucrose stearate], which also provides the best skin feel. A concentration of 3% SP70-C is sufficient to emulsify up to 60% of oil into the emulsion. Long term stability against creaming is realised by the use of hydrocolloids to increase viscosity of the external phase and a combination of microcrystalline cellulose and xanthan gum provides the best results.

JEEN International recently launched its Jeesperse ICE-T series of optimised powders that, when introduced into water at room temperature, rapidly form stable emulsions typically eliminating the use of traditional emulsifiers and allowing the addition of waxes into the system without heating. There are currently four mixtures in the range, each consisting of polymers for thickening with powdered mixtures of conventional emulsifiers and co-emulsifiers. Like with many cold-process emulsifying systems it is important to follow the suppliers mixing instructions for best results.

BergaMuls ET 1 from **Berg & Schmidt** is a vegetable fibre compound for emulsifying and thickening cosmetic emulsions. It is a mixture of β-glucan and pectin obtained from fruit and vegetables and is supplied as a white powder that can be used for both hot and cold emulsification. It has the advantage of not being affected by electrolytes, pH or oil polarities. The same company also supplies lysolecithin in various grades as BergaMuls HL, which are used as cold-processing emulsifiers.

Lecithin is the basis for many of the materials from **Lucas Meyer** and its Ecogel is a mixture of lysolecithin, sclerotium gum, xanthan gum and pullulan that provides gelling and cold-process emulsification properties. A second material from Lucas Meyer suitable for cold-process emulsification is Dermofeel Easymuls. It is an anionic emulsifier made from sunflower oil, triglycerol and citric acid from renewable plant sources and the manufacturing process uses environmentally friendly condensation reactions. Thus does not involve any kind of alkoxylated species so it is PEG and PPG free. It forms o/w emulsions of low

viscosity and rich skin feel and can be employed as the emulsifier for spray-on sun care products with up to 30% oil content and also for wet wipes and roll-on deodorants.

Sepiclear G7 [INCI: Heptyl glucoside] from **Seppic** is a 100% bio-based non-foaming surfactant for solubilising oils and perfumes in aqueous media and for use as a co-emulsifier suitable for cold-processing. It is synthesized by reacting heptyl alcohol from castor oil with glucose and is an example of the use of sustainable resources to create a material that complies with the principals of green chemistry. Also from **Seppic**, Simulgreen 18-2 also owes its origins to castor oil and glucose, this time to form hydroxystearyl alcohol and hydroxystearyl glucoside, which together provide an o/w emulsifier capable of forming lamellar structures and products that are rapidly absorbed by the stratum corneum without a soaping effect.

The search for PEG-free surfactants for solubilizing perfumes, essential oils and lipophilic substances in predominantly aqueous compositions has led to some interesting materials. Tego Solv 61 from **Evonik** is a mixture of polyglyceryl esters based on renewable materials that make it possible to obtain clear shampoos, shower gels and similar products using a significantly lower level than would be the case with PEG-40 hydrogenated castor oil. An alternative idea is behind the **Viatenza** range of water-dispersible oils from **Aldivia,** which are based on forming polyglyceryl esters of the oil itself.

Evonik also produces polyglyceryl esters for emulsification; its Tego Care PBS 6 is a mixture of polyglyceryl-6 stearate and polyglyceryl-6 behenate. Glycerin is from coconut oil and it is then polymerised to give polyglycerol; the stearic acid and behenic acids are from rapeseed and palm oil. Tego Care PBS 6 is an o/w emulsifier that can be used to create stable low viscosity emulsions and it is also a skin moisturizer.

The use of enzymes to produce ingredients is encouraged by the principals of green chemistry. **Akott** uses enzymatic processing to produce extracts of Mediterranean, organic and GMO-free plants and marine algae. Another example of this process is used by **Evonik** to produce a vegetable-based ester trade named Tegosoft OER [INCI: Oleyl erucate]. It is a high viscosity, medium spreading oil with properties similar to jojoba oil but it does not discolour either itself or the compositions containing it. Interestingly it has a higher level of purity than chemically synthesized oleyl erucate, made possible by the specificity of enzymatic processes. **Evonik** also produces isoamyl cocoate, cetyl ricinoleate and decyl cocoate and myristyl myristate by enzymatic esterification.

Utilising byproducts of the food industry is “green processing” and **Akott** creates Italine-T from otherwise wasted tomato seeds. Using cold mechanical pressing, decantation and filtration without using any solvents or added chemicals ensures the process retains all the natural nutrients present in the tomatoes. The result is a pure and 100% natural active ingredient that can be used as an antioxidant and free radical scavenger. Akott claims that it reduces skin dryness, desquamation and itchiness and increases the physiological barrier function. **Akott** also uses a novel process to sterilize plant material for its Akobiol ranges of botanical actives. The plant material is placed in a hyperbaric chamber filled with an inert gas, thus avoiding the use of chemical solvents, insecticides and other possibly toxic treatments.

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Skinveil 500 [INCI: Sericin] from Principium is a seresin protein extracted as a waste bi-product from the production of Silk. The molecular weight is 500 kDa and this exceptionally large size confers a bioactivity to the molecule that is lacking in smaller, degraded proteins from a similar source. Its high level of purity is obtained through a precisely controlled pharmaceutical grade lyophilisation process. Skinveil 500 helps to soothe skin irritation and reinforces the skin's own natural defences making it ideal for sensitive skin applications.

Rosamox from **Kemin** would appear to tick several boxes when it comes to being "Green". It comprises the active principals obtained from certified sustainably grown rosemary [*Rosmarinus officinalis*]. It is obtained by supercritical CO2 extraction and it replaces synthetic antioxidants to protect oils and fats from rancidity. It is virtually odour-free and is multifunctional, providing skin benefits including skin soothing and conditioning as well as its antioxidant properties.

A subject of discussion at In-Cosmetics was the environmental impact of using polyethylene scrub particles as exfoliates. There is a wealth of alternatives available; mostly made from waste materials such as seeds and nut shells. Almost all purveyors of cosmetic ingredients offer some of these but the most complete range appears to come from **A&E Connock** and there are some useful tips on how to suspend them in a variety of products on its web site www.connock.co.uk/

Replacing commonly used ingredients with more environmentally friendly alternatives is part of going "green" and in recent years attention on replacing volatile silicones has led to the introduction of more acceptable materials, many of which were described in the feature on silicones and alternatives in SPC Jan. 2014. A more recent introduction is Cetiol Ultimate from **BASF Care Creations**. It is a mixture of undecane and tridecane, both of which are natural-based, biodegradable, light in feel and volatile. Finsolv TN [INCI: C12-15 alkyl benzoate] is a well-known ester from **Innospec** but its alkyl chain was derived from petrochemicals. Innospec has recreated the ester with raw materials approaching 50% natural. It is trade-named Finsolv TN-G and its INCI name is unchanged and there is very little difference in its physical specification.

The majority of materials mentioned in this feature have Ecocert and COSMOS approval.

Ref 1. Green Chemistry. United States Environmental Protection Agency. 2006-06-28. Retrieved 2011-03-23.

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www.creative-developemnts.co.uk