Naturals and Green Chemistry 2018
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The acceptance that the chemical industry must not adversely affect the environment for future generations has been the driving force behind the development of green chemistry. This is not a separate branch of chemistry, but an approach that permeates every stage of process development. Sustainability is at the heart of this aspiration and sustainable development and manufacture meets the needs of the present without compromising the ability of future generations to meet their own needs. [Ref 1].

There are twelve principles of "Green Chemistry" [Ref 2]

1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

Natural ingredients for cosmetic use that have been obtained by following the principles and ideals of Green Chemistry is the focus of this feature.

A search for Green Chemistry on the Kosmet database retuned 7,722 references covering many aspects of cosmetic ingredients and production [Ref 3]. Showing that the cosmetic industry was at the forefront of applying green chemistry principles is a paper published in 2005 that describes eco-friendly synthesis of various aromatic esters for use as sunscreens and preservatives using microwave activation [Ref 4]. The search for new non-toxic, environmentally friendly and biodegradable surfactants has increased with the development of green chemistry. Non-ionic bio-surfactants, such as sugar fatty acid esters, may be obtained by enzymatic synthesis and these have application as surfactants and emulsifiers [Ref 5].

Many cosmetic ingredient suppliers have adopted the principles of green chemistry and publish their commitment to it [Ref 6]. **Laboratoires Expanscience** was a finalist in the Sustainable Beauty Awards 2017 and has pledged to ensure that by 2020 all its cosmetic active ingredients will be eco-socio designed. To achieve this, it has committed to providing information about every ingredient's security, safety, and environmental impact. Each of its materials are assessed according to the relevant criteria and given scores out of 100. As part of a continuous improvement approach, this helps determine which socio-environmental criteria have room for improvement, while maintaining the cosmetic performance and quality of the active and other ingredients. 100% of Expanscience cosmetic active ingredients launched since 2015 obtained scores of over 80/100 and 78% of the catalogue's active ingredients scored over 75/100.

A process that meets all the accepted principles of green chemistry is that developed by **Olixol** to produce pure natural seed oils using plant cells. Its patented process occurs at temperatures of less than 30^0C and no solvents or harmful chemicals are used. Non-GMO seeds of the genus of oil

required are carefully selected and, under a microscope, the seed is cracked open and the specific oil producing cells are identified and removed. The cells are placed in flasks containing a proprietary liquid media and then subdivided repeatedly into vessels of increasing size. In a continuous process in a hygienic environment at atmospheric pressure the cells are constantly fed with sugars, light and air. Oil separates naturally from the cells and is removed from the tanks. The oil is cold filtered using a food grade membrane, bottled and nitrogen blanketed within hours of being produced. Currently Borago officinalis (borage) seed oil and Simmondsia chinensis (jojoba) seed oil are available through its distributor, **A&E Connock Ltd.**

Utilising waste materials from the food industry is an example of applying green chemistry and the head, skin and backbones of farmed salmon is used as a source of valuable oils rich in PUFA and as a source of collagen and gelatine. Green methods of extraction were compared with conventional methods and found to give equal or higher yields than methods in common use [Ref 7]. **Adina Cosmetic Ingredients** has recently launched it Full Circle range of upcycled ingredients utilising waste materials from the food industry. Examples are Blueberry Necta [INCI: Vaccinium corymbosum (blueberry) seed oil] and Raspberry Necta [INCI: Rubus idaeus (raspberry) seed oil]. Following extraction of the juice by the drinks industry the waste fruit pulp is collected and cold-pressed to extract the oil from the seeds. Upcycling is then taken a stage further as the waste material following oil extraction is processed to provide natural scrubs and powders such as Blueberry Crush [INCI: Vaccinium Corymbosum [blueberry) seed] and Raspberry Crush [INCI: Rubus Idaeus (raspberry) seed].

Celus-Bi Esters are new range of materials from **Brasca** starting from the ambition of reaching 100% sustainability while delivering performance. Celus-Bi Esters are natural cosmetic ingredients created without any interference with the food supply chain. As a result, it is possible to create ingredients focusing on non-edible by-products, aiming at zero impact on the environment. One of the range, Celus-BI Light Esters, was the winner of the Cosmetorium 2017 Sustainability Award and is described as a fully biodegradable innovative high-technology ester obtained from renewable European crops using an eco-friendly process. Celus-Bi Light Ester [INCI: Tripelargonin] was compared to caprylic/capric triglyceride and found to have superior pigment dispersion properties, to provide a comparable performance in anhydrous products such as lipsticks and body oil, and has good binding properties in powder formulations. Brasca also markets Celus-BI Microbeads, which are biodegradable microspheres suitable as exfoliating agents for personal care and cosmetic products.

Using plant cells instead of whole plants is the approach used by **Vytrus Biotech** in the development of its plant cell biofactories technology platform. This technology uses plant stem cells and is described as a new, efficient and eco-sustainable way to obtain a new generation of plant extracts with high added value for dermocosmetics. It enables the exploitation of rare plants because only a few seeds or even a single plant is needed to establish a bank of plant stem cells, which may be cloned for decades. Once the cell culture is established in the laboratory there is complete independence from natural resources as the plant stem cells are reproduced sustainably in a bioreactor. The technology has been used to prepare two ranges of materials: plasma rich in cell factors (PRCF) targeting molecular synergy through controlled stress and phyto-peptide fractions (PPF), described as the first generation of plant peptides.

Examples of PRCF materials from **Vyrtus Biotech** are Arabian Cotton PRCF [INCI: Gossypium herbaceum (cotton) callus culture], which gives broad-spectrum protection against photo-aging. Luminia Granatum PRCF [INCI: Punica granatum seed cell culture lysate] combines the antioxidant and anti-inflammatory properties of pomegranate to even skin tone, enhance radiance and show a

visible brightening effect. Sensia Carota PRCF [INCI: Daucus carota sativa root cell culture lysate] targets inflammation, strengthening the skin level of tolerance and acts as a protector against inflammation, free radicals and DNA oxidation. The phyto-peptide materials include Capilia Longa PPF [INCI: Curcuma longa (turmeric) callus conditioned media] from the rhizome of turmeric, which is rich in signalling peptides and specially designed to create the optimal micro-environment to re-activate hair growth. It provides an epigenetic reset of the hair bulb and hair follicle regeneration and in-vivo studies show up to 89% hair loss reduction and up to 52% hair density increase at 150 days, with an average of 13.500 new hairs.

Oleos patented its method for extracting non-volatile compounds from vegetable matter [EP 2413706 B1] and produces several natural actives using vegetable oils as the extracting medium. Myrtle-Olive Oléoactif is an active lipid complex extracted from myrtle using deodorized olive oil, [INCI: Olea europaea fruit oil, Myrtus communis leaf extract, Olea europaea leaf extract], that is highly concentrated in phenolic acids and flavonoids and shows excellent antioxidant properties. Diam Oléoactif, [INCI: Cocos nucifera oil, oak root extract, Quercus suber bark extract] is an oily active derived from cork oak and coconut oil for sensitive and reactive skin, acting as a natural shield against inflamm'aging. Propolis Oléoactif TL is an active lipid complex derived from propolis and sunflower oil [INCI: Helianthus annuus seed oil, propolis extract] claimed to reduce the UVB-induced oxidation level of cutaneous cells and to visibly fill and smooth fine lines and wrinkles. All the Oléoactif materials are obtained using green chemistry processing and are certified 100% organic.

Ginger, red grape and frankincense are subjected to bioliquifaction technology, an enzyme based process developed by **Phenbiox**, to enable the complete recovery of plant phyto-complexes. The result is Pure-Phen [INCI: Vitis vinifera fruit extract, Zingiber officinale root extract, Boswellia serrata resin extract], a purifying, soothing and conditioning active ingredient able to help restore health to skin and scalp. Vine sap is the solution of nutrients that travel up the stem of vines in spring to reawaken the plant and stimulate budding and growth. It contains a complex mix of mineral salts, amino acids, natural saccharides, polyphenols, organic acids and auxins. **Phenbiox** has encapsulated vine sap in plant liposomes to provide LifeEssence-vitis [INCI: Vitis vinifera vine sap], which has beneficial effects on skin and hair. In-vivo data show it able to improve the condition of the skin, increasing moisturisation and elasticity, and tests on hair treated with compositions containing LifeEssence-vitis showed a notable improvement in hair elasticity and strength.

TC-USA is a company that specialises in providing butters based on octyldodecanol, beeswax and cold-pressed oils. The range includes Argan Butter, Raspberry Butter and Blueberry Butter and Pomegranate Butter. They are creamy pastes and each melt at body temperature, have superb barrier qualities, outstanding skin feel and excellent emolliency. The butters retain the properties of the seed oils from which they are derived so Raspberry Butter is rich in linoleic, alpha-linolenic, and oleic acids. The composition of omega-3 and omega-6 fatty acids reduces the effects of oxidative stress in skin plus its high levels of Vitamin E protect the skin from ROS and it has pronounced anti-inflammatory properties.

Squalane has long been used as an emollient in skin care; originally from shark liver oil production then changed to using olive oil as its source. Now **Aprinnova** produces Neossance squalane by fermentation of sugar cane. The crop is sustainably grown in Brazil without irrigation, and represents the highest biomass per hectare of all sugar sources. This innovative process gives virtually unlimited supply and lower, stable prices. Sustainability is at the core of the process as wastes are used to generate electricity, water use is minimised and biodiversity respected. The same process is used to

produce Neossance Hemisqualene, which is recommended as an alternative to isohexadecane and to silicones.

The market for vegan cosmetics has grown significantly in recent years. **BASF** has responded to this by introducing Rheocare XGN. It is the first polymer launched under the Care Creations brand consisting of pure vegan xanthan gum and is 100 % based on non-GMO renewable feedstock. Rheocare XGN is a powerful thickening agent and stabilizer for emulsion and surfactant based systems. It appears that most green chemistry claims are for skin care actives and less so for ingredients to treat hair, however **Inolex** produces a hair conditioning material that is energy efficient in its production and is completely biodegradable. It is trade named ProCondition 22 [INCI: Brassicamidopropyl dimethylamine] and prepared by a one-step aminolysis process. Hydrogenated brassica oil undergoes amidation with DMAPA, which allows for quantifiable data of reduced 'Greenhouse Gas Equivalency'.

RevCare NE 100S from **Itaconix Personal Care** is a hair styling polymer prepared according to the principles of green chemistry. It is based on itaconic acid, which is obtained from non-GMO corn, converted to sodium polyitaconate using green chemistry with mineral reagents and polymerised under controlled conditions. Itaconix claims high yield with no downstream purification required and water as the only solvent. There is low energy and labour input, very low waste, no by-products and minimal environmental controls are necessary. Recognised test protocols show it to have low aquatic toxicity and to be fully biodegradable. This naturally derived polymer offers excellent hold and anti-frizz properties and is claimed to be the first hair styling polymer to be approved by COSMOS, Ecocert, Greenlife and the USA Natural Products Association. It is water-soluble, does not require neutralisation and tests show it to exhibit superior curl retention in high humidity environments and to have outstanding sensory properties, offering a non-crispy, natural feeling to styled hair. Another itaconic acid polymer is RevCare HP, which is recommended for thermal protection of hair.

NOTE: INCI breakdowns of mixtures only show the principal ingredients and virtually all the materials described are complaint with green chemistry principles and certified as natural ingredients, however those interested are urged to obtain full information from the suppliers.

Ref 1 http://www.essentialchemicalindustry.org/processes/green-chemistry.html

Ref 2 Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30.

Ref 3 http://www.kosmet.com/abstracts/ Search term "Green Chemistry, accessed on 30/12/17

Ref 4 Villa, C., Baldassari, S., Gambaro, R., Mariani, E. and Loupy, A. (2005), Eco-friendly methodologies for the synthesis of some aromatic esters, well-known cosmetic ingredients. IJCS, 27: 11–16. doi:10.1111/j.1467-2494.2004.00246.x

Ref 5 Ruela, H. S., Sutili, F. K., Leal, I. C. R., Carvalho, N. M. F., Miranda, L. S. M. and de Souza, R. O. M. A. (2013), Lipase-catalyzed synthesis of secondary glucose esters under continuous flow conditions. Eur. J. Lipid Sci. Technol., 115: 464–467. doi:10.1002/ejlt.201200321

Ref 6 http://www.expanscience.com/en/commitments/csr-policy

Ref 7 Głowacz-Różyńska, A., Tynek, M., Malinowska-Pańczyk, E., Martysiak-Żurowska, D., Pawłowicz, R. and Kołodziejska, I. (2016), Comparison of oil yield and quality obtained by different

extraction procedures from salmon (Salmo salar) processing byproducts. Eur. J. Lipid Sci. Technol., 118: 1759–1767. doi:10.1002/ejlt.201500269

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