Feature: Natural Cosmetics
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For many centuries cosmetics could only be made from natural materials but from the early 19th century synthetic materials enabled much improved products to be prepared. A scientific basis for preparing stable properly preserved products was developed that met the physiological needs of the user. However in the mid-1960s herbal extracts suitable for inclusion in cosmetic products became commercially available and "natural" cosmetics were reborn.

The argument about what is natural has rumbled on ever since, more recently joined by the meaning of organic and when is a chemical not a chemical!

The difference between today's cosmetics that contain natural ingredients and those made prior to the 19th century are that consumers expect elegant, pleasant smelling products that meet their claims and are safe to use and there is a host of legislation that reinforces such expectations.

What are the problems of formulating natural products? First and foremost is the argument about what is natural. The argument has recently been opened in the Formulators Discussion Group [Ref 1] by Gavin Greenoak, President of the Australian Society of Cosmetic Chemists, who wrote "We (the Society) have been asked to give an opinion on the question of "Organic" and "Natural" claims. As these claims expect to convey desired qualities of safety, efficacy and environmental friendliness we understand fully the huge and growing market success that these claims enjoy but we are also a scientific society, and we cannot find any scientific basis whatever for these claims.

In reply Tony Dweck [Ref 2] wrote "Organically grown means that the environment has been an important consideration in the production of the raw material. Natural means found in nature or derived from nature. There is the third category, nature identical. We are all chemists and there is not a jot of difference between citric acid from a normally grown lemon, citric acid from an organically grown lemon or citric acid from a biological ferment or citric acid produced from a petrochemical starting point. That is chemistry! Chemists deal in the real world, marketing look for love and who-knows-what in something that has no difference in science, although all these citric acids would vary hugely in cost!"

What is clear is that adding a few drops of herbal extract to a batch of shampoo or bath foam does not make it natural, although it does enable an attractive label design. Adding less than 1% of natural oil to an emulsion does not make it natural, although many labels would have the consumer believe it so.

The other extreme are those companies that try to be wholly natural and even try to source the majority of ingredients certified as organically grown. Providing safe, effective and affordable products that meet these criteria presents particular challenges to the formulator.

Somewhere between these extremes are products that meet the majority of consumer expectations; an alliance between science and nature was how one company described it. The author has discussed numerous product briefs with clients over the years and many wish for natural claims. In soon becomes apparent that the wishes are as much negative as positive.

Not wanted are animal ingredients and those tested on animals, at least in recent years. Not wanted are materials that are obviously petroleum-based, ethoxylates and glycols. Most preservatives and especially parabens are not wanted and synthetic colours are dismissed as are aromatic chemicals in perfumed preparations. It is obvious in discussion that some of the rejections are based on deep-seated beliefs and careful thought, other times it is an attempt to find a place in a market niche and often it is knee-jerk reaction to the latest scare story in the tabloid press or on the web. Whatever the basis for the new product formulation, it raises difficulties not faced when creating main-stream preparations.

The first problem is always that of preservation; finding natural materials that foam is difficult, even more so if a surfactant product is also to have significant viscosity; emulsifiers can also be difficult although there are now some very useful ones that are naturally derived. Other problems depend on the restrictions that clients impose; avoiding ethoxylates when trying to solubilise essential oils in clear surfactant products is a particular hurdle that is difficult to overcome.

Any formulator faced with the problem of preserving natural products with minimal use of accepted preservative systems is advised to obtain a copy of Preservative-Free & Self-Preserving Cosmetics & Drugs, [Ref 3]. It discusses hurdle technology, the use of essential oils and the antimicrobial action of chelating agents, fatty acids and fatty acid esters and of surfactants and anti-oxidants. Many of the materials cited may not be acceptable to the marketing brief or suitable for the product but there are many useful ideas. Of great importance is the need to build in the preservative system at the start of formulation.

It is possible to preserve products with materials that are acceptable to the majority of natural product briefs by lowering the product pH to 4.0 – 4.8 and using potassium sorbate, which is one of the few preservatives allowed by the Soil Association when claiming organic certification. Benzoic acid may also be used at this pH; it is said to be more effective against bacteria than potassium sorbate but less effective against yeasts and moulds. Citric acid from a suitable source may be used to adjust the pH and this appears to act in synergy to improve the antimicrobial action of these two materials. Needless to say a challenge test is essential when preparing products using these principals.

If planning to add one or more botanical extracts to a product it is essential to get full disclosure of ingredients from the supplier. Many suppliers fail to understand the need for avoiding particular materials and will load the extract with a multitude of preservatives, even

when 50% of the extract is a glycol. Unfortunately glycols may also be on the not wanted list but some are less wanted than others. Even now it is common to find extracts that include five parabens and phenoxyethanol in an aqueous- propylene glycol base.

Some companies have listened and Alban Muller International provides preservative-free extracts of organically certified plants in organic-sourced glycerine and oil-based extracts in organically certified safflower oil. Euro-Gewurz GmbH offers a limited number of extracts produced by supercritical carbon dioxide extraction, which results in the lipidic components becoming available. Freeze-dried extracts in powder form are also possible, extracts of Aloe barbadensis being the best example. Ennagram produce dry extracts and powdered extracts based on Ayurveda principals are available from Biosourcing of India, and it is always possible to create one's own extracts in situ, negating the need for preserving the actual extract.

Another problem with extracts is discolouration and fall-out from clear liquid products. The extract itself may be heavily coloured or it may discolour with time. Aloe barbadensis leaf juice is an example of the latter and the pH of a product containing significant levels of it needs to be kept below 5.5 or it will go brown. Many other extracts are pH sensitive yet suppliers in general fail to mention this. In clear products the wrong pH can cause precipitation, in all products the wrong pH can inactivate any active principals that may be present.

Various natural materials contain saponins and are offered as foaming agents. Of these *Yucca schidigera* and *Quillaja saponaria* bark extract, both available from Paroxite, are possibly the best known. New offerings include Juazirine from Naturactiva, which is an extract from the *Zizyphus joazeiro* tree and Seagold 100 from Surfacare, which is a foaming material from *Laminaria digitata*. If these materials are used as the sole foaming agent the result is only likely to appeal to the ultra-purist but they can be combined with one or more acceptable synthetic surfactants.

The Swedish Society for Nature Conservation publishes a list of surfactants that are least harmful to the environment and from Germany we have the OKO Test list of materials graded for acceptability, some being more acceptable than others. The Soil Association accepts alkylglucosides, alkylpolyglucosides and alkylbetaines. Amphoacetates, sarcosinates and isethionates also appear to be generally acceptable and there are an increasing number of non-ethoxylated surfactants available. For example from Seppic we have sodium cocoyl apple amino acids and sodium lauroyl oat amino acids and from Vama there is a series of amphoacetates based on natural materials.

From a chemist's viewpoint it is very difficult to determine why one group of surfactants may be more acceptable than others but sodium lauryl sulfate and its ethoxylated sister are not

acceptable to the majority of companies wishing to make natural claims and using a different fatty chain or a different cation is not an ethical way round this, although often seen.

Natural creams and lotions are becoming easier to formulate as more suppliers provide suitable oils, waxes and emulsifiers. Almond, peach kernel, sesame and olive oils have always been used but now every seed that can yield oil is tried. The problem with natural oils is that their quality and availability varies from season to season and they may be prone to rancidity and discolouration. There are also emulsification problems, although these should not be insurmountable.

Not all oils are prone to rancidity; Limnanthes alba (Meadowfoam) seed oil is resistant and Simmondsia chinensis (Jojoba) seed oil is particularly stable but technically speaking it is a liquid wax rather than oil. Tocopherol is a natural antioxidant and is often used to protect natural oils before use and in final products. Aperoxid TLA from Crestchem is tocopherol and ascorbyl palmitate with lecithin and citric acid to be used as an antioxidant in final compositions. Many botanical extracts with anti-oxidant properties are available but generally these are water-soluble to be added to skin care cosmetics with the objective of preventing free radical attack in the epidermis. Their water-solubility and price render them generally unsuitable to protect the oil-phase.

Natural oils, fats and butters are triglycerides, classified into the three categories by their solidification temperatures after being melted. If natural oil is saponified it releases glycerine and fatty acids, which then react with the alkali used in the process. If a wax is saponified it releases fatty acids and fatty alcohols, so the effect on the composition is quite different. Triglyceride fats and oils are used in plants and animals primarily as a source of energy. Wax esters are used primarily for moisture control, protection and emolliency.

Because natural materials contain a number of different triglycerides the fatty acid profile is an important property requiring careful consideration before a selection is made. They differ in the length of carbon chain, the presence of double bonds and their iodine value. Whatever the claim the application of a cosmetic emulsion has to be a pleasing sensorial experience; oiliness increases with increasing length of carbon chain with lower numbers feeling quite dry and higher numbers of carbon atoms leading to a greasy feel. The presence of double bonds lowers the setting point of the oil and the higher the number of double bonds the higher its iodine value, and the more prone will the oil be to rancidity.

.In recent years much work has been undertaken by oil suppliers to the cosmetic industry to provide natural-derived emulsifiers that avoid some of the restrictions requested by marketing departments. One example is based on Carthamus tinctorius (Safflower) oil, which is valued for its unique blends of unsaturated fatty acids like oleic and linoleic acids that impart a light, smooth, emollient feel to the skin. Lonza claims to have extracted both the lipid components

and the oils' natural proteins and phospholipids in order to provide Natrulon OSF, an oleosome material that is self-emulsifying and that will emulsify other ingredients and it can be used for cold-processing.

From Tecomag comes olive oil glutamate, a combination of olive oil with wheat gluten that is said to be a natural emulsifier and cleansing agent. Olivem 1000, B&T Srl, is also an emulsifier derived from olive oil and both these materials are capable of producing an acceptable emulsion with no other lipid components. Other emulsifiers acceptable to the majority of natural cosmetic producers are Emuliance, INCI: Cetearyl wheat bran glycosides with cetearyl alcohol and Xyliance, INCI: Cetearyl wheat straw glycosides with cetearyl alcohol; both available from Soliance, a company that also produces a number of organically certified materials. Sasol suppliers PEG-free w/o and o/w emulsifiers under its Imwitor trade name although persuading the marketing department that diisostearoyl polyglyceryl-3 dimer dilinoleate is suitable for natural cosmetics might be an uphill struggle.

Rheological modifiers are an essential part of many cosmetic formulations but the ubiquitous carbomers are not accepted as suitable for natural cosmetics and even mined clays like Veegum are not universally approved. Xanthan gum is allowed but it does not gel however Glucovis, Chesham Chemicals, is a combination of xanthan gum with mannan, which has unique gelling properties and may be used as an emulsion stabiliser or to prepare gels and to thicken natural-based surfactant systems. Versaflex, Uniqema, is also a combination of xanthan gum with mannan but is quite different to work with and is used more as an emulsifier rather than a gelling agent.

Heliogel from Lucas Meyer is a gelling agent with emulsifying properties based on Helianthus annuus (Sunflower) seed oil and phospholipids although it's content of sodium acrylates copolymer and polyisobutene may decrease its attraction in the world of natural cosmetics. Alginates and carageenans may be more acceptable and FMC Biopolymers have a number in their product portfolio, including some with organic certification. Also from FMC is Avicel microcrystalline cellulose, which has wide application. Other cellulose derivatives are widely available and at least one will normally provide the desired properties. Starch and various modifications of it are also widely used; National Starch has a complete range that covers most applications.

When a composition is complete it normally needs an added fragrance. In the world of natural cosmetics this means adding essential oils. Disclosure of allergens has upset this somewhat and the author still has difficulty persuading clients that essential oils can contain such materials. If the composition is to be surfactant-based the oils will probably need solubilising. One of the few materials found satisfactory in this regard is Oramix CG 100, Seppic, INCI: Caprylyl/capryl glucoside, which appears equivalent to PEG-40 hydrogenated castor oil as a

solubiliser and also contributes to the foaming power of the composition. Detailed application and toxicological data is available for this material from the suppliers.

Ref. 1 Formulators Discussion Group; a web-based forum sponsored by Step Exhibitions.

Ref. 2 Dweck Data; www.dweckdata.com

Ref 3 Preservative-Free & Self-Preserving Cosmetics & Drugs, Kabara & Orth, Marcel Dekkar 1996