

Bathroom Products;
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About 45 years ago a basic shower gel was formulated using a combination of sodium laureth sulfate with lauryl betaine, preservative, colour and perfume. At about the same time a basic foam bath comprised the same ingredients and so did a simple shampoo. What has changed since? A glance along any supermarket shelf will disclose that the majority of price-conscious products are still based on those few ingredients. Closer inspection may show lauryl betaine replaced by cocamidopropyl betaine; formaldehyde replaced by isothiazolinones and the addition of a modicum of a botanical extract may have been added to grace the label but these are hardly radical changes.

The biggest change in British bathroom habits over the last four decades has been the result of widespread installation of central heating and double glazing. This has made the daily shower feasible throughout the winter. No longer are premium products aimed solely at getting users clean but at giving them a pleasant experience and imparting a skin benefit. This has led to the introduction and use of mild surfactants and ingredients that contribute to skin feel. Other driving forces have been the ever-expanding use of natural and organic claims now validated by various certification bodies, and additional product functions and claims.

A number of surfactant suppliers have developed mild surfactants from natural and sustainable sources. The SugaNate Series from **Colonial Chemical** (USA) are surfactants based on alkyl polyglucoside (APG) derivatives, which may be substituted for traditional primary surfactants in personal care formulations. Colonial claims that in the past a formulator started with irritating materials and built the formulation to mitigate irritation. SugaNate products allow a formulator to start formulating with non-irritating, products and build consumer desired aesthetic properties knowing irritation to eyes and skin will not be a problem. This allows the formulation of low or no irritation shampoos, body washes, bath gels, and personal cleansing products. The SugaNates are said to be readily biodegradable, soluble in water, easy to handle, to foam well, are gentle cleansers, and compatible with most other personal care ingredients.

Currently there are two SugaNate materials available; Poly SugaNate 100 is sodium hydroxypropyl decylglucosides cross-polymer and Poly SugaNate 160, is sodium hydroxypropyl laurylglucosides cross-polymer. They have a Green Star rating of about 6.5. The Green Star Rating [Ref 1] is a classification system designed to allow the formulation chemist to determine the natural component in products. It is a relatively simple system based on a spread sheet available on line at no cost and in use it is simply a matter of identifying the natural components in a molecule, which are first expressed as a percentage then on a scale of 1 to 10; the higher the Green Star Rating the more green the product.

Other mild surfactants available from Colonial include Polysugamates, which are APG sulfosuccinates; Polysugaphos, which are APG phosphonates, and Polysuga Betaines, which are alkyl glucosides betaine crosspolymers. The Poly SugaQuat series are made from short and long chain quats reacted onto polymerised alkyl polyglucoside sugars, yielding products that are naturally derived and cationic in character. The sugar moiety decreases the irritation substantially over traditional quats, allowing the formulator an expanded use of these materials in a variety of personal care formulations. They have the INCI names Polyquaternium-n, where n is 77, 78, 79, 80, 81 and 82.

The sugar-based surfactants from Colonial are part of a trend named “Free from” by **Cognis** which means they are preferably free from preservatives, ethoxylates, alkyl and alkyl ether

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sulfates, betaines etc. In answer to this trend Cognis has developed its green leaf method of identifying an ingredients degree of naturalness with four green leaves representing materials from 100 % natural, renewable feed stocks that have only been physically purified by water, alcohol or energy. Three green leaves are awarded to materials from renewable feed stocks that have been chemically processed using a catalyst or reaction aid and two green leaves are given to materials where at least 70% of the carbon atoms are from natural, renewable sources but if less than 70% it is only awarded one green leaf.

Having identified the “Free from” trend Cognis seeks to satisfy it with the introduction of Plantapon SF, a combination of sodium cocoamphoacetate, glycerin, lauryl glucoside, sodium cocoyl glutamate and sodium lauryl glucose carboxylate. The blend is Ecocert approved and only needs dilution, perfume and preservation to be the basis of a skin cleansing system. Viscosity may be adjusted by the addition of Lamesoft PO 65, a mixture of coco-glucoside and glyceryl oleate and resulting products are claimed to be comparable in foaming characteristics with ethoxylate-based systems but to be extremely mild and to confer additional benefits such as skin moisturising and skin smoothness.

Plantapon LGC Sorb, INCI: Sodium lauryl glucose carboxylate and lauryl glucoside, is claimed to retain the mildness of APG surfactants while improving important consumer-related attributes such as foam and sensorial acceptance. Also from Cognis, Plantapon LC 7, INCI: Laureth-7 citrate, is claimed to be particularly suitable for the sensitive skin of seniors and babies. Based on 100 % active matter, this protective surfactant can be used in non-aqueous systems such as care-treatment shower and bath oils.

Many other suppliers are available for glucoside-based surfactants: Ritafactant 138 AN is a 57% active blend of decyl glucoside and sodium lauroyl lactylate available from **Rita**. Oramix NS-100 is decyl glucoside and it is also available mixed with cocamidopropyl betaine as Oramix GB10, both from **Seppic**. AG-10LK is decyl glucoside from **Kao Corporation** and it is available mixed with ammonium laureth sulfate from Cognis as Plantaren PS-100. Coco-glucoside is available from **A&E Connock** or mixed with cetearyl alcohol as Montanov 82 from Seppic while a mix of coco-glucoside and glyceryl oleate is available from Cognis as Lamesoft PO65.

Eucarol AGE/SS from Cesalpina is an aqueous solution of disodium coco-glucoside sulfosuccinate, which shows good foaming properties and outstanding mildness. Other mild surfactants from Cesalpina include sodium coco-glucoside tartrate, trade named Eucarol AGE TT, a low foaming but exceptionally mild surfactant suggested for wet wipes, cleansing lotions and make-up removers, and Eucarol AGE EC, a 30% active solution of disodium coco-glucoside citrate. All materials in the Eucarol AGE series are Ecocert approved.

Protein-based surfactants have been available for decades but they often have problems of colour and odour; Proteol OAT from Seppic is claimed to be virtually colourless and odour-free and to have foaming properties comparable to alkyl ether sulfates. Its INCI name is sodium lauroyl oat amino acids. Oat proteins also feature in materials from **Sinerga**. Vegequat is cocodimonium hydroxypropyl hydrolysed wheat protein and Lauroate is sodium cocoyl oat amino acids. Proteol APL, INCI: Sodium cocoyl apple amino acids, is an anionic surfactant created from the acylation of amino acids characteristic of apple juice.

From **Arch Personal Care**, Amaranth S is a natural foaming peptide which functions as a secondary surfactant, high in colloidal peptides and carbohydrates. Amaranth S is non-ionic

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in nature, stable over a wide pH range and highly compatible with other ingredients. It provides excellent foam, foam density, and stability even in the presence of salt. It is extremely mild and biodegradable and the presence of the protein base enhances substantivity to skin leaving behind an elegant, conditioned feel after rinsing.

For those not wishing to have cocamidopropyl betaine listed on their product labels Lipex Shea Betaine from **AAK** is an amphoteric primary surfactant based on shea butter with foam boosting and viscosity building properties. Its INCI name is shea butteramidopropyl betaine and its shea butter origin and content of shea butter unsaponifiables contribute to the mildness and irritation reducing ability of this betaine.

The basic requirement of a shower gel is that it should cleanse; to this may be added a nice perfume and a pleasant skin feel during and after use but premium products must offer more and claims range from moisturising to anti-ageing effects and even to providing sun protection. Unfortunately, the cleansing action also removes protective lipids from the skin surface and adding emollients that remain on the skin after rinsing presents special challenges.

Two materials from **ISP** are claimed to overcome this problem by being substantive to skin: according to the ISP literature lipids found in healthy skin are largely in a lamellar gel crystalline state that is responsible for the skin's barrier function. In the stratum corneum, ceramides and cholesterol serve a vital role by acting together with fatty acids to properly organise the lipid phase of the skin. Ceraphyl RMT is castoryl maleate which forms structured lipids with fatty acids, in a manner similar to that exhibited by ceramides and cholesterol in the stratum corneum. Prolipid 161 comprising behenyl alcohol with cetearyl alcohol and cetearamidopropyldimonium chloride, spontaneously forms lamellar gel structures in water. In both cases the lamellar gel is both the deposition vehicle and the moisturiser system. Extensive test results available from ISP show significant improvements to skin topography and moisture levels when either of these materials are applied from cream body washes and shower products.

Spherulites from **Soliance** are concentric micro-vesicles encapsulating active ingredients. They are composed of alternating surfactant bilayers and aqueous phase and both hydrophilic and hydrophobic ingredients may be included within their structure. Spherulites are available in non-ionic form, which are claimed to penetrate deeply into the epidermis, and in cationic form, which makes them substantive to skin. The cationic form were originally targeted at hair products but have found application in rinse-off skin care applications. Not only do they resist being rinsed from the skin but deliver slow release benefits over several hours. Upon contact with biological surfaces the micro-vesicles gradually open through the action of cutaneous enzymes or water evaporation. As each membrane opens another layer of actives is released, prolonging the product's effectiveness over time.

Another carrier for emollients and oil-based actives is Natrasorb Bath from **AkzoNobel**. It is a modified tapioca starch that is able to absorb large quantities of oils and anhydrous liquids. The starch is processed in a manner that enables it to carry up to 16% of its weight in oils while remaining a free-flowing powder and it will dissolve in contact with water releasing the loaded ingredients into the bath. The starch itself provides a soft feel to the bath water, but does not settle or leave a film. The starch can also be blended with dry surfactant to formulate foaming bath powders with high oil content and can also be used to absorb the oils and

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fragrances used in a bath salt formula. When the oil-loaded starch is mixed with the salt granules, the starch naturally adheres well to the salt, eliminating the necessity for a fixative.

Starch-based materials of interest are also available from **Grain Processing Corporation**.

Zeina B860 hydroxypropyl starch is a cold water-soluble polymer designed to combine outstanding film-forming properties with a smooth, silky skin feel. This unique polymer has very low viscosity and is ideal for formulations requiring water-soluble film properties such as personal wash products, facial masks, shaving creams and gels and is said to contribute mildness to personal care formulae, adding functionality without adding high viscosity.

Kreglinger markets rice starch from **Beneo-Remy**, a company with a long history of investigating its properties. Many Asian cultures attribute skin caring properties to rice starch and these are validated by an investigation into its healing properties when added to bath water [Ref 2]. Organically certified rice starch in the form of large compact crystals can be obtained from Kreglinger and it is suggested that it be sprinkled directly into bath water or formulated into a bath milk or shower gel.

Water-soluble or dispersible emollients are mostly based on PEG-n glycerides. Lipex 102 E75 and Lipex 203 E70 are water dispersible non-ionic surfactants derived from shea butter and mango kernel oil. Both materials can be used in transparent surfactant based face wash and shower gels. Lipex 102-E75 is PEG-75 shea butter glycerides and Lipex 203 E70 is PEG-70 gango glycerides, both from **AAK**. Softigen 767 from **Sasol** is PEG-6 caprylic / capric glycerides. Olivem 300 from **B&T** is olive oil PEG-7 esters and from the same company, Olivem 460 is sodium PEG-7 olive oil carboxylate.

Bath oils retain their popularity and are an ideal carrier for natural oils. The Sucragels based on sucrose laurate, water and glycerine from **Alpha Chemicals** are of interest because are compatible with esters and non-polar oils, and despite their water and glycerine content, enable the formulation of crystal clear gels. Sucragel CF also contains caprylic/capric triglycerides and Sucragel AOF contains *Prunus amygdalus dulcis* (Sweet almond) oil and is available as 94% organically certified from **Colonial Chemicals**.

Many materials finding application in face washes and shower gels were initially developed for improving hair shampoo. One such example is Aquaxyl from **Seppic**. This combination of xylitol, xylitylglucoside and anhydroxylitol is a moisturiser for hair that is found to have skin moisturising and soothing properties when incorporated in personal cleansing applications.

It appears that with the exception of those wishing to be certified “Organic” whatever the cosmetic application there is a suitable silicone compound to enhance the product. **Dow Corning** HMW 2220 Non-Ionic Emulsion has been designed as a unique way of incorporating a high viscosity polymer into water-based systems for body wash applications including skin facial cleansers and shower gels. Silplex J2-S, INCI: Silicone Quaternium-20, from **Siltech** combines cationic and anionic silicone polymers and can be used in clear anionic systems to impart a velvet skin feel. These materials are new and full details are available on the web site [Ref 3]

Biosil Technologies market a number of silicone compounds of interest in shower and bath products; BioPlex SA is a complex of a sunflower seed oil derivative and a carboxy silicone with the rather long INCI designation of sunfloweramidopropyl trimethylammonium chloride PEG-8 dimethicone succinate. It is water-soluble and compatible with most surfactants and

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both the carboxy silicone portion and the sunflower seed oil derivative are said to be a highly substantive to hair and skin. Similar materials based on coconut oil or olive oil are also available as is cetyl triethylmonium dimethicone PEG-8 succinate under the trade name Cetylsil S. The description of this material in the Biosil brochure explains how cationic materials are deposited on the skin from anionic surfactant systems.

Thickening Problems

Surfactant systems based on alkyl ether sulfates are readily thickened by adding electrolyte but others can present difficulties in attaining sufficient viscosity or in controlling results however an increasing number of materials aimed at addressing these problems are now available. Rheocare TTA from **Cognis** is a liquid, acrylic emulsion polymer used as a rheology modifier designed to suspend, thicken, and enhance the appearance of surfactant-based cosmetic cleansing preparations. Due to its special rheological behaviour it is possible to stabilise air bubbles, peeling particles, and encapsulated actives in body cleansing formulations and is able to stabilise silicone and water insoluble actives. Also from Cognis, Arlypon TT is a high performance thickening agent that combines associative and micellar thickening behaviour to ensure optimum viscosity. It is a combination of PEG/PPG-120/10 trimethylolpropane trioleate and laureth-2.

Elfacos T 212, INCI: PPG-14 palmeth-60 hexyl dicarbamate, is an associative thickener from **AkzoNobel** designed to build viscosity with mild surfactants. It is suitable for use as a rheology modifier in clear formulations and can be used to provide conditioning effect and as a suspending agent. Carbopol Aqua SF-1 from **Noveon** is a cross-linked acrylic polymer dispersion designed to impart suspending, stabilising and thickening properties to a variety of surfactant-based personal cleansing products.

Solubilising Problems

Higher priced shower gels and bath additives often include relatively high levels of perfume and emollients, which are difficult to solubilise without destroying product viscosity and suppressing foam. **Cognis** claims that Eumulgin ES, INCI: PPG-5-laureth-5, has outstanding solubilising properties for vegetable and synthetic oils, natural extracts and perfumes in surfactant media. It is said to be easy to handle, is clear and fluid at low temperatures. PPG-1-PEG-9 lauryl glycol ether is available as Eumulgin L and it also appears in combination with coceth-7 and PEG-40 hydrogenated castor oil as Eumulgin HPS. It is said to give good results with different oils in surfactant media and to provide excellent sensorial properties in the final formulation.

Croda offers three materials said to provide solubilising properties and thickening power to surfactant systems. Promidium 2 is PPG-2 hydroxyethyl coco/isostearamide; Promidium CO is PPG-2 hydroxyethyl cocamide and Promidium LTS combines PPG-2 hydroxyethyl cocamide with PEG-150 distearate. Promidium CO is recommended as a viscosity and foaming alternative to the traditionally used cocamide DEA but without any of the safety concerns associated with it. Promidium 2 has attributes approaching more that of cocamide MEA and these two materials are generally used in typical ethoxylated surfactant systems. Promidium LTS is recommended for more difficult to thicken systems such as those based on amphoteric surfactants and alkyl polyglucosides.

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Also from **Croda** is Procetyl AWS: it is PPG-5 ceteth-20 and is said to solubilise some of the most challenging oils and lipophilic actives into clear detergents without affecting foam. In combination with Crodafos O3A, INCI: Oleth-3 phosphate, it forms a microemulsion that releases oils upon dilution and leaves an emollient film on the skin after rinsing. Effective and efficient solubilisation requires the optimum solubiliser to oil ratio, and whilst it is common to have a greater quantity of solubiliser compared to oil, the closer the ratio is to 1:1, the more efficient the solubiliser. Croda has determined that Procetyl AWS with Crodafos O3A is most effective when used at a starting solubiliser to oil ratio of 3:1. It is advised to use Procetyl AWS and Crodafos O3A in a ratio of 2:1. A micro-emulsion is formed by heating the materials with water to 80C. This can then be added to a surfactant system such as a bath additive, face wash or shower gel and the Croda literature gives many examples of how suitable oils can be incorporated using this system.

The Procetyl AWS/Crodafos O3A system can be extended to incorporate many other materials into surfactant systems. Worth consideration are the Zenibee Butters from **Zenitech**, which are a series of natural oils, cold pressed to retain naturally occurring antioxidant and other attributes. The oils are combined with octyl dodecanol and beeswax to form products that melt at body temperature, have superb barrier qualities, outstanding skin feel, and excellent emolliency. Currently the range includes blueberry, pomegranate, argan, macadamia, orange, raspberry, avocado, lime, and carnauba.

For those seeking ethoxylate-free solubilising Oramix CG 110 from **Seppic**, INCI: Caprylyl capryl glucoside, is said to be useful for dissolving essential oils. From **Sinerga** comes Natisol, INCI: Cocoyl proline, a natural perfume and essential oil solubiliser.

Ref 1 <http://www.greenstarproducts.org/>

Ref 2 Effect of Rice Starch as a Bath Additive on the Barrier Function of Healthy but SLS-damaged Skin and Skin of Atopic Patients; Acta Derm Venereol 2002; 82: 184–186

Ref 3 http://www.siltechpersonalcare.com/whats_new_page.html

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www.creative-developments.co.uk