Bathroom Products;
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John Woodruff

Generally speaking, people like to be clean and to get clean water is not enough. It has been said that the care given to personal hygiene is a measure of civilisation; certainly, the Ancient Greeks and Romans took it very seriously. Pliny (AD 79) wrote that soap making was invented by the Gaul's, who used animal fat and alkali from wood ash or lime. Apparently goat fat and the ashes of beach wood gave the best results and the remains of a soap factory were found in the ruins of Pompeii.

In the late 13th or early 14th century soap making was established in Marseilles, where the industry thrived because of its proximity to the sources of wood ash from the forests of that region plus olive oil, lime and barilla, which are coastal plants and seaweeds, the ash of which yields sodium carbonate that is used to harden soap. In the late 18th century Nicholas Leblanc patented a method of obtaining sodium carbonate from sodium chloride. This process was rendered obsolete in the 1860s by the Solvay process that synthesised sodium carbonate from sodium chloride and calcium carbonate, a process that is still in use today.

Animal and vegetable oils are triglycerides and soap is the product of saponifying them with an alkali to produce a metallic stearate and glycerin. For such an old industry it is somewhat surprising that new patents related to soap formulation and production are still being filed. USP 7,919,442 describes a method for preparing multiphase toilet soap, which results in a toilet soap with speckles and stripes. USP 8,017,567 describes a personal cleansing bar with free fatty acid and quaternary surfactant synergism. It also describes how the addition of talc in varying percentages increases qualities to the user such as fragrance deposition, freshness, smoothness, lather and creaminess.

USP 8,546,315 also looks at the effect of adding talc to toilet soap and discusses the addition of various surfactants to improve its lathering properties. USP 8,492,323 looks at ways of improving soap lather by adjusting the ratios of the fatty acids in the soap making process. It is also of interest in that it mentions almost all possible additives to soap grouped under various headings. USP 8,563,494 claims iridescent soap bars containing ethoxylated alcohols.

When soap is used for washing free alkali is released and this saponifies any sebum and natural oils on the skin, enabling them to be readily removed by rinsing. Thus, in use the soap has a high pH, around 9.5 – 10.5, and this can result in significant drying of the skin and subsequent irritation. An alternative are syndet bars using synthetic surfactants and USP 5,300,249 claims a mild personal cleansing bar composition with balanced surfactants, fatty acids, and paraffin wax. Syndet bars do not saponify natural skin oils but emulsify them into oil-in-water emulsions that can be rinsed away.

The pH of personal cleansing products is an important attribute and its effect on the skin has been the subject of many studies, summarised in a paper by Sven Munke *et al* in an article first appearing in the IFSCC Magazine [Ref 1]. It describes a project conducted to evaluate the effect of application of surfactant systems of different pH on the skin surface pH. The optimum pH at the skin surface is 5 – 5.3 and even short-term elevation of about 0.5 pH units produces functional abnormalities such as decreased epidermal barrier cohesion. It was found that a single treatment with soaps leads to a pH increase of approximately 1.5 to 3.0 units and a single use of skin pH

balanced products like syndet bars elevates the skin surface pH by approximately 0.5 to 1.5 units.

Munke concluded that not only the given acidic pH of a cleansing product but also the composition of the surfactants is important to maintain the physiological skin surface pH and thus epidermal barrier function. An acidic pH alone is no guarantee for protection of the physiological skin surface pH. An acidic product pH has to be combined with the right surfactant system to minimise the effect of cleansing products on the skin pH, wrote Munke.

Because of the drying effect of toilet soaps, face washes based on mild cleansing aids and/or containing additives to impart additional mildness have risen in popularity. Shower gels still tend to be based on less mild systems but the popularity of the daily shower is tending to merge the two products so many of the materials described in the next section are applicable to both types of product.

Amino-acid based surfactants are generally recognised as being mild and can be substituted for the commonly used fatty-chain anionic surfactants in personal cleansing products. Amino-acid surfactants produce substantial foam and leave a soft mild and smooth after-wash feel on the skin. Examples are the Eversoft products from **Sino-Lion** based on either potassium or sodium cocoyl glycinate and available as either 30% active solutions or as a 95% active powder.

From **Ajinomoto** we have Amisoft CS-11 [INCI: Sodium cocoyl glutamate]; Amisoft HS-11P (F) [INCI: Sodium stearoyl glutamate] and Amisoft ECS-22SB [INCI: Disodium cocoyl glutamate], which, as well as for face and body washes is also recommended for bath and hair. **Shanghai Oil Enterprises** offers these plus TEA-cocoyl glutamate and various glutamates are also available from **Guangzhou Tinci Materials Technology Co. Ltd. Clariant** offers sodium cocoyl glutamate as Hostapon KCG and **BASF** has a number of glutamates available under its Plantapon trade name including sodium stearoyl glutamate.

The Plantapon trade name is also used by **BASF** for Plantapon LGC Sorb, a mixture of sodium lauryl glucose carboxylate and lauryl glucoside that has good foaming properties and shows excellent dermatological compatibility, making it suitable for shower gels, facial washes and bubble baths. Glucosides are in common use for personal cleansing products and are widely available singly or in mixtures, e.g. lauryl glucoside with cocamidopropyl betaine is available as Plantacare K55 from **BASF.** For more foam the same combination is also found with sodium laureth sulfate such as in Marlinat 24/70 from **Sasol Olefins & Surfactants**.

Decyl glucoside, xylose and decyl alcohol are the main constituents of Appygreen 812 from **Soliance,** which is said to work in synergy with SLES to optimise cleansing, improve the viscosity of the formula and to effectively increase the quality of foam.

Using sodium laureth sulfate (SLES) as the primary surfactant is still the most popular approach for body washes and foam baths because of its excellent flash foaming properties combined with low odour, minimal colour and low cost. To this are added secondary surfactants to improve foam texture and stability and reduce the irritation potential of the SLES. Cocamidopropyl betaine remains the most popular but the glutamates and glucosides already mentioned find application in the milder versions.

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Other secondary surfactants include the sarcosinates such as sodium lauroyl sarcosinate produced from natural fatty acids and the amino acid, sarcosine and lactylates like sodium cocoyl lactylate, which is the sodium salt of the coconut acid ester of lactyl lactate. This is available as Pationic SCL from **RITA Corporation**. Sodium stearoyl lactylate is available from **AAK Surfactants** as Akoline SL and these anionic emulsifiers can be used as co-surfactant foam boosters and moisturisers in shower gels.

Another method of reducing potential irritation from face and body washes is by the addition of special additives like Arlasilk PTC [INCI: Cocamidopropyl PG-dimonium chloride phosphate] from **Croda.** It is said to be substantive to skin, offering excellent sensorial benefits for personal wash products while providing antimicrobial and preservative boosting effects.

For an optimised blend of mild foaming detergents, waxes and structuring agents **Croda** suggests Arlatone MAP [INCI: Disodium lauryl sulfosuccinate, sodium cocoyl isethionate, Zea mays, cetearyl alcohol, aqua, hydrogenated castor oil, glycerin, titanium dioxide]. It facilitates the production of white, creamy personal care formulations, especially where '2-in-1' combined cleansing and moisturising benefits are claimed.

Still with **Croda**, Crovol A70 [INCI: PEG-60 almond glycerides] is a water dispersible emollient and solubiliser and functions as a superfatting and conditioning agent without adversely affecting foam volume. Solubilising lipids in personal washing preparations can be difficult but Natragem S140 from **Croda** is designed to do this. Comprising polyglyceryl-4 laurate/sebacate and polyglyceryl-6 caprylate/caprate in aqueous solution it can be used to solubilise hydrocarbons, esters and essential oils and it can give clear solutions in cleansing preparations. Experiment shows it to be more efficient at doing so than polysorbate-20 and PEG-40 hydrogenated castor oil. It has also been determined that NatraGem S140 has proven counter irritancy benefits and does not affect the foaming properties of a formulation.

Monoalkyl phosphate esters are known to be mild to the skin yet to still deliver copious volumes of dense, stable foam and to impart a silky skin feel with a talc-like after feel to skin. Two examples are available from **Sino Lion** as EverMAP 24 K50 [INCI: Potassium C12-14 alkyl phosphate] and EverMAP 160K [INCI: Potassium cetyl phosphate]. The 24 K50 can be used to prepare clear foaming products whilst the 160K can be used to prepare cream face and body washes.

From **Global Seven** Hetoxol Guerbet Ethoxylates are a range of non-ionic surfactants that help increase foam volume and stability when used in combination with other surfactants and exhibit excellent wetting and emulsification properties There are six items in the range and examples are Hetoxol I-20-20, which is a octyldodeceth-20 with an HLB 14.9 and Hetoxol 1-20-2 that is octyldodeceth-5, HLB 4.9.

Ingredients based on olive oil are perceived as being mild to the skin and the **B&T Company** is well known for its Olivem range of surfactants and emulsifiers based on this material. Olivems 400, 450 and 460 are all sodium PEG-7 olive oil carboxylate of different activity levels. They have good foaming properties and although anionic in character they show amphoteric behavior and are compatible with anionic, non-ionic and many cationic systems. They are said to be show excellent dermatological

compatibility and to impart an emollient feel to skin when used in face and body washes. They reduce the irritation of SLES when used as secondary surfactants and can be added to bar soaps. Olivem 300 is PEG-7 esters of olive oil and is a mild emollient and non-foaming cleanser. It is 100% active and is recommended to reduce irritation caused by commonly used surfactants and as a refatting agent and a co-emulsifier for O/W systems.

Olive oil-based surfactants are also available from **B.C Cosmetics & Food**, which supplies olive oil PEG-7 glycerides as Beautyolea S3 and sodium PEG-7 olive oil carboxylate as Beautyolea S4. The same company also supplies a number of amphoacetates based on natural oils and butters including argan, babussa, olive, rice and sweet almond oils under its Beautycare trade name.

Another mild surfactant suitable for face washes and shower gels is Lipex Shea Betaine from **AAK** [INCI: Shea butteramidopropyl betaine]. It is an amphoteric surfactant that improves the viscosity and foaming properties of rinse-off formulations; it is mild and non-irritant and is free from ethoxylates. Eucarol AGE surfactants from **Lamberti Spa** also includes ethoxylate-free materials such as AGE/ET [INCI: Sodium coco-glucoside tartrate], AGE/SS [INCI: Disodium coco-glucoside sulfosuccinate] and AGE/EC [INCI: Disodium coco-glucoside citrate]. They are described as surfactants with optimum skin tolerance showing superior mildness to the eye yet with foaming properties comparable to traditional anionic surfactants.

This article has focused on delivering effective cleansing from mild surfactant systems however depositing skin benefit agents from products designed to rinse off the body is more difficult. N-Hance SP-100 [INCI: Acrylamidopropyltrimonium chloride/acrylamide copolymer] from **Ashland** may be added to bath and shower gels to improve skin feel after bathing or showering. N-Hance SP-100 also functions as a deposition polymer in body wash systems by forming a coacervate with anionic surfactants, promoting the deposition of silicone and other emollients onto skin.

Another approach to improving deposition is to use spherulite technology. When surfactant molecules are dispersed in water, as the concentration of surfactant increases, their molecules spontaneously arrange themselves into micelles and other energetically stable configurations including spherulites. They are discrete onion-like structures that can contain useful cosmetic ingredients, which make spherulites valuable encapsulation systems. Spherulites containing actives are stable when included in rinse-off products and they will be deposited onto skin and hair when the rest of the product is rinsed away [Ref. 2]. **Soliance** has pioneered Spherulite technology and supplies them encapsulating both water-soluble and oil-soluble actives.

A workshop presentation by Peter Clark at Formulate 2013 [Ref 5] described the formulation of structured surfactant systems, which are systems where the surfactants are in liquid crystalline phases and of articular interest are lamellar phases. These are formed at higher surfactant concentrations than micelle phases and when lamellar phases are sheared they form multi-lamellar vesicles or spherulites. Not all surfactants and surfactant mixtures form spherulites but **Innospec** provides blends that may be used to create them. One such is Iselux SLC [INCI: Aqua, sodium lauroyl methyl

isethionate, sodium lauroamphoacetate, cocamide MIPA], which can deliver high levels of oils or silicones to the skin from shower gels.

Next month this feature is continued with the focus on delivering active ingredients from different cleansing and treatment systems.

Ref 1 Munke S. et al, The impact of cleansing products on the skin surface pH, IFSCC Magazine Vol 16, No 1, January/ March 2013, pp. 17-24.

Ref 2 Brockway, B., in praise of spherulites – delivering actives to skin and hair from rinse-off products. Cosmetic Science Technology, 2012.

Ref 3 Clark, P., Formulating sulfate-free structured surfactant systems; Formulate 2013

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