Bathroom Products;
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Once upon a time, long, long ago, bathrooms were cold draughty places where people bathed once a week, even if they weren't in need. Now, with double glazing, central heating and equipped with at least a shower and a bath they are places where users can disappear for extended periods of pampering. If the magazines are to be believed this applies to men as well as women.

The first stage for either sex is cleansing, and because of the frequency of use and other modern trends mildness is the keyword for almost all products. There are also niche markets that demand organic materials, no ethoxylated compounds, no parabens, no perfumes and even no "chemicals". Other niche markets rely on quirky messages, high levels of perfumes or essential oils, new presentations and not least, on beautiful packaging.

Cleansing may be as simple as a shower; or as time consuming as a pre-treatment wash, an exfoliating scrub and a moisturising balm to follow. The cleansing regime may include face masks, salts scrubs, AHA products, cleansing emulsions, or be oil-free, surfactant-free, preservative-free and even water-free: there are no shortages of challenges thrown down by the marketing department for the formulator to grapple with.

In its simplest form a shower gel consists of sodium laureth sulfate with cocamidopropyl betaine plus colour, perfume and preservatives. This will give copious foam, be easy to rinse away and will cleanse the skin. For label dressing a dash of botanical extract may be added. To improve the product it needs to impart a pleasant skin feel during and after use; rheology modifiers like the PEG-150 distearate, glutamates and xanthan gum add to skin feel. To add mildness and to improve foaming characteristics caproyl lactylate, which is said to be an excellent foam booster and stabiliser when used in conjunction with cocamidopropyl betaine may be added. Alternatives are alkyl polyglycosides, sodium lauroyl isethionate, sodium lauroyl sarcosinate and sodium lauryl sulfoacetate, which is an excellent foaming, wetting, emulsifying and cleansing surfactant with good stability in hard water. It is possible to formulate reasonable products using these materials and avoid ethoxylated compounds altogether, but the end result costs more and there is a loss of product efficacy. A possible alternative to ethoxylated compounds is sodium C14-16 olefin sulfonate. Sodium lauroyl glutamate and sodium cocoyl glutamate also foam well and because of their amino acid origins, impart a pleasant skin feel and have moisturising properties. ***Further ideas were published in SPC – Surfactants***

Zschimmer & Schwarz supply glutamates under the trade name Protelan AGL 95. They are described as extremely mild and effective liquid emulsifiers for cold and hot processed emulsions. A major benefit is the great flexibility offered to the formulator. Nearly all kinds of oils can be emulsified with Protelan AGL 95 and by using polymeric thickeners; viscosity can be adjusted in the formulations. This allows the application of high amounts of oils and emollients to the skin. Additionally, acyl glutamates leave a perceivable and smooth feel on the skin and form particularly creamy and stable foam. Mild and gentle cleansing emulsions can be formulated in combination with traditional surfactants, which impart a smooth, velvety feel to the skin. In laboratory tests Zschimmer & Schwarz demonstrated that cold produced emulsions based on sodium cocoyl glutamate, in combination with oils of different polarities such as dimethicone, paraffin liquidum, isopropyl palmitate and glycine soja (soybean) oil all show excellent long-term stability regarding viscosity, pH value, particle size, touch and optical effect. Acyl glutamates are also available from Ajinomoto Co. Inc., Clariant International Ltd. and Vama Farmacosmetica SRL.

Many suppliers claim that the surfactants they produce are exceptionally mild but it is not a parameter that is easy to measure, especially if animal testing is not to be used. At the IFSCC Congress, Florida 2004, a paper entitled The Effect of Surfactants on Skin as Measured by Squamometry: A Sensitive Way to Observe Sub-Clinical Irritant Dermatitis was given by Morrison, Paye, Charbonnier and Maibach, which described a method of quantifying mildness. It was found that squamometry measurements could detect minor differences in mildness, or more precisely, in irritation, and these findings were more accurate than instrumental and clinical examination techniques.

Although cleansing is an important step in personal care and no other treatment can commence until the cleansing phase has been completed it received scant attention at the IFSCC Congress, 2004. One poster, Quantifying Cleansing Efficacy of Facial Cleansers Using Objective Measurements by Di Qu covered the background attributes needed for efficient cleansing. He described the types of soils that need to be removed as dead skin cells, sebum, makeup, surface grime, or any other contaminants from the environment including various micro-organisms. Di Qu said that evaluation of efficacy on antimicrobial products has been well established while for the rest of soils, the cleansing efficacy of various products is primarily evaluated by subjective means such as user groups or panel tests.

Di Qu first defined the cleansing efficacy as the percent change in the colour of a makeup-stained surface relative to that of an unstained surface after a cleansing application. Silicone based facial make-ups were used to stain the surface of Transpore tape and an ink-rub tester was used to provide rubbing action to clean the surface. A flow meter was used to control the velocity of rinse water after cleansing and a colorimeter was used to measure the changes in all three colour coordinates, L*, a* and b*. Results of cleansing efficacy were charted for a number of surfactants and surfactant blends and mildness, cost and foaming ability were compared. Thus TEA cocoyl glutamate and sodium cocoamphoacetate gained good foaming and cleansing scores and were exceptionally mild but they were also the most expensive. Sodium C14-16 olefin sulfonate was good for foam and cleansing and is relatively inexpensive but was an irritant; similar scores were obtained for sodium laureth sulfate and ammonium laureth sulfate.

Not included in the study above was a mixture of sodium dicocamide PEG-15 sulfate with sodium lauroyl lactylate, sold under the name Ceralution F from Condea Vista through S. Black. It is one of the so-called Gemini surfactants, which consist of two surfactant moieties; a hydrophilic group and a hydrophobic chain joined with a spacer, said to offer many benefits to personal care systems based on surfactants, including smaller bubbles, a pleasant, creamy consistency, longer draining times and easier foam generation. Gemini surfactants form stable liquid crystalline gel networks for o/w emulsions that need to withstand high oil contents, extreme pH values or high levels of electrolytes. The bi-layer structure of the Gemini surfactant system makes it compatible with skin ceramides and provides skin barrier properties. Cerulation is said to be compatible with anionic and cationic surfactants, is extremely mild, is effective at levels as low as 0.50% and adds volume and body to hair and a silky smooth feel to skin.

Cream body washes are shower gels that include high levels of emollients or which contain a moisturising emulsion. There are various ways of creating such formulations but stability can be suspect. Worth looking at are a new class of surfactants available from Orafti through Adina Chemicals under the trade name of Inutec. Inutec surfactants are obtained by grafting inulin with hydrophobic chains, resulting in high-performance dispersants and emulsifiers. They stabilise oil droplets and hydrophobic particles against coalescence and flocculation through steric stabilisation. Inulin consists mainly of ß (2-1) fructosyl-fructose links and is described as a linear polyoxyethylene backbone to which fructose moieties are attached. On an industrial scale, inulin is extracted from Cichorium intybus (Chicory) roots. Primary skin irritation, acute ocular irritation and acute oral toxicity tests, sensitisation and mutagenicity studies show the safety of Inutec surfactants. They are biodegradable, do not show any aquatic toxicity, are ethylene oxide free and are derived from a vegetable source. Two products are of particular interest; Inutec H25 is pure inulin and is considered as a totally naturally derived hair and skin conditioner and moisturising agent and Inutec SP1, which is an inulin derivative and is an efficient emulsifier and emulsion stabiliser. In addition to making standard o/w emulsions, Inutec SP1 is ideal for manufacturing stable shower cream formulations.

Formula for Cream Body Wash; provided by Adina Chemicals.

Ingredient	%w/w	Trade Name
Helianthus annuus (Sunflower) seed oil	9.00	
Skin lipid mix	0.10	Questamix H
Ammonium lauryl sulfate (70% Active)	9.00	
Pentaerythrityl tetracaprylate/caprate	1.00	Neoderm PTC
Perfume	0/50	
Aqua (Water)	To 100%	
Inulin lauryl carbamate	0.20	Inutec SP1
Inulin	1.50	Inutec H25
Xanthan gum	0.50	Keltrol T
Acrylates/C10-30 alkyl acrylate crosspolymer	0.70	Carbopol 2020
Preservatives	qs	As required
Cocamidopropyl betaine	3.50	
Sodium hydroxide 10%	qs	To pH 4.7 – 5.2

Surfactants that form stable liquid crystalline gel networks give rise to structured surfactant systems, which have remarkable suspending and dispersing properties. Most surfactants form a G-phase either at ambient or at some higher temperature when mixed with water in certain specific proportions. However such G-phases cannot usually be used as structured suspending systems. Useful quantities of solid render them non-pourable and smaller amounts tend to sediment. The main types of structured system used in practice are based on dispersed lamellar, spherulitic and attenuated lamellar phases. Dispersed lamellar phases are two phase systems in which the surfactant bilayers are arranged as parallel plates to form domains of G-phases which are interspersed with an aqueous phase to form an opaque gel-like system. Spherulitic phases comprise well defined spheroid bodies, usually referred to in as spherulites, in which surfactant bilayers are arranged as concentric shells. The spherulites usually have a diameter in the range 0.1 to 15 microns and are dispersed in an aqueous phase in the manner of a classical emulsion, but interacting to form a structured system. Many structured surfactant systems are intermediate between dispersed lamellar and spherulitic, involving both types of structure. Usually systems having a more spherulitic character are preferred because they tend to have lower viscosity.

Manufacturers are somewhat reluctant to divulge the actual mixtures that provide these properties although further information is available after signing confidentiality disclosure agreements. Rhodia is providing structured surfactant systems under its Miracare trade name. The structured network is described as like layers of onion skin and can hold up to 20% of oils, including mineral oil, vegetable oil and silicone fluids. The system also may be used to suspend exfoliants in body scrubs and lipo-beads in cleansing preparations. The moisturising performance of formulations with this technology was assessed on humans using TEWL and Corneometer studies and the results demonstrate extended moisturising benefit, lasting up to 24 hours in some cases. Structured surfactant formulations provide a novel appearance and sensorial attribute, and true two-in-one moisturising body wash products can now be prepared with proven effect.

As well as leading to improved shower products structured surfactant systems are also used in the latest generation of two-in-one conditioning shampoos. Huntsman has recently advanced the potential application of this technology to shampoos by developing optically clear structured systems that can be made using surfactant,

carbohydrate and water [USP 6,770,612]. The technology provides polymer-free, transparent formulations having excellent suspending power, low freezing point and a wide thermal stability range.

Presentations at Formulate 2004 included a number that described personal cleansing products. They have already been covered in SPC ?.

As well as the surfactant system cleansing products generally contain additives to condition hair or provide skin feel and moisturising properties to skin. The addition of a traditional humectant such as a polyalcohol like glycerine would appear to be contra-indicated because of its water solubility. However a patent [USP 6,183,732] recently granted to Johnson & Johnson claims that when the polyalcohol is present in association with a mixture of at least two polyquaternary compounds, one of which is a cationic copolymer and one of which is an amphoteric copolymer, then deposition of the humectant occurs. A preferred example contains 4% glycerine, 15% sodium laureth sulfate, 0.20% Polyquaternium-7 and 0.10% Polyquaternium-39.

Cleansing wipes and towels continue to grow in popularity. A novel idea patented by Kao Corporation [USP 6,492,307] is a two sided sheet; one side holding a solvent for removing oil-based makeup and the second side holding an aqueous-ethanol composition to remove oily residues from the first cleansing and all water-soluble grime. The composition and structure of the sheet is very important as it has to retain the two different liquids and these are separated by an impermeable barrier.

Cleansing different types of soil by using two-in-one packaging is also the subject of a patent filed by P&G [USP 6,673,755]. The compositions comprise a cleansing phase containing surfactant and water; and an active phase containing a lipophilic carrier and a skin active agent. The cleansing and active phases are physically separated from one another and dispensed as a dual stream that mixes on application. Preferred embodiments are further defined by selected lipophilic carrier rheologies, defined active phase particulates for improved skin feel, and selected chronic skin active agents for use in the active phase.

Not all bathroom products contain water: the following examples of water-free cleansers were kindly supplied by Cornelius Produce Company.

Water-free Cleanser 1

Ingredient	**%w/w**	**Trade Name**
TIPA-laureth sulfate	20.00	Zetesol TP200
Laureth-4	30.00	Multifan CPA
Cocamide DEA	6.00	Purton CFD
Parfum (Fragrance)	1.00	
Helianthus annuus (Sunflower) seed oil	Qs 100	

Water-free Cleanser 2

Ingredient	**%w/w**	**Trade Name**
MIPA-Laureth Sulfate (&) Cocamide DEA (&) Laureth-4	56.00	Zetesol 100
Essential oil	5.00	

Isopropyl palmitate	2.00	
Simmondsia chinensis (Jojoba) seed oil	1.00	
D-Panthenol	0.70	
Glycine soja (soybean) oil	32.30	

The formulations are suggested as starting points for salt or sugar scrubs. Still with water-free formulations Cornelius also provided the following formulations:

Blooming Rice Oil

Ingredient	**%w/w**	**Trade Name**
Oryza Sativa (Rice) bran oil	To 100%	
Oleth-5	3.00	Ritoleth 5
Sodium isostearoyl lactylate	6.50	Pationic ISL
Phenoxyethanol	0.10	
Parfum (Fragrance)	qs	

Blooming Shower Oil

Ingredient	**%w/w**	**Trade Name**
Paraffinum liquidum	To 100%	Light mineral oil
Paraffinum liquidum & Capric/CaprylicTriglyceride & Hydrogenated Styrene/Isoprene Copolymer	40.00	Transgel 110
Oleth-5	7.50	Ritoleth 5
Sodium isostearoyl lactylate	3.50	Pationic ISL
Parfum (Fragrance)	0.70	

The blooming shower oil is described as suitable for people with dry skin who don't want to use aggressive surfactant based products in the shower. This product is a slightly thickened mineral oil with some blooming active which allows for the product to be washed off easily leaving the skin feeling really smooth and moisturised.