nappi



Evonik's portfolio of biosurfactants

WORKHORSES

The role of surfactants in home & personal care

COSMETICS & SURFACTANTS

An in-depth look at chemistries



Household and Personal Products Industry

FEATURES

Soap & The Virus 4 Ricardo Diez, PhD asks, "Are all formulas the same?"

Surfactants in 6 Household, Personal **Care & Institutional Cleansers: Recent** Trends

The role of surfactants in household and personal care. Robert Y. Lochhead, PhD explains how each class works, current issues, recent advances & relevant inventions.

12 **Greener & Better**

Evonik has a new portfolio of biosurfactants that meet the highest standards in sustainability and functionality.

Fear & Lathering 17

In a marketplace awash with pampering attributes, rising concern about coronavirus in the US is shifting the conversation back to cleansing.

22 How Did We Get Here?

Written by Ricardo Diez, PhD, it is an update of a presentation that he made at the IFSCC

27 Just Hit Refresh

This year has been all about clean including advanced shampoo, conditioner and treatments for the scalp.

A Clean Commitment 34

In a pandemic, clean matters more than ever, which explains the gains in fabric care sales.







Why Surfactants Are Essential Ingredients

he COVID-19 pandemic has consumers and fast-moving consumer goods companies rethinking everything. Supply chains are getting revamped, distribution channels reevaluated and finished products reformulated. But for all the changes, strong demand remains for surfactants. According to Fortune Business Insights (FBI) predicts that the escalating need for home care products among the urban population will bolster the healthy growth of the market for years to come. At the same time, increasing consumer consciousness toward personal hygiene owing to the spread of various diseases and viruses will help expand the market. As a result, FBI predicts the global surfactant market will enjoy a CAGR of 4.9% to reach \$60.5 billion by 2027.

Interestingly, the pandemic didn't curtail consumer demand for environmentally-friendly products. Even during lockdowns, shoppers continued to look for effective bio-based formulas that were better for them and the planet. In fact, demand for biobased surfactants is rising faster than the overall market. With that in mind, Evonik has introduced a new range of biosurfactants that are just as effective, yet greener than traditional surfactants. The benefits of RewoFerm are detailed on p. 12 in this eBook.

Also in this issue, long-time household and personal products industry chemist Ricard Diez, PhD, explains the role of surfactants in cosmetics formulations and how cleansers are imperative to keeping consumers safe in a pandemic. Read Soap & The Virus, starting on p. 4. Dr. Diez performs double duty in this eBook with an article on current surfactant trends in personal care which addresses current controversies such as 1,4 dioxane and sulfate-free formulations. Turn to page 22 to learn more.

Of course, no publication devoted to surfactants is complete without input from renowned surfactant industry expert Robert Y. Lochhead. In this issue, Dr. Lochhead details the role of surfactants in personal care and home care formulations, and reviews some of the latest research in biosurfactants. His in-depth article begins on p. 6.

This eBook also features roundup article on two multibillion dollar categories that are driven, in large part, by the efficacy of surfactants. In Just Hit Refresh (p. 27), Melissa Meisel reports on the latest advances in shampoos and conditioners. And in A Clean Commitment (p. 34), we provide an update on how the laundry detergent industry is thriving during the pandemic.

We hope you enjoy this surfactant eBook sponsored by Evonik.

Tom Branna VP/Editorial Director tbranna@rodmanmedia.com



Soap & The Virus Are all formulas the same?

By Ricardo Diez, PhD

E HAVE heard it many times: "Wash your hands with soap, for no less than 20 seconds." We have also heard, read or even watched YouTube videos explaining that soap makes the virus ineffective because it "dissolves" the fatty membrane that surrounds it.

But what kind of soap are we talking about? An Ivory bar made of real soap? Or a Dove bar with no soap? Or a liquid hand soap that has no soap at all, either? Do all of these soaps work the same when confronting the virus? Soap is the original surfactant and the key component of the classic bar. But when we say "liquid hand soap" we normally refer to products that are made with surfactants rather than soap.

This "dissolving" of the fatty membrane comes from the detergent properties that are intrinsic to soap and cleansing surfactants. In fact, detergent comes from the Latin word "detergeo" for cleaning. Therefore, surfactants remove the lipid envelope of viruses the same way they remove the lipids in our skin and hair, or the oily stains in our clothes.

A recently-published paper¹ explains that the action of soaps on the virus involves more than this mechanism of detergency. And this "more" results in the finding that not all "soaps" are equally effective in deactivating the virus. We must indicate that the study was done before the appearance COVID-19. It uses two other corona viruses (H3N2 and H5N3).

HOW IT WORKS

In the paper, the interaction of the viruses with solutions of sodium laureth sulfate (SLES), sodium lauryl sulfate (SLS), and soap (potassium oleate) is investigated using isothermal titration calorimetry. The data reveals that these three surfactants interact differently with the virus resulting in different deactivation effectiveness. Soap showed the best deactivation results, followed by SLS. The least efficient was SLES.

Guided by the calorimetric results, the paper identifies an additional mechanism of interaction besides detergency. It involves electrostatic interactions between the surfactant and the virus'



characteristic spikes or corona. The spikes are proteins that mediate the entry into host cells. The strength of the electrostatic interaction affects the efficacy of the products.

Reading the paper, it became difficult not to relate to the similarity of these findings with the two mechanisms of interaction of surfactants with skin and even hair. During the cleansing process, surfactants interact with the lipids and with the proteins in the corneocytes of the stratum corneum. The removal of lipids results in skin or hair dryness, while the interaction with the corneocytes yields skin irritation.

Therefore, and from this perspective, there should be no surprise that what makes soap and SLS more irritating to the skin than other surfactants; i.e., their strong interaction with corneocytes, is what provides effectiveness in deactivating the spikes of the virus.

We can assure you that surfactants have been forming micelles in water well before micellar cleansers and micellar shampoos arrived on the market. In fact, all you need to make a micellar solution, as per scientific definition, is to dissolve in water with as little as 0.1% surfactant. The individual molecules of surfactant will assemble into these physical structures known as micelles. At low concentrations, the micelles will be spherical, about 3nm in diameter. We could visualize the radii of the sphere as the surfactant molecules. And they do this themselves. Therefore, no complicated development research projects are required to make micelles.

The surface of the micelles is electrically charged. This charge, called the Zeta Potential (ZP), can be measured experimentally and even theoretically with quantum chemistry, and it is generated by the charge of each surfactant molecule. It just so happens that soap and SLS have large ZP values. This results in strong

interaction with proteins. In our skin, the proteins are in the corneocytes, and in the virus in the spikes. On the other hand, SLES has lower ZP and this makes it "milder" to corneocytes, and as the paper shows, it was also less effective against the virus.

The extrapolation of the paper's findings, in terms of the electrostatic interaction with the virus, suggest that the so-called sulfate-free surfactants would be less efficient against the virus because of their lower ZP.

There is an issue that the paper did not address and that may have helped to ascertain how much of the superior effectiveness of soap comes from the molecule itself; i.e, the carboxylic end group; and how much from the intrinsic alkalinity of soap solutions, with a pH near 10. This could have been achieved by testing a solution of SLS with the pH adjusted to 10.

Regardless, it is evident from the paper that good old soap remains a very effective cleanser. The specific soap used in the test was potassium oleate but soaps made with different fatty acids neutralized with an inorganic alkali would have done well in the test, too.

Do not forget that the Centers for Disease Control advises that washing your hands with plain soap and water is one of the best ways to prevent the spread of infections and decrease the risk of getting sick. We will assume that plain soap means exactly that: soap.

References:

 Kawahara T, Akiba I, Sakou M, Sakaguchi T, Taniguchi H (2018) Inactivation of human and avian influenza viruses by potassium oleate of natural soap component through exothermic interaction. PLoS ONE 13(9): e0204908



Surfactants in Household, Personal Care & Institutional Cleansers: Recent Trends

ROBERT Y. LOCHHEAD, PHD EXPLAINS HOW EACH CLASS WORKS, CURRENT ISSUES, RECENT ADVANCES AND RELEVANT INVENTIONS.

By Robert Lochhead, PhD FRSC

aundry detergents, household and institutional cleansers, shampoos and body washes are the highest volume products in the Happi sector, and personal care is the most lucrative segment.¹ Next to water, surfactants are the predominant materials used in this sector and they function to clean and to confer stability on emulsions and dispersions. Soap has been used for millennia^{2,3,4} and the basics of detergents has been known for more than a century. The term "surfactant" is an abbreviation for "surface active agent," signifying that these substances confer special properties on surfaces and interfaces.

It is beyond the scope of this brief chapter to discuss the physico-chemical mechanisms of surfactants, a subject that has been discussed elsewhere.⁵

NEW LOW ENERGY SURFACES NEED BETTER & FASTER WETTING

In cleaning operations, the rate of achieving a low surface tension is important, and the parameters of interest are dynamic surface tension⁶ and dynamic contact angle, especially for innovative materials with better hydrophobic surfaces. During cleaning, penetration into a fabric or porous surface is favored by a high dynamic surface tension and a low dynamic solid/liquid interfacial tension.⁷

Surfactant Cleaning Mechanisms: Both surfactant adsorption at interfaces and micellization are fundamental to the function of cleaning. The main function of each of these products is to remove dirt, grime, oils and waxes, and unwanted particulate matter from human and/or inanimate surfaces.

Surfactants remove oils from skin and hair surfaces by several mechanisms. There are four main mechanisms for removing oils. These are (a) roll-up, (b) emulsification, (c) penetration and (d) solubilization.⁸

CLEANSING ALONE IS NOT ENOUGH

Today's consumer expects products that cleanse, condition, facilitate cleansing, remove odors and fragrance the body with a pleasant lingering aroma. Moreover, awareness of the importance of the microbiome is forcing a rethink of whether cleaners should be designed for nonselective eradication of all microorganisms on our surfaces.⁹

For example, personal cleanliness is often associated with the absence of a sweaty odor, which arises from the interaction of bacteria with apocrine gland secretions,^{10,11,12} whereas sebum is the semifluid secretion of the sebaceous glands of mammals, consisting chiefly of fat, keratin and cellular material.¹³ Sebum serves to protect and lubricate skin and hair. Sebaceous secretions favor growth of facultative anaerobes such as *Propionibacterium acnes*,^{14,15} which releases free fatty acids onto the skin,^{16,17} contributing to the acidic pH of the skin surface,^{18,19} and inhibits the growth of many common pathogens such as *Staphylococcus aureus* and *Streptococcus pyogenes*.²⁰ Consequently, the presence of sebum and the symbiotic microorganisms that it supports may be beneficial to the health of the skin.

Whereas laundry and dishwash detergents should ideally remove all oils, sebum and particulates, cleansers for skin and hair should be designed to remove the particulates and leave desirable sebum on the surface.

The trend toward naturally-derived products is changing ingredients and supply chains. The straightforward way to pivot to biosurfactants is merely to convert existing surfactants to bio-based carbon and to ascertain the bio-based content by radiocarbon dating,^{21,22} (ASTM D6866).²³

There are a number of new bio-based surfactants. Lower carbon footprints can be achieved by using bio-derived surfactants, such as alkyl polyglucosides, in products for lower energy use during cleaning.²⁴ Acyl amino acids are biosurfactants used for cleaning in detergents, emulsifying in food products and shampoos, soaps, moisturizing agents in personal care. For instance, acyl glycinate is a personal care surfactant that provides cleaning and skin benefits. Evonik has developed a process using genetically modified cells to economically produce essentially pure acyl glycinate.²⁴

Compared to the conventional Schotten Bauman process, a new lower cost, low-energy process for synthesizing N-acyl-amino acid surfactants produces purer acylamino acids at higher actives which reduces the energy of transportation.²⁵ The purity enables formulators to finely tune the thickening of shampoo compositions. Moreover, the acylamino acids act as solubilizers in aqueous solution, and this facilitates their betainization.

Rhamnolipids are emerging as mild surfactants that are "biobased, biodegradable and sustainable," according to Hans Henning Wenk, VP of R&D Care solutions at Evonik.²⁶ Rhamnolipids are composed of one or two rhamnose units covalently attached to one or two β – hydroxy fatty acids (see image at right).

Rhamnolipids are effective foaming cleansers that are relatively impervious to water hardness, are mild on the skin, and have a low carbon footprint. Various carbon chain lengths and different numbers of rhamnose units offer choice to the formulator. Rhamnolipids are produced naturally by *Pseudomonas aerginosa* in oil-rich



Figure 1: Generalized structure of rhamnolipids.

media; the rhamnolipids emulsify the oil to enable the microorganism to use it as a food source. Rather than using the pathogenic strain, *Pseudomonas aerginosa*, Evonik's patents describe the biosynthesis of rhamnolipids using genetically-modified strains of the well-known GRAS microorganism *Pseudomonas putida*,^{27,28} with a sugar feedstock rather than unsustainably harvested tropical oils.^{29,30}

Dialkylamido derivatives of rhamnolipids provide fragrance retention on hair, and shine, combability and shapeability.³¹ Alkyl esters of rhamnolipids are nonionic surfactants that leave the skin feeling soft and smooth, especially after shaving.³²

Sophorolipids are biosurfactants synthesized by yeasts. They are used in hard surface cleaning; for example, for cleaning oil-soiled surfaces in off-shore locations, effective cleaners contain sophorolipids (for example, Evonik's Rewoform surfactants) with biodegradable sorbitan esters and conventional betaines, nonionic alkyl ethoxylates, alkyl polyglucosides or lauryl ether sulfates.³³

Hard surface cleaners should be designed to "wash away" oils, grime and particulates. Many current hard surface cleaners leave residual films of bactericidal surfactants or disinfectants, but such residuals are being de-emphasized due to concerns that they could stimulate the emergence of tolerant or resistant pathogens.³⁴ Synthetic cationic surfactants and biosurfactants have been proposed as microbiocides against bacteria, lipid-coated viruses and bio-films. In the US, antimicrobial claims would cause these products to be regarded as over-the-counter drugs by the FDA, and/or require them to be registered as disinfectants by the EPA.

Chelants (termed "builders" in the art of detergents) are added to detergent formulations to sequester the hard water ions, to ensure adequate concentrations of surfactant, and prevent deposition of metal salts. Traditionally, soluble inorganic phosphates or polyphosphates were used as for this purpose, but there are efforts to reduce or eliminate sources of phosphorus due to concerns of eutrophication of waterways. They are sometimes replaced by polyacrylates which prevent the deposition of calcium carbonate, calcium oxalate, calcium sulphate, barium sulphate and other low solubility salts.³⁵ Maleic acid tetrapolymers have been advanced as efficient antiscalants.³⁶

Environmentally-friendly, low temperature dishwashing are in vogue. To conserve energy in institutional dishwashing, lower temperature washes are desired. This has led to searches for better non-phosphate, more environmentally friendly chelators. Promising chelators are aminocarboxylates, such as the trisodium salt of methylglycinediacetic acid.³⁷ Combinations of aminocarboxylates and polyacrylates provide synergistic chelation that prevents scale during low-temperature institutional dishwashing.³⁸

Transparent Builder Compositions: Aminocarboxylates are hygroscopic and this creates storage challenges for solid compositions. Moreover, if aminocarboxylates are formulated as concentrated solutions, they crystallize and separate which detracts from their visual attractiveness, especially for unit dosage products in clear capsules. Resistance to such crystallization can be formulated by combining the aminocarboxylate with another acid, such as citric or acetic acids, in compositions at pH 8 or below.³⁹ It is postulated that, crystallization is prevented by molecular interaction between the citric acid and aminocarboxylate.

However, methylglycineacetate may damage decorative patterns or lettering on glassware, and this high-cost chelator is suited only to high-end applications. To remedy these shortcomings, alternative aminocarboxylates have been postulated. Examples are trisodium 2,2'-((l-carboxypropan-2-yl)azanediyl)diacetate, tetrasodium 2,2'-((2,2-dimethylpropane-1,3-diyl)bis (azanediyl))disuccinate, tetrasodium 2,2', 2",2",2"-((cyclohexane-1,4diylbis(methylene))bis(azanetriyl))tetraacetate, tetrasodium 2,2'-((cyclohexane-1,4-diylbis(methylene))bis (azanediyl))disuccinic acid, and trisodium (1-carboxypropan-2-yl)aspartate.⁴⁰

Preventing Copper Deposition on Hair: One interesting example of synergistic chelation is the use of histidine and ethylenediamine N,N' disuccinic acid to prevent deposition of copper on hair from water used during shampooing, conditioning, and/ or leave-on treatments.⁴¹ Copper deposition on hair can facilitate Redox reactions that can damage the hair and alter the effect of hair coloring treatments. Histidine preferentially chelates copper rather than calcium, and this makes it useful to prevent copper deposition on hair from hard water.

Surfactant Micelles Exist in a Wide Variety of Shapes and Sizes: The shapes of micelles are determined by the shapes and packing of their constituent surfactants. Packing Factor theory relates the shapes of the molecules with the resulting micelle shape⁴² (see image, top right). The packing factor of a surfactant molecule is the volume of the tail group divided by the volume of the cylinder subtended by the head group to the length of the tail group. The fraction, v/al, is known as the packing factor.

Conical-shaped surfactant molecules have a packing factor of 1/3, and they pack into spherical-shaped micelles. Higher surfactant or salt concentrations, and/or mixing with cosurfactant,

Effect of Molecular Structure on Micelle Shape and Size



Packing factor = v/al_c

Figure 2. The packing factor of a surfactant molecule is the volume of the tail group divided by the volume of the cylinder subtended by the head group to the length of the tail group. The fraction, v/al, is known as the packing factor.

causes the molecules to change toward a more cylindrical shape on average, and this causes the micelle structures to be rod-like or worm-like, with packing factors around 1/2. Lamellar layers result when the packing factor is 1. The same surfactant can adopt different micelle shapes depending upon, for example, the concentration of surfactant, the pH of the solution, or the presence of salt ions.⁴³

Above a certain concentration (the critical overlap concentration, C*) the worm-like micelles entangle and form micellar networks. Shampoo and surfactant gel formulators often rely upon an entangled micelle structure to give their product the viscosity and rheology desired by consumers.

At higher concentrations, the mutual repulsion of rod-like micelles causes them to align in hexagonally-packed arrays; a structure that is known as hexagonal lyotropic liquid crystal phase or



Figure 3. Ionic surfactant micelles change shape as a function of ionic strength and surfactant concentration.

LIQUID CRYSTALLINE PHASES



Figure 4. Increase in surfactant concentration causes micelles to transition from spheres to rods to hexagonal phase to lamellar phase to inverse hexagonal phase to inverse micelles.

hexagonal gel phase. Hexagonal phases are often clear ringing gels. Gel phases are useful structurants for surfactant-based formulations. Further increase in the packing factor leads to the planar surfactant bilayers of lamellar phase, and further increases favor the formation of inverse phases which feature micelles with aqueous cores. Slight changes in such bilayers result in a rich, and useful hierarchy of lamellar phases including vesicles, liposomes^{44,45,46} and gel phases. Vesicle and liposome structures are characteristic of conditioners.⁴⁷ Lamellar phases are also useful for the stabilization of emulsions.^{48,49,50,51}

Hydrotropes: The trend toward higher surfactant actives concentrations has accelerated in recent years, driven by the desire to reduce plastic packaging and carbon footprint. Simple micelles with rapid micellization/demicellization kinetics are sought for optimal laundry cleaning but they often have higher–order amphipathic structures. Upon dilution they can deposit rubbery particles of cubic, hexagonal or lamellar phases on fabrics. Apart from the undesirable aesthetics, the gel particles contain surfactant that cannot participate in the cleaning process, lowering the efficiency of cleaning. Hydrotropes accelerate the transition to simple micelles upon dilution. Hydrotropes reside at the periphery of surfactant micelles, forcing the surfactants' hydrophilic groups apart, and thereby increasing the curvature of the micelle surface. In essence, hydrotropes decrease the packing factor and enable functional, efficient concentrated detergents.⁵²

Like hydrotropes, many preservatives and fragrances selectively partition into the micelle rather than into the cell membranes of microbial contaminants, compromising preservation and olfactory perception.⁵³ This challenge has been overcome, in part, by including 2-methyl-1,3- propanediol as a sole preservative for aqueous surfactant compositions at neutral or slightly alkaline pH.⁵⁴

Micellar Water: The term "micellar water" was introduced to describe efficient, mild facial cleansers. The term "micellar" in

these products cannot signify a technological breakthrough, because the term "micelles" had been used and the mechanism of surfactant cleaning had been known for more than half a century before the introduction of this product category. Micellar cleansers are formulated with mild surfactants at low surfactant concentration, at the natural pH of skin.⁵⁵ A typical micellar water makeup remover contains PEG-6 caprylic/capric glycerides.⁵⁶ One such material, Tegosoft GMC 6³⁷ is described as "a hydrophilic emollient, soluble in aqueous surfactant solutions, which solubilizes oils and oil-soluble ingredients. It results in surfactant preparations with good foamability and moisturizing, superfatting effects with solubilization and emulsification properties. PEG-6 caprylic/caprate glycerides is a hydrophilic linker, a term which is synonymous with "hydrotrope."⁵⁸

Other predominant ingredients in micellar water are glycerin, propylene glycol and Poloxamer 181. The glycols and/or a poloxamer help to solubilize facial oils and waxes. The typical surfactants that are used have CMCs below 1%. Micellar waters are leave-on products and it is important that they are not sticky but impart a silky skin after-feel. This is achieved by including xylitylglucoside, anhydroxylitol and xylitol to moisturize the skin, improve water circulation and reduce water loss.⁵⁹ Cotton swabs finish the cleansing by removing the soil by capillary action.



For some applications, like automatic dishwashing, foam is not desirable.

Foam: Foaming is a cue to the consumer that the product is working, and it also floats away hydrophobic particles.⁶⁰ Surfactants facilitate foaming of liquids.⁶¹ Foams and foaming comprise three distinct processes, namely foam initiation and formation, foam stability, and foam drainage and rupture.^{62,63,64}

Self-foaming facial cleansers convey light, but efficient cleansing actions that are mild to the skin.⁶⁵ The influence of the surfactant packing factor on foaming is demonstrated by self-foaming compositions with glycerin content approaching 50%, which require surfactants having very low packing factors, below 0.25.⁶⁶

Defoaming: While foaming is desired in applications such as hand dishwashing and shampooing, there are other applications for which foam must be minimized. These include hard surface cleaners, machine dishwashing, and vertical axis washing machines. Oils, hydrophobic particles and sebum induce defoaming by introducing Marangoni instability. When the oil cannot spread, it can still cause defoaming if the droplet is capable of bridging the two faces of a foam film.⁶⁷ Some nonionic surfactants (typically Poloxamer block copolymer) have cloud points higher than the temperature of storage but lower than the wash temperature and they can be used as stimuli-responsive defoamers.⁶⁸

Oily soil acts as a foam suppressor and, since foam is a cue to the consumer that the detergent is working, there is a need to extend the duration of foam during washing. One way to remove the oil during washing is to include fatty acid transforming enzymes, such as oleate hydratases, in the detergent formula.⁶⁹

Foaming cleansers tend to remove the skin's natural oil barrier, and this can lead to dry, chapped skin. The paradox of including emollient oils in foaming cleansers has been tackled by suspending the oil droplets with nonionic crosslinked semi-hydrophobic copolymers, and nonionic associative thickeners, with fatty acid soaps.⁷⁰

References

- 1. https://www.alliedmarketresearch.com/surfactant-market
- 2. B. Casselman, At the wording Desk, pp 254-255, Trafford Publishing 2016.
- Jewish News Syndicate, (August 17, 2020), 1,200-year-old soap factory uncovered in southern Israel, Available at https://www.jns.org/1200-year-old-soap-factoryuncovered-in-southern-israel/
- Lochhead, R. Y.; W. J. Hemker; J. Y. Castaneda; D. Garlen; "Novel Cosmetic Emulsions," Cosmetics and Toiletries, 101(11), 125 (1986).
- Lochhead, R.Y., "Basic Physical Sciences for the formulation of cosmetic products", Chapter 3 of K. Sakamoto, R.Y. Lochhead, H. Maibach, Y. Yamashita, "Cosmetic Science and Technology, Scientific Principles and Applications", Elsevier, 2017
- Derrick Anderson, Erik C. Olson, Melissa Martinez-Crowley. Hard surface cleaning compositions with reduced surface tension, U.S. Patent Application 2021/0002586, Jan. 7, 2021, Applicant: Ecolab USA Inc.
- Victor Fuk-Pong Man, Derrick Anderson, Gang Pu, Jimmy Stokes, Kaustav Ghosh. Methods of cleaning and soil release of highly oil absorbing substrates employing optimized extended chain nonionic surfactants. U.S. Patent Application 2021/0047588, Feb. 18, 2021. Ecolab USA Inc.

- Lochhead, R.Y., Shampoo and conditioner science, Chapter 3 of Practical Modern Hair Science, (Trefor Evans and R. Randall Wickett, editors), Allured Press Business Media, 2012.
- Grice, Elizabeth A., and Julia A. Segre. "The Skin Microbione." Nature reviews. Microbiology 9.4 (2011): 244–253. PMC. Web. 6 June 2016.
- 10. Emter R, Natsch A. The sequential action of a dipeptidase and a β -lyase is required for the release of the human body odorant 3-methyl-3-sulfanylhexan-1-ol from a secreted Cys-Gly-(S) conjugate by Corynebacteria. J. Biol. Chem. 2008;283:20645– 20652.
- Decreau RA, Marson CM, Smith KE, Behan JM. Production of malodorous steroids from androsta-5,16-dienes and androsta-4,16-dienes by Corynebacteria and other human axillary bacteria. J. Steroid Biochem. Mol. Biol. 2003; 87:327–336.
- Martin A, et al. A functional ABCC11 allele is essential in the biochemical formation of human axillary odor. J. Invest. Dermatol.2010;130:529–540.
- The American Heritage Science Dictionary. Retrieved June 06, 2016 from Dictionary.com websitehttp://www.dictionary.com/browse/sebum
- Marples M. The Ecology of the Human Skin. Bannerstone House, Springfield, Illinois: Charles C Thomas; 1965.
- Leeming JP, Holland KT, Cunliffe WJ. The microbial ecology of pilosebaceous units isolated from human skin. J. Gen. Microbiol. 1984;130:803–807.
- Ingham E, Holland KT, Gowland G, Cunliffe WJ. Partial purification and characterization of lipase (EC 3.1.1.3) from Propionibacterium acnes. J. Gen. Microbiol. 1981;124:393–401.
- Marples RR, Downing DT, Kligman AM. Control of free fatty acids in human surface lipids by Corynebacterium acnes. J. Invest. Dermatol. 1971; 56:127–131.
- Roth RR, James WD. Microbial ecology of the skin. Annu. Rev. Microbiol. 1988;42:441–464.
- 19. Elias PM. The skin barrier as an innate immune element. Semin. Immunopathol.
- Aly R, Shirley C, Cunico B, Maibach HI. Effect of prolonged occlusion on the microbial flora, pH, carbon dioxide and transepidermal water loss on human skin. J. Invest. Dermatol.1978;71:378–381.
- Thorsten Bastigkeit, Tyler Mikkelsen, Daniel S. Wood, Daniel L. Carter, Pamela Lam, Eco-friendly laundry detergent compositions comprising natural essence, US Patent 7,648,953, Jan.19,2010, Assignce: The Dial Corporation.
- Wei Sun, Liquid detergent compositions that include a mixture of ecologically-responsible surfactants, US 2021/0054305, Feb.25,2021. Assignee: Henkel IP & Holding GmbH.
- 23. ASTM. https://www.astm.org/Standards/D6866.htm
- 24. Liv Reinecke, Steffen Schaffer, Katrin Grammann, Maik Olfert, Nicole Decker, Nils Arto, Hans-Georg Hennemann. Byosynthetic production of acyl amino acids, US Patent Application 2017 /0130248, May 11, 2017. Assignee: Evonik Degussa.
- Stefan Julian Liebig, Dominik Schuch, Jan Marian von Hof, Kathrin Daniela Brandt, Maximilian Vogt, Hans Henning Wenk, Method for producing surfactants, US Patent Application 2019/0135734, May 9, 2019, Assignee: Evonik Degussa GmbH.
- Craig Bettenhausen, Rhamnolipids rise as a green surfactant, C&E News, June 13, 2020, Volume 98, Issue 23
- Oliver Thum, Steffen Schaffer, Christoph Schorsch, Mirja Wessel, Cells and method for producing rhamnolipids using alternative glucose transporters, US Patent Application 2019/0233856, Aug. 1, 2019. Assignce Evonik Goldschmidt GMBH
- Schaffer, Steffen; Wessel, Mirja; Thiessenhusen, Anja; Stein, Nadine. Cells and methods for producing rhamnolipids, US Patent 9,580,720, February 28, 2017. Applicant: Evonik Goldschmidt GMBH.

- Schaffer, Steffen Thiessenhusen, Anja, Zellen und Stein, Nadine. Cells and method for producing rhamnolipids, WO 2012013554, Anmelder Evonik Goldschmidt GMBH.
- Thomas Haas, Thomas Biilter, Stefan Buchholz, Simon Beck, Rhamnolipid synthesis, US Patent Application 2018/0066297, Mar. 8, 2018. Applicant: Evonik Goldschmidt GMBH
- 31. Xin Lu, Sandra Nattland, Monica Desiree van Logchem, ; Hans Henning Wenk, Fabien Cabirol, Verena Dahl, Ralph Scheuermann, Kathrin Daniels Brandt, Jochen Kleinen, Rhamnolipid amides for hair scent. US Patent Application 2019/0040095, Feb. 7,2019. Assignce Evonik Goldschmidt GMBH
- 32. Xin Lu, Sandra Nattland, Monica Desiree van Logchem, Hans Henning Wenk, Fabien Cabirol, Verena Dahl, Ralph Scheuermann, Kathrin Daniela Brandt, Jochen Kleinen, Rhamnolipid esters as nonionic surfactants for cosmetic use, US 2019/0256542, Aug. 22, 2019, Assignce Evonik Goldschmidt GMBH.
- 33. Zheng Xue, Andras Nagy, Dennis Parrish, Sam Christy, Jennifer Goodyear, Jeff Davidson. Biodegradable cleaning composition, US 2020/0199492 Jun. 25, 2020, Assignce Evonik Goldschmidt GMBH
- S. Levy, Antibacterial household products: Cause for Concern, Emerging Infectious Diseases, Vol 7, No 3, Supplement, June 2001.
- Acumer 1000 scale inhibitor, https://aniq.org.mx/pqta/pdf/Respaldo/ACUM-ER%201000%20(HT).pdf
- K.A. Rightmire, C.M. Silvernail, Detergent composition containing a tetrapolymer, US Patent Application 2021/0040419, Feb 11, 2021. Applicant Ecolab USA.
- BASF, First things first: clean dishes, Trilom M, https://www.homecare-and-i-and-i. basf.com/solutions/i-i/food-service-and-kitchen-hygiene/first-things-first-cleandishes
- 38. Erin Dahlquist Howlett, Carter Martin Silvernail, Steven E. Lentsch, Terrence P. Everson, Phosphorus free low temperature ware wash detergent for reducing scale build-up, US Patent Application 2021/0032575 Al, Feb. 4, 2021, Applicant: Ecolab USA Inc.
- H.J.M. Arlabosse, O.C.TP. Beers, R.J.Moll. Detergent Solid Composition comprising aminopoylycarboxylate and organic acid. US Patent Application 2021/0040417, US Patent Application 2021/0040418 Feb 11, 2021, Applicant: Conpoco d/b/a/ Unilever.
- 40. Shawn Marie Dougherty, Rong Xu, Jeffrey Michael Clauson, Brendan Patrick Abolins, Kenneth Flint, Mounir Izallalen, Nicholas M. Martyak, Ryan M. Thayer, Aminocarboxylate chelating agents and compositions containing them. US Patent Application 2021/0047590, Feb. 18, 2021, Assignee: Eastman Chemical Company.
- 41. J. Marsh, C. Kelly, Method of inhibiting copper deposition on hair, US Patent Application 2021/022977, Jan 28, 2021, Applicant; The Procter & Gamble Company.
- 42. J. N. Israelachvili , D. J. Mitchell and B. W. Ninham, Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers, J. Chem. Soc., Faraday Trans. 2, 72, 1525-1568, (1976)
- S. J. Candau, A. Khatory, F. Lequeux, F Kern, Rheological behaviour of wormlike micelles: Effect of salt content, Journal de Physique IV, 03, C1, 197-209 (1993).
- 44. Bangham, A. D.; Horne, R. W., "Negative Staining of Phospholipids and Their Structural Modification by Surface-Active Agents As Observed in the Electron Microscope." Journal of Molecular Biology 8 (5): 660–668, (1964).
- Horne, R. W.; Bangham, A. D.; Whittaker, V. P. (1963). "Negatively Stained Lipoprotein Membranes." Nature 200, 1340, (4913).
- Bangham, A. D.; Horne, R. W.; Glauert, A. M.; Dingle, J. T.; Lucy, J. A. (1962). "Action of saponin on biological cell membranes." Nature 196: 952–955.

- Michael James Cooke, Thuy-Anh Pham, Andrew Malcolm Murray, Conditioning shampoo comprising an aqueous conditioning gel phase in the form of vesicles, US Patent Application US20110243870 A1, Oct 6, 2011.
- Friberg, S.E., Liquid crystalline phases in emulsions, Journal of Colloid and Interface Science, Volume 37, Issue 2, October 1971, Pages 291-295.
- Friberg, S.E., Emulsion Stability, Emulsions A Fundamental and Practical Approach, Volume 363 of the series NATO ASI Series pp 1-24.
- Friberg, S.E., Concepcion. Solans, Surfactant association structures and the stability of emulsions and foams, Langmuir, 1986, 2 (2), pp 121–126.
- Friberg, S.E., Micelles, microemulsions, liquid crystals, and the structure of stratum corneum lipids, J Soc Cosmet Chem, 1990, 41, 155-171
- Friberg, S. E; Lochhead, R.Y.; Blute, I.; Waernheim, T: "Hydrotropes –Performance Chemicals;" J. Dispersion Sci. Tech.; p 243, Vol 25 (3).; 2004.
- Al-Bawab, A.; Bozeya, A.; Friberg, S.E. and Aiken, P.A., Geranyl Acetate Emulsions: Surfactant Association Structures and Stability, Journal of Dispersion Science and Technology, 31:606–610, (2010).
- Jiinichen, J.; Petersen, W.; Microbiologically stable surfactant-containing, formulation, U.S. Patent Application 2019/0254942, Aug. 22, 2019, Assigned to Evonik Degussa GmbH.
- https://www.cosmeticsbusiness.com/news/article_page/Surfactants_for_trending_ bathroom_products/115374
- 56. https://www.bioderma.co.id/en/our-products/sensibio/h2o
- 57. https://www.ulprospector.com/en/na/PersonalCare/Detail/1483/52179/TEGO SOFT-GMC-6?st=1&sl=101261991&crit=a2V5d29yZDpbVEVHT1NPRITCriB HTUMgNl0%3d&ss=2&k=TEGOSOFT%c2%ae|GMC|6&t=TEGOSOFT%c2 %ae+GMC+6
- Chu, J. et al, Lecithin-linker formulations for self-emulsifying delivery of pharmaceuticals, International J. Of Pharmaceutics, 471, 92-102, (2014)
- https://www.seppic.com/sites/seppic/files/2018/04/05/eu07382-on-the-go-moisturizing-body-fluid-soft-and-powdery-touch-complete-gb.pdf
- Seher, A.,; Ahmed, N.; Jameson, G.J.; Collection of hydrophobic particles in the froth phase, Int. J. Miner. Process. 64, 101–122, (2002).
- Pugh, R. J. Foams and Foaming. In Handbook of Applied Colloid and Surface Chemistry; Holmberg, K., Ed.; John Wiley & Sons: New York, 2001
- 62. Mysels, K.J.; Soap Films: Studies of their thinning, Pergamon Press: Oxford (1959).
- 63. Garrett, P.R.; The science of defoaming, CRC Press, 2014.
- 64. Zhang, H., a; Miller, C.A., a, Garrett, P.R., b and Raney, K.H., Mechanism for defoaming by oils and calcium soap in aqueous systems, Journal of Colloid and Interface Science 263 (2003) 633–644
- Stebbins, N.D.; Hara, R.; Halpern Chirch, S.; Perfluoro-free self-foaming facial cleanser composition, US Patent Applications 2021/0030652, and 2021/0030659, Feb.4, 2021. Assignee: L'Oréal.
- Yang, L.; Tsaur, S.L.; Hermanson, K.D.; Low viscosity, high polyol self-foaming composition, US Patent Application 2020/0383889, Dec. 10, 2020, Assignee: Conopco, Inc., d/b/a Unilever.
- 67. Garrett, P.R.; J. Colloid Interface Sci. 76 (1980) 587.
- 68. BASF, Pluronic 31R1, https://hcii.basf.us/products/pluronic-31r1/
- Lant, N.J.; Bettiol, J.P.; Gonzales, D.A.; Detergent composition, US Patent Application 2021/0054311, Feb.25, 2021, Applicant: The Procter & Gamble Company
- Qu, X.; Cho, K.H.; Figura, B.D.; Zhang. Y. Foaming cleanser compositions containing a non-polar oil and amphiphilic polymer, US Patent Application 2021/0038494, Feb. 11, 2021. Applicant: Lubrizol Advanced Materials, Inc.



Greener & Better

EVONIK HAS A NEW PORTFOLIO OF BIOSURFACTANTS THAT MEET THE HIGHEST STANDARDS IN SUSTAINABILITY AND FUNCTIONALITY.

Dr. Hans Henning Wenk, Evonik

or the past century, the cleansing properties of virtually all household cleaning and cosmetic products have been obtained from surfactants derived from petrochemical sources. In response to shifting consumer demand toward sustainable products, this fast-growing \$40 billion global market for surfactants is now undergoing a rapid transition toward green surfactants that are fully biodegradable, minimize CO2 emissions and are not harmful to aquatic or other natural organisms.

However early generations of bio-based surfactants developed since 2000 have faced several challenges relating to raw material sourcing and manufacturing that constrict their green credentials. Most of all, there have been few, if any, bio-based surfactants that have been able to generate the cleaning and foam-generating functional properties of traditional raw materials. To address these unmet market needs, Evonik, one of the world leaders in specialty chemicals and a market innovator for green biosurfactants used with household cleaning products, has developed a new portfolio of biosurfactants that meet the highest standards in sustainability and functionality.

AN OVERVIEW OF SURFACTANTS

Surfactants are amphiphilic molecules with surface tension properties that enable the efficient breakdown of the interface between water and other particles. The molecules feature hydrophobic (water-repelling) and hydrophilic (water-loving) parts that naturally bond with each other to form spherical micelles. Each of these parts work in unison, with the hydrophobic tail being attracted to substances such as oil or dirt while the hydrophilic head then draws these particles toward the micelle's core.

This physico-chemical reaction, followed by the rapid dissolution of such particles in water, makes surfactants an attractive active ingredient for use with a range of personal care and cleaning applications. In prod-



Figure 1: A surfactant molecule highlighting its hydrophilic and hydrophobic (lipophilic) elements

ucts such as dishwashing detergents, surfactants can account for up to around 30% of total content volume. Their functional effectiveness plays a major role in determining rates of brand preference among consumers. Accordingly, the global market for surfactants is highly competitive. The market was valued at \$40 billion in 2020 and is expected to increase to \$52 billion by 2025 for a CAGR of 4.5%.¹

The first generation of synthetic surfactants were known as branched alkylbenzene sulfonates (BAS), which were used from the 1930s until they were phased out across most international markets in the 1960s. Within most global regions and for most applications, BAS was replaced by another anionic class of surfactants known as linear alkylbenzene sulfonates (LAS) which has superior biodegradability properties.

Extracted from benzene (crude oil), LAS surfactants are legally required in most nations to be degradable within four weeks. While the overwhelming majority of LAS can be removed from the water supply during initial processing at sewage treatment plants, studies indicate that higher concentrations of LAS can be toxic to certain aquatic and soilbased organisms such as bacteria, algae, fish and crustaceans.² Furthermore, petrochemical-derived LAS can contribute greenhouse gas emissions of 2.36 kg CO2 eq / kg LAS until its End-of-Life (EoL).³

THE MARKET SHIFT TO GREEN SURFACTANTS

Increasingly, global demand for surfactants used in household and personal care products is being determined not only by the functional performance of the active ingredient, but also by its sustainability as consumers and regulatory agencies seek more environmentally-friendly solutions. This demand for sustainable cleaning products has given rise to a new era of bio-based surfactants that are based on biological raw materials. The annual worldwide market for bio-based surfactants (partially bio-based surfactants, fully bio-based surfactants and biosurfactants, which will be detailed here) was estimated to be \$5.52 billion in 2022, with a CAGR of 5.6% from 2017 to 2022.⁴

There are three separate classes of bio-based surfactants. First are partially bio-based surfactants, where fatty alcohols and acids are derived from the natural fats and oils from natural sources including soya, palm and palm kernel, rapeseed, sunflower, tallow and coconut. Examples of partially bio-based surfactants include alkyl ether sulfates and coconut-oil-derived cocamidopropyl betaine (CAPB). However, most of the oils used to create these surfactants are sourced from tropical regions, where it can be challenging to obtain certifications that confirm the use of sustainable practices for harvesting, or the use of non-exploitive hiring practices for local workers and communities. In addition to the use of hazardous raw materials during harvesting, further processing is typically required to obtain the necessary functionality for their use with most personal and home care applications. These additional processing steps can involve the use of petrochemical-based substances or moieties that are also less sustainable.

The second category are fully bio-based surfactants such as alkylpolyglycosides (APGs) which are plant-based but still manufactured by a chemical process. Like partially bio-based surfactants, they can be derived from tropical oils and involve the use of hazardous raw materials or processes. Certain functionality gaps, such as being less gentle to the skin, may also affect the performance and consumer preference of such surfactants.



Figure 2: The market shift for surfactants derived from petrochemicals to green biosurfactants



Figure 3: Evonik manufacturing and supply chain process for its biosurfactants

The third, and most recent category of surfactants are known as biosurfactants. These 100% natural surfactants are excreted by an organism during biological synthesis. Companies such as Evonik can utilize established fermentation-based processes to create biosurfactants from oils, sugars or a combination of the two.

Biosurfactants are the first class of surfactant that are not only environmentally friendly, but capable of delivering rates of functionality that are equivalent, or even superior to, traditional petrochemical-based surfactants. In addition to coming from renewable, non-tropical raw materials, biosurfactants are gentle on the skin, impervious to hard water, possess excellent cleansing and foam cleaning characteristics, are 100% biodegradable and are well tolerated by aquatic organisms.

GREEN BIOSURFACTANTS FOR A RANGE OF APPLICATIONS

Evonik has developed two glycolipid-based platforms of biosurfactants known as sophorolipids and rhamnolipids. This portfolio gives the company significant flexibility to address the specific requirements of a range of personal care and household cleaning applications. Consisting of a carbohydrate moiety linked to fatty acids, Evonik's two glycolipid-based platforms are manufactured at commercial scale at efficiencies that make them attractive for use by companies seeking more sustainable brands that can still attain desired high levels of functionality.

SOPHOROLIPIDS

A select number of yeasts such as *Candida bombicola* can be utilized to produce sophorolipids through raw materials such as sugar and rapeseed oil. Their potential for use as surfactants was first identified in the 1980s; however, the original processes developed for their production were unfeasible for commercial use. During the past decade, however, Evonik's bio-based materials unit that is part of the nutri-

tion & care division, together with other parties including Evonik's long-term innovation center Creavis, sought to develop a new commercially scalable biological production process.

In 2016, this R&D project culminated in the successful commercial launch of Evonik's platform of sophorolipids. Manufactured at the Evonik Fermas facility in Slovakia, an advanced and highly efficient process is utilized for extraction, synthesis and purification (Figure 3). Special yeasts are grown in a bioreactor feeding on plant-based sugars and oils, resulting in the production of the raw sophorolipid material during metabolism. A purification process then separates the microorganism from the sophorolipid material until it is ready for storage and supply.

One active ingredient developed by Evonik that is based upon its sophorolipid platform is REWOFERM[®] SL ONE. This composition features a mix comprising 40% sophorolipid lactones and sophorolipid acid combined with water and 1% free fatty acids and salt to create an amber-colored, low-viscosity aqueous solution.

In hard water, a mixture with REWOFERM[®] SL ONE performed significantly better in grease removal compared to a standard cocamidopropyl betaine (CAPB)-based alternative. Foam production in mixtures



REWOFERM[®] SL ONE in hard water



Figure 5.: Foam production under dirty conditions replacing part of CAPB with REWOFERM® SL ONE

containing REWOFERM[®] SL ONE was also up to 50% higher under dirty conditions compared to the CAPB-based alternative. Compared to CAPB and another common surfactant known as sulfosuccinates, RE-WOFERM[®] SL ONE was found to be the mildest option analyzed in red blood cell (RBC) tests with an L/D value of 1000, supporting its categorization as a non-irritant. In terms of sustainability, it easily met all



DISCOVER THE SOUL AND SCIENCE OF BEAUTY

intoBeauty[®]

Have you already joined us on intoBeauty[®]? From within Evonik's customer portal for the personal care industry, you have access to videos, information and documentation on our products and formulation concepts. After registering and entering intoBeauty[®], you can explore the portal and experience interactive online tools 24/7 on any device. Find out more about the world of your future personal care formulation and visit intobeauty.evonik.com!

.....

www.evonik.com/personal-care

Evonik Personal Care @EvonikPC

@evonikpc



requirements including aerobic degradation, anaerobic biodegradation and low aquatic toxicity to earn the favored EU Ecolabel status.

One of the first companies to sell products containing Evonik's sophorolipids was Ecover, a leading Belgian-based global supplier of organically produced washing and cleaning products.

Various detergents and cleaning products containing Evonik's sophorolipids are now available on supermarket shelves.

RHAMNOLIPIDS

Rhamnolipids consist of one or two rhamnose sugar groups that are attached to one or two hydroxy fatty acid chains. As a biosurfactant, the sugar groups fulfill the hydrophilic function of attracting water while the hydrophobic fatty acids latch onto oils and other substances. Scientists discovered in the 1960s that certain soil-dwelling bacterium from the Pseudomonas family could naturally produce rhamnolipids.

However, it was only following the decoding of the bacteria's genome in 2000 that Evonik was able to develop a fermentation-based manufacturing process that complemented its established commercial capabilities. Evonik's process converts sugars into rhamnolipids via the use of a well-researched bacteria known as *Pseudomonas putida*. Fermentation takes place in bioreactors at room temperature under energy-efficient conditions. No chemical processing or derivatization is required once the substance has been isolated in the fermentation broth. As with Evonik's manufacturing process used for sophorolipids highlighted earlier, further purification is then required to meet the high-quality requirements of use for home and personal care applications.

Evonik's rhamnolipids are completely biodegradable irrespective of the presence of oxygen, and require no tropical oils as feedstock. They are also able to remove oils or dirt as reliably as petrochemical-based synthetic surfactants even in hard water, have exceptional foam-forming properties, and provide a mild, gentle feeling on the skin.

RHEANCE[®] One is one rhamnolipid-based product now available from Evonik within its RHEANCE[®] glycolipid platform for use in rinse-off applications such as facial cleansers, oral care and baby wipes. Available as a low viscosity aqueous solution that is slightly yellow in appearance, it is easily processible and easy to handle in formulations between 1 and 8% in concentration. Foaming and viscosity properties can be easily tuned to address specific formulation requirements by adjusting the pH value.

RHEANCE[®] One is fully biodegradable under both aerobic and anaerobic conditions, with aquatic toxicity levels far lower than CAPB or other common surfactant alternatives. Furthermore, this multifunctional solution features excellent mildness to the skin and mucous membranes and is highly efficient in solubilizing various essential oils, fragrances and flavors. When tested with long-lasting facial and eye makeup, RHEANCE[®] One demonstrated significantly higher makeup removal than common alternatives.

Evonik and Unilever are in a long-term collaboration for the commercial manufacturing and supply of Evonik's rhamnolipids for use in a range of Unilever's green household cleaning products. In 2019,



Figure 6: A Unilever advertisement promoting the 100% biodegradability of Quix hand dishwashing liquids in Chile.

Unilever launched its first ever hand dishwashing liquid product utilizing Evonik's rhamnolipids in Chile under its Quix brand (Figure 6). This launch represented the first time a cleaning product utilizing a rhamnolipid-derived surfactant was commercially used in the world.

The partnership with Evonik was highlighted by Unilever earlier this year as one key pillar of its Clean Future initiative, which seeks to fundamentally change the way in which some of the world's best-known cleaning and laundry products are created, manufactured and packaged. Clean Future is unique in its intent to embed the principles of a circular economy into both packaging and product formulations at the commercial scale of global brands to eliminate or reduce their carbon footprint.

CONTINUED INNOVATION FOR A SUSTAINABLE FUTURE

Evonik will continue to expand its portfolio of biotechnology-derived ingredients to strengthen its position as a leading provider of sustainable solutions that are able to excite both suppliers and consumers of household cleaning and cosmetic products. In parallel, the leading global specialty chemical company remains committed to expanding its commercial manufacturing capabilities to support growing demand for glyocolipid-based surfactants including rhamnolipids and sophorolipids.

Reference Sources

- ResearchandMarkets. Surfactants Market by Type, Application, and Region Global Forecast to 2025. June 30, 2020.
- Ivanković, Tomislav & Hrenović, Jasna. Surfactants in the Environment. Archives of Industrial Hygeine and Toxicology. April 2010.
- Daniel P. Fogliatti, Scott A. Kemppainen, Tom N. Kalnes, Jiqing Fan, and David R. Shonnard. Life Cycle Carbon Footprint of Linear Alkylbenzenesulfonate from Coconut Oil, Palm Kernel Oil, and Petroleum-Based Paraffins. ACS Sustainable Chemistry & Engineering 2014 2 (7), 1828-1834 DOI: 10.1021/sc5001622
- MarketsandMarkets. Biosurfactants Market by Type (Glycolipids (Sophorolipids, Rhamnolipids), Lipopeptides, Phospholipids, Polymeric Biosurfactants), Application (Detergents, Personal Care, Agricultural Chemicals, Food Processing), and Region -Global Forecast to 2022. December 2017.



Fear and Lathering

IN A MARKETPLACE THAT'S AWASH WITH PAMPERING ATTRIBUTES, RISING CONCERN ABOUT CORONAVIRUS IN THE US IS SHIFTING THE CONVERSATION BACK TO ONE OF SOAP'S MOST IMPORTANT ROLES.

By Christine Esposito, Managing Editor

OR THE past year, US consumers have been emptying shelves of disinfectants, wipes, facemasks and even toilet paper amid rising concerns about novel coronavirus CO-VID-19. There's been a similar run on personal cleansers, too. IRI reports that sales of hand sanitizers soared 79.6% in US multi-outlets and liquid hand soap sales rose by 7.5% for four weeks ended Feb. 23, 2020. Yet while hand washing with soap remains a leading mechanism to ward off the spread of the illness—a message promoted by all health organizations and NGOs worldwide—consumers weren't raising the bar, so to speak. Bar soap sales fell 1.5% during that same period, according to IRI.

The bar soap stats are much more the norm for the \$5.1 billion soap category (see chart), which posted a 1.3% sales gain for the 52 weeks ended Jan. 26, 2020. Liquid body wash and liquid hand wash

sales during that time rose 3% and 4.1%, respectively (although unit sales were down for both). Non-deodorant and deodorant bar soap sales declined. Hand sanitizer sales were up a scant 0.8%.

The arrival of COVID-19 came to fore during the height of flu season in the US-a time when messaging about handwashing is typically at its loudest. Health experts have long promoted handwashing with soap as the best weapon to ward off all kinds of viruses and germs, and an outbreak like COVID-19 puts this simple, yet effective practice back in the spotlight.



To mark Global Handwashing Day last year, Dial and Big Brothers Big Sisters of America taught children healthy hygiene habits.

The overall soap category recorded a 1.3% gain to \$5.17 billion with unit sales down 2.6%, and most subsectors posted typical performance–but that was before COVID-19 began its global spread. Below are sales in total US–Multi Outlets (grocery, drug, mass market, military and select club and dollar retailers) for latest 52 weeks ending Jan. 26, 2020.							
	Dollar Sales	Change Y/A	Unit Sales	Change Y/A			
Liquid Body Wash/All Other	\$2,688,792,800	3.0%	582,011,394	-2.1%			
Non-Deodorant Bar Soap	\$1,090,183,817	-3.0%	248,104,599	-5.2%			
Liquid Hand Soap	\$852,270,362	4.1%	362,275,389	-0.5%			
Deodorant Bar Soap	\$308,375,284	-3.8%	95,353,361	-6.7%			
Hand Sanitizers	\$224,817,629	0.8%	109,672,763	-3.0%			
Heavy Duty Hand Cleaner	\$6,947,403	-1.3%	2,821,270	-5.2%			

SOAP SECTOR

Source: Market Advantage; IRI Liquid Data

Handwashing is "one of the simplest things people can do—and is one of the most effective. CDC is putting that message out. We are trying to amplify the CDC messaging," Martina Spinatsch, vice president of R&D, Dial, told Happi in a phone interview last year.

This 70-year old leading brand invests time and resources to publicly promote healthy hand hygiene as it connects to charitable causes at the same time. For example, Dial last year reconnected with Big Brothers Big Sisters of America to promote healthy hygiene habits in connection with Global Handwashing Day (October 15). At one local event with Big Brother Big Sisters in Connecticut, the brand used glitter to represent germs, and showed children how soap works better to remove germs better than just water alone.

Adults might benefit from a similar refresher course.

According to Spinatsch, consumers need to get back to basics when it comes to hand washing.

"First off, it's important to use soap or a handwashing product that has surfactants. Washing with just water is less effective. The surfactant helps remove dirt and germs. Second, everyone is so busy and so focused on moving to the next thing, that they don't spend enough time," she said alluding to the CDC's guidelines of handwashing for 20 seconds. "Scrub your whole hands, your palms, the top, in between fingers, finger tops."

CLEAN WITHOUT COMPROMISES

Consumers who increase their hand washing as COVID-19 cases increase can rely on leading brands that are crafting soaps that deliver cleaning power without tradeoffs.

"We know consumers want to be able to wash their hands thoroughly. So, we design our hand soap formulations with this in mind and we test them extensively to ensure that they are gentle on skin and hydrating," according to Spinatsch.

Even with a long history of trust that's been built up, Dial continues to evolve its collection to meet consumers where they are.

"We want to make sure we are curating, selecting and offering new items to meet consumers' expectations. Consumers trust us to deliver what they want," Spinatsch told Happi. To that end, the company in April introduced the Dial Pure Collection. It includes Dial PureMicellar Foaming Hand Wash, a non-antibacterial hand wash with active micelles that is available in three scents (Seafoam, Hyacinth and Juniper), and Dial Pure Moisture Body Wash, which has a multi-layered formula that contains renewable sunflower oil. The wash is available in three light scents, including a rosy floral with a light powdery undertone to sandalwood, which has a warm and woody opening note. Both formulations are free from parabens, phthalates, silicone, SLS and SLES and come in bottles made with 50% post-consumer recycled plastics—attributes sought by today's consumers.

"For a legacy brand, like Dial, it is important to evolve with changing consumer expectations," Spinatsch said.

Another venerable personal care brand has expanded its soap



Dial's new Pure Micellar Foaming Hand Wash and Pure Moisture Body Wash (right) are free from parabens, phthalates, silicone, SLS and SLES and come in bottles made with 50% post-consumer recycled plastics.



HARNESS THE POWER OF CLEAN AND GREEN IN YOUR BOTTLE

Biosurfactants from Evonik

Evonik's biosurfactants make a clean sweep – literally. They not only remove grease and dirt but are also eco-friendly and gentle on the skin. Other performance advantages include exceptional foam-forming properties and hard water compatibility. They are 100 percent biodegradable and also impact the environment less than conventional surfactants. All our biosurfactants are produced from bio-based raw materials without the use of tropical oils.

evonik.com/cleaning



in Evonik Cleaning Solutions





Tom's of Maine has added a new Prebiotic line that includes its first liquid hand wash and bar soap.

offerings. Tom's of Maine recently launched a line of natural prebiotic personal care products, including bar soap and a liquid hand wash formulation, the first in the company's 50-year history.

Prebiotics offer plenty of growth opportunities. According to a recent survey conducted by PSB Research on behalf of Tom's of Maine, more than half of Americans believe the gut could benefit from a healthy balance of good and bad bacteria, but significantly fewer realize other areas of the body like the skin need this balance.

According to Justin Boudrow, personal care brand manager, Tom's has been studying the benefits of supporting "good bacteria' in personal care for several years."

Tom's of Maine Prebiotic Body Wash & Bar Soaps are sulfate-free formulas that retain skin's natural moisture and gently cleanse. The washes are offered in Fresh Apple, Gentle Lavender, Soft Rose and Blood Orange scents. The bar soap, which uses Rainforest Alliance Certified palm oil, comes in Fresh Apple and Soft Rose.

The Prebiotic Liquid Hand Soap helps support the growth of good bacteria found on hands and palms, while retaining skin's natural moisture. It is available in Fresh Apple, Gentle Lavender, Soft Rose, Blood Orange and Peppermint.

As body washes remain a popular format in the US, Nivea this season expanded its range with a line that marries on-trend scents with skin care attributes. Launched in February, Nivea Body Wash with Nourishing Serum is a portfolio of 10 body washes enriched with a unique blend of plant-derived oils, essential skin lipids and vitamins. The varieties are spread across three platforms—Nourishing, Refreshing and Pampering. Options include Shea Butter Body Wash, Basil & White Tea Body Wash, Wild Berries & Hibiscus Body Wash, and Coconut & Almond Milk Body Wash, to name a few.

NOT YOUR MOTHER'S BATH TIME

Wellness continues to influence the personal care space—but this concept is nothing new to the bath category; soap brands have long touted a good soak in the tub as a means to get away from it all without leaving home. Companies are rolling out formulations that tap into overarching health and wellness trends that are top of mind with today's consumers.

Take J.R. Watkins. Just last month this heritage brand launched the Luxe Line, marking its foray into luxury body care category. Exclusive to Ulta, the range includes Bath Elixir, described as a liquid bath soak made with a proprietary blend of natural extracts that is an alternative to salt soaks and bath bombs; Creamy Body Wash; Aromatherapy In-Shower Mist; and Sugar Body Polish, which exfoliates and then lathers into a foaming cleanser.

Luxe offers three options—Detox, Sleep and Awaken. The Sleep line has a blend of natural extracts to calm the mind, relax the body and

encourage a restful night's sleep with ingredients such as lavandin, orange and calendula and a scent that features coconut notes from the top to the base. The Detox Line features key ingredients of ginger, witch hazel, chamomile, calendula, cactus water and jojoba oil. The Awaken range is formulated with similar components as Detox, but has coriander, which enhances mood, and bergamot, which is said to reduce nervous tension, according to J.R. Watkins. The range is 98% natural and is free from parabens, sulfates and silicones



Also new in the specialty bath sector is Spongellé's Wild Flower Collection of body wash infused buffers

Nivea rolled out Body Wash with Nourishing Serum, a line with 10 new products.

which eliminate the need for multiple bath products including loofah, smoother, massager, body wash, moisturizer and exfoliator, which in turn saves consumers money and time, according to Spongelle, LLC. Inspired by rolling meadows of organic florals, each exfoliating buffer sponge combines time-release technology with a built-in body wash that's infused with herbal extracts such as yuzu, edelweiss and vetiver. Each buffer provides 14-plus washes.

Of course, bath time isn't just for adults; kids are bigtime tubby takers. Natural brand Babo Botanicals, which is now a decade old,



J.R. Watkins' new range taps into wellness.

CLEANING UP THEIR ACT

Men are adding products to their grooming routines, but it appears there's room for improvement when it comes to their basic skills. According to a poll of more than 1,000 men age 18 and above conducted by AcuPoll for skin care brand Tiege Hanley, one-third of men admit that they don't wash their faces on a daily basis. Younger men

are more likely to drop the ball on their daily face wash routine, with half of men age 18-24 admitting that they don't wash their faces daily. Further, 63% of men do not regularly use face wash and 11% say they've never even tried it. One-third of men surveyed said they wash their faces with bar soap.

Method is offering men both options in its Method Men line. Body wash and bar soaps (including one with exfoliating properties) come in a range of modern scents such as Sea + Surf, Juniper + Sage and Bergamot + Lime, according to the company, which sells



has rolled out a limited-edi-

tion Birthday Bubbles Plant Based Bubble Bath & Wash.

Available on babobotani-

cals.com, it features organic

chamomile, calendula and

aloe vera-sure to please

mom-and scent of warm

birthday cake scent-which

cently expanded its shelf pres-

ence to Target, which means

450 store locations across the

US will sell its bestselling prod-

ucts, including EWG-Verified

Sensitive Baby Fragrance Free

Shampoo & Wash, Moisturiz-

ing Baby Oatmilk Calendula

Shampoo & Wash and Mois-

turizing Baby Oatmilk Calen-

dula Bubble Bath.

In addition, the company re-

will be welcomed by kids.

Cora, an indie feminine care brand, has added a personal cleanser for the entire body.

Hail a Ride and Hand Sanitizer



Lyft riders can spritz on Everyone's Hand Sanitizer Hand sanitizer sales have been surging as consumers look for hygiene products that can be used away from home as the spread of novel coronavirus cases throughout the world continues. As store shelves empty, finding a bottle of sanitizer has become akin to looking for a needle in a haystack.

But there's one unlikely place where consumers are likely to find a dose–in their ride share. Everyone recently announced exclusive partnership with Lyft in an effort to provide its Everyone Hand Sanitizer Sprays to Lyft drivers with the goal to assist riders and drivers in living a healthy and safe lifestyle. The rideshare industry recently acknowledged that the novel coronavirus could pose a material risk to business and this is just a small step in the effort to address the larger concern. Through this strategic partnership, Everyone will be providing Lyft driver hubs in 10 major cities–

including Atlanta, Boston, Chicago, Los Angeles, Miami, New York City, Sacramento, San Francisco, Seattle and Washington, D.C.–with an initial delivery of up to 2,000 units per city of Everyone Hand Sanitizer Spray for use in driver vehicles. Everyone expected to deliver 9,000 sprays by the end of April.

them online and inside Target as well as on Amazon.

Additional brands targeting men are also incorporating facial cleansers into their stables.

Bevel—part of Walker & Company, which was acquired by Procter & Gamble in late 2018—kicked off 2020 with national retail expansion and an expanded product range. Among its new offerings are exfoliating body washes formulated with charcoal and argan oil. Bevel offers three scents—Dark Cassis, Black Bergamot and Supreme Oak.

On the female side of the personal care category, Cora, an indie brand that has shaken up the feminine care category with organic products, has expanded beyond pads and tampons. In April the company rolled out One Wash, a pH-balanced cleanser designed for the entire body, including one's most intimate areas. The wash is formulated with a tri-oil blend of hemp, sunflower and shea as well as red raspberry and B-vitamins. The scent is derived from notes of sandalwood, lavender and mandarin, according to Cora, which is based in the San Francisco Bay area.

Whether it's a product for boys or girls, the hands or elsewhere, soap brands must continue to raise the bar—and body wash—to insure they're addressing the needs and desires of today's consumers.



How Did We Get Here?

A FAST-PACED REVIEW OF THE HISTORY OF SURFACTANTS IN THE PERSONAL CARE SPACE AND A LOOK AT MODERN ISSUES SUCH AS 1,4 DIOXANE AND SULFATE-FREE.

By Ricardo Diez, PhD

t may sound surprising, but the fact is that most of the surfactants used today in personal cleansing products were synthesized by German chemists in the 1920s and 1930s. These patents are such masterpieces of practical synthesis that little room was left for the development of new surfactants for future chemists. For many, this moment in time represents the beginning of the modern cosmetic industry. A selection of those patents is shown in references 1–8. Interestingly, these surfactants were not invented to make shampoos or with the cosmetic industry in mind, but for industrial applications, and most precisely for washing natural fibers, mainly wool, prior to the dying process. And yet, their research has transformed the personal care industry and human health.

The best way to appreciate the need and value of their discoveries is washing your hair with soap—that was the only material available for this purpose in the 1930. Just dissolve 5 to 10 grams of soap in warm water, followed by shampooing. Please, keep your eyes closed or better yet, wear swimming goggles! Then, rinse with plenty of water, and take your time combing your hair. You may always consider a final rinse, before combing, with water and vinegar to help remove the soap scum left on your hair.

History was made in 1933 when Procter & Gamble launched Drene, the first shampoo of the modern era. At that time, P&G was just another soap producer. But the company's vision to introduce these surfactants in a shampoo, which was in direct competition with its key product, soap, changed P&G forever, and put it on the road to become the largest fast-moving consumer products company in the world.

Drene was formulated with SLS, synthesized not by a P&G researcher, but Heinrich Bertsch, a German chemist. His patent¹ is a great example of how our industry was founded by great chemistry, combined with great skills in formulating consumer products. But World War II came soon after that, putting a brake on surfactant expansion. After the war, the rise of these materials as soap replacements, especially in shampoos, was unstoppable.

During the 1950s, Unilever launched the first "bar soap with no soap," Dove.⁹ It was formulated using cocoyl isethionate, also synthesized in Germany in the 1930s. Its limited water solubility made it optimum for bars.

The surfactants that have become the most widely used globally,



the ether sulfates, took a bit longer to arrive on the scene due to the difficulty of the additional ethoxylation step. Performance-wise, the ether sulfates erased all the weaknesses of SLS in terms of mildness, clarity, haze point and sensitivity to water hardness. All these surfactants, synthesized almost a century ago, are known as primary anionic surfactants, and are presented in Table 1. As indicated, some made it into personal cleansers very quickly, others needed more time. Those in groups 1 and 2 have the same "water solubilizing" group, the sulfonate (SO3-) group, even though this word does not show in the name of most of them.

The term "primary surfactant" was coined to indicate that any one of them could be used as the sole surfactant to formulate a cleanser, even if some deficiencies were present. The "anionic" part refers to the chemical nature of the solubilizing group used in the synthesis process.

A "surfactant evaluation process" started in the industry in the 1960s. It involved all the aspects shown in Table 2. Unknown to many is the large body of research in the areas of biodegradation, human safety and environmental impact. The many books and papers available in these topics reflect the continuous effort of many decades. The evaluation concluded with the ether sulfates at the top of the list. The fact that they could also be used in other consumer products, such as laundry detergents, household cleaners, and dishwashing liquids, also helped to put them at the top.

THE PERFECT COUPLE

The secondary surfactants appeared as early as the 1950s. Unlike a primary surfactant, a secondary one does not render by itself a cleansing product of acceptable quality. But magic happens after mixing it with a primary anionic surfactant because this results in a product with nicer and more stable lather, Plus, it has the added benefit of achieving good viscosity by just adding salt. The simplicity of formulating shampoos simply mixing primary and secondary surfactants propelled the launch of many of today's shampoo brands. The difficult part was, of course, making the surfactants.

The alkanolamides, originally synthesized by Stepan, became very popular. Cocamide DEA became a staple of the industry. Decades later, the discovery that this amide had nitrosamines resulted in the voluntary move by the industry to stop using them. I must clarify than another member of this family, Cocamide MEA, a wax, has no nitrosamines, and has remained a key secondary surfactant because of its ability to build "structured systems." These micellar structures are required to avoid stability problems when other important ingredients, such as silicones, petrolatum, oils, antidandruff powders, are added as part of the formulation.

But the most critical discovery in this field was made by a selftrained chemist, Hans Mannheimer, who in 1948 invented the amphoteric surfactants.¹⁰ He did not go too far with them as primary surfactants, but after a decade of perseverance and changes in the synthesis process, he made one of the most important discoveries in our industry, the anionic-amphoteric blend.¹¹

His amphoterics, (INCI: amphoacetates) surpassed the alkanolamides in the key property of mildness, and most importantly, they reduced the irritation of anionic surfactants. But the alkanolamides dominated the market because of lower cost and, surprise again, because mild products were of no marketing interest at that time. Johnson & Johnson was the exception with the launching of its iconic baby shampoo.¹² This was the first product that used today's widelypopular anionic-amphoteric system. But we needed to wait until the mid-1960s for the arrival of the most widely-used secondary surfactant.

Performance attributes

in all cleansing products (shampoos, shower gels, Hand and facial cleansers)

Manufacturing

Batch vs. continuous Feedstock global availability Global production facilities Cost

Environmental / Safety

Biodegradation Human Toxicity Eco-toxicity Human Sensitization Skin / eye irritation

Table 2. Surfactant Evaluation Process over 50 years

LOST IN THE (CHEMICAL) TRANSLATION

Under the title "Bubble Bath Composition," a Goldschmidt patent¹³ describes the structure of today's ubiquitous cocamidopropyl betaine (CAPB). It had all the required properties to become the secondary surfactant of choice, beginning with price and ease of use. It quickly became the key companion in Europe to the ether sulfates in the recently-introduced showers gels and later, in the hand and facial cleansers.

In the 1980s, a misconception roiled the market; a misconception that exists today. It all started when mild products became an important marketing trend. The original amphoterics, the amphoacetates, had quickly established themselves as the gold standard for mildness, thanks to the popularity of the J&J shampoo. But somehow, CAPB started to also be called amphoteric, perhaps due to some "similarities" in the chemical structures. But CAPB is not amphoteric, much less an amphoacetate. The Goldschmidt patent does not describe CAPB as amphoteric. The point here is not so much how similar or not their chemical structures, but the fact that transforming CAPB into an amphoteric also resulted in perceiving the betaine at the same level of mildness and irritation reduction of the original amphoacetate.

But amphoacetates and CAPB do not have the same mildness. And the amphoacetates do not have the impurities or by-products associated with the allergic reactions reported for CAPB. They are also more difficult and expensive to produce. In essence, to the undeniable good properties of CAPB as s secondary surfactant, "transforming it" into an amphoteric, aureole of mildness included, did also help in making it the secondary surfactant of choice.

A GIFT FOR FACIAL CLEANSERS

The evaluation process of the surfactants in Table 1 that started decades ago revealed that a good number of them delivered shampoos and showers gels of inferior performance to the ether sulfates. In addition, the formulas had a higher cost reflecting the higher cost of the surfactants. It is always desirable to have a "good price" in products that are used often by all family members.

Interestingly, the differences in the performance requirements of the various cleansing products, transformed, for example, a foam deficiency in shampoos into a strength in the new category of facial cleansers, where ease of rinsing is very important. Also, the higher price of facial products allowed to formulate them with more expensive surfactants.

In addition, and very importantly, some of the surfactants had sensorial benefits that, while unnoticed in shampoos, were of value in facial cleansers. A clear example is the lauryl phosphates (Box 4 in Table 1), deficient in shampoos, but used in one of the first facial cleansers because of their excellent feel, mildness and rich lather.

This logical evaluation process, based on assigning the surfactants to the most suited type of cleanser according to their strengths and weakness, resulted in two main categories—commodities and specialties. The commodities were the laureth and lauryl sulfates, and the olefin sulfonates, best suited for shampoos, shower gels and hand cleansers. The rest were named "specialties," ideal for facial cleanser. Today, we still benefit from this approach in the multitude of facial cleansers formulated with specialty surfactants. Then, about 15 years ago, a disruption occurred.

THE SULFATE-FREE DISRUPTION

Assume, for a moment that there is a Cosmetic, Food and Drug Administration. If there were such a thing, there would be no sulfatefree products in the market the way they exist now. And no need for the following paragraphs:

There is no science, no technology, and no clear consumer benefits behind the sulfate-free (SF) products. The SF movement started about 15 years ago as the typical internet "conspiracy." Then it ex-



EMPOWER YOUR BODY'S NATURAL SHIELD

With solutions from the ceramide expert

Pollution, the aging process, seasonal factors, UV irradiation and predisposition: There are many threats to disrupt our natural protective skin and hair barrier. Evonik's ceramide and sphingolipid technologies preserve and maintain this barrier. Our actives keep skin hydrated and protect hair from damage. The result is a more vital, smooth and healthy look. With more than 25 years of experience in ceramides, we offer a comprehensive portfolio to boost formulations with ceramides.

www.evonik.com/personal-care

in Evonik Personal Care

@EvonikPC

@evonikpc



panded to hair salons where stylists got commission to sell the new "SF shampoos" to their clients.

The SF movement could have died by itself or remained isolated to a limited market. But, unfortunately, some sectors of the industry realized that SF products could be the way to enter or compete in the crowded shampoo shelves. The veracity of the claims against the regular, sulfate-based products was irrelevant.

Basically, consumers have been fed misinformation. Once they believed it, a sector of the industry had "no alternative" but to offer them products addressing the misinformation that had been created. With some exceptions, the major shampoo brands resisted the SF move for some time, but they have all capitulated in recent years. They have no alternative. If a loyal consumer of brand X wants a SF shampoo, and brand X does not offer it, that once-loyal consumer will go to another brand.

Those of us who with years in the industry were amazed observing that what we have always called specialty surfactants were renamed as the new "sulfate-free" surfactants, assigning to them all sort of fantastic benefits that we never saw in our research. Changing the name from specialties to SF surfactants was not the problem. The problem was that using them in shampoos and shower gels resulted, as expected, in inferior products at higher cost. How do you sell this combination? Marketing them as the necessary higher cost that you must pay, in both price and performance, for "safer and milder" products. And the higher the cost, the "safer and milder" the product.

Recently, there has also been "innovation" in some SF brands, including some major names. To overcome the performance weakness of the SF surfactants, the solution has been to redefine the concept of sulfate-free products. As a result, not all the sulfate surfactants are bad because some are good, really good. SLS remains as bad as always, but the siblings ALS and coco sulfate are fine and dandy. The given explanation is so ridiculous that it clearly shows the real intentions of the SF products.

1,4 DIOXANE IN ETHER SULFATES

1,4 dioxane (1,4 D) is considered a "possible carcinogen" by the International Agency for Research on Cancer (IARC). This classification is based on sufficient evidence in experimental animals and inadequate evidence in humans. The first studies with animals were conducted adding 1,4 D to drinking water.

The 1,4 D that is present in ether sulfates is primarily generated during the sulfonation process of the starting ethoxylated fatty alcohol. The mechanism is known, as are the manufacturing conditions required to minimize its formation. In addition, a "stripping-off" process is available to further reduce the content. At present the industry can manufacture ether sulfates with as little as 5ppm of 1,4 D at 70% active, equivalent to 0.07ppm per 1% active surfactant. 1,4 D poses no risk to the consumer during the actual shampooing or showering, either from inhalation or skin absorbance. This is part of the misinformation on this important issue. The real risk is that 1,4 D ends up in the water we drink. The US Environmental Protection Agency has established a maximum concentration of 1,4 D in drinking water at 0.35ppb. At this level, it expected to cause no more than one extra case of cancer in one million people. Some states have their own regulations.

It should be noted that not all the 1,4 D detected in tap water comes from personal care products. Other sources are non-cleansing consumer products, and the various industrial uses of this compound. The contribution of 1,4 D from each potential source is not exactly known, and it could vary from location to location.

A recent proposed regulation by the State of New York setting the maximum content of 1,4 D in cosmetic cleansers to 1ppm is a welcome sign. It is also the appropriate response to a cosmetic industry that has failed to address an issue that has been lingering for nearly four decades.

The commercially available ether sulfates mentioned before will permit formulating cleansers with up to 14% active ether sulfate and meet the NY State regulation. This 14% active surfactant is well within the formulation requirements for practically of cleansers.

The lack of response of the industry to set a limit to the content of 1,4 D in cleansers, the equal lack of response to contain and address the rampant misinformation on the dangers of 1,4 D to the consumer, and worst of all, the attitude of some sectors to capitalize on the misinformation and offer alternative products, has created a negative image of a surfactants family that from an overall performance standpoint remains unmatched.

References

- 1. U.S. Patent 1,968,797 to H. Bertsch (1934).
- 2. U.S. Patent 1,968,793 to American Hyalsol (1934).
- 3. U.S. Patent 1,968,794 to American Hyalsol (1934).
- 4. U.S. Patent 1,906,484 to I.G. Farben (1933).
- 5. U.S. Patent 1,932,180 to I.G. Farben (1933).
- 6. U.S. Patent 2,174,761 to GAF (1939).
- 7. U.S. Patent 2,183,853 to I.G. Farben (1939).
- 8. U.S. Patent 2,220,099 to GAF (1940).
- 9. U.S. Patent 2,894,912 to Lever Brothers (1959).
- 10. U.S. Patent 2,528,379 to H. Mannheimer (1948).
- 11. U.S. Patent 2,781,349 to H. Mannheimer (1957).
- 12. U.S. Patent 2,990,069 to Johnson & John- son (1961).
- 13. U.S. Patent 3,328,307 to Goldschmidt A.G. (1967).

ABOUT THE AUTHOR

Ricardo Diez, PhD, is currently an adjunct professor at Rutgers University where he teaches two courses on applied cosmetic science in the Masters of Business and Science. He has more than four decades of experience in the industry in both consumer product companies (Procter & Gamble, Dial Corp and Chanel), and raw material producers (Miranol, Stepan and Huntsman). He has obtained patents in the fields of raw materials synthesis and consumer product technologies. Diez gives courses and webinars for the International Federation of Society of Cosmetic Chemists (IFSCC), the SCC of the US, and the Center for Professional Advancement.

diezr@hotmail.com



Just Hit Refresh

THIS YEAR HAS BEEN ALL ABOUT CLEAN INCLUDING ADVANCED SHAMPOO, CONDITIONER AND TREATMENTS FOR THE SCALP.

By Melissa Meisel, Associate Editor

LEAN IS critical when it comes to washing hands to eliminate germs. In fact, 2020 took cleanliness to a whole new level. It's quality over quantity when it comes to shampoos, conditioners and other scalp cleansers as products have to preserve color and moisturize extra-dry ends for those who can't visit the salon as much as in previous years. According to Philip Pelusi, salon industry veteran and expert source for Happi.com, times have certainly changed when it comes to how often we cleanse our hair.

"We can go back just a couple decades to where 'wash, rinse and repeat' was an everyday mantra," he told Happi. "Fast forward to 2020 where that routine has become passé' and almost frowned upon. Today, cleansing hair less frequently practically gives one bragging rights. A time when clients and stylists alike compare notes on their shampooing routines as frequently as they discuss the latest hair trends."

Marketers are following suit when it comes to the creation of shampoos and conditioners for the season. Since self-care is also paramount right now for shoppers, new products feature premiere components and recyclable packaging to tap into the demand for global wellness.

"Our perspective is to think of hair as the finest garment one owns. Easy to do since our hair is the most important fabric we wear, so given that, it deserves the highest level of preservation," added Pelusi.

While macro trends surrounding sustainability and wellness impact ingredient preferences, consumers still value safety and efficacy above all else, added Clare Hennigan, senior beauty analyst, Mintel, Chicago.

"Consumers are looking for natural and clean beauty products. This will mean something different to each shopper, from using natu-



Bravo Sierra recently added a dry shampoo to its portfolio.

rally occurring ingredients, eliminating harmful ones, or not testing products on animals," added Tiffany Hogan, principal analyst at Kantar, Columbus, Ohio.

Professional hair product sales in June 2020 were 98% of the June YAG totals, according to the most recent findings from Kline Pro, Kline's salon retail products and services database. In fact, shampoos and conditioners were ahead of last year at +6% and +12%, respectively. This is welcome news for an industry that nearly shut down from mid-April through most of May 2020.

Hair care products that provide color care benefits have always had the highest category share but that share climbed to 34.0% in the second quarter, peaking in April at 43.7%. Since most salon doors were shuttered at this time, ordering online and curbside pickup from salons became a lifeline, according to Kline Pro.

In prestige beauty, hair care product sales rose by 11% to \$232.5 million for the third quarter of 2020, with all areas of the category growing except for hair styling, according to The NPD Group. Hair masks, hair color and other hair care including primers and treatments were among the fastest-growing areas of the market. For the nine months through September 2020, hair product sales as sold in prestige rose 4%, according to NPD Group. Shampoo sales generated \$106.6 million and increased 10% during these months, while conditioner jumped 8% to \$101.6 million. However, dry shampoo slipped 16% to \$41.8 million.

"Hair continues to grow in a stormy year, with double-digit gains across most areas of the market," said Larissa Jensen, beauty industry advisor, The NPD Group.

Shampoo sales rose 2.4% to \$3.3 billion, according to data from Information Resources Inc. (IRI) for total US multi-outlet (supermarkets, drugstores, mass market retailers, military commissaries and select club and dollar retail chains) for the 52 weeks ended Oct. 4, 2020. Conditioner sales climbed 7.1% to \$2.4 billion. For more information by category, check out the chart on p. 29.

CONSUMER DIRECTION

The pandemic impacted people's hair color and hair styles, as well as how people care for their hair at home. According to Emily Boulin, Sally Beauty SallyCrew ambassador and professional stylist, Baltimore MD, with social distancing the new norm in day-to-day life, consumers who regularly visited the salon are recreating their favorite salon hair treatments and services at home.

"As a professional stylist, I've received more questions than ever about scalp health and breakage remedies," she told Happi. "As people continue to work from home and participate in fewer social activities, most are not washing their hair as often...although stylists recommend not washing your hair every day, not washing it enough results in natural oils, dirt, and product residue building up on the base of the hair which can lead to scalp irritation. To help with this issue, it's important to invest in a sulfate-free shampoo."

All signs point to the internet when it comes to where shoppers are buying more these days.

"Sales in their traditional sense has changed during COVID," Kevin Hughes, artistic director with Moroccanoil, Palm Springs, CA., told Happi. "It shifted to a majority of online sales but so many stylists put on their entrepreneur hat and set up ways to safely get shampoos, conditioners, and styling products to their clients. I think it helped so many because it gave a bit of normalcy during such a difficult time."



Pantene is branching out with Nutrient Blends.

SALES RISE IN SHAMPOO, CONDITIONER CATEGORIES Data from Information Resources Inc. (IRI) for total US multi-outlet for the 52 weeks ended Oct. 4, 2020.								
	Dollar Sales		Unit Sales		Price per Unit			
Product	Current	% Change vs YA	Current	% Change vs YA	Current	Change vs YA		
Shampoo	\$3,300,625,985	2.4%	\$607,041,082	-4.8%	\$5.44	\$0.38		
Regular Shampoo	\$2,319,609,762	1.5%	\$467,350,223	-6.0%	\$4.96	\$0.36		
Dandruff Shampoo	\$647,067,509	2.0%	\$93,859,118	-3.0%	\$6.89	\$0.34		
Shampoo and Conditioner Combo Pack	\$333,948,714	10.9%	\$45,831,741	5.5%	\$7.29	\$0.35		
Hair Conditioner/Creme Rinse	\$2,400,066,429	7.1%	\$454,618,511	-0.5%	\$5.28	\$0.37		

Source: Market Advantage TSV; IRI Liquid Data

Hughes added that consumers are craving shampoos and conditioners that will protect their investment, as in hair color or smoothing treatments.

"They need their hair color to last as long as possible while keeping it looking fresh and healthy. They are looking for hydration without weighing the hair down. They don't want anything that will strip their color or make their hair feel dry," he explained, adding that Moroccanoil just launched Blonde Perfecting Purple Shampoo that works miracles on keeping brassy tones out of hair.

Dr. Rocio Rivera, vice president and head of scientific communications at L'Oréal Paris, New York, agreed that color-treated hair continues to be a focus in terms of how to ensure the hue stays fresh and unaltered as long as possible.

"L'Oréal Paris' Ever Collection continues to be a collection that consumers gravitate towards," she told Happi. "The line contains no sulfates and is an affordable color protection option for shampoos, conditioners and treatments."

NEW & IMPROVED

Procter & Gamble updated its hair care portfolio with new and improved versions of staple shampoos and conditioners. For example, Herbal Essences is on a mission to bring plant power to every shower. This year, its six sulfate-free shampoos have a new look and the same performance, according to the company. That means tons of lather and fragrance, while still meeting the strict clean beauty standards of the Environmental Working Group (EWG).

Not all plants are created equal, so only the most powerful plants make it into Herbal Essences bottles, according to the brand. That's why the Royal Botanic Gardens, Kew, one of the world's leading authorities on plants, certified botanicals in the bio:renew lineup. In addition to Herbal Essence's 90% naturally-derived formulas and signature scents, its bio:renew lineup has something for everyone with offerings for all hair types. Consider Herbal Essences Birch Bark Extract Collection. This range is free from sulfates, colorants, parabens and mineral oil, and provides a gentle, yet effective cleanse to help moisturize hair. The collection features birch bark and sustainably harvested aloe with an aroma of dewy floral bouquet, aquatic/marine and a lingering scent of warm amber.

Meanwhile, the Herbal Essences Honey & Vitamin B Collection is PETA Cruelty-Free and is free from sulfates, colorants, parabens and mineral oil. The collection features honey and sustainably harvested aloe endorsed by Kew Gardens as well. It leaves hair shiny and hy-



The latest creation at Aveda is the Botancial Repair range.



Head & Shoulders has an apple cider vinegar formula.

drated with a comforting scent of honey, jasmine and creamy vanilla. The pandemic didn't stop the search for new sources of nutrients and new hair secrets from around the globe, as seen with its expanded Nutrient Blends collection. According to the company, Pantene

ed Nutrient Blends collection. According to the company, Pantene Nutrient Blends Shampoo, Conditioner and Treatment collections are discovered and curated by Pantene's global team of scientists to ensure hair gets all the nutrient-rich ingredients it needs—and nothing it doesn't, with sulfate, silicone, paraben, dye and mineral oil-free formulas. Next month, Pantene adds Baobab Hydrating Glow and Pure Clean & Clarify. Meanwhile, Head & Shoulders chemists are working with natural ingredients, like apple cider vinegar, to solve scalp concerns such as dandruff and buildup. Apple cider vinegar is known to be antifungal, a disinfectant, rich in minerals and acidic, which helps to bring the scalp back to a balanced state, according to P&G. Head & Shoulders Apple Cider Vinegar Collection is formulated with apple cider vinegar as well as active zinc pyrithione to target the scalp. The collection features three products that are said to work to remove impurities, excess oils and buildup on the scalp.

This month, Aveda launched an entirely new damage repair at-home and professional range. Botanical Repair is a collection that transforms hair using plant-powered technology that instantly strengthens and repairs hair through a combination of five different products, including a shampoo, conditioner, strengthening leave-in treatment and two hair masques.

According to the company, Aveda's bond-building treatment makes hair "5x stronger in as few as 10 minutes." It strengthens and repairs to dramatically reduce breakage, and helps protect hair during a color service, leaving hair stronger, visibly revived, shiny and full of life. The collection includes a shampoo, conditioner, leave-in treatment and two masques for both light and rich levels.

NATURAL SELECTION

Got greens? Fekkai's new CBD Scalp Calming collection includes a shampoo, hydrating conditioner, hydrating mask and supreme oil formulated with a proprietary blend of non-THC broad-spectrum CBD from organically cultivated hemp extract grown in the US. According to the company, it helps soothe sensitized/stressed scalp, deeply hydrate hair for a clean and healthy glow, hydrate the body and provide calming nourishment.

Indie brand Hempz rolled out a CBD, Eucalyptus and Tea Tree Oil Haircare Collection, which includes herbal shampoo, conditioner, conditioning mist, a hair mask and scalp serum. The products in the collection are infused with 100% pure natural hemp seed oil, CBD and signature blends of eucalyptus and tea tree oils.

"The ideal balance of hydration, antioxidants, vitamins and key amino acids will transform your hair from dull and lifeless to healthy, calm and beautiful," said Jennifer Weiderman, chief marketing officer for TSG Consumer Partners, which makes the Hempz collection, in a Zoom event with beauty editors this season.

The collection is THC-free, dye-free, gluten-free, paraben-free, cruelty-free and 100% vegan. The products are available at hempz. com, in Ulta stores and on ulta.com. It will expand nationally in 2021, according to Weiderman.

Zotos Professional, also part of Henkel, recently launched a CBD and hemp seed oil infused hair care brand called Wellphoria. The range contains a blend of 99% pure CBD at 50ppm and hemp seed oil.

John Paul Mitchell Systems' (JPMS) new Paul Mitchell Clean Beauty is vegan and cruelty-free. Formulas contain ingredients such as argan oil, almond oil, aloe vera, hyaluronic acid, amaranth ex-



Antibacterial hair care is from Biosilk.

tract, pea protein, olive and oat peptide and include shampoo, conditioner and leave-in treatment.

In the age of COVID-19, when everyone's looking for new ways to sanitize and stay safe, BioSilk's newest innovation is part of its existing Health + Beauty Division and features shampoo, conditioner, and a hair/body mist options to rid hair of grime and germs, while making it feel silky smooth. Farouk Systems Inc. is taking hair care to the next level by launching BioSilk Health + Beauty Antibacterial Hair Care Line.

After initially launching the Antibacterial Hand Soap and Antibacterial Lotion in August as part of BioSilk's Health + Care division, the brand expanded its offerings to include Antibacterial Shampoo, Rescue Moisturizing Conditioner and Hair & Body Mist, as well as a Trio Kit. The Antibacterial Shampoo and Hair & Body Mist contain benzalkonium chloride (0.10%), an antimicrobial that's said to rid hair of 99.9% of germs, while the Rescue Moisturizing Conditioner is packed with essential nutrients to soothe and seal in moisture for silky, smooth hair, said the company. This trio, infused with lavender and natural aloe vera, is designed to eliminate germs and bacteria while softening and replenishing tresses.

Kérastase has once again combined advanced technology with sensorial experience for an updated hair care system, Chronologiste, a collection that completely invigorates hair from scalp to tip. Targeting the dimensions of aging for both scalp and hair, each product features revitalizing actives including hyaluronic acid, vitamin E and abyssine from the sea.

The Pre-Cleanse Régénérant is a revitalizing pre-shampoo that deeply cleanses scalp and roots with charcoal, removing impurities, unclogging pores and toning the scalp for a balanced foundation. Meanwhile, the Huile de Parfum is a fragrant treatment that leaves



Chronologiste by Kerastase Paris revitalizes strands.

hair nourished and radiant. Designed by master perfumer Alberto Morillas of Firmenich, the fragrance includes a crisp, citrusy top note, with floral notes of tea rose, peony and magnolia and a woody base. Along with restoring shine, the oil reduces breakage and provides added strength to the hair fiber.

Landing stateside this season from the UK is Lee Stafford. Its hair lengthening shampoo is billed as a growth-stimulating formula packed with moisture regulating proteins to feed and energize the scalp. According to the company, it stimulates the metabolic activity of the hair bulb cells and encourages blood flow to the root, helping to stimulate growth. Moisture-regulating proteins and wheat starch feed the scalp for softer, smoother and healthier hair. This gentle, revitalizing cleanser contains fresh apple and lemon extracts to add shine to hair while anti-oxidizing green tea extract helps to protect it



Indie brands such as Bounce Curl target curly and textured hair.

from heat damage and breakage.

Meanwhile, Black woman-owned, clean luxury hair care brand Meraki launched Quartz Conditioner. According to the company, each Meraki product is activated with a gemstone, and this conditioner features clear quartz to "help provide balance mentally, emotionally and spiritually." Meraki Quartz Conditioner delivers deep nourishment to hair strands along with the "elevated vibes of clear quartz crystals" and a fragrance of real gardenia flowers and lavender. With rich butters, precious oils and hair repair agents, this conditioner also offers high hydration levels. White willow bark balances the scalp while amla, ginseng, yerba mate and sage stimulate circulation, enhancing hair growth and strength, said the company.

For those plagued by greasy, clumpy, stiff, dry and dull locks, Bounce Curl's Turmeric Hair Detox Mask is said to be an ultimate



Herbal Essences' sulfate-free Honey & Vitamin B hair care.

treatment to refresh and revitalize overwhelmed hair. Cleansers can easily remove style product residue and pollutants but can also be especially rough for those with curly hair. The Tumeric Hair Detox Mask cleanses, purifies and removes product buildup, according to the indie beauty brand. Key ingredients include organic apple cider vinegar, organic aloe barbadensis leaf juice, charcoal, turmeric, camellia sinesis, chamomile, biotin and vitamin B3. Also new at Bounce Curl is its Ayurvedic Deep Conditioner.

And don't forget dry spray. Bravo Sierra, the wellness brand with a military heritage, introduced a climate-friendly Dry Shampoo that was field-tested and developed based on direct feedback from more than 1,000 active duty military members to ensure it meets the highest performance standard. Rather than using traditional hydrocarbon-based propellants, Bravo Sierra adopted a climate-safe propellant technology from the auto industry to eliminate VOCs within its aerosol makeup. The dry shampoo adds volume and texture, leaving hair looking and feeling thicker. It provides a cooling sensation when sprayed onto the scalp for a refreshing experience and does not leave a white cast so it can be used on all hair colors. Five percent of company revenue is donated to MWR programs, dedicated to improving the quality of life for vets and active duty military members and their families.

WHAT'S OUTSIDE COUNTS, TOO

John Frieda Hair Care recently launched packaging that uses 50% less plastic and reduces product waste. The tube-like-pouch (TLP) was developed and commercialized by Cincinnati-based Kao USA Inc. and has a structure that uses 50% less plastic than John Frieda's current 8.45oz tube, and because the material is ultra-flexible, it allows every last drop of product to be squeezed out. The product

range offered in TLP includes John Frieda Frizz Ease Daily Nourishment shampoo and conditioner and Sheer Blonde Highlight Activating shampoo and conditioner. All are available exclusively for a limited time in select 200 Walmart stores and Walmart.com.

The new packaging at John Frieda follows in step with Kao's Kirei Lifestyle Plan announced in 2019.

P&G Beauty has also unveiled its newest packaging move in the hair care sector that it says is designed to change the way consumers buy, use and dispose of their shampoo bottles. Next year, Head & Shoulders, Pantene, Herbal Essences and Aussie brands will launch a shampoo refill system in Europe with a new reusable 100% aluminum bottle and recyclable refill pouch, made using 60% less plastic (per ml versus standard brand bottle). The announcement was made during a live panel of sustainability experts at the Reuters Responsible Business Summit.

P&G Beauty says it is on track to reduce virgin plastic usage by 50% in shampoo and conditioner bottles by the end of 2021 when, through collective efforts to reduce, reuse and recycle, will result in 300 million fewer virgin plastic bottles being produced yearly.

JPMS is committed to making 10 of its 12 product lines vegan by 2023 and is rethinking its packaging, too.

The company is moving toward 75% post-consumer recycled plastic. It also pledges to plant one million trees by 2022 and remove single-dose plastic by 2023.

COMING UP NEXT

Elements of hygiene will enter the clean beauty conversation in hair care further down the line in 2021, noted industry experts.

"Consumers will be looking for products that are not only clean and sustainable, but also safe and protective," noted Hogan of Kantar.

According to Rivera of L'Oréal Paris, repair continues to be a key trend in hair care. "It's about being able to repair damaged hair from brushing, heating, harsh coloring or even just pollution and friction," she said.

Looking ahead, Pelusi believes shampoos and conditioners will have an ingredient philosophy similar to the diligent health perspective people have now for what they put inside their bodies.

"The vitamin, powder mix supplement and food industries are, in a good way, overflowing with options for people to improve their health," he told Happi. "We believe this mentality will, as it already has, overlap into consumer demand for new ways to improve their health via their hair and scalp."

This inspired Pelusi to create his proprietary Tela Beauty Organics by Philip Pelusi Hair Immunity Complex, a composition of pre- and probiotic enzymes and fermented sea kelp.

"We approach the need for good bacteria to maintain a healthy scalp the same way digestive pre and probiotics do for the gut," he said. "Healthy hair comes from a healthy scalp which requires the right balance of good bacteria. So, the formulation of shampoos and conditioners will be based on a meticulous approach to health as opposed to cosmetic appearance."



BOTTLE YOUR SUSTAINABILITY GOALS

Minimize your environmental footprint with our emollients

Are you interested in meeting consumer's sustainability demands? Contact us to find out how our enzymatic emollients, produced through a unique green chemistry process, can help you.

Our data shows how this eco-efficient process, powered entirely by renewable energy, leads to an improved impact on global warming through a smaller carbon footprint compared to conventional chemical production. Create a skin care product with any skin feel you want using emollients that support climate relief.

www.evonik.com/personal-care



@EvonikPC

@evonikpc





A Clean Commitment

IN A PANDEMIC, CLEAN MATTERS MORE THAN EVER, WHICH EXPLAINS THE GAINS IN FABRIC CARE SALES DURING THE PAST YEAR.

By Tom Branna, Editorial Director

ash your hands for 20 seconds with antibacterial soap, of course, but be sure to wipe down that countertop, too, and, while you're at it, throw another load of laundry in the washer. About a year after consumers around the world heard the term, "coronavirus," the emphasis on clean has touched the very fabric of their lives. Sales of hard surface cleaners, disinfectants and hand sanitizers have soared during the past 12 months, but laundry detergent, bleach and other fabric care formulas have also benefitted from heightened awareness about germs, according to industry observers.

"Detergent and complementary products such as fabric, liquid softeners and dryer sheets increased as detergent increased," said Ellen Chen, research analyst at Euromonitor International. "We've also seen powder detergent and bar detergent increase from previous declines, supporting the fact that more consumers are doing laundry during the pandemic. More specialty products such as fine fabric detergent saw a decline."

In the US, sales of laundry detergent jumped 5.9% to nearly \$8 billion, according to IRI (see chart, p. 52). Euromonitor analysts attribute the gains, in part, to a propensity for overdosing among consumers who tend to use more than is required. Along with a lack of knowledge, even among regular users, this behavior stems from elevated health concerns during COVID-19. In consumers' minds, this follows a straightforward logic that more product will clean more effectively.

But no matter what the reason nor the season, Procter & Gamble dominates the US fabric care category, year-in and year out. Among liquids, P&G brands hold six of the top 10 spots. Within unit dose, Procter's Tide and Gain brands hold eight of

UNIT DOSE DRIVES DETERGENT GAINS

The pandemic has helped lift demand for laundry detergents as consumers realize the value of clean. Here are laundry detergent sales for the 52 weeks ended November 1, 2020 in US multi-outlet (grocery, drug, mass market, military and select club and dollar retailers).

Product	Dollar Sales		Dollar Share of SubCategory		Unit Sales		Price per Unit	
	Current	%Change vs YA	Current	Change vs YA	Current	%Change vs YA	Current	Change vs YA
LAUNDRY DETERGENT	\$7,935,902,156	5.9%			963,094,206	-1.5%	\$8.24	\$0.57
Liquid Laundry Detergent	\$5,780,299,263	5.3%	100.00	0.00	722,876,899	-1.9%	\$8.00	\$0.55
Procter & Gamble	\$3,298,573,668	8.9%	57.07	1.88	335,165,033	3.9%	\$9.84	\$0.45
Church & Dwight Co Inc	\$1,090,410,892	4.3%	18.86	-0.19	178,514,610	-6.6%	\$6.11	\$0.64
The Dial Corp	\$497,419,909	-5.5%	8.61	-0.99	73,295,915	-14.4%	\$6.79	\$0.64
The Sun Prods Corp	\$482,152,947	-9.3%	8.34	-1.34	72,469,375	-16.3%	\$6.65	\$0.51
Private Label	\$150,958,105	5.2%	2.61	0.00	20,212,343	1.2%	\$7.47	\$0.28
Other Laundry Detergent (Packet/Bar)	\$1,634,298,176	11.5%	100.00	0.00	181,556,985	2.5%	\$9.00	\$0.72
Procter & Gamble	\$1,318,410,719	13.6%	80.67	1.53	123,864,698	2.6%	\$10.64	\$1.03
The Sun Prods Corp	\$116,535,164	-6.6%	7.13	-1.38	16,351,449	-14.6%	\$7.13	\$0.61
Church & Dwight Co Inc	\$65,599,979	-7.4%	4.01	-0.82	11,997,924	-13.2%	\$5.47	\$0.34
The Dial Corp	\$56,594,948	50.8%	3.46	0.90	11,777,358	45.5%	\$4.81	\$0.17
Private Label	\$46,975,555	5.3%	2.87	-0.17	5,184,564	-1.3%	\$9.06	\$0.57
Powder Laundry Detergent	\$521,304,717	-4.0%	100.00	0.00	58,660,321	-7.1%	\$8.89	\$0.29
Procter & Gamble	\$374,425,680	-3.3%	71.82	0.52	32,680,985	-6.8%	\$11.46	\$0.41
Fabrica de Jabon La Corona	\$73,479,928	1.3%	14.10	0.75	17,474,646	1.3%	\$4.20	\$0.00
Church & Dwight Co Inc	\$32,552,179	-4.2%	6.24	-0.01	2,781,813	-8.6%	\$11.70	\$0.54
Private Label	\$14,476,500	-0.5%	2.78	0.10	931,624	0.5%	\$15.54	-\$0.16
The Sun Prods Corp	\$9,505,949	-30.2%	1.82	-0.68	1,146,118	-36.0%	\$8.29	\$0.69

Source: Market Advantage TSV; IRI Liquid Data.

the top 10 spots and, even in downtrodden powder, four P&G brands are in the top 10. In an effort to build on that lead, P&G rolled out Tide Hygienic Clean Heavy Duty 10X laundry detergent collection which, P&G maintains, provides an effective odor and stain removal at the microscopic level. Also new at Tide is One Wash Miracle, a premium, liquid detergent that eliminates odor and buildup while removing tough stains in just one wash.

Despite Procter's dominance, other detergent makers insist there is plenty of room for growth. Henkel's North American laundry and home care business grew last year, particularly within the laundry detergent and fabric conditioner categories, according to Patrick Davis, chief marketing officer, US laundry and home care division.

"This is a trend we've seen throughout 2020 as fabric care has become more important during the pandemic with people doing more wash loads or washing clothes more frequently," observed Davis. "Our Snuggle dyer sheets sales, for example, are up both year-over-year and year-to-date."

Consistent category growth has encouraged others to make a go of it in the laundry detergent market. Reckitt Benckiser entered the



Henkel uses a digital influencer program on social media to promote Snuggle SuperCare.

laundry space last year with the introduction of Botanical Origin. RB comes at the category with two differentiators—online-only sales and plant-based ingredients. According to RB, online laundry household penetration increased from 8.1% in 2019 to 25% by the end of November 2020. Of all household products, laundry saw the highest uptick of increase consumption during COVID-19, according to Nielsen data. Botanical Origin is available exclusively through Amazon and a dedicated website. The online-only approach enables RB to validate its proposition and deliver a robust test and learn strategy, according to company executives. By doing so, RB can get quick feedback from consumers and determine the right channel and messaging strategy to its goals.

"Botanical Origin breaks those barriers as we offer plant-based products that really work, without having to pay a premium," said a company spokesperson. "We have seen that the interest for plant-based is still very much there, but the pace of category share growth has slowed from previous years."

Based on internal consumer research, RB expects that as the US recovers from COVID-19 more people will again be comfortable switching to plant-based products and have a mix of conventional and more sustainable options in their homes. Botanical Origin laundry detergent contains 67% USDA-certified biobased ingredients and the Botanical Origin fabric softener is 71% biobased. Both are sensitive, hypoallergenic and dermatologisttested with no dyes, brighteners, parabens, phosphates, artificial preservatives or chlorine.

RB's research found that when it comes to plant-based solutions, there are two key barriers for consumers: 1. The belief that plant-based doesn't work as well as conventional options, and 2. They aren't willing to spend more on plant-based, which is traditionally more expensive. It's early, but so far, RB executives like what they see.

"We're seeing very positive results from consumers as our brand has over a 4.3 average rating on Amazon.com," said the spokesperson. "We're seeing strong growth month-on-month since launch. We expect 2021 to be a key year for educating and encouraging the big change towards plant-based cleaning solutions that really work."

Feedback from consumers has been positive, too. Here's just some of what they had to say:

- "The scent is amazing! I have the lavender scent. I am vegan and have been searching for a sustainable option for detergent that is also effective, and I have finally found it. I will definitely purchase Botanical Origin in the future."
- "This detergent scared me as I hate scent on my clothing. I usually refrain from any scent at all. But this cleaned heavy dirt well. It is heavy scent in the bottle but my bedding, towels, etc. are not heavily scented. I usually get a headache in a matter of minutes. But I did not with this. I will buy it again."
- "Works great for baby's [sic] and adults! My son has sensitive skin, and I mean very sensitive, but this fabric softener doesn't break him out at all. Awesome."

Henkel isn't the only company with an Amazon-only launch. In November, Whirlpool introduced a concentrated liquid laundry detergent called Swash on Amazon. Its foray into the liquid laundry detergent category is an ultra-concentrated (8x) formulation that's said to wash up to 83 regular loads, and can be used in all machines. The packaging comes with "precision pour cap" that dispenses the detergent in a pre-measured dose to limit residue and other buildup in the washer, according to the company.

Why all of the interest from new players? According to Filip Hoffmann-Häußler, senior consultant at Euromonitor International, leading brands performed strongly during 2020 as consumers were willing to spend their money on products they trust. Yet, evidence suggests that consumers have equally started to experiment with new brands.

"When demand surged, some retailers ran out of stock, which resulted in consumers trialing new brands or moving their home care purchases online," explained Hoffmann-Häußler. "This has helped smaller brands and e-commerce pure players to increase their reach, cannibalizing sales of established brands in the market. Private label has also seen strong demand among increasingly price-sensitive consumers. Depending on the severity of the economic consequences deriving from the pandemic as we transition into 2021, this can be expected to continue and intensify as a trend."

Ironically, these COVID-19 consumption drivers are partly

counterbalanced by the effects of home seclusion, as consumers across the world are still exposed to some level of restriction on movement.

"With fewer occasions out of the home and flexible working arrangements in place, dressing up for work or social gatherings has become less common, which is especially true during the months of home seclusion, observed Hoffmann-Häußler.

CONSUMER TRENDS

All the concerns about germs makes consumers less likely to leave heaps of dirty clothes lying about.

"Since the beginning of the pandemic, we've noticed a significant increase in the weekly number of loads consumers are doing, and clothes are being washed more frequently primarily to remove germs and bacteria from household items and to wash clothing after being out in public," observed Davis, who noted, however, the average size of each load is smaller than before, with consumers doing more medium vs. large loads. At the same, time, the Henkel executive said consumers are also taking extra precautions by increasing wash temperatures for additional sanitization and purchasing more sanitizers/bleach products than before. IRI data backs that up; bleach sales soared 33% during the most recent 52-week period.

"Additionally, consumers normally tend to gravitate toward a brand they've tried before when their preferred product is unavailable, however, amid the pandemic, they appear to be more willing to try a brand they've never bought before," he added.

Davis told Happi that it is clear that the pandemic created a major shift in consumer behaviors and attitudes during the past



DTC has been the right business model for Truman's and other startups.



Dropps revamped its packaging to eliminate labels.

several months. He predicted that as the world continues to battle COVID-19 in the US, and consumers continue to use more laundry products, the need for fabric care is expected to grow.

"For example, consumers may increasingly look to products like All Free Clear Clean & Care, which is formulated with keratin and vitamin E to provide extra protection for fabrics," he added.

This shift in behavior has also driven Henkel to rethink how and where it is reaching consumers.

"We have focused more heavily on digital marketing to ensure we're connecting with consumers who are more likely to make purchases online vs. instore during the pandemic," said Davis. "One example of this is the recent launch of Snuggle SuperCare that included a digital influencer program on social media, focused primarily on Instagram."

Euromonitor analysts agree that direct-to-consumer and ecommerce have also significantly increased in popularity during 2020. Multinationals, startups and established players have all found success with the DTC model.

Dropps' sales have doubled every year for the past four years and growth in 2020 was even better, according to Founder and CEO Jonathan Propper. The company moved entirely to DTC four years ago and Propper said getting off the shelf has been Dropps' ticket to success.

"Politicians tell us the system is rigged, but no system is more rigged than retail shelves," explained Propper. "You can build a better mousetrap and offer the best margins, but if you're not big, you're not in the middle of the shelf."

He called Dropps the most concentrated unit dose formula on the market, a concept that consumers readily understand. "Our mantra is 'eliminate the stupid.' It makes no sense to ship traditional liquid laundry detergent across the country to put it in a machine that adds water."

With a plant-based formula that is equal to that of the multinationals, Propper and his team have stepped up their sustainability message, eliminating plastic containers and, most recently, in November, eliminated labels on its compostable cardboard boxes and replaced them with water-based inks.

"There's an issue with labels and biodegradability," he explained. "Using water-based ink reduces costs, saves time, gives us manufacturing flexibility and even acts as a metaphor in that we are getting rid of labels."

Dropps may have been the first startup to challenge the multinationals with unit dose formats and environmentally-friendly formulas, but since then, other marketers have entered the category.

Truman's debuted in 2019, with a line of home cleaning products. It entered the toilet bowl cleaner, laundry detergent and dish care space right as the pandemic was taking hold in the US, but Company Co-Founder Alex Reed called it perfect timing as consumers were adjusting to working-from-home conditions.

A BOOST FOR SUBSCRIPTIONS

"It's odd to say it, but the pandemic has been a tailwind for a subscription-based business," said Reed. "It was always a challenge to sell liquids online, so cleaning products never had a solid foothold in ecommerce, but there's been a big shift to e-commerce for laundry and similar categories."

The pandemic also caused a sharp reduction in acquisition costs, as online advertising costs per impression were cut in half.

"Big companies were boycotting Facebook in the Spring and local restaurants were closed, which created more inventory for companies like ours," explained Reed.

No wonder then, that leading industry players as well as smaller businesses are experimenting with subscription models and auto-replenishment to retain their customer base.

"An increased focus on hygiene has led to a heightened level of competitiveness among FMCG players, as well as appliances companies who seek to benefit from an increased demand for hygiene by selling their own laundry detergents," explained Hoffmann-Häußler. "This will further proliferate with an increased household penetration of connected washing machines that come with auto-dosing functionality."

Propper says he's not concerned about competition from multinationals or startups.

"We're in a very big market that's growing 6% a year, and a market that size can float all boats," he insisted.

Sapadilla Soap Company maintains that its point of differentiation is its 100% pure blend of essential oils. According to Melanie Blumenthal, manager of digital, social and public relations, that aspect of the brand connects with consumers who are looking for premium products that are free of artificial colors or fragrance.

"We just conducted some consumer research and found that

our audience is in the 35 to 65 age range," noted Blumenthal. "We had thought the age would skew younger, but in today's climate it makes sense because people are looking for more natural formulas."

MORE NEW PRODUCT DEVELOPMENT

Despite the uncertainty surrounding the pandemic, Henkel launched several fabric care products through its various brands this year. For example, the Snuggle's SuperCare line is built off the success of its sister line, SuperFresh, according to Davis. The new line focuses on providing superiority in fabric and color care protection to consumers, which is underlined by the line's key message, "Keeps Clothes Looking Newer Longer."

Also new is a Free Clear Clean & Care line through the All brand. It uses a new fabric formula with keratin and vitamin E to help smooth fibers and promote elasticity. Similar to All's other products, Free Clear Clean & Care is 100% free of perfumes and dyes, and hypoallergenic helping to make clothes feel comfortable on sensitive skin.

In terms of eco-friendly products, Henkel introduced an All eco variant that provides the same cleaning power of its regular All detergent, but with a 99% bio-based formula and at a mid-tier price point. That introduction dovetails with current trends in the market, say analysts.

"Interestingly, a lot of new products are natural ones that focus on ingredient transparency and bio-based formulas, such as RB's Botanical Origin; natural scents, like Gain's Essential Oil, and Henkel's new All Vitamin E detergent," explained Chen of Euromonitor. "Consumers are seeking additional benefits to their products, and manufacturers are trying to differentiate themselves by adding natural fragrances and fabric conditioning."

That search for natural, or at least better-for-the-planet options, transcends formulations and includes interesting packaging options. Packaging and formats of products such as powder detergent (Blueland), refillable (Blueland and Cleancult), compostable packaging (Cleancult), and more concentrated formula (Seventh Generation).

"P&G has been doing really well, especially with their Tide brand. They are dominating within the laundry tablets category, especially as consumers typically associate pods with Tide pods, similar to Kleenex and tissue," Chen said. "P&G's success demonstrates how consumers have been turning to familiar brands that they trust to do the job."

ACI IN ACTION

The current crisis hasn't just impacted how consumers clean clothes and how soapers sell products. The pandemic is reshaping how industry associations conduct business. This issue of Happi includes coverage of online annual meetings of the Household and Commercial Products Association (p. 58) and the Society of Cosmetic Chemists (p. 73). This month, it's the American Cleaning Institute's chance to step up to the monitor for its virtual summit, which will take place April 25-29. In an interactive twist, ACI is planning six informal hot-topic discussion sessions moderated by industry peers with attendees as the panelists. Registrants are invited to suggest or vote for topics, which will be announced this month.

Other sessions will include how the supply chain responded to COVID-19, the latest in sustainable packaging, a global industry update, a look at emerging technology and of course, the State of the Association address by ACI President and CEO Melissa Hockstad, who noted that throughout 2020, ACI was in contact with federal, state and local legislators on a host of issues.

"In New York, we are consistently working to ensure that implementation of its 1,4-dixoane law will not lead to the clearing of retail shelves of safe and effective cleaning products," Hockstad explained. "At the federal level, ACI has urged the Environmental Protection Agency to consider the fact that 1,4-dioxane was a manufacturing byproduct."

Those efforts paid off last month when EPA issued a supplemental draft risk evaluation of 1,4-dioxane, which found that regular use of surface cleaning, laundry, dishwashing and, general purpose cleaning products does not pose an unreasonable risk to consumers.

In New York, ACI is working with the Department of Environmental Conservation to get a clear understanding of the product sell-through process, when the ruling goes into effect on Jan. 1, 2022. In related news, ACI is keeping an eye on New Jersey, where concerns have been raised regarding 1,4-dioxane levels in drinking water.

Key issues that ACI continues to work on include ingredient communication, where ACI is calling for a federal policy to govern cleaning product communication through virtual meetings and briefings with members of Congress and their staffs.

Another area of work for ACI is on the issue of topical antiseptics. The US Food and Drug Administration continues to acknowledge the in-depth research that's been undertaken by ACI and its members through the years.

"The Agency actually told us, and I quote, 'FDA believes that ACI continues to demonstrate its ongoing progress in conducting the necessary safety and efficacy studies.' It's really important to get that type of feedback from FDA," explained Hockstad.

These multiyear research projects are critical to ensuring that antiseptic products that contain these important ingredients remain available to the consumer, commercial and health care marketplaces, she added.

"That's so critical especially now, with what is going on in the world today."

To keep its members updated about all of these activities in a pandemic, the Association launched a series of webinars called ACI Presents which covers topics such as FDA's temporary changes to hand sanitizer rules, EPA updates and the Association's partnership with the Centers for Disease Control.

"It enables our members to stay up-to-speed on things in a

virtual format," concluded Hockstad. "The webinars have been well-received and something that we will be continuing in 2021."

At press time, ACI had conducted five webinars and had more than 2,000 attendees. Clearly, online is on-target, for associations, for marketers and their suppliers, both now and for the foreseeable future.

WHAT'S NEXT

How soap companies plan to address the future varies, of course. For example, Truman's continues to eye new categories in the new year, but Reed is understandably cautious.

"In 2021 we are going to be careful," he told Happi. "One mistake is expanding too fast. For us, our market penetration gives us so much runway, but we want to pick our spots. We are working on some new categories, but I can't promise when we will launch them."

Meanwhile, RB is new to the laundry category, but the company is working on developing more online friendly formats such as unit doses and concentrates to better serve its online customers.

According to Chen of Euromonitor, antibacterial claims are becoming more important, but there could be more awareness raised among consumers about more specialty products like fabric sanitizer.

"In the US, consumers still believe that clean clothes is hygienic enough," she added.

But whatever the format, the emphasis will be on clean for years to come. Chen's colleague, Hoffmann-Häußler observed that hygiene and healthy living were integral components of many consumers' lives prior to COVID-19, with strong links to urbanization and global warming. The latter resulted in sustainability moving to the center of attention, accelerated by the media, governments, consumers and manufacturers. Going forward, he expects efficacy will continue to be a key driver of consumer decisions, especially when "normal" life begins to resume.

"While sustainability will continue as a long-term shift, consumers are less likely to be willing to compromise on cleaning performance. The strong performance of bleach, home care disinfectants and laundry sanitizers in 2020 bears testimony to this shift in priority," he explained. "This contrasts with the direction in which the industry had started to move over recent years, with a clearly defined trend toward gentle, eco-friendly and non-toxic ingredients. Manufacturers are well advised to build this new understanding into their R&D thinking as we transition to the new normal."

As a result, he expects sustainability will likely be addressed through new packaging formats, compaction, refills to combat plastic waste and broader environmental and social sustainability campaigns. Take RB, for example, which aims to reach 100% post-consumer recycled plastic use for Botanical Origin by 2022 and by 2025 launch new, renewable packaging.

"You'll see a lot of headlines in the home cleaning space in 2021," Reed predicted. "There is a lot of investment in startups, and there will be more activity, more innovation and more M&A. There is a lot of excitement to come."