The Presidential Green Chemistry Challenge Awards Program:
Nomination for 2012 Award

NATRASURF™ PS-111 polymeric surfactant: Achieving next generation mildness in personal care products with a reduced environmental footprint

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Most recent milestone: As of January 2011, Johnson & Johnson Consumer & Personal Products Worldwide (Johnson & Johnson), in partnership with AkzoNobel Surface Chemistry (AkzoNobel), has completed development and commercial scale-up of the NATRASURF™ PS-111 polymeric surfactant. The first products utilizing the PS-111 technology, the AVEENO® Pure Renewal line of shampoos, will launch in December 2011, and product development for launches under other Johnson & Johnson brands is ongoing for 2012 and beyond.

TSCA Statement: As a cosmetic ingredient regulated under the FFD&C Act, PS-111 is currently TSCA exempt.

Award category: The nominated technology is not eligible for the small business or academic awards.

Focus area: NATRASURF™ PS-111 is being nominated for Focus Area 3, *The design of greener chemicals*.

Work conducted in the United States: All aspects of NATRASURF™ PS-111 ideation, research, development, scale-up, and manufacture have taken place in the U.S. The technology is a collaborative effort involving multiple U.S. locations of Johnson & Johnson and AkzoNobel.

1. Abstract

The production of personal cleansing products, such as shampoos, body washes, and facial cleansers, consumes sizable and ever-increasing volumes of surfactants. Intended for human contact, these products must be carefully formulated to ensure that they are gentle and nonirritating, yet they must still deliver consumer acceptable performance and aesthetics. The classical approach for achieving the mildness associated with personal cleansers involves the use of petroleum-derived synthetic detergents which are largely nonrenewable. While these well-established surfactants are safe and cost-effective, there are still opportunities for innovative improvements in mildness, renewability, manufacturing processes, and biodegradability.

Johnson & Johnson and AkzoNobel have collaborated to develop NATRASURF™ PS-111, an innovative, starch-based polymeric surfactant (PS) for the formulation of mild personal care products. PS-111 is based on the patented discovery that PSs overcome the problem of surfactant-induced irritation because they lack the ability to penetrate into living tissue. NATRASURF™ PS-111, the first ever personal care ingredient of its kind, delivers the performance of traditional surfactants (e.g. cleansing and foaming) with the added benefit of virtually no irritation potential.

The development of NATRASURF™ PS-111 was guided by green chemistry principles to produce an ingredient that minimizes environmental impacts throughout its life cycle. PS-111 is a 90% renewable material derived from the reaction of hydrolyzed potato starch with an alkenylsuccinic anhydride. This low temperature, aqueous esterification process offers many advantages over traditional esterification routes, including energy efficiency and atom economy. The starch ester chemistry used for PS-111 is nonirritating to skin and eyes, nonallergenic, nontoxic to humans and aquatic organisms, nonbioaccumulative, and is readily biodegradable.

PS-111 is supplied to manufacturers as a self-preserving, spray dried powder, which eliminates the need for chemical preservatives and reduces the energy demand associated with the respective storage and shipping of conventional aqueous surfactant solutions.

PS-111 has the potential to revolutionize personal cleansing while eliminating the use of millions of pounds per year of nonrenewable and poorly biodegradable surfactants and emulsifiers. Furthermore, this technology can be readily leveraged for use in agricultural, household, and industrial product formulations and applications. NATRASURF™ PS-111 exemplifies how green chemistry can enable cost-effective, sustainable materials that benefit both consumers and the environment without sacrificing performance or efficacy.

2. Health and environmental issues associated with personal cleansing products

The most critical benefit of personal cleansing is the reduction of disease transmission and infection that accompanies good personal hygiene. Cleansing also provides a variety of important physical and emotional health benefits, such as improved skin health and personal appearance. Thus, in both developed and emerging markets around the world, consumer demand for personal cleansing products continues to increase, driving the development of new and innovative products. Consequently, surfactant production and usage continues to expand to meet this ever-increasing demand. Although personal cleansing with surfactant-based products provides many health benefits to consumers, such product usage is not without health and environmental consequences.

Health concerns and the need for mild cleansers: During cleansing, surfactants can adsorb onto and diffuse into the skin and damage its structure by denaturing proteins, disrupting and disorganizing lipid bilayers, and solubilizing and removing lipids.[1] Surfactants in contact with the skin can cause damage to the skin barrier and increase transepidermal water loss, leading to symptoms such as tightening of the skin, dryness, roughness, and scaling.[2] Prolonged damage of the skin barrier and underlying epidermal tissue may elicit an inflammatory response in the skin, resulting in symptoms that include erythema and pruritis. This combination of barrier damage and inflammation are collectively referred to as *irritation*, and surfactants can exhibit significant irritation potential if they are not properly designed and formulated for personal care applications.

Continual improvement of mildness is a key imperative in the design of personal cleansers. The ultimate goal is to provide consumers with aesthetically-pleasing and efficacious products that adequately remove dirt, sebum, and pathogens without presenting an irritation hazard to the skin, eyes, or mucosa. However, more often than not, key performance attributes, (e.g. lathering and cleansing), may suffer at the expense of maintaining mildness.

Environmental concerns: From an environmental perspective, the high volume usage of surfactants in cleansing products is of special concern, as virtually all of these chemicals will ultimately be discharged into wastewater upon product usage (i.e. rinsed down the drain). Surfactants with poor biodegradability should be excluded from cleansing products to prevent the build-up of environmentally-persistent and potentially toxic compounds in the ecosystems where wastewater is discharged. Additionally, because surfactants are high production volume chemicals, any negative environmental impacts of the processes and waste streams associated with their production will carry significant consequences. Thus, it is critical that personal cleansing formulations and their surfactant components be designed to have minimal environmental impact throughout their life cycles.

3. Polymeric surfactant (PS) technology for improving mildness

The development of innovative technologies for mild cleansing remains a key R&D initiative at Johnson & Johnson to ensure continued success as a market leader in personal cleansing products under brands that include JOHNSON'S® Baby, AVEENO®, and NEUTROGENA®.

Inspired by the *micelle penetration model* of surfactant irritation proposed by Moore et al,[3] researchers at Johnson & Johnson have pioneered the control of micelle penetration as a new approach to formulating mild cleansers.[4] To attain new levels of mildness in cleansing products, the team envisioned a class of nonpenetrating surfactants made possible by covalently linking surfactant molecules together to form PSs.

Accordingly, Fevola et al.[5] demonstrated that PSs can be used to achieve tremendous improvements in mildness over conventional small molecule surfactants via a *hydrodynamic size exclusion* mechanism. Due to the polymeric nature of these molecules, PSs and PS micelles are too large to penetrate into tissue and cause irritation, rendering them extremely benign. However, PSs still provide the same benefits as conventional surfactants, such as cleansing and foaming. PSs can also be formulated with conventional surfactants to form larger mixed micelles that demonstrate improved mildness over traditional surfactant blends. In fact, PSs are perhaps the gentlest foaming surfactant ingredients ever developed, and PS technology represents the most significant innovation in mild cleansing since the introduction of No More Tears® formulas by Johnson & Johnson in 1959.

To initially enable their invention and prove the concept of PSs as ultra-mild, nonpenetrating surfactants, Johnson & Johnson researchers relied on synthetic PSs derived from the polymerization of ethylenically unsaturated monomers sourced from petrochemical feedstocks.[5] Although such PSs proved to be extraordinarily nonirritating and provided adequate foam performance, these materials were deemed unsuitable for commercial application because they were nonrenewable and not readily biodegradable. Therefore, to responsibly commercialize PS technology for application in consumer products, the Principles of Green Chemistry[6] were employed to guide development of an affordable, renewable, and environmentally safe PS ingredient.

4. Green chemistry for the commercialization of PS technology: NATRASURF™ PS-111

Following a comprehensive review of many possible chemistries, the production of PSs via modification of naturally-occurring polysaccharides was identified as the "greenest" and most commercially feasible route. The most critical design criterion for NATRASURF™ PS-111 was ingredient safety, and a key factor in selecting modified starch chemistry for commercialization was the acceptability of analogous chemistries for use in food applications,[7] which indicated a low risk of toxicity from the onset of development. To complete development and commercialization of the new technology, Johnson & Johnson established a partnership with AkzoNobel, a worldwide leader in starch chemistry. The result of the companies' joint development efforts is NATRASURF™ PS-111 (INCI[*] Name: *Sodium Hydrolyzed Potato Starch Dodecenylsuccinate*), the first PS ingredient of its kind designed for personal care applications (Figure 1).[8]

[*]International Nomenclature of Cosmetic Ingredients

NATRASURF™ PS-111 is a low molecular weight (MW) hydrolyzed potato starch that is homogeneously substituted with hydrophobic dodecenylsuccinate ester groups to provide surface-activity. The novel physical properties of PS-111 were achieved via identification and precise control of multiple design factors (e.g. starch source, hydrolyzed starch MW and MW distribution, hydrophobic carbon chain length, and degree of hydrophobic substitution) to yield a proprietary PS having high surface and interfacial activity, high foaming, high solution clarity, low color, low solution viscosity, and most importantly, maximum mildness.[8]

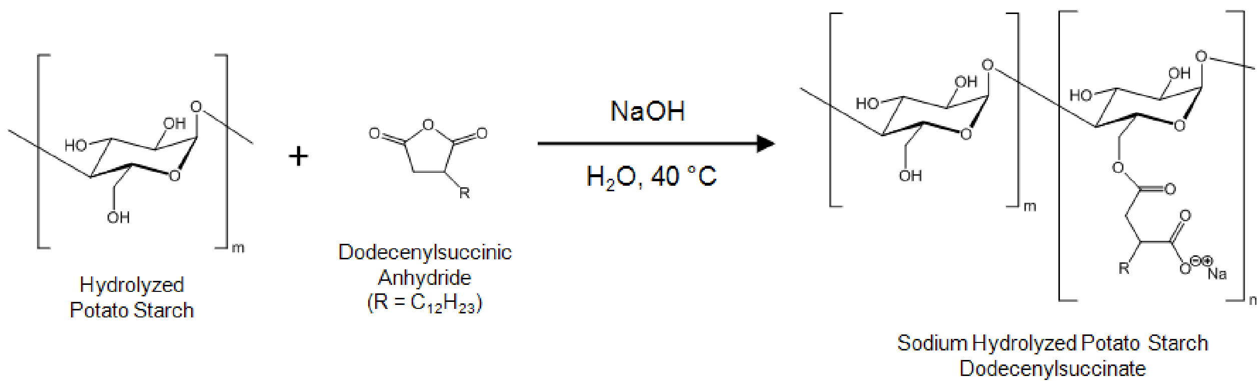

Figure 1. Synthesis of NATRASURF™ PS-111, Sodium Hydrolyzed Potato Starch Dodecenylsuccinate.

Table 1 summarizes the alignment of PS-111 and its manufacturing process with key principles of green chemistry. The starch ester chemistry was selected for its high renewable content (90 wt%) and for rapid biodegradation via enzymatic cleavage of the α-(1→4)-*D*-glucosidic and dodecenylsuccinate ester bonds. Figure 1 depicts the synthetic route used to manufacture PS-111. This one-step, base-catalyzed process utilizes a highly-activated cyclic anhydride reagent for esterification, enabling a low temperature, solvent-free, and atom economical derivatization of the starch precursor in near 100% yield. Real-time monitoring and in-line process controls enable precise control of reaction conditions (temperature, pH, and reagent addition rate) to favor esterification and minimize hydrolysis of anhydride reagent and starch ester product. The anhydride route offers many benefits over other esterification routes, which suffer from critical drawbacks. For example, the direct condensation of fatty acids with starch under heat and vacuum 1) requires higher energy input, 2) results in heterogeneous substitution of the starch, and 3) is accompanied by significant degradation of the starch, whereas the reaction of starch with fatty acid chlorides requires toxic, corrosive reagents (e.g. PCl_3 or $SOCl_2$) to generate the acid chloride intermediates, requires organic solvents, and produces stoichiometric amounts of undesired NaCl as a byproduct.

An important feature of PS-111 is the ability to supply the material as a spray dried powder. The spray drying process reduces the shipping weight of PS-111 by up to 70%, which reduces the fuel consumption and emissions associated with transportation of the material. Also, PS-111 powder is self-preserving due to its low water activity, eliminating the need to add preservative chemicals to the ingredient for shipping and storage. Nevertheless, PS-111 powder readily dissolves in water at ambient temperature (20 – 25 °C) due to its low MW and hydrophilic character, allowing for "cold" processing upon compounding into formulations.

NATRASURF™ PS-111 has undergone comprehensive safety and toxicological testing, and the results confirm that PS-111 is perhaps the gentlest surfactant ever employed at Johnson & Johnson. In over 50 years of evaluating eye mildness, Johnson & Johnson had never tested a surfactant as benign to the eyes as PS-111. When evaluated in the transepithelial permeation assay, an in vitro alternative to the Draize rabbit eye model, PS-111 proves completely nonirritating and significantly better than the mildest known surfactants. Furthermore, PS-111 does not elicit eye sting or redness when tested in human volunteers, and it is as gentle to the eyes as pure water.

Table 1. Alignment of NATRASURF™ PS-111 technology with key principles of green chemistry.

Principle	NATRASURF™ PS-111 attributes
Pollution prevention	• PS-111 starch ester is inherently non-PBT and readily biodegradable
Design for degradation	
Atom economy	• Noncondensing esterification via anhydride route does not produce stoichiometric small molecule byproducts • All reactants incorporated into PS-111 product – no separations required
Design safer chemicals	• Nonirritating to skin and eyes, nonallergenic; does not penetrate skin barrier • Nontoxic to aquatic organisms and readily biodegradable • Delivers benefits of small molecule surfactants without associated irritation
Safer solvents and auxiliaries	• Aqueous process, no organic solvents • PS-111 powder is self-preserving and does not require addition of chemical preservatives
Design for energy efficiency	• Esterification via exothermic anhydride route – low temperature (ca. 40 °C), ambient pressure reaction requiring minimal heat input • PS-111 supplied as spray dried powder to reduce fuel consumption and emissions associated with transportation and storage • Powder dissolves in water at ambient temperatures for "cold" processing
Use renewable feedstocks	• 90 wt% of molecule is derived from potato starch • Potential for 100% renewable feedstocks once bio-based sources of maleic anhydride and dodecene become commercially-viable
Reduce derivatives	• One-step reaction, no intermediates or protecting groups
Real-time analysis for pollution prevention	• Real-time monitoring and in-line controls optimize process conditions to favor esterification and minimize hydrolysis
Inherently safer chemistry for accident prevention	• Esterification via anhydride route does not require high heat and vacuum • Safer, easy-to-handle reactants and products; no organic solvents

PS-111 is also extremely mild to skin. When tested in the EpiDerm™ in vitro skin equivalence model and in exaggerated patch studies on human volunteers, the results for PS-111 were identical to those of deionized water controls, and PS-111 proved significantly less irritating than the leading commercial benchmarks for mildness. In vitro genotoxicity testing in the Ames model confirmed that PS-111 is nonmutagenic, and PS-111 proved to be nonallergenic in the human repeated insult patch test (HRIPT) model. Additionally, an in vivo skin penetration model using Raman confocal microscopy was employed to demonstrate that PS-111 does not perturb the skin barrier, a strong indication that the molecule is unable to penetrate the stratum corneum of the skin. Indeed, PS-111 is so benign that it can be left on the skin without fear of irritation, allowing it to be used in water-conserving "rinseless" cleansers (e.g. disposable wipes) and as an emulsifier for leave-on products (e.g. creams and lotions).

NATRASURF™ PS-111 also demonstrates exceptional environmental safety. The starch ester chemistry of PS-111 inherently minimizes its risk of being a persistent, bioaccumulative, and toxic (PBT) compound, rendering it ideal for use in rinse-off cleansing applications. PS-111 meets the criteria for ready biodegradability defined by OECD 301B, achieving 84% aerobic degradation in 28 days. Given its extremely high water solubility, negative log K_{ow} (oil-water partition coefficient), and propensity for enzymatic degradation, PS-111 does not present a risk of bioaccumulation. PS-111 is nontoxic to aquatic organisms, exhibiting EC_{50} values of >100 mg/L in both invertebrates (*Daphnia magna*) and algae (*Desmodesmus subspicatus*).

5. Life cycle considerations and benefits of applying green design principles

In a recent case study of 12 polymeric materials, Tabone et al.,[9] demonstrated a qualified positive correlation between adherence to green design principles and a reduction of environmental impacts of production. They also concluded that atom economy in particular is an indicative predictor of low life cycle environmental impacts. Based on these findings, NATRASURF™ PS-111 is expected to provide many positive impacts over its life cycle and across the value chain; these benefits are summarized in Figure 2.

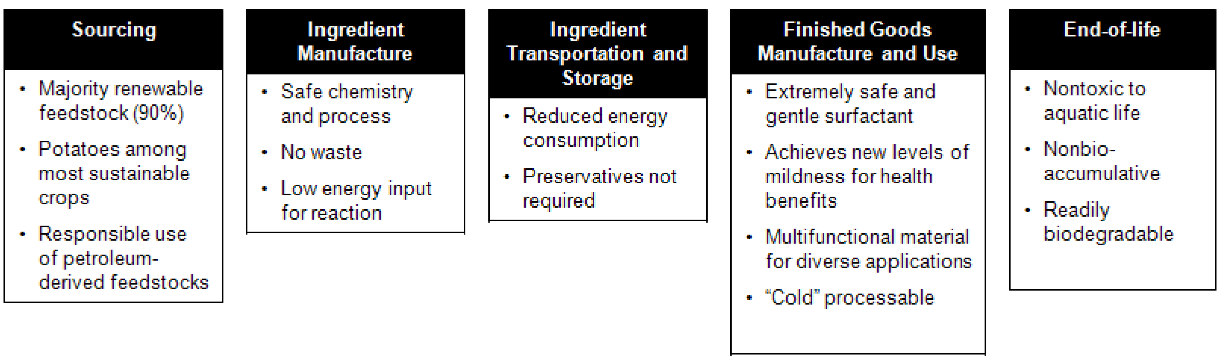

Figure 2. Positive impacts of NATRASURF™ PS-111 across the product life cycle.

Given the novelty of the NATRASURF™ PS-111 polymeric surfactant, a full life cycle analysis (LCA) of PS-111 is presently beyond the scope of this nomination due to a paucity of data and the absence of suitable competitive technologies for benchmarking. Additionally, the use and end-of-life stages for products containing PS-111 will vary dramatically depending on product formulations and applications (e.g. rinse-offs vs. wipe-offs/leave-ons), further complicating any full LCA at this time.

Those familiar with the principles of green chemistry and engineering will recognize that trade-offs are an unavoidable aspect of designing new chemicals. Landis and coworkers[9, 10] have shown that the most critical trade-offs associated with biobased materials is that their benefits, such as decreased fossil fuel consumption and reduced global warming potential, may come at the cost of 1) environmental impacts, including eutrophication and eco-toxicity due to fertilizer and pesticide usage, respectively, and 2) increased energy usage and waste generation from the conversion of biofeedstocks into intermediates and then to polymers. They concluded that the use of renewable resources must minimize these trade-offs to have a positive impact on the material life cycle.

NATRASURF™ PS-111 effectively minimizes such trade-offs in several ways. In terms of agricultural production, current practices in sustainable potato farming have enabled producers to significantly reduce fertilizer and pesticide usage,[11] and the starch precursor for PS-111 is derived from non-genetically modified (non-GMO) potatoes that are compliant with the pesticide minimal risk levels (MRLs) for food grade potatoes. Additionally, potatoes require less irrigation compared to other crops (e.g. corn),[12] and are thus preferable in terms of water conservation. In terms of chemical processing, unlike most biobased polymers, PS-111 is based directly on the naturally-occurring polymer (starch) and does not require biological or chemical conversions of the starch into monomers for subsequent polymerization reactions; thus, PS-111 conserves energy and reduces waste generation relative to other biobased materials.

6. Conclusion

NATRASURF™ PS-111 is a polymeric surfactant that delivers unparalleled mildness with reduced environmental impact and greater sustainability compared to traditional surfactants. To promote long-term sustained acceptance of this technology in the marketplace, emphasis was placed on delivering superior properties and performance, while simultaneously improving material and energy efficiencies and reducing environmental footprint, all within a cost structure that is competitive with current mild surfactants for personal care. However, the applications of PS-111 are not limited to personal care, and it is envisioned that this transformational technology will be leveraged for the formulation of products in the home care, industrial/institutional sanitation, and agricultural chemical markets, including products geared toward the US EPA's Design for the Environment (DfE) program.

7. References – please click on underlined hyperlinks for further information

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