Surfactants and Detergents Interest Area
Technical Program Abstracts

Table of Contents

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S&D 1: Chemical and Surfactant Enhanced Oil Recovery (EOR)

Chairs: U.P. Weerasooriya, University of Texas, USA; and S.K. Kiran, CESI Chemical, Canada

Propoxylated Anionic Gemini Surfactants as Model Compounds for Enhanced Oil Recovery. J. Cai, K.A.N. Upamali, S. Rajapaksha, D.S.P. Lansakara-P, U.P. Weerasooriya, and G.A. Pope, Center for Petroleum & Geosystems Engineering, University of Texas at Austin, USA.

A series of new propoxylated anionic Gemini surfactants were synthesized with different anionic groups, different length of PO group and linking spacer group. These compounds can be scaled up commercially to meet the demands of petroleum industry and the cost of them was competitive compared to commercial surfactants. With two hydrophilic head groups introduced into the structure, the propoxylated anionic Gemini surfactants showed high water solubility in high salinity environment. The CMC values of these molecules were three orders of magnitude lower than those single chain surfactants, which showed the potential of utilizing these surfactants at low concentrations. The optimal salinity (minimum IFT condition) ranged from 70,000ppm to 210,000ppm TDS for the products tested. Microemulsion phase behavior experiments were carried out for different crude oils with propoxylated sulfate Gemini surfactants. Gemini disulfates can generate good synergy with single chain sulfate or carboxylate surfactant to emulsify crude oils with ultra-low IFT. The ASP coreflood was performed by producing 91.3% of the waterflood residual oil saturation. The final oil saturation was about 0.025. The Gemini disulfates retention was low (0.042mg/g). The experiments show the possibility that anionic Gemini surfactants can replace internal olefin sulfonates as a new major surfactant in EOR study.

Latest Developments in Chemical Enhanced Oil Recovery. U.P. Weerasooriya, G.A. Pope, and K.A.N. Upamali, University of Texas at Austin, USA.

New technologies have been developed to meet the needs of challenging reservoir conditions. High temperatures and high salinities along with high hardness levels are among these challenges. New surfactants and co-solvents have been developed to improve the oil recovery with reduced loss of chemicals due to retention. Cost effective commercial production of these chemicals will also be discussed.

Improved Handleability of High Active Internal Olefin Sulfonates for Enhanced Oil Recovery Through the Use of Viscosity Modifiers. T.E. King[1], H. Huh[1], L.E. Pretzer[1], M.J. Doll[1], and J. Barnes[2], [1]Shell Global Solutions (US) Inc., USA, [2]Shell Global Solutions International B.V., The Netherlands.

Internal olefin sulfonates (IOS) are anionic surfactants that are being used in chemical enhanced oil recovery projects. Highly concentrated versions exhibit non-Newtonian rheological behavior and very high viscosities, up to several million centipoise at near zero shear and 20°C. These properties pose challenges when transporting to and handling and solubilizing at field injection facilities. These challenges are addressed with the incorporation of viscosity modifiers. Several viscosity modifiers were evaluated. All surfactants tested had an active matter greater than 65wt% and varied nominal carbon chain lengths ranging from 15 to 32. This paper examines the impact on the rheological properties at different temperatures with the addition of the modifiers. Aqueous solubility and phase behavior tests results on select samples to verify no negative impact with the addition will be presented. For the case of an IOS 20-24, a significant viscosity drop at the same temperature and shear rate was observed. The material went from a paste-like to a more liquid-like consistency that resulted in a shift from non-Newtonian to Newtonian-like behavior with no impact on performance. The overall net benefit includes ease of handling, reduced transportation cost, and improved logistical operations in managing the field injection facilities and requirements.

Evaluating Surfactants Using Potentiometric Titration. L.B. Carey, Metrohm, USA Inc., USA.

Surfactants are added into many industrial applications to improve surface chemistry functions such as emulsification, lubricity and foaming. Development of surfactants with improved capabilities leads to more complex matrices that are often difficult to evaluate. Concentrations of anionic, cationic and nonionic surfactants vary across the many formulations of products made for the pharmaceutical, detergent or cosmetic industry. In this talk, learn how to best use potentiometric titration to evaluate surfactants in a wide variety of samples.

Multi-walled Carbon Nanotubes in Enhanced Oil Recovery: Part I. Surfactant Carriers. C. Chen, M.J. Kadhum, B.J. Shiau, and J.H. Harwell, University of Oklahoma, USA.

Purified multi-walled carbon nanotubes (MWNT) exhibit unique and attractive properties for applications in oil production. The combination of their large specific surface area and the strong affinity toward surfactants makes them candidates for delivering surfactant deep inside the reservoir. In field applications, surfactant flooding may not be an economic EOR alternative due to excessive surfactant adsorption losses onto the rock matrix. To overcome this, we propose injecting MWNT as carriers for surfactant, so that the surfactant can reach the O/W interface, where it will lower the O/W interfacial tension, enabling release of oil while mitigating surfactant losses.

As a proof of concept a binary surfactant system (an ethoxylated alcohol and a propoxylated alcohol sulfate) was successfully developed targeting a model crude in 10% brine.

This binary system not only exhibits ultralow interfacial tension for a model crude (i.e., 0.007mN/m), but also maintains a stable MWNT dispersion.

Surfactant-loaded nanoparticles injection results in higher oil recovery in sand pack experiments as compared to a surfactant-only system. Results also indicate the strong interactions between MWNT and surfactant hydrophobic tails can drastically alleviate the attraction between the rock surfaces and the surfactant, implying great potential in improvement of total recovery using low surfactant concentrations.

Characterization of Guerbet-based Alkoxylate Sulfates for EOR Application. T. Nguyen, C. Stoute, G. Russell, L. Matheson, and G. Trahan, Sasol Performance Chemicals, USA.

Heavy alcohol Guerbet-based alkoxy sulfate extended surfactants with high number of propoxy (PO) and ethoxy (EO) units were evaluated for use in EOR applications. This research focuses on characterizing these surfactants by their characteristic curvatures (Cc) based on the hydrophilic/lipophilic deviation (HLD) concept. C28 Guerbet alcohol-based alkoxy sulfates were made with different PO/EO ratios. The effect of the PO/EO ratio on the Cc value was evaluated. In addition to Cc values, the ability of these surfactants to reduce the interfacial tension and solubilize various oils, including crude oil, was also investigated. This research determined the contribution of adding each unit of PO and EO to the Cc value of the surfactant. The finding is useful in designing surfactant molecules that are desirable in chemical EOR formulations under a certain reservoir temperature and salinity conditions.

Single-well Surfactant Flooding in Extreme Total Dissolved Solids Conditions. M. Budhathoki, S. Bang, S. Wang, L. Jin, B. Roberts, A. Jamili, J.H. Harwell, and B.J. Shiau*, University of Oklahoma, USA.

Field-pilot surfactant flooding was executed in a single-well test at a location in northwestern Oklahoma. The challenges of formulating in a heavy brine (total dissolved solids of 301,710mg/l) were overcome using a surfactant and co-surfactant system exhibiting robust phase stability while producing ultra-low IFT microemulsions. Based on encouraging laboratory results, an *in situ* partitioning tracer test and a single-well surfactant test were designed to verify the extent of oil mobilization under reservoir conditions, at a total depth of 5866ft, rock permeability of 750 minidarcy, and temperature of 125°F. In the field test, a binary surfactant-only system, comprised of an alkyl alkoxy sulfate and an alkyl ethoxy sulfate, was injected as the chemical slug. Ethyl formate was used as the partitioning tracer together with other short-chain alcohols to assess the oil mobilization. Laboratory optimization tests showed that keeping the chemical slug size constant and increasing surfactant concentration increases overall oil recovery. The field injection protocol involved a 0.5PV surfactant slug at 0.5wt%, which gave 41% oil recovery based on the sand pack study. Numerical simulation was applied to interpret the field data collected. The results show 73% reduction in the residual oil saturation near the well bore, demonstrating the efficacy of this surfactant-only system in an ultra-high TDS brine.

Developments in Flowback and Hydrocarbon Production Enhancement in High Temperature and TDS Environments in Hydraulic Fracturing. L. Do, A. LaBlanc, K. Harkness, and B. Mueller, Nalco Champion—An Ecolab Co., USA.

During hydraulic fracturing, a large amount of aqueous fluid is introduced into the formation. This fluid becomes trapped within the fracture and formation, experiencing high temperature (e.g., 300°F) and/or accumulating large amount of total dissolved solids (e.g., 300,000ppm) from the formation. This process, which can include lengthy shut-ins, leads to fracture conductivity damage via mechanisms such as water blockage and fines migration. This damage can be mitigated by the use of flowback aids which are stable to these conditions, enhancing fracture clean-up and thereby hydrocarbon production.

This paper presents the development of flowback aids, consisting of surfactants and microemulsion packages, which are effective for fracture clean-up and production enhancement under harsh conditions. The optimized surfactant systems were formulated into microemulsions with plant-derived oils to evaluate the possibility of an added advantage of microemulsions over surfactant systems. The results showed that the optimized flowback aids packages attained ultralow interfacial tension values with both Bakken crude oil and Eagle Ford condensate over an extended period of time and over a wide range of temperature and TDS values. The developed flowback aids can be used for fracturing or refracturing with high TDS produced waters.

Some Key Features to Consider When Studying Acrylamide-based Polymers for Chemical Enhanced Oil Recovery. A. Thomas[1], N. Gaillard[1], C. Favéro[1], and S. Dufour*[2], [1]SNF Floerger, France, [2]SNF HC, USA.

Among Chemical Enhanced Oil Recovery methods, polymer flooding is a straightforward technique with a long commercial history and proven results. It consists of injecting polymer-augmented water to improve the sweep efficiency in the reservoir and provide mobility control between the water and hydrocarbons. However, implementing successfully a polymer flood in the field requires specific know-how, to avoid polymer degradation and associated viscosity loss. The first stage begins with the proper selection of polymer for the reservoir, which is highly dependent on water quality, temperature, permeability and the presence of contaminants. The next step is the design and selection of equipment for the dissolution and ultimately injection of the polymer solution into the reservoir. The goal is to allow for adequate hydration, maturation and transport of the solution, while

avoiding any type of degradation that can occur either chemically or mechanically.

Another aspect to be assessed is degradation of any back-produced polymer. Several prior studies have shown there is no influence of polymer on the separation of crude and water; the polymer being water-soluble. However, in some cases, a treatment may be necessary prior to any water treatment processes to avoid any difficulty with surface facilities and plan optimum efficiency.

S&D 1.1: Hard Surface Cleaning

Chairs: T. Zander, Henkel, USA; and E. Theiner, Air Products & Chemicals Inc., USA

How a New Builder in Automatic Dishwashing Detergent Became Ready Biodegradable in the US: Widespread Microbial Adaptation in the Field. J.N. LePage[1], E. Bisinger[1], C. van Ginkel[1], T. Federle[2], N. Itrich[2], K. McDonough[2], J. Menzies[2], K. Casteel[2], and E. Schaefer[3], [1]AkzoNobel, USA, [2]Procter & Gamble, USA, [3]Wildlife International, USA.

L-GLDA (Glutamatediacetate) is a new chelate introduced in the US as a phosphate replacement in an automatic dishwashing detergent several years ago. Before introduction, L-GLDA failed multiple ready biodegradation screening tests (OECD 301B). However, results from a continuous activated sludge treatment test (OECD 303A) predicted that an inoculum pre-exposed to L-GLDA would degrade it after a lag period. Introduction of this new chemical into wastewater offered a unique opportunity to monitor for microbial adaptation in the field. Within several months, WWTP inoculums that had previously produced negative results, measuring 9-21% CO_2 production, demonstrated that L-GLDA was "ready biodegradable" (65-100% CO_2). Additionally, a decrease in the measured lag period was observed with adaptation time. This is the first systematic study showing how a newly introduced chemical, that consistently failed ready biodegradation tests in the US became ready biodegradable across a wide geographical region. While only ready test results using non exposed inoculum are allowed when registering new chemicals, this work demonstrates that when pre-exposure occurs under realistic conditions, laboratory tests can accurately predict real world behavior indicating the importance of considering potential adaptation in regulatory assessments.

Dishwashing Products: Ensuring High Performance in the Post-phosphate Era. T.J. Burns[1], A.C. Lee[1], and T.R. Graham[2], [1]Novozymes North America, Inc., USA, [2]Rivertop Renewables, Inc., USA.

Dishwashing product formulas have changed substantially in recent years, necessitated by shifts in ingredient options in order to maintain and improve high levels of performance in both automatic and manual use scenarios. We will review the recent evolution of formula compositions in this, the "post-phosphate" era, with particular attention to the increased dependence on functionality related to enzymes and other bio-based ingredient classes such as newer novel builders. We will present survey information on changes and trends in ingredient composition in N. American consumer dishwashing products, and share related performance-test results to arrive at an understanding of the benefits and challenges of the current formulas in this cleaning sector.

Innovation in Hard Surface Cleaning Products—An Upstream Perspective Combining Science and Sustainability for a New Generation of Ingredients. C.J. Wilson, Eastman Chemical, USA.

Consumers and end users continue to demand higher performance, safety, and value from their hard surface cleaners, while regulators and other third party influencers continue to whittle down the available raw materials that can be used in those products. How to achieve the optimal balance, given the many limitations in place, has become an ongoing challenge for formulators, especially with the overall trend to reduce or eliminate solvents (a crucial ingredient to dissolve the most difficult soils). In order to help meet these needs, raw material manufacturers are developing innovative technologies that can address many of the current issues facing formulators of hard surface cleaners. We will explore opportunities to create next-generation cleaners that are highly effective, gentle on a wide range of surfaces, and safer for the users and the environment. The ultimate goal is to develop and deliver hard surface cleaners valued by customers with no trade-offs.

Improving the Performance and Reducing the Cost of Autodish Washer Formulations with Novel Copolymers of Itaconate Acid. Y.G. Durant and B. Jiang, Itaconix Corp., USA.

Poly(sodium itaconate) has been used in the recent years as a cost effective and 100% sustainable alternative solution to phosphates, citric acid, and petroleum-based chelants, such as EDTA and other amino acetates. We have recently improved this polymeric chelant through the copolymerization of itaconic acid and sodium styrene sulfonate for optimal performance in ADW formulas. The novel copolymer has exceptional binding capacity for calcium and magnesium while remaining soluble during wash and rinse cycles with the combination of specific dispersants. The resulting combination offers excellent performance for filming and spotting scores in ADW tests. This polymeric chelant can be used at a reduced dosage, providing significant cost savings over the most recent advances in amino acetates chelants.

New-to-the-world Metathesis-based Amide Surfactant Provides Solvent-like Function for Substantially Aqueous Cleaners, and a New Cleaning Mechanism in Aqueous Formulation with Terpenes. R.A. Masters, M.J. Nepras, and M. Wiester, Stepan Co., USA.

N,N-Dimethyl 9-Decenamide, a new-to-the-world surfactant molecule based on Nobel Prize-winning metathesis technology, brings new and enhanced cleaning mechanisms to water-based cleaners and removers. This is a unique low-HLB nonionic molecule that can H-bond via amide and C=C pi electrons, allowing aqueous formulations to work like an

organic solvent. A formulated aqueous blend of this unique amide with terpenes creates a new cleaning mechanism beyond dissolution and roll-up, one that de-colorizes metal charge-transfer-complex chromophores without the need for oxidizing bleach, functioning in a 95+% water-based cleaner. A live demonstration of this new mechanism will be included in the presentation.

S&D 2/SCC 2: Surfactants in Cosmetics

This session developed in conjunction with the Society of Cosmetic Chemists.
Chairs: M.S. Vethamuthu, Ashland Specialty Ingredients, USA; and D. Abbeduto, Society of Cosmetic Chemists/Colonial Chemical, Inc., USA

Interaction Between Skin and Surfactants: A Review.
P. Giacomoni, Elan Rose International, USA.

Surfactants are amphiphilic substances used in skin-care products such as cleansers and emulsions. The scientific literature reports experimental observations about the interaction of surfactants with human skin.

When in cleansers or rinse-off products, surfactants provoke the removal of surface lipids with the alteration of the lipid-moisture balance of the skin and excessive dryness as net result. This has depends on the type of surfactant and on the "formula" (e.g. soap *vs* syndet bars). When in emulsions or other leave-on products, surfactants disorganize the lamellar structure of the lipids in the *stratum corneum*. This can facilitate the penetration of allergens such as those contained in cosmetic fragrances.
In vitro, surfactants in the growth medium are toxic to cultured cells and induce cell death by breaking open the cell membrane. This mechanism has been invoked to understand the observation that some surfactants behave as irritants when topically applied. *In vivo*, topically applied surfactants induce xerosis and dissolve specific proteins in the *stratum corneum.*

When in shampoos, surfactants can provoke an undesirable stinging of the eyes during the rinse process. The intensity of the stinging is a function of the size of the micelles, which can be modulated by appropriate ingredients.

Multi Domain Silicone Quaternary Polymers. T. O'Lenick, Siltech LLC, USA.

A series of silicone quaternary polymers have been developed that contain water soluble quaternary groups and water insoluble groups on the same silicone polymer backbone. This development allows for PEG/PPG free silicone polymers that are available in a range of solubility for use in personal care formulations. The ability to change the ratio of these water soluble to water insoluble cationic group within a polymer allows for the synthesis of water soluble, water dispersible and water insoluble polymers. In addition to providing conditioning effects, these products are emulsifiers, and have great aesthetics on the skin. The ability to modify the aesthetics provided by the emulsifier is critical since it has recently been shown that the emulsifier determines the initial feel of an emulsion on the skin not the oil phase.

Reassessing the Foam-boosting Properties of Alkanol Amides. R. Galleguillos and L. Lipp, Lubrizol Co., USA.

The foam boosting properties of alkanolamides and a Glucamate ester, MEGCCO, in various aqueous surfactant systems was investigated using meticulous foam tests. This work was conducted to unambiguously establish the relative foam boosting strength of these molecules on the foam of systems based on the anionic/betaine pair of surfactants. The RAFFA burette method, a Bikerman cylinder variation, and the Foam Double Logistic, FODL, a new method developed by us, were employed to measure foam properties such as flash foam, foam density, foam decay, rates of aeration and lathering as well as the quality of the texture of the foam. The results indicated that the foam boosting effect of alkanolamides was not significant in most of the surfactant systems studied. We found that cocamidopropyl-betaine up to 2wt% was sufficient to improve the foam properties of the anionic surfactant. It was discovered that MEGCCO's foam boosting properties were comparable to the alkanolamides in cases where some degree of foam improvement was observed. These results contradict the widely accepted notion that alkanol amides are strong foam boosters. Furthermore the precision of our foam test methods can be used to design surfactant systems with different foam properties as needed in specific applications.

Surfactants in Personal Care Applications: Advances in Role and Selection of Multifunctional Rheology Modifiers.
M.S. Vethamuthu, E. Di Antonio, S. Ozkan, V. Johnson, and H. Fares, Ashland Specialty Ingredients, USA.

Objective: The aim of this work is to present recent advances in polymeric multi-functional rheology modifiers used in surfactant rich cosmetic products. The presentation would highlight the key functionality, rheological profiles, and parameters used to select polymer mixes to achieve optimum yield stress, shear thinning profile, and good pump ability from typical packaging components used for dispensing.

Method and Results: Steady and dynamic rheological experiments were performed on cosmetic formulations using an AR-G2 stress controlled rheometer. Cone and plate geometry with 60mm radius and cone angle of 2^{o} over a stepped stress ramp from 0.1-100Pa at 2 minutes per step was used to measure the rheological profile at 25 & 45^{o}C. The results will be discussed with respect to zero shear viscosity, yield stress and flow profile for a wide range of polymer structured compositions.

Discussion and Conclusion: The suspension stability of formulations strongly depends on the value of the yield stress and zero shear viscosity. The rheological performance parameters also depend on the composition, namely polymer selected, surfactant types; mix ratio, pH, and co additives. Over structuring formulations will result in unacceptable flow properties and contribute to poor tactile or negative foam sensory ratings during use.

Quantifying Technical Changes in Hair Properties After Treatment. T.A. Evans, TRI Princeton, USA

An ability to technically assess ingredient and product-induced changes in hair is essential to cutting through nebulous consumer language and understanding underlying functionality. For example, it is evident that aesthetically-pleasing lubrication is the source of hair "conditioning" and a plethora of other consumer expressions (softer, smoother, repaired, moisturized, etc.). Further insight and contemplation leads to the conclusion that the sizable daily-use hair care industry simply revolves around laying down and removing of surface deposits – along with the construction of new and attractive marketing messages relating to this technical feat.

Without denigrating the undeniable benefits of such products, certain other hair-related attributes associate with the internal structure (i.e. the cortex) and are therefore unaffected by these treatments. Therefore, we are presented with direction for creating new, novel products that alter hair's properties in ways that have not previously been possible.

This presentation will discuss instrumental assessments of hair's structure and properties to better understand product efficacy and direct future endeavors.

Various Oil Micro-emulsions and Their Possible Benefit for Beauty and Personal Care Products. G.A. Smith, Huntsman Performance Products, USA.

Microemulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant. The aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons and olefins. In contrast to ordinary emulsions, microemulsions form upon simple mixing of the components and do not require the high shear conditions generally used in the formation of ordinary emulsions.

Microemulsion are having unique properties, namely, ultralow interfacial tension, large interfacial area, thermodynamic stability and the ability to solubilize otherwise immiscible liquids. With our unique system, no salts are necessary and microemulsions have been developed with Essential Oils, Vegetable Oils, Mineral Oil, Octyl Methoxycinnimate, Silicone Oil, and esters.

The micro-emulsions may potentially be used to add these solubilized materials to various beauty & personal care products.

Dealing with Rheological Realities—A Guide to a Clean and Satisfying Life. J.M. Chandler, ACT Solutions Corp., USA.

Consumers do not purchase (and repurchase) such personal cleansing products as shampoos, body washes, facial cleansers, and hand washes merely for their cleaning ability. There is a whole consumer experience that comes into play. A large part of consumer delight, or lack thereof, for a product comes with the flow properties. High measured (Brookfield) viscosity is typically more appealing, offering the allure of richness and high content of good things inside. Unfortunately, many 'thick and rich' formulations exhibit a variety of negative rheological traits.

This presentation will look into how viscosity is built in personal cleansing products, and provide some insight into dealing with formulation issues related our increasingly 'free' consumer society. Getting the rheology right in a personal cleansing product is a big key toward gaining consumer acceptance and excitement. Anything they can buy will clean. So, with the destination assured, it is about the journey.

Natural Fragrance Solubilizers. D. Abbeduto, Colonial Chemical, Inc., USA.

As formulators of personal care products continue to look for alternatives to ethoxylated materials, fragrance solubilization has been an area with few viable alternatives. Now, and increasing number of formulation solutions have become available. A variety of commercially available non-ethoxylated and naturally certified solubilizers will be reviewed with regard to properties, certifications, and usage.

Of particular interest to formulators using these products is the ability to solubilize essential oils using two common techniques: premixed with fragrance and added to fragrance/water mixtures. The efficiency of these solubilizers to produce clear aqueous mixtures in combination with a variety of common essential oils will be examined, as well as how they compare to traditional ethoxylates using the same formulation techniques and clear mixture endpoint.

Performance varies dramatically by essential oil polarity, formulation technique, and solubilzer used. The results will assist formulators to improve their selection of appropriate technologies.

S&D 2.1: New Forms: Applied and Theoretical Aspects

Chairs: K. Genco, Arkema Inc., USA; and S.M. Raders, Lubrizol Corp., USA

Synergistic Effect of Surfactant and Enzymes During Dry-grind Ethanol Fermentation on Distillers Corn Oil Distribution and Recovery. L. Fang, T. Wang, and B.P. Lamsal, Iowa State University, USA.

Distillers corn oil (DCO) is a valuable co-product from dry-grind ethanol fermentation, which is used as animal feed additive and in bio-fuel production. DCO is present in various forms, including oil adhering on surfaces of wet grains (such as cell wall and protein matrix). Such oil is difficult to move from wet cake to thin stillage by subsequent decanting and separate from the thick stillage. The effect of surfactant (polyoxyethylene (20) sorbitan monooleate) addition during fermentation on DCO partition and DCO recovery from thick stillage was investigated. We found that about 10% DCO present in whole stillage adhered to solid surface, and this could be washed from wet cake to thin stillage by surfactant (200~500ppm) added in fermentation step. The stirring rate in fermentation had a significantly positive effect on oil partition in thin stillage, and surfactant addition can reduce the requirement of high speed stirring for the desired oil partition. Moreover, a synergistic effect between enzymes (protease and non-starch carbohydrate hydrolyzing enzyme) and surfactant during fermentation step was observed for partitioning of DCO to the thin stillage. Enzymes reduced the size of solid by hydrolysis and released more DCO from the corn matrix, but also created a more complicated surface which can adsorb more DCO.

Insights into the Mechanism of Textile Greying During the Consumer Laundry Process. M. Job and M. Dreja, Henkel AG & Co. KGaA, International Research Laundry & Home Care, Germany.

Whiteness is still one of the biggest needs, which consumer address to a detergent. On one hand, stain removal has an important impact on the whiteness of textiles. On the other hand, it is the anti-redeposition performance of a detergent as secondary washing effect that correlates to the degree of greying after several washes.
Carboxymethylcellulose (CMC) is one of the key ingredients with regard to improving the secondary detergency and is used in almost all standard powder detergents. In order to clarify the mechanism behind the performance of CMC, we have conducted an investigation of the interaction of modified cellulose on model surfaces. We correlated the results to tests, which we did under consumer relevant conditions. We will show that the dynamic ad- and desorption of CMC on cellulosic textiles during the washing process influences the redeposition of soil. These results will help to find new and more potent anti-grey ingredients for laundry detergents.

Foaming Properties of Methyl Ester Sulfonate (MES) for Laundry Detergents. H. Watanabe, Y. Ito, C. Endo, and Y. Kaneko, Lion Corp., Japan.

Methyl Ester Sulfonate (MES), derived from sustainable palm oil, is an attractive anionic surfactant used in laundry detergents for machine washing because of its superior features like excellent detergency, high calcium tolerance, carbon neutrality, and lower foaming ability. However, anionic surfactants used in detergents for hand washing must have high foaming ability, in addition to detergency, so that damage to the fabric during the washing process is prevented. Therefore, we tried to improve the foamability and foam stability of MES for hand washing by adding commonly used surfactants as foam boosters. We characterized the foamability of the mixed micellar solutions on the basis of dynamic interfacial tension and foam stability in the presence of calcium oleate particles, which is generated from human sebum soil and acts as an antifoam, by measuring the contact angle between the liquid drop and the soil surface. The enhancement of foaming and foam stability could be attributed to the decrease in dynamic interfacial tension and increase in wettability, respectively. This study confirmed that the degree of foaming and foam stability of MES can be enhanced by adding surfactants.

Performance and Properties of a New Generation of a Readily Biodegradable Chelating Agent: GLDA. J.N. LePage, P.D. Kincaid, K. Chatterjee, and J. McVeigh, AkzoNobel, USA.

L-GLDA (Glutamatediacetate) is one of several readily biodegradable chelating agents recently introduced to the U.S. market as a replacement for phosphates in auto dish washing detergents. While replacement of phosphate was mandated by regulation, there is now significant and growing interest in replacing EDTA and conventional chelates in other cleaners and applications. While GLDA is not as strong a chelate as EDTA, GLDA offers several unique benefits. Besides having a more favorable environmental profile, GLDA offers high water solubility (>50%) over a wide pH interval. Such high solubility allows for the preparation of highly concentrated liquid cleaners with low water content and for compatibility in PVOH single dose pouches. Strongly alkaline and acidic cleaners containing high levels of GLDA are also possible. Like EDTA, GLDA is a strong enough chelate to boost the effectiveness of preservatives thus allowing less of the preservative to be used, but unlike EDTA, GLDA is still effective with many enzymes used in cleaners. GLDA meets all requirements of EPA's Safer Choice program, is listed on CleanGredients, is approved for Direct Release to the environment and is the only stronger chelate that is USDA certified as being 58% biobased.

Dendritic Methods for Surfactants and Carrier Applications: Design, Synthesis, and Characterization. C.N. Moorefield, University of Akron, USA.

The advent of highly branched, dendritic, macromolecules has fostered many new joint research opportunities by facilitating precise control of functional group and component placement in composite materials. Commercial availability of these tree-like building blocks has served as a driving force for cross-disciplinary research and development; however, greater choice in molecular frameworks is desirable. Construction of Newkome-type, predesigned 1 → 3 *C*-branched, monomers used for amide-based, dendritic scaffolding, provides advantages in enhanced stability and processibility of dendrimer polymer additives. The synthesis of a series of surfactants and composite additives was undertaken using these unique aminotriester monomers with the goal to obtain enhanced stability with respect to temperature, pH, and concentration, as well as handling characteristics with regard to material transport and delivery. Key requirements of these materials include the ability to easily modify the frameworks through either carbodiimide coupling reactions or simple nucleophilic substitutions. The simple protection-deprotection sequences used for the amide-based dendritic surfactants has also led to the development of novel ricinoleic-type branched surfactants.

S&D 3: *Journal of Surfactants and Detergents* (*JSD*) Selected Papers

Chairs: G.A. Smith, Huntsman Performance Products, USA; C. Rodriguez-Abreu, International Iberian Nanotechnology Lab. (INL), Portugal; and N.A. Falk, Clorox Services Co., USA

HLD Optimum Formulation as the Main Principle for Breaking Emulsions: Recent Advances on the Demulsifier Performance in Crude Oil Dewatering. J.L. Salager, A.M. Forgiarini, and J.G. Delgado, Lab FIRP, University of the Andes, Venezuela.

Forty years ago a correlation between the characteristic physico-chemical variables of a surfactant-oil-water system was found as a numerical condition to attain a minimum interfacial tension in a formulation scan. Later, this so-called optimum formulation was also found to correspond to the most unstable emulsion. Many reasons were proposed to explain this coincidence, particularly the elimination of the Gibbs-Marangoni stabilization mechanism.

In the past decade new experimental techniques were developed and the attainment of an optimum formulation by producing an interfacial mixture of an added hydrophilic surfactant, called demulsifier, with the lipophilic natural surfactants present in crude oil (asphaltenes, resins, acids, etc.) was corroborated to be the main principle of crude oil dehydration. The so-called proportional regime condition allows to characterize the surfactant aspect of asphaltenes, which can be separated from their role as polar oil reducing the EACN. I also allows to compare the performance of different demulsifiers with different crude oils. Secondary effects dealing with the self-association of asphaltenes, bulk and interfacial rheology, solvent-like and other additives may be dealt with at optimum formulation to make the emulsion even more unstable, i.e. to improve performance.

Capillary Curves for the Design of Cleaning Processes. S. Quraishi, M. Bussmann, and E.J. Acosta*, University of Toronto, Canada.

This presentation summarizes the findings of the article "Capillary Curves for Ex-situ Washing of Oil-Coated Particles" published in the *Journal of Surfactants and Detergents* (J. Surfactants Deterg. 2015, 18 (5), pp. 811-823). In that work, it was determined that the removal efficiency of oil deposited on sand is determined by the balance of forces at the oil/water and solid/fluid interfaces. These forces were quantified through dimensionless film and particle-based Weber and capillary numbers. The Weber number speaks to the ratio between the inertial forces that help remove the oil, and the surface tension forces that keep the oil attached to the surface. The capillary number speaks to the ratio between shear forces that tend to remove the oil from the surface, and the surface tension forces. These number were then use to represent the fraction of oil retained by the particles as a function of these dimensionless numbers to generate capillary curves similar to those used in enhanced oil recovery. These curves reveal the existence of a critical film-based Weber number and a particle-based capillary number that can be used in the design or evaluation of washing processes. Additional examples will be discussed and the potential use of these dimensionless numbers in detergency and hard surface cleaning applications.

Surfactants Based on Bis-galactobenzimidazolones: Synthesis, Self-assembly, and Ion Sensing Properties. L. Lakhrissi[1,3], N. Hassan[2], B. Lakhrissi[1], M. Massoui[3], E.M. Essasi[3], J.M. Ruso[2], C. Solans[4], and C. Rodriguez-Abreu*[5], [1]Universite Ibn Tofail, Morocco, [2]University of Santiago de Compostela, Spain, [3]Universite Mohamed V, Morocco, [4]Consejo Superior de Investigaciones Cientificas (CSIC), Spain, [5]International Iberian Nanotechnology Lab. (INL), Portugal.

Sugar-based surfactants, with their low toxicity and excellent biodegradability, i.e. reduced environmental impact, offer an attractive alternative to more conventional non-ionic surfactants such as poly(ethyleneoxide) alkyl ethers. We have synthesized a series of new non-ionic amphiphiles based on bis-galactobenzimidazolones by grafting alkyl bis-benzimidazolone units as hydrophobic tails on hydroxypropyloxygalacto-pyranose moieties as hydrophilic heads. Their surface and self-aggregation properties in water were evaluated. The compounds show very low critical micellar concentrations (CMCs) that decrease with increasing chain length; values for the minimal area per molecule at the interface follow the same trend. The synthesized compounds also form hexagonal liquid crystals in water for a certain range of hydrophobic tail lengths. On the other hand, the new amphiphiles show characteristic UV–Vis absorption and fluorescence emission bands associated with the benzimidazolone moiety. The fluorescence emission is quenched with a certain degree of selectivity by cations, due to their strong affinity towards the benzimidazolone group, which shows ion complexation properties. Hence, the reported new amphiphiles are candidates as self-assembling chemosensors.

Viscoelastic Behavior of Alkyl Ether Sulfate Systems Containing Sodium Carbonate. S.T. Adamy, Church & Dwight Co., Inc., USA.

Relaxation behaviors in systems containing sodium alkyl ether sulfate and sodium carbonate were studied. The anionic surfactants were commercial grade systems with average chain lengths of twelve carbons and either one, two, or three ethoxy (EO) groups. It was found that viscosity maxima in the three systems were achieved at particular salt levels that increased with an increase in the number of EO groups. Relaxation, studied through the performance of frequency sweeps while measuring complex, elastic, and loss moduli, in the optimized systems were studied. Temperature

was varied between 5 and 45°C. While characterization of relaxation in terms of the Maxwell model adequately described data below the threshold of ?t < 1, the model failed to adequately describe behavior at higher frequencies. A modified expression with an additional relaxation mode adequately described relaxation throughout the frequency range studied. Temperature dependencies provided estimates of activation energies which were consistent with literature values for reptation modes of relaxation. Studies of ultrasonic attenuation in the surfactant systems were also studied and provide insights into motions on faster time scales.

Cold-water Detergency of Vegetable Oils and Semi-solid Fats Using Surfactant Mixtures: HLD Concept and Initial Probing of Mechanisms. L.D. Do[1], C. Attaphong[2], J.F. Scamehorn[3], and D.A. Sabatini*[3], [1]Corsitech, USA, [2]King Mongkut's Inst. of Technology, Thailand, [3]University of Oklahoma, USA.

In spite of the increasing interest in cold temperature detergency of vegetable oils and fats, very limited research has been published on this topic. While extended surfactants have shown promising detergency with vegetable oils at ambient temperature, the excessive salinity requirement (4-14%) for these surfactants has limited their application. In this work, published in *JSD*[*], we investigated the mixture of a linear C_{10}–$_{18}$PO–$_2$EO–$NaSO_4$ extended surfactant and a hydrophobic twin-tailed sodium dioctyl sulfosuccinate surfactant for cold temperature detergency of vegetable oils and semi-solid fats. Four vegetable oils of varying melting points (from -10 to 28°C) were studied (canola, jojoba, coconut, and palm kernel oils). At temperatures above the melting point, this surfactant mixture achieved greater than 90% detergency with only 0.5% NaCl. While detergency performance decreased at temperatures below the melting point, it was still superior to that of a commercial detergent (up to 80 vs. 40%). Further, results show that the experimental microemulsion phase behaviors correlated well with predictions from the hydrophilic–lipophilic deviation concept. This presentation will also present more recent (unpublished) work probing the fundamental processes affecting cold water detergency of solid nonparticulates (fats/waxes below their melting point).

*Do, L.D., Attaphong, C., Scamehorn, J.F. and Sabatini, D.A. "Detergency of Vegetable Oils and Semi-Solid Fats using Microemulsion Mixtures of Anionic Extended Surfactants: The HLD Concept and Cold Water Applications." Journal of Surfactants and Detergents. 2015, 18, 373-382.

Elucidation of the Mechanism of Softening Effect of Fabric Softener. T. Igarashi, N. Morita, Y. Okamoto, and K. Nakamura, Kao Corp., Japan.

Mechanism of softening effect was known to be caused by the lubrication between fibers. We proposed new theory that important main factor of softening effect was formation inhibition of bound water consisted by hydrogen network between single fibers.

Properties of Surfactants Based on Sulfoxide Esters. B.P. Grady, University of Oklahoma, USA.

This talk will discuss new and novel non-ionic surfactants containing a sulfoxide hydrophilic moiety within the main chain. Although not new, the sulfoxide headgroup has been very rarely studied and has the advantage over more common ethylene oxide headgroups as not having a cloud point. The particular manifestation of sulfoxide uses an ester moiety which allows for control of the number of sulfoxide groups on a single molecule, similar to the ethylene oxide moiety. This talk will discuss in detail the structure and physical chemistry of these molecules. Equilibrium and dynamic surface tension, critical micelle concentration, Draves Wetting, adsorption on solid surfaces, and micelle structure via scattering will be reported and compared to other similarly structured surfactants.

Performance of New Biodegradable Di-sulfonate Surfactants as Hydrotropes in High-temperature and Salinity Environments. C.J. Tucker, A.M. Behhe, and E.D. Daugs, The Dow Chemical Co., USA.

Propyl alkyl ether sulfonate (PAES) surfactants, recently developed by The Dow Chemical Company, show excellent electrolyte, hard water, and caustic solubility, with attractive ECOTOX profile and biodegradability. Due to their unique structure and properties, they are good candidates for use as hydrotropes in formulations containing nonionic surfactants. The goal of these studies was to evaluate hydrotropic efficiency of PAES materials via cloud point analysis. The effects of PAES alkyl tail length, concentration, and mono- and di-sulfonate components on the cloud point of TERGITOLTM 15-S-9 in solutions of varying electrolyte strength were investigated. In the presence of high electrolyte levels, PAES 12C had the highest hydrotropic efficiency of all materials tested, including commonly used commercial hydrotropes. Disulfonate components of the PAES materials were found to be more efficient hydrotropes than mono-sulfonate in high electrolyte and elevated temperature environments for all tail lengths tested. The di/mono ratio and tail length were found to be critical parameters.

S&D 4/BIO 4.1: Biosurfactants and Biodetergents

This session developed in conjunction with the Biotechnology Division.
Chairs: D.K.Y. Solaiman, USDA, ARS, ERRC, USA; D.G. Hayes, University of Tennessee, USA; and H.E. Byrne, Huntsman Performance Products, USA

A Survey of Biosurfactant Rhamnolipid Production and Applications. D.K.Y. Solaiman and R.D. Ashby, USDA, ARS, ERRC, USA.

Rhamnolipids (RLs) are microbial-produced glycolipids in pilot-scale production for applications in niche markets. Presently, RL is mainly used as biobased surfactants in cleaning-product formulation. However, other properties of RL could present new opportunities for their commercial applications. In this review presentation, various production systems for RLs will be surveyed to evaluate the volumetric productivity potentials of the processes. The antimicrobial and other biological activities of RLs will also be reviewed to provide data-set useful for product developments.

Rhamnolipid Composition, Modification, and Soil Adsorption. S. Miao[1,3], S. Soltani Dashtbozorg[1,2], A. Sancheti[1], K. Invally[1], and L.K. Ju*[1], [1]University of Akron, USA, [2]Chromatan Corp., USA, [3]George Washington University, USA.

Rhamnolipids are well known microbial surfactants. We recently investigated the potential effects of cultivation factors, mainly substrate and cultivation time, on the congener composition of rhamnolipids produced along anaerobic *Pseudomonas aeruginosa* fermentation. We also converted rhamnolipids to several derived compounds, ranging from nonionic surfactants to polymers. For applications as agricultural biopesticide or bioremediation, we further characterized the soil adsorption behaviors of rhamnolipids. Results of these studies will be presented.

A New Synthetic Platform to Create Known and Novel Bioinspired Glycolipids. C.J. Boxley[1], J.E. Pemberton[2], and R.M. Maier[2], [1]GlycoSurf, LLC, USA, [2]University of Arizona, USA.

Since their initial discovery and introduction to the marketplace in the 1960's, microbially produced glycolipids (biosurfactants) have experienced a steady rise in interest and potential applications as "green" alternatives to traditional petroleum-based specialty surfactants. This is due to a combination of their environmentally friendly characteristics, including low toxicity and ready biodegradability, as well as their excellent surfactant attributes. A new technology recenlty introduced builds on these advantages by providing a platform to synthesize a wide variety of glycolipids. This presentation will discuss some of the advantages associated with using synthetic approaches to produce glycolipids including: 1) the ability to chemically synthesize single congeners rather than undefined and unreproducible congener mixtures as produced by biosynthesis, 2) the ability to tailor both the head and tail groups to produce surfactants with a wide range of properties that can be used for specific applications, and 3) the potential to use waste stock materials to produce these surfactants cheaply.

Novel Sophorolipid-based Biosurfactants by Metabolic Engineering: Production and Application. I.N.A. Van Bogaert[1], S.L.K.W. Roelants[2], and W. Soetaert[1,2], [1]Ghent University, Belgium, [2]Bio Base Europe Pilot Plant, Belgium.

Through metabolic engineering of the unconventional yeast *Starmerella bombicola* we created several new-to-nature and tailor-made biosurfactants. Indeed, despite the clear advantages of biosurfactants, their overall use is hampered by the lack of structural variation. This is in sharp contrast to chemically produced surfactants where one can introduce variation by simply changing the building blocks. Structural variation is essential as (bio)surfactants find application in a very broad range of sectors. We alleviated this fundamental limitation by developing a generic biotechnological production technology for glycolipid biosurfactants, based on the very efficient biosurfactant producing yeast *S. bombicola*. By metabolic engineering, most structural parts of the glycolipid biosurfactant molecule can be controlled: fatty acid tail, sugar moiety, acetylation and lactonization. For each target molecule, an industrial applicable fermentation and downstream process was developed and the molecules are evaluated for various applications such as cleaning, cosmetics, medics and nanoscience. Our approach thus covers the whole innovation chain from basic research to production and application development. To achieve this goal, a complementary consortium of academic and industrial partners was formed that covers the whole range of required expertise.

Sophorolipid Modifications: Advantages of a New Pathway. D.W.G. Develter, Ecover Coordination Centre, Belgium.

As sophorolipids are finding their way to the detergent and cosmetic market, the search for higher foaming sophorolipids continues. A state of the art overview of chemical and biotechnological modifications is given which shows that none of the commercially viable modifications outperforms wild type sophorolipids. Finally the synthesis of a modified sophorolipid species is described, the physicochemical behaviour of which for the first time ever exceeds that of wild type sophorolipids.

Surfactants Based on Algae Oil. G.A. Smith, Huntsman Performance Products, USA.

Modern day surfactants are based on natural, petrochemical or a combination of natural and petrochemical feedstocks. With the recent emphasis on sustainability,

surfactants based on natural feedstocks are of considerable interest. Palm-based natural alcohols are produced in regions where deforestation is a concern, have long supply chains to developed markets and is a food source for human beings.

An alternative feedstock which overcomes the deforestation concerns and is not used for food is algae. There are thousands of different algae species which can grow in fresh or salt water. Work was performed to optimize the growth conditions for different types of freshwater algae in laboratory photobioreactors (PBR). Light frequencies and fertilizer concentrations were varied to achieve the optimum growth conditions.

The oil extracted from algae was used to make nonionic surfactants by low temperature transesterification with an ethoxylated polyol. The process is fast and produces only trace amounts of dioxane and residual EO. The products are light colored, low viscosity liquids with no gel phase upon dilution in water. Surface properties and detergency looks similar to conventional natural alcohol ethoxylates. Work was performed to optimize the molecular structure for different applications including detergency, rheology modification and foam control for home and personal care products and polyurethane foam applications.

Next Generation Castor Oil Ethoxylates. H.E. Byrne, G.A. Smith, M.T. Meredith, and C. Cleary, Huntsman Performance Products, USA.

Castor oil ethoxylates (COEs) have been widely used for emulsification properties in industries such as agriculture, metal working and personal care. The main technology available on the market uses direct ethoxylation on castor oil to obtain this vegetable based surfactant. Although the older technology is still used today, in the more recent years, it was found that you could obtain castor oil ethoxylates by scrambling ethoxylated glycerin and castor oil triglycerides. Compared to the old technology, this new route helps to keep both the hydroxyl group intact and the levels of 1,4-dioxane low.

In this work, an investigation was carried out in order to see what benefits would be shown with the new COE technology compared to the direct ethoxylation products. Properties compared include EO or 1,4-dioxane content, cloud points and foam profiles among many others. Comparisons with industry specific formulations will also be reported.

New and Emerging Biobased Surfactants: A Review. D.G. Hayes, Dept. of Biosystems Engineering & Soil Science, University of Tennessee, USA.

This presentation will review three new biobased surfactants described in recent issues of the Journal of Surfactants and Detergents (JSD). First, in a series of two papers, Cai and coworkers have developed a nonionic surfactant formed from low molecular weight chitosan and an epichlorohydrin-derivatized form of dehydroabietic acid, a derivative of pine tree rosin (JSD 17:493 [2014] and 18: 463 [2015]). The derivatives lowered the surface tension of water to 36 mN/m and were effective emulsifiers. Second, Negm and coworkers have produced biobased surfactants formed through esterification of jatropha oil fatty acid ethoxylates and p-aminobenzoic acid, the latter derived from vanillin (JSD 18:1011 [2015]). The derived surfactants were effective as anticorrosion inhibitors on carbon steel. Third, Heidelberg and co-workers produced sugar-based surfactants that contained an amide linkage for use as an oil-based emulsifier through converting the primary OH group of methyl glucoside into an azide group, and then forming an amide linkage between the azide group and a fatty acyl derivative through the Staudinger coupling reaction (JSD 17:1141 [2015]). The surfactants possessed a high Krafft point temperature and tended to form hexagonal phases in solution; but, long-chain derivatives were capable of emulsifying water into oil.

S&D 4.1: New Technologies in Industry

Chairs: J. Coope-Epstein, Sun Products Corp., USA; and W.W. Schmidt, Consultant, USA

Cellulosic Polymer Technologies for Fabric, Hard Surface, and Personal Care Applications. J.E. Shulman, J. Todd, and J. Hayes, Dow Chemical, USA.

There are several distinct types of cellulosic polymers which a formulator can utilize to achieve a variety of care benefits. Conventional cellulosics, such as hydroxyethyl cellulose (HEC) and hydroxypropyl methyl cellulose (HPMC), offer advantages in initial foam generation and stabilization (in the presence of soil) and improved sensorial benefits in manual dishwashing and shampoos. Novel cationic cellulosics have been shown to enhance fabric softening, reduce creasing, and enhance fragrance deposition without the associated negatives on clay soil redeposition in liquid laundry applications. These modified cationic polymers can also be delivered in different formats (including fragrance enhancers and pre-treaters) in a through the wash or rinse added approach. The success of a given cationic cellulosic is strongly dependent upon the polymer backbone, nature of the charge type, and relative hydrophilicity/hydrophobicity of the composition and the type of matrix being employed.

Sokalan® HP20 as a Foam Stabilizer and Performance Booster in Manual Dishwashing Detergents. S. Gross and K. Salmon, BASF Corp., USA.

In this presentation, a performance improvement observed with low levels of Sokalan® HP20 (ethoxylated aziridine homopolymer) in manual dishwashing detergents is introduced. Several typical manual dishwashing formulations containing Sokalan® HP20 exhibit increased plate count relative to identical formulations without Sokalan® HP20 according to the “standard plate test”, ASTM D4009, Method A, Soil B. The use level of Sokalan® HP20 is 0.4% wt. active in the formulations, and only 4ppm active in the dishwashing test solution. The work suggests that polymers can interact with soils, thereby reducing the defoaming effect of the soil. Sokalan® HP20 can also reduce viscosity of 20-30% active surfactant solutions more effectively than ethanol, and is non-volatile and non-flammable. Market trends in Manual Dish, test formulations and performance data will be presented.

Foam Longevity for Manual Dish Detergents. J.J. Sabelko, C.C. Cypcar, and K. Wilzer, Lubrizol Corp., USA.

Foam longevity is a key performance indicator for consumers using manual dish products. The longer the foam is stable and visible during the wash time, the better the performance of the dish detergent.

To meet this consumer need Lubrizol introduced two new high performance polymers designed to improve foam longevity and performance of a wide range of liquid detergent products. Noverite™ 311 and Noverite™ 315 polymers consist of a unique ampholytic terpolymer structure that enables foam stabilizing performance by synergistically interacting with the surfactants in the detergent products. You can create cost-effective formulations with long-lasting foam in the presence of organic soil loads typically found in cleaning applications.

Noverite™ 311 and 315 polymers are easy to use liquids that are effective at low dosage levels. The polymers are suitable for use in translucent to clear formulations and compatible with a wide range of surfactants. Examples will be demonstrated for manual dish detergents. The technology also provides foam stabilization in other common detergents, including high-suds manual laundry detergents, liquid multi-purpose detergents, and car wash detergents. Extend the cleaning performance of your detergents with long-lasting foam and less detergent per wash with Noverite™ 311 and 315 polymers.

Study for Enhancing Detergency on Lipid Stains by Hydrophilic Treatment of Cotton Fibers. M. Fukui, T. Hayashi, T. Kurokawa, H. Shindou, and T. Okamoto, Lion Corp., Japan.

After repeated wearing and washing, solid lipids from sebum easily accumulate on cotton clothes. In this study, we tried to remove these hydrophobic solid lipid more efficiently by adding soil-release function to cotton fibers for the lipid being removed more easily on top of the conventional approach of selecting surfactants, enzymes, and chelating agents for this purpose. To achieve this objective, we evaluated a variety of polymers and found that a polymer with a cotton-adsorption site, as well as a hydrophilic group exhibited the soil-release effects and was able to reduce the accumulation of solid lipids after repeated wearing and washing. Furthermore, we found that the soil-release polymer inhibited yellowing of the cloth. Especially, the polymer showed the significant effect on saturated fatty acids that accelerate yellowing by liquid lipids such as squalene.

Formulating Liquid Detergents with Enzymes and Strong Chelators. H. Lund, Novozymes A/S, Denmark.

Household care liquid laundry detergents can benefit by including chelators in order to prevent negative influence of metal ions in the wash water on f.ex. surfactant performance, incrustation, chalky or iron deposits in the machine, and/or fabrics. The stronger these chelators bind calcium and other transition metals the stronger benefit or lower dose will be needed. Another well-known and inevitable performance driver of modern liquid detergents are multienzyme solutions. The Gordic knot is, however, that some enzyme classes, ex proteases and amylases are more sensitive to strong chelators hence limiting the flexibility for the soapers to choose the best from the worlds of both enzymes and chelators in their quest for developing sustainable detergents.

Invisible Stain Removal Intervention Using Enzymes—Protecting Fabrics from Residual Soiling Effects. V.M. Casella, D. Rhine, and M. Bullock, Novozymes North America, Inc., USA.

The benefit of using enzymes in detergents to remove a variety of highly visible and problematic stains from fabrics is well known. An under-appreciated benefit of enzymes is their utility to remove highly substantive "invisible" macromolecules from fabrics that can act as attractants for soils and dyes released during the laundering process. Over time, these interactions can lead to dingy and unappealing fabric appearance. In this presentation, the attraction of common stain components (e.g., starch, guar, proteins, and fats) to fabric and the subsequent interaction with wash dispersed soils is described. The ability of enzymes to prevent/minimize these soil build-up effects is presented.

Zap the Oil Away with Lipase. T.B. Green, A.C. Lee, P. Haasis, and D. Showmaker, Novozymes, N/A., USA.

Consumers rank oily/buttery/greasy foods as some of the most difficult stains to remove in laundering. As a result, many garments often require many rounds of washing, or they are ruined and discarded because of this frustration with incomplete removal of oils. We will demonstrate the influence of several factors on the removal of oily stains. These factors include oil stain properties, pretreatment times, surfactant interactions, surfactant types, and washing machine types. Several types of stains will be examined using top and front loaders in both consumer and professional washing scenarios.

Alkylphenol Ethoxylate Elimination as an Opportunity for Performance Enhancement. E. Theiner, A. Fonseca, and K. Yacoub, Air Products & Chemicals, Inc., USA.

Growing concern around the toxicological profile of alklyphenol ethoxylates (APE), as well as indications of change in the regulatory landscape affecting these materials, are driving an effort to formulate these materials out of cleaning products, particularly those for industrial and institutional uses. Although the task may be onerous, there are many opportunities for cost savings and improved efficacy by using some basic strategies. This talk will discuss some of those strategies and associated tools so that a formulator may take advantage of these market drivers.

S&D 4.2/EAT 4: Delivery and Dispersed Systems

This session developed in conjunction with the Edible Applications Technology Division.
Chairs: S. Ghosh, University of Saskatchewan, Canada; and E. Szekeres, Method Products, Inc., USA

Engineering Interface of Encapsulation Systems to Limit Oxidation and Controlling Release of Bioactives. N. Nitin[1], Y. Pan[1], and R.V. Tikekar[2], [1]University of California, Davis, USA, [2]Dept. of Nutrition & Food Science, University of Maryland, USA.

Limiting oxidation and controlling the release of encapsulated compounds are the key goals for the rational design of encapsulation systems. This presentation will focus on our efforts to characterize the role of interfacial composition and its engineering in influencing oxidation processes during accelerated testing and the release of bioactives during simulated digestion. Specifically, the role of interfacial thickness and composition, layer by layer coatings and localization of antioxidants at the interface in influencing the oxidative barrier properties of the encapsulation systems will be discussed. The results will demonstrate the role of interfacial design in reducing permeation of radicals and oxidation of a model encapsulated bioactive in encapsulation systems. To advance understanding of the role of engineered structures in influencing the delivery and bioavailability of bioactives, development of a real time measurement approach to characterize interactions of encapsulation interface with digestive environment as a function of interfacial composition and structure will be presented. The results will illustrate a novel approach to analyze the dynamics of nanoscale structures during digestion processes and their relationship with release and delivery of bioactives.

Forming Essential Oil-loaded Hollow Solid Lipid Micro- and Nanospheres with Antimicrobial Properties Using Supercritical Fluid Technology. J. Yang, C.R. Kok, R. Hutkins, and O.N. Ciftci*, Dept. of Food Science & Technology, University of Nebraska-Lincoln, USA.

The main objective was to form essential oil-loaded novel hollow solid lipid micro- and nanospheres with antimicrobial properties using a simple and green method based on supercritical fluid technology. Hollow solid lipid micro- and nanospheres were formed from fully hydrogenated soybean oil using atomization of the carbon dioxide (CO_2)-expanded lipid. Particle formation conditions of 50µm nozzle diameter, 60°C, and 200bar CO_2 pressure yielded hollow solid lipid spheres ($d_{50\%}$ = 278nm). Shell thickness of the hollow spheres decreased with increasing pressure. Decreasing the nozzle diameter yielded the polymorphism of the particles from β to α. Clear dispersions of essential oil-loaded nanoparticles in water (d_{mean}= 173nm, polydispersity index (PDI)= 0.3) was formed by separating the microparticles in water by filtration. Hollow spheres were loaded with peppermint essential oil spontaneously during the particle formation with loading efficiencies up to 74%. Essential oil-loaded particles showed antimicrobial activity against selected microorganisms. Release properties and the morphology of the particles studied during storage showed that supercritical CO_2-assisted atomization process is a promising method to form hollow solid lipid micro- and nanospheres to develop "natural" antimicrobials for food systems.

The Effect of Contact Force on Coalescence of Water Droplets Suspended in Bitumen. S. Goel[1], S. Ng[2], and A. Ramachandran[1], [1]University of Toronto, Canada, [2]Syncrude Canada Ltd., Canada.

In the oil-sands industry, the presence of water in bitumen is highly undesirable in downstream unit operations. Therefore, processes such as centrifugation and inclined settling are currently used to achieve the separation of water from bitumen froth. They are, however, ineffective in removing extremely fine water droplets, which can form a significant fraction of the residual water content in bitumen after separation. The aim of this project is to understand the practically-relevant parameter regimes which will facilitate the coalescence of these extremely fine droplets with themselves or with larger drops. Accordingly, this will lead to the generation of larger droplets which can be further removed by conventional separation methods. Currently, the project is focused on conducting coalescence experiments in microfluidic device to determine the contact forces, bitumen solution properties and water chemistry that lead to coalescence of water droplets suspended in bitumen. In our experiments, coalescence time decreases with an increase in contact force and pH. Additionally, coalescence time increases with increasing bitumen concentration. Moreover, these experiments have also been quantified to develop coalescence time vs. contact force curves for different bitumen to solvent ratios and pH. Our results show that coalescence process is relatively faster beyond a critical force.

An In-depth Look at the Stabilization Factors Behind Low to Very Low Fat Spreads. K. Bhattacharya and P.G. Kirkeby, DuPont Nutrition Biosciences Aps, Denmark.

Retail or table margarines with about 82% fat content have become less popular with consumers globally. They are replaced with lower fat spreads with fat content ranging from 60% to as low as 15% and are being sold under the banners of 'low fat' or 'low calorie' products. However stability of such low fat water-in-oil emulsions is often a problem for producers affecting shelf life and consumer acceptance due to imperfection in taste and texture. There is also a growing preference of ambient stable low fat spreads from sustainability view point by the producers and retailers which require more careful selection of emulsifiers, fat blends and overall composition. Stability of different low fat systems depends on the synergy between the choice of fat blends,

choice of emulsifiers and hydrocolloids and their interaction with other food additives. Processing conditions also play a very important role. The present work discusses in details the role of different distilled monoglycerides, structuring emulsifiers, alginates and pectins for emulsion stabilization of fat spreads having 60% to 15% fat in conjunction with varying processing parameters. Analytical data includes Solid Fat Content and water droplet size distribution by p-NMR, confocal laser imaging, rheology, texture analyses, and sensory evaluations.

Studies on Preparation of Margarine from Di–acyl Glycerol Rich Oleogel. M. Ghosh[1], D.K Bhattacharyya[1], N.R. Bandyopadhya[1], and M. Ghosh*[2], [1]Indian Inst. of Engineering Science & Technology, IIEST, India, [2]University of Calcutta, India.

Di-acyl glycerol (DAG) rich oils are gaining importance in the field of nutrition due to their suppressive effect on postprandial serum triglyceride elevation and body fat accumulation. Recently, novel kinds of products are being developed in the name of oleogel using liquid oils and appropriate food grade oleogelators. Objective of the present study was to prepare oleogels obtained from DAG rich oil and to prepare margarine from these oleogels. DAG rich rice bran, soybean, sunflower and palmolein oil and combination of palm stearin and cetyl oleate were used as gelators to prepare oleogels. For preparation of margarine, lecithin and monoglycerides were used as emulsifier along with 14% water and 1% NaCl. The products thus formed, had the desired textural and thermal properties along with suitable shelflife. All the margarine samples were smooth spread, homogeneous in texture. The samples did not lose their structural integrity after the application of load on to the gels. The peak melting temperatures of the margarine samples varied from 47°C to 54°C. The dilatation value of all the margarine samples decreased with increase in temperature. These oleogel products were very stable against oxidation during storage and thus proved their suitability as shortening or margarine-base stock.

Fully Water-dilutable Microemulsions for Delivery of Riboflavin. N. Garti, N. Lidich, and A. Aserin, Hebrew University, Israel.

Riboflavin (vitamin B2) is a naturally occurring micronutrient found in relatively high levels in, or added to, various foods and beverages. It plays an important role in biochemical redox reactions in humans and animals. It also acts as an antioxidant and is essential for the health of skin, hair, eyes, and liver.

Microemulsions (MEs) are isotropic and thermodynamically stable nanosized mixtures of water, oil, and amphiphiles.

In the present study, a ribophlavin phosphate (RFP)-loaded MEs were prepared and structurally characterized. The selected ME components self-assemble, forming transparent, thermodynamically stable, non-viscous and fully water-dilutable structured systems. RFP incorporation does not disorder the ME structure. We found that in formulations with up to 40wt% water, the hydrophilic surfactant headgroups and cosolvent strongly bind water molecules (DSC and SD-NMR). Above 60wt% water, globular, O/W nanodroplets, ~14nm in diameter, are formed (SAXS, cryo-TEM, and SD-NMR). The structure of MEs loaded with 0.14 to 4.25wt% RFP (0.29–8.89mmol per 100g formulation) is not significantly influenced by the presence of the RFP.

Microfluidics to Study Emulsifier Adsorption and Emulsion Stability. K. Muijlwijk, C.C. Berton-Carabin, and C.G.P.H. Schroën, Wageningen University, The Netherlands.

To understand droplet formation and stabilization, technologies are needed that combine micrometer length and millisecond time scales. Microfluidics are used to bridge this gap, and the present work shows that droplet formation and stability in food emulsions can be investigated in close detail through high speed recording and image analysis. The dynamic interfacial tension during droplet formation was measured in the millisecond range with a microfluidic Y-junction that was purpose built and validated extensively. This method allows exploration of surfactant behaviour at the oil-water interface, which is not possible through any other technique at this very short time scale. Emulsion stability under flow was measured with a microfluidic coalescence channel. Results include coalescence measurements of protein stabilised emulsion droplets and we show that emulsions are stable at low protein concentrations.

We discuss underlying principles of these microfluidic methods and their potential for the food industry, which we believe to be very versatile, since the flow conditions during production and storage can both be covered adequately. Through this, we give evidence that microfluidic investigations can add greatly to the knowledge needed for the rational design of large scale emulsion production.

S&D 5: Rheology in Colloidal and/or Surfactant Systems

Chairs: B.P. Grady, University of Oklahoma, USA; and S. Natali, Halliburton, USA

A Comparative Study of the Rheological and Sensory Properties of a Petroleum-free and a Petroleum-based Cosmetic Cream. F.C. Wang ***(Surfactants and Detergents Division Student Award Winner)*** and A.G. Marangoni, University of Guelph, Canada.

Increasing demand from green cosmetics has driven the industry to develop alternatives for petroleum-based cosmetics. In this study, a petroleum-free skin cream has been developed using food-grade ingredients. The rheological and sensorial properties of this experimental petroleum-free skin cream were compared to a commercially available petroleum-based skin cream. Specifically, large amplitude oscillatory shear (LAOS) characterization of the two skin creams was performed. The petroleum-free skin cream showed similar linear and non-linear viscoelastic rheological properties, comparable moisture barrier functions, and consumer acceptance as the commercially available skin cream. A schematic diagram aiming to correlate the physical and sensorial properties of skin cream was also proposed at the end of the work. A petroleum-free skin cream has been developed using an MG-structured emulsion. This novel cosmetic cream showed comparable skin barrier function and rheological profiles with a commercially-available skin cream.

The Effect of a Yield Stress on the Drainage of the Thin Film Between Two Colliding Newtonian Drops. S. Goel and A. Ramachandran, University of Toronto, Canada.

Coalescence of drops immersed in fluids possessing a yield stress (Bingham fluids) has been of interest to many industries, such as the oil extraction, cosmetics, and food industries. Unfortunately, a theoretical understanding of the drainage of the thin film of Bingham fluid that develops between two drops undergoing a collision is still poorly understood. In this work, we examine this problem for low capillary numbers via a combination of scaling analysis and numerical simulations. There are three key features of the film drainage process of Bingham fluids. First, the introduction of a yield stress in the suspending fluid retards the drainage process relative to Newtonian fluid of the same viscosity. Second, the presence of yield stress prolongs the spherical regime of the drainage process and delays transition into the dimpled regime. This is contrasted with Newtonian case. Third, below a critical height, drainage can be arrested completely due to the yield stress. This critical height scales as $G_0^2R^3/s^2$, where G_0 is the yield stress, R is the drop radius and s is the interfacial tension, and is, surprisingly, independent of the force colliding the drops. This and other distinguishing characteristics of the drainage process will be elucidated in the presentation.

Alcohol Ethoxylate Blends for Viscosity Improvement of Laundry Detergent Formulation. T. Nguyen, T. Weemes*, C. Stoute, and S. Lyons, Sasol Performance Chemicals, USA.

Viscosity control plays an important role in creating a liquid laundry detergent product that meets consumer needs. Besides the reason for the appearance of the liquid detergent, high viscosity can cause liquid flow and stability problem while low viscosity can cause mechanical loss of the detergent during the machine washing process. Therefore, it is important to formulate a liquid laundry detergent with reasonable viscosity. In this research, the effect of alcohol ethoxylates made from different types of alcohol feedstocks on viscosity improvement for laundry detergent formulation was evaluated. These alcohol feedstocks include single alcohols or blends of alcohols with different structures such as the degree of branching, the type of branching, and the length of the hydrophobe. The clarity of the formulation or the solubility of the alcohol ethoxylates in the formulation was also evaluated. It was found that alcohol ethoxylates with a certain type and degree of alcohol branching can produce the desirable formulation viscosity and clarity.

Controlling the Lubrication Properties Between Silica Surfaces Induced by Mixed Anionic-amphoteric Surfactant Micellar Solutions. K. Ichihashi[1], C. Akabane[1], M. Kasuya[2], and K. Kurihara[2], [1]Lion Corp., Japan, [2]Tohoku University, Japan.

Synergism in mixed anionic-amphoteric surfactant solutions is effective for producing detergent performances. Previously, we reported that controlling the molar ratio of a mixed sodium polyoxyethylene alkyl ether sulfate and dodecyldimethylamine oxide (AES/DDAO) micellar solution is effective to induce spontaneous emulsification in the absence of salts or co-solvents and can reduce the time required to remove oily soil from hard surfaces. Here, in this system, we also found that the slipperiness on dish surfaces caused by aggregation and adsorption of surfactants during washing can be reduced by controlling this ratio of AES/DDAO. We characterized the lubrication properties from the difference of aggregation behavior of surfactants between SiO_2 surfaces by using resonance shear measurements. This study confirmed that by this control of AES/DDAO, the degree of viscosity increase of the micellar solutions confined between SiO_2 surfaces can be inhibited, as can the degree of friction decrease between surfactant adsorption layers on SiO_2 surfaces. Therefore, controlling the molar ratio of a mixed anionic-amphoteric surfactant solution is effective to inhibit the slipperiness. Using body motion analysis, we also demonstrated that this inhibition of slipperiness improves the posture of the dishwasher and increases arm movement during dishwashing.

Marangoni Flow at the Interface Between Oil and a Flowing Aqueous Solution of Surfactants or olyelectrolyte/Surfactant Complexes. G. Dunér, T.M. Przybycien, S.G. Garoff, and R.D. Tilton*, Carnegie Mellon University, USA.

Marangoni flow is caused by an interfacial tension gradient along a fluid interface. When an aqueous surfactant solution passes in laminar flow along the initially clean interface with a confined oil film, surfactant adsorption rates vary with position and time and set up a time-dependent interfacial tension gradient. This transient stress enhances interfacial transport in the direction parallel to the bulk aqueous flow. The opposite occurs upon rinsing. The objective of this work is to experimentally and theoretically assess the magnitude of Marangoni flows induced by surfactant convective diffusion at an oil/water interface, including the effects of surfactant complexation by polyelectrolytes that often accompany surfactants in commercial products. Marangoni velocities produced by transient surfactant adsorption or desorption can be hundreds of times greater than the baseline interfacial velocity, and the net displacement of an interfacial fluid element over one cycle of surfactant adsorption and rinsing can be significant. Polyelectrolyte complexation can dramatically enhance Marangoni velocities and net displacements. This may play an important role in interfacial transport, for example of entrained particulate matter in cleaning, dermatological or personal care applications where the dynamics of an oil/water interface are important.

S&D 5.1: General Surfactants

Chairs: P.T. Sharko, Shell Global Solutions (US) Inc., USA; and R.T. Zehr, Church & Dwight Co. Inc., USA

New Cosmetic Applications of Castor Oil. S.S. Awbrey[1], T. Alexander[1], and E.M. Hernandez*[2], [1]Envirosource, Inc., USA, [2]Advanced Lipid Consultants, USA.

Castor oil (CO) is one of the most widely used ingredients in cosmetic products and has been used traditionally in many therapeutic applications including the treatment of some skin conditions and in digestive remedies. Castor oil is extracted by pressing and solvent extraction processes or a combination of both. The chemical composition of the oil is mainly triglycerides of ricinoleic acid (90%). The stability and versatility of ricinoleic acid is the main reason for its high value in the cosmetics and chemical industries. Other applications include lubricants, process oils, oleochemicals, paints, coatings, inks, polyurethanes, polyesters, polyamides and other polymers. This presentation will discuss several preparation techniques of a novel product prepared from a blend of modified castor oil and castor oil-derived hydroxy stearic acid (HSA). Samples tested were prepared at several ratios (1:1-3:1) of CO and HSA and at several reaction temperatures and contact times. The final product had characteristics resembling of petroleum jelly, i.e., viscosity, melting point and emolliency. It was an effective ingredient in skin lotions and other cosmetic products. It was also easier to be removed from biological surfaces than petroleum jelly which was more sticky and difficult to remove. This new castor oil blend was tested as an effective cosmetic's jelly from a renewable source.

More Accurate HLD Parameters for Anionic Surfactants. C.Y. Su, M. Budhathoki, B.J. Shiau, and J.H. Harwell, Inst. of Applied Surfactant Research, University of Oklahoma, USA.

A modified approach based on the hydrophilic-lipophilic deviation (HLD) concept is proposed to determine quickly the HLD parameters, Cc and K, of surfactant candidates that are unlikely to create middle phase microemulsions without introducing alcohols. The procedure requires the new surfactant be blended with a reference surfactant such as sodium dihexyl sulfosuccinate (SDHS), then the optimal salinity be determined against oils of varying equivalent alkane carbon number (EACN). Surprisingly, the resulting plots of the log of the optimal salinity vs EACN for the SDHS system does not follow the common linear correlation when used with oils such as benzene and toluene, or with *n*-alkanes with EACN >9. This behavior prompted us to suggest new values of K (0.07) and Cc (-1.51) for SDHS, which are different from those previously reported. The observed K and Cc-values for several test surfactants using this modified HLD approach are quite similar to the values of the same surfactants measured without a reference surfactant. This validates the robustness of this new approach in accurately determining HLD parameters of anionic surfactants and measurably improves the predictability of mixture HLD values.

Heat of Wetting as a Substitute for Contact Angle Measurements. B.P. Grady, J.S. Weston, J.H. Harwell, and R.E. Jentoft, University of Oklahoma, USA.

Measurement of the contact angle of a powder is difficult and has significant limitations. Performing this measurement at elevated temperatures and/or pressures is even more difficult. We will demonstrate that using the heat of wetting at room temperature is able to give better information for a wider variety of surface energies vs. using the Washburn method for powders. We have also extended the method to one hydrophobic surface at different temperatures, including temperatures above 100°C. Measurements have been made with pure water, as well as with water containing CTAB, SDS, and C12E6 at different concentrations. The addition of surfactant causes the heat of wetting to become more exothermic as expected, with little difference between the different surfactants.

The USDA BioPreferred® Program: An Opportunity in the Biobased Products Niche. M. Wheat, USDA, BioPreferred® Program, USA.

Biobased products manufactured from agricultural, forestry, or marine materials are attractive for their technical qualities as well as their potential renewability, biodegradability, lower toxicity, and economic impact. Managed by the US Dept. of Agriculture (USDA), the goal of the BioPreferred Program is to increase the purchase and use of biobased products. The two major parts of the program are:

- mandatory purchasing requirements for federal agencies and their contractors; and,
- a voluntary labeling initiative for biobased products.

Learn about the USDA BioPreferred Program's regulatory agenda and how the program designates categories of products, both consumer products as well as intermediate ingredients, for mandatory federal purchasing. This presentation will also discuss the regulation of products carrying the USDA Certified Biobased Product label and discuss the benefits of obtaining a label for a product. As biosurfactants and bio-detergents continue to gain traction in diverse fields such as environmental clean-up, industrial and household cleaning, medicine, agriculture, and food processing, it will be important to understand the BioPreferred Program, its regulations, and their impact.

You will also learn about a recent economic study, the first of its kind in North America, which highlights the significant long-term prospects for growth in the biobased products industry and the industrial sectors impacted. The report examines the current state of play of the global bioeconomy and the specific economic impacts of biobased

industry across the United States.

Bio-based Ethylene Oxide—The Road to 100% Sustainable Nonionic Surfactants. B.S. Jaynes, Croda, Inc., USA.

In April of 2015, ground was broken on a $170 million plant in New Castle, Delaware, that will produce sustainable ethylene oxide (EO) from bio-based ethanol. With EO production beginning in early 2017, this facility will allow the commercial preparation of a range of ethoxylated surfactants and emulsifiers that are 100% bio-based, addressing the industry's growing demand for sustainable, non-petrochemically derived raw materials. Currently, the ethoxylation process is used to generate a range of products for emulsification, including ethoxylated alcohols, carboxylic acids, and bio-based esters. While the hydrophobic portions of many of these products are naturally sourced from plant oils, there has been no corresponding source for non-petrochemical EO in North America until this time. With this new bio-based EO, the ethoxylated products can be produced with 100% bio-based content, allowing customers to choose fully sustainable products without sacrificing any performance. The chemical production of these ethoxylated products will be presented, along with a summary of bio-based materials that are enabled by this technology.

The Development of a High Performance, yet Economic and Mild, P-free Automatic Dishwasher Detergent. R. Nolles, Cosun Biobased Products, USA.

As of January 1st, 2017 the EU regulation will come in place, stating a limitation of 0.3 grams of the total phosphorus content in the standard dosage in consumer ADW detergents. Since phosphates provide multiple functions, reformulation requires the use of several alternative ingredients. Overall, the cleaning performance of phosphate-free formulations can be restored to par level. Achieving good performance on spotting and filming however, remains challenging. And this applies to a greater extent when striving for excellent secondary cleaning performance in sustainable formulations. As a result of the abovementioned, new P-free ADW detergents have been developed for the European market focusing on maintaining high performance at an economic cost price.

At the same time in North-America there is a still-existing gap between the performance of ADW detergents and the consumer expectation. The lessons learnt from reformulating for the European market can be implemented in formulations for the North-American market.

Built on a base of sodium citrate and sodium carbonate, using synergies between performance ingredients, an excellent performing ADW detergent formulation was developed. Since the formulation does not contain any strong chelating agents, which are considered to be corrosive, it is very mild towards sensitive materials in the dishwasher and the dishes itself. Prolonged wash tests (up to 20 washes) with high levels of soiling show superior results on spotting and filming of for instance glassware. All of this is obtained at a raw material cost level that can compete with national brand equivalent cost price.

S&D-P: Surfactants and Detergents Poster Session

Chair: M. Wint, Amway Corp., USA

1. **Antimicrobial Properties of Bio-based Surfactants.** K.Z. Ren and B.P. Lamsal, Iowa State University, USA.

Bio-based surfactants are either microorganism produced or enzymatically synthesized surfactants. These surfactants could have two functions: emulsifiers and antibacterial agents. Antimicrobial property of several lab-synthesized bio-based surfactants (glucose palmitate ester, glucose laurate ester, surfactin, and fatty acid glutamic acid) was examined against *Salmonella enteritidis,* and *Listeria monocytogenes*. Different concentrations of the bio-based surfactants were applied to the Brain Heart Infusion broth with 10^5 CFU/mL pathogens to test the inhibitory effect. The broth were transferred into bio-screen wells and incubated for 48 hours. The turbidity of the broth were determined every 30min at 600nm. Result indicated that glucose palmitate, surfactin had inhibitory effect to the two pathogens. Glucose palmitate demonstrated the strongest inhibitory effect at 0.67mg/mL: it inhibited growth during stationary stage and reduced the final bacteria amount by one third fold. Surfactin showed similar effect at all concentrations (0.156mg/mL to 2.5mg/mL). Fatty acid glutamic acid did not have obvious antimicrobial effect. For glucose laurate, it was surprising that higher level (2mg/mL) promoted the pathogen to grow, which may indicate that glucose laurate provided metabolic substances for bacteria to grow. The minimum inhibitory concentrations for these bio-based surfactants will be determined.

2. **Chemocleavable Surfactants Bearing Polyethylene Glycol Derived from Diethyl Tartrate.** D. Ono[1], R. Uematsu[2], S. Kawano[1], H. Sato[1], M. Shizuma[1], and A. Masuyama[2], [1]Osaka Municipal Technical Research Inst., Japan, [2]Osaka Inst. of Technology, Japan.

Development of surfactants with excellent surface-active properties, additional functions, or good biodegradability has become desired. We have been investigating the preparation and properties of a series of acid- and alkali-cleavable surfactants which are designed to decompose into non-surface active species under mild conditions after fulfilling their original functions such as emulsification, solubilization, micellar catalytic activity, and so on. The decomposition properties can be controlled through adjustment of the solution's pH.

In this work, one-chain and double-chain chemocleavable nonionic surfactants bearing a 1,3-dioxolane ring were prepared by acid-catalyzed condensation of diethyl tartrate with fatty ketones, followed by a reaction with polyethylene glycol without any expensive reagents or special equipment. We confirmed that they have good surface-active properties. The biodegradabilities of these cleavable surfactants after 28 days are more than 60% according to guideline OECD 301C with activated sludge. Their detergency on artificially soiled cotton cloth was better than the reference detergent according to the Japan Industrial Standard Method. The reference detergent consisted of sodium n-dodecylbenzenesulfonate, which is a popular component in commercial detergents.

3. **Syntheses and Surface Active Properties of Fluorosurfactants Having Short Perfluoroalkyl Groups.** B.M. Lee[1,2], E. Kang[2], and G. Jung[2], [1]Korea Research Inst. of Chemical Technology, Republic of Korea, [2]University of Science & Technology, Republic of Korea.

Fluorosurfactants show excellent surface-active properties compared to normal hydrocabon derived ones. But the major disadvantage of fairly long fluorosurfactant such as PFOA is a suspecting endocrine disruptor.
In this study, fluorosurfactants having 2 ~ 6 difluoromethylene groups were synthesized. The surface tensions of those at 1% aqueous solution are between 13.84 and 24.11dyne/cm.

4. **Organomodified Silicones in Household Care Applications.** M. Hisamoto and A. Nagy, Evonik Corp., USA.

A novel organomodified silicone has been studied for multiple application areas, including fabric softening and hard surface treatment. An optimized production process resulted in a new amino-functional polymer with a more uniform microstructure. This new structure enables the user to improve fabric conditioner formulations, including softening, rewet and fragrance retention. In addition, this polymeric additive can also contribute to clean and protect hard surfaces with higher efficiency while improving their aesthetic appearance. Test methods, formulation procedures and comparative data will be discussed.

5. **Surfactants with Glycerol and Sophorose Headgroup.** S.S. Bhagwat, S.P. Sulakhe, and V. Dengle-Pulate, Inst. of Chemical Technology, India.

We present two new surface active molecules where the polar headgroup is of natural material origin. Lauramididopropyl glyceryl dimethyl ammonium chloride, or LGDMAC, is a quaternary ammonium surfactant where glycerol contributes towards the hydrophilic part of the molecule. The CMC (1.2mM) is comparable to conventional quaternary ammonium compounds, while the C20 (0.27mM) is lower. The foamability of this molecule is also comparable to conventional surfactants. The dynamics at low concentration is superior to CTAB while its antimicrobial activity is somewhat lower. This molecule is more likely to be used as a mixture with other conventional surfactants and hence its mixture equilibrium properties were also studied, including with some conventional surfactants such as Triton X-100, Lauryl alcohol ethoxylates, etc., as well as with the salt

of its raw material the lauramidopropylamine. Sophorose is another such natural hydrophilic molecule which can work as a polar headgroup. In the present work, sophorolipids were prepared by using fatty alcohols, and, hence, the molecule remains a nonionic one. Application of this molecule (CMC~0.02mM and CMC<25mN/M) can be as a single material or, more likely, as a mixture with other bulk surfactants.

6. **Optimization of Nanoemulsion Fabrication Using Microfluidization: Role of Surfactant Concentration on Formation and Stability.** S. Uluata[1,2], D.J. McClements[2,3], and E.A. Decker[2,3], [1]Dept. of Food Science, University of Massachusetts Amherst, USA, [2]Dept. of Food Technology, Inonu University, Turkey, [3]Dept. of Biochemistry, King Abdulaziz University, Saudi Arabia.

Nanoemulsions have some important potential advantages over conventional emulsions for certain commercial applications due to increase the bioavailability of lipophilic bioactives. In this study, the factors influencing droplet size and stability in oil-in-water nanoemulsions fabricated from a hydrocarbon oil and an anionic surfactant were examined. These nanoemulsions were produced by a high pressure homogenizer using sodium dodecyl sulfate (SDS) as a surfactant. The influence of homogenization pressure, number of passes, surfactant concentration, and cosolvent addition was examined. The droplet size decreased with increasing homogenization pressure, number of passes, and surfactant concentration.

Nanoemulsions with low turbidity and small droplet diameters (~62nm) could be produce under optimized conditions. Interestingly, the creaming stability of the nanoemulsions depended on droplet size and free surfactant concentration, which was attributed to a depletion flocculation effect. These results show the importance of optimizing surfactant levels so as to produce small droplets that are also stable to creaming.