

S&D 1: Fabric Care Performance Boosters and New Benefits

Chairs: Kathleen Stanton, American Cleaning Institute, USA; and Tyler Smith, Lightbox Laboratories, LLC, USA

Rational Design of Lipases: A Case Study. Jakob Skjold-Jørgensen*, *Novozymes A/S, Denmark*

When it comes to caring for their clothes, consumers want to save time and money with a high expectation on performance. With an increasing number of consumers using the “Quick wash” cycle to save time, water and energy costs, concerns with incomplete stain removal also arise. Average wash temperatures have been falling driven by appliance manufacturers designing machines to meet Energy Star requirements. Colder wash cycles address key consumer needs of fabric care and preservation, but cleaning efficiency is lower than with warm water. This talk demonstrates how catalytic enzymes enable better cleaning with shorter wash cycles and colder wash temperatures.

Engineering an Improved Cellulase for Fabric Care in Liquid Detergents. Christian Adams*¹, Andre Krouwer², and Arjen J. Hoekstra², *¹DuPont Industrial Biosciences, USA; ²DuPont Industrial Biosciences, The Netherlands*

A global fabric care study carried out by DuPont highlighted considerable consumer dissatisfaction with pilling and color fading on garments after using most detergents. In general, liquid detergents provide better fabric care properties than laundry powders, and in most mature markets, including North America; liquids have become the dominant product format. Cellulase is known for providing multi cycle fabric care benefits such as pilling prevention and color maintenance. However, liquid detergents provide a challenge to the product formulator for delivering robust fabric care performance with cellulase, especially in the presence of proteolytic enzymes. In liquid

detergent formulations protease may negatively impact the cellulase activity over time, resulting in loss of fabric care properties. Therefore, an improvement of the storage stability properties of cellulase is required. DuPont has applied molecular modelling software and structure function analysis to generate hypotheses about regions of the enzyme that may be susceptible to instability. Functional studies identified the cleavage sites where we could influence the properties of improved performance and stability. These improved properties of the new cellulase were confirmed in application studies under North American wash conditions, as well as storage stability trials in typical US liquid detergents comprising protease.

Breakthrough Solution for Odor Reduction in Cleaning Products. Anita Augustyniak, and Yvon G. Durant*, *Itaconix, USA*

Odor management is a core component of cleaning functions. Odor in various textiles, such as laundry, sport equipment, upholstery and carpets are assaulted by combinations of odors ranging from pet urine to bodily fluids to food waste. Odor management in cleaning products is often a combination of detergency (odor extraction to solution), oxidation and masking. However, some odors are persistent even after oxidation and recur once masking has dissipated. This is due to the high susceptibility of the human nose to a set of odors that we culturally associate as unwanted. Thiol and amine derivatives are some of the most persistent molecules that can be detected by our noses at sub ppb level. A breakthrough strategy is to add molecules that have the ability to complex malodorants into non-volatile molecules.

Complexes of Zinc-polyitaconate have the property of maintaining zinc ions in solution across a wide range of pH, in complex aqueous matrices, while drying to a non-oily residue. The zinc atom is able to coordinate with thiols or amines, to create Lewis acid-base complexes that are non-volatile, while remaining in solution. Formulated products containing these neutralizing metal-organic complexes are offering novel performance in odor reduction, while eliminating unwanted residues on fabric.

Study on Bacterial Control During Washing with Laundry Detergent. Nanami Sasaki*, Keisuke Mori, Takahiro Hayashi, Misa Nakagawa, Masayoshi Oishi, Hiroaki Shindo, Hiroyuki Masui, and Takahiro Okamoto, *Lion Corporation, Japan*

In recent times, awareness on personal hygiene has been increased year by year, especially, consumer needs on odor care in daily life has become higher. In response to this needs, many kinds of study on odor care have been conducted in the fabric care field. So far, most of studies have been done focusing on 1) removing sebum soil, nutrition for bacteria, from fabric, or 2) preventing bacteria growth on fabric as a counter-measure for bacteria generating malodor. In this study we focused on the effect of bacteria present in washing tubs to reduce fabric malodor. First, we studied bacteria flora of bio-film on washing tub surfaces in 14 houses by using gene-sequences homology comparison. From this data, we found that some kind of bacteria detected commonly in most houses have clear relation with malodor of washing tubs. These bacteria grew up and formed bio-film to stick firmly to the surface. These bacteria transferred to clothes during washing process then it became a cause of clothes malodor. Next, we tried to reduce the effect of bacteria on washing tub surface by approaching 1) to remove bio-film or to inhibit bio-film forming, and 2) to

prevent transfer of bacteria from bio-film to clothes during washing. As a result, we found a specific enzyme itself and further the combination of the enzyme with some detergent components are effective for the purpose.

Laundry Detergency of Solid Non-particulate Soil or Waxy Solids: Relation to Oily Soil Removal Above the Melting Point. David A. Sabatini*¹, John Scamehorn¹, Jarussri Chanwattanakit², and Sumaeth Chavadej², ¹*University of Oklahoma, USA*; ²*Chulalongkorn University, Thailand*

In this work, methyl palmitate or palmitic acid methyl ester, a monoglyceride, was used as both a model solid fat below the melting point and as an oily soil above the melting point. An anionic extended surfactant [branched alcohol propoxylate sulfate sodium salt (C123-(PO)4-SO4Na)] was used to remove methyl palmitate from cotton and from polyester. Above the melting point (~30°C) of methyl palmitate, the maximum oily soil removal was found to correspond to the lowest dynamic interfacial tension (IFT), as is common with liquid soils. Below the melting point, the lower the contact angle of the wash solution against the soil (indicating higher wettability), the higher the solid fat soil detergency. The removed methyl palmitate was found to be mostly in unsolubilized droplets or particles with a small fraction of micellar solubilization for both solid and liquid forms. The presence of surfactant can prevent the agglomeration of detached methyl palmitate particles in both liquid and solid forms, reducing redeposition and enhancing detergency. Below the melting point, the surfactant aids the solution wetting the surfaces, then penetrating the waxy solid, causing detachment as small particles, and dispersion of these particles. Unlike particulate soil detergency, electrostatic forces are not an important factor in fatty soil detergency.

Polymers and Detergency—A Complex Game of Interactions. Keith E. Gutowski¹, and Dieter Boeckh*²,¹*BASF Corporation, USA*; ²*BASF SE, Germany*

Liquid laundry detergents are formulations predominantly based on surfactants. Polymers are added at much lower levels serving a variety of purposes like hardness- and rheology-management, soil-dispersion or the prevention of redeposition of soils or dyes. Primary and secondary detergency are areas that can be significantly relevant for the application of polymers. While initially, when polymers were introduced to laundry detergents, the focus was on anionic polymers, the scope of polymers applied today has widened and includes functional polymers with cationic character as well as nonionic amphiphilic structures. The variability and characteristics of functional polymers allows choices how the polymer can interact with the complex colloidal and interfacial situation found in a liquid detergent and during laundry. Charge, size and polarity as well as distribution of functionality determine if and how polymers associate with surfactants, interfaces and hardness ions. A study of the colloidal chemistry of selected polymers in mixed polymer-surfactant systems is presented. The influence of the selected surfactant system as well as of water hardness on association concentrations and phase behavior is studied. Examples show how modeling can help understand the solution behavior of these polymers and how they are affected by the presence of surfactant and hardness ions. The influence of observed properties and association phenomena on detergency are discussed and examples are shown that were obtained in model experiments.

Protect and Care—Silicone Effects for Perceivable Benefits. John H. Richards*, *Wacker Chemical Corporation, USA*

Consumers are continually seeking ways to maintain, refresh and enhance garment properties. Silicones utilized as rinse cycle additives generate many perceivable consumer benefits. Color fastness and shape retention are two such effects that can be defined and quantified via application testing. An overview of novel silicone chemistries that protect fabrics will be provided, along with relevant practical test results. Performance characteristics of treated garments are highlighted along with product recommendations for achieving the desired effects.

S&D 1.1: New Technologies in Industry

Chairs: Eric Theiner, Evonik Corporation, USA; and Hongwei Shen, Colgate Palmolive Co., USA

Surface Restoration Achieved Using STEPOSOL[®] CITRI-MET via Partial Softening and Cure of Existing Polymer Coatings Ron A. Masters*, *Stepan Company, USA*

STEPOSOL[®] CITRI-MET is a concentrated, natural-oil-based cleaning blend that contains Nobel Prize winning metathesis and Stepan commercial amidation chemistry. Launched September 2015, this product serves multiple applications, depending on dilution, from heavy oilfield equipment cleaning to household all-purpose cleaning. At a ten to twenty-fold dilution range, a unique restorative effect is observed for many surfaces. Originally thought to be a deeper, more effective cleaning than traditional cleaners, further development has revealed that this is a new technology where existing surface coatings are slightly softened and mobilized, and when spread and left to dry, provides a restoration effect, as if the original coating were reapplied. This presentation will include the technical basis for the effect, visual examples, and a live demonstration.

Viscosity Control for a Vesicle Suspension System with Non-adsorbed Polymer Ryo Inoue*¹, Asami Miyajima¹, Taku Ogura¹, Otto Glatter², and Norio Tabori¹, ¹*Lion Corporation, Japan*; ²*University of Graz, Austria*

Consumers' need of long-lasting fragrance for the fabric-care category has been steadily increasing in recent years. Therefore, a number of liquid laundry products containing encapsulated fragrance have been launched. In order to satisfy both the prevention of floating capsule particles and easy pouring in liquid products, it is necessary to have a structural viscosity as a solution property. In this study, we attempted to control structural viscosity for vesicle suspensions formed by cationic

surfactant triethanolamine-based esterquat (TEQ) as ingredients of softener. We found that the addition of a non-adsorbed polymer which cannot interact with the vesicle membrane is effective in this system by utilizing the techniques of rheological measurements, differential scanning calorimetry and dynamic light scattering. Thus, we considered that the main factor of structural viscosity is depletion flocculation induced by the coexistence of the two different particle sizes represented by the surfactant vesicles and by non-adsorbed polymers. To understand the flocculation behavior of this system more clearly, we examined the effect of the particle size, concentration of vesicles and non-adsorbed polymers on the viscoelastic behavior. As a result, the flocculation force calculated from viscoelastic property became strong with increasing size and concentration of the non-adsorbed polymer. It can be deduced that the flocculation mechanism is based on the theory of depletion interaction.

Potential of Biosurfactants as New Performance Ingredients in Liquid Laundry Alexander Schulz* and Michael Dreja, *Henkel AG & Co. KGaA, Germany*

The main target for a detergent from a consumer viewpoint is the removal of soil and stains. Since the invention of modern detergents, the consumer goods industry is working to fulfil those needs. More recently, growing environmental awareness of industry, regulators and customers leads to additional requirements which can be met today via innovations in sustainability. Modern detergents have to work well at low temperatures during the wash, and its ingredients have to be well biodegradable. Surfactants can be derived from sustainable natural

sources, among them biosurfactants produced by microorganisms. Integrating biosurfactants into market-relevant detergent formulations remains challenging, due to their availability, performance profile and since the vast majority of consumers are reluctant to pay extra for “green” claims. Indeed, not all biosurfactants are in general more sustainable when e.g. land use, energy consumption and biodegradability are considered. Due to these complex requirements, we use several methods to assess the use of biosurfactants for liquid laundry applications. We start with the evaluation of physico-chemical parameters like the critical micellar concentration of the pure surfactant, but also of blends with other surfactants. At the same time, we evaluate what the end consumer can perceive by assessing compatibility, stability and performance, via washing trials with suitable sets of stains. Especially on various fatty stains like lard, sebum, and oil, biosurfactants show unique properties, and understanding these properties is important for the creation of future detergents. Correlating these results with the physico-chemical parameters enables us to understand underlying interactions and to make predictions about the best detergent formulations to fulfil consumer needs.

Elucidation of Softening Mechanism in Rinse Cycle

Fabric Softeners Takako Igarashi*, Koichi Nakamura, Masato Hoshi, Teruyuki Hara, Hironori Kojima, Masatsugu Itou, Reiko Ikeda, and Yoshimasa Okamoto, *Kao Corporation, Japan*

In our previous study, we proposed that the inhibition of the formation of hydrogen bonding network between single fibers made of bound water was important. Based on this proposal, we have continued to get a deeper-insight about the reason why and how the comfortable softening is realized with the point of adsorption status of cationic vesicles to the yarns.

Development of a Spherulite Structured Liquid Cleanser at Reduced Surfactant Concentrations

Peter R. Hilliard*, *Colgate Palmolive Co., USA*

Delivering moisturizing benefits to the skin's surface from a body cleansing liquid presents several challenges. One particular challenge is the need to deliver significant amounts of oil to the skin while maintaining formula stability and foaming properties. Spherulite based structured surfactant systems can be used to develop cleansing liquids capable of suspending and delivering significant concentrations of oil to the skin. However, these formulations tend to contain significant concentrations of surfactants in order to maintain the spherulite structures and suspension properties. We will discuss chemistries and processes that produce structure at lower spherulite based surfactant concentrations. These low spherulite concentration structured formulas are significantly more effective delivering oils to the skin than normal high concentration spherulite formulas. In addition, a low concentration spherulite system is much more effective than a standard oil/water emulsion in delivering oils to the skin's surface during washing procedures. The hypothesized mode of action is based on formation of a unique “honey comb” ordering of the spherulites leading to structure at much lower surfactant concentrations. This is very different from that observed in a normal spherulitic system based on volume exclusion and tight packing of the spherulite structures. The oil is dispersed within the “honey comb” formations, is released during a catastrophic breakdown of the structure upon dilution, and potentially presenting a high localized concentration of the oil to the skin. In addition, since less surfactant is required to produce a structured formula capable of suspending the oil phase, it is hypothesized that less of the oil will be emulsified during washing and resulting in a further increase in the amount of oil deposited on the skin.

Examples of experiments supporting this hypothesis will be discussed.

Noverite™ Polymers for Window and Bathroom Cleaners: Improved Anti-fog, Reduced Hard Water Spotting, and Easier Soap Scum Removal Jobiah J. Sabelko*, Chris Cypcar, and Eve De Maesschalck, *Lubrizol Advanced Materials, Inc., USA*

Consumers have increasingly busy lifestyles and desire cleaning products that make the cleaning process easier and more effective. Product differentiation is also critical to success in this crowded marketplace and typically requires providing innovative functionality to traditional products. In response to these market needs, Lubrizol has developed Noverite™ 301, 310 and 311 polymers, novel functional additives for window and bathroom cleaners with long-lasting effects. These high performance surface-substantive polymers have shown excellent capability to provide hydrophilic properties to hard surfaces. The resulting water sheeting effect inhibits fogging on glass, reduces the formation of hard water spots, and provides easier removal of soap scum on bathroom surfaces. The Noverite™ polymers are water soluble, easy to use liquid additives that are effective at low dosage levels. They are compatible with a wide range of surfactants and over a broad pH range thereby providing great formulating flexibility and are also suitable for products that demand high clarity. Noverite™ polymers allow for the development of cost-effective cleaners that prevent fogging, hard water spotting and soap scum build up, making the cleaning process easier and less time-consuming.

Hydrotroping Properties of Naturally-derived Surfactants in Alkaline Formulations Robert J. Coots*, and Dennis Abbeduto, *Colonial Chemical, Inc., USA*

Surfactant chemicals that are classified as hydrotropes serve an important function in formulating cleaning products for many different applications. The ability of a water insoluble detergent ingredient to be solubilized into an aqueous alkaline solution, is an important requirement when formulating such products. In the last few years, we have seen a shift in attitude of both consumer and industrial consumers toward using ingredients that are from natural, renewable sources. This has given rise to several new products that are derived from natural feedstocks designed to compete in this area of surfactant chemistry. This talk will give detailed information about hydrotropes that are derived from natural sources and their performance compared to traditional hydrotropes, that are derived from petroleum-based feedstocks.

S&D 2: New Trends in Cleaning: Hard Surface, Detergency, Hand Dish, and Autodish

Chairs: Paul Sharko, Shell Global Solutions, Inc., USA; and Masaki Tsumadori, Senior Advisor, R&D, Kao Corporation, Japan

Improving Hand Dishwashing Liquid Cleaning

Performance with Enzymes Lotte J. Jensen-Holm¹ and Thomas J. Burns*², ¹*Novozymes A/S, Denmark;* ²*Novozymes North America, Inc., USA*

Hand-dishwashing (HDW) product formulations have historically focused on continuous optimization of the surfactant and fragrance systems. Innovation is now increasingly dependent on more-novel ingredients such as enzymes. To benefit from the well-known ability and speed of enzymes to quickly break down starch and protein, HDW formulations require state-of-the-art technology to ensure formulation compatibility as well as stability. We evaluated the ability of enzymes to enhance performance by dismantling complex burnt-on and dried-in food-soils. In addition to those results, the presentation will focus on how to overcome the technical formulation challenges to ensure this improved performance in hand dishwashing solutions.

Glucamides - Versatile Sugar Surfactants for Sustainable Cleaning of Hard Surfaces Carsten Cohrs*, Florian Schinle, Gabi Ohlendorf, and Christine Müller, *Clariant, Germany*

To meet the trend of renewable based and environmentally safe surfactants we investigated Glucamides or N-Methyl-N-Acyl Glucamines as a new type of highly renewable, non-ionic sugar surfactants. They are readily biodegradable and are safe for the aquatic environment. Depending on the hydrophobic moiety of the molecule wetting ability, foam performance and cleaning effect can be modulated to cover a broad field of applications. Therefore we assumed them to be an ideal new product group for hard surface applications. In the homecare segment they may be used for a variety of applications. In hand dishwashing liquids, green hand dishwashing liquids can be formulated without loss in performance against standard products. Highly concentrated liquids are accessible without volatile organic solvents. The liquids have a very low impact on the environment. Selected Glucamides can deliver caring benefits to hands after

the wash up and still add to the foam mileage of the hand dishwashing liquid. In hard surface cleaning short chain exhibit superior wetting performance. Their excellent lime scale removal power combined with excellent compatibility with all kind of surfaces, especially sensitive plastic materials makes them the ideal solution for bath cleaners. In addition, Glucamides leave low residue and streaks on the cleaned surfaces, maintaining their shiny appearance. Finally members of the Glucamide family are also excellent rinse surfactant for automatic dishwashing as they reduce spots and films significantly.

Novel Dishwashing Process Converting Fatty Soil into Surfactant Mariko Kagaya*, and Takaya Sakai, *Kao Corporation, Japan*

Sodium poly (oxyethylene) alkyl ether carboxylate (EC) is known as a low irritated anionic surfactant and has been applied to many kinds of detergents and industrial chemical products. Recently we found that EC performs excellent detergency for fatty soil. In order to reveal the mechanism for it, we investigated the triangle phase diagram of EC, a component of fatty soil and water by means of microscopic observation, small angle x-ray scattering (SAXS) and DSC measurement. As a result, EC aqueous solution and oleic acid, which is one of the components of fatty soil, form lamellar liquid crystal (LLC) in very broad composition and concentration range in the phase diagram. The cleansing mechanism for fatty soil is thought to be that EC solution penetrates into fatty soil and forms LLC with oleic acid. In this LLC, fatty acid, which is soil, also works as a surfactant and it becomes high concentrated surfactant solution. As high concentrated surfactant solution (LLC) is formed inner soil itself, the other soil components can be removed by liquid crystal emulsification with much less power than the normal emulsification. In fact, it is confirmed that EC solution removes the whole fatty soil without rubbing. From above, EC performs not only high detergency but also spontaneous dishwashing for fatty soil converting soil

into surfactant. It might lead sustainable process decreasing the amount of surfactant. Moreover this cleansing can provide consumer low mechanical power cleansing with mildness to the skin.

Increasing the Performance of Automatic Dishwashing with Enzymes Roberta Mustacchi¹, Lotte J. Jensen-Holm^{*1}, and Thomas J. Burns², ¹*Novozymes A/S, Denmark*; ²*Novozymes North America, Inc., USA*

In this presentation we will focus on showing the ability of enzymes to save time and effort in the wash process and we will prove how enzymes can significantly increase the overall wash performance on hard to remove complex soils. We will also illustrate the novel methodology used for evaluating performance and the materials available for reproducing such results in any laboratory.

Cracking the Code for Spotless Dishes Peter Miller* and Keith E. Gutowski, *BASF Corporation, USA*

In 2010, a post-phosphate landscape created some major challenges for automatic dishwashing detergent formulators, and many consumers were left with dirty dishes. Six years later, formulators have come up with inventive ways to replace and even exceed the performance gaps left by the removal of phosphate. One of the largest gaps has been the spotting and filming performance, largely influenced by the level of minerals in the wash water and the degree to which these minerals can be sequestered in the wash. Formulating with the chelating agent sodium methylglycine diacetate (MGDA), in combination with other sequestrants, can virtually eliminate spotting and filming without major concessions on cost or other performance criteria.

Future Trends in Auto-dish Wash Detergents Mike Orr*, Nilgun Aksoy, Rob Roggeband, and Graham A. Sorrie, *The Procter & Gamble Co., UK*

Consumers continue to demand outstanding cleaning and shine performance from auto-dish detergents. To delight the consumer, The ADW innovator has to deliver top class cleaning performance through a skilled integration of a diverse palette of chemistries that does not require phosphate or, in some

regions, phosphonates. Cleaning: the palette of chemistry the ADW formulator can chose range across bleach for beverage removal, enzymes (protease for protein soils such as meat and egg and amylases for starch related pasta and rice), alkalinity for hydration of burnt soils and surfactant for grease removal. Shine: combinations of polymers, builders and crystal growth inhibitors are available to deliver shine across the full range of consumer relevant substrate. Yet the top unmet consumer need continues to be on tough baked on soil removal. Delivering against this consumer need will become even more challenging as the industry and consumers will try to save energy behind lower temperatures and with shorter wash cycles, which pose new technical challenges such as dissolution of tablets, grease cleaning, organic film formation, and need for higher levels of enzymes/efficient enzymes under these conditions. In addition there are space constraints within the unit dose form to be compatible with machine dispenser drawers. The ADW formulator will need look to increasingly sophisticated chemistries in order to balance these challenges and, in the process, continue to demonstrate good product stewardship in the area of human and environmental safety. The partnership of the Dishwashing Appliance Industry is a requisite to achieve these goals.

In Situ Monitoring of Soil Removal Processes from Hard Surfaces Using Quartz Crystal Microbalance Technique Yu Kanasaki^{*1}, Yasuyuki Kobayashi², and Keiko Gotoh³, ¹*Nara Women's University, Japan*; ²*Osaka Municipal Technical Research Institute, Japan*; ³*National Institute of Technology, Nara College, Japan*

The trace-level surface contaminants significantly impact on the quality of the products such as hard disk, silicon wafer and semi-conductor, and therefore their removal by cleaning should be necessary. To improve the removal efficiency of the contaminants, the mechanism of the removal process should be revealed. In this study, to investigate removal behavior of trace-level contaminants from various hard surfaces in aqueous solutions, we performed in-situ monitoring of contamination removal process using a quartz crystal microbalance (QCM). The QCM electrodes consist of carbon, silica, and gold, which were used as model hard

surface substrates. For comparison, a polymer film, was prepared on the QCM. Stearic acid (SA) was deposited as trace-level contaminants onto the QCM by the Langmuir-Blodgett (LB) technique. Immediately after immersion of the QCM in the aqueous solution containing sodium hydroxide (NaOH) or alkyl sulfate (AS), the QCM frequency was recorded. The apparent equilibrium removal efficiency and the rate constant of the SA-LB film were determined from the frequency vs. time curve. In the NaOH solution, the SA-LB film was efficiently removed from all substrates due to neutralization. On the other hand, in the AS solution, the removal efficiencies of the SA-LB film from the carbon, gold and polymer substrates were small. It seems that the SA-LB film deposited on the substrate in contact with its hydrophobic part is difficult to remove by the penetration of the surfactant. As expected, the SA-LB film deposited on the silica substrate in contact with its hydrophilic part was rapidly removed.

Silicone-free Rubber and Plastic Dressing for Enhanced Carwashing

Danielle Goodwin¹ and Dave McCall^{2*},
¹Madonna University, USA; ²USA

Unlike most detergent processes, successful washing of an automobile involves more than just soil removal. Once clean, the various surfaces of the vehicle are expected to have a high gloss. Achieving sufficient shine usually requires the application of an additional product. Rubber and plastic surfaces are generally treated with a silicone blend, which produces a very high gloss. However, the silicone film is wet and tends to sling off the surface when the car is in motion and is prone to quick resoiling when dirt impacts the wet film. A new rubber and plastic dressing product has been formulated which produces a durable, glossy film on treated surfaces in the form of a dry film. The film is a blend of polymers and waxes and includes an exclusive gloss agent specifically synthesized for this application. Since the film is dry, it remains in place after application, resists soil, and survives multiple cleaning cycles.

Methane Sulfonic Acid and Methylglycinediacetic Acid Benefits in Acidic Bathroom Cleaning Formulations

Kevin M. Salmon*, and Stephen F. Gross, BASF Corporation, USA

In this presentation, a performance synergy is explored between a combination of methane sulfonic acid (MSA) and methylglycinediacetic acid (MGDA) in an acidic bathroom cleaning formulation. For home care applications, MSA must be partially neutralized to an acceptable pH (>2.3). Buffering of strong acid solutions to higher pH normally results in loss of primary cleaning performance, due to acid neutralization and acid salt formation. Surprisingly, a significant increase in primary cleaning performance vs. calcium stearate is observed when the pH is adjusted using MGDA as opposed to NaOH. Further development work was performed to generate a formulation with improved performance to market products at a greatly reduced activity. Market trends in Hard Surface (specifically bathroom care), test formulations and performance data will be presented.

Spontaneously-generated Peeling of Keratin Grime from Hard Surfaces by the Effects of Permeation, Chelation, and Swelling

Yosuke Watanabe*, Asako Kawasaki, Yukihiro Kaneko, and Ryoji Yasue, Lion Corporation, Japan

In a bathroom, various grime stick and accumulate to the hard surfaces easily and strongly by repeating dipping and drying with soiled bathtub and showering water. In this study, we report a new mechanism of bath cleaning whereby the detergent can wash out the grime from hard surfaces without a great deal of time and effort. For easy cleaning, we focused on the binding state between the bath grime and the hard surfaces, and tried to weaken the bond strength by permeating and chelate effects of detergents. We confirmed that a main component of the bathtub grime is a complex of calcium and a keratin protein derived from human skin by using FT-IR and EDS-SEM measurements, and keratin grime is remarkably swollen with water by depriving it of calcium ion with chelating agents by using ICP and FT-IR measurements. Further, we found that the swelling rate is increased by permeating effect of anionic surfactants and glycol solvent by using dynamic surface tension measurement and the advanced swelling

induces spontaneously-generated peeling of keratin grime from the hard surfaces by using video microscope measurement. The results demonstrate that the binding state between the bath grime and the hard surfaces can be weakened by permeating effect of surfactants / glycol solvent and swelling effect of chelating agents.

S&D 2.1: General Surfactants

Chairs: Sanja Natali, USA; and Phillip Vinson, The Procter & Gamble Co., USA

A New Approach to Developing Surfactants

Soluble in Highly Alkaline Systems Renae Bennett, Eric Theiner*, Khalil Yacoub, Brian Smith, and Larry Meyers, *Evonik Corporation, USA*

Cleaning systems with high levels of actives allow more economical distribution of concentrated products as well as the benefit of bringing high performance products to bear in difficult soil removal systems such as those found in food and beverage plants. To date, there have not been many materials that provide a high degree of solubility in heavily built alkaline systems while maintaining the performance that results from good surface and kinetic action. This presentation will discuss a new approach to the problem and the resulting surfactants that are unique to the industry.

Assessment of Narcotic-like Effects of Surfactants Using a Larval Zebrafish Neurobehavioral Assay

Harry W. Broening*¹, Lisa Truong², Jane K. La Du², Greg J. Carr¹, J. F. Nash¹, George P. Daston¹, and Robert L. Tanguay², ¹*The Procter & Gamble Co., USA*; ²*Oregon State University, USA*

The intoxicating (narcotic) potential of ingredients used in consumer products can result in adverse outcomes following accidental exposures. These effects are often characterized as drowsiness, lethargy, or non-responsiveness in emergency treatment situations. Thus, it is important to identify ingredients with narcotic potential in order to assess the likelihood that a formulation may produce symptoms of narcosis following accidental ingestion. To rapidly screen and evaluate the narcotic-like effects of chemicals, a neurobehavioral assay was developed using early life-stage zebrafish. The assay is based on locomotor responses stimulated by a light-to-dark

photo-transition in 5 days post-fertilization (dpf) larvae. Larval zebrafish are exposed to test materials beginning at 5 dpf and locomotor activity assessed using video tracking. Locomotor activity is stimulated using alternating 3 minute light/dark periods and activity recorded for 8 light/dark cycles. Narcotic potency is determined as the concentration at which locomotor activity is reduced by 50% (IC50). A variety of test materials have been evaluated including linear alcohols and surfactants. The narcotic potency of linear alcohols (C2 to C12) was observed to increase with carbon number. Ethoxylation (EO) of alcohols to produce alcohol ethoxylate (AE) surfactants altered narcotic potency in a biphasic manner, increasing narcotic potency at low EO but decreasing narcotic potency at high EO. Anionic surfactants (alkyl ethoxy sulfates, linear alkylbenzene sulfonates) were an order magnitude less potent narcotic agents in comparison to AEs. These studies collectively demonstrate the utility of the larval zebrafish model to detect and characterize narcotic agents.

Counterion Binding on Coacervation of Dioctyl Sulfosuccinate in Aqueous Sodium Chloride

Shengbo Wang, Changlong Chen*, Ben Shiau, and Jeffrey Harwell, *University of Oklahoma, USA*

Large amounts of surfactant coacervation work focused on complex coacervation, such as mixture of surfactant and polymer, or mixture of different species of surfactants, seldom on the simple coacervation of single conventional surfactant in aqueous phase. This study aims to investigate evolution of dioctyl sulfosuccinate (AOT) /sodium chloride coacervation in aqueous solution associated with change in counterion binding degree. In this work, coacervation phase boundary of AOT in the presence of sodium chloride was

obtained by spectrophotometer in terms of turbidity measurement. The activity of counterion was measured by sodium ion electrode probe. Electro kinetic parameters such as Zeta potential and hydrodynamic aggregate size were investigated by dynamic lighting scattering (DLS). Also, the formation of coacervate, an electrostatically-driven phase separation, is mathematically illustrated through DLVO theory, essentially a balance between electrostatic repulsion and van der Waals attraction for colloid system. A monotonic decreasing AOT coacervate boundary was observed with increase in NaCl concentration. The degree of counterion binding, calculated by modified Corrin-Harkins equations, revealed a 3-segment behavior of AOT in salt solution. Colloid size distribution was conducted with DLS, where a micelle-vesicle-coacervation process was observed in accordance with a sharp change in zeta potential. Electron microscopy also verified the evolution of coacervation in aspect of morphology. DLVO theory calculation shed lights on how to promote or avoid coacervate. Counterion binding degree plays an important role in the formation of surfactant aggregates. A further study of binding degree facilitates to understand coacervation.

Strategies for Drop-in Replacements for Active Ingredients in Existing Liquid Laundry Detergent Formulations Thu Nguyen, Christian Jones*, and Tamra Weemes, *Sasol Performance Chemicals, USA*

Viscosity control plays an important role in creating a liquid laundry detergent product that meets consumer needs. Beside 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 by

selecting the suitable surfactants. The objective of this research is to investigate the salt-viscosity response of alcohol ethoxylate sulfate anionic surfactants, alcohol ethoxylate nonionic surfactants and mixtures of the two. These surfactants are also tested in different laundry detergent formulations for their viscosity performance. Parameters affecting the salt-viscosity response to be studied include the degree of ethoxylation, the hydrophobe structure of the surfactants and the anionic/nonionic surfactant ratio. The viscosity is measured using a Brookfield viscosimeter at room temperature. The stability of the laundry detergent formulas is evaluated visually based on the formulation clarity and homogeneity at 4 and 40°C. As different formulations require different viscosities, the finding of this study will provide guidance for screening potential alcohol ethoxylate sulfate/alcohol ethoxylate surfactants individually or in combination for a new formulation as well as selecting a drop-in replacement of each surfactant or surfactant combination in an existing formulation to achieve the desirable formula viscosity.

Synthesis, Characterisation, and Surface Activity of Purified Sodium Lauroyl Isethionate.

Mohammed I. Jeraal*, David Harbottle, and Kevin Roberts, *University of Leeds, UK*

In recent decades, synthetic detergents such as sodium cocoyl isethionate (SCI) have become a popular alternative to saponified soaps as a result of their comparatively higher stability in hard water and increased mildness. Despite widespread adoption by the personal care industry, there is a notable lack of knowledge with respect to their fundamental chemical and physical properties. In the current study, a compositional analysis was executed on a hydrolysed coconut oil blend typically used to synthesise SCI. The most abundant lauryl constituent was subsequently synthesised at

the 1L scale. The crude isethionate product was purified by repeat recrystallisation in methanol and any incremental increase in purity was measured by titration with benzethonium chloride. The chemical identity of the resulting surfactant was verified by FTIR, NMR and LC-MS. A combined TGA-DSC thermal analysis was used to determine the solid-liquid phase behaviour of the pure isethionate species. Sodium lauroyl isethionate was isolated to a purity of 97% by LC MS. The thermal analyses indicated a melting temperature range of 223-225°C with significant decomposition beyond 300°C. A critical micellar concentration of 5.4 mM at 18°C was determined by tensiometric analysis, thus confirming the surface activity of the isethionate ester derivative. Commercial isethionate esters typically range between 70 and 85% so this research provides an insight into the preparation and performance of isethionate esters of a higher purity. Future research aims to blend different purified isethionates to determine the effect of varying chain length distributions on the phase behaviour of naturally derived synthetic detergents.

Synthesis of Isomerically Pure 2-Phenyl Linear Alkyl Benzene Sulfonates Richard L. Pederson*, *Materia Inc., USA*

Linear alkylbenzenes are primary surfactants used in household cleaners and detergents. The demand for linear alkyl benzene sulfonates continues to grow because of their low cost, strong performance, and biodegradability. One of the "holy grails" of the detergent industry is more concentrated cleaning power. Industrial experts have described the superior cleaning performance of the 2-phenyl linear alkyl benzene sulfonate (2-PhLAS) isomer over the other LAS isomers (e.g., the 1-, 3-, 4-, 5- and 6-PhLAS). This presentation will describe the synthesis of isomerically pure 2-

phenyl linear alkylbenzenes and 2-phenyl linear alkylbenzene sulfonates. A series of 2-PhLAS were synthesized with chain lengths ranging from 10 to 16 carbons. These isomerically pure 2-PhLAS compounds were independently tested to determine if enhanced detergency performance was achieved when compared to commercial LAS. Results from the detergency tests will be included in this presentation.

The Effect of Regular Surface Patterning on Surfactant Adsorption Brian P. Grady* and Joshua J. Hamon, *University of Oklahoma, USA*

Using e-beam lithography and reactive ion etching, we have created surfaces that we have termed pillars (a relatively flat surface with nanoscale size) and troughs (a relatively flat surface with nanoscale size with walls on either side). Using atomic force microscopy, we have examined these surfaces in water after surfactant adsorption and compared those to the same surfaces with no confinement. Results in terms of the thickness of the layers will be presented, and molecular dynamic simulations under similar confinement will also be presented.

Rheology Modifications for Functional Markets

David R. Allen, Aaron W. Sanders*, Elodie Shaw, Ginger Wren, Dawn Friesen, Eric Weber, and Kelly Buchek, *Stepan Company, USA*

The use of rheology modifiers is widespread in the functional additives markets. Surfactant based solutions can offer alternatives to the traditional polymeric based systems. In the oilfield viscoelastic surfactant formulations and foamed fluids have found several niche applications, including hydraulic fracturing, gas well deliquification, and EOR. Viscoelastic surfactants form a self healing "pseudo polymer" that can be easily broken down when required. Foams create a novel shear thinning or thickening fluid, that can modify the

density of a liquid making it easier to lift, but also can slow the propagation of gas in porous media. In the agrochemical area, formation of nano-sized vesicles through a self-assembly process using at least two surfactants can provide liquids which are both shear thinning and have high elasticity. These properties are the basis for strong suspensive systems which can be utilized in agrochemical suspension concentrate or suspoemulsion delivery systems. This talk discusses some of the recent advances in the rheology of surfactant systems and foams in the functional products area.

Development and Characterization of a New Class of Castor Oil Ethoxylates Cornell Stanciu*, Jorge M. Fernandez, and Ning Xie, *Sasol North America, USA*

A new class of castor oil ethoxylates with significantly improved efficacy has been developed using a narrow range catalyst. The unique structure of the castor oil triglyceride allows for the formation of highly effective surfactants especially when saponification can be mitigated through the use of a very selective catalyst. These products display distinct features compared to other traditionally base-catalyzed analogs on the market, making them particularly suitable for agricultural and oilfield applications. This paper describes the thorough analytical characterization (NMR, wet chemistry, HPLC, MALDI-TOF) we pursued in order to understand the noticeable differences in behavior compared to similar products manufactured via alternative catalytic methods. It also shows the main surfactant characterization methods (ST, IFT) utilized for the product. A report on the performance of these molecules in agricultural and oilfield markets with the new applications developed is also presented.

The Effect of Small Molecules on Cetylpyridinium Chloride's Behavior in Solution and at Interface

Hongwei Shen*, Chi-Yuan Cheng, Kevin Chi, Donghui Wu, Venda P. Maloney, and Ravi Subramanyam, *Colgate Palmolive Co., USA*

Cetylpyridinium chloride (CPC) has been widely used in many consumer products as emulsifier, antibacterial agent, and / or preservative. Understanding how small molecules in the formulations impact CPC's behavior and activity is critical for developing efficacious new products for consumers. In this study, the effects of two small molecules, sodium benzoate and benzyl alcohol on CPC's behavior in solution and at interfaces were investigated by NMR, dynamic light scattering (DLS), and surface/interfacial tension (SFT/IFT) techniques. It was found that sodium benzoate significantly altered the size and dynamics of CPC aggregates, while benzyl alcohol had minimum effect. In an effort to understand the observed CPC behavior change, the interaction of these small molecules and CPC at molecular level was investigated by Nuclear Overhauser Effect NMR Spectroscopy (NOESY). NOESY results suggest that the aromatic ring of negatively charged sodium benzoate strongly interacted with CPC while benzyl alcohol did not. It is believed that electro-static interaction dominates the effect of small molecules on CPC in aqueous formulations and results in observed behavior change.

S&D 3: *Journal of Surfactants and Detergents*—20th Volume Celebration Honoring Milton Rosen

Chairs: Dennis Murphy, Stepan Company, USA; and Arun Ramchandran, University of Toronto, Canada

Gemini Surfactants Based on Linear Alkylbenzene Sulfonate for Use in Liquid Laundry Detergents

George A. Smith*, *Huntsman Corporation, USA*

Linear Alkylbenzene sulfonate (LAS) is the largest production volume anionic surfactant in the world. It has a clean bill of health in terms of environmental and ecotoxicity and is the main frame surfactant in most laundry powder formulations. LAS suffers from some deficiencies including poor hard water tolerance and limited solubility in aqueous solution because of its propensity to form lamellar phases. With the shift from powders to liquids in many countries, the demand for LAS has decreased. To obtain better performance in liquid formulations, Huntsman has been investigating the use of gemini and oligomer surfactants based on LAS. A gemini surfactant is two has two hydrophilic headgroups and two hydrophobic tails chemically connected by a spacer group close to the headgroups. In general, gemini surfactants have very low critical micelle concentrations (CMC), have better foaming, wetting and emulsification properties than conventional single chain surfactants. Huntsman has been looking at using electrostatic interactions rather than covalent bonds to form gemini surfactant structures for use in liquid formulations. A number of different commercial bola-type connecting molecules can be used to form gemini-like surfactants. Ethyleneamines and multifunctional polyetheramines are very effective at forming gemini and oligomeric surfactant structures in aqueous solution by simple mixing. These structures have much reduced CMC, foaming properties and can build viscosity in low active detergent formulations without the need for added

salt. Detergent properties are also superior to LAS on a variety of soil types. The presentation will discuss the physiochemical and performance properties of gemini and oligomeric surfactants based on LAS.

Silicone Surfactants in Oil Based Systems Tony O'Lenick*, *Siltech LLC, USA*

Over the years Dr. Rosen has examined, characterized, and evaluated many different types of surfactants and their ability to function for very specialized applications. His in depth studies that provide structure/ function insights into surfactants in which traditional fatty surfactants are placed into water has inspired expansion into non-traditional systems. Professor Rosen's approach to evaluating standard surfactants has been expanded into looking non-traditional surfactant systems. Such systems are those in which silicone / hydrocarbon surfactants are added to oil based systems. Our laboratory has become increasingly interested in understanding the function of such surfactants in anhydrous systems. These systems take advantage of the fact that hydrocarbon and silicone are immiscible in each other and have surface activity. These surfactants, when properly chosen will lower surface tension, provide wetting, foam and function that are directly analogous to what fatty surfactants do in aqueous systems. It is perfectly legitimate to ask what is the CMC of cetyl dimethicone in mineral oil or in olive oil. Using the techniques that have allowed us to understand traditional surfactants it is possible to understand the function of non-traditional systems that are already in use in several industries. This paper will

discuss the properties of silicone surfactants used in oil based anhydrous systems and compare them to standard surfactants in aqueous systems.

Synergism and Interaction of Surfactants in Enhancing Performance in Personal Care and Industrial Formulations Manilal Dahanayake*, *Surfactant Solution Experts LLC, USA*

The interfacial and colloidal properties of a solution of two or more surfactants may be quite different from those of the individual surfactants in solution. Mixtures of surfactants can exhibit synergy if the surfactants attract each other sufficiently, either through mutual electrostatic attraction of oppositely charged hydrophilic groups or through van der Waals attraction of their hydrophobes. The interactions between surfactants can be measured and quantified by the so called "beta" parameters related to their activity coefficients in the mixture. Mixing different charge types of surfactant that exhibit synergism is an important method in enhancing performance properties. Synergism in surfactant mixtures leads to less surfactant utilized to obtain the same level of performance, with consequent economic and environmental benefits as well as enhancing surface activity, spreading, wetting, foaming, detergency and many other phenomena. Recent advances in design of surfactants to optimize interactions and synergism in surfactant mixtures has further led to several new and novel opportunities in practical applications. Some of these developments such as mitigating the irritancy in personal care formulations, use of bio-enhanced surfactant-adjuvants to reduce usage levels of many highly toxic agrochemicals and enhanced recovery of oil and gas (EOR) by the use of viscoelastic surfactants will be highlighted in this talk.

Surfactant Mixtures: Synergism in Solubilization,

Microemulsions, and Detergency David A. Sabatini*, *University of Oklahoma, USA*

Journal of Surfactants and Detergents – 20th Volume Celebration (in honor of Milt Rosen)
Surfactant mixtures have the potential to achieve ultra-low CMC values, greatly enhance solubilization, produce middle phase microemulsions, and corresponding ultra-low IFTs, and thus enhance system performance in a range of applications. This presentation will summarize research published in JSD that focused on surfactant mixtures to achieve these objectives, including anionic-cationic surfactant mixtures as well as other mixtures. The role of surfactant mixtures in detergency will be discussed as well.

Surfactant-polymer Interaction Yun-Peng Zhu*, *Lubrizol Advanced Materials, Inc., USA*

Polymers are widely used together with surfactants in many applications. To understand the interaction of surfactants and polymers is of great significance to developing the beneficial properties while avoiding unwanted problems. Here, a study to investigate the interaction of common surfactants with polymers was carried out and the properties including rheology control, viscosity enhancement, and water solubility improvement were discussed in terms of the interaction between surfactant-polymer. Furthermore, a brief introduction of the application of polymer with surfactants to detergents was provided.

Improve Low Tension Formulation Robustness in Enhanced Oil Recovery with Properly Optimized Surfactant Mixture Jean-Louis Salager*, and Ana M. Forgiarini, *Universidad de Los Andes, Venezuela*

Enhanced Oil Recovery requires the attainment of ultra low interfacial tension between crude oil and the injected aqueous phase. It is known that the lower the minimum tension is, the narrower

the range of formulation over which it would take place. Consequently, the general rule is that the lower the tension, the more accurate should be the surfactant formula, and the worse will be the robustness. This is a very serious problem since the injected formulation is likely to be altered as the surfactant slug progresses through the petroleum reservoir. However, there are two ways to avoid it. The first one is to use an injected formula as insensitive as possible from the variable likely to be altered like the salinity, temperature, or surfactant mixture characteristics. This can be attained in some cases with complex surfactant mixtures whose components partitioning may be used to counteract the spontaneous change. The second way to improve robustness is to use an artifact in which the spontaneous alteration will result in a transition followed by the opposite retrograde transition, thus producing two optimum formulation zones taking place one after the other. It is shown that such an extended low tension zone may be attained to compensate a spontaneous change in aqueous pH, in brine salinity, and in surfactant originally injected composition.

Accounting for Ion Specific Effects in the Hydrophilic/Lipophilic Difference (HLD) Equation

Brock A. Trotter, Mohannad Kadhum, Ben Shiau, and Jeffrey Harwell*, *University of Oklahoma, USA*

The Hydrophilic/Lipophilic Difference (HLD) Equation correlates the phase behavior of surfactant/oil/water systems with temperature, electrolyte concentration, oil type, and surfactant selection. A Winsor Type III microemulsion is a separate, surfactant-rich phase that forms in equilibrium with excess oil and water. Varying the amount of an added simple electrolyte can induce the formation of a Type III microemulsion from an oil/water/surfactant system. The concentration of sodium chloride at which equal volumes of oil and water partition into the middle phase is called the

optimal salinity. We have observed large changes in optimal salinity when varying the cation of an added salt. Results with potassium, calcium, magnesium, cesium, rubidium and lithium chloride salts are presented. The observed shifts in optimal salinity are consistent with the Hofmeister series; for example, potassium, the weakest chaotrope, reduces the optimal salinity, while lithium, the strongest kosmotrope, increases the optimal salinity. These results suggest additional strategies for formulators in a variety of application areas from enhanced oil recovery, to cleaning systems, to drug delivery. We present suggested adjustments to the calculation of the optimal salinity in the HLD equation to account for these effects.

Use of High Throughput Technologies to Accelerate Formulation Development Christopher J. Tucker*, Michael Tate, and John Ell, *The Dow Chemical Company, USA*

Colloid and interface science is a multidisciplinary field at the intersection of chemistry and physics. Many of the most interesting aspects of the field occur in multiphase materials or systems at or near phase transitions. We have utilized fundamental studies of the properties and phase behavior of complex systems such as emulsions, microemulsions and surfactant blends with polymers and other materials to impact performance of formulated products in multiple applications. In order to facilitate these studies, we have developed a range of high throughput formulation and characterization methods that have reduced the experimental time required to study structure property relationships and generate complex phase diagrams. The effectiveness of these tools and methods can be maximized if they are combined with experimental design approaches to generate predictive models to optimize performance in different applications. The products impacted are diverse and include

consumer and personal care products, paints and coatings, food additives, drug and Agricultural products, and microelectronic device fabrication.

Samuel Rosen, Milton Rosen, and Visions of a Future Honoring a Legacy Charles E. Hammond*, *Flotek Chemistry, USA*

"Surfactants and Interfacial Phenomena", 4th Edition, was published by Wiley in 2012. The book includes many tables that painstakingly tabulated references of data. As the number of surfactant publications per year continues to grow, how will similar data be collated and tabulated in the future? This presentation will briefly discuss how the world of surfactant oil water systems may be augmented by "big data".

S&D 3.1: New Encapsulation and Delivery Systems

Chairs: Sam Adamy, Church & Dwight Co. Inc., USA; and Michael Miguez, Shell Global Solutions, Inc., USA

HLD-based Method to Customize Lecithin-linker SMEDS Delivery Systems Mehdi Nouraei*, and Edgar Acosta, *University of Toronto, Canada*

Lecithin-linker microemulsions have been used as platform for designing fully dilutable self-microemulsifying delivery systems (SMEDS). A platform SMEDS formulation composed of ethyl caprate (oil), lecithin (surfactant), glycerol monooleate (lipophilic linker, LL) and polyglycerol caprylate (hydrophilic linker, HL) displayed a fully dilutable path suitable in the absence of active ingredient. Introducing ibuprofen as a model active ingredient resulted in a phase separation along the dilution line. To address this issue, the Hydrophilic Lipophilic Difference (HLD) framework was used to quantify the effect of ibuprofen on the lipophilicity/hydrophilicity of the formulation. Using this methodology, the SMEDS-drug interaction was quantified by calculating the shift in optimum salinity for loaded and unloaded systems over a phase scan. It was determined that introducing ibuprofen produces a positive HLD shift. The HLD framework was then used to predict the required type of hydrophilic linker and the proportions of LL: Lecithin: HL to restore (recover) the fully dilutable path. Implementing the proposed changes resulted in a fully dilutable SMEDS loaded with ibuprofen upon exposure to simulated intestinal fluid (SIF). The results of this study suggest that the HLD is a useful tool to quantify the impact of active-formulation interaction and prescribe the necessary changes to restore the formulation. Although the active in this formulation was a drug, the concept could also be used in the delivery of nutraceuticals, cosmeceuticals, and active ingredients for agrochemicals.

Study of Fragrance Bloom, Release, and Retention on Substrate from Surfactant-rich Cosmetics

Martin S. Vethamuthu*, Sergio Lira, Edward DiAntonio, and Hani Fares, *Ashland Specialty Ingredients G.P., USA*

Objective: This study discusses a new and effective in vivo method to study fragrance bloom and release kinetics from formulations containing neat and encapsulated fragrance oils in surfactant rich cosmetics. **Method:** The instrument used to screen cosmetic compositions for improved fragrance retention components is an Agilent HP7890B GC/5977C MSD with GERSTEL MPS robotic sampler, equipped with a DB-624 capillary column (30m, 250 mm and 1.40 μ m film thickness). An area of 18cm² of the inside arm was washed with 3.3 mg/cm² of a shower gel formulation and rinsed with tap water for 30 seconds and dried. Subsequently the area of the arm was exposed to the twister bar or SPME fiber for 15 minutes, this step is repeated at intervals of 1 hour for a total time of four hours, after extraction the twister bar / fiber is removed and placed into a clean glass thermal desorption tube for GCMS analysis. **Results:** The technology screening process helps identify fragrance encapsulates and polymeric deposition aids that capture, interact and retain fragrance ingredients on skin during the wash process. **Discussion and Conclusion:** The headspace GC instrumentation coupled with the appropriate SPME fiber or twister bar is capable of monitoring the time dependent release/ retention profiles of fragrance ingredients from the substrate. The results from this study show polymeric deposition technology when combined with micro-encapsulation routes provides the best approach to significantly improve fragrance delivery from rinse-off cosmetics.

Microencapsulation Robert S. Bobnock*, *Encapsys, USA*

Microencapsulation can be defined in a myriad of ways usually closely related to the core, wall material and/or release mechanism being utilized. The technology has been around for many decades and it continues to experience new advances followed by patent protection as more and more companies and their researchers test the boundaries of encapsulation chemistry and physics. Microcapsules are common in many of the major markets including but not limited to consumer products, pharmaceutical, paper, agrochemical, food, microorganisms and many others. This review will explore wall materials, core materials, release mechanisms, and the reality of using microencapsulation for a new benefit with the possibility of creating a competitive advantage.

Waterborne Silicone Delivery Brett L.

Zimmerman*¹, and Leon Marteaux², ¹*Dow Performance Silicones, USA*; ²*Dow Performance Silicones, Belgium*

The targeted delivery of actives has generated significant interest globally, largely driven by ever changing and demanding consumer perceived needs. Whether from environment concerns (solvent and waste minimization) or just application performance optimization, the waterborne delivery of silicone and other high value actives are becoming prominent fixtures in academic and industrial project lists. The purposeful use of surfactants to stabilize droplets, to direct actives to surfaces, and to provide a template for interfacial polymerization once only prevalent in applications like beauty care are now finding utility in textiles, construction, and even electronics. Silicone emulsions, water based elastomers, and encapsulation in general will be covered. The inherent properties of silicones and how they are delivered, possible use of silicone

elastomers as delivery medium, and various Si specific encapsulation routes will also be discussed.

Delivery Systems in Detergent Products Johan Smets*, *The Procter & Gamble Co., USA*

The freshness experience from fabrics during/after the laundry process is of outermost importance of the appreciation of the detergent products being used for the laundry process. The detergent industry is one of the biggest customers of the perfume business. The optimal use of perfume materials is of outermost importance in the strive for efficient material use and can be effectively done via several approaches as evidenced by the huge amount of patent activity in this domain since the late '80s. In the strive for optimal use of perfume materials in the detergent business, multiple factors are into play, for most i) bring the signal perfume materials to places where it matters and ii) release at the appropriate time in the appropriate amounts. We will present a showcase on a perfume delivery technology being used in detergent business. We will describe the various aspects that were important to the commercialization path of the perfume delivery technology, what was important for deposition, and for headspace release in combination with the perfume material choice. The perfume delivery technology is based upon the use cationic polymers with substantivity to specific perfume raw materials. It has been evidenced that the approach can enhance dramatically perfume deposition and the head space release above dry fabrics can be significantly increased by the technology approach. We have also been researching the impact of the rheological parameters of the technology versus the efficiency of the technology. We will present how these rheology aspects of the technology represented a huge challenge that was turned into an opportunity. Furthermore, we will cover how scale up and process challenges were overcome to

implement the technology for a wide range of businesses.

Dual Action Malodor Benefit Capsules for Enhanced Freshness Evan Beach*, Ron Gabbard, Yabin Lei, Sean Wetterer, and Li Xu, *International Flavors & Fragrances Inc., USA*

Superior, long-lasting fabric freshness is increasingly demanded by modern consumers of laundry detergents. Often, delivering this benefit is dependent on covering or reducing undesirable or unpleasant odors – malodors - that may arise as a result of washing practices, the environment, or wear. To that end, innovative scent and delivery technologies have been developed to ensure a preferred sensorial experience in this technically challenging application. In this presentation, we report on the additional malodor reduction benefits of a novel capsule system that combines two proven modes of action: the perceptual

coverage of traditional encapsulated fragrance and the malodor elimination of a physico-chemical absorber. Malodor coverage efficacy is quantified using ratings of malodor reduction reported by trained sensory panelists and application relevant standardized malodor mixtures. Elimination efficacy against a series of malodor molecules of interest is demonstrated using instrumental testing. The resulting combination results in an enhancement of freshness over standard detergent benchmarks in application testing that simulates a full laundry cycle. Secondary benefits of the new technology include a long-lasting fragrance delivery profile and the potential for activated release of fragrance during periods of motion or exertion, which may precede malodor development.

S&D 4: Chemicals and Surfactants in Enhanced Oil Recovery

Chairs: Upali Weerasooriya, University of Texas, Harcros Chemicals & Ultimate EOR Services, USA; and Ben Shiau, University of Oklahoma, USA

Enhanced Oil Recovery via Targeted Emulsified Solvent Injection (TESI) Aurelio Stammitti*, and Edgar Acosta, *University of Toronto, Canada*

Based on 2013 Canadian oil production statistics, surface mining and steam injection are the two main recovery methods from oil sands. The former is used up to 70m depth, and the latter for depths greater than 150m. However, no method is implemented to recover heavy oil within 70 to 150m in depth. In this work, emulsified-solvent formulations near the phase inversion point or PIP (exhibiting ultralow interfacial tension) were injected into a column packed with bitumen-coated sand. Five emulsified-solvent formulations around the PIP having a water-to-solvent volumetric ratio of 10 were injected into artificial oil-sand packed columns at 9.2 m/day. The effluent was collected in a fraction collector and the overall recovery was determined by mass balance in each experiment. Our preliminary results showed that at least 90% of the original oil in place can be recovered using surfactant concentrations below 1% and salinities close to 1% NaCl. The proximity to the PIP (as determined via the Hydrophilic-Lipophilic-Difference or HLD framework) influenced not only the fraction of oil recovery, but also the pressure drop observed in the process. The results will be discussed in light of dimensionless number, particularly the capillary number that relates the hydrodynamic shear to the interfacial forces retaining the oil in the porous media.

Highly Branched Heavy Guerbet Alkoxylate Sulfates as EOR Surfactants and Crude Oil IFT Reduction Thu Nguyen*¹, Christian Jones¹, and Greg Trahan², ¹*Sasol Performance Chemicals, USA;* ²*Sasol North America, USA*

This study focuses on evaluating the performance of highly branched heavy Guerbet alkoxylate sulfates as EOR surfactants and finding a new effective method of selecting appropriate surfactant systems for crude oil IFT reduction. Therefore, this research has two objectives. The first objective is to compare the IFT reducing capability of highly branched heavy Guerbet alkoxylate sulfates to that of conventional light alkoxylate sulfates. The second objective is to develop a method for identifying an effective surfactant system for a new crude oil based on its SARA (saturates, aromatics, resins and asphaltenes) analysis. Our previous study showed that heavy Guerbet alkoxylate sulfates have higher solubilization capacity for oils than light alkoxylate sulfates. This study further demonstrates that highly branched Guerbet alkoxylates with proper PO/EO ratios can lower the IFT for crude oils as much as light alkoxylate sulfates. A number of crude oils were also studied and characterized into two groups based on their SARA analysis. The crude oils that have the ratios of each of light hydrocarbon (<C15), saturates, resins and aromatics content to asphaltenes content (referred to as composition ratios) of less than 10 are considered as heavy crudes due to the high content of asphaltenes. For the crude oils with composition ratios that are 2-3 orders of magnitude higher, they are considered as light crudes. It was found that the IFT for all crude oils with composition ratios of

less than 10 was similar by the same surfactant system.

A Novel Approach to Determine HLD Parameters Demonstrated with Internal Olefin Sulfonates

Chien-Yuan Su¹, Ben Shiau², and Jeffrey Harwell²,
¹*Institute of Applied Surfactant Research, University of Oklahoma, USA;* ²*University of Oklahoma, USA*

The hydrophilic-lipophilic difference (HLD) equation has shown utility in guiding surfactant formulations for Winsor I, II and III microemulsions in various applications. A major limitation, however, is the difficulty of obtaining the head group constant (K), the characteristic curvature (Cc), and the temperature dependence (αT) of the surfactants. This paper illustrates the facile determination of these parameters using a reference surfactant with a series of internal olefin sulfonates (IOS). IOS surfactants are a multicomponent mixture of hydroxyalkane sulfonate, alkene sulfonate, and di-sulfonate molecules with twin-tailed structures, which are unable to form middle-phase microemulsions without introducing alcohols at ambient temperature. In this work, the IOS surfactants were blended with a reference surfactant, an alkyl propoxysulfate, C10-(PO)₄-SO₄Na, to aid in the formation of middle-phase microemulsions with a series of alkanes at room temperature. From these studies the K and Cc values of the IOS surfactants were individually determined by the plots of optimal salinity against alkane carbon number (ACN) combined assuming the applicability of a linear mixing rule. In addition, the determination of the temperature constant (αT) of one IOS surfactant was shown using this novel approach. Finally, the practical application of the HLD parameters combined with the HLD equation was demonstrated for guiding the optimal microemulsion formulation at high temperature. The accuracy of the HLD parameters determined in this work was thus demonstrated.

Oil-induced Formation of Wormlike Micelles and Their Use in Nanoparticle Stabilization Francis Choi*, and Edgar Acosta, *University of Toronto, Canada*

Controlled nanoparticle synthesis using self-assembled structures produced with surfactants and microemulsions have been widely used due to their consistency in structure, and tunability. Though effective in synthesis, the stability of the resulting suspensions is relatively poor. The ease in modifying the structures of lyotropic liquid crystals into wormlike micelles (WLMs) through composition, however, provides flexibility in nanoparticle stabilization after synthesis. We have studied the formation of WLMs in microemulsions and their application in nanoparticle stability. WLMs have typically been produced using systems of surfactant, water, and salt. Recently, we found the addition of a fatty acid ester to an extended anionic surfactant-water-NaCl system containing spherical micelles, induces the formation of oil-swollen WLMs and liquid crystals. The construction of phase diagrams show WLM formation requires two conditions: a low oil content, and surfactant-oil-water systems with a hydrophilic-lipophilic-difference (HLD) value equal or greater than zero. Rheological measurements also indicate a large increase in the storage modulus (G') from liquid-like to solid-like behavior when these conditions are satisfied. Sedimentation tests for iron oxide and titanium dioxide suspensions show that the stability occurs in regions of the phase diagram containing WLMs. The G' of these suspensions increase upon the addition of particles, suggesting the particles act as junctions in networks of entangled WLMs that further increase the viscoelasticity to achieve exceptional stability. This phenomenon offers the possibility of formulating wormlike micelles from a variety of surfactant-water systems previously incapable of producing

these phases, leading to an increased flexibility in the formulation of nanoparticle suspensions.

Interaction of Alkalis with Acidic Crude Oils

Himanshu Sharma*¹, Krishna Panthi¹, Jun Lu², Upali Weerasooriya³, Gary A. Pope¹, and Kishore K. Mohanty¹, ¹University of Texas, Austin, USA; ²University of Tulsa, USA; ³University of Texas, *Harcros Chemicals & Ultimate EOR Services*, USA

A large amount of oil is left unrecovered after primary and secondary floods due to high capillary forces. Low IFT surfactants can recover this trapped oil by lowering the interfacial tension. An alkali is added with surfactants to lower their adsorption on the rock surface and generate in-situ soap with acidic crude oils. The objective of this study is to investigate the interactions of alkalis with acidic crude oils (NH₃, NaOH, Na₂CO₃, and NaBO₂). Alkali scans with acidic crude oils were performed, with and without adding cosolvents, and low IFT regions were identified. An organic alkali was studied, in addition to conventional alkalis, for performing ACP floods. The type and amount of soap formed with different alkalis were investigated. The effect of cosolvent type was studied. Oil recovery corefloods were performed to compare ACP floods with ASP floods for the same oil. ACP formulations developed using ammonia and sodium hydroxide were found to be similar; showing low IFT at lower salinities. An incremental addition of calcium ions resulted in gradually transforming the phase behavior towards Winsor type II. Favorable ACP phase behaviors were obtained on adding a more hydrophilic cosolvent. Good oil recoveries were observed during ACP corefloods in sandstone cores. The results of ACP floods were found to be as good as those of the ASP corefloods in some cases. The interaction of alkalis with acidic crude oils is not well understood. This study is aimed at improving that understanding so that ACP and ASP floods can be designed effectively.

Enhancing Foam Stability in Porous Media by Applying Nanoparticles

Shengbo Wang*, Changlong Chen, Mohannad Kadhum, Ben Shiau, and Jeffrey Harwell, *University of Oklahoma, USA*

The utilization of nanoparticles dispersions in foam flooding has become an attractive chemical EOR technique as compared to the conventional surfactant only foaming system. This study is to expand our understanding of utilizing multi wall carbon nanotube (MWNT) on foam stability in porous media. We developed several foaming agent formulations (surfactant and polymer) in the presence of MWNT in 3% salinity (NaCl, 2.4wt%, CaCl₂, 0.6wt %). The dispersion stability of the MWNT and the viscosity of the solutions were measured. Foam was generated in-situ, one-dimensional flow-through tests were performed by co-injecting air and foaming solution containing either the foaming agents-only or the foaming agents in the presence of MWNT. During each experiment, the pressure drop (Δp) and the nanoparticles recovered across the sand-pack were monitored. Injection rate, gas fraction and the effect of MWNT stabilized foams in porous media were investigated. The results reveal that foams stabilized by nanoparticles are able to generate stronger foams leading to apparent higher Δp by introducing MWNT total concentration as low as 60ppm. Δp profile varies with gas fraction which largely affects the foam texture. Also, our data indicate the viscosity of foaming agent solutions influences Δp values. Adding MWNT to the foaming agent solutions appears beneficial to the flooding as surfactants adsorb to nanoparticles which facilitates surfactants partitioning to the G/L interface. Thus, addition of nanoparticles in the developed surfactant-polymer foam formulations can lead to formation of stronger high-quality foams in porous media, which improves the sweep efficiency and increases the oil recovery.

New Surfactants and Cosolvents for Chemical EOR Processes Pinaki Ghosh, Krishna Panthi, Himanshu Sharma, Upali P. Weerasooriya, and Kishore K. Mohanty, *University of Texas, Austin, USA*

A large amount of oil is left unrecovered from oil reservoirs after primary and secondary floods due to various reasons. Among these factors, high capillary forces (between oil and water) and poor sweep efficiency are largely responsible for trapping of oil in the porous media. Surfactants that can lower the interfacial tension with oil have traditionally been studied to improve the oil recovery. Studies have shown that a significant improvement in oil recovery can be achieved by injecting suitable surfactants in the reservoir. However, traditionally used surfactants suffer from severe limitations due to their limited applicability in a high salinity/hardness and a high-temperature environment. These surfactants tend to be unstable (not soluble) under these conditions and therefore cannot be used for improving the oil recovery. Novel surfactants that are stable under a high salinity/hardness/temperature environment would expand the applicability of surfactant EOR to such reservoirs. In addition to an ultralow interfacial tension, a favorable microemulsion rheology is critical in lowering the surfactant requirement. Cosolvents have shown to lower the microemulsion viscosity, lower surfactant retention and improve the oil recovery. Alkali cosolvent polymer (ACP) floods have been developed recently for acidic crude oils, employing in-situ generated Naphthenic soap as the surfactant. Improved cosolvents are critical to the success of the above-mentioned processes. In this study, new surfactants and cosolvents for chemical EOR were developed and their applicability in chemical EOR processes such as ASP/SP floods, ACP floods, and foam floods was investigated. Promising results were obtained using these new surfactants and cosolvents. They were found to interact

synergistically with traditionally used surfactants, give ultralow IFT ASP/SP/ACP formulations and show enhanced foam stability in high-temperature/high-salinity environment.

Solid-Liquid-Liquid Wettability and Its Prediction with Surface Free Energy Models Aurelio Stammitti*, and Edgar Acosta, *University of Toronto, Canada*

Understanding wettability of immersed solids is important for applications such as enhanced oil recovery, multiphase flow in pipes and porous media, oil-water separation, and bacterial attachment. Significant research efforts have been undertaken to characterize wettability of low-energy surfaces like polymers and coatings exposed to air, and to a lower extent under immersed conditions. Furthermore, wettability alteration through structured/functionalized surfaces has been the focus of recent experimental development. However, little attention has been paid to immersed high-energy surfaces and no models are available to predict their wetting behavior. In this work, the solid-liquid-liquid wettability of glass, mica, stainless steel, PTFE and PMMA immersed in isopropyl alcohol (IPA) aqueous solutions equilibrated with toluene was determined via the contact angle (θ) of toluene drops (measured through the toluene phase) deposited using the inverted sessile drop method. The Geometric Mean and Neumann's Equation-of-State (EQS) models were assessed for the prediction of θ using a fitted or assigned solid-aqueous phase interfacial energy (γ_{sw}). Results plotted as $IFT \cdot \cos\theta$ vs. IFT show a smooth wetting transition from hydrophilic to hydrophobic with decreasing IFT for stainless steel and glass. Mica remained hydrophilic, while PTFE and PMMA hydrophobic running parallel to the $\theta=0^\circ$ line, consistent with literature data. Neumann's EQS was able to describe the trends for glass, stainless steel and mica, suggesting that probably γ_{sw} is

approximately constant for these systems. Neumann's EQS offers a promising simple prediction tool for immersed high-energy surfaces.

Static Adsorption Study of Alcohol Propoxy Sulfate Surfactants onto Crushed Berea Sandstone

Daniel F. Wilson*, Laurie A. Poindexter, and Greg Trahan, *Sasol North America, USA*

For chemical enhanced oil recovery (CEOR) applications, surfactant adsorption in porous media is one of the major criteria which determine both the technical and economic viability of surfactant based flooding applications. In this study, static adsorption measurements were carried out with several representatives of anionic alcohol propoxy sulfate surfactants onto crushed Berea sandstone. Although there are other studies in the literature that independently evaluate the strong roles that mineralogy, temperature, pH, inclusion of other chemicals, and brine salinity play on the adsorption capacity of surfactant on a solid surface, these parameters were maintained as constants for this work. The focus for this study was instead placed solely on the surfactants being evaluated with regard to alcohol structure, length of the hydrophobe, neutralization process, and variable PO extensions available. Chemical-flooding schemes for recovering residual crude oil saturation from reservoirs have often struggled due to loss of chemicals by adsorption to the reservoir rock. An increased understanding on how various surfactant parameters may affect surfactant adsorption are helping lead to enhancements in manufacturing, minimizing surfactant loss, and improving the overall economic efficiency of surfactant based CEOR processes in the field.

A Novel Microfluidic Platform to Measure the Dissolution Rate of Drops Emulsified in an Immiscible, Surfactant-containing Suspending

Medium Sachin Goel*¹, Samson Ng², and Arun Ramchandran³, ¹*Dept. of Chemical Engineering and Applied Chemistry, University of Toronto, Canada;* ²*Syncrude Canada Limited, Canada;* ³*University of Toronto, Canada*

It is well known that the dissolution rate and solubility of drops of one liquid emulsified in a second, immiscible liquid phase can be enhanced significantly by the presence of surfactants in the continuous phase. While methods for measuring solubility abound in the literature, measurement techniques for the dissolution rate are rare. In this study, we present a new, robust microfluidic platform for determining the dissolution dynamics of an individual drop in an immiscible suspending medium. We demonstrate this technique for emulsions of water in bitumen, which contains natural surfactants that enhance water solubilization. This is a difficult system for dissolution measurements due to the opacity of bitumen, but our shallow microfluidic channels allow us to clearly image the water-bitumen interface. We show that depending on the bitumen composition, water chemistry, and flow conditions, the time for water dissolution in bitumen is governed either by interfacial phenomena or by mass transfer between the bulk bitumen phase and the water-bitumen interface. In the latter case, we can also calculate the solubility of water in bitumen, provided an independent measure of the size of the water-carrying species is available. Water-in-bitumen emulsions are extremely stable, and any sub-micron emulsified water droplets, which are difficult to remove even by ultracentrifugation, are also counted as solubilized water in traditional solubility measurements. Our single drop dissolution technique avoids this complication. Lastly, our microscale results can also predict the time required to completely solubilize a spherical drop in a suspending medium at the macroscale

BIO 4.1 / S&D 4.1: Biosurfactants, Bio-derived Surfactants, and Biodetergents

Chairs: Heather Byrne, Huntsman Performance Products, USA; Douglas G. Hayes, University of Tennessee, USA; and Daniel Solaiman, USDA, ARS, ERRC, USA

Tailoring of Mannosylerythritol Lipids by Pseudozyma Species Using Different Renewable Feedstocks Susanne Zibek*, *Fraunhofer IGB Institute for Interfacial Engineering and Biotechnology, Germany*

Currently, sustainable surfactant products with decreased carbon footprint and complete biodegradability are highly demanded. This requires the introduction of new compounds and production processes based on renewable resources. Microbial biosurfactants meets organic criteria and shows also a broad spectrum of molecule diversity. Mannosylerythritol lipids (MEL), produced by fungi of the genus *Pseudozyma* and *Ustilago*, are among the most promising microbial biosurfactants with application potential in personal care, technical uses and pharmaceuticals. MEL can be composed of a group of four variants (A to D), which are classified by the degree of acetylation, which affects the polarity of the biosurfactant and by that, their spectrum of application. Depending on the strain and feedstock (fatty acid chain length, unsaturation), unique MEL mixtures can be produced. Therefore, we evaluated the effect of different feedstocks on the production of MEL by various *Pseudozyma* strains. The results are used to develop strategies for structure-tailoring of the surfactants by enzymatic, process engineering or metabolic engineering methods. This way a portfolio of MEL-derivatives with enhanced hydrophilicity or hydrophobicity was generated. The created portfolio of MEL-derivatives ranges from diacylated and acetylated molecules with hydrophobic properties especially suitable as emulsifier and cosmetic ingredients to monoacylated hydrophilic MEL for applications in aqueous solution. In order to make more types of

biosurfactants in sufficient amounts and desired performance available, we are developing scalable production processes (fermentation and downstream processing) for several glycolipids. Our current optimized fermentation processes deliver product concentrations more than 120 g/L for mannosylerythritol lipids.

Integrated Bioprocess Design for the Production of Tailor-made Glycolipids Using *Starmerella bombicola*: Promising Results from Application Testing

Lisa Van Renterghem^{1*}, S. Roelants^{1,2}, N. Baccile³, K. De Schampheleere⁴, M. Höfte⁵, Q. Christiaens¹, M. Hartmann¹, S. Verweire¹, and W. Soetaert^{1,2}, ¹*Ghent University, Centre for Industrial Biotechnology and Biocatalysis, Ghent, Belgium*, ²*Bio Base Europe Pilot Plant, Ghent, Belgium*, ³*Université Pierre et Marie Curie, Laboratoire de Chimie de la Matière Condensée, Paris, France*, ⁴*Ghent University, Environmental Toxicology Unit, Ghent, Belgium*, ⁵*Ghent University, Phytopathology Unit, Ghent, Belgium*

Biosurfactants are an emerging class of surfactants produced by microorganisms, offering a more environmentally friendly alternative compared to traditional surfactants. One type of glycolipid biosurfactants are sophorolipids (SLs), naturally produced by the non-pathogenic yeasts from the *Starmerella* clade in high amounts (> 200 g/L), explaining its large industrial interest. Due to unique expertise gathered at InBio.be, *Starmerella bombicola* can be genetically engineered to alter the production towards one specific sophorolipid or novel glycolipid, transforming *S. bombicola* into a real platform organism.

This research focuses on developing an integrated bioprocess design (IBPD) strategy for the production of new-to-nature glycolipids using

genetically engineered *S. bombicola* strains. In this strategy, the entire innovation chain is considered: from genetic engineering to medium optimization, fermentation and downstream processing, to final application testing.

The application testing is very important to define possible applications of the tailor-made molecules. Since biosurfactants can be employed in so many fields of industry, this is a complicated task, and therefore a multidisciplinary collaboration was set up. Different possible applications of tailor-made glycolipids were assessed and some very interesting leads were found, showing that there are real opportunities in various markets/applications. For example, a new method to encapsulate iron oxide nanoparticles into liposomes was discovered. Antimicrobial characteristics were assessed for various tailor-made glycolipid molecules for selected bacteria and fungi. An ecotoxicological evaluation of the novel-made glycolipids display much higher (or even not-determinable) EC50 concentrations compared to traditional surfactants, making them very promising alternatives.

This portfolio of tailor-made sophorolipid biosurfactants with varying characteristics and properties will lead to an improved market penetration of biosurfactants in the future.

Microbial Biosurfactants, from Lab to Market:

Hurdles and How to Take Them Sophie LKW Roelants*¹, Bernd Everaert¹, Emile Redant¹, Brecht Vanlerberghe¹, and Wim Soetaert², ¹*Bio Base Europe Pilot Plant, Belgium*; ²*Centre for Industrial Biotechnology and Biocatalysis (InBio.be), Ghent University, Belgium*

Microbial biosurfactants have been holding the promise as the environmental friendly alternative for petrochemical derived surfactants for many years. The real lift off of this technology is still expected, but some important recent developments were done. On one hand, large companies are investing in this technology and a

few products can actually be found on the market today. Dedicated and valorization oriented research at Universities on the other hand has enabled the generation of potent microbial strains, ready to move ahead in the innovation chain. In this paper, we will use an example to show how the integration of process (fermentation and purification) development, optimization, scale up and application testing has been key for biosurfactant technologies to move further ahead in the innovation chain. The production of a new type of sophorolipid, by a strain with lower inherent productivities compared to the wild type sophorolipid producing organism, was optimized by process development and scale up. This resulted in a substantial (x4) increase of the productivity and thus a significant reduction of the production price. Moreover, scaling up the process enabled us to generate large samples for dedicated application testing and perform both a techno economic analysis (TEA) as a life cycle assessment (LCA), sometimes resulting in surprising findings. Sensitivity analysis of the TEA and LCA studies enabled us to identify hotspots for price and impact reduction respectively. The combination of the described efforts and strain engineering is expected to result in a real commercial breakthrough of microbial biosurfactant the coming years.

Sophorolipids in Hard Surface Cleaning

Applications Zheng Xue*, Dennis Parrish, Jeff Davidson, Samuel Christy, Andras Nagy, Miyako Hisamoto, and Terrence Everson, *Evonik Corporation, USA*

Microbial biosurfactants produced by fermentation exhibit favorable properties such as low toxicity, skin mildness, and biodegradability. In particular, there is significant commercial interest in sophorolipids, owing to the nonpathogenic character of the production host and the high

yields. Sophorolipids are glycolipids biosurfactants consisting of a sophorose sugar head and a hydrophobic fatty acid tail. The carboxylic end of this fatty acid can be free, forming the acidic structure, or internally esterified at the 4 position of the sophorose head, forming the lactone structure. The lactone form is only stable at neutral or slightly acidic conditions due to the hydrolysis of ester bond at high alkalinity. The narrow pH range for stability against hydrolysis poses significant challenges for utilizing sophorolipids in hard surface cleaning formulations, which are usually formulated at alkaline conditions of $\text{pH} \geq 10$ to saponify fatty deposits. Sophorolipids formulation at neutral pH with cleaning performance comparable to conventional high pH cleaners were developed, through tuning the hydrophilic-lipophilic balance of the formulation to obtain strong emulsification. The effects of sophorolipids on detergency are investigated using interfacial rheology and interfacial tension measurements. Formulation procedures and comparative results will be discussed.

Sophorolipid Biosurfactant Against Bacteria

Relevant to Tooth Caries and Skin Hygiene Daniel K.Y. Solaiman^{*1}, Richard D. Ashby¹, Joseph Uknalis², Aixing Fan³, and Laurence Du-Thumm³, ¹USDA, ARS, ERRC, USA; ²USDA, ARS, ERRCA, USA; ³Colgate Palmolive Co., USA

Sophorolipid (SL) is glycolipid biosurfactant produced by yeast. Its general antimicrobial activity was previously reported. In this paper, we present the antimicrobial activity of SL specifically against oral and skin bacteria. Using a microplate to continuously monitor cell growth, we found complete inhibition of cell growth at SL concentrations ≥ 1 mg/ml (1,000 ppm) for oral *Lactobacilli* tested and ≥ 50 $\mu\text{g}/\text{ml}$ (50 ppm) for the oral *Streptococci*. SEM study of SL-treated *L. acidophilus* (overnight; 1 mg/ml) suffered extensive

cell lysis; *S. mutans* (at SL=130 $\mu\text{g}/\text{ml}$) showed extensive lesions on cell surface but no lysis. SL (at *Lactococci*, as shown by increased cell-doubling time (T_d) and decreased final cell density (by $A^{600\text{nm}}$) in concentration-dependent manner. SL at *Streptococci*, as evidenced by a prolonged lag-time of growth curves in a concentration-dependent manner but no differences in T_d and the final $A^{600\text{nm}}$. Standard Minimal Inhibitory Concentration (MIC) test was also performed towards a broad array of oral and skin bacteria. Superior antibacterial properties were achieved against 3 oral *Streptococci* species tested (MIC < 4ppm). Good antibacterial properties (MIC=19-39 ppm) were also achieved towards some Gram-positive skin bacteria such as *S. haemolyticus*, *C. striatus* and pathogenic *S. aureus*. However, its efficacy towards Gram-negative *E. coli* is only moderate (MIC=312-625 ppm). In conclusion, the results presented demonstrated the high value of SL as antimicrobials for applications in oral and skin care industries.

A Journey to Standardisation of Bio-based

Surfactants in Europe Juergen G. Tropsch^{*1}, Christophe Sené², Thierry Beaudouin², Stephen Mudge³, and Horacio Hormazabal⁴, ¹BASF SE, Germany; ²Stepan, France; ³BSI, UK; ⁴AFNOR, France

The European Commission has decided in 2011 to become the first bio-based economy. In the following, the EU issued a mandate to CEN to develop a standard on bio-based surfactants among other product groups. A new working group within CEN was created to deal with the standardization process (CEN/TC-276 WG3). The working group issued the technical specification CEN/TS 17035 which will be published in April 2017. The CEN/TS 17035 specifies the thresholds on the biomass content (5%, 50% and 95%) and the naming as well as the methods to determine the

thresholds (e.g. radiocarbon method according to EN 16640). The reasoning for the thresholds as well as our approach on the environmental and societal criteria will also be explained. Further work of the working group will include the finalization of a European Norm (EN) and a Technical Report (TR) in 2017. There is planned also an ISO standard on bio-based surfactants. The standard might be used in European ecolabels and in public procurement.

Oil Seed-extracted Oleosome Emulsifiers for Sun Protection Products Soo In Yang*¹, Shuanghui Liu¹, Geoffrey Brooks¹, Yves Lanctot¹, and James V. Gruber², ¹*Botaneco Inc., Canada*; ²*Botaneco Inc., USA*

As a repository of new life energy source in oil seeds, oil bodies or oleosomes are structurally unique due to their uniformly embedded protein stabilizers into the phospholipid-surrounded triacylglycerol core. This naturally-engineered structure provides a foundation for the biochemically programmed collapse and release of oil from the oleosomes in a tightly controlled manner. The oil in the oleosomes are dispersed in the aqueous phase of the cells with the help of the physically stabilized structure by the surface proteins. This structural benefit yields a protective mechanism against coalescence of oil droplets; thus, also increasing the surface area. These physico-chemical barriers provide steric and electrostatic stabilization to the oleosomes, leading to a stable emulsion system. Oleosome itself is an oil-in-water emulsion, but it also possesses an excellent surface active characteristic, thus suggesting its great potential as an emulsifier. We extracted oleosomes using a patented non-solvent-based aqueous extraction process. The purified mixture of oleosome-containing liquid fraction in water with D-glucono-1,5-Lactone, sodium benzoate, and citric acid, has been studied for its potential use as an emulsifier for sun protection

products. Our clinical studies demonstrated oleosomes are hypoallergenic and emollient with high water resistance. When applied for sun protection products, where active ingredients are oil soluble UV filters, oleosomes resulted in great emulsion stability and outstanding functionality, specifically boosting sun protection factor (SPF) significantly. This outcome was delivered by diminishing the use of the aggressive UV filters by up to 9 - 10 folds, achieving the same levels of SPF as market-leading products.

The Antibacterial Property of Fatty Acyl Glutamic Acid and Proposed Mechanism Buddhi Lamsal, and Kangzi Ren*, *Iowa State University, USA*

Fatty acyl Glutamic acid (FA-Glu), a highly water-soluble acyl lipoprotein biosurfactant produced by bacterial fermentation, was studied as an antibacterial agent against foodborne-pathogens. The objective of this study was to determine the how the FA-Glu interacted with bacterial cell membrane to achieve bactericidal effect. The minimum inhibitory concentrations of FA-Glu and other bio-based surfactants against *E.coli* O157:H7, *Salmonella enteria* and *Listeria monocytogenes* were determined and compared. The mechanism of FA-Glu antibacterial property was studied. Cell content leakage test by spectrometry indicated FA-Glu caused significant leakage of cytoplasmic protein and DNA. The differential scanning calorimetry study of FA-Glu interaction with artificial cell membrane revealed that FA-Glu disrupted the cooperativity of phospholipid bilayer structure by interacting with the hydrocarbon chain, reducing phase transition temperature and enthalpy change. The interaction with different types of phospholipids indicated that bio-based surfactant were more effective against Gram-positive bacteria compared to Gram-negative ones. The major phospholipid (DPPE) in Gram-negative *E.coli* O157:H7 is harder to disturb

than the major phospholipid (DMPG) in Gram-positive *Listeria monocytogenes*. Composition of various proteins (from cytoplasm, cell membrane and cell wall) of FA-Glu treated and control bacteria will be examined by SDS-PAGE to determine whether FA-Glu interacted with a specific protein or show the detergent solubilization effect. The study will provide information on possible development of disinfectant formulation using this novel bio-based surfactant.

Triglyceride Derived Surfactants and Interesterification: Synthesis and Performance Properties Heather E. Byrne*¹, George A. Smith², and Angela Garibay-Lewis², ¹*Huntsman Performance Products, USA*; ²*Huntsman Corporation, 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. Investigations showed benefits to these newer castor oil ethoxylates which in turn led to further experimentation in order to see if we could derive an estolide with this generation of COE. Once able to synthesize the interester of the castor oil ethoxylate, several performance tests were run to see what benefits, if any, were seen. This data along with other comparison data will be discussed in depth.

S&D 5: Foam Boosting and Control

Chairs: Warren Schmidt, Consultant, USA; and Martin Severance, Dow Corning Corporation, USA

Mechanism of Action of Silicone-based Foam

Control Agents Jacqueline L'hostis*, Chamee Chao, and Stéphanie Lobry, *Dow Corning, Belgium*

In recent years, the “High-Efficiency” (HE) home washing machines have increased in usage in North America. This design of the machine (horizontal drum), combined with more concentrated and anionic-rich detergent formulations is leading to increased foaming conditions. This high foam ability needs to be efficiently controlled to avoid interference with the cleaning action, and even an undesirable overflow of the washing liquor out of the machines. The mechanism of action of Silicone-based foam control agents will be discussed, explaining their ability to control foam at very low dosage in an extremely large scope of detergent concentrations, formulations and foaming conditions due to their inherent silicone properties. This specific foam control mechanism, different from soap, makes silicones extremely attractive especially when formulation space is needed such as in highly concentrated detergent formulations.

Nonionic Surfactant Foam Control Technology for

HE Laundry Michael D. Capracotta*, Shakera Thamanna, Kevin M. Salmon, and Stephen F. Gross, *BASF Corporation, USA*

Foam control in machine washing applications has long been important in enabling optimal cleaning, but is even more important in modern appliances that apply “smart” technology during cleaning cycles. For example, HE laundry machines can detect foam present in the drum and will continue to rinse until the foam is dissipated. As a result, foam control technology in detergent formulations is a key factor in minimizing rinsing times, impacting both water and energy use. With

this in mind, BASF has evaluated several low foaming nonionic surfactants for use in HE laundry detergents. Both structure-property trends with respect to defoaming will be explored and synergistic combinations of defoamers will be reported.

High Performance Surfactant Blends with High Bio-based Content

Scott Jaynes*, *Croda, Inc., USA*

Domestic production of bio-based ethylene oxide (EO) made from corn ethanol will begin in late 2017 at Croda’s Delaware manufacturing site. This renewable EO will be utilized on-site to produce ethoxylated surfactants with high levels of bio-based content. The availability of these plant-based surfactants will allow home care product formulators to more easily meet the rising demand from their customers for products made with bio-based materials. As an example of products available with increased bio-based content, a family of high performance surfactant blends will be presented. These surfactant blends have been carefully designed to give optimal performance in specific application areas, saving time for formulators who would otherwise need to prepare and test numerous blends of individual surfactants. “Blend NC” is a blend of nonionic alcohol ethoxylates and a cationic surfactant, delivering a highly effective grease cutting product for household or I&I degreasers. “Blend CS” is a blend of an alkylpolyglucoside (APG) with an alcohol ethoxylate that has the high caustic compatibility of an APG, but with the added cleaning power of an ethoxylate. Lastly, a new “Blend CIP” will be introduced for application in Clean-in-Place (CIP) and other I&I areas, with excellent caustic stability and very low foaming. All of these products will

have bio-based content of >60% when Croda's bio-based EO manufacturing plant comes on line in late 2017.

Driving Foam Performance with Surfactant

Interactions Eric Theiner* and Renae Bennett, *Evonik Corporation, USA*

It is common to report foaming properties for neat surfactants in dilute solutions, but it is less common to report foaming characteristics for combined surfactant systems. Unfortunately, surfactant systems are rarely used as neat materials. The presented study presents a large body of data developed from High Throughput Experimentation to determine foam behavior for a base set of combined surfactants. Also to be presented is the analysis undertaken in an attempt to develop a set of rules to guide surfactant

selection for a given foam profile.

Foam Optimization Strategies in Various Consumer Relevant Applications Shui P. Zhu*, and Sangeeta Ganguly-Mink, *Stapan Company, USA*

It is well established that each distinct application formulation or product needs a suitable foam profile. Some need high and sustainable foam such as hand dish washing detergents and shampoos, and some need low and fast-collapsing foam such as auto dishwasher detergents and swimming pool disinfectants. This presentation introduces some basic foam optimization principles, technologies and formulations with ingredients such as anionic, nonionic, amphoteric, and cationic surfactants, cosurfactants, specific/multivalent counterions etc.

S&D 5.1: Sustainability in Surfactants, Polymers, and Detergent Chemicals

Chairs: Keith Genco, Arkema Inc., USA; and Troy Graham, Lightbox Laboratories, LLC, USA

The Unbeatable Beet: The Power of Microcellulosic Fibers Unraveled Robert Nolles*, *Cosun Biobased Products, USA*

Royal Cosun invested in an integrated cascading biorefinery to refine sugar beet pulp and isolate high-value components. The patented microcellulosic fibers (MCF) obtained from this biorefinery is a particulate cellulose material containing at least 60% cellulose, 0.5-10% pectin and 1-15% hemicellulose, and has typical particle dimensions within the range of 25-75 μm . This parenchymal cellulose based material, which comprise cell wall derived networks of cellulose based fibers and nanofibrils, can be used to structure liquids and for stabilization of suspended particles. In an aqueous environment MCF forms a particle gel and creates a physical 3D network that shows superior particle carrying properties. This physical network tends to be stronger than chemical networks being built by nano-fibers. Hence, the yield point of MCF exceeds the yield point of well-known viscosifiers like CMC, xanthan gum and acrylics. More importantly, the properties of the network built are maintained under a broad pH range, at elevated temperature levels and are virtually unaffected by electrolytes known to disrupt chemical networks. Introduced in liquid compositions MCF delivers high zero shear viscosity and strong shear thinning behavior. MCF is suitable to structure laundry detergents, fabric softeners, abrasive cleaners and personal care products like shampoos and body washes. In laundry detergent MCF will enable effective suspension of encapsulated fragrances. In toilet bowl cleaners, strong shear thinning behavior allows easy application using a spray bottle and high zero shear viscosity supports vertical cling. In abrasive

cleaners MCF has the capability to suspend particles, preventing sedimentation in the bottle.

Co-valorisation of Palm Oil Processing By-products as Soaps Teerasak Punvichai*, *Prince of Songkla University, Thailand*

The palm oil refining industry generates spent bleaching clay (SBC) and palm fatty acid distillate (PFAD) as by-products. Both containing fatty acids and/or acylglycerols (22.4% of waste oil in SBC), the study concerns the co-valorization through the manufacture of soap. The analysis showed free fatty acid content and saponification value of 60.5% and 182 mg KOH/g, and 88.4% and 204.5 mg KOH/g respectively. This data was used for computing the stoichiometric amount of NaOH to be used for producing soap at 40°C with a varying proportion of water introduced through the basic solution. From SBC the maximum soap content 43.9% (dry weight) was obtained by reacting it with 13% w/w of NaOH (based on waste oil content) and using 30% w/w of water (both forming the basic reacting solution). With PFAD the maximum soap content 89.2% was obtained with 14.6% of NaOH and 15% w/w of water. In the case of mixtures of both by-products, the maximum yield 92.5% was obtained for a SBC:PFAD ratio of 1:5 w/w and with 14.3% of NaOH and 35% of water, and it was found that the maximum yield required an increasing amount of soaps when decreasing the SBC:PFAD ratio. Soaps with maximum content were tested for cleaning efficiency. PFAD and waste oil soaps gave the lowest reduction of microbial count after hand washing (37 and 30% respectively), while it was improved to 49% in the case of SBC-soap. The best score, 74%, was measured when using soaps made from SBC and

PFAD mixtures. This synergy could be due to abrasive or absorption effect of the clay combined to the high soap content.

Sustainable Suds Manufacturing Kaj A. Johnson*,
People Against Dirty (Method/Ecover), USA

Most of us spend our days working hard to select the very best ingredients, mix and rigorously test them. We strive to make awesome products that delight our consumers, families, and friends. We do all of this using years of experience with ingredients, with input from suppliers and partners, and innovation from conferences just like this. We consider where these ingredients come from, how they will be used, and what happens to them after they are finished. We want to be certain that we are making valuable & high performance products that are truly sustainable. With all this focus on optimizing our products, it's easy to neglect the role that manufacturing plays in sustainability. A couple of years ago, People Against Dirty (Method & Ecover Brands) had the opportunity to build a sustainable manufacturing plant from the ground up. This opened the opportunity to start from scratch- what ideas make sense? how do we do them? And, most importantly, how can we drive benefits as a B-Corp? We wanted to drive practices that reflect our company philosophy to make a positive impact on the environment and consumers. We certainly made a few mistakes along the way but we also learned a lot. Here is a fun look at some things we would like to share with you today about our South Side Soap Box, our sustainable factory.

Readily Biodegradable Builders—Selecting the Right One(s) Patrick Kincaid*, Butch Dery, James N. LePage, Kuntal Chatterjee, and Jeanne-Marie McVeigh, *AkzoNobel, USA*

Today's cleaning formulators are fortunate to have a wide range of safe and readily

biodegradable builders to choose from. Narrowing the field of choices prior to formulation development is an important 1st step in the process. Besides safety and regulatory implications, and 'green' and biobased certifications, several important physical / chemical properties to consider are strength of binding with Ca and other metal ions as well as Ca chelation value, if a solid or liquid / gel is needed, solubility of the builder at a specific pH and other considerations. A review of the attributes and properties of 'green' commercial builders – including citrate, MGDA, GLDA, IDS, EDDS and polyitaconic acid will be presented. Acceptance and use of these products in commercial formulations is growing rapidly with their specific usage tending to fall into specific cleaning products and applications – such as gel and solid ADW products, I&I cleaning and water softening.

How to Improve the Long Term Performance of Autodish Washer Formulations Yvon G. Durant*¹ and David A. Pears², ¹*Itaconix, USA*; ²*Revolymex, UK*

Itaconic acid polymers have been used in recent years as a cost effective and sustainable alternative solution to amino carboxylate based builders. We have recently improved these polymeric chelants through the copolymerization of itaconic acid with sodium styrene sulfonate for optimal performance in ADW formulas. We have previously presented in-formula performance results. These new copolymers are showing a significant advantage regarding metal erosion. Polyitaconate have high binding constants for calcium, but relatively low binding for metals such as iron, aluminum, nickel, copper and gold. We have conducted a study of these metals in the presence of chelants relevant to ADW formulations. Upon extended exposure of glasses and dinnerware with metal decorations, we recorded significant reduction in metal erosion.

The use of polyitaconate chelants in ADW practically eliminates the long term performance concerns associated with some amino carboxylate builders.

Dispersants for Reduction of Spotting in Automatic Dishwashing Paul P. Mercado¹, Eric P. Wasserman¹, Severine S. Ferrieux², and Scott A. Backer*¹, ¹*The Dow Chemical Company, USA*; ²*The Dow Chemical Company, France*

Dow Home Institutional and Personal Care has been developing and evaluating a series of acrylic polymers to act as next generation dispersants for automatic dishwashing formulations. The performance requirements for dispersants have changed significantly as classical phosphate-based formulations are being phased out due to environmental regulations in Western Europe. Currently, no single performance replacement for phosphates has been identified, and new materials and formulations are currently being developed at all levels of the market in order to meet this need. A series of terpolymers containing acrylic acid, AMPS, and a dicarboxylic vinyl monomer (maleic acid, itaconic acid) at specific ratios was prepared and tested in several ADW formulations under various conditions (temperature, water hardness, machine model). Several of the tested terpolymers

provided exceptional spot reducing performance on glassware and stainless steel, regardless of other changes made to the formulation (dispersant type/loading, surfactant type/loading). This novel benefit would allow formulators to achieve maximum shine utilizing a dispersant alone, while optimizing the surfactant system for primary cleaning and other benefits. Best performance was obtained from mixtures of the terpolymer with a second specialty dispersant.

Advancing Sustainable Chemistry: Chemical Footprint Reduction at GOJO Antonio Quinones-Rivera*, *GOJO Industries, USA*

In 2015, at the 10th Annual BizNGO Chemical Footprint Project Conference in Boston, GOJO announced its commitment to reduce its Chemical Footprint by 50% by the year 2020. In this presentation we will discuss the definition of Chemical Footprint, share some of the strategies we have implemented to determine and reduce our Chemical Footprint, and describe some of the tools we have developed to communicate our progress in reducing our Chemical Footprint.

EAT 5 / S&D 5.2: Interfacial Phenomena in Complex Food Systems

Chairs: Nitin Nitin, University of California, Davis, USA; and Ozan Ciftci, University of Nebraska-Lincoln, USA

Effect of Membrane-associated Peptide on the Dynamics of Bicontinuous Microemulsions via Quasi-elastic Neutron Scattering and Neutron Spin-echo

Douglas G. Hayes*¹, Veerendra K. Sharma², Volker S. Urban², Hugh M. O'Neill², S. Venkatesh Pingali², Michael E. Ohl², Eugene Mamatov², and Madhusudan Tyagi³,
¹University of Tennessee, USA; ²Oak Ridge National Laboratory, USA; ³National Institute of Standards and Technology, USA

A grand challenge for the soft matter scientific community is to obtain a deeper understanding of dynamics at several different length and time scales. This paper will describe the short- and long-range dynamics of bicontinuous microemulsions (BMEs), a potentially useful biomembrane mimetic system, by quasi-elastic neutron scattering (QENS) and neutron spin echo (NSE), respectively. The investigation focuses upon the effect of melittin on BMEs formed by water/sodium dodecyl sulfate (SDS)/1-pentanol/dodecane. Melittin is an antimicrobial peptide (AMP) with potential utility as an agent against antibiotic-resistant microorganism and cancer, among others, and penetrates within the surfactant monolayers of the BMEs. (BMEs may be a potentially valuable delivery system for AMPs.) QENS analysis indicated two distinct motions of the BME surfactant monolayers, namely (i) lateral motion of the surfactant on the surface of the oil channels and (ii) internal motion of the surfactants. It is found that melittin hindered both the lateral and the internal motion, thereby acting as a stiffening agent. NSE analysis indicated that melittin has a slight, lesser, impact on the long-range dynamics.

Structuring Food Emulsions Through Lipid Crystallization at the Oil-Water Interface Dérick Rousseau*, Ryerson University, Canada

Incorporation of emulsions into processed foods offers significant possibilities in regards to texture improvement, cost reduction, and health enhancement. In both oil-in-water and water-in-oil emulsions, an emerging tool is the use of direct lipid crystallization at

the oil-water interface, which can strongly impact emulsion kinetic stability against coalescence and phase separation, functionality and rheology. This presentation outlines some of the factors that govern interfacial crystallization, notably emulsion dispersed phase volume fraction, lipid surface activity and liquid-solid phase transition temperature as well as molecular complementarity between the crystallizing lipid and interfacially-bound emulsifier. Specific examples of the impact of interfacial crystallization discussed include the ability of crystalline shells to transform water-in-oil emulsions into reservoirs for the controlled release of aqueous compounds as well as their capacity to protect oil cargos during in vitro digestion of oil-in-water emulsions.

The Effect of Interfaces in Nanodroplets Loaded With Nutraceuticals on Their Release from Drinks to Human System Nissim Garti*, Hebrew University, Israel

Dilutable microemulsions (DME) are nanodroplets composed of oil phase, surfactants, cosurfactants and cosolvents (no water) and other ingredients that facilitate formation of concentrates with the capability of being diluted with any amount of water and inverting from W/O to bicontinuous and to O/W nano structures. The phase diagrams describing these formulations are termed "U-type phase diagrams" and the structures are termed "umbrella type droplets". The concentrates are loaded (solubilized) with bioactives (guest molecules) that are lipophilic and insoluble in water. The systems are transparent, Newtonian and thermodynamically stable. The bioactives are, in most cases, located at the interface of the structures along any dilution stage. The loaded nutraceuticals are, upon dilution, forming soft drinks. The structures are consisting also of additional ingredients allowing the bioactives to 'survive' the acidic conditions of the human stomach and are aimed to be released from the guts jejunum membrane "on demand" to the blood stream. We will bring few such examples including CBD (the non narcotic fraction of Cannabis) and other antioxidants and nutraceuticals.

The formulations are derived from Monte Carlo Dynamic Simulations calculations, and advanced analytical tools, to determine the location of the solubilized nutraceuticals at any stage of its dilution and across the guts membrane.

***In situ* Observation of Template Effects of Emulsifiers with Different Fatty Acid Moieties** Chinami Ishibashi*¹, Hondoh Hironori², and Satoru Ueno², ¹*Hiroshima University, Japan*; ²*Graduate School of Biosphere Science, Hiroshima University, Japan*

Template effect is the promotion of fat crystallization by crystallized emulsifiers that were nucleated prior to fat. Although an impurity effect also promotes a nucleation of fat crystals on the surface of an emulsifier, the crystallization mechanism is different between template and impurity effects. Many previous studies reported that the similarity in fatty acid composition between a fat and an emulsifier should be important for the template effect. An emulsifier crystal having similar fatty acid packing to a fat crystal would provide a favorable spot for fat crystal nucleation. The molecular interaction at the fat-emulsifier interface will promote the orientation of fat crystals. However, there are few reports about the fat crystal orientation promoted by the template effect, and the difference between template and impurity effects are not concerned so much. The purpose of this study is *in situ* observation of crystallization behavior of fat crystals on an emulsifier crystal in order to reveal the difference between the template and the impurity effects. We used palm-mid-fraction (PMF) as an oil phase and sorbitan tripalmitate (STP), sorbitan tristearate (STS) and sorbitan tribehenate (STB) as an emulsifier. The results were as follows; (i) When fatty acid moiety of emulsifier were similar to those of fat, PMF crystals oriented along the STP or STS crystals, suggesting template effect. (ii) When fatty acid moiety of emulsifier did not show the similarity to those of fat, PMF randomly crystallized around STB crystals, suggesting impurity effect.

Thermodynamics and Adsorption Mechanisms for Hydrophobic Food Surfactants at Interfaces Stephanie R. Dungan*, *University of California, Davis, USA*

Lipid amphiphiles are found widely in foods and other biological materials. Their tendency to accumulate and lower the energy of interfaces plays a critical role in food processing and ing metabolic actions such as digestion and cellular transport. Interpretation of interfacial phenomena is often based on studies of water-soluble molecules, whose behavior is heavily influenced by the hydrophobic effect. Instead, in this presentation, the behavior of water-insoluble surfactants at oil/air, oil/water and air/water interfaces will be discussed. Equilibrium surface tension (oil/vapor) measurements of various triacylglycerol or free fatty acid molecules as a function of temperature were used to assess surface excess internal energy and entropy. Length of the acyl chain is the main feature to influence surface excess energy, in contrast to degree of saturation or triacyl or monoacyl character. These findings clarify the very subtle effects of composition on surface tension of food oil mixtures. Our understanding of the behavior of lipid phases alone can then be extended to oil/water mixtures, where lipid amphiphiles have a much more pronounced and complex effect on interfacial tension. Dynamic interfacial and surface tensions were also probed, using drop profile tensiometry, for caprylic acid, monocaprylin and phosphatidylcholine. When the amphiphile is dissolved as individual molecules in a triglyceride or water phase, transport to the interface is driven by diffusive mechanisms. Phospholipid transport kinetics are more complex, as these molecules are nearly soluble in both triglyceride and water. Their adsorption kinetics are much slower, and heavily dependent on the structure of the vesicle dispersion.

An In-depth Look at Bakery Applications of a Structured Monoglyceride Gel Alejandro G. Marangoni¹, and Kaustuv Bhattacharya*², ¹*University of Guelph, Canada*; ²*DuPont Nutrition & Biosciences ApS, Denmark*

After successfully addressing the use of trans fat in the food industry the focus is now on reduction of saturated fats and in certain parts of the world palm oil

and its derivatives due to sustainable issues. The primary approach has been replacing fats rich in saturated fatty acids with structured liquid oils using different ingredients and techniques. But not all solutions are food approved or have wide range acceptable application opportunities. The present work is based on oleogel emulsion technology using an emulsion structured by crystalline multi-layers of monoglyceride interspersed with water in presence of anionic co-emulsifiers in the alpha polymorphic form. This technology is appropriate for manufacturers of oils and fats, bakery products, and others, who want to improve the sustainability footprint and health benefits of their existing products. By using this technology, 'palm free', zero trans and reduced saturated fats can be claimed. The solution is oil source independent providing freedom of choice for the manufacturer. A diverse range of bakery applications including analytical data on the emulsion oleogel and dough containing such using NMR, Confocal laser imaging and Rheology will also be highlighted.

Improve Foam Properties—Multifunctional Cellulose Polymer Terry Crutcher*¹ and Bert Kroon², ¹*Ashland Specialty Ingredients G.P., USA*; ²*Ashland Specialty Ingredients, The Netherlands*

Many household and personal care wash applications exhibit trade mark foamability and rheological aesthetics that consumers have come to expect and enjoy. The foam profile of a consumer product may serve as an indicator of its performance in the minds of many end users. It is becoming more of a challenge to deliver cost efficient and robust foam performance as traditional foaming ingredients like alkanolamides and alkyl sulfates are of toxicological concern. Today there is a need for better more efficient eco-friendly foaming technologies that satisfy finished goods manufacturers' desire for more sustainable high performance products with reduced surfactant/chemical content in the effluent. It has been found that a modified polysaccharide derivative reduces the surface tension at the air liquid interface sufficiently to boost and stabilize foaming in care compositions like hand dish detergent, hand soap, and hard surface

cleaners. Additionally these naturally derived cellulosic polymers build rheology, improve skin feel, and mildness of cleansing compositions in which they are incorporated. Research will be presented to validate equivalent foamability at reduced surfactant concentration. The data to confirm the foam enhancing properties of a multifunctional naturally derived modified hydroxypropyl methyl cellulose polymer.

Interfacial Interaction and Emulsification Behaviour of Lentil Protein Isolate and Fenugreek Gum Complexes Supratim Ghosh* and Natalie Longmore, *University of Saskatchewan, Canada*

The aim of this work was to improve solubility and emulsification behaviour of lentil protein isolates (LPI) by their interaction with fenugreek gum (FG). Complex formation between the protein and polysaccharide molecules was studied as a function of pH (7 to 1.5), and mixing ratios (1:3 to 3:1). The soluble complexes at pH 2 and 7 were further used to investigate the interfacial and emulsification behaviour. At a total biopolymer concentration of 0.1 wt% significant decrease in oil/water interfacial tension was observed. From 23.9 mN/m for pure oil/water interface, it decreased to ~17 and ~13 mN/m, at pH 2 and 7, respectively. No significant change in interfacial tension between the LPI-FG complex and pure LPI was observed. In contrast, presence of FG significantly decreased interfacial storage modulus and the values were higher at pH 2 compared to pH 7, which was ascribed to strong -ve charge on both the biopolymers at pH 7 leading to a weaker interfacial interaction. The mixed biopolymer solutions were used to prepare 1 wt% oil-in-water emulsions using multiple passes through a high pressure homogenizer at pH 2 and 7. Stable emulsions were generated at both pHs where the average droplet diameters were less 500 nm. Results showed that presence of FG significantly improved emulsification behaviour of LPI due to improved solubility, and lowering of the interfacial modulus of the complex. Interfacial complexation between LPI and FG could be a novel way to utilize natural ingredients in the development of food emulsions for beverage application.

S&D-P: Surfactants and Detergents Poster Session

Chair: Mike Wint, Amway Corporation, USA

1. Studies on Dispersion of Various Size of Ethyl Cellulose in Colloidal Solution and Their Foam Ability

Hongche Noh*, Hanyang University, South Korea

Foam has been studied in various fields, such as household goods and foods, in addition to surfactants. In this paper, the stability and structure of foam were studied using nanoparticles. Ethyl cellulose (EC) colloidal solution with high dispersibility was prepared by anti-solvent precipitation. Especially, the particle size was controlled by changing the concentration and temperature. This EC colloidal solution was mixed with sodium dodecyl sulfate to study the stability and structure of foam. EC was measured by dynamic light scattering (DLS), zeta potential and scanning electron microscope (SEM). Foam ability was analyzed by dynamic foam analyzer.

2. Chemocleavable Nonionic Surfactants Bearing Mono-dispersed Polyethylene Glycol Derived from Diethyl Tartrate

Daisuke Ono*¹, Makoto Okumura², Shintaro Kawano¹, Hirofumi Sato¹, Motohiro Shizuma¹, and Araki Masuyama^{2,1} Osaka Municipal Technical Research Institute, Japan; ²Osaka Institute of Technology, Japan

It has become of special interest to develop the "chemocleavable" surfactants which are designed to be decomposed into nonsurface-active species under mild conditions after fulfilling their original functions such as emulsification, detergency, micellar catalytic activity, and so on. We have been investigating the preparation and properties of a series of acid- and alkali-cleavable surfactants and reported that they were applicable as detergent and emulsifier of emulsion polymerization. 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 mono-dispersed polyethylene glycol. We confirmed that they have good surface-active properties. The emulsion stability of these surfactants was similar to that of typical surfactants. 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. The new surfactants do not require any expensive reagents or special equipments for their preparation and might improve the efficiency of waste water treatment and of polymer purification in the emulsion polymerization process.

3. Thermogravimetric and Rheological Evaluation of Mucilage Flax with Potential Application in Microencapsulation of Bioactives Substances

Jaime Reyes Hernandez*, Concepción Lopez Padilla, Josefina Gallegos Martinez, and Paola Algara Suarez, Universidad Autónoma de San Luis Potosí, Mexico

The goal of this study was evaluated rheological (G'), thermogravimetric parameters (weight loss) and pH sensibility of mucilage flaxseed for application in microencapsulation. Methods: Thermogravimetric analysis (weight loss) of mucilage flax (MF) was performed in a TGA TA-Q500, Samples (~5mg) were heated from 35°C to 600°C at 10°C/min in N₂ atmosphere. The gelation of systems with MF was developed with ramp 80°C to 25°C at 1°C/min. Rheological analysis was

developed in mechanical spectrometer MCR 101 with parallel-plate geometry (PP-50) under static conditions at 25°C and 37°C. Gel sensibility to pH was developed at pH of 2 and 7. Results: Thermogravimetric analysis of mucilage flax showed two important weight loss; the first was at temperature of 255.7°C and was associated to breakdown and weight loss of monosaccharide and disaccharides. The second weight loss was observed at 297°C, these temperatures can be associated to different composition of proteins present in MF. Storage module values (G') increased as the concentration of MF increased, however G' values was considerably higher at 2 and 3% of MF ($G' \approx 500$ MPa) than 1% ($G' \approx 5$ MPa). The higher resistance structural of gel was observed at pH 2 than pH 7. Conclusions: Concentrations higher of 2% suggested the possibility of developing gels with good viscoelastic properties and higher resistance to pH 2 for be used in microencapsulation of bioactives substances. Knowledge of these mechanisms may be helpful for the understanding of these phenomena and improving the control of the viscoelastic properties and therefore their functionality.

5. High Foaming, Bleach Stable Surfactant

Alternative to Laurylamine Oxide Benjamin J. Markovitz, Ryan C. Vikan, Tenu A. Adeosun, William B. Hehemann, and Philip C. Benes*, *Nease Co., USA*

This poster for the surfactants and detergent division, foam boosting and control session, will focus on a high foaming, bleach stable alternative to laurylamine oxide (LAO). LAO has been a workhorse surfactant in the field of chlorine bleach stable foaming cleaners. However, while LAO offers good bleach stability and Ross-Miles foaming performance, it only provides somewhat limited Draves wetting and surface tension reduction performance in cleaning formulations. In contrast,

secondary alkane sulfonates (SAS) provide limited Ross-Miles foaming performance but show good chlorine bleach stability, Draves wetting, and surface tension reduction performance. By modifying a secondary alkane sulfonate, a high foaming, chlorine bleach stable surfactant was created. This product retains chlorine bleach stability equal to LAO and has improved Ross-Miles foaming, Draves wetting and surface tension reduction performance over LAO at both room temperature and at reduced temperature. When formulated at equal actives to LAO it exhibits improved performance and equal performance at 75% of LAO active. The modified secondary alkane sulfonate product provides the opportunity for manufacturers of cleaning and detergent products to either enhance the performance of existing LAO containing formulations and/or reduce the overall surfactant loading (cost) in cleaning formulations.

7. Selective Synthesis of Sugar Mono Fatty Acid Ester Using Ion-exchange Resin as Catalyst

Tomone Sasayama*¹, Yuto Kamikanda², and Naomi Shibasaki-Kitakawa³, ¹*Dept. of Chemical Engineering, Tohoku University, Japan;* ²*Tohoku University, Japan;* ³*Graduate School of Engineering, Tohoku University, Japan*

Sugar fatty acid ester has been received much attention as a bio-based surfactant. It is industrially produced by transesterification of sucrose and fatty acid methyl ester using homogeneous alkali catalyst such as Na_2CO_3 . However, reduced pressure condition for removing by-product, methanol, is required to shift the equilibrium toward the product and a complicated operation for removing the catalyst from the product is also necessary. These cause an increase in the production cost. We have proposed that the porous type anion-exchange resin has a high catalytic activity for transesterification of acylglycerols under mild condition. In this research,

sugar ester is synthesized using the resin catalyst at 60°C under atmospheric pressure. Sucrose and methyl oleate are used as model feedstocks, dimethyl sulfoxide, as solvent. In the batch experiments, we find that sugar ester is rapidly produced under the specific condition that the resin is first added to the sucrose solution and then methyl oleate is added to the solution. In the continuous experiments using the reactor packed with the resin, sucrose solution is first supplied to the reactor for saturation and then the mixed solution of sucrose and methyl oleate is fed to the reactor for ester synthesis. At steady state, the conversion of 50% is obtained at the residence time of 1.5 h and mono ester is selectively produced (>95wt%).

8. Synthesis of Mild Natural Micro Beads Face Scrubber Rohan S. Mestri*, Harshada S. Patil, and Amit P. Pratap, *Institute of Chemical Technology, India*

Daily cleansing does not remove dead epithelial cells and impurities which are trapped in pores of skin. These dead cells and impurities affect the skin life if it is trapped in pores of skin, resulting in the less life of skin, problems of acne and blackheads. Solution of these problems is use of face scrubbers ones or twice a week which is exfoliating, mild and contains natural traditional ingredients. The mild micro beads face scrubber contains Gram flour, aloe vera, sugar, starch, milk, skin care oil etc. in this scrubber-beads are outer cover with Gram flour and inside is oil. When we massage with this beads outer layer are exfoliate dead skin and black heads and inside oils is spread on skin which will help to growth of new fresh cells. The result is ever youthful and fresh look.

9. Manufacturing of Detergent Tablet Rohan S. Mestri*, *Institute of Chemical Technology, India*

A soap or detergent is a material which when dissolved in water, aids the removal of dirt or foreign matter from surface. The tablet form of the detergent powder is one of the new formats of the detergent. It is the compact form of detergent powder with highly active ingredients. The tabulated form of detergent will reduce the volume of the powder due to compact format it affects the transportation and packing cost. The detergent formulation content the Linear alkyl Benzene Sulphonate (LABSA), Sodium Tripolyphosphate (STPP), Sodium hydroxide (NaOH), Sodium Silicate, Sodium Sulphate. The tablet form of the detergent powder is comparatively new. It is the compact form of detergent powder with highly active ingredients. The tabulated form of detergent is expected to reduce the volume of powder due to compactness. The detergent formulation contains Linear Alkylbenzene Sulphonate (LABSA), Sodium Tripolyphosphate (STPP), Sodium hydroxide (NaOH), Sodium Silicate, sodium sulphate etc. Detergent powder is mixed with various disintegrating agents like corn starch, sodium carboxy methyl cellulose (Sodium CMC). Detergent tablet is instantly disintegrated when contacted with water. It is less or no hygroscopic in nature and one or two tablets are enough for the washing instead of one scoop.

11. Salt-thickening Effect in the Quaternary Ammonium/Carboxylate Surfactants Mixtures by Forming Entangled Wormlike Micelles Liming Zhang*, Wanli Kang, Derong Xu, Meng Yang, Qiong Zhou, Jiatong Jiang, and Hairong Wu, *China University of Petroleum (Beijing), China*

Surfactants impact a lot on fracturing fluids which play a critical role in the effect of the hydraulic fracturing. However, formation fluids contain large quantities of inorganic salts. When the fracturing fluids are injected into the formations, precipitation appears, leading to a loss

to the fracturing effect and damages to the formations. Thus, compatibility with the formation fluids is essential to EOR. The rheological behaviors of the mixtures are measured by the mechanical Rheometer, and the morphologies of the aggregates in the solutions are observed with Cryo-transmission electron microscopy (Cryo-TEM) and Freeze-fracture transmission electron microscopy (FF-TEM). The results show that viscosities of the mixed solutions are quite low when the total mass concentrations are lower than 3.0%. They behave like Newtonian fluids. After adding NaCl and CaCl₂, there is an obvious increase in viscosity and viscoelasticity. Moreover, the salt-thickening effect becomes better with the increasing inorganic salt to some extent. NaCl has an outstanding viscosity-thickening ability than that of CaCl₂. Importantly, no precipitation appears until the NaCl concentration reaches 25%. In addition, micrographs exhibit that transformation occurs from spherical micelles to the wormlike micelles. The larger of the inorganic salt concentration, the closer of the entangled wormlike micelles pack. The microstructures are in accordance with the salt-thickening effect in theory, indicating a good compatibility with the formation fluids. This work has extended the understanding of salt-thickening effect which is related to the forming of wormlike

micelles. It provides guidance for the application to EOR as well as other industries.

12. Turkish Demographic Profile, Homecare Detergent Market Volumes and Customer Expectations Kutluay Kabaday*, Saruhan kimya, Turkey

Turkish demographic profile, specifications, population, median ages, housewife profiles, house profile and economical data, GDP per capita values among years and forecasted values also comparison to some other countries. Turkish retail prospect, market types, market share details, product groups, tonnages, incomes and strategies, yearly changing market share values. Discount market types, numbers. Total Turkish homecare detergent sector economical values and product groups. Homecare detergents as laundry, dishwashing, surface group and softener volumes, annual growing rates, forecasts for each group as income and tonnages, customer expectation in homecare detergent business, marketing strategies. Also there are a detailed customer profile survey analyzes of customer purchasing behaviours.