A New Emulsification Method

with Application for Cleaning Oil Spills

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ABSTRACT

The clean-up and removal of oil spilled in the marine environment and in coastal and inland waters is a challenging task. Each of the available clean-up technologies has significant disadvantages. Current oil dispersants are successful at distributing small oil droplets through the water column, but they do not prevent fouling of birds, animals, and plants. By developing an oil antideposition agent that is composed of commercially available food-grade materials, our research team has provided an economical and environmentally friendly option for oil spill treatment. Our antideposition agent relies on a novel emulsification system that combines amphiphilic polysaccharides and natural bilayer-forming surfactants. This system uses a combination of steric stabilization and lamellar stabilization to disperse the oil into discrete droplets and prevent that treated oil from wetting or sticking to hydrophobic substrates, such as bird feathers.

INTRODUCTION

Following the recent Deepwater Horizon incident in the Gulf of Mexico, more than one million gallons of dispersant were deployed to the site of the spilled oil. The clean-up strategy in this case was to keep the oil at sea until it was microbiologically degraded. However, the dispersant that was used is also a good wetting agent. Such wetting agents rapidly lower interfacial tension and, as such, they exacerbate fouling of solid substrates, such as bird feathers. There is a need for biodegradable oil dispersants that resist wetting and spreading on solid substrates. In response to this incident, we devised antidepositing dispersants to mitigate the deposition of oil on solid coastal surfaces, including soil, sand, plants, and wildlife (especially birds). As a result of a RAPID NSF Project (1047662), we demonstrated an improved approach for the treatment of oil spills at a laboratory scale. This approach arose from our discovery that soy lecithin, which is biodegradable in the marine environment, seemed to act as a chaperone and anchor for cellulosic antideposition agents to the oil/water interface. The cellulosic agents act as steric stabilizers to prevent fouling of solid surfaces by the dispersed oil. These cellulose ethers are listed as TSCA-exempt (40 CFR 710(B)), and they are not likely to accumulate in the food chain, due to their water solubility and high molecular weight (bioconcentration potential is low). They are nontoxic to fish and aquatic organisms on an acute basis, and they are expected

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to slowly biodegrade in the aquatic environment. All of the materials used for our oil antideposition agent are available in large quantities and are economically feasible for oil clean-up use.

Using high throughput formulation techniques, a large number of compositions comprising oil, lecithins, and cellulose ethers were screened. These compositions were evaluated for interfacial tension, rheology, and dispersion in water, and phase diagrams for these compositions were generated to search for a dispersant with the best-suited characteristics for an antideposition aid. The NSF RAPID project demonstrated proof of principle by showing that some of the formulations had the propensity to prevent oil fouling of feathers. We found only a few of the dozens of grades of cellulose ethers to be optimal antideposition agents for oil. Moreover, we found that known performance in fresh water was not adequate to predict performance in sea water. The NSF AIR grant (1127846) allowed our team to develop the new antideposition oil-dispersant technology from the proof-of-principle stage to a working prototype that could be demonstrated to potential customers.

OIL SPILL CLEAN-UP BACKGROUND

Oil Spill Effects

Because oil spills are a manmade disaster, the severity and repercussions are difficult to predict. Several variables influence the severity of an oil spill: the grade of oil, the amount of oil spilled, the location of the oil spill, and the weather conditions at the time of the spill. It is well accepted that crude oil contains toxic components that cause damage to marine life, ranging from poisoning to the physical smothering of animals. Though the oil may not always immediately kill the marine life, the side effects of exposure could lead to long-term harm to animal reproductive cycles and offspring.[1] Some of the most vulnerable inhabitants of open water are seabirds. Because the birds are on the open-water surface, they come into direct contact with the floating spill. Birds that dive for food or gather on the sea surface are especially at risk. Though many birds die because they ingest the oil while attempting to clean themselves, most oil-spill-related bird deaths are caused by starvation, body heat loss, and drowning from the damage done to their feathers.[2]

Oil Spill Clean-Up Methods

Currently, a wide range of methods are used to combat oil spills. The method of response to any oil spill depends upon the nature and extent of the oil spill and the resources available at the time of the incident. Floating surface oil can be mitigated by surface dispersants, controlled burns, booms and skimmers, sorbent materials[3] (such as polyester fiber mats, super-hydrophobic absorbents,[4] hair mats, hay, or pine shavings), and water-oil separating devices.[5] The oil can be gelled or consumed by biological agents or oil-eating mushrooms.[6] It can be manually cleaned up or left for natural processes to remove the pollution. In general, contingency planning is restricted to small spills. The response to large spills usually involves aerial observations, protective strategies, containment and recovery, and finally, the use of dispersants for shoreline protection and the dispersal of large oil slicks.

EMULSIFICATION BACKGROUND

Oil dispersants are generally comprised of solvents to reduce the viscosity of the oil slick and surfactants that are used to emulsify the oil. Surfactants are molecules that contain two parts: a hydrophobic segment that is expelled by water and a hydrophilic segment that interacts strongly with water. Such molecules are said to be amphipathic, meaning that they interact with both the oil and water phase.[7] It is this amphipathic behavior that can be used to disperse the oil slick. As the surfactant self-assembles with the hydrophilic segments in the water phase and the hydrophobic segments in the oil phase, the interfacial tension between the oil and water is reduced enough to break small oil droplets away from the slick and distribute them through the water column (*Figure* 1).

Though the droplets are small and dispersed, many current dispersant systems utilize surfactants that are also good wetting agents. Therefore, the oil droplets can still accumulate on surfaces that come into contact with them before they are biologically degraded. We have

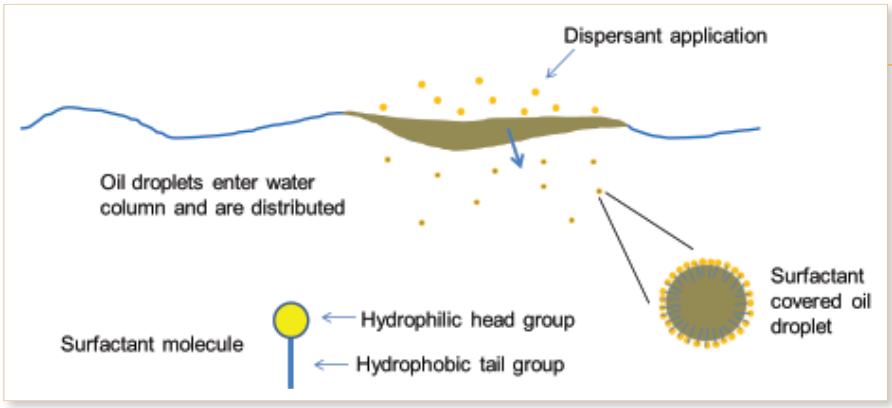

Figure 1—Illustration of the dispersant action of surfactants with oil slicks.

Figure 2—Oil dispersed with dioctylsulfosuccinate and alkylsorbitan ethoxylate is deposited on feathers, as seen in this microscope image of the droplets readily spreading onto and between the barbs of the feather.

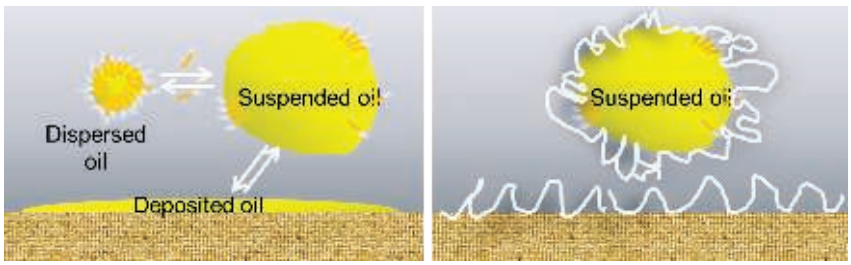

Figure 3—In the presence of insufficient conventional dispersants, there is a three-way equilibrium between dispersed oil, suspended oil, and oil deposited on adjacent surfaces (left); adsorption of lyophilic polymer on the oil droplets and on the substrate causes repulsion between the droplet and the surface and mitigates deposition. Sufficient anchoring on the oil droplet can prevent deposition even on "bare" surfaces.

seen this behavior in our laboratory experiments using an oil emulsion stabilized by di-2-ethylhexylsulfosuccinate and ethoxylated sorbitan mono-oleate (surfactants similar to those used in the current Corexit® dispersant that was applied in the Gulf of Mexico and good wetting agents). The dispersed oil droplets immediately wetted bird feathers (*Figure* 2).

Anti-redeposition Agents for Laundry

The initial reason for the development of anti-redeposition agents was the widespread use of synthetic fabrics in clothing. Prior to the use of synthetics, laundry detergents were successful at removing soil from cotton fabrics without redeposition issues. However, after the introduction of synthetic fabrics with hydrophobic properties, such as polyester, the soil that was removed from the cotton fabrics would transfer to the synthetic fabrics during rinse cycles. Several types of polymers can act as anti-redeposition agents. Carboxymethylcellulose (CMC) is commonly used to both coat the fabrics themselves and adsorb onto the soil particles to prevent redeposition through steric repulsion (*Figure* 3). Polyelectrolytes, such as polycarboxylates, are also used as anti-redeposition agents for synthetic fabrics to prevent soil redeposition through electrostatic effects. These polymer properties were the inspiration for our research to provide an anti-deposition agent for oil spill clean-up. Unfortunately, the materials we screened from traditional laundry applications (a freshwater environment) were not suitable for use in seawater applications, due to precipitation by the salts present in seawater.

Lecithin as an Emulsion Aid

Molecules of surface active agents self-assemble into micelles, which are the agents that keep oil droplets suspended in the water phase. The shapes of surfactant molecules and the way they can be packed, known as the "packing factor theory," plays an important role in determining micelle shape (*Figure* 4).[8] The fraction, v/al, is known as the packing factor. When the packing factor has a value of 1/3, the surfactant molecule can be approximated by a conical shape and the molecules pack into a sphere (*Figures* 5 and 6). When the packing factor has a value of 1, the surfactant molecules pack as planar bilayers in a so-called lamellar structure (*Figure* 7). Commercial lecithin is a mixture of several natural phospholipids (phosphatidyl choline, phosphatidyl inositol, phosphatidyl ethanolamine, and phosphatidic acid) in oil. These phospholipids, with two hydrophobic tails, have a packing factor of 1 and generally form a bilayer structure or lamellar structure (*Figure* 7).

Lecithin is known to stabilize emulsions and is used in many food and medical products because of its digestibility and biocompatibility for humans. However, there is limited research available for the cellulose and lecithin systems in combination. A fundamental study[9] directed to the stability of whipped cream comprising vegetable oil and stabilized by lecithin and hydroxypropylcellulose revealed that there was an induction time for the onset of a measurable interfacial pressure conferred by hydroxypropylcellulose alone, and this induction time ranged from under a second to about 2.5 hours, depending on the polymer concentration. The interfacial storage modulus peaked with increasing surface pressure, a phenomenon which the authors attributed to polymer brush formation due to hydrophobic interaction between the exposed polymer chains. In the presence of lecithin, the interfacial storage modulus increased quasilinearly while the surface pressure and the interfacial loss tangent decreased with surface pressure, which the authors attributed to domination of the interfacial properties by the rate of adsorption of lecithin and the lecithin becoming more structured with time.

Since there appeared to be competition for the oil/water interface between the lecithin and the hydroxypropylcellulose when used together, the authors conclude that "the skill for the technologists consists in the right mixture, as both compounds compete for the same interface."[9] However, for application to marine oil spills, the technologists' skills are not adequate to control concen-

tration and mixing conditions. Fortunately, our laboratory testing has shown that when the lecithin and cellulose are preformulated before application to the oil/water system, stable droplets are achieved using typical dispersant application levels.

OIL ANTI-DEPOSITION AGENT DEVELOPMENT

General Requirements

It was imperative that the only materials considered for this research were those available in vast quantities at short notice, and this curtailed our possible choices of materials. The challenge was approached using high throughput screening techniques to quickly screen candidate dispersant systems. In our initial laboratory investigation, we discovered that the best commercial candidates currently used in laundry detergents (such as sodium carboxymethylcelluloses) were precipitated by the calcium in seawater and thereby rendered virtually useless. We also discovered that our second-best selected candidates, nonionic cellulose ethers, did not adsorb spontaneously to the oil/water interface in the dilute concentrations that would be expected from deployment in the sea. In order to overcome this deficiency, we investigated the approach of incorporating the nonionic cellulose ethers in hydrophobic liquids to enhance adsorption at the oil/water interface. We have discovered that soy lecithin (which is biodegradable in the marine environment) chaperones nonionic celluloses to the oil/water interface. This characteristic behavior could be viable in dispersing spilled oil and preventing it from fouling coastal substrates. Using high throughput formulation techniques, a large number of compositions comprising oil, grades of lecithin, and cellulose ethers were screened. Once the screening revealed a smaller subset of suitable candidates, further evaluation methods needed development to choose the best lecithin and the best cellulose type.

Inverted Contact Angle

Because our project was focused on rapid product development in addition to scientific study, we needed a fast and pragmatic approach to evaluate our compositions at a simulated oil/water interface to provide some insight into the role of each candidate formulation in order to select a target composition. We devised a contact angle method and built an apparatus (*Figure* 8) to measure contact angles of an antideposition-agent-treated oil droplet contacting a simulated oil surface from underneath the water. The oil surface was simulated using a polypropylene (hydrophobic) plaque. The use of a solid hydrophobic surface allowed the operator to photograph the treated oil as it contacted the surface and to photographically record the process of the treated oil interacting with the simulated oil/water interface for scrutiny

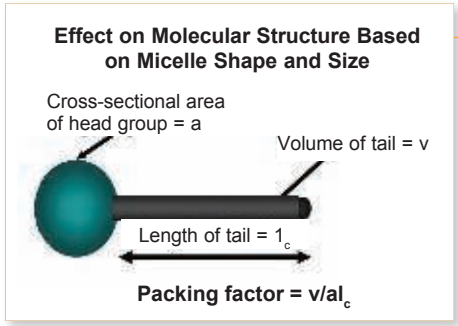

Figure 4—The packing factor of a surfactant molecule is the volume of the tail group divided by the volume of the cylinder created from the cross-sectional area of the head group and the length of the tail group.

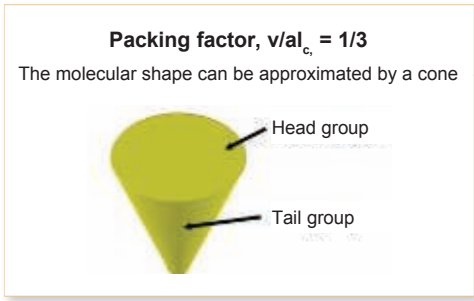

Figure 5—Surfactant molecules having a packing factor of 1/3 have a shape that can be approximated by a cone.

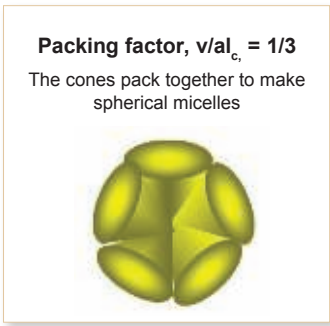

Figure 6—These conical molecules pack naturally into a sphere.

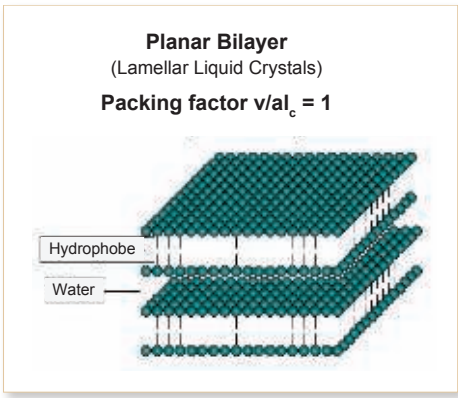

Figure 7—Surfactant molecules with a packing factor of 1 pack naturally into bilayer planes.

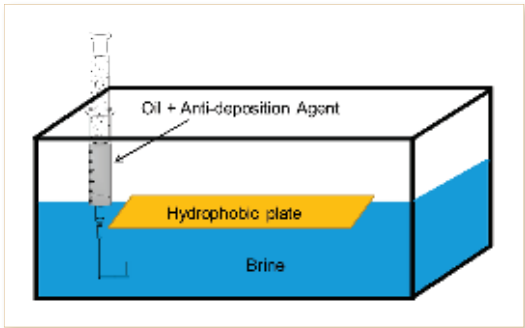

Figure 8—The contact angle device that we constructed to measure the contact angle of the treated oil at a simulated oil/water interface.

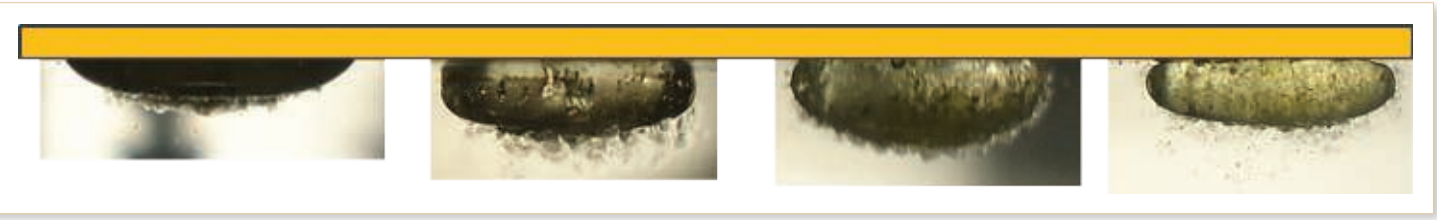

Figure 9—Contact of the antideposition-agent-treated oil with a polypropylene disc floating on water allowed an assessment of the processes that occurred when the compositions adsorbed at the oil/water interface. The cellulosic polymer can clearly be seen exuding as microgels from the droplets at different rates. The yellow bar represents the polypropylene surface.

Figure 10—Instantaneous fouling of an untreated duck feather with colored oil (left). The untreated oil completely wets the feather and is not readily removed from the feather even with agitation of the feather in the water. When a duck feather is immersed in oil dispersed with the antideposition agent in salt water, the oil droplets begin to lift away from the feather after simple immersion (right). Further agitation of the feather removes the treated oil.

and analysis by the entire technical team. The results of some of these contact angle measurements are shown as an example in *Figure* 9.

Measurements from this study revealed that the cellulose tended to dissolve in the aqueous medium and escape from the lecithin formulation when used at low concentrations in the final formulation. As the cellulose component was increased to approximately 50% by weight of the composition, formulations in which the cellulose ether remained at the interface of the dispersed oil phase and conferred "nonstick" properties were attainable. When bird feathers were applied to the surface of the water containing the treated droplets of oil, the droplets loosely flocculated, but they did not spread on the feathers (or other hydrophobic fabrics). Also, with mild agitation or rinsing of the feather with fresh brine, the treated oil droplets were washed away from the surface of the feather (*Figure* 10).

Microscopic Evaluation of Antideposition

Microscopic images of the feathers treated with our antideposition-agent-dispersed oil show that the oil was stabilized against deposition on the feather (*Figure* 11), and the droplets are easily removed by rinsing with clean salt water. On the other hand, when we applied an emulsion stabilized by di-2-ethylhexylsulfosuccinate and ethoxylated sorbitan mono-oleate (the surfactants similar to those used in the current Corexit dispersant that was applied in the Gulf of Mexico) the emulsion immediately broke and the oil spontaneously and immediately coated the feathers (*Figure* 12). It has been long known that dialkylsulfosuccinates are good wetting agents[10] and the behavior observed is exactly what would be expected from a good wetting agent.

Atomic Force Microscopy Study of Antideposition

Further study of the antideposition-agent-treated oil was done using atomic force microscopy (AFM). A hydrophobically modified silicon wafer was exposed to a brine solution containing the antideposition-agent-treated oil. *Figures* 13a and 13b show that the droplets of oil did settle onto the test surface. In fact, *Figure* 13b shows several hollow droplets, indicating that the oil was indeed encapsulated by the lecithin and cellulosic poly-

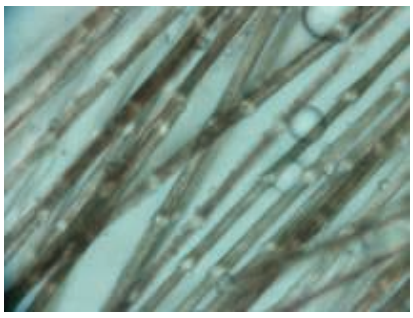

Figure 11—Oil dispersed with the antideposition agent is stabilized against deposition on duck feather fibers.

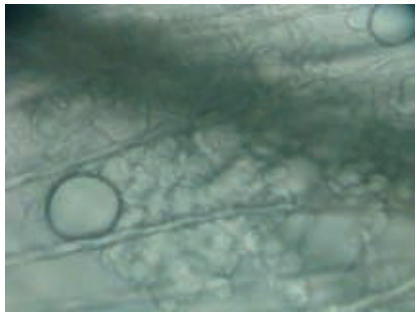

Figure 12—Oil dispersed with dioctylsulfosuccinate and alkylsorbitan ethoxylate is deposited on feathers.

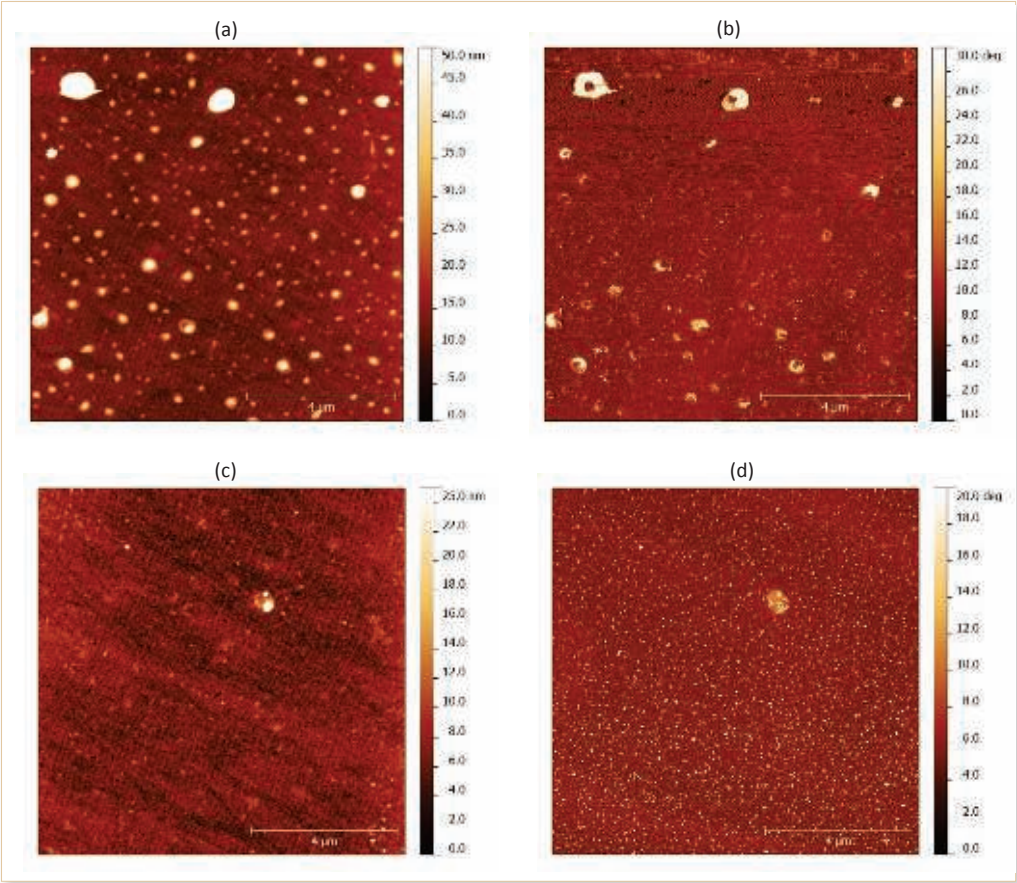

Figure 13—AFM height (left) and phase (right) images of antideposition-agent-treated oil settled on silicon dioxide QCM sensors after introduction of the solution (a and b), and complete droplet removal after a rinse by seawater (c and d).

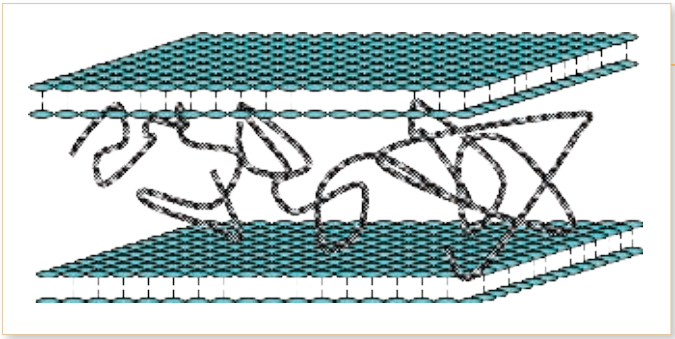

Figure 14—Illustration of the ability of the cellulosic polymers to enter the d-spacing of the lecithin.

mers. After rinsing by salt water (*Figures* 13c and 13d), the same test surfaces showed no remaining droplets.

Hypothesis of Mechanism

It is our current understanding that the antideposition agent sterically stabilizes the oil droplets against deposition because the lecithin multilayers adsorbed at the oil interface serve to anchor the cellulose ether polymers to the interface. However, at this stage, that hypothesis is informed speculation. Previous studies by Lochhead and Welch[11] showed that hydrophobically modified hydroxyethyl cellulose created a stable single lamellar phase when the cellulosic was mixed with surfactant B-phase, but created a segregated polymer and surfactant when the same polymer was mixed with D-phase. The only difference between these two surfactants is the d-spacing of the lamellar phase, which is greater for B-phase than for D-phase. Lochhead and Welch[11] concluded that the different results arose from the hydrodynamic volume of the polymer, which was able to penetrate B-phase but could not enter the galleries of D-phase.

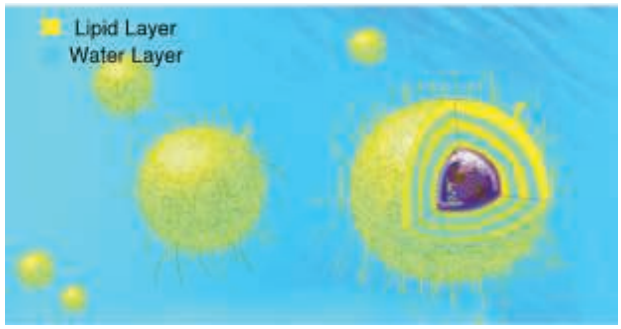

Figure 15—Illustration of the method of encapsulation for antideposition treatment of oil droplets. The lecithin bilayers form around the oil droplet and anchor the cellulosic polymer in the d-spacing of the bilayers. (Note: illustration not to scale)

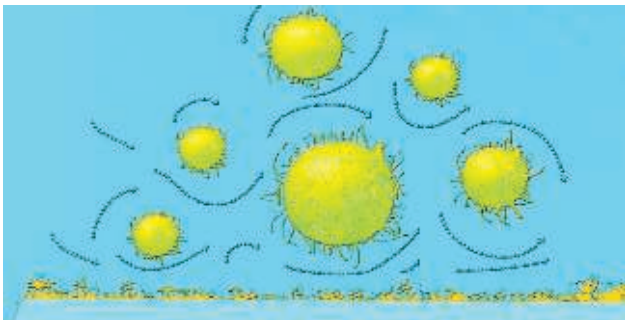

Figure 16—The cellulose that is anchored to the droplets acts to provide steric stabilization from agglomeration and provides "nonstick" properties when in contact with hydrophobic surfaces such as bird feathers.

From this previous research, we infer that the cellulosic polymer chains are anchored to the lecithin bilayers by their penetration into the d-spacing of the bilayers (*Figure* 14). The lecithin/cellulose system is successful because the lecithin disperses the oil droplets, and the cellulose provides steric stabilization against agglomeration of treated droplets and provides steric repulsion between the treated droplets and hydrophobic surfaces (*Figures* 15 and 16). This prevents the wetting and sticking of the treated oil onto surfaces like bird feathers. We are in the process of studying the mechanistic properties of the antideposition agent to be able to predict which cellulose ether molecular properties and which lecithin multilayers would provide the most desired dispersant action and droplet stabilization under the less precise application conditions to spilled oil in the marine environment.

CONCLUSIONS

We have developed a treatment for oil slicks that disperses the oil into discrete particles and prevents those treated particles from sticking to substrates such as bird feathers. Our antideposition agent is made of food-grade materials that are biodegradable. One of the major components in the formula is soy lecithin, which is known to increase bioremediation of oil spill sites by providing a phosphorous and nitrogen source to natural microbes at the site of the spill. We have successfully scaled the prototype to the kilogram scale with 50 kilograms available for sampling. We are currently pursuing toxicity testing and looking for partners to begin larger-scale trials, including field testing.

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