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- New Challenges, Solutions and Trends

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Stepan Company: Structured Surfactants as Rheology Modifiers in Agricultural Product Formulations

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History of structured liquids

Surfactants in the bulk aqueous phase self-assemble into various aggregate forms, such as lamellar, hexagonal or multi-lamellar vesicles (figure 1). This phenomenon is largely driven by the surfactant concentration and chemistry. These various phases impart unique physical properties to the surfactant solution, particularly at high concentrations where shear-thinning suspensive systems can be obtained.

First appearing more than 30 years ago, examples harnessing the self-assembly of surfactants are numerous across many disciplines. In 1985, multi-lamellar vesicles were used in laundry liquid to suspend sodium tripolyphosphate crystals, allowing higher loading of the builder than previously attainable. Although these systems can be employed by using high surfactant loadings, it was discovered that various additives, such as salts or oils, can force the conformation of surfactants into multi-lamellar vesicles at much lower concentrations. While additives improve practicality and cost by reducing the surfactant load, they limit the scope of formulations where this technology can be used.

Structured liquids in agrochemical formulations

Herein, Stepan Company presents a novel method for preparing suspensive systems by using a combination of high and low HLB surfactants, thereby eliminating the need for additional additives. We apply this technology to agrochemicals, allowing us to develop formulations not achievable through conventional methods.

An optimized ratio of a low HLB surfactant to high HLB surfactant, in the presence of water, forms vesicles that measure approximately 100 nanometers in size, resulting in a translucent liquid. These packed vesicles create a thick fluid with high yield stress, capable of suspending a range of materials, from solid pesticides to oil adjuvants. These fluids are also shear-thinning, non-thixotropic and have high elasticity.

The conventional rheology aids found in agricultural formulations have many limitations. For example, some pesticide actives are incompatible with xanthan gum and fail to solvate regardless of how much or how long shear was applied. Xanthan gum and other rheology aids can also present incompatibilities when electrolytes are built into a formulation concentrate or when diluted into liquid fertilizers. Additionally, low pH systems can cause issues with xanthan gum, even when an acid-stable grade is used. To evaluate a structured surfactant system in low pH, a carbaryl suspension concentrate (SC) was developed and evaluated for stability against xanthan gum controls at varying pH levels. All samples containing xanthan gum showed significant separation and hard packing, while the structured surfactant formulations remained stable at an elevated temperature.
Identifying structuring components

To identify the optimum ratio of low HLB to high HLB surfactant, the formulation liquids are first evaluated without any component suspended. Several samples should be prepared varying the ratio of surfactants and visually inspected for stability. High shear energy is not necessary to incorporate the structured surfactants, unlike with xanthan gum and other rheology aids.

After some mixing, air would have been incorporated, and the presence of suspended air bubbles over time gives an early indication of the suspensive system. Promising samples are then placed for temperature stability testing at 54°C and for freeze thaw evaluations at -15°C. An example of sample preparation with ratios and stability observations can be seen in figure 2.

Once a ratio is identified for a structured system, the formulation can be prepared with solid pesticide particles or the liquid oil adjuvant suspended. With a suspended component, small adjustments to the HLB ratio may be necessary for an optimized formulation. The type of surfactant chosen for the low and high HLB structurants can also be selected to perform more than one function, such as a dispersant or wetting agent, for example.

Rheological properties of structured liquids

To determine if a strong suspensive system was developed, we can characterize the rheological profile of the formulation. A four-pound per gallon atrazine SC was developed with structured surfactant technology and evaluated against a control formulation containing xanthan gum. An oscillation stress sweep of these two formulations reveals a more robust system and stronger structure at rest. Additional rheological methods were performed on the structured surfactant system, including a thixotropic loop, to show rapid recovery of the internal structure and temperature ramp to illustrate similar viscosities over a range of temperatures, compared to xanthan gum control.

Structuring in the presence of electrolytes or oil

Formulations can also be structured in the presence of electrolytes. It is important to start evaluating HLB ratios with the electrolyte present at the targeted level to determine which ratio will work best. A combination potassium and isopropylamine (KIPA) glyphosate salt was structured and evaluated for stability without any additional component suspended. That same structured formulation was then used to suspend atrazine particles for a combination KIPA glyphosate and atrazine formulation. The structured glyphosate-atrazine formulation showed superior dilution performance, compared to a generic KIPA glyphosate formulation tank mixed with a generic atrazine SC at the same active levels. The tank mixed material flocculated immediately upon dilution and after one hour had 7.5% separation, while the structured combination dilution had trace levels of cream sedimentation (As shown in figure 3).

An oil adjuvant can also be suspended through structured surfactant technology. Similar to structured KIPA glyphosate with suspended atrazine, rapeseed oil was suspended in KIPA glyphosate. When a generic rapeseed oil crop oil concentrate and a generic KIPA glyphosate formulation were combined without structured technology, the formulations separated, demonstrating that additional surfactant would be necessary or the materials would require tank mixing instead. In addition, both oil and...
pesticide particles can be suspended together in one formulation concentrate, as seen in the rapeseed oil and suspended atrazine combination that was developed.

**Field trial data**

Stepan conducted field trials with two different structured Atrazine SC formulations, a neutral pH and low pH chassis, along with a commercial standard and xanthan control formulation. The results showed similar or improved performance in three weed varieties, using a 10-ounce per acre use rate, while comparing seven days of control against 28 days of control (As shown in figure 4).

The future work with structured surfactants will continue to focus on unique combination formulations and identification of advantages over existing conventional technology.

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3. Tai Ho Tan, Build Liquid Detergent Compositions, EP0074134, 1984
About Stepan Agricultural Solutions

To help meet ever-changing market dynamics, Stepan Agricultural Solutions offers a robust pipeline of innovative products and actively seeks to be the strategic supplier of choice for your agricultural chemical needs. Our global research network and geographic footprint is such that we can effectively meet the needs of our customers around the globe. In addition, our industry-leading, in-house formulation expertise in emulsifiable concentrates, microemulsions, suspension concentrates and dry products provides a value-added service to help solve customers’ most difficult challenges.

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Stepan
Agricultural Solutions
Today’s increased global demand for food, feed, fibers and biorenewable fuels, coupled with climate change and the need to conserve natural resources, presents complex challenges for the agricultural industry. The industry’s response has been to focus on technology enhancements in three critical, interdependent areas – biology, chemistry and sustainability — and to enhance productivity through the use of agricultural chemicals.

**Major Technologies and Products**
Stepan Agricultural Solutions leverages the company’s core technologies of sulfonation, alkoxylation, amidation, oxidation, quaternization, and polymerization to deliver a complete line of products that meet our customers’ needs.

Stepan offers a broad product portfolio including, but not limited to, dispersants, emulsifiers, solvents, and specialty blends:

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<th>Dispersants</th>
<th>Emulsifiers</th>
<th>Solvents</th>
<th>Specialty Blends</th>
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<td>CaDBBSA</td>
<td>Vegetable oil-based methyl esters</td>
<td>Active ingredient-specific</td>
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<tr>
<td>Phosphate esters</td>
<td>Block copolymers</td>
<td>Dimethylamides</td>
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<td>Polyarylphenol ethoxylates</td>
<td>Ethoxylated alkyl phenols</td>
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<td>Lignosulfonates</td>
<td>Ethoxylated sorbitol esters</td>
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<td>Ethoxylated castor oils</td>
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Stepan Company is committed to innovation and new product development in partnership with our customers. In listening closely to our customer’s needs, Stepan is focused on the continued development of environmentally-sustainable solvents, improved adjuvant technologies, and our novel polymeric dispersant technology.

**Digital Tool Box**
We know immediate access to information and ease of use is important when making product selection. Rely on Stepan Company to offer you the right tools. Our most recent development, the Online Product Attribute Library (OPAL), is a customized private portal that is ideal for formulators looking for a more comprehensive technical data set, which includes chemical structure, fundamental surfactant properties, and advanced performance properties.

**Agricultural Solutions Manufacturing and R&D Sites**

![Map of Agricultural Solutions Manufacturing and R&D Sites](image_url)