ACULYN™ 22 Rheology Modifier/Stabilizer
A Very Efficient Thickener for Difficult to Thicken Surfactant Systems

This bulletin focuses on our ACULYN 22 rheology modifier, a very efficient thickener for difficult to thicken surfactant systems. Our ACULYN rheology modifiers find utility in an ever-increasing breadth of personal care applications because of their unique ease of use, wide compatibility, cost effectiveness and favorable balance of rheological properties.

Rohm and Haas Company is committed to providing technology enhancement to the personal care industry. To learn how our expertise in polymers and preservatives can spark your own creativity, please contact us.

Description

ACULYN 22 rheology modifier is an anionic hydrophobically modified alkali-soluble acrylic polymer emulsion (HASE) with unusually high aqueous thickening and stabilizing efficiency. This thickener is a liquid, cold-processable product that instantaneously thickens upon neutralization providing ease of handling and increased manufacturing efficiency. ACULYN 22 is offered at 30% solids and is compatible with high levels of surfactants. The polymer has a well-established toxicological profile and is safe in normal use.

CTFA/INCI Name: Acrylates/Steareth-20 Methacrylate Copolymer

Features

- High efficiency
- Yields clear gels
- Highly associative
- Very pseudoplastic
- High surfactant synergy
- Synergistic interaction with inorganic clays
- Particulate stabilizer
- Emulsion stabilizer
- Foam stabilizer
- Broad pH range stability
- Peroxide compatible
- Salt tolerant
- Shear tolerant
- High yield value
- Instant neutralization/thickening
- Cold-processable
- Liquid
- Broad compatibility

Benefits

- Easy to handle
- No preparation necessary
- Non hygroscopic
- Increased manufacturing efficiency
- Allows for use of continuous production processes with use of in-line static mixers
- Can be processed with membrane pumps and, when diluted, with turbine mixers and high speed propellers
- Able to formulate clear products
- Can be used with electrolytes
- Synergistic interaction with surfactants, particulates and hydrophobic raw materials
- Stabilization of hydrophobic (low solubility) components
- Compatible with nonionic, anionic, Zwitterionic and some cationic surfactants
- Ability to stabilize suspensions
- Mild, soft, non-greasy, non-sticky
- Stable in pH 5.5 to 12 formulations
- Thickens and stabilizes hydrogen peroxide
- Does not promote or support contamination, unlike natural thickeners
- Flexibility in choice of preservative system
- Supported by comprehensive environmental, health and safety data

Applications

- Anti-dandruff shampoos
- Bath foams
- Curl activators
- Depilatories
- Emulsifier free formulations
- Foaming facial cleansers
- Hair styling gels
- Liquid soaps
- Lotions
- Moisturizing creams
- Shampoos
- Shower gels
- Skin masks
- Waterless hand cleaners
- Wave sets
ACULYN 22 Chemistry

ACULYN 22 is a Hydrophobically-modified Alkali Soluble Emulsion (HASE). HASE polymers are synthesized from an acid/acrylate copolymer backbone and a monomer that connects the hydrophobic groups as side chains. The polymer is made through emulsion polymerization.

ACULYN 22 is synthesized from acrylic acid, acrylate esters and a steareth-20 methacrylate ester. The general structure for ACULYN 22 is shown to the right.

Mechanism of Action

ACULYN HASE rheology modifiers are able to thicken by two mechanisms that can act simultaneously and are synergistic, i.e. by the effect of charge-induced polyelectrolytic chain extension and by association of hydrophobe groups.

When the acid groups present in the ACULYN HASE molecules are neutralized with inorganic bases or organic amines, they become anionically charged and water-soluble. ACULYN 22 thickens above pH 6.5. ACULYN HASE rheology modifiers dissolve and swell due to charge-charge repulsion and therefore thicken instantly.

When ACULYN HASE polymers swell, the pendant hydrophobic groups are free to build associations with one another and with other hydrophobes available in the formulation, such as surfactants, particulates, emulsion droplets and dyes. This phenomenon creates a network structure that results in a significant viscosity build.
These associative structures can also act to stabilize and disperse particulates in a formulation.

And because of the ethoxylated hydrophobic group on the rheology modifier, ACULYN 22 can also act as a primary emulsifier for some emulsion systems, such as water-resistant sunscreens, to minimize the level of surfactant or emulsifier.
Features of HASE Rheology Modifiers

The chart to the right shows features indicative of the behavior of HASE rheology modifiers under different conditions. Please note that these behaviors may vary to some extent according to specific formulations.

All ACULYN rheology modifiers are easy to formulate, have good to excellent salt tolerance, compatibility with anionics and nonionics and low odor. HASE polymers have excellent shear thinning properties and good stability in two-part peroxide systems. Blending of the ASE and HASE chemistries can offer further enhancements and synergies.

<table>
<thead>
<tr>
<th>Feature</th>
<th>ACULYN 22</th>
<th>ACULYN 222</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ease of formulation</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Associative</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Salt tolerance</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>NaCl</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Di/trivalent ions</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Shear thinning behavior</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Solvent compatibility</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Low pH compatibility</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Anionic surfactant compatibility</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nonionic surfactant compatibility</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Zwitterionic surfactant compatibility</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Cationic surfactant compatibility</td>
<td>Some</td>
<td>Excellent</td>
</tr>
<tr>
<td>Peroxide stability</td>
<td>No</td>
<td>Excellent</td>
</tr>
<tr>
<td>1 part system</td>
<td>No</td>
<td>Excellent</td>
</tr>
<tr>
<td>2 part system</td>
<td>No</td>
<td>Excellent</td>
</tr>
<tr>
<td>Lack of odor</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

ACULYN 22 Behavior Profile

ACULYN 22 rheology modifier possesses many properties that make this polymer highly desirable for use in personal care applications, as shown by the data presented below.

Rheology

Effect of Shear Rate

ACULYN 22 thickener is a low-viscosity dispersion that becomes a highly viscous clear solution when neutralized with alkali. Provided that proper mixing conditions are used, ACULYN 22 thickens instantaneously upon addition of base, allowing rapid preparation of solutions and products. There is no need for pre-wetting, high shear mixing or long soak times.

The presence of the C₁₈ hydrophobe causes neutralized solutions of ACULYN 22 to be very pseudoplastic, in general showing a high degree of shear thinning because of easily broken van der Waals forces. The yield value also allows the thickener to stabilize suspensions, while still being pourable.

The alkaline solutions are clear, and their flow properties are characterized by a complete lack of stringiness and tackiness and by shear thinning. At the same time, the solutions are viscous at low shear rates. The log-log plot of apparent viscosity vs. shear rate is linear for the sodium salt over the range of spindle rotation rates between 0.5 and 60 rpm. The shear thinning behavior in the following graph is measured in water and the behavior can change in formulations.
Effect of Temperature

Thickening with ACULYN 22 undergoes a modest decrease as the temperature rises from 20°C to 75°C.

Compatibility

Surfactant Synergies

General Effect of Surfactants

Certain anionic and nonionic surfactants give a synergistic increase in the viscosity and thickening efficiency of neutralized ACULYN 22 solutions. 10 to 1000 fold increases in viscosity can be achieved. Each surfactant has an optimum concentration at which maximum viscosity is obtained.
With sodium lauryl sulfate (SLS), for example, the maximum occurs at a level of 40% based on the concentration of ACULYN 22 thickener. The effect of SLS on solution viscosity as a function of the level of ACULYN 22 thickener and the effect of SLS as a function of SLS concentration are shown in the graphs below.

Thickening of Acid-Containing Surfactants Solutions

At high levels of anionic surfactants, acid-containing aqueous solutions with ACULYN 22 display a high degree of thickening. By using a mixture of two surfactants, one an anionic (major component) and the other an amide (minor component), clear thickened compositions are obtained with ACULYN 22 at pH 1 to 7. The presence of amide surfactant is necessary to ensure clarity in these formulations. Applications for these formulations include clear, low pH shampoos.

To correctly prepare these products, the ACULYN 22 is dispersed in the water and the two (or more) anionic surfactants are added with stirring. The solution is neutralized with caustic or other base and allowed to stir for 15 minutes. Finally, the acidity is adjusted to the required level by adding citric acid (pH 4.5 to 7) or hydrochloric acid (pH 1 to 7) to the neutralized solution of the surfactants and thickener. Addition of cationic ingredients, if any, should occur after the pH is lowered to 6.0 or less to minimize the potential interaction of the carboxyl functionality.

The graph and table below show the Brookfield viscosity of a typical formulation over a broad range of low pH.
The graph below presents the effect of pH on the viscosity of formulations based on various anionic surfactants with ACULYN 22.

The table shows the viscosity values at pH 5, 12 rpm for different formulations at various pH levels:

### Acid Shampoos

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>SLS (28%)</th>
<th>SLES (27%)</th>
<th>TEALS (40%)</th>
<th>AOS (40%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids As supplied</td>
<td>17.0</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Lauramide DEA</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Cocamide DEA</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Miranol C2MSF (70%)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>ACULYN 22 (30%)</td>
<td>1.0</td>
<td>1.5</td>
<td>5.0</td>
<td>1.5</td>
</tr>
<tr>
<td>NaOH (10%)</td>
<td>0.09</td>
<td>0.14</td>
<td>1.4</td>
<td>0.14</td>
</tr>
<tr>
<td>Water</td>
<td>32.1</td>
<td>27.6</td>
<td>44.6</td>
<td>48.1</td>
</tr>
</tbody>
</table>

Viscosity, Brookfield, cps @ pH 5, 12 rpm

- SLS: 2100
- SLES: 900
- TEALS: 3000
- AOS: 5700
Salt Tolerance

Neutralized solutions of ACULYN 22 can thicken salt solutions. The thickening efficiency decreases with increasing level of salt, and solutions with low concentrations of thickener are particularly sensitive to the presence of salt. Addition of low levels of surfactant, even when salts are present, substantially increases the thickening efficiency of ACULYN 22.

ACULYN 22 also has a tolerance for other salts. Divalent salts such as magnesium chloride will have an impact on viscosity, more of an impact than monovalent salts such as sodium chloride or sodium acetate.
Synergies with Inorganic Clays

Adding low-cost bentonite clays appreciably increases the thickening efficiency of neutralized ACULYN 22. Combining appropriate levels of ACULYN 22 thickener and bentonite clays can produce free-standing gels.

Effect of Bentonite Clay on Viscosity of Neutralized Aculyn 22

Values are low shear viscosities (Brookfield RVF at 0.5 rpm).
The figures give the ratios of clay to polymer for each curve.
Mixes of Bentonite with the Aculyn 22 polymer show a significant yield stress (point).

pH Tolerance

Thickening drops precipitously below pH of about 7, a range in which the polymer is insoluble. With sodium hydroxide as the base, the viscosity reaches a maximum and remains steady over the pH range from 7.5 to 12. ACULYN 22 can thicken aqueous solutions containing a high level of surfactant below pH 6.5.
Performance

Extremely Efficient Thickener

ACULYN 22 achieves thickening of solutions at very low concentrations and is therefore very efficient and cost effective. The thickening efficiency of ACULYN 22 is significantly superior compared to other types of thickeners such as cellulosics and carbomers. ACULYN 22 can be neutralized with sodium hydroxide, ammonia, soda ash (sodium carbonate), and triethanolamine as well as other bases.

Formulation and Use Guidelines

ACULYN 22 rheology modifier is compatible with surfactants, solvents, oils and salts commonly found in cosmetic and toiletry products. These products undergo instantaneous thickening when neutralized with base.

This product is supplied as a low viscosity emulsion and can be incorporated directly into formulations with none of the concerns about dissolution, particulate clumping or dusting problems that can be encountered with dry products. ACULYN 22 is also cold processable.

Because thickening occurs instantaneously upon neutralization with base, in-line mixing with static mixers is possible. Upon neutralization, the ACULYN 22 emulsion becomes a clear, highly viscous solution.

The preferred order of addition when using ACULYN 22 rheology modifier in aqueous formulations is as follows:

1. Add ACULYN 22 to the water
2. Add other ingredients from the most acidic to the most alkaline
3. Add the neutralizing agent

If this sequence is not desirable, Aculyn HASE and ASE polymers can be added directly to an alkaline formulation after first diluting the Aculyn 22 product with two parts of water. Addition of the water prevents gel particles (small particles with neutralized swollen surfaces and unneutralized cores that will take considerable time to dissolve completely).

Preparation of Emulsions and Dispersions

Neutralized ACULYN 22 thickener can also be used to make oil-in-water emulsions of organic liquids such as mineral oil, lanolin or kerosene. ACULYN 22 can also be used to suspend fillers and pigments, such as calcium carbonate, silicate clays and titanium dioxide, in water.

If ACULYN 22 is being used in an emulsion formulation, the general order of addition is as follows:
1. Add ACULYN 22 to the water phase at temperature
2. Add the other water phase ingredients
3. Mix separately the oil phase ingredients at temperature
4. Mix the oil phase into the water phase maintaining temperature
5. Neutralize the ACULYN 22 polymer
6. Cool the mixture with constant stirring
7. Add the preservative (if any) at a safe temperature

**Environmental, Health and Safety Record**

**Toxicology**

**Acute Toxicity Profile**

<table>
<thead>
<tr>
<th>Test/Species</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oral LD$_{50}$ – rat</td>
<td>&gt;5.0 g/kg non-toxic</td>
</tr>
<tr>
<td>Dermal LD$_{50}$ – rabbit</td>
<td>&gt;5.0 g/kg non-toxic</td>
</tr>
<tr>
<td>Eye irritation – rabbit</td>
<td>Non irritating (US and EEC)</td>
</tr>
<tr>
<td>Skin irritation – rabbit</td>
<td>Slightly irritating (US); Non irritating (EEC)</td>
</tr>
</tbody>
</table>

US — United States classification  
EEC — European Economic Community classification

**Sensitization Toxicity Profile**

<table>
<thead>
<tr>
<th>Test/Species</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitization, Guinea pig</td>
<td>Non sensitizer</td>
</tr>
</tbody>
</table>

**Genetic Toxicity Profile**

<table>
<thead>
<tr>
<th>Test/Species</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ames Test</td>
<td>Non mutagenic with and without metabolic activation</td>
</tr>
</tbody>
</table>

**Ecotoxicity Profile**

<table>
<thead>
<tr>
<th>Test/Species</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daphnia magna EC$_{50}$ — 48 hr</td>
<td>&gt;1000 mg/L — non toxic</td>
</tr>
<tr>
<td>Rainbow Trout LC$_{50}$ — 96 hr</td>
<td>&gt;1000 mg/L — non toxic</td>
</tr>
<tr>
<td>Bluegill Sunfish LC$_{50}$ — 96 hr</td>
<td>&gt;1000 mg/L — non toxic</td>
</tr>
</tbody>
</table>

**Overall Evaluation**

ACULYN 22 is considered non-toxic by single oral and dermal exposure, produces minimal to no irritation to the eyes and skin, a non-sensitizer, non-mutagenic in the Ames assay and non-toxic to aquatic organisms. This material is safe and appropriate for use in a broad range of rinse-off and leave-on personal care applications.

ACULYN 22 is cleared under the major chemical inventories such as CTFA, MITI, EINECS, TSCA, AICS and Canada.
Storage and Handling

Storage

Keep from freezing; material may coagulate. The minimum recommended storage temperature for these materials is 1°C/34°F. The maximum recommended storage temperature is 49°C/120°F. These materials may coagulate if exposed to temperature outside this range. The coagulation process is irreversible.

Material Safety Data Sheets

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Material Safety Data Sheets outlining known health and safety hazards and handling methods for our products are available on request.

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