ACULYN™ 33  Rheology Modifier/Stabilizer
A Cost-Effective Thickener for Formulations Containing Polar Solvents

This bulletin focuses on our ACULYN™ 33 rheology modifier, a cost-effective thickener particularly suited for formulations containing polar solvents. 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.

CTFA/INCI Name: Acrylates Copolymer

Description
ACULYN 33 rheology modifier is an alkali-swellable anionic acrylic polymer emulsion (ASE) that is lightly crosslinked to impart a short pseudoplastic flow. It is a liquid, cold-processable product that instantaneously thickens upon neutralization providing ease of handling and increased manufacturing efficiency. This thickener is offered at 28% solids and is compatible with peroxide and other oxidizing agents, electrolytes, polar solvents and zinc pyrithione. The polymer has a well-established toxicological profile and is safe in normal use.

Features
- Stable in highly alkaline systems
- Particulate suspension
- Polar solvent compatibility
- Instant neutralization/thickening
- Short flow
- Cold-processable/Liquid
- Yields clear gels
- Divalent ion tolerance
- Excellent viscosity stability
- Peroxide compatible
- Flat pH/viscosity response
- Lack of odor
- Excellent high shear stability

Benefits
- Easy to handle
- Formulations exhibit little viscosity drift
- No preparation necessary
- Compatible with nonionic and anionic surfactants
- Non hygroscopic
- Thickens and stabilizes hydrogen peroxide
- Increased manufacturing efficiency
- No odor/color change in two-part peroxide formulations
- Allows for use of continuous production processes with use of in-line static mixers
- Permits stable formulations with particulates
- Can be processed with membrane pumps and, when diluted, with turbine mixers and high speed propellers
- Formulation ability with zinc pyrithione
- Ability to stabilize suspensions
- Less sensitive to water hardness
- Able to formulate clear products
- Does not promote or support contamination, unlike natural thickeners
- Mild, soft, non-greasy, non-sticky
- No watery feel upon skin contact
- Flexibility in choice of preservative system
- Improved pickup properties
- Supported by comprehensive environmental, health and safety data
- Formulation of spreadable lotion products that flow readily from the container
- Allows for stable, viscous formulations in polar solvents

Applications
- Alcohol and glycol-containing formulations
  - Astringents
  - Cleansers
- Anti-dandruff shampoos
- Depilatories
- Hand Soaps
- Lotions
- Make-up creams and lotions
- Peroxide-containing formulations
  - Hair dyes
  - Hand disinfectants
  - Permanent wave neutralizers
- Solvent gels
ACULYN 33 Chemistry

ACULYN 33 is an anionic Alkali-Soluble polymer Emulsion (ASE). ASE polymers are synthesized from acid and acrylate comonomers and are made through emulsion polymerization.

The general structure for ACULYN 33 is shown to the right.

Mechanism of Action

ACULYN ASE polymers thicken via a non-associative mechanism. Non-associative rheology modifiers do not interact with surfactant structures, particulates or insoluble emulsion droplets.

Non-associative polymers thicken by structuring the continuous phase and through chain entanglement. This can stabilize pre-dispersed insolubles by significantly slowing their motion.

Physical and Chemical Characteristics

These properties are typical but do not constitute specifications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry</td>
<td>ASE polymer</td>
</tr>
<tr>
<td>Association</td>
<td>none</td>
</tr>
<tr>
<td>Ionic nature</td>
<td>anionic</td>
</tr>
<tr>
<td>Appearance</td>
<td>milky liquid</td>
</tr>
<tr>
<td>Solvent</td>
<td>water</td>
</tr>
<tr>
<td>Solids, %</td>
<td>28</td>
</tr>
<tr>
<td>pH (as supplied)</td>
<td>3.0</td>
</tr>
<tr>
<td>Density</td>
<td>1.05</td>
</tr>
<tr>
<td>Equivalent weight*</td>
<td>218</td>
</tr>
<tr>
<td>Rheology</td>
<td>short, buttery</td>
</tr>
<tr>
<td>Shear thinning</td>
<td>moderate</td>
</tr>
<tr>
<td>Viscosity, mPa s (as supplied)</td>
<td>10</td>
</tr>
<tr>
<td>Pseudoplastic index</td>
<td>5.0</td>
</tr>
<tr>
<td>(viscosity @ 6 rpm/viscosity @ 60 rpm)</td>
<td>(2% solids in water)</td>
</tr>
</tbody>
</table>

*grams of dry polymer neutralized by 1 equivalent (40 grams) of NaOH.
Features of ASE Rheology Modifiers

The chart to the right shows features indicative of the behavior of ASE 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. ASE polymers have excellent solvent stability and excellent 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>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ease of formulation</td>
<td>Excellent</td>
</tr>
<tr>
<td>Associative</td>
<td>No</td>
</tr>
<tr>
<td>Salt tolerance</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>Good</td>
</tr>
<tr>
<td>Di/trivalent ions</td>
<td>Good</td>
</tr>
<tr>
<td>Shear thinning behavior</td>
<td>Good</td>
</tr>
<tr>
<td>Solvent compatibility</td>
<td>Excellent</td>
</tr>
<tr>
<td>Low pH compatibility (&lt; pH 6)</td>
<td>No</td>
</tr>
<tr>
<td>Anionic surfactant compatibility</td>
<td>Excellent</td>
</tr>
<tr>
<td>Nonionic surfactant compatibility</td>
<td>Excellent</td>
</tr>
<tr>
<td>Cationic surfactant compatibility</td>
<td>No</td>
</tr>
<tr>
<td>Peroxide stability</td>
<td></td>
</tr>
<tr>
<td>1 part system</td>
<td>No</td>
</tr>
<tr>
<td>2 part system</td>
<td>Excellent</td>
</tr>
<tr>
<td>Lack of odor</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

ACULYN 33 Behavior Profile

ACULYN 33 rheology modifier possesses many properties that make this polymer highly desirable for use in personal care applications, as shown in the data presented below.

Rheology

Shear Thinning

Solutions incorporating ACULYN 33 exhibit shear thinning properties with a short flow.
Temperature Sensitivity

The relative degree of the shear thinning nature of these solutions is closely related to that of the cellulosic thickeners. Thickening undergoes a modest decrease throughout a temperature range from 20°C to 75°C.

Compatibility

Cationic Compatibility

Polymeric cationics, as well as some large, bulky quaternary materials, can possibly be incorporated in formulations containing ACULYN 33. The optimum order of addition in these instances generally requires the ACULYN 33 to be neutralized with a base prior to the addition of any cationics.

pH Tolerance

ACULYN 33 is an effective stabilizer/thickener over the pH range of 6.0 to 12.5.
Peroxide Stability

ACULYN 33 is stable in systems containing hydrogen peroxide. Because hydrogen peroxide is only stable under acidic conditions and is most often supplied at a pH of 4, and ACULYN 33 does not thicken until neutralized (pH > 6.5), the use of ACULYN 33 in peroxide-containing formulas is restricted to two-part systems.

Peroxide and ACULYN 33 can be mixed together forming a stable mixture (part A), with alkali and any other component forming part B. When the two parts are mixed, thickening will occur instantaneously.

### Peroxide Stability with ACULYN 33 (3% Polymer Solids, pH 3.5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peroxide Retained, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 weeks at 25°C</td>
</tr>
<tr>
<td>3% Hydrogen Peroxide + ACULYN 33</td>
<td>71.1</td>
</tr>
<tr>
<td>3% Hydrogen Peroxide (No polymer)</td>
<td>82.2</td>
</tr>
<tr>
<td>12% Hydrogen Peroxide + ACULYN 33</td>
<td>87.4</td>
</tr>
<tr>
<td>12% Hydrogen Peroxide (No polymer)</td>
<td>83.0</td>
</tr>
</tbody>
</table>

Performance

**Film Formation**

Films of neutralized ACULYN 33 are clear and somewhat brittle. Soft flexible films can be prepared with the addition of glycols. Films cast from the ammonium or volatile amine salts are less sensitive to water than those prepared from sodium or potassium salts.

**Particulate Suspension**

Particulates can be stabilized by ACULYN 33. The table on the next page illustrates stable kaolin clay slurries created with low levels of ACULYN 33. Formulators of liquid and cream-based makeup will find ACULYN 33 a valuable addition to their array of formulation aids. Formulations containing pigments difficult to suspend such as red iron oxide (Fe₂O₃) can be thickened/stabilized with ACULYN 33. And because of its ability to suspend particulates, ACULYN 33 can be employed to stabilize suspensions of zinc pyrithione in anti-dandruff shampoos.
ACULYN 33 can also be used with titanium dioxide (TiO₂) in sunscreens to give an excellent feel with ample playtime. The polymer is also compatible with other inorganic UV absorbers.

**Neutralization Options**

ACULYN 33 can be neutralized by a wide range of both inorganic and organic bases. Choice of base is dependent upon intended applications, specific ingredients and personal preference. In many simple aqueous systems the choice is often sodium hydroxide, potassium hydroxide, or ammonium hydroxide.

In emulsified lotions and creams, alkanol amines are often used. Typical choices include triethanolamine (TEA), diethanolamine (DEA), aminomethylpropanol (AMP) and aminomethylpropanediol (AMPD).

For products with high levels of organic solvents, the alkanol amines or higher molecular weight, more oil-soluble amines are preferred, such as Quadrol (tetrahydroxypropyl ethylenediamine) and Ethomeen C/-25 (PEG-15 cocoamine) supplied by Akzo Nobel.

Choice of amine can somewhat affect the formulated viscosity. The table below shows TEA to be slightly more efficient for ACULYN 33 in increasing viscosity of water. Subtle properties such as product feel can be altered by choice of amine.

### ACULYN 33 Neutralization with Various Bases
(1% solids, Brookfield Viscosity (cps) @ 12 rpm)

<table>
<thead>
<tr>
<th>Base</th>
<th>pH 7</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄OH</td>
<td>3700</td>
<td>3200</td>
</tr>
<tr>
<td>TEA</td>
<td>5500</td>
<td>5500</td>
</tr>
<tr>
<td>KOH</td>
<td>3900</td>
<td>4300</td>
</tr>
</tbody>
</table>

**Thickening of Polar Solvents**

ACULYN 33 is an effective thickener for a variety of alcoholic solutions. The thickening efficiency for the sodium form of ACULYN 33 in these polar solvents is shown in the table and graph below. Sodium hydroxide was used to neutralize ACULYN 33 in these solutions. More hydrophobic organic amines would be more appropriate for less polar solvents.
ACULYN 33 can be efficiently used to thicken up to 60% solutions of isopropyl alcohol. For optimum results when formulating with high levels of alcohols, it is recommended, if possible, to add approximately one-half of the required alkali for neutralization prior to the addition of the alcohol, followed by the balance of the alkali.

**Formulation and Use Guidelines**

ACULYN 33 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 33 is also cold processable.

Because thickening occurs instantaneously upon neutralization with base, in-line mixing with static mixers is possible. Upon neutralization, the ACULYN 33 emulsion becomes a clear, highly viscous solution.
The preferred order of addition when using ACULYN 33 rheology modifier in aqueous formulations is as follows:

1. Add ACULYN 33 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 ASE polymers can be added directly to an alkaline formulation after first diluting the ACULYN 33 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 completely dissolve).

If ACULYN 33 is being used in an emulsion formulation, the general order of addition is as follows:

1. Add ACULYN 33 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 33 polymer
6. Cool the mixture with constant stirring
7. Add the preservative (if any) at a safe temperature

**Environmental, Health and Safety Record**

**Acute Toxicity Profile**

<table>
<thead>
<tr>
<th>Test</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>Slightly irritating (US); Non irritating (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

**Genetic Toxicity Profile**

Toxicity data for a compositionally similar product are shown below:

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

**Human Toxicity Profile**

<table>
<thead>
<tr>
<th>Test</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitization/irritation — Single application</td>
<td>Non sensitizing and Non irritating</td>
</tr>
</tbody>
</table>
Overall Evaluation

ACULYN 33 is considered non-toxic by a single oral dose and dermal exposure, produces minimal to no irritation to the eyes and skin, non-mutagenic in the Ames assay, non-irritant and non-sensitizer in Human Patch testing 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 33 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

Rohm and Haas Material Safety Data Sheets (MSDS) contain pertinent information that you may need to protect your employees and customers against any known health or safety hazards associated with our products. Under the OSHA Hazard Communication Standard, workers must have access to and understand MSDS on all hazardous substances to which they are exposed. Thus, it is important that you provide appropriate training and information to your employees and make sure they have available to them MSDS on any hazardous products in the workplace.

Upon initial shipment of non-OSHA-hazardous and OSHA-hazardous products (including samples), Rohm and Haas Company sends the appropriate MSDS to the recipient. If you do not have access to one of these MSDS, please contact your local Rohm and Haas representative for a copy. Updated MSDS are sent upon revision to all customers of record. MSDS are also sent annually to all customers receiving products deemed hazardous under the Superfund Amendments and Reauthorization Act (SARA). MSDS should be obtained from suppliers of other materials recommended in this bulletin.

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