Clay Control Basics

Clay swelling in shale formations during drilling or well completion can have a tremendously adverse impact on oil and gas operations. Traditionally, preventing clay swelling in oilfield operations by aqueous-based systems has been achieved using large concentrations of inorganic salts, mainly potassium chloride (KCl). However, effective clay control requires high concentrations, which can be difficult to apply. GVision methods of clay control involve either water-soluble or water-insoluble products to achieve cloud point under site-specific work conditions.

Minerals, including clay, are the primary component of most shale. They are composed of layers of clay flakes, forcing them apart. Clay flakes are made up of a number of thin, flaky clay minerals. Clay flake size and composition affect the rate of water penetration into the shale, while amines and ammonium compounds inhibit swelling by chemical means. Amines/quaternary compounds inhibit swelling by changing the ionic strength of the water. Adsorption onto crystal surfaces and drawing by osmosis between the clay flakes and water molecules induces swelling.

The leading global producer and supplier into a wide range of industries is Huntsman Corporation. Huntsman is a publicly traded global manufacturer and marketer of differentiated chemicals with 2016 revenues of approximately $10 billion. Our chemical products number in the thousands and are sold worldwide to manufacturers serving a broad and diverse range of consumer and industrial markets. We operate more than 100 manufacturing and R&D facilities in approximately 30 countries and employ approximately 15,000 associates within our 5 distinct business divisions including the Polyurethanes, Performance Products, Advanced Materials, Surface Specialty, and Electronic Materials division that we intend to spin-off as Venator Materials Corporation. For more information about Huntsman, please visit the company’s website at www.huntsman.com.

Huntsman Performance Products

Performance Products brings together innovative and world-leading process technologies to produce more than 1,000 products used for manufacturing products that enhance people’s lives.

- **Amine**: Largest global producer of specialty amines used in composites, coatings, fuel and tube additives, and gas treating.
- **Maleic Anhydride**: The leading global producer and supplier into industries such as unsaturated polyester resins, food, oil additive, and medical.
- **Surfactants**: Integrated producer of a wide range of products for films and personal care, oleochemicals, agriculture, and process industries.
- **Ethylene and Derivatives**: Highly integrated manufacturer of ethylene, ethylene oxide, ethylene glycol and other derivatives.

The division has 14 manufacturing plants and had 2016 revenues of USD 2.1 billion.

About Huntsman

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Clay Control Basics

The clay minerals, generally crystalline in nature, typically have a flaky structure. Clay flakiness makes them ideal for use as a number of oil and gas industry products. Clay minerals are commonly used in oil and gas drilling fluids, to stabilize clay minerals in the reservoir and to control drilling fluid rheology.

Clay minerals are generally composed of silicate sheets held together by hydrated layers of clay. Clay minerals include illite, montmorillonite, kaolinite and attapulgite. Clay minerals are scheelite crystal structure and their properties depend on the type of clay.

Shale is a type of sedimentary rock composed chiefly of clay and other fine-grained materials. Shale is a low-temperature, low-pressure sedimentary rock. Shale is a major source of natural gas and oil. Clay minerals are composed of silicate sheets held together by hydrated layers of clay. Clay minerals include illite, montmorillonite, kaolinite and attapulgite. Clay minerals are scheelite crystal structure and their properties depend on the type of clay.

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Huntsman Clay Control Chemicals

By use of the proper concentration of SURFONIC® OFS 500 or SURFONIC® OFS 600 stabilization agent with a SURFONIC® L4 series solvent and KCl, the cloud point of the clay control fluid can be adjusted to a particular drilling environment. Amine compounds are often more effective when applied as ammonium salts.

Cloud Point Shale Inhibition

**Tested on Khvalynsky brown “chocolate” clay from Volgograd region in Russia, 3% shale inhibitor. Different clays may produce different results.

Several laboratory methods of evaluating shale inhibitor efficiency are being used industry wide. Huntsman clay control mud formulations for 16 hours at 90°C (194°F) in a rolling oven and screened through a 0.85 mm sieve. Surviving Dispersion Test (Hot Rolling):

- Flower and inhibitor in water were filtered through a specialty paper filter while the instrument measured the speed dispersion test, clay retained,** 

- pH < 10 pH > 10

- 94

- 84

- 50

- 33

- 11

- 30

- 40

- 5

- 0 6 12 1 8 2 4 3 0 3 6 4 2 4 8 5 4 60 66 72

- 90

- 30

- 45

- 15

- 15

- 35

- 45

- 5

- 0

- 0

- 6 12 1 8 2 4 3 0 3 6 4 2 4 8 5 4 60 66 72

- 90

- 30

- 45

- 15

- 15

- 35

- 45

- 5

- 0

- 0

- 6 12 1 8 2 4 3 0 3 6 4 2 4 8 5 4 60 66 72

- 90

- 30

- 45

- 15

- 15

- 35

- 45

- 5

- 0

- 0

- 6 12 1 8 2 4 3 0 3 6 4 2 4 8 5 4 60 66 72

Amine/Quaternary Shale Inhibitors

Several laboratory methods of evaluating shale inhibitor efficiency are being used industry wide. Huntsman clay control agents and their acetic salts have been rigorously tested in accordance with published protocols.

**Capillary Suction Test (CST):** Often used as a preliminary screening method. Smears of bentonite clay, silica flour and inhibitor in water were filtered through a specialty paper filter while the instrument measured the speed of filtration. Faster filter time indicates less swelling and improved performance.

**Dispersion Test (Hot Rolling):** Shale pieces between 4.75 and 6.7 mm size were tumbled in water base drilling mud formulations for 16 hours at 90°C (194°F) in a rolling oven and screened through a 0.85 mm sieve. Surviving chips were washed and dried. Higher retained weights of shale indicate improved shale stabilization.

<table>
<thead>
<tr>
<th>Clay Inhibitor</th>
<th>Capillary Suction Test Efficiency, %</th>
<th>Dispersion Test, Clay Retained,**</th>
<th>Dispersion Test, Clay Retained,**</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFS 125 (L4-2)</td>
<td>90</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>OFS 126 (L4-3)</td>
<td>90</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>OFS 127 (L4-4)</td>
<td>90</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>OFS 500 Shale Stabilizing Agent</td>
<td>90</td>
<td>80</td>
<td>70</td>
</tr>
</tbody>
</table>

**Note:** Results taken from five different shales at different concentrations and conditions. Differences may arise between different shale samples. The following are key points with SURFONIC® OFS 500 Shale Stabilizing Agent:

- No inhibitor YP

- 1% Surfactant:

- 5% Surfactant:

- 10% Surfactant:

- 15% Surfactant:

**Note:** Potassium chloride for controlled testing of bentonite in water base drilling mud was used as a stabilizing agent. Several experiments were used to select the ratio for the system.

Different clays may produce different results.

**Dynamic Linear Swelling:** The ORITE Swellmeter measures clay swelling at wellbore conditions. Compressed Globe of bentonite was submerged in a drilling mud at high temperature and the time of water swelling mounted over time. Less swelling indicates improved clay inhibition performance.

**Mud Rheology:** Bentonite was incrementally added to water base drilling muds (3% KCl) until the mud became too thick to measure their viscosities. The ability to absorb more bentonite indicates improved clay inhibitor performance. Baselines representing the uninhibited system and 5% KCl are added for reference.

<table>
<thead>
<tr>
<th>Bentonite, lbs/barrel</th>
<th>KCI Solution (%</th>
<th>Visc. @ 3 rpm, Fann Units</th>
<th>Yield Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>0</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>150</td>
<td>10</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>150</td>
<td>15</td>
<td>40</td>
<td>100</td>
</tr>
</tbody>
</table>

**Key Points in Polyols Applications**

- Partial replacement for KCl:

- Highly soluble in salt water. Should not phase on surface water at temperatures below cloud point.

- Cuttings may be easily rinsed and recycled back into the mud.

- May be formulated with SURFONIC® L4 series solvent to give a wide range of system cloud points to match bottom hole circulating temperatures.

- “On the fly” adjustments may easily be conducted to get suitable clay points on drifting conditions change.

- Additional benefits include fabrication of the drill stem and cleaning of the drill bit.

**Effect of Polyol Concentration on Cloud Point of KCI Solutions**

<table>
<thead>
<tr>
<th>Test</th>
<th>1% Surfactant</th>
<th>5% Surfactant</th>
<th>10% Surfactant</th>
<th>15% Surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>YP</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>Vis.</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>70</td>
</tr>
</tbody>
</table>

**Testing**

- At 55%, 150 lbs/barrel of bentonite in water base drilling mud was added to 1% of surfactant package in KCl. After 15 minutes the cloud point was measured. The rate of cloud point formation was decreased to 15 minutes with 1% of surfactant package.

- 5% Surfactant:

- 10% Surfactant:

- 15% Surfactant:

- 20% Surfactant:

**Note:** Polyols are used as cloud point modifier when used in combination with SURFONIC® OFS 500 Shale Stabilization Agent. Dosage: 1% total surfactant package in KCl.

**Cloud Point of OFS 600 Shale Stabilizing Agent for Cloud Point Shale Control:**

- No inhibitor YP

- 1% Surfactant:

- 5% Surfactant:

- 10% Surfactant:

- 15% Surfactant:

**Note:** Surfactant was used as a stabilizing agent. Dosage: 1% total surfactant package in KCl.
**Huntsman Clay Control Chemicals**

By use of the proper concentration of SURFONIC® OFS 500 or SURFONIC® OFS 600 stabilization agent with a SURFONIC® L4 series solv and KCI, the cloud point of the clay control fluid can be adjusted to a particular downside environment. Amine compounds are often more effective when applied as ammonium salts.

### Chemical Mode of Action

- **Lubricant Applications**
  - **Amine/Quaternary Shale Inhibitors**
    - Agents and their acetate salts have been rigorously tested in accordance with published protocols.
    - Mud formulations for 16 hours at 90°C (194°F) in a rolling oven and screened through a 0.85 mm sieve.

### Dispersion Test (Hot Rolling)

- Shale pieces between 4.75 and 6.7 mm size were tumbled in water base drilling muds (3% inhibitor) until the muds became too thick to measure their viscosities. The results were calculated.
Huntsman Clay Control Chemicals

By use of the proper concentration of SURFONIC® OFS 500 or SURFONIC® OFS 500 stabilization agent with a SURFONIC® L4 series solvent, the cloud point of the clay control fluid can be adjusted to a particular downhole environment. Amine compounds are often more effective when applied as ammonium salts.

Amine/Quaternary Shale Inhibitors

Several laboratory methods of evaluating shale inhibitor efficiency are being used industry wide. Huntsman clay control agents and their acetic salts have been rigorously tested in accordance with published protocols.

Cloud Point Shale Inhibition

- Shale inhibitor performance booster
- Blocks H2O access to clay, cloud point inhibitor
- Partial or total KCl replacement
- Binds clay platelets
- Cloud point modifiers

Polyols Applications

- Additional benefits include lubrication of the drill stem and cleaning of the cuttings
- May be formulated with SURFONIC® L4-3 solvent as cloud point modifier when used in combination with SURFONIC® OFS 500 Shale Stabilization Agent. Dosage: 1% total surfactant package in KCl.

Different clays may produce different results.

Dynamic Linear Swelling: The OFITE Swellmeter measures clay swelling at wellbore conditions. Compressed pills of bentonite were submerged in a 5% KCl solution for 10 hours at 90°C (194°F) in a rolling oven and screened through a 0.85 mm sieve. Surviving Bentonite was washed and dried. Higher retained weights of shale indicate improved shale stabilization.

Key Points in Polyol Applications

- Partial replacement for KCl
- Highly insoluble in salt water. Should not plug a screen on surface water at temperatures below cloud point.
- Cuttings may be easily rinsed and recycled back into the mud.
- May be formulated with SURFONIC® L4-3 solvent to give a wide range of system cloud points to match both hot circulating temperatures.
- “On the fly” adjustments may easily be conducted in situ to give suitable clays on drilling conditions change.
- Additional benefits include lubrication of the drill stem and cleaning of the cuttings.

Adjustment of Cloud Point with SURFONIC® L4-3 Solvent

- Different clays may produce different results.
- Tested on Khvalynsky brown “chocolate” clay from Volgograd region in Russia, 3% shale inhibitor. Different clays may produce different results.
- Polyols and their acetate salts have been rigorously tested in accordance with published protocols.

Cloud Point Concentration on Cloud Point of KCl Solutions

- 1% Substituted
- 2% Substituted
- 5% Substituted

Adjustment of Cloud Point with SURFONIC® OFS 500 Solvent

- No inhibitor
- YP 20
- No inhibitor
- YP 10

Acidochlor PFF

- No inhibitor
- YP 50
- No inhibitor
- YP 10

Acidochlor PFF

- No inhibitor
- YP 50
- No inhibitor
- YP 10

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- Highly insoluble in salt water. Should not plug a screen on surface water at temperatures below cloud point.
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Shale is a type of sedimentary rock composed chiefly of silt and clay. There are many different types—bituminous shale, oil shale and gas shale—all of which are important sources of fossil hydrocarbons. Clay swelling in shale formations during drilling or well completion can have a tremendous adverse impact on oil and gas operations. Traditionally, preventing clay swelling in oilfield operations by aqueous means has been achieved using large concentrations of inorganic additives such as potassium chloride (KCL). However, effective clay control requires high concentrations, which can be difficult to apply. Flexible methods of clay control include both polymers and ammonium compounds. Polymers stabilize clays by reducing the rate of water penetration into the shale, while ammonium compounds inhibit swelling by chemical means. One effective way to isolate clays from water inflow involves the use of water soluble polymer compounds to achieve a cloud point under down-hole conditions. At temperatures above the cloud point, the precipitated polymer forms a barrier that not only protects the formation but also improves the rate of water penetration into the shale, while ammonium compounds inhibit swelling by chemical means.

Huntsman’s leadership position comes from its range of technologies, world-scale integrated manufacturing capabilities, and global distribution network.

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• Maleic Anhydride: The leading global producer and supplier into industries such as unsaturated polyester resins, food, oil additive and coatings
• Surfactants: Integrated producer of a wide range of products for home and personal care, coated agriculture, and process industries

Contact a Huntsman sales representative to discuss your oilfield requirements.

www.huntsman.com/Performance_products