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# Polymers for Temperature Independent Viscosity

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## Abstract

Traditional oil-based drilling muds containing organoclay viscosifiers demonstrate a temperature dependent rheology. As the temperature of the mud decreases the viscosity goes up, and as the temperature of the mud increases, viscosity goes down. This phenomenon is particularly evident in offshore drilling where the fluid can experience temperatures of 40°F in the riser and temperatures of over 300°F at the bottom of the borehole. The dramatic differences in viscosity in the riser and near the bottom of the hole can lead to pressures exceeding the fracture gradient of the formation and other fluid management issues. A study was conducted to determine the effectiveness of two new flat rheology polymer chemistries at minimizing the rheological differences across a broad temperature range. The polymers were added to an organoclay containing mud and the before and after rheological properties were measured at 40, 100 and 150°F.

Rheological testing on the mud containing only organoclay showed a 65% decrease in YP and a 67% decrease in the 6 rpm reading from 40 to 150°F. The mud containing organoclay in addition to the flat rheology polymer showed only a 12% decrease in YP and no change in the 6 rpm reading from 40 to 150°F. PV was similar for both muds. The addition of the flat rheology polymer greatly eliminated the rheological change across the temperature range. This flatter rheology profile is ideal for offshore drilling.

## Introduction

Drilling offshore presents challenges that are not encountered when drilling onshore. One of the biggest challenges is that the ocean temperature gradient and local geothermal gradient are both influential to the rheology of drilling fluids. As one goes deeper in the water column, temperatures decline. As one goes deeper in the ground, temperatures increase. Figure 1 illustrates this phenomenon. Conventional drilling fluids are temperature dependent, meaning that their rheology is influenced by the temperature experienced. The dramatic changes in temperature experienced when drilling offshore can cause controlling ECD and other fluid properties to become difficult or impossible. Drilling fluids which are temperature independent eliminate or drastically reduce fluid management issues.

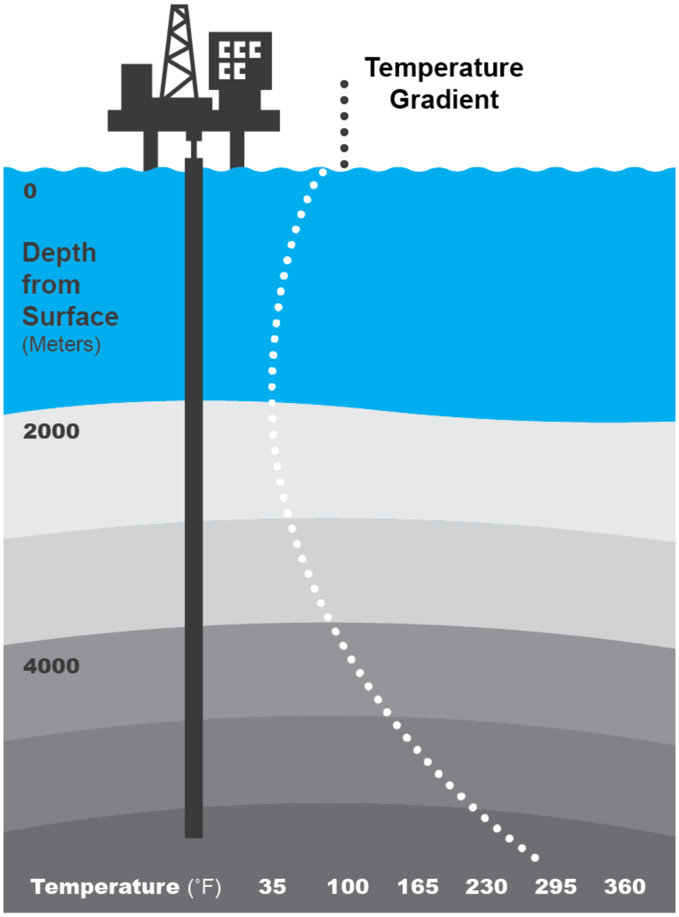


**Figure 1. Typical offshore temperature gradient.**

Conventional oil-based drilling muds containing organoclay viscosifiers demonstrate temperature dependent rheology. As the temperature of the mud decreases, the viscosity increases, and as the temperature of the mud increases, viscosity decreases. This phenomenon is particularly evident in offshore drilling, where the fluid can experience temperatures of 40°F in the riser and in excess of 300°F at the bottom of the hole. These differences in temperature cause differences in viscosity in conventional drilling fluids and can lead to exceeding the fracture gradient of the formation as well as other fluid management issues.

A study was conducted to determine the effectiveness of two new flat rheology polymer chemistries at minimizing the rheological differences in oil-based drilling fluids across a broad temperature range. The polymers were added to organoclay containing mud. Rheology was measured at 150°F and then hot rolled at temperatures up to 250°F. Selecting the best flat rheology polymer chemistry for a drilling fluid depends on the amount of organoclay present in the fluid and the temperature that the fluid will experience at the bottom of the hole.

## Polymer Chemistries

Two new polymer chemistries were developed to provide temperature independent rheology in OBM and were tested in the study.

The first polymer (Polymer 1) can be described as a solution of an alkyl-ammonium salt of a polycarboxylic acid. This chemistry was developed for drilling fluids which will not see BHT above 200°F and/or which have organoclay loadings below 2 lb/bbl.

The second polymer (Polymer 2) can be described as a solution of polyamine amides of unsaturated polycarboxylic acids. This chemistry was developed for drilling fluids which will see BHT above 200°F and/or which have higher loadings of organoclay.

Typical properties and solvent content of the two chemistries can be seen in Table 1.

**Table 1. Properties of Polymer 1 and Polymer 2.**

| | Density at 68°F | Flash Point | Solvents |
|---|---|---|---|
| Polymer 1 | 0.97 g/ml | 217.0°F | Propylene Glycol |
| Polymer 2 | 0.93 g/ml | 109.4°F | C10-11 Isoparaffin and Butylglycol |

## Test Formulations and Experimental Methods

To study the effects of Polymer 1 and Polymer 2, two test fluid systems were prepared using commercially available materials. Both systems used the same synthetic base fluid, oil-to-water ratio, brine phase salinity, and surfactant package. The mud weights ranged from 12.0 to 13.0 ppg with oil to water ratios of 75/25. The internal phase was a 25% weight to volume calcium chloride brine. The brine was emulsified with a commercially available combination emulsifier/wetting agent package. The organoclay content ranged from 1-3 lb/bbl. API grade barite was used for the weighting agent as this would be worst case scenario in terms of sag. Lastly, 20 lb/bbl simulated drill solids were included in the system on the premise that they would be present in almost every case in the field: recycled mud or fresh drilling cuttings.

Each mud was evaluated for rheology and emulsion stability following API 13B-2 procedures for oil-based drilling fluids. Rheology and emulsion stability values were measured using an OFITE 900 viscometer and OFITE Emulsion Tester Model 131-50. Formulation 1 and Formulation 2 show the components and mixing order. After low shear mixing, the fluids were homogenized at 6,000 rpm until the fluid reached 150° F to ensure stability. The rheological properties were measured at 150° F on a digital viscometer. The fluids were then transferred to heat aging cells, pressurized, and hot rolled overnight at 150 - 250° F depending on the test system.

**Formulation 1. 13.0 ppg 75/25 Synthetic Based Mud**

| | lb/bbl | Mix Time (min) |
|---|---|---|
| C16-C18 Internal Olefin | 148.6 | |
| Organoclay | 1 | 5 |
| Lime | 6 | 5 |
| Emulsifier | 15 | 5 |
| 25% $CaCl_2$ Brine | 83.7 | 10 |
| API Barite 4.1 | 270 | 5 |
| Simulated Drill Solids | 20 | 5 |
| Polymer 1 | 0 - 1.2 | 5 |
| *High sheer on Silverson overhead mixer at 6,000 rpm until 150°F* | | |

After removing the cells from the roller oven, they were allowed to cool to ambient temperatures before venting and opening the cells. The cells were mixed and rheology was measured at several temperatures from 100 to 150° F. The mud contents were returned to the aging cell and re-mixed for five minutes. Finally, sufficient volume was poured into the chiller unit to obtain the 40° F rheology. The result summary of the testing on Formulation 1 can be seen in Table 1. Full testing results can be viewed in Appendix 1.

**Table 1. Results for Formulation 1 After Hot Rolling for 16 Hours at 150°F.**

| Tests at 40°F | Organoclay Only | Organoclay and 1.2 lb/bbl Polymer 1 |
|---|---|---|
| YP | 29 | 16 |
| 6 rpm | 14 | 11 |
| 10 min gel | 14 | 17 |
| Electrical Stability | N.M. | N.M. |

| Tests at 100°F | Organoclay Only | Organoclay and 1.2 lb/bbl Polymer 1 |
|---|---|---|
| YP | 14 | 14 |
| 6 rpm | 8 | 11 |
| 10 min gel | 8 | 15 |
| Electrical Stability | N.M. | N.M. |

| Tests at 150°F | Organoclay Only | Organoclay and 1.2 lb/bbl Polymer 1 |
|---|---|---|
| YP | 12 | 15 |
| 6 rpm | 5 | 11 |
| 10 min gel | 5 | 18 |
| Electrical Stability | 412 | 864 |

Formulation 2 used a different flat rheology polymer that was designed to work with higher loadings of organophilic clays and at higher temperatures. In this round of testing, the amount of polymer was held constant at 0.6 lb/bbl while the organoclay content varied between 1 and 3 lb/bbl.

The muds were first hot-rolled overnight at 250° F. Then the mud were vertically static aged for 96 hours at 250° F. The muds were then re-homogenized for five minutes at 6,000 rpm on a Silverson mixer. The last step was to determine if the components degraded or the emulsion droplets increased in size during the static aging period. The result summary of the testing on Formulation 2 can be seen in Table 2. Full testing results can be viewed in Appendix 2.

**Formulation 2. 12.0 ppg 75/25 Synthetic Based Mud**

| | lb/bbl | Mix Time (min) |
|---|---|---|
| C16-C18 Internal Olefin | 148.6 | |
| Organoclay | 1-3 | 5 |
| Lime | 6 | 5 |
| Emulsifier | 15 | 5 |
| 25% $CaCl_2$ Brine | 83.7 | 10 |
| API Barite 4.1 | 190 | 5 |
| Simulated Drill Solids | 20 | 5 |
| Polymer 2 | 0.6 | 5 |
| *High sheer on Silverson overhead mixer at 6,000 rpm until 150°F* | | |

**Table 2. Results for Formulation 2 after Static Aging for 4 Days at 250°F.**

| Tests at 40°F | 1 lb/bbl Organoclay and 0.6 lb/bbl of Polymer 2 | 2 lb/bbl Organoclay and 0.6 lb/bbl of Polymer 2 | 3 lb/bbl Organoclay and 0.6 lb/bbl of Polymer 2 |
|---|---|---|---|
| YP | 9 | 11 | 17 |
| 6 rpm | 4.9 | 6.0 | 9.1 |
| 10 min gel | 5 | 7 | 11 |
| Electrical Stability | N.M. | N.M. | N.M. |

| Tests at 120°F | 1 lb/bbl Organoclay and 0.6 lb/bbl of Polymer 2 | 2 lb/bbl Organoclay and 0.6 lb/bbl of Polymer 2 | 3 lb/bbl Organoclay and 0.6 lb/bbl of Polymer 2 |
|---|---|---|---|
| YP | 5 | 8 | 13 |
| 6 rpm | 3.2 | 5.4 | 9.1 |
| 10 min gel | 5 | 6 | 10 |
| Electrical Stability | 175 | 279 | 407 |

## Conclusions

Offshore drilling conditions create difficulties in managing drilling fluid properties, especially with respect to rheology. Combinations of temperature independent polymers and organoclays can be used to create viscosity profiles which vary little across the expected operating temperature range. The choice of polymer depends on the amount of organoclay required in the system as well as the maximum expected exposure temperature of the drilling fluid. Polymer 1 works very well in systems where less than 2.0 lb/bbl of organoclay is used and where maximum temperatures will not exceed 200°F. Polymer 2 showed better performance in fluids that contained higher levels of organoclay necessary for reducing barite sag and in fluids that will experience temperatures greater than 200°F.

Both of these flat rheology polymers include an oil wetting component which often generates higher ES values. Moreover, as flat rheology systems tend to employ high loading levels of emulsifiers, it is worth comparing the aged systems before and after re-shearing. As seen in this study, the components are still functional.

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## Nomenclature

| | |
|---|---|
| *Organoclay* | *=quaternary ammonium compound treated clay* |
| *°F* | *=Degrees Fahrenheit* |
| *YP* | *=Yield Point* |
| *PV* | *=Plastic Viscosity* |
| *ppg* | *=pounds per gallon* |
| *lb/bbl* | *=pounds per barrel* |
| *75/25* | *=volume ratio of 75% base fluid and 25% brine* |
| *N.M.* | *=Not Measured* |
| *OBM* | *=Oil-base Mud* |

## References


1. Lee, J., Friedheim, J., Van Oort, E.: "A New Approach to Deepwater Drilling Using SBM with Flat Rheology." ADE-04-DF-HO-37. AADE - 1st industry paper on flat rheology with organoclays
2. van Oort, E., J. Lee, J. Friedheim and B. Toups; "New constant-rheology Synthetic-based Mud for Improved Deepwater Drilling", SPE 90987, SPE Annual Technical Conference and Exhibition, Houston, Texas, Sep. 26-29, 2004
3. Cameron, C.: "Deepwater Drilling Fluids – What's New?", AADE-05-NTCE-79, AADE 2005 National Technical Conference and Exhibition, Houston, Texas, April 5-7, 2005. Discusses "clay free" muds as one method to improve flat rheology
4. Mullen G., Tanche-Larsen, P., Clark, D., Giles, A.: " The Pro's and Con's of Flat Rheology Drilling Fluids." AADE-05-NTCE-28, AADE Drilling Fluids Conference, Houston, Texas, April 5-7, 2005. States that Organoclays tend to give better barite sag performance over polymers
5. Lu S., Perez J, Brignac C., Roy, S, Lattanzi S.: "The Missing Pressure Factor in Deepwater SBM." AADE-17-NTCE-058, AADE Drilling Fluids Conference, Houston, Texas, April 4-5, 2017.


## Appendix 1. Full Test Results for Formulation 1.

| | Base Mud | | | 1.2 lb/bbl Polymer 1 | | |
|---|---|---|---|---|---|---|
| **Test Temp. (°F)** | 40° | 100° | 150° | 40° | 100° | 150° |
| **Before Hot Rolling** | | | | | | |
| **600 rpm** | 200 | 83 | 55 | 179 | 91 | 65 |
| **300 rpm** | 120 | 49 | 34 | 102 | 58 | 44 |
| **200 rpm** | 91 | 38 | 26 | 76 | 46 | 36 |
| **100 rpm** | 60 | 27 | 18 | 49 | 33 | 27 |
| **6 rpm** | 18 | 10 | 6 | 15 | 16 | 15 |
| **3 rpm** | 15 | 8 | 5 | 13 | 15 | 14 |
| **PV** | 80 | 34 | 21 | 77 | 33 | 21 |
| **YP** | 39 | 15 | 14 | 25 | 24 | 22 |
| **10 sec gel** | 15 | 8 | 5 | 14 | 10 | 14 |
| **10 min gel** | 16 | 9 | 5 | 19 | 16 | 18 |
| **ES** | – | – | 572 | – | – | 742 |
| **After Hot Rolling 150° F** | | | | | | |
| **600 rpm** | 185 | 89 | 53 | 195 | 89 | 63 |
| **300 rpm** | 107 | 51 | 32 | 106 | 52 | 39 |
| **200 rpm** | 80 | 39 | 24 | 75 | 40 | 31 |
| **100 rpm** | 51 | 26 | 16 | 45 | 27 | 22 |
| **6 rpm** | 14 | 8 | 5 | 11 | 11 | 11 |
| **3 rpm** | 11 | 7 | 4 | 10 | 10 | 10 |
| **PV** | 78 | 38 | 21 | 90 | 38 | 24 |
| **YP** | 29 | 14 | 12 | 16 | 14 | 15 |
| **10 sec gel** | 11 | 7 | 4 | 11 | 9 | 11 |
| **10 min gel** | 14 | 8 | 5 | 17 | 15 | 18 |
| **ES** | – | – | 412 | – | 779 | 864 |
| **After Hot Rolling 250° F** | | | | | | |
| **600 rpm** | 168 | 75 | 50 | 176 | 81 | 56 |
| **300 rpm** | 92 | 42 | 29 | 95 | 46 | 33 |
| **200 rpm** | 66 | 31 | 21 | 68 | 35 | 25 |
| **100 rpm** | 40 | 20 | 14 | 40 | 23 | 17 |
| **6 rpm** | 9 | 6 | 4 | 10 | 8 | 7 |
| **3 rpm** | 7 | 5 | 3 | 8 | 7 | 6 |
| **PV** | 76 | 33 | 21 | 81 | 35 | 23 |
| **YP** | 17 | 8 | 9 | 15 | 12 | 10 |
| **10 sec gel** | 7 | 5 | 3 | 9 | 7 | 6 |
| **10 min gel** | 7 | 5 | 3 | 11 | 10 | 9 |
| **ES** | – | 385 | 219 | – | 530 | 595 |

## Appendix 2. Full Test Results for Formulation 2.

| **Organoclay** | **1 lb/bbl** | | **2 lb/bbl** | | **3 lb/bbl** | |
|---|---|---|---|---|---|---|
| **Polymer 2** | **0.6 lb/bbl** | | **0.6 lb/bbl** | | **0.6 lb/bbl** | |
| **Test Temp. (°F)** | 40° | 120° | 40° | 120° | 40° | 120° |
| **Before Hot Rolling** | | | | | | |
| **600 rpm** | 132 | 66 | 144 | 73 | 167 | 82 |
| **300 rpm** | 74 | 41 | 82 | 47 | 96 | 54 |
| **200 rpm** | 55 | 33 | 61 | 38 | 71 | 44 |
| **100 rpm** | 34 | 23 | 39 | 27 | 46 | 32 |
| **6 rpm** | 9.0 | 10.1 | 11.2 | 12.4 | 13.7 | 16.5 |
| **3 rpm** | 8 | 9 | 9 | 11 | 12 | 15 |
| **PV** | 57 | 24 | 62 | 26 | 71 | 28 |
| **YP** | 17 | 17 | 21 | 21 | 25 | 26 |
| **10 sec gel** | 8 | 9 | 9 | 11 | 12 | 15 |
| **10 min gel** | 9 | 9 | 12 | 13 | 15 | 17 |
| **ES** | – | 519 | – | 616 | – | 756 |
| **Muds static aged at 250°F for 4 days** | | | | | | |
| **600 rpm** | 122 | 48 | 142 | 56 | 158 | 65 |
| **300 rpm** | 66 | 27 | 77 | 32 | 88 | 39 |
| **200 rpm** | 47 | 20 | 54 | 25 | 63 | 30 |
| **100 rpm** | 27 | 13 | 31 | 16 | 38 | 21 |
| **6 rpm** | 4.9 | 3.2 | 6.0 | 5.4 | 9.1 | 9.1 |
| **3 rpm** | 4 | 3 | 5 | 5 | 8 | 9 |
| **PV** | 56 | 22 | 65 | 24 | 71 | 26 |
| **YP** | 9 | 5 | 11 | 8 | 17 | 13 |
| **10 sec gel** | 4 | 3 | 5 | 5 | 8 | 7 |
| **10 min gel** | 5 | 5 | 7 | 6 | 11 | 10 |
| **ES** | – | 175 | – | 279 | – | 407 |
| **Silversoned at 6,000 rpm for 5 minutes** | | | | | | |
| **600 rpm** | 124 | 56 | 137 | 63 | 151 | 70 |
| **300 rpm** | 72 | 36 | 79 | 40 | 88 | 45 |
| **200 rpm** | 53 | 28 | 60 | 32 | 67 | 36 |
| **100 rpm** | 34 | 20 | 39 | 23 | 43 | 27 |
| **6 rpm** | 9.6 | 8.1 | 12.6 | 10.1 | 15 | 12.3 |
| **3 rpm** | 8 | 8 | 11 | 9 | 14 | 12 |
| **PV** | 52 | 21 | 58 | 23 | 63 | 25 |
| **YP** | 20 | 15 | 22 | 18 | 25 | 20 |
| **10 sec gel** | 9 | 8 | 12 | 9 | 14 | 12 |
| **10 min gel** | 12 | 9 | 15 | 11 | 18 | 14 |
| **ES** | – | 471 | – | 558 | – | 667 |