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# Enhanced Fluid Viscosity Using Novel Surfactant Chemistry Purposely Designed for Low-Aromatic Mineral and Synthetic Base Fluids

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## Abstract

Increased regulation and stakeholder concern has provided the impetus for an increase in the use of environmentally friendly additives for hydrocarbon extraction. One of the biggest challenges in replacing established chemistries with greener solutions is to ensure that effectiveness and performance are not sacrificed when evaluating the environmental footprint of the material under consideration.

The trend towards more environmentally responsible drilling fluids has profoundly influenced the design of both aqueous and non-aqueous drilling fluids. The development of non-aqueous drilling fluids (NADF's) has evolved significantly within the last several decades with the introduction of low and non-aromatic base fluids, and particularly so with the introduction of synthetic base fluids in the early 1990's[1]. Chief among the challenges in using low or non-aromatic base oils is the ability to efficiently exfoliate organophilic clay and generate viscosity, particularly low shear-rate viscosity. Among the materials previously used to effectively build viscosity in non-aqueous organoclay-based systems are ethanol and methanol. These two materials have health, safety and environmental concerns related to their flash point and toxicity, respectively. Much of the literature involving benign polar activators uses a "one size fits all" approach, with propylene carbonate and water being the most recommended materials. Additionally, polymeric viscosifiers are sometimes added to compliment or completely substitute the viscosity generated by organophilic clay in non-aqueous drilling fluids[2].

This work details the selection of novel nonionic surfactants for efficient organophilic clay viscosity generation in synthetic base fluids. These specialized surfactants function in place of traditional organoclay polar activators in aliphatic base oils. Furthermore, the nonionic surfactant packages can be customized to function exceptionally well in different synthetic base fluids such as esters and olefins, although this work focuses on synthetic fluids based on natural gas feedstock using Fischer-Tropsch technology.

## Introduction

The ability to provide adequate suspension capacity in specialized polymer slurry concentrates and in increasingly difficult drilling conditions is critical. An adequate viscosity profile is especially important during the makeup of non-aqueous drilling fluids and in slurry concentrates that precludes the use of water or environmentally detrimental products in the formulation. The structure and make-up of the base fluid, such as branching and carbon chain length, will have a strong influence on the degree of organoclay exfoliation and consequently the ability to build good fluid viscosity. As an example, propylene carbonate functions quite well in linear paraffins, but is not able to provide equal functionality in highly branched and naphthenic base oils. The differences in rheological and fluid loss properties in simple comparisons between different base fluids in identical formulations have been previously demonstrated[3]. Specific nonionic surfactants can be used to increase the rate of organoclay exfoliation in cases where traditional polar activators and other viscosifiers fall short.

Several nonionic surfactants have been evaluated for their ability to firstly, increase the exfoliation rate of organoclay and secondly, for their performance along with the components making up a non-aqueous drilling fluid. Ideally, the model surfactant is able to help viscosify the base oil with organoclay as the primary viscosifier and also enhance the properties of the drilling fluid. Prior research has shown that the composition of the base oil has a significant impact on the base oil properties of kinematic viscosity and pour point among others. These inherent properties, in turn, influence the rheological profile and properties of a given non-aqueous drilling fluid. In this paper, we have focused our attention on synthetic Fischer-Tropsch-based paraffin drilling fluids.

## Nonionic Surfactants

Nonionic surfactants can generally be described as having an uncharged hydrophilic head and a hydrophobic tail (Figure 1). Fatty alcohol ethoxylates are composed of an alcohol hydrophobe reacted with varying moles of ethylene oxide. The choice of alcohol hydrophobe as well as the degree of ethoxylation has significant consequences on the performance of the nonionic surfactant. The alcohol hydrophobe may be derived from a variety of sources including oleochemical and synthetic feedtsocks. The hydrophobe can vary in chain length from C4 to C20+. Depending on the source of the alcohol hydrophobe, it can be linear, semi-branched or completely branched and have many different isomers[4]. The degree of branching will dictate a certain molecular structure that influences the performance of the alcohol ethoxylate

(Figures 2-4 are representative structures out of many isomer possibilities).

Nonionic surfactants are naturally good choices for this application due to their general tendency not to negatively interact with other elements of the drilling fluid such as the primary emulsifier and wetting agents. Additionally, these types of surfactants have previously been shown to have hard water stability and maintain effectiveness across a wide range of alkalinities and salinities[4].

## Synthetic Paraffin

Offshore disposal regulations are administered by many regulatory agencies around the world including the US EPA and OSPAR. These regulatory bodies, among others, have set the definitions assigned to the different base oils used in NADF's. The two main categories of drilling fluids can be described as petroleum derived fluids and synthetic fluids. Mineral oils and enhanced mineral oils are petroleum derived fluids and have improved health, safety and environmental profiles compared to diesel, thanks in part, through their severe hydrotreatment and adjustment of flash point and other properties. Synthetic fluids are recognized as being a manufactured fluid oligomerized from chemical feedstocks[5]. Among the most popular synthetic fluids are esters, internal olefins and paraffins derived from Fischer-Tropsch synthesis. The synthetic fluid used for this study is a Fischer-Tropsch derived paraffin.

## Methods and Materials

Five different alcohol ethoxylate surfactants were tested in first, an all oil screening formulation. The three best performing surfactants from the all oil screening work were then tested in a 12.0 ppg and 16.0 ppg NADF. A general description of the surfactants used in this study can be found in Table 1.

### *Screening in All Oil System*

Several nonionic surfactants were screened in all oil system at a 1.1% concentration by volume in FT based paraffin using a wet-processed organophilic clay (Table 2). Previous screening in mineral oil-based linear paraffin determined that the optimal hydrophilic-lipophilic balance (HLB[6]) value of the nonionic surfactants in generating viscosity and fluid stability is between 12.5 and 13.4.

1. The fluids were sheared for 1 minute at low setting on the Ultra TURRAX T25 basic disperser.
2. The fluid viscosity was conducted immediately after mixing at room temperature on the GRACE M3600 Viscometer.

The surfactants contributing most to the efficient exfoliation of the organoclay as determined by viscosity profile (Figure 5) were then chosen as additives in the 12.0 ppg and 16.0 ppg NADF's.

### *Surfactant Testing in NADF*

Table 3 lists the formulation for a 12.0 ppg 70/30 Oil Water Ratio (OWR) NADF. Table 4 lists the formulation for a 16.0 ppg 80/20 OWR NADF.

1. The NADF was mixed on OFITE 2 speed laboratory mixers at moderate to high shear.
2. The fluid was then sheared for 5 minutes on a Silverson L4RT at 6,000 rpm.
3. The fluid was immediately transferred to a heating cup and tested on the GRACE M3600 Viscometer at 150°F.
4. After completing the rheology readings, 30 ppb of Rev Dust was added to the fluid and mixed for 1 minute on the OFITE laboratory mixer.
5. The fluids were dynamically aged in pressurized stainless steel ageing cells at 300°F for 16 hours.
6. After ageing and cooling, the fluids were re-homogenized for 1 minute and retested for rheology on the GRACE M3600 Viscometer.

### *Barite Sag Testing*

Increasingly long laterals in extended reach drilling (ERD) have sharpened the focus on the importance of proper fluid rheology within the last decade. A property of drilling fluids receiving scrutiny is the fluid's ability to maintain cuttings and other solids, including the weighting agents, in suspension. This has also evolved with the understanding that dynamic sag as opposed to static sag has the greater propensity to generate significant differences in fluid density[7]. To that end, the dynamically aged fluid was tested for Sag Factor (SF) as follows:

1. 250 mL of the NADF was added to a graduated cylinder and aged at room temperature at a 45° angle on a G10 Gyrotory Shaker by New Brunswick Scientific at 15 rpm for 16 hours (figure 6).
2. The Barite Sag Factor (SF) was calculated in equation 1 below by comparing the density of the bottom of the fluid to the density of the top of the fluid where a value greater than 0.52 indicates a greater potential for the fluid to sag[8].

**Equation 1**

Sag Factor = density of the bottom / (density of the top + density of the bottom)

## Results and Discussion

The research completed with regards to best-fit rheological models is exhaustive. Historically, the most often used model is the Bingham Plastic model where plastic viscosity (PV) and yield point (YP) are generated from the 600 and 300 rpm dial readings on the FANN®35A viscometer.

### *Plastic Viscosity*

The value of PV, in centipoise (cP), represents the viscosity of the fluid extrapolated to infinite shear rate (equation 2). Plastic viscosity can be generally described as the resistance to flow caused by mechanical friction. For this reason, low PV values may translate to greater fluid energy at the bit and also greater flow in the annulus for hole cleaning. It is increasingly important to minimize PV in light of longer and smaller diameter tubulars in extended reach drilling and coiled tubing.

The general upper limitation of the PV has previously been mentioned as being twice the mud weight in lbs per gallon.

**Equation 2**

Plastic Viscosity (PV) = 600 rpm dial reading – 300 rpm dial reading

The initial plastic viscosity of the 12.0 ppg NADF blank mud increased slightly with the addition of a commercially available polymeric viscosifier, typically used to aid in viscosity generation in non-aromatic base fluids from 34 cP to 38 cP. The addition of the nonionic surfactants all reduced the PV, with the short chain linear surfactant having the greatest effect, reducing the value to 22 cP. The addition of simulated drill solids (Rev Dust) at 30 ppb before dynamically aging the fluid at 300°F caused an increase in the PV as expected. The samples formulated with the nonionic surfactants had PV values lower than the blank and polymeric viscosifier samples. The lowest value was again seen in the short chain linear hydrophobe-based surfactant. Although the SCL and MCL surfactants had similar profiles, the mid chain branched surfactant had significantly higher values that approached the values seen in the blank formulation. At the higher density fluid, the difference (increase) in plastic viscosity was not significant going from 12.0 ppg to 16.0 ppg. The addition of 30 ppb of Rev Dust and dynamic ageing caused significant increases in the blank and polymeric viscosifier formulations as seen in figures 9 and 10.

The theorized explanation of organoclay exfoliation in this case involves the use of nonionic surfactant to overcome the Van der Waals forces keeping the clay platelet edges stuck together. Coupled with high shear, the solvent or base oil is then able to solvate the quaternary amine used to make the clay organophilic and exfoliate the platelets creating viscosity. Excess use of surfactant has the potential to also disrupt the clay edge to clay edge interactions and affect the viscosity profile. The nonionic surfactant also appears to mitigate the friction caused by the increase in particles, especially in the high density fluid.

### *Yield Point*

The yield point (YP) is another parameter of the Bingham Plastic rheological model. The value of YP, in lb/100ft², represents the shear stress at a shear rate of zero. This translates to the shear stress required to move the fluid (also described as the yield stress). The YP has previously been used as an indicator of the ability of a mud to lift cuttings out of the annulus. An optimum YP value has been described as being between 10-25[9].

**Equation 3**

Yield Point (YP) = 300 rpm dial reading – plastic viscosity

The yield point after ageing showed increased stability in the fluids formulated with the nonionic surfactants, except the fluid formulated with the mid chain branched surfactant which had a significantly higher yield point. The shape and size of the hydrophobe, represented in figure 3, may have contributed to the material behaving in a more lipophilic fashion than indicated by its calculated value. The effect was not observed in the higher density fluid, possibly due to the decreased water (brine) phase content.

### *Low Shear Yield Point*

One of the short comings of the Bingham Plastic rheological model is that it uses high shear values (600 and 300 rpm dial readings) to extrapolate a low shear rate value (YP) resulting in higher than realistic values. The Herschel-Bulkley rheological model provides a better model to determine yield stress. The low shear plastic viscosity is calculated using equation 4 below. These values may be significantly lower than the values calculated using equation 3. The LSYP is often used as an indicator for sag potential and also as an indicator of the force required to get a drilling fluid to flow. Ideally, the LSYP value is the minimum value required to maintain cuttings and weighting material in suspension where an optimum value lies between 5 and 15[2].

**Equation 4**

Low-Shear Yield Point (LSYP) = (2 X 3rpm dial reading) – 6rpm dial reading

It is interesting to note that although the actual values between the parameters of YP and LSYP differ significantly, the trends seen in each parameter were nearly identical. The LSYP of several aged samples was compared to the sag factor of those samples to determine if indeed the higher LSYP produced lower sag factors. In this testing the LSYP values did not differ significantly, but a general trend was observed that lower LSYP values resulted in higher sag factor values.

## Conclusions

- The use of specific nonionic surfactants with an HLB between 12.5 and 13.4 allow for the efficient exfoliation of organoclay in synthetic paraffin.
- Short and mid chain linear hydrophobe-based surfactants are able to decrease the plastic viscosity of NADF's at different densities and maintain the improvement after ageing at high temperature (300°F) and contamination with simulated drill solids.
- The branching in mid chain branched hydrophobe-based surfactants results in a more compact hydrophobe structure that may contribute to higher "performance" HLB than what is calculated by molecular weight and moles of ethoxylation.
- Both the short and mid chain linear hydrophobe-based surfactants demonstrated stable rheological profiles after ageing.
- The NADF's formulated with the short and mid chain linear hydrophobe-based surfactants demonstrated lower LSYP values than the blank formulation as well as the formulation with an added viscosity material but did not demonstrate high SF values.

## Acknowledgments

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this work.

## Nomenclature

*NADF* =*Non-Aqueous Drilling Fluid*
*US EPA* =*United States Environmental Protection Agency*
*OSPAR* =*Oslo/Paris Convention for the Protection of the Marine Environment of the North-East Atlantic*
*HLB* =*Hydrophilic Lipophilic Balance*
*ERD* = *Extended Reach Drilling*
*PV* = *Plastic Viscosity*
*YP* =*Yield Point ( lb/100ft²)*
*LSYP* =*Low Shear Yield Point ( lb/100ft²)*
*SCL* = *Short Chain Linear Surfactant*
*MCL* =*Mid Chain Linear Surfactant*
*MCB* =*Mid Chain Branched Surfactant*
*MCFB* =*Mid Chain Fully Branched Surfactant*
*OWR* =*Oil Water Ratio*
*HR* = *Hot Rolled*
*cP* =*centipoise*

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## Tables

**Table 1 – Nonionic Surfactants Tested**

| Hydrophobe | Hydrophobe Carbon Chain Length | HLB |
|---|---|---|
| Short Chain Linear (SCL)* | <10 | 12.7 |
| Mid Chain Linear (MCL)* | 10-15 | 13.4 |
| Mid Chain Branched (MCB)* | 10-15 | 13.4 |
| Mid Chain Fully Branched-1 | 10-15 | 12.5 |
| Mid Chain Fully Branched-2 | 10-15 | 13.2 |

**Table 2 – Surfactant Screening Formulation**

| Basic surfactant screening formulation | | |
|---|---|---|
| 100 | mL | Synthetic Paraffin |
| 3.0 | grams | organophilic clay |
| 1.1 | mL | nonionic surfactant |

**Table 3 – 12.0 ppg 70/30 OWR NADF**

| Additives | Units | Blank | Polymeric Viscosifier | SCL Surfactant | MCL Surfactant | MCB Surfactant |
|---|---|---|---|---|---|---|
| **Synthetic Paraffin** | bbl | 0.557 | 0.557 | 0.557 | 0.557 | 0.557 |
| **Organophilic Clay** | ppb | 5 | 5 | 5 | 5 | 5 |
| **Polymeric Viscosifier or Surfactant** | ppb | 0 | 1.1 | 1.1 | 1.1 | 1.1 |
| **Lime** | ppb | 6 | 6 | 6 | 6 | 6 |
| **1° emulsifier** | ppb | 8 | 8 | 8 | 8 | 8 |
| **Wetting agent** | ppb | 1 | 1 | 1 | 1 | 1 |
| **25% $CaCl_2$ brine** | bbl | 0.254 | 0.254 | 0.254 | 0.254 | 0.254 |
| **Barite** | ppb | 218 | 218 | 218 | 218 | 218 |
| **Rev Dust*** | ppb | 30 | 30 | 30 | 30 | 30 |

*Rev Dust added after initial rheology readings, but before dynamic ageing.

**Table 4 – 16.0 ppg 80/20 OWR NADF**

| Additives | Units | Blank | Polymeric Viscosifier | SCL Surfactant | MCL Surfactant | MCB Surfactant |
|---|---|---|---|---|---|---|
| **Synthetic Paraffin** | bbl | 0.517 | 0.517 | 0.517 | 0.517 | 0.517 |
| **Organophilic Clay** | ppb | 3 | 3 | 3 | 3 | 3 |
| **Polymeric Viscosifier or Surfactant** | ppb | 0 | 1.1 | 1.1 | 1.1 | 1.1 |
| **Lime** | ppb | 4 | 4 | 4 | 4 | 4 |
| **1° emulsifier** | ppb | 8 | 8 | 8 | 8 | 8 |
| **Wetting agent** | ppb | 1 | 1 | 1 | 1 | 1 |
| **25% $CaCl_2$ brine** | bbl | 0.143 | 0.143 | 0.143 | 0.143 | 0.143 |
| **Barite** | ppb | 447 | 447 | 447 | 447 | 447 |
| **Rev Dust*** | ppb | 30 | 30 | 30 | 30 | 30 |

*Rev Dust added after initial rheology readings, but before dynamic ageing.

**Table 5 – 12.0 ppg 70/30 OWR NADF Rheology Sweep at 150°F**

| 12.0 ppg NADF Initial Dial Reading @ 150°F | | | | | | |
|---|---|---|---|---|---|---|
| **Shear Rate** | **Speed** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** |
| **(1/S)** | **(Rpm)** | **Blank** | **Polymeric Viscosifier** | **SCL Surfactant** | **MCL Surfactant** | **MCB Surfactant** |
| **1021.38** | **600** | 94 | 125 | 64 | 65 | 66 |
| **510.69** | **300** | 60 | 87 | 42 | 40 | 40 |
| **340.46** | **200** | 48 | 72 | 31 | 29 | 28 |
| **170.23** | **100** | 34 | 56 | 20 | 18 | 18 |
| **102.14** | **60** | 27 | 47 | 16 | 14 | 13 |
| **51.07** | **30** | 22 | 39 | 12 | 10 | 10 |
| **10.21** | **6** | 13 | 27 | 7 | 5 | 6 |
| **5.11** | **3** | 12 | 25 | 7 | 5 | 5 |
| **10 sec gel** | | 12 | 23 | 7 | 5 | 5 |
| **10 min gel** | | 13 | 24 | 9 | 7 | 7 |

**Table 6 – 12.0 ppg 70/30 OWR NADF Dynamically Aged, Rheology Sweep at 150°F**

| 12.0 ppg NADF Dynamically Aged Dial Reading @ 150°F | | | | | | |
|---|---|---|---|---|---|---|
| **Shear Rate** | **Speed** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** |
| **(1/S)** | **(Rpm)** | **Blank** | **Polymeric Viscosifier** | **SCL Surfactant** | **MCL Surfactant** | **MCB Surfactant** |
| **1021.38** | **600** | 109 | 146 | 69 | 67 | 138 |
| **510.69** | **300** | 62 | 87 | 42 | 40 | 95 |
| **340.46** | **200** | 46 | 67 | 30 | 30 | 76 |
| **170.23** | **100** | 30 | 44 | 19 | 20 | 53 |
| **102.14** | **60** | 22 | 33 | 14 | 16 | 41 |
| **51.07** | **30** | 15 | 23 | 12 | 12 | 30 |
| **10.21** | **6** | 8 | 13 | 6 | 7 | 15 |
| **5.11** | **3** | 8 | 13 | 6 | 6 | 13 |
| **10 sec gel** | | 8 | 15 | 7 | 7 | 15 |
| **10 min gel** | | 9 | 28 | 8 | 7 | 15 |

**Table 7 – 16.0 ppg 80/20 OWR NADF Rheology Sweep at 150°F**

| 16.0 ppg NADF Initial Dial Reading @ 150°F | | | | | | |
|---|---|---|---|---|---|---|
| **Shear Rate** | **Speed** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** |
| **(1/S)** | **(Rpm)** | **Blank** | **Polymeric Viscosifier** | **SCL Surfactant** | **MCL Surfactant** | **MCB Surfactant** |
| **1021.38** | **600** | 90 | 136 | 68 | 65 | 65 |
| **510.69** | **300** | 53 | 92 | 39 | 35 | 36 |
| **340.46** | **200** | 40 | 76 | 29 | 26 | 25 |
| **170.23** | **100** | 26 | 57 | 18 | 16 | 15 |
| **102.14** | **60** | 20 | 48 | 14 | 13 | 12 |
| **51.07** | **30** | 15 | 40 | 10 | 9 | 8 |
| **10.21** | **6** | 9 | 27 | 5 | 4 | 4 |
| **5.11** | **3** | 11 | 26 | 5 | 4 | 4 |
| **10 sec gel** | | 8 | 25 | 9 | 4 | 4 |
| **10 min gel** | | 9 | 26 | 7 | 5 | 6 |

**Table 8 – 16.0 ppg 80/20 OWR NADF Dynamically Aged, Rheology Sweep at 150°F**

| 16.0 ppg NADF Dynamically Aged Dial Reading @ 150°F | | | | | | |
|---|---|---|---|---|---|---|
| **Shear Rate** | **Speed** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** | **Dial Reading (deg)** |
| **(1/S)** | **(Rpm)** | **Blank** | **Polymeric Viscosifier** | **SCL Surfactant** | **MCL Surfactant** | **MCB Surfactant** |
| **1021.38** | **600** | 161 | 287 | 109 | 92 | 88 |
| **510.69** | **300** | 89 | 194 | 61 | 50 | 49 |
| **340.46** | **200** | 64 | 147 | 44 | 36 | 36 |
| **170.23** | **100** | 39 | 95 | 27 | 22 | 23 |
| **102.14** | **60** | 28 | 71 | 19 | 17 | 17 |
| **51.07** | **30** | 19 | 48 | 14 | 12 | 12 |
| **10.21** | **6** | 9 | 22 | 7 | 6 | 6 |
| **5.11** | **3** | 9 | 21 | 7 | 5 | 6 |
| **10 sec gel** | | 8 | 22 | 7 | 5 | 6 |
| **10 min gel** | | 10 | 25 | 7 | NA | 6 |

## Figures

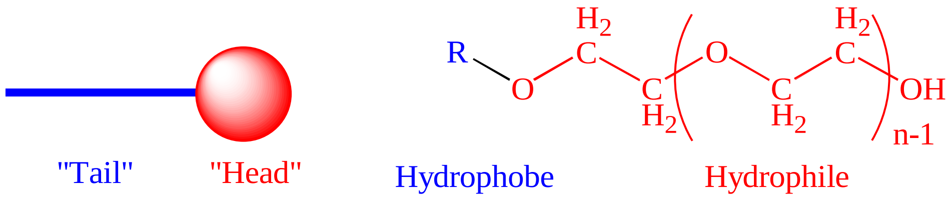
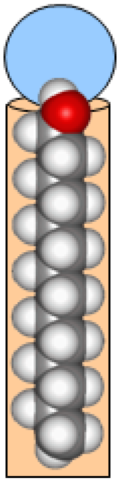
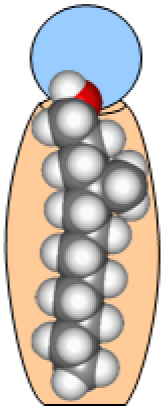


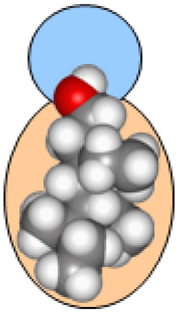
**Figure 1 – general alcohol ethoxylate structure**



Linear C14
1-tetradecanol
**Figure 2**



Semi-branched C13
4- methyl-1-dodecanol
**Figure 3**



Branched C13
6-methyl-3,5-diethyl-1-octonal
**Figure 4**

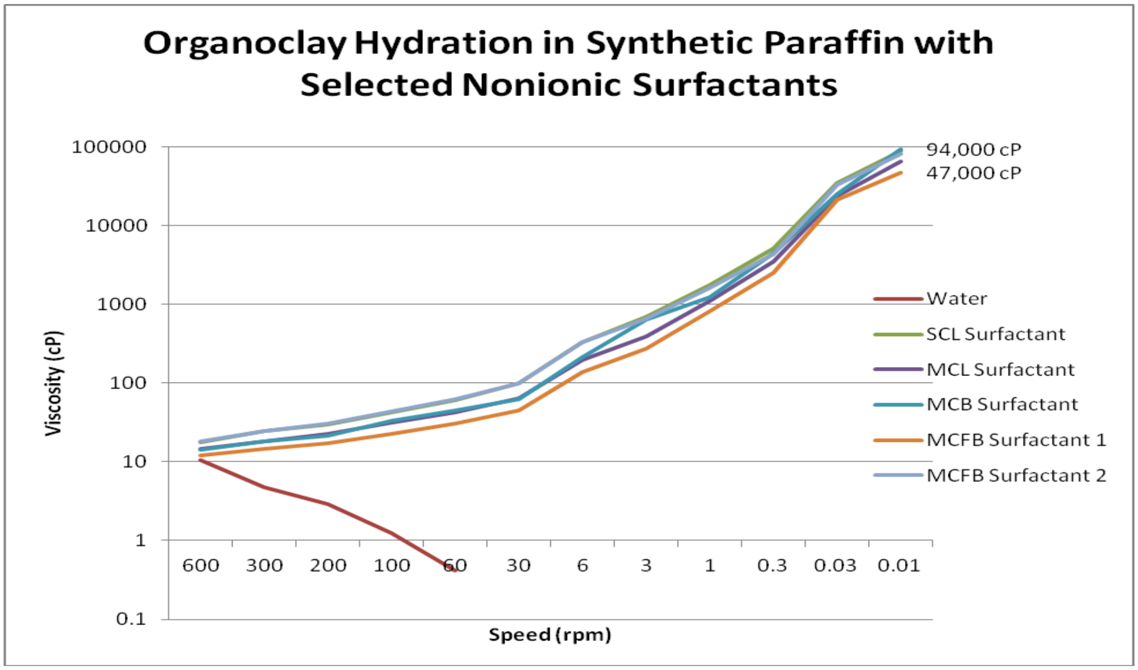


**Figure 5 – Viscsoity of organoclay mixed with different surfactants.**

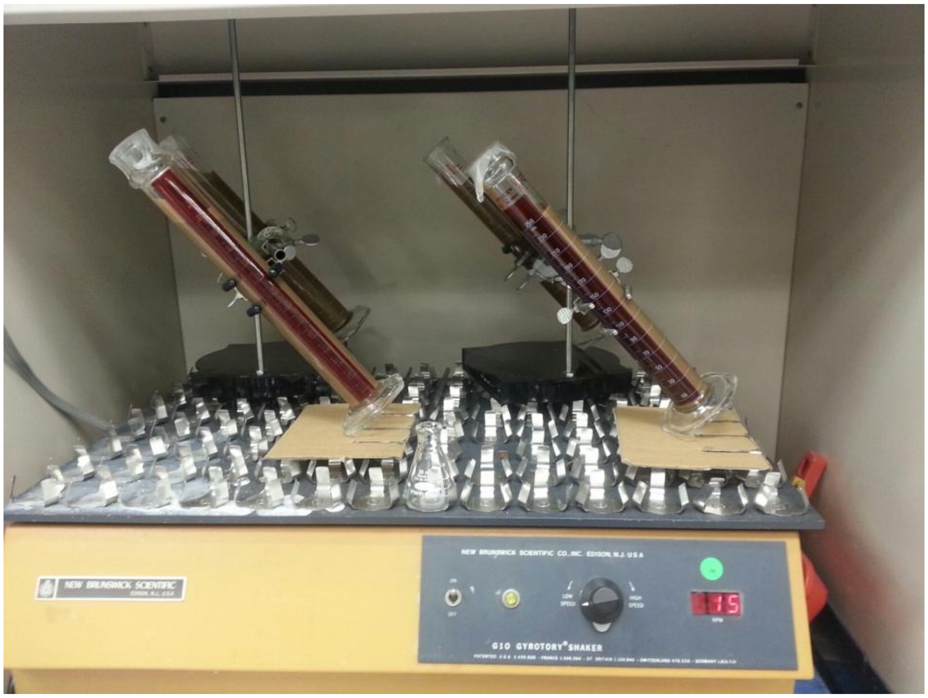


**Figure 6 – Barite Sag testing of NADF.**

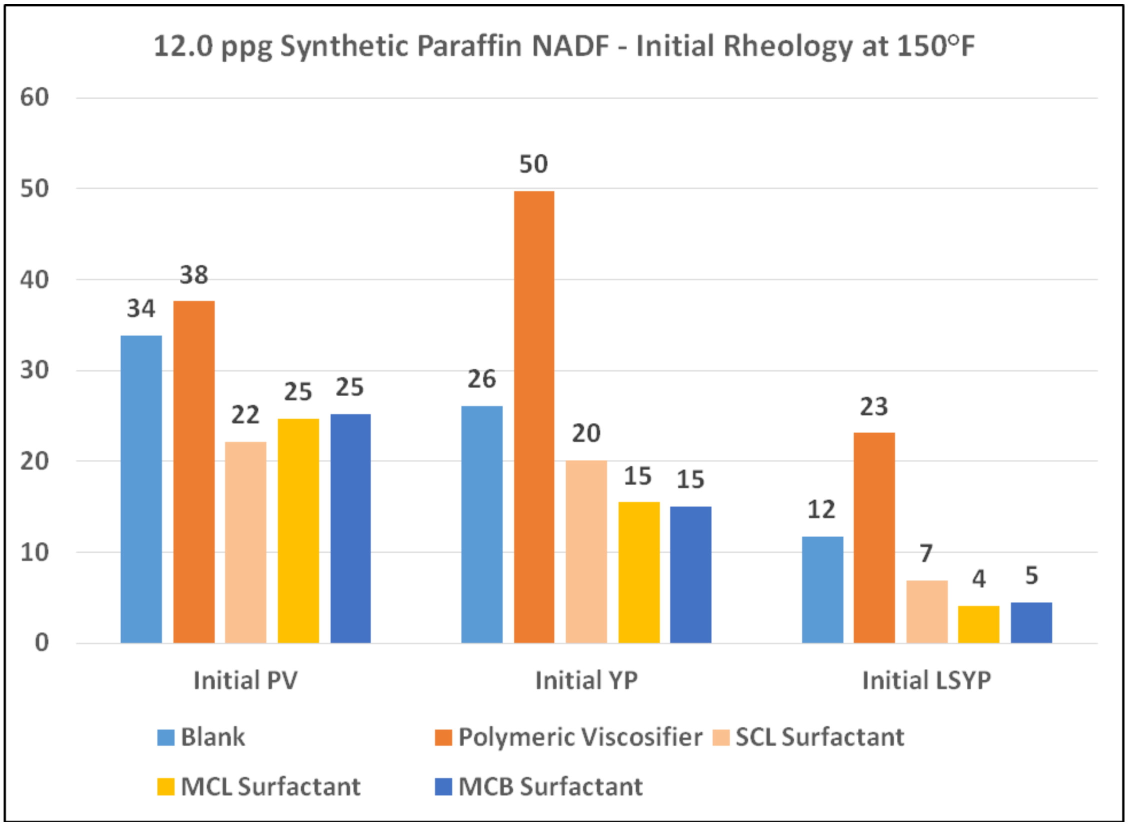


**Figure 7 – Initial PV, YP, and LSYP of 12.0 ppg NADF**

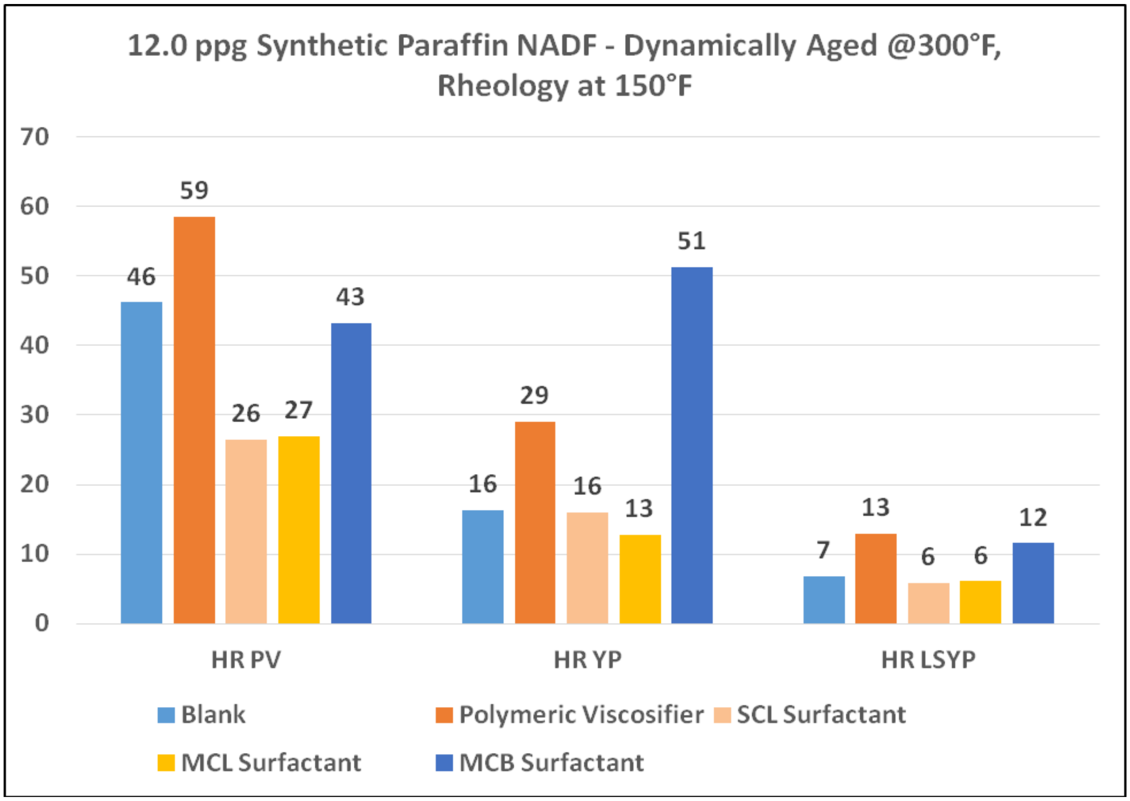


**Figure 8 – Hot Rolled (HR) PV, YP, and LSYP of 12.0 ppg NADF**

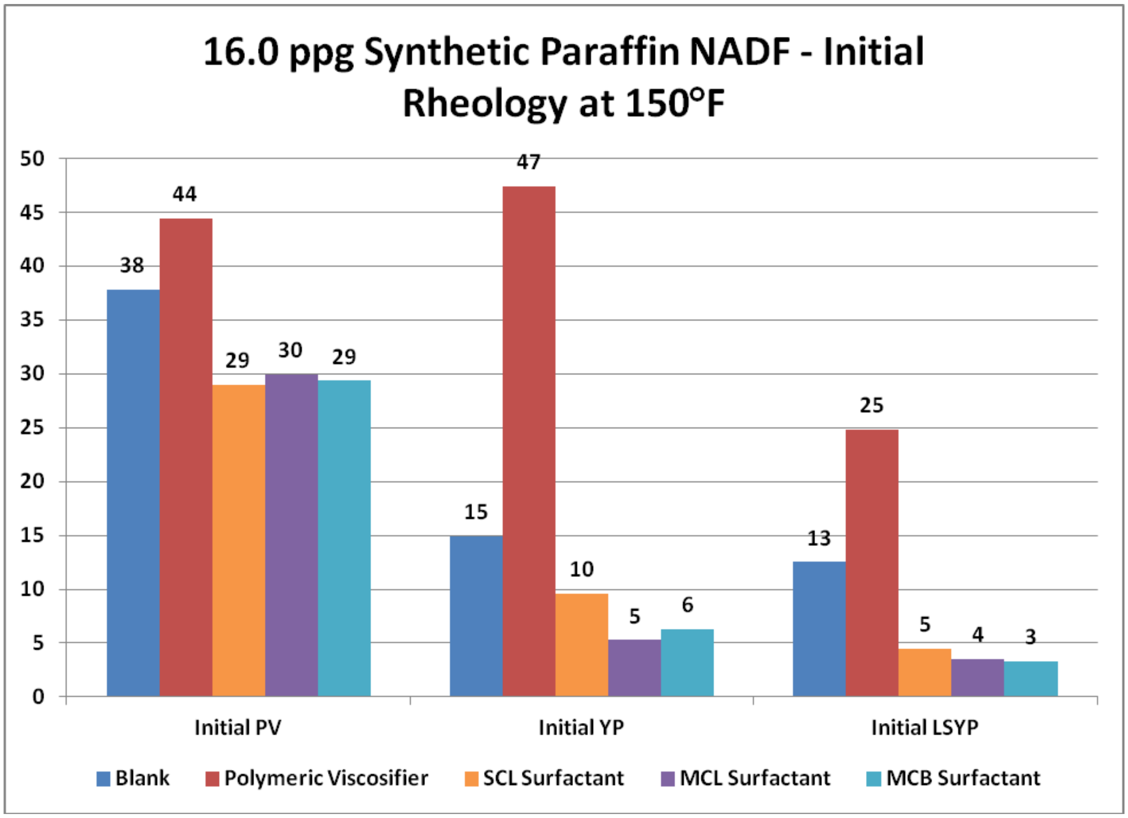


**Figure 9 – Initial PV, YP, and LSYP of 16.0 ppg NADF**

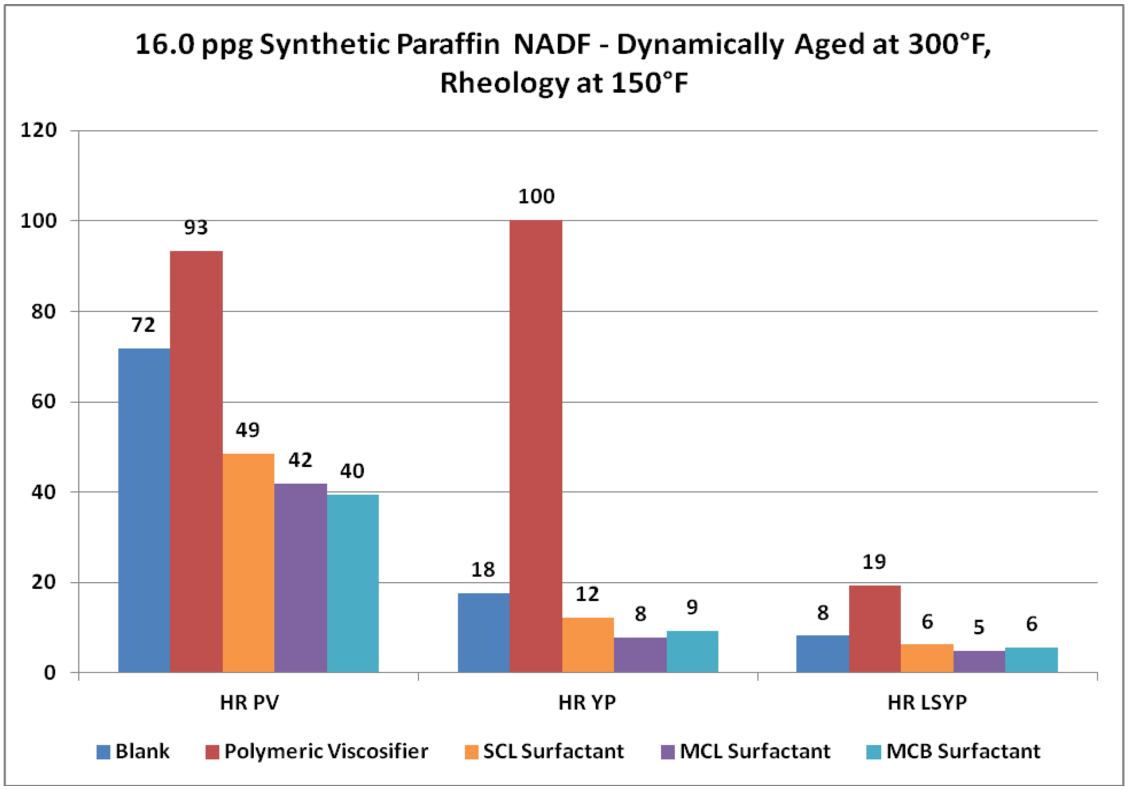


Figure 10 – Hot Rolled (HR) PV, YP, and LSYP of 16.0 ppg NADF

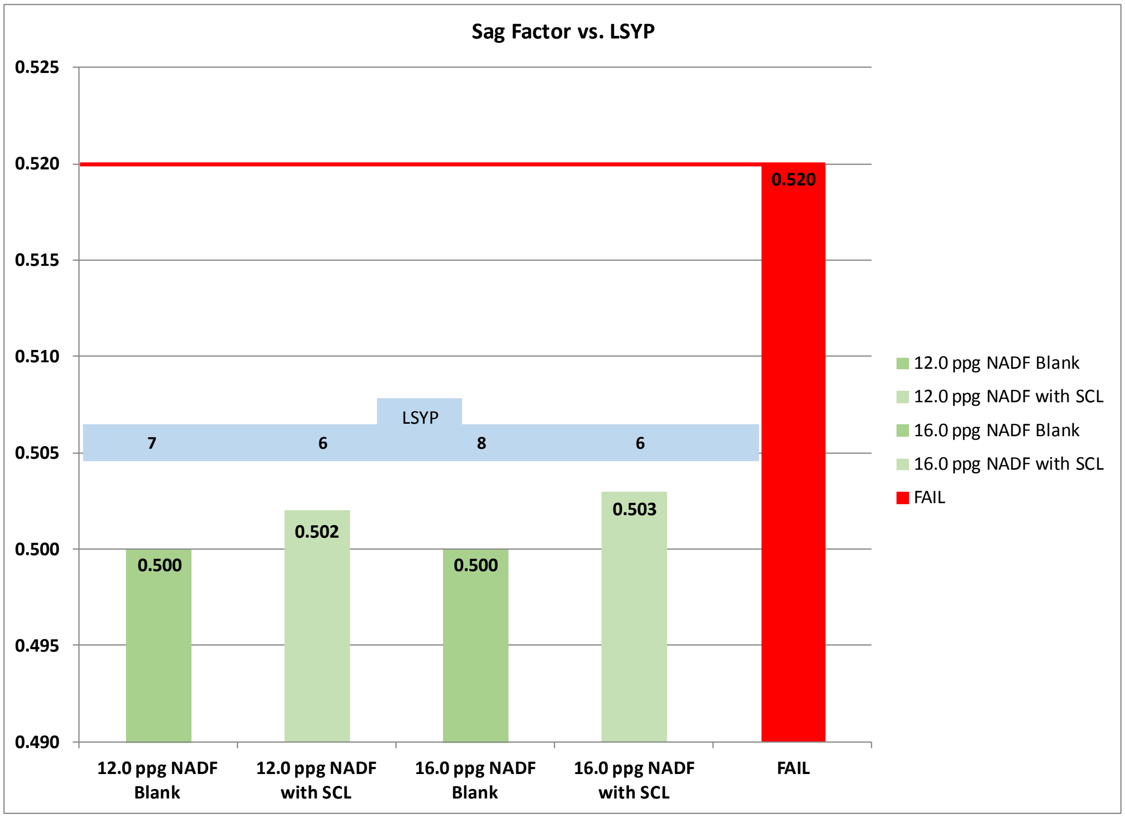


Figure 11 – Sag Factors of NADF's with and without short chain linear surfactant