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Robust invert emulsifier and fluid loss performance from a novel spray-dried additive

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Abstract

In the area of invert drilling fluid additives, Ingevity presents a novel spray-dried additive (SDA) that is easy to handle, and delivers superior emulsification and fluid loss performance. Detailed testing was done to determine its performance in different base oils (mineral and diesel), at various mud weights (12.5 to 16.6 ppg), in distinct contaminants, and at elevated temperatures. The SDA was compared to industry standard additives in these invert emulsion drilling fluids, characterized by fluid viscosity and high-pressure, high-temperature (HTHP) filtrate loss testing.

For emulsification, the novel SDA required much lower dosage than standard additives used to deliver stable invert emulsion fluids. In terms of fluid loss, the novel SDA outperformed conventional emulsifier and fluid loss additive (FLA) combinations at an improved (lower) dosage. Lastly, the SDA gave equal or lower drilling fluid plastic viscosity than the liquid emulsifiers of the study, differentiating it as a good candidate for low equivalent circulating density drilling fluids. The novel SDA demonstrated superior performance in various mud weights, base oils, contaminants and at elevated temperatures.

Introduction

When discussing the properties of liquid oilfield chemicals in the context of sustainability, the comparative advantages of equivalent solid products include improved handling since limitations of pour point and product viscosity are eliminated. Furthermore, flowable solids have a reduced storage footprint and lower transportation costs due to lighter packaging compared to drummed liquids. Disposal costs for bagged solid products are also much less than drummed liquids, as they do not require cleaning and disposal of steel drums.

Some oilfield chemicals behave as dual-functional additives, offering a further sustainable advantage. This provides bonus logistical and sustainability benefits in consolidating two products on-site with concomitant reduction in transport costs, storage space needs and associated greenhouse gas emissions.

For the reasons described above, drilling fluid industry players have sought to develop solid substitutes for conventional liquid emulsifiers. For example, reports of invert emulsifiers adsorbed on various media such as silica, clay, diatomaceous earth, asphalt, carbon and the like. [Albrighton et al. 2019; Gupta et al. 2019; Lifton et al. 2017; Ray and Richard 2020]

We've discovered that the SDA at 100% activity, furnished handling, increased performance and sustainability advantages, exceeds those of conventional emulsifier/FLA combinations.

This report describes our development of such an advantageous additive, and highlights comparative performance, handling and sustainability benefits. This paper outlines the development and optimization of a 100% active dual-function fluid loss/emulsifier SDA suitable for invert emulsion drilling fluids.

The novel SDA for invert emulsion drilling fluids is shown to deliver:

- Combined filtrate loss and emulsifier behavior
- 100% active product in a flowable powder form
- Reduced footprint on rigsite where space is a premium, such as in remote offshore locations
- Lower transportation costs
- Decreased environmental impact
- Improved metering at rig site (ability to add 40 lb package unit, v. 400 lb package unit)
- No pour point limitations
- Lower effective dose

Materials and Methods

Development of Novel SDA

The development of the novel SDA employed two sets of design of experiments (DOE), a screening followed by an optimization. The synthesis of the novel SDA was based on our extensive experience developing invert emulsifiers from tall oil chemistry with respect to HTHP fluid loss performance and rheology. The tall oil reaction product was saponifed and diluted to provide appropriate viscosity for spray drying.

Performance Testing Fluid Preparation and Procedure

The fluid formulation in **Table 1** was used to assess the HTHP fluid loss and rheology performance of the SDA. This fluid formulation was developed to test industry primary emulsifiers (Maghrabi et al. 2018) and a standard dosage of liquid primary emulsifier is 6 ppb and FLA at 6 ppb (1 ppb refers to 1 g in 350 mL of fluid). However, the SDA was tested at a primary emulsifier dosage from 3 ppb to 6 ppb in absence of FLA to exhibit its superior ability to perform at a lower dosage. The secondary emulsifier (SE) used throughout testing was a commercially available liquid emulsifier.

Table 1: 16.6 ppg conventional formulation without FLA

Mud Additives	Specific Gravity	Mass (g)	Mix Time (mins)
Low sulfur diesel	0.86	As required	2
Spray-dried additive (PE)	1.10	3.0-6.0	
Alkalinity control agent	2.21	3.0	3
Secondary emulsifier (SE)	0.92	3.0	
$CaCl_2$ brine, WPS = 33.5% w/w	1.33	As required	10
Organoclay	1.60	2.0	15
Weighting agent	4.20	As required	10
Mix time total			40
OWR	70:30		
Hot roll for 16 hours at 150°F			

The fluid formulations were massed according to calculations determined when altering dosage of components to arrive at the designated final mud weight. They were mixed in stainless steel 48070 malt cups on a multimixer Model 9B, 5 spindles with sine-wave impeller blades (9B29X) approximately one-inch, single speed of 11,500 rpm. The fluid formulation was then transferred to pint jars, sealed with tape and hot rolled in a 5-roller oven (Model 173-00-RC) for 16 hours at 150 F. If hot rolling temperature was above 150 F, the mud formulations were transferred to stainless steel aging cells with appropriate nitrogen pressure and hot rolled in a 5-roller oven for 16 hours at the desired temperature.

After hot rolling for 16 hours, the fluids were transferred back to malt cups and remixed on the multimixer for five minutes. The rheology was then measured at 120 F on a Model 900 Viscometer according to API 13B-2 (7.3.2 Determination of Viscosity and Gel Strengths Using a Direct Reading Viscometer procedure) and characterized by Bingham plastic viscosity (PV), Bingham yield point (YP) and gel strengths at 10 seconds and 10 minutes. Of note, all rheology shown is only after hot roll (AHR) of 16 hours at designated temperature. Immediately following, the electrical stability (ES) was measured at 120 F using a Model 23E Electrical Stability Tester.

HTHP fluid loss was conducted using a 175 mL, 4-unit filter press with regulators and temperature controllers (Model 170-00-4S) at desired temperatures after equilibrating cell temperature for 45 minutes with 500 psi differential pressure per API 13B-2 recommendation. Fluid loss was measured after a duration of 30 minutes.

The majority of the performance testing was conducted using the conventional 16.6 ppg fluid. Listed below are the additives used in this formulation. Worth noting, there was no separate FLA used in the formulations. The novel SDA performed as both primary emulsifier (PE) and FLA.

- Base oil (diesel or mineral oil)
- Novel SDA PE
- Alkalinity control agent
- Commercially available SE
- $CaCl_2$ for water phase salinity (WPS)
- Weighting agent for fluid density adjustment

Results and Discussions

Optimization of Final Formulation for the SDA and Performance Testing

After screening SDA products from the initial DOE, conclusions pointed to creating an optimized DOE around the formulation which had the best overall performance in HTHP fluid loss and rheology stability.

Passing fluid loss performance is considered less than 10 mL fluid with no water in the filtrate as indicated by a red line on figures. **Figure 1** demonstrates the HTHP fluid loss results from the dosage study showing 3 ppb to 6 ppb SDA absent of a separate FLA. Even at half of the typical liquid PE dosage of 6 ppb, there was passing FL performance. The rheology showed stability across the varying SDA doses and the ES values were similar as shown in **Table 2**.

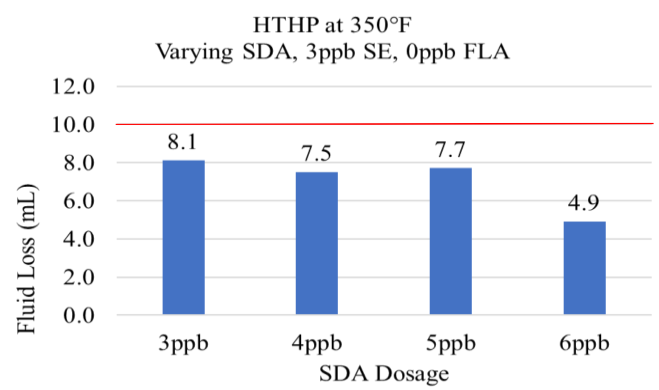

Figure 1: Fluid loss performance at varying dosage of SDA product without additional FLA included

Table 2: Rheology and electrical stability of the SDA at varying dosage in **Table 1** fluid formulation

	SDA			
Rheology @ 120°F	3 ppb	4 ppb	5 ppb	6 ppb
600 rpm (D.R.)	92.1	91.3	92.2	98.1
300 rpm (D.R.)	53.6	51.3	52.4	56.0
200 rpm (D.R.)	40.3	38.5	38.9	41.7

100 rpm (D.R.)	25.7	24.2	24.4	26.2
6 rpm (D.R.)	7.6	6.7	6.5	7.1
3 rpm (D.R.)	6.4	5.6	5.6	5.9
PV (cP)	38.6	40.0	39.8	42.2
YP (lb/100ft^2)	15.0	11.4	12.7	13.8
10" Gel (D.R.)	7	6	6	7
10' Gel (D.R.)	7	7	7	7
ES (V) @ 120˚F	354	362	375	425

Comparison of SDA with Commercially Available PE (liquid)

The SDA was compared to commercially available primary emulsifiers using the fluid formulation in **Table 1**. As shown below in **Figure 2**, utilizing 4 ppb SDA provided fluid loss performance comparable to a system comprising 12 ppb combined primary emulsifier and fluid loss additive: an 8 ppb total additive savings was achieved. The SDA passes with less than 10 mL with no water in the filtrate. Water in filtrate may be a sign of emulsion instability. Only when the commercially available PEs are dosed higher at 6 ppb with the addition of 6 ppb FLA does the commercially available PEs pass FL performance as shown in **Figure 3**. The SDA not only requires less dosage for PE, but there is no need for an additional FLA in the fluid formulation. The overall rheology was similar between the commercially available PEs to the SDA; however, the YP (100lb/100ft^2) was slightly improved by the SDA whereas the ES value of the SDA was comparable to the commercially available PEs (**Table 3**).

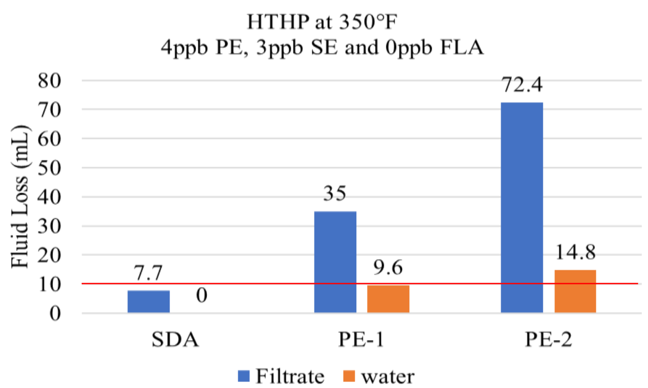

Figure 2: Fluid loss performance of commercially available PE versus the SDA in the absence of a FLA

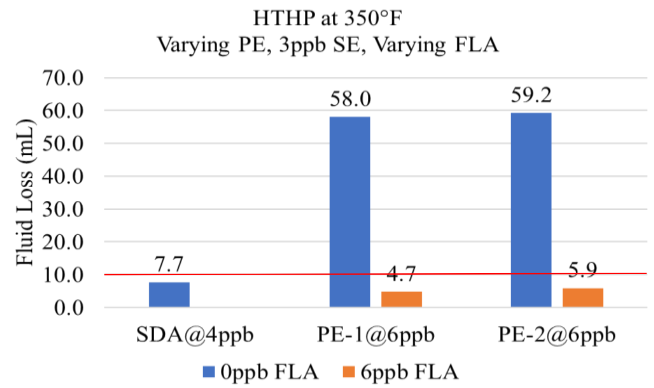

Figure 3: Comparison of commercially available PE dosed to show required amount for FL performance compared to SDA

Table 3: Rheology comparison of commercially available PEs and the SDA from the passing HTHP FL results in Figure 3

Rheology @ 120˚F	SDA	PE-1	PE-2
600 rpm (D.R.)	100.8	105.7	99.6
300 rpm (D.R.)	60.2	57.9	53.7
200 rpm (D.R.)	45.5	42.2	39.1
100 rpm (D.R.)	29.7	24.8	24.1
6 rpm (D.R.)	9.4	6.6	6.6
3 rpm (D.R.)	7.8	5.5	5.6
PV (cP)	40.6	47.8	45.9
YP (lb/ 100ft^2)	19.6	10.1	7.8
10" Gel (D.R.)	8	6	6
10' Gel (D.R.)	9	8	7
ES (V) @ 120˚F	380	384	421

Performance of SDA in Various Conditions: *Base Oils*

The SDA was tested using different base oils (diesel and mineral oil) in the fluid formulation shown in **Table 1**. The change of base oil did not affect the FL performance of 4 ppb SDA as PE without FLA. **Figure 4** demonstrates the results of the HTHP fluid loss at 350 F. The change of base oil did affect the rheological profile by significantly decreasing the Bingham YP and 10-minute gel strength. This low rheology issue was mitigated by increasing the amount of organoclay in the fluid formulation. The increased organoclay slightly improved FL performance in the mineral oil fluid formulation as exhibited in **Table 4**.

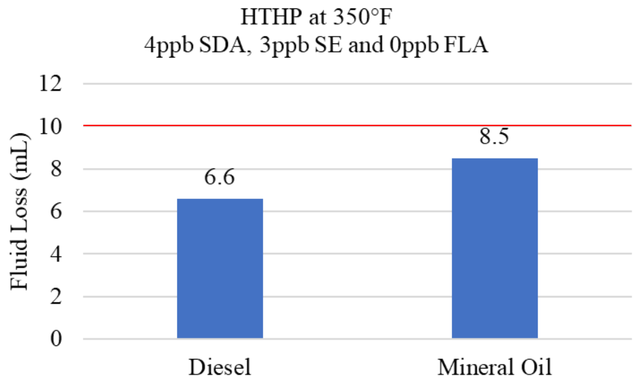

Figure 4: Fluid loss performance of SDA as PE comparing different base oils before additional organoclay

Table 4: Effect on rheology of varying base oil in conventional 16.6 ppg fluid formulation with 4 ppb SDA as PE without FLA

Rheology @ 120˚F	Diesel	Mineral Oil	Min. Oil w/ Additional Organoclay
600 rpm (D.R.)	94.1	49.0	71.1
300 rpm (D.R.)	55.5	23.8	37.1
200 rpm (D.R.)	42.4	16.2	26.1
100 rpm (D.R.)	27.6	8.3	15.1
6 rpm (D.R.)	8.6	0.6	2.8
3 rpm (D.R.)	7.4	0.4	2.0
PV (cP)	38.6	25.2	34.0
YP (lb/ 100ft^2)	16.9	-1.4	3.1
10" Gel (D.R.)	8	0	2
10' Gel (D.R.)	8	0.5	3
ES (V) @ 120˚F	393	288	318
FL (mL) @ 350˚F	6.6	8.5	5.4

Performance of SDA in Various Conditions: Mud Weights (16.6 ppg and 12.5 ppg)

The SDA was tested in various mud weights to see the effect on HTHP fluid loss and rheology. **Table 1** describes the formulation of the 16.6 ppg fluid formulation in which most of the performance testing was conducted. As discussed throughout the paper, the SDA had superior HTHP fluid loss performance at a low dosage of 4 ppb without FLA.

The 12.5 ppg fluid formulation, as shown in **Table 5**, provided a different composition of additives as compared to the conventional 16.6 ppg fluid. The lower HTHP temperature (250 F vs 350 F) was expected to require lower dosages of the SDA to meet performance properties. The SDA was tested in this formulation using only 3 ppb SDA without FLA.

Table 5: 12.5 ppg fluid formulation without FLA

Mud Additives	Specific Gravity	Mass (g)	Mix Time (mins)
Low sulfur diesel	0.86	As required	2
Alkalinity control agent	2.21	7.0	
Organoclay	1.60	5.0	10
Spray-dried additive (PE)	1.10	3.0	5
Secondary Emulsifier (SE)	0.93	1.9	
Wetting agent	0.94	1.7	
$CaCl_2$ brine (WPS = 25% w/w)	1.24	As required	10
Weighting agent	4.20	As required	5
Simulated drilled solids	2.50	50.0	5
Mix time total			37
OWR	70:30		
Hot roll for 16 hours at 250˚F			

As shown below in **Figure 5**, the SDA was successful at providing passing HTHP fluid loss below 10 mL filtrate in both diesel-based mud weight formulations. In addition, the SDA gave stable rheology in both mud weight formulations with slightly lower measurements in the 12.5 ppg. More noticeable is the comparison of gel strengths and ES. The SDA gave slightly more overall stable rheology in the 16.6 ppg fluid (**Table 6**).

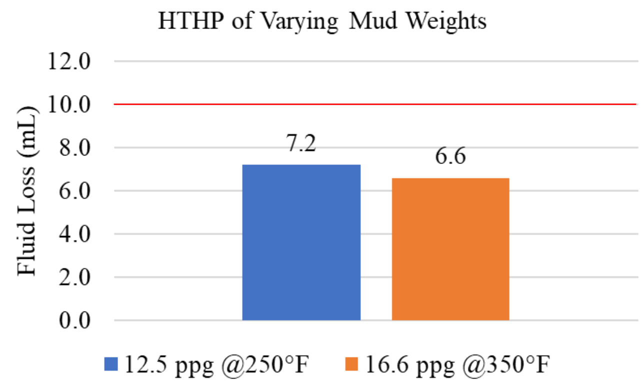

Figure 5: SDA HTHP fluid loss performance testing at varying mud weight diesel-based fluids without FLA

Table 6: Rheology of varying mud weight diesel-based fluids using SDA as PE without FLA

Rheology @ 120˚F	12.5 ppg fluid	16.6 ppg fluid
600 rpm (D.R.)	84.6	94.1
300 rpm (D.R.)	45.9	55.5
200 rpm (D.R.)	32.2	42.4
100 rpm (D.R.)	18.2	27.6

6 rpm (D.R.)	3.7	8.6
3 rpm (D.R.)	3.1	7.4
PV (cP)	38.8	38.6
YP (lb/ 100ft^2)	7.1	16.9
10" Gel (D.R.)	5	8
10' Gel (D.R.)	10	8
ES (V) @ 120˚F	235	393

Performance of SDA in Various Conditions: *Contaminants*

After an initial 16-hour hot roll at 150 F, contaminants were introduced to the base fluid formulation found in **Table 1**. 50 ppb of Rev Dust and 10% w/v sea water were used as the contaminants, with no contaminants added to the control. All fluids were then hot rolled for another four hours at 150 F before HTHP fluid loss and rheology were measured. **Figure 6** illustrates the SDA was able to maintain passing FL below 10 mL even after contamination; however, rheology and ES were affected (**Table 7**). As expected, the fluid containing the 50 ppb Rev Dust increased the rheological profile while slightly decreasing ES as compared to the control. The 10% w/v sea water contamination showed a slight increase in rheology, but drastically decreased the ES by half.

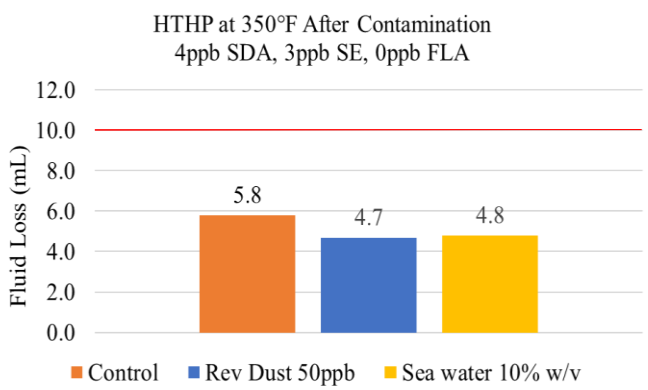

Figure 6: HTHP fluid loss results after contamination and additional hot roll four hours at 150 F

Table 7: Rheology and ES of fluid formulations after contamination and additional hot roll four hours at 150 F

Rheology @ 120˚F	Control	50 ppb Rev Dust	10% w/v Salt water
600 rpm (D.R.)	91.8	143.3	109.9
300 rpm (D.R.)	55.2	84.9	66.0
200 rpm (D.R.)	42.6	64.2	50.4
100 rpm (D.R.)	28.6	41.3	33.5
6 rpm (D.R.)	10.5	11.9	11.5
3 rpm (D.R.)	9.3	10.5	10.2
PV (cP)	36.6	58.5	44.0
YP (lb/ 100ft^2)	18.6	26.4	22
10" Gel (D.R.)	9	11	11
10' Gel (D.R.)	10	13	11

ES (V) @ 120˚F	546	419	267

Performance of SDA in Various Conditions: *Elevated Temperatures (Hot Roll and HTHP)*

The fluid formulation found in **Table 1** was hot rolled and HTHP fluid loss tested at elevated temperatures. The fluid formulation that was hot rolled at 150 F and HTHP fluid loss tested at 350 F served as the control. As demonstrated in **Figure 7**, even with temperatures as high as 375 F, the SDA was successful at passing the HTHP fluid loss below 10 mL. The differences between the measured value of the elevated temperatures as compared to the control can be contributed to the normal variance when retested. As shown in **Table 8**, the gel strengths and ES characteristics were most affected by the elevated temperatures.

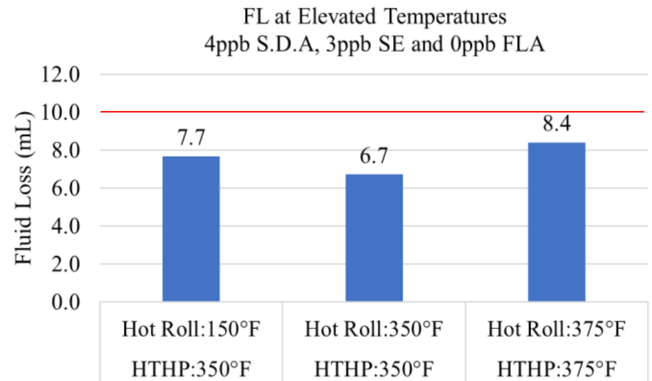

Figure 7: Fluid loss after elevated variation of hot roll and/or HTHP temperatures

Table 8: Comparison of rheology after variation in temperatures of hot roll and/or HTHP with the same fluid formulation

Rheology @ 120˚F	HR: 150°F HTHP:350°F	HR: 350°F HTHP:350°F	HR: 375°F HTHP:375°F
600 rpm (D.R.)	100.8	103.5	110.0
300 rpm (D.R.)	60.2	57.2	58.9
200 rpm (D.R.)	45.5	41.0	41.9
100 rpm (D.R.)	29.7	23.3	23.8
6 rpm (D.R.)	9.4	4.0	3.8
3 rpm (D.R.)	7.8	2.7	2.8
PV (cP)	40.6	46.4	51.1
YP (lb/ 100ft^2)	19.6	10.8	7.9
10" Gel (D.R.)	8	3	3

10' Gel (D.R.)	9	4	4
ES (V) @ 120˚F	380	159	194

Conclusions

The SDA was developed from a DOE varying the ratio of components. The paper demonstrates the favorable emulsifying and fluid loss characteristics of the SDA in a multitude of performance variables.

- SDA had the lowest threshold concentration as compared to commercially available PE, while requiring no supplementary FLA for passing HTHP fluid loss performance with comparable rheological profile.
- SDA successfully performed fluid loss test using various base oils in the formulation. Rheology was lower in mineral oil but mitigated by adding more organoclay to the formulation.
- There was no fluid loss performance decline, with comparable rheology when testing SDA in formulations with varying mud weights and components.
- SDA had high tolerance to drilled solids and salt water. Contaminants (50 ppb Rev Dust and 10% w/v salt water) had no effect on HTHP fluid loss passing performance when added to base formulation.
- The SDA passed HTHP fluid loss of elevated hot roll and HTHP conditions at 350 F and 375 F using the low 4 ppb threshold concentration of SDA with no supplemental FLA.

Performance testing in a multitude of variable conditions, the SDA successfully delivered a stable fluid formulation with controlled fluid loss and stable rheology at a lower threshold than commercially available PEs. In addition to this SDA having superior HTHP fluid loss performance in numerous conditions, it has operational business value propositions.

This SDA is 100% active in a flowable powder making it valuable in cold climates where pour point is an issue. The product also reduces the overall PE concentration and eliminating the necessity of an additional fluid loss additive. In addition to lower threshold concentrations, the packaging of the SDA allows for more precise dosing tailored to each well's specific needs while promoting a safer work environment by eliminating the need of 55-gallon drums and therefore disposal and storage costs.

Acknowledgments

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Nomenclature

10" Gel =10-minute Gel Strength
10' Gel =10 Second Gel Strength
cP =Centipoise
D.R. =Dial Reading
ES =Electrical Stability
°F= =Degree Fahrenheit
FL= =Fluid Loss
g =grams
HR = Hot Rolled
HTHP =High-temperature, High-pressure
lb =pound
mL =Milliliters
OWR =Oil Water Ratio
PE = Primary Emulsifier
ppb =lb/bbl
ppg =lb/gal
PV =Plastic Viscosity
rpm =Revolutions per Minute
SE =Secondary Emulsifier
WPS =Water Phase Salinity
w/v =Weight/Volume
YP =Yield Point

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