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Designing Advanced Emulsifiers for High-Performance Synthetic Fluids: From Drawing Board to the Challenging Wells

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Abstract

Methods have been created to provide a pathway for developing enhanced emulsifiers to meet the needs of high-performance invert emulsion drilling fluids. Furthermore, this suite of techniques can be expanded to other components, enabling development and performance optimization to meet a wide range of drilling fluid requirements based on data-driven methods.

Exploration and development of challenging assets drives a need for high-performance drilling fluids with improved stability and tightly controlled properties. Emulsifiers are the backbone of invert-emulsion fluids and require extensive testing during development. However, historically it has not been clear why most emulsifiers suffer from similar performance issues and, more importantly, what makes one emulsifier more stable compared to others.

This paper introduces a suite of methods to address these challenges and provide an improved technique to optimize the emulsifier for drilling applications. Through an evaluation of the chemical weak points, the prediction of chemical transformation over long-term application enables innovative chemical analyses and evaluation. Performance improvement of the optimized emulsifiers compared to incumbents is validated through a design of experiment (DoE) methodology. The implementation of new analytical methods and the use of digital models provides improved repeatability to develop the appropriate emulsifier chemical composition.

Introduction

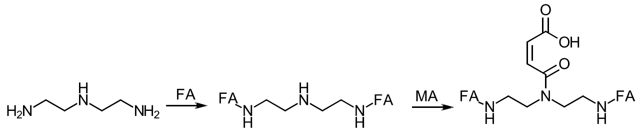
Invert-emulsion drilling fluids have dominated the high-tier market because of their superior performance—improved thermal stability, formation protection, lubricity, tolerance to contaminants, and drilling performance. Since the inception of invert-emulsion fluids, advancements have been mainly made in changes of base oil to improve environmental profile, weighting materials, and oil/water ratios. Little has changed in emulsifier chemistry used in invert emulsions. The dominant emulsifier type used in invert fluids is amidoamine based on DETA, TOFA, and maleic anhydride. Despite much effort on developing novel emulsifiers, amidoamines are still the workhorse of the industry. Surprisingly, there is not a thorough and detailed investigation of amidoamine chemistry that is supported by high-quality analytical data.

In the absence of structure-activity information, the only reliable testing method is performance testing in whole mud formulations with all other components included. Performance testing is time- consuming and still does not explain why two similar products can behave differently. Without a thorough understanding of what molecules are responsible for emulsifier performance; performance testing is the only feasible approach. To properly evaluate performance of an emulsifier, a large matrix of experiments is necessary because performance testing needs to be completed under a variety of conditions that may be possible in the real world. Alternatively, performance testing done under a limited set of conditions with fewer tests may be insufficient to describe how the product will work in the real world.

This paper discusses amidoamine optimization in the context of deepwater GoM applications. GoM drilling fluids have a unique set of requirements (such as performance across a wide temperature range 40–350 degF) and therefore, unique demands for the emulsifier. This wide temperature range along with additional requirements of extended stability under static conditions means that fluid components must be hydrolytically stable and cannot exhibit strong HLB dependence with temperature. Also, surfactants cannot cause excessive gelation at 40 degF. These requirements limit the plausible emulsifier chemistry to the same raw materials that are currently used. To improve performance of amidoamines that have been used for decades, new structure-activity test methods are needed. This paper explores new analytical methods to improve quality of amidoamine emulsifier and outlines simple steps to improve emulsifier performance without changing the basic chemistry.

Emulsifiers

The basic structure of amidoamines that have been used in the invert emulsions has not changed much over decades. The basic composition is based on DETA and TETA reactions with fatty acids followed by capping the intermediate with an anhydride to produce an anionic emulsifier (Figure **1**) . Over the years various efforts were made to create nonamidoamine emulsifiers and some of these efforts were quite successful[1] with developing new emulsifiers for RDF. However, emulsifiers for invert emulsion fluids are still amidoamines. Development efforts for nonamidoamine emulsifier are ongoing. In parallel, we have undertaken the effort to optimize amidoamine chemistry.



FA = fatty acid (oleic)
MA = Maleic anhydride/acid

Figure 1. Proposed reaction pathway to synthesize amidoamines.

Manipulation of Amine Surfactant Chemistry

The basc structural features of an amidoamine surfactant molecule is shown in Figure **2**.

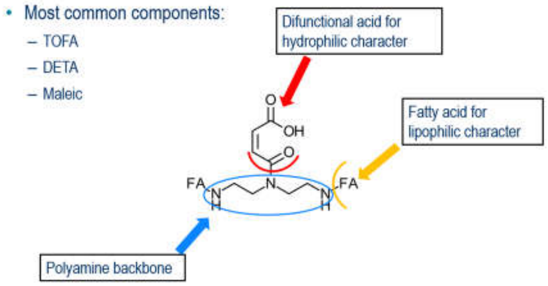


Figure 2. General description of amidoamine emulsifier used for invert emulsions and potential sites for modification.

One can envision that attaching different pieces in LEGO®-like fashion will allow us to tune emulsifier properties and optimize the performance. Change of fatty acid tail groups and the head-group will affect polarity of the molecule and make it more oil or brine soluble. Changing the structure of the head-group can also affect how the surfactants pack at the interface and, therefore, change how the emulsion behaves. These properties can improve emulsion stability and change emulsion viscoelastic properties, which directly impacts performance of a drilling fluid.

We determined that tuning solubility of surfactant by changing the alkyl groups is impractical. Currently TOFA is used. TOFA is C18 fatty acid that is predominantly oleic and linoleic acids with other minor components. TOFA is unsaturated fatty acid which gives a lower melting point. The only available substitutes for TOFA are saturated fatty acids. Using these fatty acids causes the drilling fluid to form strong gels at 40 degF presumably because fatty acid tails crystallize from the solution. Even shorter fatty acids exist that remain liquid at 40 degF; however these are likely to be too short to make an effective invert emulsifier.

DETA, TETA, and other backbone choice is also limited once the manufacturing process of this material is considered. DETA is the only product available in relatively pure form while DETA and heavier homologs are complex mixtures. The complexity per se is not an issue; however, heavier-than-DETA homologs have more secondary nitrogen atoms that are less reactive, which means it takes more energy to synthesize the emulsifier. Furthermore, TETA and above have tertiary nitrogen atoms that are completely unreactive. With exception of DETA, composition of these is variable, further complicating the effort of producing a consistent product.

Lastly, the selection of capping agent is the area where there is the most flexibility in tuning the molecule. We have tried many mono- and polyfunctional carboxylic acids. These can either be in the form of acids or anhydrides. Attempts have been made with capping agents as simple as acetic acid (Figure **2**, red bracket) but very high HPHT fluid loss was observed. Most likely without the free acid group, HLB of the surfactant is too low. Reacting various other difunctional acids we learned that the main challenge with this step is completion of the reaction. Even with highly reactive capping agents, such as maleic, succinic, and glutaric anhydrides we observed that this reaction step did not proceed as planned.

Emulsifier Structure Analysis

The two-step reaction pathway for amidoamine emulsifier synthesis is depicted in Figure **1**. Typically, base oil, surfactants, and pour point depressants are added to the product to meet handling requirements, and QC procedures are applied to the final blend. Complex composition of the blend precludes effective analysis of the amidoamine resin itself. To address these issues, we isolated the resin as the most complex component of the emulsifier package and devised QC protocols to identify potential issues in each reaction step.

Both synthetic steps consist of reacting fatty acids and anhydrides with amines (Figure **1**). Analysis for acids is a convenient way of determining the extent of reaction, and a common approach is to measure acid number, i.e., the content of unreacted carboxylic groups in the product. However, due to the different acids used in the process (fatty acid and maleic acid), this simple measurement is not enough, and a detailed compositional analysis is required. To overcome this problem, GC analysis coupled with BSTFA derivatization was applied to make the unreacted acids more volatile for effective GC analysis.

Chemical analysis results showed that ~5 wt% TOFA and a substantial amount of maleic acid were present in the final product. On a molar basis, TOFA reaction with

DETA proceeded well so excess TOFA was not deemed critical. Presence of excess maleic acid pointed at issues with the second capping step of the reaction. This was further confirmed by amine number measurement of the amidoamine resin.

Generally, insufficient reactivity in step 2 of the reaction (Figure **1**) should result in a product with a high amine number. Amine number is a common specification for amidoamines; however, the standard measurement protocol relies on aqueous titration and is not necessarily suitable for amidoamine emulsifiers. Accuracy of results can be hampered by poor solubility of emulsifier in aqueous media. Furthermore, unreacted amine is still present in the form of ammonium ion, which may further hamper the titration.

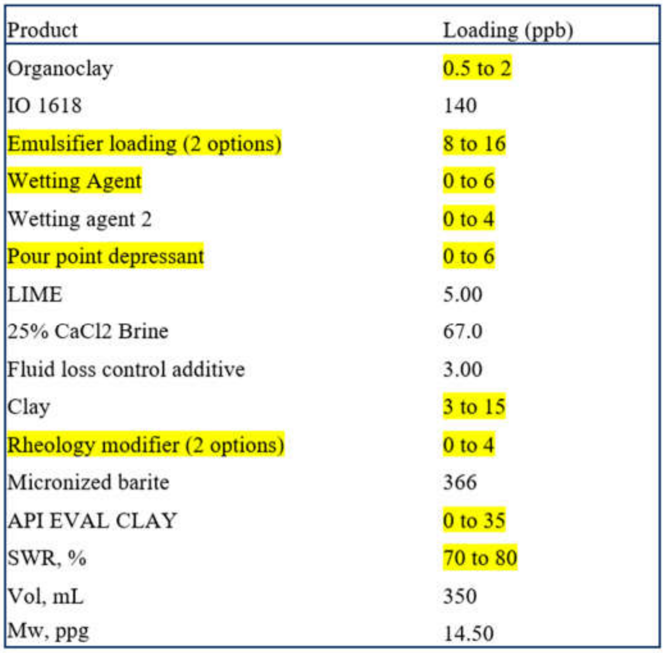
To address these issues, we applied a special titration method by dissolving the surfactant in glacial acetic acid and titrating with a solution of perchloric acid in acetic acid. Endpoint was detected by the change in the electrode [4,6]. Amine number measured by the new method accurately correlated to excess of maleic acid that we quantified previously by BSTFA method.

From these analyses, it became apparent that traditional synthesis of amidoamines suffered from an incomplete maleic addition step. Armed with this new understanding, the manufacturing process was modified to ensure completion of the second reaction step. With the new reaction protocol, both amine number and acid number decreased as expected from better completion of the reaction.

Drilling Fluids Formulations

To verify and quantify performance gains with the improved emulsifier, we applied design of experiments to screen a large variety of conditions and create a mathematical model of fluid properties and composition response. The variables used to generate response surface are shown in Figure **3**. The components that were not part of the study, such as base oil, brine, and barite, were adjusted accordingly to keep the fluid at 14.5 ppg and desired OWR.

All samples were prepared in one lab barrel quantity by adding ingredients during mixing on the Hamilton Beach mixer and then shearing on Silverson for 5 min at 6,000 rpm. Samples were hot rolled for 16 h at 280 degF prior to measurements. HPHT fluid loss was performed using filter paper disks at 280 degF with 500-psi pressure differential.



Product	Loading (ppb)
Organoclay	0.5 to 2
IO 1618	140
Emulsifier loading (2 options)	8 to 16
Wetting Agent	0 to 6
Wetting agent 2	0 to 4
Pour point depressant	0 to 6
LIME	5.00
25% CaCl2 Brine	67.0
Fluid loss control additive	3.00
Clay	3 to 15
Rheology modifier (2 options)	0 to 4
Micronized barite	366
API EVAL CLAY	0 to 35
SWR, %	70 to 80
Vol, mL	350
Mw, ppg	14.50

Figure 3. Matrix for emulsifier evaluation study. Yellow highlights are components that were changed.

This approach and the variables to be tested, outlined in Figure **3**, created a test matrix of 76 experiments. Design-Expert software (Stat-Ease, Minneapolis, MN, USA) was used to generate fluid compositions and for all subsequent data processing. While experimental matrix is quite extensive, the resultant response surface provides a quantitative description of fluid behavior In a variety of conditions and imparts confidence to our conclusions on emulsifier differentiation. The metrics for emulsifier evaluation were based on fluid properties of interest to the Gulf of Mexico (GoM) market and included several rheological parameters at 40 and 150 degF, HPHT fluid loss, and electrical stability.

Normally, it would be very difficult to create a matrix of 76 truly distinct experiments by hand without making many tests too similar. More so, simultaneous analysis of 76 data tables consisting of dozens of variables and response values is all but impossible for a person to do. The benefit of using DoE software is the ability to review a large amount data in easy-to-understand graphical format. An example of a data dashboard is shown in Figure **4**.

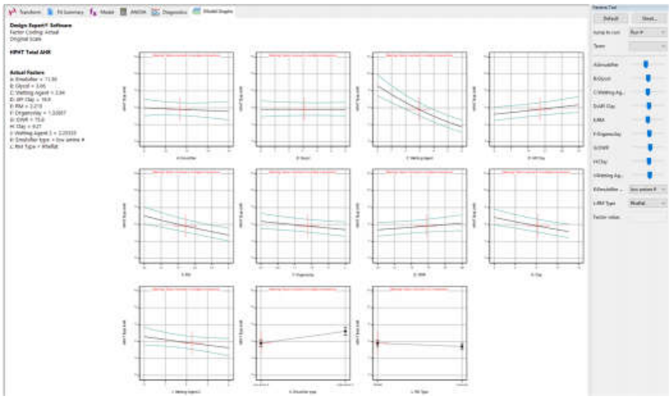


Figure 4. DOE data dashboard for fluid loss parameter.

Here we can see trends and effects of different components on HPHT fluid loss. It is known that drilling fluid formulating and testing produces inherently yield variable results. Depending on the quality of the model, confidence intervals on the trends also change, which makes it easier to estimate if the effect is real or within the typical noise of the measurement. Furthermore, with a mathematical model as shown in Figure **4**, it is now possible to do virtual drilling fluid formulations, i.e., predict fluid properties from composition without having to run additional tests. This is particularly useful because we can evaluate the difference in two emulsifiers (old and new) under all possible combination of factors.

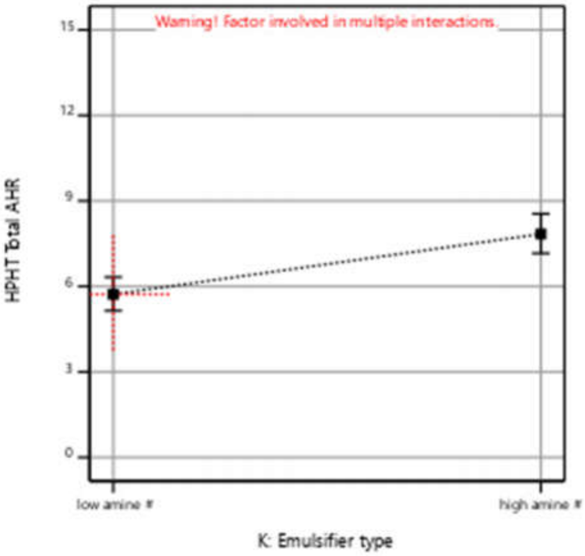


Figure 5. HPHT fluid loss comparison between new (left side) and old (right side) emulsifier.

From the analysis of emulsifier performance, the following conclusions can be made regarding key fluid properties:

- 600 rpm at 40 degF—minimal difference
- 3 rpm at 40 degF—minimal difference
- 10-min gel at 40 degF—minimal difference
- 3 rpm at 150 degF—minimal difference
- 10-min gel at 150 degF—slightly higher gels for new emulsifier
- HPHT fluid loss—substantial differences, detailed description below
- Electrical stability—no difference

Together, these results suggest that improvements we made to the emulsifier resulted in an improvement of emulsion stability, as seen in the HPHT fluid loss test, without detrimental effects on rheology. Fluid loss results from this DoE study showed substantial differences in the emulsifier but not under all conditions. The quantity of emulsifier matters when evaluating the performance. For example, at 8-ppb emulsifier, the new amidoamine had a noticeably lower fluid loss (Figure **6**).

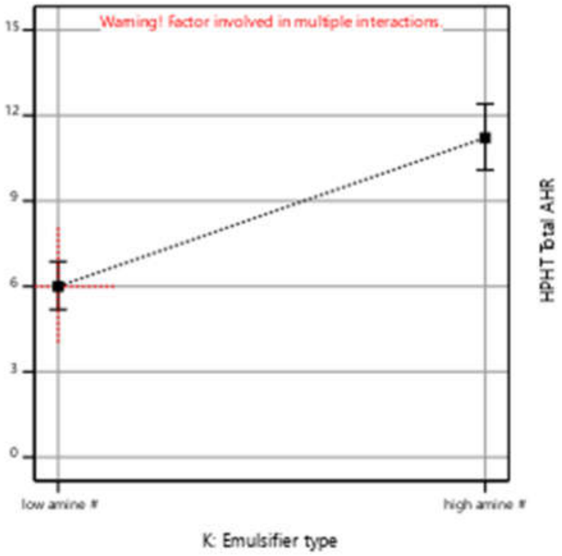


Figure 6. Comparison of HPHT result at 8-ppb emulsifier (new or old).

Increasing concentration of emulsifier to 14 ppb negated the benefit of using the new product with respect to fluid loss (Figure **7**). These factors are easily visualized using the mathematical model in the DoE software (Figure **4**), allowing to observe the effect of this virtual formulation in real time.

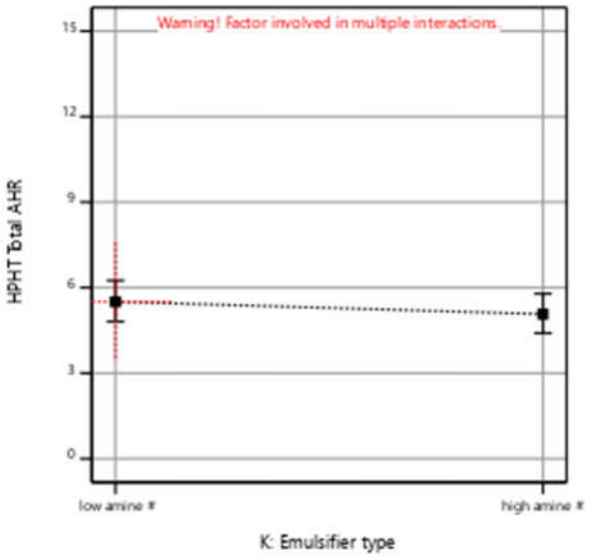
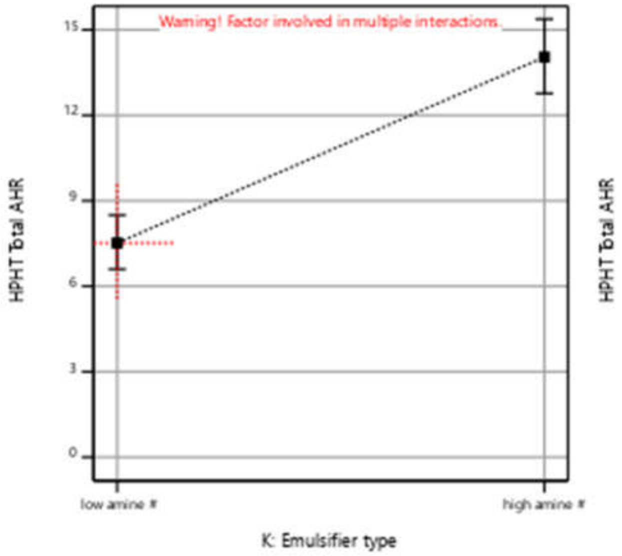


Figure 7. Comparison of HPHT result at 14-ppb emulsifier (new or old).

In addition to demonstrating the effect on fluid loss vs emulsifier type and loading, this study has shown multiple factor interactions, something that would not be easily observable if the study was performed by some other methods besides generating a response surface. For example, it was observed that changing wetting agent number 2 showed a larger detrimental effect on the old emulsifier (Figure **8**).



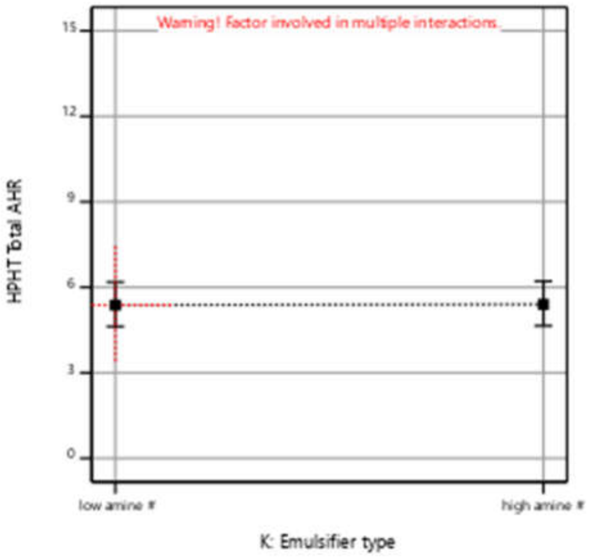


Figure 8. Changes in HPHT performance by keeping emulsifier quantity the same and changing the wetting agent 2. No wetting agent 2 (top) and 3.5-ppb wetting agent 2 (bottom).

While emulsifier comparison is the focus of this paper, it is worth noting that a substantial amount of additional information can be extracted from this digital model. For example, ES does not change between emulsifiers, but HPHT fluid loss does. Perhaps this means that ES does not really explain emulsion stability of the drilling fluid.

Also, tolerance to API clay contamination shows that increased amounts of API clay worsen fluid loss, but the relative difference between emulsifiers does not change; therefore, it is not highly likely that making these types of changes to emulsifier chemistry will improve clay tolerance.

The improved emulsifier imparts stability to the fluid in static aging under high temperature conditions at 280 and 325 degF. As shown in Table 1 and Table 2, there were no substantial changes to fluid rrheology, ES, and HPHT fluid loss after 7-day static compared to the properties of AHR fluid.

Explanation for Improved Emulsifier Stability

While it is not necessary to understand the underlying mechanisms of why one product performs better than another it is helpful. We believe the reason new emulsifier performs better is because a combination of amidoamine and fatty acids are commonly used so unreacted emulsifier with high amine number forms a salt with fatty acids, which itself can act as an emulsifier. Illustration of this property is shown in Figure **9**. Fatty amine does not work as emulsifier at all and fatty acid is a poor emulsifier, but stoichiometric ratio of the two makes an emulsion.

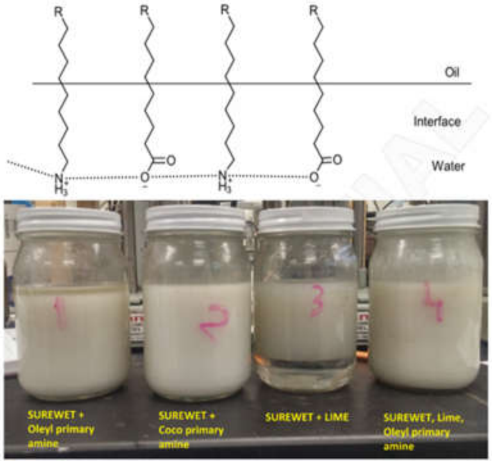


Figure 9. Fatty amines with fatty acids make an emulsifier that has only temporary staying power.

The same process is likely to occur in the drilling fluids where high amine number emulsifier is mixed with fatty acids, which results in a metastable emulsion. However, the issue with this approach is that fatty acid and amine salt is broken up with lime. Time and temperature accelerate this process. This may be the reason why at lower temperatures emulsifiers with incomplete reaction may work OK but fail at higher temperatures. And for similar reasons, why incompletely reacted emulsifier may be OK AHR but poor after 7-day static aging—amine salts break down by action of lime.

We postulate that the mechanism responsible for emulsion degradation that we are describing is also the same mechanism responsible for deactivating reaction product rheology modifiers. A lot of rheology modifiers list amine salts on their SDS. Alternatively, rheology modifiers, such as dimer amine form salts in solution. Many of these serve as excellent rheology modifiers at low temperatures, but their effect disappears when samples are hot rolled at higher temperatures.

Conclusions

Amidoamines are widely accepted emulsifiers for invert drilling fluids with risks and benefits well characterized. The benefit of developing improved amidoamines vs introducing completely new chemistries is a lower risk to operations. We relied on our understanding of organic chemistry mechanisms, improved product analysis methods, and digital modeling to demonstrate that we can improve emulsifiers that have been in use for decades. We have shown that amidoamine chemistries have potential to create high-performing emulsifiers without relying on exotic chemistry.

With improvements to manufacturing and QC procedures, we demonstrated that amidoamine emulsifiers can perform well up to 280 degF and, potentially, extend performance to 325 degF and beyond.

Acknowledgments

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Nomenclature

DETA = diethylenetriamine
TOFA = tall oil fatty acid
HLB = hydrophilic lipophilic balance
HT = high temperature
HPHT = high pressure high temperature
ECD = effective circulation density
LSRV = low shear rate viscosity
ppb = pounds per barrel or grams per 35 0Ll

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Table 1. BHR, AHR, ASA 7-day at 280 F fluid properties based on new emulsifier. 14.3ppg fluid 77/23 OWR.

Heat Aging Temp, °F	INITIAL			280			280		
Heat Aging, hr				16			160		
Static/Rolling				D			S		
Mud Weight, lb/gal	14.30			14.30			14.30		
Rheology Temp, °F	**40**	**100**	**150**	**40**	**100**	**150**	**40**	**100**	**150**
R600 , °VG	186		54	174	83	56	181	86	59
R300, °VG	100		30	96	47	33	101	49	36
R200 , °VG	71		22	69	34	26	72	36	27
R100 , °VG	39		13	39	22	17	41	22	18
R6 , °VG	6.0		3.0	9.0	9.0	9.0	8.0	8.0	9.5
R3, °VG	4.5		3.0	7.0	9.0	9.0	6.5	7.5	9.0
PV, cP	86	0	24	78	36	23	80	37	23
YP, lb/100ft²	14	0	6	18	11	10	21	12	13
LSYP, lb/100ft²	3	0	3	5	9	9	5	7	9
10-sec Gel, lb/100ft²	7		4	10	12	16	10	14	20
10-min Gel, lb/100ft²	17		9	27	33	37	30	37	34
Static Shear, lb/100ft²									
E.S. @150°F, V			591			512			550
HTHP Temp, °F						280			280
HTHP FL, ml						1.7			2.5
Water in HTHP Filtrate, ml						0			0

Table 2. BHR, AHR, ASA 7-day at 325 F fluid properties based on new emulsifier. 14.3ppg fluid 77/23 OWR.

Heat Aging Temp, °F	INITIAL			325			325		
Heat Aging, hr				16			16+160		
Static/Rolling				D			S		
Mud Weight, lb/gal	14.29			14.29			14.29		
Rheology Temp, °F	**40**	**100**	**150**	**40**	**100**	**150**	**40**	**100**	**150**
R600 , °VG	237		58	182	85	58	170		61
R300, °VG	132		32	100	48	34	93		36
R200 , °VG	93		23	71	35	25	67		27
R100 , °VG	53		14	41	23	16	37		18
R6 , °VG	10.0		4.0	9.0	8.5	7.0	6.5		7.0
R3, °VG	7.5		3.0	8.0	8.0	7.0	5.0		6.5
PV, cP	105	0	26	82	37	24	77	0	25
YP, lb/100ft²	27	0	6	18	11	10	16	0	11
LSYP, lb/100ft²	5	0	2	7	8	7	4	0	6
10-sec Gel, lb/100ft²	8.5		4	9	10	8	5		7
10-min Gel, lb/100ft²	15		6	19	21	18	33		31
Static Shear, lb/100ft²									<10
E.S. @150°F, V			334			667			474
HTHP Temp, °F						325			325
HTHP FL, ml						2.4			4.4
Water in HTHP Filtrate, ml						0			0