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Rheological properties of RHMOD-INVERT^{TM}—A Study on a novel oil-based drilling fluid with high thixotropy

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Using conventional oil-based drilling fluids typically involves the disadvantages of low borehole cleaning efficiency, easy cuttings bed formation and drill pipe sticking. In order to address these problems, we developed the gemini surfactant SRHJ-1, after which we manufactured the oil-based drilling fluid RHMOD-INVERT^{TM}. This new drilling fluid demonstrates excellent rheological properties, including low viscosity and high shear. The microscopic structure of the drilling fluid was observed through freeze-fracture electron microscopy. Then, combining high-temperature, high-pressure rheometry with optical microscopy, the RHMOD-INVERT^{TM} drilling fluid was analyzed both macroscopically and microscopically. The observation data showed strong van der Waals forces active between emulsion droplets, organic clay, and other solid-phase particles, resulting in close interactions and the formation of network-like aggregates. Due to these forces, the new drilling fluid exhibits a "cake batter" structure. Emulsion droplets, organic clay, and other solid-phase particles, when at rest, form a complex, three-dimensional piling structure in space, which has a higher suspending power. When flowing, the reticular formation can be destroyed even under extremely low shear stress, facilitating the flow of the drilling fluid. This is manifested as low viscosity and high shear on the microscopic level. The new drilling fluid was applied in field tests to several deep horizontal wells, including WS1-H2, GS3, and XS1-H8, where it demonstrated stable performance. The rheological properties of low viscosity and high shear make it easier to overcome challenges in the cuttings, carrying, and sticking phenomena in deep horizontal wells in tight gas reservoirs, while simultaneously improving the drilling efficiency.

Keywords: Emulsion, high thixotropy, low viscosity and high shear, oil-based drilling fluid, rheology.

INTRODUCTION

Oil-based drilling fluids (OBDFs) possess excellent capacities for inhibitive activity, lubrication, and pollution reduction. In drilling projects, these fluids can be used to inhibit the hydration swelling of shale, prevent the collapse of borehole walls, and reduce hole shrinkage [1]. When applied to high-temperature deep wells and wells with large displacement or complex structures, OBDFs can prevent borehole instability in complex strata, thereby ensuring safe and rapid drilling [2-3].OBDFs have undergone rapid changes through research conducted in foreign countries. In fact, the application rate of OBDFs has reached over 80% in North America and Mexico. Baroid and M-I Corporation have developed high-performance, OBDF systems such as INNOVERT and INTOL^{TM}, based on FACTANT and VETSAMUL, respectively [4-6]. High-performance emulsifiers are important for developing desirable OBDFs; however, the development of emulsifiers has fallen far behind in China compared with other regions of the world. At present, single-chain and single-functional-group surfactants are extensively used in China. These surfactants are low in both emulsification efficiency and resistance to high temperature; therefore, they are added in large amounts to OBDFs, leading to unstable performance, poor shear thinning ability, high viscosity, and low shear. As a result, these OBDFs may present problems of low borehole cleaning efficiency and easy cuttings bed formation, such that they are unsatisfactory for horizontal wells and wells with complex structures [7-9].To address these defects, we developed a high thixotropy OBDF called RHMOD-INVERT^{TM} that incorporates the SRHJ-1 emulsifier. This new drilling fluid achieves low viscosity and high shear, and it was applied successfully to several horizontal wells in deep tight gas reservoirs in the Daqing oilfield (horizontal wells WS1-H2 and XS1-H8). RHMOD-INVERT^{TM} also resolves the frequent phenomena of low borehole cleaning efficiency, cuttings bed formation, low drilling speed, and drill pipe sticking in complex structure wells.

EXPERIMENTAL

Development of new emulsifier and high thixotropy OBDF

Working mechanism of new emulsifier, SRHJ-1

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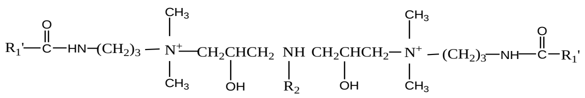
We prepared the new emulsifier using the organic acids N-Vinylpyrrolidone and epichlorohydrin as raw materials, in an attempt to address the problems of instability and hydrolysis under certain temperatures and in alkaline environments. The gemini emulsifier SRHJ-1 was synthesized through a three-step method. Fig. 1 shows the molecular structure of the SRHJ-1 emulsifier, which is a dimer with two head groups introduced to enhance the adsorption capacity on the oil-water interface. The two alkyl chains of the emulsifier molecule display strong intramolecular interactions, increasing the strength of the interfacial film between oil and water and thereby promoting the emulsification capacity. On the oil-water interface, both intramolecular interaction in the alkyl chains and intermolecular interaction based on hydrogen bonding occur, greatly improving the formation and stability of a water-in-oil emulsion[10]. The bi-layer structure of the gemini emulsifier SRHJ-1 enables a tighter molecule arrangement on the oil-water interface. In solutions, the emulsifier exists as a suspension of micelles with low curvature. In low-concentration liquids, the emulsifier exists as wormlike or linear micelles, which intertwine to form a network structure. This unique feature provides high viscoelasticity [11-16] and the shear properties of non-Newtonian fluids [17] to the solution into which the emulsifier is added.

In rheological terms, a stress must act on the fluid in order for the fluid to flow. Gel strength is defined as the maximum elastic deformation of the fluid before it is made to flow. When added to fluid, SRHJ-1 can increase the elastic deformation and gel strength of the emulsion. When left standing, the emulsion will increase in elasticity as well as in gel strength and suspending ability. Because the SRHJ-1 emulsifier is easily dissolved in the dispersed phase, it will not increase friction within the continuous phase. While increasing the yield point-plastic viscosity ratio, the SRHJ-1 emulsifier does not increase plastic viscosity itself [18].



注： R_1： $C_{15}H_{31}$□ $C_{17}H_{32}OH$ R_1'□ $(C_{17}H_{33}O(C_6H_9NO)m)n$ R_2： $C_{18}H_{29}$， m≥ 1□ n≥ 2

Fig. 1. Molecular structure of SRHJ-1 emulsifier

Performance evaluation of SRHJ-1

Using a DSX500 opto-digital microscope, we evaluated the morphology of an emulsion formed by adding SRHJ-1 emulsifier and assessed the suspending performance of the emulsifier. We then determined the capacity of the organic clay-containing emulsion to improve shear strength. The base fluids used were inverse emulsions with an oil-to-water ratio of 80:20.

Microscopy of emulsion formed by SRHJ-1

Under the microscope, we observed changes in emulsion droplet size and morphology after hot aging at a high temperature, and we compared these results with an emulsion formed by Span-80. Figs. 2 and 3 show the differences in droplet size using the two emulsifiers. Compared with Span-80, SRJH-1 produced a smaller droplet size and a more uniform size distribution after hot aging [19], indicating its higher emulsification capacity.

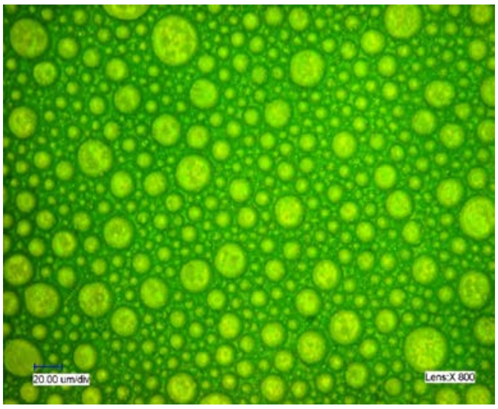


Fig. 2. Emulsion droplets formed by Span-80

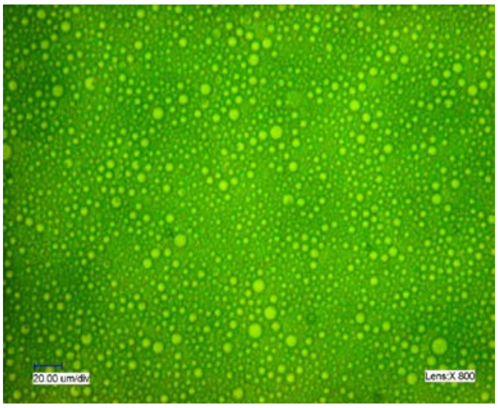


Fig. 3. Emulsion droplets formed by SRHJ-1

(Note on emulsion formulation: a) oil-to-water ratio 80:20, $CaCl_2$ concentration 20%+4.0% Span-80+3.0% oleic acid+3.0% naphthenamide; b) oil-to-water ratio 80:20, $CaCl_2$ concentration 20%+3.0% SRHJ-1+1.0% naphthenamide; conditions of hot aging at a high temperature 260°C/16 h in both a and b)

Suspending performance

Loss factors of emulsions formed with different emulsifiers in static states were determined using Rheolaser™ (Fig. 4). The loss factor is a measurement of suspending performance, defined as the ratio of the loss modulus to the modulus of elasticity. The smaller the value, the higher the suspending performance, and the lower the possibility of static settlement of the solid phase under the action of weight [20]. As Fig. 4 shows, the loss factor of the emulsion formed by SRHJ-1 decreased fastest compared with several other emulsifiers developed by foreign researchers, and it stabilized after about 7 min. In actual applications, the new emulsifier's macroscopic performance corresponded well with its microscopic performance. This emulsifier improved the rheological properties, thixotropy, and suspending performance of the OBDFs, thereby promoting borehole cleaning efficiency.

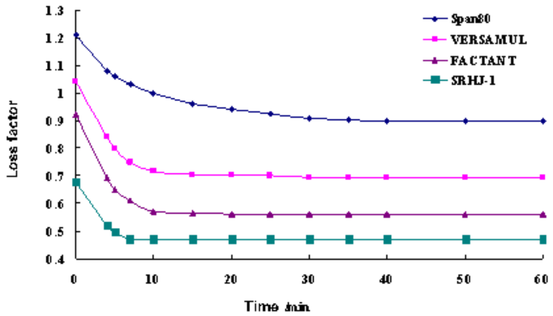


Fig. 4. Loss factors of emulsions formed with different emulsifiers

Capacity of organic clay-containing emulsions to improve shear strength

Separate water-in-oil emulsions were prepared with Span-80 and SRHJ-1, with different amounts of organic clay added. The corresponding changes in yield point were then determined (Fig. 5). The results indicate that SRHJ-1 demonstrated a better capacity for improving shear strength. Even at a small addition amount of 0.3%, SRHJ-1 worked synergistically with the organic clay to improve emulsification efficiency. The mixture of SRJH-1 and the organic clay enhanced the overall performance of the OBDF.

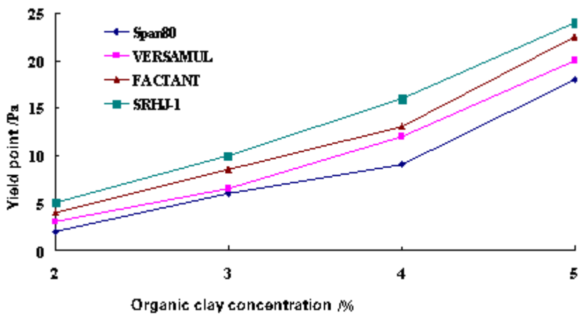


Fig. 5. Effect of SRHJ-1 on the yield point of organic clay-containing emulsions

Establishment of high thixotropy OBDF system

Gemini emulsifiers, when used synergistically with conventional emulsifiers, can greatly enhance emulsification performance[21-22]. We combined SRHJ-1 with naphthenamide, a conventional emulsifier, as well as a filtrate reducer, organic clay, and wetting agent. We then prepared a high thixotropy OBDF system, RHMOD-INVERT™, which demonstrated resistance to temperatures as high as 260°C. Its performance properties are shown in Table 1. The formula of the drilling fluid system consists of biodiesel, 20% $CaCl_2$ water solution (oil-to-water ratio 80:20), 3.0-3.5% SRHJ-1, 1.0-1.2% naphthenamide, 4% organic clay, 1.5% calcium oxide, 3-5% filtrate reducer, 2-4% wetting agent, 4% ultrafine calcium carbonate (1250 mesh), and barite powder. The performance of the new drilling fluid system was verified by field tests in several deep horizontal wells (WS1-H2, GS3, and XS1-H8). Its rheological features of low viscosity and high shear are effective in resolving common problems with OBDFs, such as difficulty in cuttings carrying, pipe sticking, and the instability of deep wells in tight gas reservoirs. The horizontal completion length of the WS1-H2 well was 1704.35 m, and the mechanical drilling speed was as high as 1.8 m/h; both of these values set new records in the field.

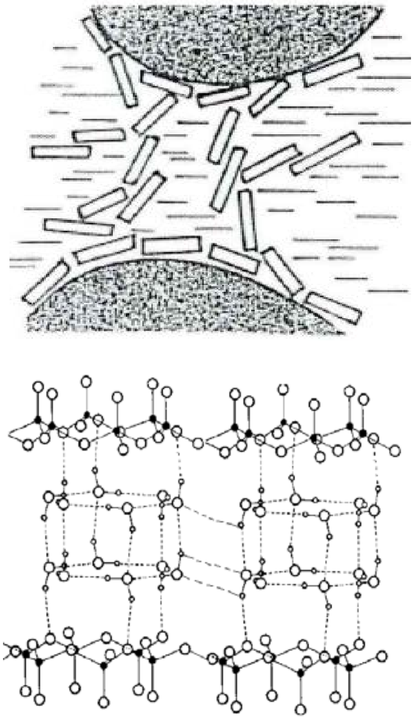
Table 1. Performance parameters of RHMOD-INVERT™

Experimental conditions	AV/ mPa·s	PV/ mPa·s	YP/ Pa	Gel/ Pa/ Pa	YP/PV	ES/ V	FL_{HTHP}/ mL
Before aging	26	18	8	3.5/5.0	0.44	1653	/
260°C/16 h	27	19	8	4.0/6.5	0.42	1644	8.2
260°C/48 h	29	20	9	4.0/6.5	0.45	1613	8.4
260°C/72 h	30	21	9	3.5/6.0	0.43	1548	8.4

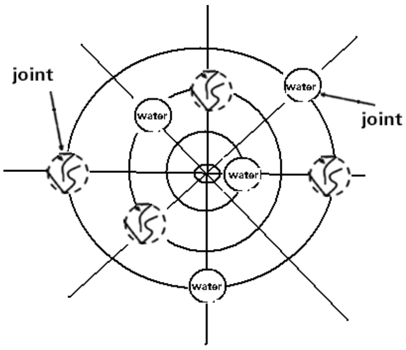
RESULTS AND DISCUSSION

Hypothesis of the microscopic structure of high thixotropy OBDF

The low viscosity and high shear properties of RHMOD-INVERT™ can be explained on the basis of microscopic factors. These rheological features may be caused by the intertwining of wormlike or linear micelles, which form a stereoscopic cake batter structure through interactions with quaternary ammonium clay. The hypothesized forms of interactions between emulsion droplets and solid-phase particles are illustrated in Fig. 6. When left standing, the elasticity of the emulsion droplets formed by SRHJ-1 continues to increase, giving the emulsion high gel strength and suspending performance. Moreover, strong van der Waals forces are created between the emulsion droplets and the organic clay, forming a cake batter structure that correlates to the interactions between emulsion droplets, organic clay, and other solid-phase particles. This system is associated with higher gel strength and suspending performance. The drilling fluid system's shear stress τ_y was only 2.71 Pa as the fluid flowed. This suggests that the reticular formation can easily be destroyed even under an extremely small shear stress, facilitating the flow of the drilling fluid.



a. Stereo view of the cake batter structure



b. Planar view of the cake batter structure

Fig. 6. Hypothetical microscopic structure of the high thixotropy OBDF

Verification of the rheological properties of high thixotropy OBDF

In order to determine its rheological properties, samples of the drilling fluid were cryopreserved in liquid nitrogen, which helped preserve its flow characteristics. Then, Cryo-scanning electron microscopy (Cryo-SEM) was used to investigate the drilling fluid's microstructure development. Moreover, a HTHP rheometer was used to test the new fluid's unique rheological properties.

Microscopic analysis

We used a DSX500 opto-digital microscope combined with Cryo-SEM to observe the microscopic structure of RHMOD-INVERT™. First, the moving fluid was flast frozen in -173°C liquid nitrogen, and images were taken using a transmission electron microscope with 100 KV accelerating voltage. Figs. 7 and 8 are the high-magnification images and Cryo-SEM images, respectively. As indicated in Figs. 7 and 8, the water-in-oil emulsion formed by SRHJ-1 enjoyed high stability and was resistant to the breaking of the emulsion. Moreover, there were more emulsion droplets formed, with smaller droplet sizes and a more uniform size distribution. Aggregates formed between the emulsion droplets and organic clay particles through hydrogen bonding. Based on these factors, a cake batter structure was observed as the form of interaction between emulsion droplets, organic clay, and other solid-phase particles; this structure provides higher gel strength and yield point. The emulsion droplets, organic clay, and other solid-phase particles interact by van der Waals forces, which are easily broken by high shear rate, leading to "shear thinning."

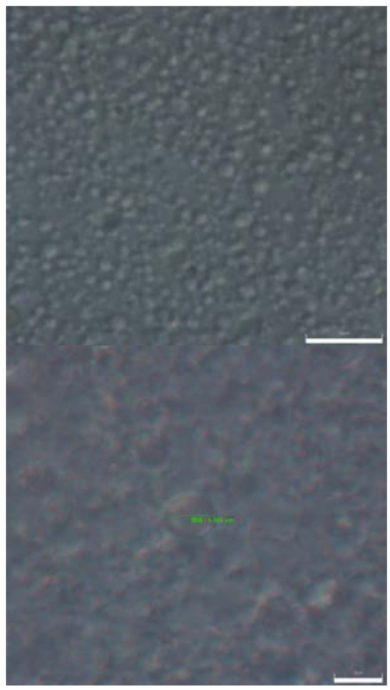


Fig. 7. SEM images of high thixotropy OBDF

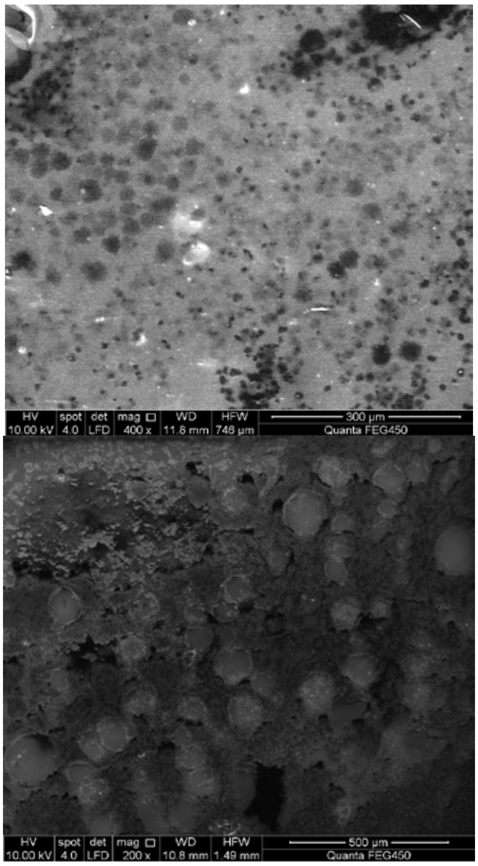


Fig. 8. Freeze-fracture electron microscopy images of high thixotropy OBDF

Macroscopic analysis

To characterize the macroscopic properties, a DHR-2 rheometer was applied to both conventional drilling fluid and RHMOD-INVERT^{TM} at 50°C. The rheological curves at high temperature and high pressure were then plotted so as to compare the rheological differences between the two. Figs. 9 and 10 show the changes to viscosity and shear stress, respectively, with shear rate. According to Fig. 9, the viscosities of both drilling fluids declined sharply at a shear rate of 0-100s^{-1}, which is typical of non-Newtonian fluids. With the shear rate fixed, the viscosity of RHMOD-INVERT^{TM} was obviously lower than that of the conventional drilling fluid, indicating a stronger shear thinning effect. This is conducive not only to increasing the drilling speed, but also to carrying cuttings in a circular space.

However, neither the Bingham model nor the power law model can accurately depict the rheological properties of these OBDFs. As Fig. 10 illustrates, the conventional OBDF more closely resembles a dilatant fluid at a shear rate of 0-1000 s^{-1}. As the shear rate increases, some particles intertwine together to form a reticular structure, which causes the flow resistance to increase, resulting in the rheological features of high viscosity and low shear during the drilling operation. This is not favorable for borehole stability or the carrying of cuttings. In contrast, RHMOD-INVERT^{TM} conforms to the Herschel-Bulkely equation[23], expressed as $\tau=\tau_y+K\gamma^n$, which provides a more accurate model. The emulsion droplets formed by SRHJ-1 show a constant increase in elasticity in a static state, providing the emulsion with higher gel strength and suspending performance, also known as high shear. The initial shear stress τ_y of the flowing drilling fluid is only 2.71 Pa, which means both that the fluid can flow under minimal shear stress and that the drilling fluid is superior in thixotropy.

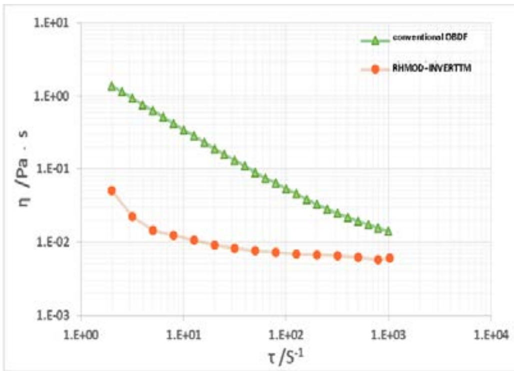


Fig.9. Viscosity-shear rate curves for different OBDFs

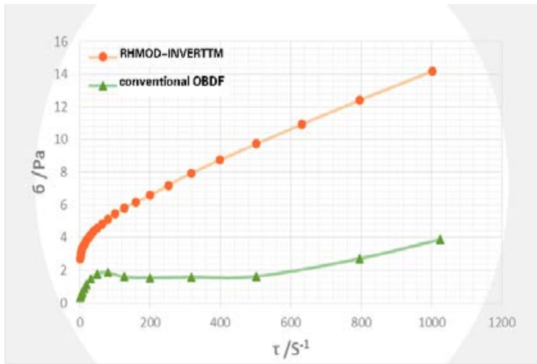


Fig.10. Shear stress-shear rate curves for different OBDFs

CONCLUSIONS

We developed a gemini emulsifier, SRHJ-1, for use in OBDFs. This emulsifier demonstrated excellent performance and compatibility with conventional emulsifiers. This emulsifier can increase the yield point of emulsion droplets, enhancing the strength of the interfacial film between oil and water. When added to a high thixotropy OBDF, SRHJ-1 can provide high shearing force and suspending ability. Based on

SRHJ-1, we then prepared a high thixotropy OBDF, RHMOD-INVERT^{TM}, which can resist high temperatures (260°C). Field tests proved the low viscosity and high shear of RHMOD-INVERT^{TM}, which has a unique cake batter structure. This three-dimensional piling structure, which is helpful in enhancing suspending performance, is formed by the interactions between emulsion droplets, organic clay, and other solid-phase particles.

Microscopic and macroscopic analyses of RHMOD-INVERT^{TM} indicate the formation of reticular aggregates comprised of emulsion droplets, organic clay, and other solid-phase particles. This drilling fluid system conforms to the Herschel-Bulkely equation and shows a good correspondence between its microscopic and macroscopic features.

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РЕОЛОГИЧНИ СВОЙСТВА НА RHMOD-INVERT^{TM} - ИЗСЛЕДВАНЕ НА НОВА СОНДАЖНА ТЕЧНОСТ НА ОСНОВАТА НА МАСЛО С ВИСОКА ТИКСОТРОПИЯ

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(Резюме)

Използването на конвенционални сондажни флуиди на основата на масло обикновено включва недостатъците на ниска ефективност на почистване на сондажа, лесно образуване на коритото и слепване на сондажните тръби. За да се справим с тези проблеми, ние разработихме повърхностно-активния агент SRHJ-1, след което произведохме сондажната течност RHMOD-INVERT^{TM}, базирана на нефт. Тази нова сондажна течност показва отлични реологични свойства, включително нисък вискозитет и висока степен на срязване. Микроскопската структура на сондажния флуид се наблюдава чрез електронно микроскопия с фрагментиране чрез замразяване. След това, съчетавайки високотемпературна реометрия с високо налягане с оптична микроскопия, сондажният флуид RHMOD-INVERT^{TM} беше анализиран както макроскопски, така и микроскопски. Данните от наблюденията показват силни сили на ван дер Ваалс, които са активни между емулсионни капчици, органична глина и други частици в твърда фаза, което води до близки взаимодействия и образуване на мрежови агрегати. Поради тези сили новата течност за пробиване показва структура на " тесто за торта". Емулсионните капчици, органичната глина и другите частици в твърда фаза, когато са в покой, образуват сложна, триизмерна пространствена структура на, която има по-висока задържаща сила. Когато тече, ретикуларното образуване може да бъде унищожено дори при изключително ниско срязване, улесняващо протичането на сондажната течност. Това се проявява като нисък вискозитет и висока степен на срязване на микроскопично ниво. Новият пробивен флуид беше приложен при полеви тестове в няколко дълбоки хоризонтални кладенци, включително WS1-H2, GS3 и XS1-H8, където показа стабилна производителност. Реологичните свойства като нисък вискозитет и висока степен на срязване улесняват преодоляването на недостатъците при сондирането в дълбоки хоризонтални кладенци, в тесни газови резервоари, като същевременно се подобрява ефективността на пробиване.