

## Mesophase Chemistry for Enhanced Cleaning of Oil-Based Sediments

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### Abstract

Cleaning tanks and mud pits with oil-based sediments is a challenging task that requires large amounts of energy and generates large volumes of waste that are problematic for disposal. The duration of the cleaning operation is particularly critical as the assets cleaned (storage tanks, boats, rig tanks, etc.) represent direct or indirect costs to the owner when not in operation.

Current cleaning solutions are not efficient and require many hours of labor to complete a single cleaning job. Operators and service companies have successfully used mud as a cleaning fluid, but the applicability of this solution is limited by large increases in the volume of new mud, the availability of space to store the mud, and the erosion of wet parts in the system.

A water-wetting mesophase fluid formulation has been developed that quickly fluidizes oil-wet solids in the water phase. This reduces the time for cleaning the tank, a critical success factor for an economically feasible operation. The new product is evaluated and compared against incumbent products in the field. Unlike other cleaning solutions, the mesophase product shows no negative effect when used in sea water.

Laboratory results on interfacial tension measurements, contact angle measurements and bottle cleaning tests are presented to show the cleaning efficiency of the mesophase product. Contact angle measurements show a complete change from an oil-wet surface ( $>70^\circ$ ) to water-wet surface ( $< 20^\circ$ ) when cleaned with the novel mesophase fluid formulation.

### Introduction

The removal of oil-based sediments in storage tanks, mud pits and mixing tanks at the mud plant and at the rig pose one of the biggest challenges for cleaning crews. Traditional methods require many man hours, generate a large volume of waste and can potentially expose cleaning crews to hazardous solvents and fumes. Often times, removal of the sediments require the worker to enter the tanks, a situation that can be extremely dangerous, especially in confined spaces and hot weather.

One commonly used method includes using base oil to break up the oil-wet solids and then re-using the contaminated oil to build new mud. This method can lead to excess inventory and therefore requires additional storage space. Another method is to use high-pressure water jetting to break apart oil-based residue. This method requires hours of continuous pressure washing and leads to a large amount of waste water. Disposing of this waste adds additional cost to the total cleaning operation.

The use of washing solvents, together with pressure washing, have made the tank cleaning process a little more efficient, but the amount of time required and waste generated is still of great concern.

The industry is in great need for an effective cleaning solution that is easy to use, fast acting and environmentally friendly. The availability of advanced formulation and evaluation methods now enable us to systematically develop products specifically for the oil industry. In this paper, we demonstrate the use of Interfacial Tension (IFT) measurements, contact angle measurements and bottle cleaning tests to selectively design an effective mesophase treatment for cleaning oil-based sediments in mud pits and tanks.

### Laboratory Evaluation

A mesophase cleaning product (MCP) has been formulated and optimized by measuring the IFT between the cleaning product and the base oil. For the best cleaning performance, it is desired to have the lowest possible IFT. The product is further evaluated by measuring the contact angle of a water drop on surface exposed to the oily sediments and then comparing the contact angle after the substrate is treated with the mesophase cleaning product. Contact angle measurements provide a good visual verification of change in surface wettability from oil-wet to water-wet. Moreover, this laboratory test indicates if a particular treatment fluid will make the solids water-wet and easily dispersible. Finally, the products were evaluated using a bottle cleaning test. For comparison purposes, a generic cleaning product was also tested.

### Formulation and Interfacial Tension Measurements

A number of new surfactant blends formulated with fresh water and sea water were developed. In general, land rigs have access to freshwater while offshore rigs have seawater readily available. Consequently, a blend should be able to clean in both aqueous phases. Invert emulsion drilling fluids contain a base oil external phase with an aqueous, often brine internal phase. The source of the oily residue comes from the nature of the base oil itself. As the oil from the drilling mud is cleaned, the internal phase is released adding cations (hardness) to the mix, complicating the cleaning process. While there are hundreds of mud/base oil/brine combinations, the MCP formulation was selected because of its ability to exhibit low IFT properties at a low concentration with varying degrees of hardness and for a wide range of oils.

**Figure 1** shows the dynamic IFT measurement of the 0.5% and 2% surfactant solution with a series of base oils. According to **Figure 1**, the mesophase cleaning fluid is able to produce low IFT in a range of  $10^{-1}$  to  $10^{-4}$  mN/m with the oils studied.

### Contact Angle Measurements

Contact angle measurements are a good indicator of a treatment fluid's ability to change oil-wet surfaces to a water-wet state. The cleaning performance of the MCP was assessed using contact angle measurements. A 14lb/gal synthetic-based mud (SBM) was used to treat the glass slide to make the surface oil-wet. **Figure 2a** shows the SBM coated glass slide and the corresponding contact angle is shown in **Figure 2b**. The contact angle for the SBM treated substrate was measured to be greater than  $70^\circ$ . The SBM treated slide was then rinsed with a 3% MCP solution. Additionally, SBM treated slides were also washed with a treatment fluid currently used for cleaning mud tanks and pits in the industry. **Figure 3a** shows the contact angle after rinsing with 3% MCP solution. The contact angle of  $\sim 15^\circ$  indicates the MCP is efficient in cleaning the oil-based residue and in increasing the wettability of the substrate; as a typical contact angle of a clean glass substrate is approximately  $\sim 25^\circ$ . **Figure 3b** shows the contact angle measurement for conventional cleaning product. The contact angle indicates that the surface remains oil-wet after the treatment.

### Bottle Cleaning Tests

Further performance testing was conducted using the bottle cleaning test. An 18lb/gal oil-based mud was prepared, and the laboratory sample vials were coated with the mud as shown in **Figure 4**. The vials were stored in the oven at  $150^\circ\text{F}$  for 3 hours. Water, MCP and other generic cleaning products were added to each vial, and the vials were agitated for 1 minute. The contents from the vials were poured out and then rinsed with a steady stream of water. **Figure 5** shows the vials after the final water rinse. **Figure 5a** shows poor cleaning for the vial treated with tap water, as expected. Slight improvement is observed when the mud-coated vial is washed with 6% of a generic wash solution (see **Figure 5b**). Under the same washing conditions however, **Figure 5c** show that 3% MCP solution leaves very little residue on the side of the vial. A final water rinse of the vials treated with 6% generic wash solution and 3% MCP solution indicate that the latter is more efficient in changing the wettability of the oil-based solid residue to water-wet. **Figure 6a** and **b** show images of the vials after final water rinse for 6% generic wash solution and 3% MCP solution, respectively. The results clearly indicate that the MCP treatment is very effective in cleaning oil-based sediments from the glass vials.

The performance of the wash solution was also tested in salt water as in many remote areas fresh water may not be readily available. The performance of MCP was not affected when using sea water, whereas the performance of the generic wash treatment was observed to be significantly reduced. **Figure 7a** and **b** shows the glass vials after rinsing with generic wash solution and MCP in sea water, respectively.

### Effect of MCP contamination on the Mud properties

There are concerns about the possibility of cleaning products contaminating the mud in an event of accidental release. Many products have shown a negative effect on the electrical stability (ES) of the oil-based mud, i.e., weakening the emulsion in the oil mud. **Figure 8** shows the effect of MCP contamination on electrical stability of the mud. There was no significant change observed in the ES of the mud for up to 5 lbs per bbl contamination. The ES decreased only by 50 points when more than 15 lbs per bbl are added to the mud. The amount of MCP used in contamination studies is significantly larger than what would be experienced in the field. The reduction in ES was easily recovered by adding 0.5 lb per bbl of emulsifier.

### Field Test

To validate the laboratory testing results, the MCP was used to clean mud mixing tanks at a liquid mud plant (LMP) in Louisiana. The tanks are often used to make heavy muds and therefore contained large amounts of oil-based mud residue (see **Figure 9**). Approximately 100 bbl of fresh water were added to the 500 bbl capacity mixing tank, followed by 100 gallons of MCP (2.4%). The mixture was agitated using 3 gun lines for 30 minutes (**Figure 10**). The pill almost immediately turned muddy, indicating that it contained water-dispersed solids. The treatment mixture was transferred to an adjacent mixing tank that also contained oil-based mud residue. A fresh MCP pill was prepared in the first tank and then the mixture was agitated in both tanks to clean the oil-based residue. After additional mixing, the solution was drained from the tanks and inspected. **Figure 11** shows that the tank was significantly clean, especially in the areas where there was good mixing and agitation, **Figure 12**. More importantly, all of the solids were transformed water-wet and were easily moved with a water hose. Some solid residue remained under the gun lines where there was very low agitation. Even though these solids remained in the tanks, they were easier to break up and they dispersed when sprayed with water.

The use of MCP not only saved total time for cleaning the tanks it also helped minimize the amount of waste generated, which is normally a significant cost for the operator.

### Conclusions

In this paper, we have demonstrated the development and evaluation of a mesophase product for cleaning oil-based sediments. The product can be used both in fresh water as well as in sea water without compromising its performance. The MCP was tested in the field that effectively reduced the total time required to clean tanks containing oil-based residue. The MCP is effective at low concentrations and has no adverse effect on mud properties in the event of accidental contamination.

It is important to note that the performance can be greatly enhanced by having good mixing ability. The use of high-pressure water jets can be extremely beneficial in

cleaning hard-to-reach areas. Therefore, a mechanical means, together with this MCP treatment, can reduce additional cleaning time as well and enable cleaning around gun lines and in areas where there is poor or no agitation.

### Acknowledgments

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### Nomenclature

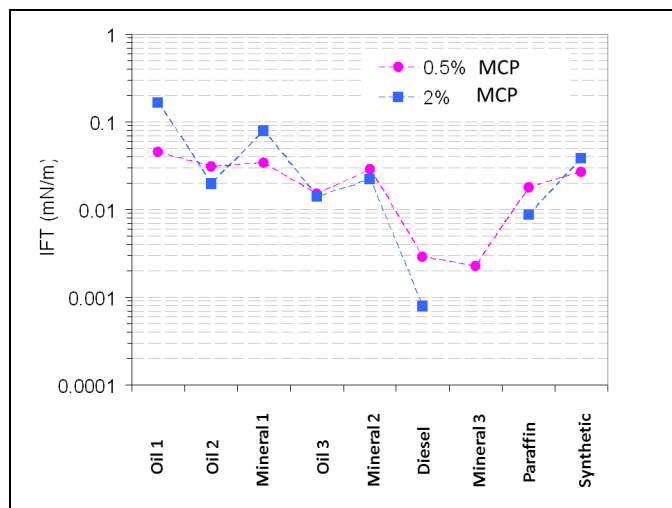
*MCP*= Mesophase Cleaning Product

*SBM*= Synthetic Based Mud

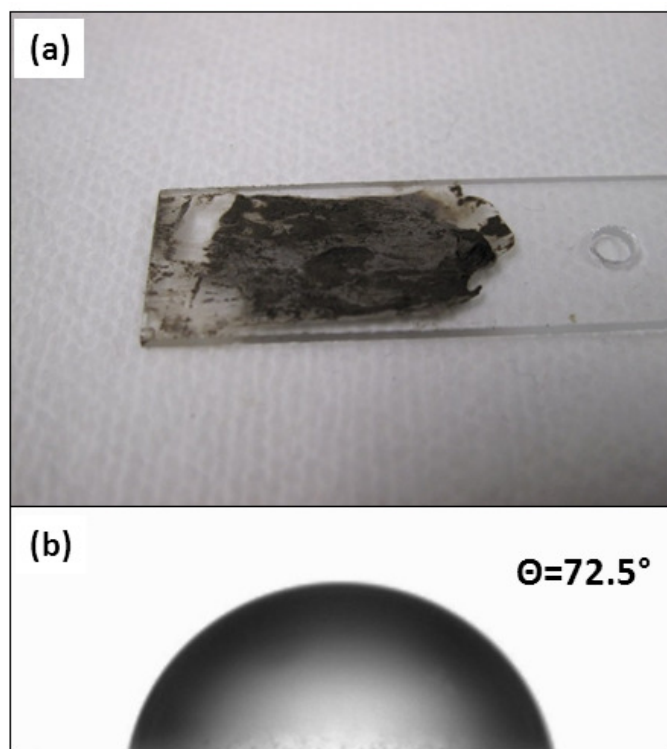
*IFT*= Interfacial Tension

*LMP*= Liquid Mud Plant

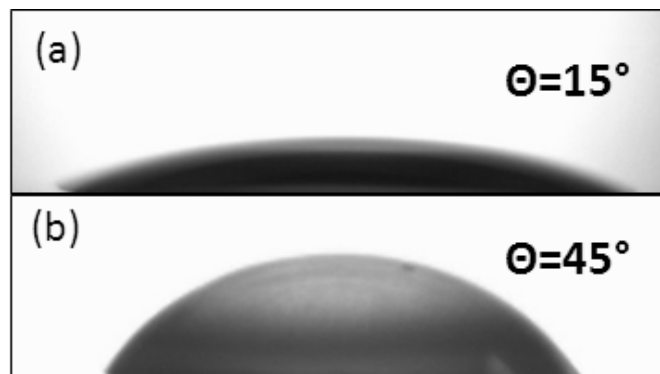
*Lb*= poundBbl= Barrels



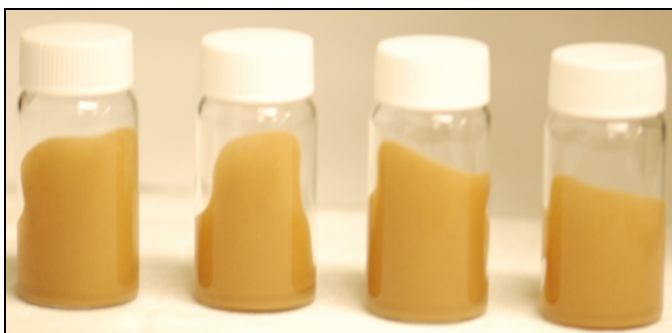
**Figure 1:** Dynamic IFT measurements of 0.5% and 2 % cleaning solution with various types of oils.



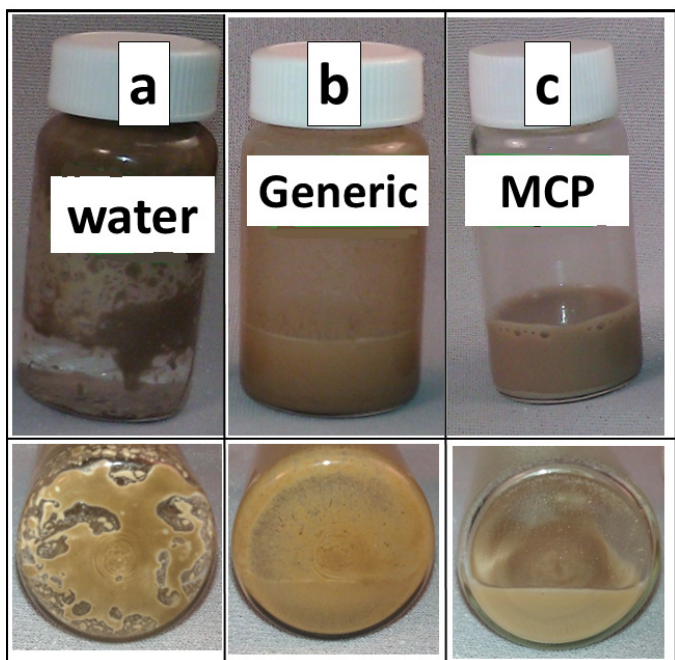
**Figure 2:** (a) SBM-treated slide and (b) contact angle of 73° was measured on the mud-treated slide.



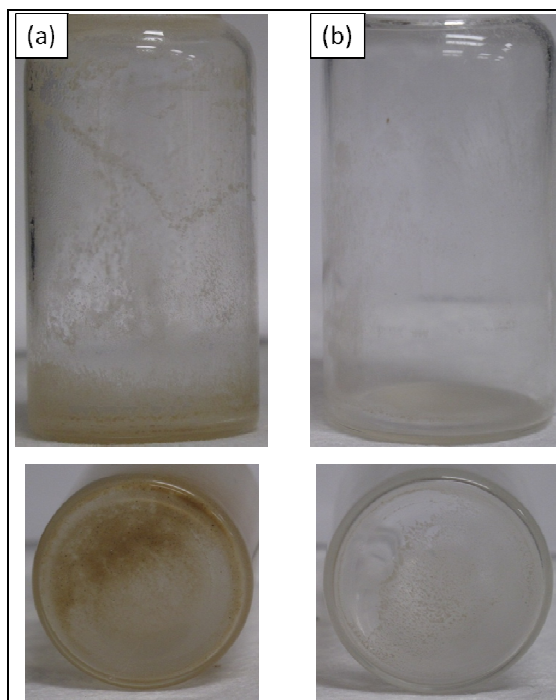
**Figure 3:** (a) The contact angle was measured to be 15° after the slide was treated with MCP and (b) 45° when treated with a generic cleaning product.



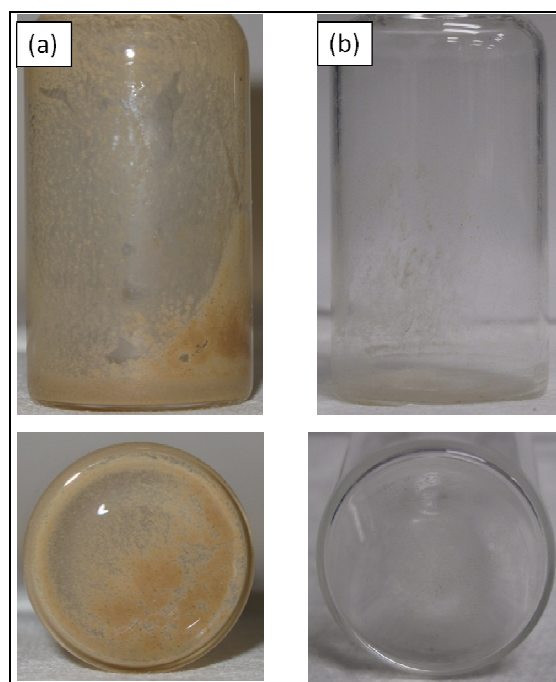
**Figure 4:** Glass vials coated with OBM and aged in an oven at 150°F.



**Figure 5:** SBM-coated vial treated with (a) water, (b) generic cleaning product and (c) mesophase cleaning product.

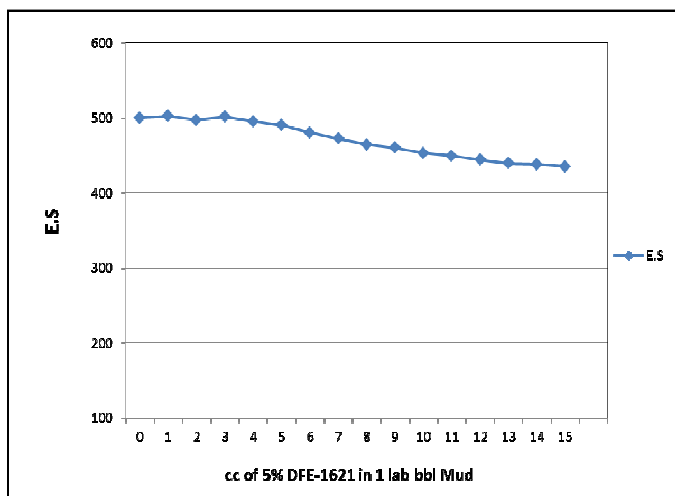


**Figure 6:** Glass vials rinsed with a steady stream of water after (a) treatment with generic cleaning product and (b) treatment with mesophase cleaning product in fresh water.



**Figure 7:** Glass vials rinsed with a steady stream of water after (a) treatment with generic cleaning product and (b) treatment with mesophase cleaning product. Both were formulated in sea water.





**Figure 8:** The effect of MCP contamination on the ES of the mud. No adverse affects is observed in the event of accidentally contaminating the mud with MCP.



**Figure 10:** MCP mixed inside the tank and agitated using the gun lines.



**Figure 9:** Oil-based mud residue settled in the mixing tank. Areas inside the tank have large sediment deposits accumulated over a period of time.



**Figure 11:** Inside the tank is considerably cleaner with solids easily dispersed in water.



**Figure 12:** Sides inside the mixing tank where there was maximum agitation were completely free from oil-wet sediments.