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Dispersion of High Viscosity Oils

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ABSTRACT 300275:

This study evaluated the effectiveness of three dispersants in simulated seawater on five different fuel oils (both intermediate fuel oils (IFOs) and heavy fuel oils (HFOs)) with viscosities ranging from 1,079 to 6,615 cSt and densities ranging from 0.995 to 0.998 g/cc. The three dispersants were COREXIT® 9500 dispersant, a dispersant under development by ExxonMobil – ED-6™ gel dispersant, and FINASOL™ OSR 52 dispersant. Testing was done at two dispersant-to-oil ratios (DOR) – 1:20 and 1:10.

All three dispersants were effective (70%+ dispersant effectiveness (DE)) for fuel oils with a viscosity less than 2,000 cSt - IFOs 180 and 380. The dispersants were less effective (16 to 58% DE) for the higher viscosity oils (ranging in viscosity from 4,258 to 6,615 cSt). Increasing the amount of dispersant from a DOR of 1:20 to 1:10 significantly improved DE. For example, the DE of the two HFOs studied increased from less than 42% to greater than 56% using COREXIT 9500™ dispersant.

The results of our bench-scale study indicate that dispersants can disperse heavy fuel oils and, therefore, could be a response option for spills of these products in a marine environment.

INTRODUCTION:

The application of dispersants, either subsea or on the surface is now a well-established technology that can attenuate the impacts of a marine oil spill. Dispersants act by breaking up a surface slick or subsea jet of oil into small droplets that are retained in the water column. This mitigates the impacts of a surface slick on marine mammals, birds, and turtles, and prevents spilled oil from reaching sensitive shorelines. The increase in surface area and the dilution that occurs after the small droplets disperse in the water column significantly enhances the ability of naturally occurring petroleum degrading microorganisms to biodegrade the oil.

There are rules of thumb that are often used to predetermine whether or not dispersants may be effective on oil spills. One of these is that the viscosity should be less than 10,000 cSt. Many oils, particularly fuel oils, may rapidly weather into this viscosity range within a few hours after a spill – particularly a spill in cold water. Hence, dispersants are typically not often considered for spills of many fuel oils. Fuel oil spills, however, are significantly more common than crude oil spills (Etkin, 2006). Also, this rule of thumb was developed several decades ago and modern dispersants have been developed to be more effective on viscous oils.

There are a number of ways to assess dispersant effectiveness (DE) ranging from bench-scale tests to at-sea trials. Tests at all scales have limitations, however. At-sea trials have challenges of logistics, cost, permitting, and data collection. Large-scale wave-basin tests are generally considered to be most representative of at-sea trials (Belore et al, 2005) but they also have limitations. They may not simulate the natural spreading that occurs in the open sea (Nedwed and Coolbaugh, 2008) and it can be difficult and expensive to run a large number of tests. Bench-scale tests have more bias when compared with large-scale or at-sea trials. For the bench-scale tests, it can be challenging to match real-world mixing energies, and natural spreading may be compromised even further. Also, all dispersant-effectiveness tests have the artificiality of time. That is, tests are conducted for generally very short periods of time – usually <30 minutes. This time limit is not an issue for readily dispersed oils but it can become an issue for more viscous oils because they take more time to thin and disperse. In actual field conditions, there are no time limits on dispersion allowing viscous oils to disperse over many hours.

The results of any confined dispersant-effectiveness test may not be considered representative of expected real-world dispersion, particularly for viscous oils that need to spread thin to effectively disperse (Nedwed and Coolbaugh, 2008). Positive results from bench-scale tests can be considered a good indicator of dispersion at sea because restricted spreading may potentially negatively bias bench-scale results. On the other hand, negative or poor results of bench-scale tests may not necessarily mean that dispersants will not work on viscous oil at sea. Keeping these limitations in mind, bench-scale tests, however, provide a useful screening tool for rapidly evaluating DE for a variety of crudes using multiple dispersants at varying dispersant-to-oil ratios (DOR).

Three widely used bench-scale test methods available to determine dispersant effectiveness (DE) are the ExxonMobil Dispersant Effectiveness Test (EXDET), the EPA's Baffled Flask Test (BFT) and the UK-developed Warren Spring Laboratory test (WSL) (Clark et al., 2005). Of these three test methods, SL Ross and MAR (2011) reported that EXDET test results most closely matched large-scale Ohmsett test results. All three bench-scale test methods were found to underestimate large-scale tests, with EXDET tests showing the least underestimation at 6-33%. Note that the primary difference between these three methods is the mixing energy imparted to the oil-water mixture, and Clark et al (2005) reported that the EXDET test has a mixing energy "intermediate of the range between the BFT and the WSL test." Clark et al (2005) further noted that the turbulent regime found in the BFT was equivalent to low-energy breaking waves.

This paper describes a study that used the EXDET test to evaluate the effectiveness of three dispersants on five different fuel oils (both intermediate fuel oils (IFOs) and heavy fuel oils (HFOs)) with viscosities ranging from 1,079 to 6,615 cSt and densities ranging from 0.995 to 0.998 g/cc. The three dispersants were COREXIT® 9500, ED-6™ (a dispersant under development by ExxonMobil) and FINASOL™ OSR 52, and were tested at two DORs – 1:20 and 1:10.

EXPERIMENTAL METHODS:

The EXDET test was performed by adding crude oil (1 mL) to a 250-mL separatory funnel containing artificial seawater with a salinity of 35 PPT (parts per thousand). Dispersant was then added to each separatory funnel at a DOR of 1:20 (50 µL) or 1:10 (100 µL) drop wise on top of the oil surface to ensure good contact between dispersant and oil. For our study, each test was run in triplicate and the room temperature was noted. The separatory funnels were mounted on a wrist-action shaker and mixed for 15 minutes. At the 15-min mark, while still shaking, a sorbent pad (1.0 inch square spill pad weighing approximately 0.15 g) was placed on the surface of the shaking mixture and shaking continued for an additional 5 min. After a total of 20 min of mixing, the water fraction was then collected in a 500-mL separatory funnel for extraction with methylene chloride. Methylene chloride (50 mL) was added to the water fraction and shaken for approximately 10 seconds and allowed to settle before the extract was collected. A second 50-mL extract was similarly collected and combined with the first extract and the absorbance of the composite noted using a UV-VIS spectrophotometer at 460 nm. Methylene chloride (50 mL) was also added to the original 250-mL separatory funnel containing the sorbent pad, and the funnel was shaken for 5 min before collecting the extract. A second 50-mL extract was similarly collected and combined with the first aliquot and its absorbance measured at 460 nm. If required, the extracts were diluted with methylene chloride to obtain readings in a linear range of measurement. The combined absorbance of the water and the sorbent pad extract were added and constituted 100% of the original undispersed oil. The ratio of the absorbance of the water extract to the combined total provided the fraction of dispersed oil or dispersant effectiveness.

Seawater (SW) was formulated using a commercially available sea salt to a salinity of 35,000 mg/L or 35 parts per thousand (PPT).

Properties of Oils Tested

Five fuel oils were studied that ranged in viscosity from just over 1,000 cSt to over 6,615 cSt at 25 °C, and ranging in density from 0.955 to 0.998 mg/L (Table 1). These represent a range of fuel oils that might be used in marine shipping. Some of these fuel oils are in the range of viscosities that might be considered non-dispersible or poorly dispersed based on the rule of thumb cited above.

Table 1. Properties of HFOs/IFOs studied

Oil	Density at 25 °C	Kinematic Viscosity at 25 °C
	g/mL	cSt (mm^2/s)
IFO 180	0.955	1,079
IFO 380	0.992	1,181
HFO 1	0.992	4,258
HFO 2	0.993	4,406
IFO 550	0.998	6,615

IFO – Intermediate Fuel Oil; HFO – Heavy Fuel Oil

RESULTS AND DISCUSSION:

DE results for the five fuels oils studied at a DOR of 1:20 using the dispersants COREXIT 9500®, ED-6™ and FINASOL™ OSR 52 are shown in Figure 1. IFO 180 and IFO 380, with viscosities less than 1,200 cSt at 25 °C were readily dispersed with a minimum DE of 70% with all three dispersants studied.

As expected, the DE was lower for the more viscous oils HFO 1 and 2 with a viscosity range of 4,258 to 4,406 cSt at 25 °C. FINASOL™ OSR 52 dispersant had a greater dispersion effectiveness (DE approximately 57%) than COREXIT 9500™ and ED-6™ dispersants (DE ranged from 28 to 42%) for the two HFOs tested.

For IFO 550, the most viscous oil tested, the DE was the lowest. However, COREXIT® 9500 and ED-6™ dispersants still had substantially equal dispersion effectiveness of greater than 40% for IFO 550.

Thus, the results of this study show that (1) no single dispersant was the most effective for all oils tested, and that some dispersants were more effective than others for certain oils, and (2) although viscosity in general is an important factor in determining DE, other factors such as the chemistry of the oil is also relevant in determining how well the oil may be dispersed. Also, considering the potential negative bias of these bench-scale tests, these oils may still readily disperse at sea as even the most viscous oil in our bench-scale tests was more than 40% dispersed using at least one of the dispersants tested.

The ED-6™ gel dispersant was designed to release surfactants slowly so as to be more effective for viscous oils. The 15-min duration EXDET test may not have been sufficiently long to allow ED-6™ dispersant to be fully effective, and that a longer duration test may show ED-6™ dispersant to be as/more effective than the other dispersants tested for these oils. Future plans include repeating these tests with a modified EXDET test that continues for more than 15 minutes and/or allows more time for the ED-6™ dispersant to soak with oil before initiating mixing.

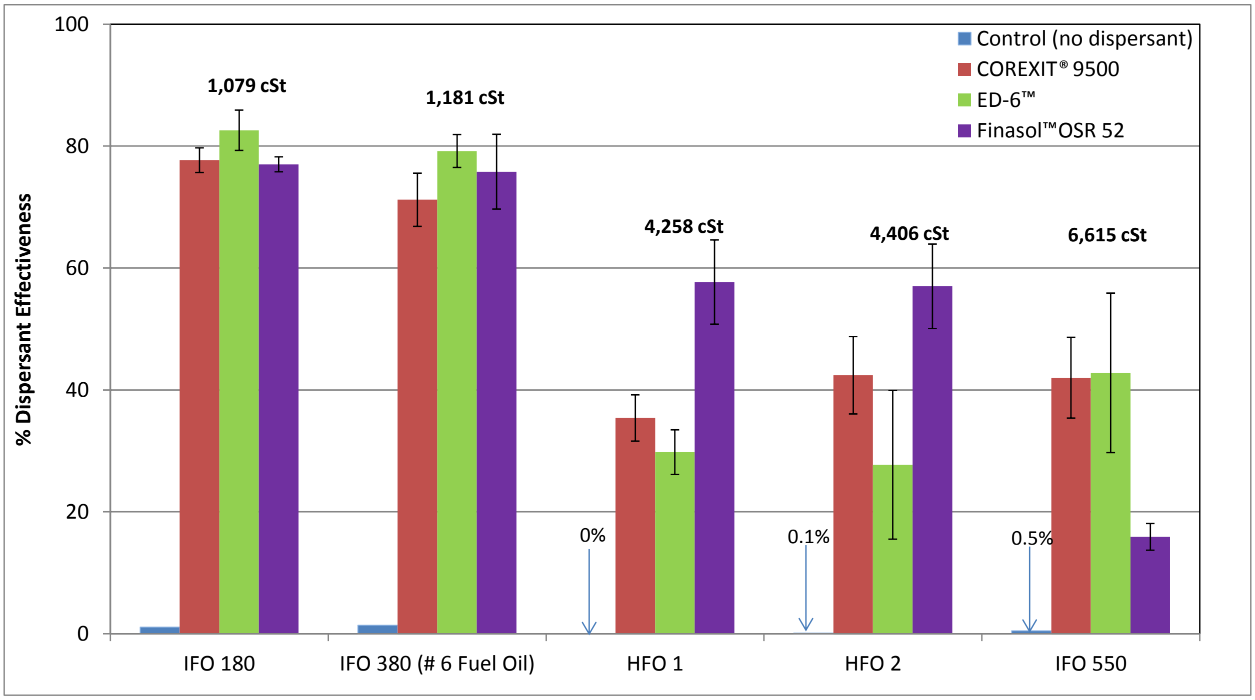

Figure 1. Dispersant effectiveness for five fuel oils at a DOR of 1:20.

The higher viscosity oils were tested at a higher DOR of 1:10 using COREXIT 9500™ and ED-6™ dispersants. At this higher DOR, the DE for both HFOs improved (see Figure 2) from about 40% or less at a DOR of 1:20 to greater than 55% at a DOR of 1:10. The DE of the IFO 550 however remained unchanged, indicating that viscosity may well be limiting DE and that a higher DOR application may not increase DE.

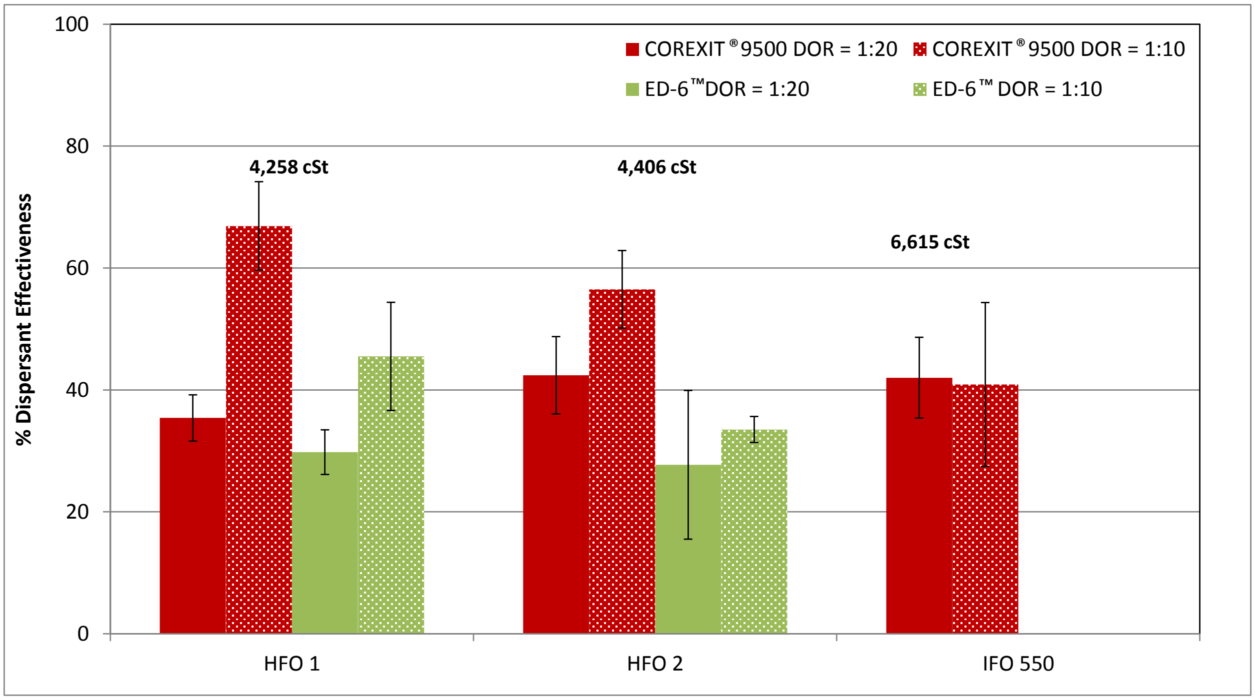

Figure 2. Comparison of dispersant effectiveness for higher viscosity oils at DORs of 1:20 and 1:10 using COREXIT® 9500 and ED-6™.

CONCLUSIONS:

The dispersants tested readily dispersed (greater than 70% DE) oils with a viscosity less than 1,200 cSt. For oils with a viscosity between 4,200 and 6,600 cSt, dispersants were less effective under the test conditions with DE ranging from 16 to 58% at a DOR of 1:20 and from 34 to 67% at a DOR of 1:10.

The results of these bench-scale tests showed that dispersants can disperse viscous fuel oils. A DE greater than 40% was achieved for IFO 550, the highest viscosity fuel oil tested in this bench-scale study. Considering the limited test duration and the limited spreading of oil in bench-scale tests, significantly greater than 40% dispersion may be achievable in a real spill. Thus, the results of this study support consideration of dispersants as an oil spill response option for marine spills of heavy/viscous fuel oils.

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