ASSESSING DISPERSANT EFFECTIVENESS FOR HEAVY FUEL OILS USING SMALL-SCALE LABORATORY TESTS

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ABSTRACT

Four bench-scale dispersant tests were used to evaluate three dispersants, Corexit 9500, Superdispersant 25 and Agma Superconcentrate DR 379 with an IFO (Intermediate Fuel Oil) 180 and an IFO 380. Dispersant effectiveness was assessed using the Swirling Flask Test (SFT) and Baffled Flask Test (BFT) developed by the U.S. Environmental Protection Agency (EPA), the Exxon Dispersant Effectiveness Test (EXDET) developed by ExxonMobil, and the Warren Spring Laboratory (WSL) test utilized in the United Kingdom. This study allows comparisons among the small-scale laboratory tests and provides a basis to compare dispersant effectiveness data with findings from at-sea field trials and wave basin studies conducted with the same dispersants and oils. No single dispersant preformed with the highest effectiveness under all test methods, but the data demonstrate that viscous oils such as IFO 380s could be dispersed under the right conditions. The results show that laboratory tests with greater mixing energy yield the highest estimates of dispersant effectiveness.

INTRODUCTION

A number of small-scale laboratory tests have been designed and utilized for a variety of purposes, most commonly, screening and/or comparing dispersant formulations for dispersant effectiveness under standardized conditions. Clayton et al. (1993) described various test systems used around the world, contrasted their design basis, and provided insights into why different systems provide different dispersant effectiveness results. While most test systems generally provide higher effectiveness data for easily dispersed oils, results can become highly disparate when testing more viscous products of heavy oils or weathered crudes or when attempting to correlate laboratory data with dispersant effectiveness observations from the field (MSRC, 1993; Fiocco et al. 1999a, 1999b). This paper summarizes results of a series of laboratory dispersant effectiveness tests conducted with heavy fuels and provides a basis for comparisons among test methods and with studies conducted in test basins and at-sea trials.

Four bench-scale dispersant tests were used to evaluate three dispersants, Corexit 9500 (9500), Superdispersant 25 (SD 25) and Agma Superconcentrate DR 379 (AGMA), with two heavy fuel oils. The test oils were an IFO (Intermediate Fuel Oil) 180 (viscosity 2075 cP at 15°C) and an IFO 380 (viscosity 7100 cP at 15°C). These dispersants and IFOs were the same materials tested in June 2003 at-sea field trials in the UK (Colcomb et al., 2005), and the October 2003 studies conducted at the MMS wave basin (OHMSETT) in Leonardo, New Jersey (Trudel et al. 2005).

Dispersant effectiveness was assessed using the Swirling Flask Test (SFT) and Baffled Flask Test (BFT) developed by the U.S. Environmental Protection Agency (EPA), the Exxon Dispersant Effectiveness Test (EXDET) developed by ExxonMobil, and the Warren Spring Laboratory (WSL) test developed and used in the United Kingdom. However, all dispersant/oil combinations were not tested with each bench-scale test method due to constraints of time, resources and programmatic focus. Nevertheless, the assemblage of laboratory data does allow useful comparisons among small-scale laboratory tests and provides a basis to compare with findings from the at-sea field trials and wave basin studies.

The SFT, currently EPA's official protocol for listing oil spill treatment products on the National Contingency Plan product schedule, and the newly developed BFT, which is being proposed as EPA's eventual replacement for the SFT, were both used as part of this investigation. Both IFO 180 and IFO 380 were tested at two different dispersant-to-oil ratios (DOR), 1:25 and 1:50, with 9500. SD 25 was tested only with IFO 380 at the same two DORs.

ExxonMobil Dispersant Effectiveness Test (EXDET) was developed by Exxon (Becker et al, 1991) to test dispersants using a moderate level of mixing energy. EXDET is a simple and effective screening method used by ExxonMobil to evaluate dispersant formulations and assess scores of test oils for R&D and contingency planning decisions. It was used to assess each IFO and each dispersant combination using DORs of 1:10, 1:25 and 1:50. A fourth dispersant, Corexit 9527, also was tested at these DORs to evaluate its efficacy against the other dispersant formulations.

The WSL test is used in the UK as the regulatory screen for dispersant effectiveness. For this paper, WSL tests were conducted as preliminary evaluations to assist in selection of test dispersants that could be effective on heavy oils. Oils for WSL tests were IFO 180 and 380 obtained from other sources and had properties slightly different from those IFOs used in the 2003 at-sea trials. The results are included in this paper as the data are likely representative of those for the at-sea test oils, and they provide insights into how the bench scale tests produce different results. Only Corexit 9500 was tested against the IFO 180 with the WSL, using a DOR of 1:10, 1:25, 1:50 and 1:100. All three dispersants were tested with the IFO 380 at DORs of 1:25, 1:50 and 1:100.

MATERIALS AND METHODS

SFT and BFT Tests

In the SFT test, the required quantity of pre-mixed oil and dispersant is added to the seawater in a swirling flask positioned on an orbital shaker (Clayton et al. 1993), then mixing the contents for 10 min, allowing a 10-min settling time, and then extracting the contents with dichloromethane (DCM) and measuring the concentration of oil dispersed in the water by spectrophotometry at three different wavelengths. The SFT recently came under scrutiny by the EPA because of the lack of reproducibility in the hands of different analysts (Venosa et al., 2002). Sorial et al. (2004a and b) conducted factorial experiments that produced data explaining why the SFT was poorly reproducible and repeatable. This research resulted in the development of a new test that EPA will soon be adopting as a replacement for the SFT, called the Baffled Flask Test (BFT), which uses a commonly available trypsinizing flask having four baffles in it. The irregular geometry of the BF results in an over-and-under motion of water flow somewhat more representative of the type of mixing that occurs from breaking waves at sea. The mixing regime was recently measured and compared with the turbulence in a wave tank capable of producing regular and breaking waves (Kaku et al., 2005; Venosa et al., 2005). Turbulence in the BFT was found to be equivalent to low energy breaking waves in the wave tank.

The SFT and BFT procedures are similar. In the standard SFT, dispersant and oil are premixed at a DOR of 1:10. A small volume, 100 µl, of the mixture is layered atop 120 mL of artificial seawater (Instant Ocean). The flask is shaken at 150 rpm for 10 min at 17°C, then allowed to sit quiescent for 10 min. After pouring off the first few mL from the spout flask, 30 mL is then extracted with DCM and the absorbance at 340, 370, and 400 nm read in a UV-visible spectrophotometer. The procedure is replicated 4 times.

The standard BFT differs slightly. First, 100 µL of oil is layered atop 120 mL Instant Ocean. Then, 4 µL or 2 µL dispersant (DOR = 1:25 or 1:50, respectively) is added carefully to the slick, taking care that the dispersant touches the oil first, not the water. The flask is placed on the orbital shaker and mixed for 10 min at 200 rpm, and then allowed to stand quiescent for 10 min. After draining the first 2 mL from the stopcock at the bottom, 30 mL is then drained and extracted as above. Analysis was by spectrophotometry as with the SFT. All tests are done in quadruplicate. Six-point calibration curves are set up for both methods, and response factors ranged between 90 to 110% of the mean in order to be accepted.

EXDET Test

The EXDET test (Becker et al., 1991) has a mixing energy intermediate of the range between the SFT and that of the Warren Springs test. EXDET is conducted using four 250 ml separatory funnels clamped to a standard Burrell Wrist-Action Shaker. The separatory funnels are filled with approximately 250 ml of seawater, and test oil is added to each. Dispersant is then added to the surface of the oil at the desired DOR. The funnels are shaken on the Wrist-Action Shaker for 15 minutes to disperse the oil in water. While still shaking, sorbent pads are then added to the water surface, and shaking is continued for an additional 5 minutes. The water is drained and the dispersed oil is extracted from the water with solvent. The non-dispersed oil remaining in the funnel and on the pad is then extracted separately.

The oil content of the two extracts is determined using a spectrophotometer at an appropriate wave-length setting (e.g., 460nm). The extracts are diluted to obtain a reading in the linear range, e.g., 0.1 to 1.1. The ratio of dispersed oil to dispersed plus undispersed oil is determined based on the dilution and absorbance measurement of each extract. The procedure is repeated for each pair of extracts, and the percent dispersed oil calculated for each. The average and standard deviation for the four data points (or more, if desired) are then calculated.

WSL Test

The WSL test method is based on a method originally devised by Labofina (Fina Limited's research laboratories) (Martinelli, 1984). 250 mL of synthetic seawater at 10°C is placed in a 250 mL separatory funnel, and the flask is placed in a motor-driven rack within a temperature controlled chamber at 10°C. 5mL of the test oil is placed on the water from a syringe, and a stop-clock is started. The oil is allowed to rest of the water surface for 1 minute. 0.2 mL of the test dispersant is then added from a syringe in a drop-wise fashion to the oil, the droplets of dispersant being added in a spiral fashion to ensure that the dispersant is distributed over the oil as evenly as possible. The stopper is placed in the flask. When the stop-clock indicates that 2½ minutes have elapsed (1 minute of the oil resting on the water surface, 1/2 minute to add the dispersant and 1 minute for the dispersant to soak in), the end-over-end rotation of the flask is started. The flask and its contents are rotated at 33 ± 1 rpm for two minutes. The flask is stopped in the vertical position and the contents allowed to stand for exactly one minute before 50 mL of the oily water is drained into a flask and collected in a 50 mL measuring cylinder.

The oily water is transferred to a 100 mL separatory funnel and extracted with dichloromethane and dried through solid anhydrous sodium sulfate. The absorbance at 580 nm is used to quantify the amount of oil with reference to a calibration graph for the test oil.

TEST RESULTS

Results from the SFT experiments are summarized in Figure 1. Based on the results of tests with the IFOs and Corexit 9500, it was clear that the SFT did not cause significant dispersion of either fuel oil. Maximum dispersion effectiveness for 9500 was measured at slightly more than 7% for IFO 180 and just under 5% for IFO 380. SD 25 was not tested with the SFT; rather, testing efforts were progressed to the higher mixing energy BFT.

Figure 2 summarizes results from the BFT with Corexit 9500 and Superdispersant 25. The Agma dispersant was not tested in the BFT system. The BFT generated much higher levels of dispersion for both oils compared to the SFT. In regards to 9500, decreasing the DOR from 1:25 to 1:50 resulted in a minor (4%) decline in effectiveness for the IFO 180 (Figure 2a). However, for the heavier fuel oil, IFO 380 (Figure 2b), the decline was much more significant (24%). SD25 dispersed IFO 180 slightly better than 9500 and IFO 380 slightly less effectively. A DOR of 1:50 was not studied for SD25. Nonetheless, it is clear that both dispersants were able to disperse both heavy fuel oils despite their high viscosity, with the IFO 180 more easily dispersible. The BFT demonstrated this dispersibility potential, but the SFT did not.

Dispersants were tested in the EXDET test at DOR of 1:10, 1:25, and 1:50. Corexit 9527 was added to the test materials to assess its effectiveness relative to 9500, which was developed for dispersing heavy and weathered oils. In addition to quantifying percent oil dispersed, we conducted a qualitative determination of the relative size of the dispersed oil droplets generated by each dispersant for the test oils. In all EXDET tests (Figures 3 and 4), 9500 gave the highest result (29%-64% for IFO 180, 19%-52% for IFO 380, over all DOR ranges). The SD 25 and the Agma product gave low results when tested at DORs of 1:50 and 1:25 (4%-18% for IFO 180, 4%-6% for IFO 380). At DORs of 1:10 on the IFO 180, Superdispersant 25 yielded 40% EXDET effectiveness while the Agma product result was 34%. Similarly, for IFO 380 treated at a 1:10 DOR, SD 25 result was 27% while Agma dispersant result was 18%. Corexit 9527 showed an intermediate result in the EXDET test (23% to 51% for IFO 180, 9%-34% for IFO 380, over all DOR ranges).

In all tests, the smallest dispersed oil droplets were observed for 9500 and the relatively largest droplets observed for SD 25 and the Agma product. Intermediate droplet sizes were observed for oils treated with 9527. These results are all qualitative, visual observations, without a reliable reference to specific droplet size ranges.

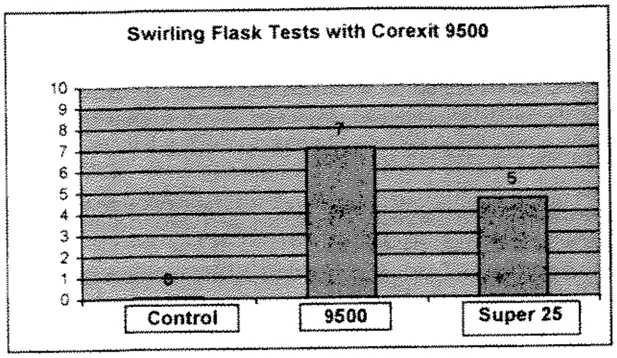

FIGURE 1. PERCENT EFFECTIVENESS OF COREXIT 9500 FOR IFO 180 AND 380 AS MEASURED IN THE SWIRLING FLASK TEST (SFT).

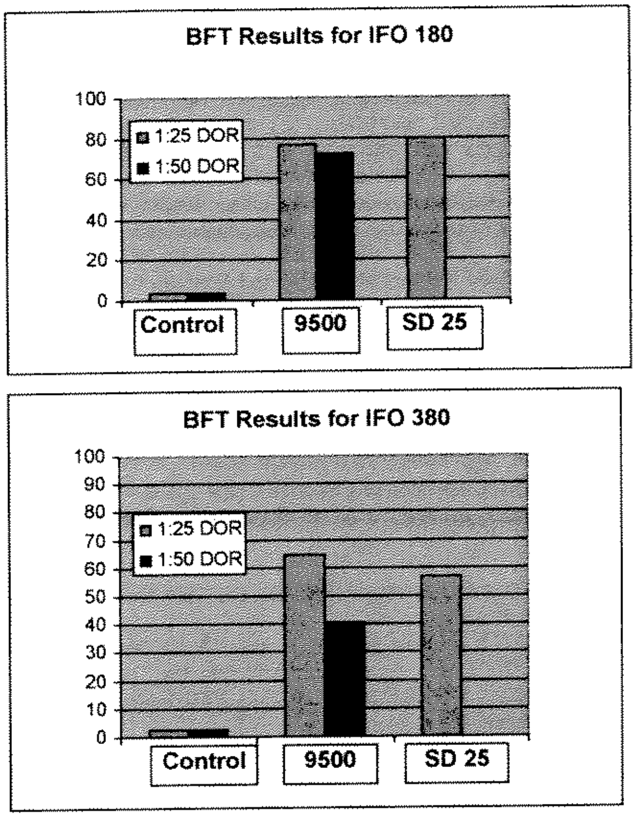

FIGURE 2A AND B. PERCENT EFFECTIVENESS OF C9500 AND SUPERDISPERSANT25 FOR IFO 180 (A) AND 380 (B) AS MEASURED IN THE BAFFLED FLASK TEST (BFT).

In the WSL tests, the IFO 180 was dispersed by Corexit 9500 with efficiencies greater than 60 percent for all DORs tested (Figure 5). Because the focus of the overall testing program was to find oil in a viscosity range that approached the limits of dispersibility, the focus moved to testing the heavier IFO with all the dispersants.

CONCLUSIONS

A comparison of the results from each test method for dispersants tested at a DOR of 1:25 shows the range of differences that various methods can generate (Figure 7a and b). Readers are reminded to apply any laboratory data with caution when making decisions for real world oil spill response. Laboratory testing along with wave basin and field studies can generate a higher degree of confidence in understanding the limits of dispersants in treating heavy oils. However, some of the simple processes used during controlled studies to ensure adequate mixing of oil and dispersant, uniformity of oil slick thickness, minimum overwashing of oil with waves, and other factors maximizing dispersant-oil interactions, may not be represented under real world conditions. This increases the degree of uncertainty when attempting to extrapolate laboratory test data to assess dispersant performance under actual spill conditions. In addition, studies such as those by Canevari et al. (2001) demonstrate that there are a wide range of differences in key physical and chemical properties of heavy oils, which can greatly enhance or reduce their propensity to be dispersed. Results of tests from only two IFOs can provide only some of the answers on limits of dispersing viscous oils.

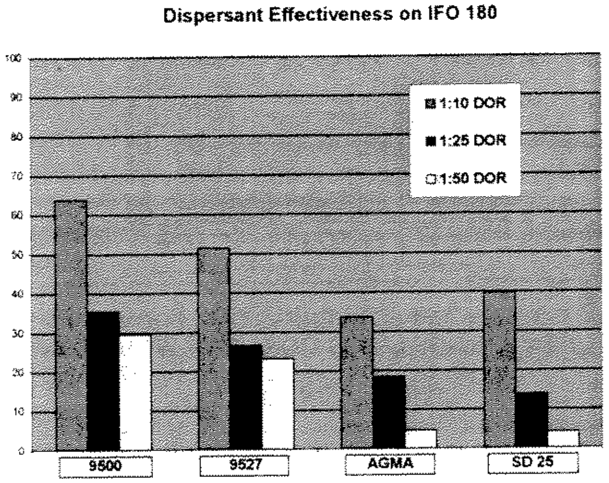

FIGURE 3 RESULTS OF EXDET TESTS WITH IFO 180 AND FOUR DISPERSANTS, COREXIT 9500, COREXIT 9527, SUPERDISPERSANT 25, AND AGMA DR 379.

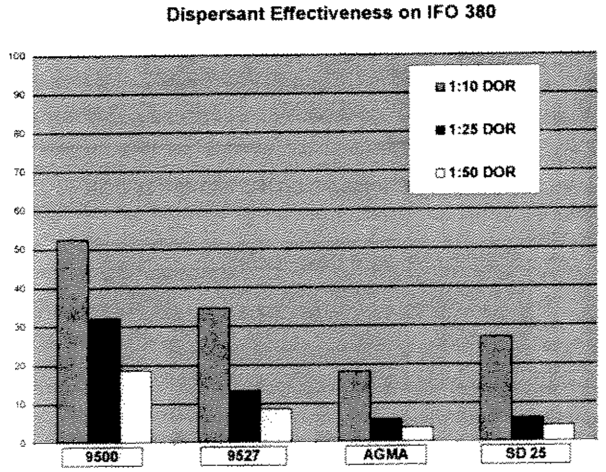

FIGURE 4. RESULTS OF EXDET TESTS WITH IFO 380 AND FOUR DISPERSANTS, COREXIT 9500, COREXIT 9527, SUPERDISPERSANT 25, AND AGMA DR 379.

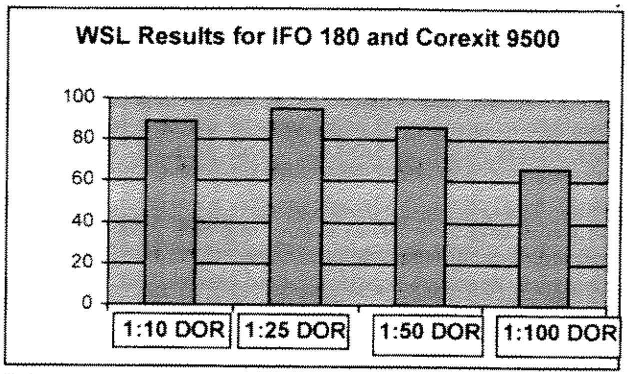

FIGURE 5. COREXIT 9500 EFFECTIVENESS ON IFO 180 USING THE WARREN SPRINGS LABORATORY TEST.

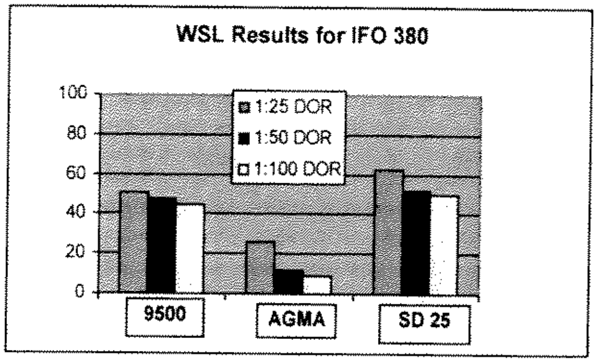

FIGURE 6. EFFECTIVENESS DATA FROM WARREN SPRINGS LABORATORY TEST WITH 3 DISPERSANTS, COREXIT 9500, AGMA DR 379, AND SUPERDISPERSANT 25.

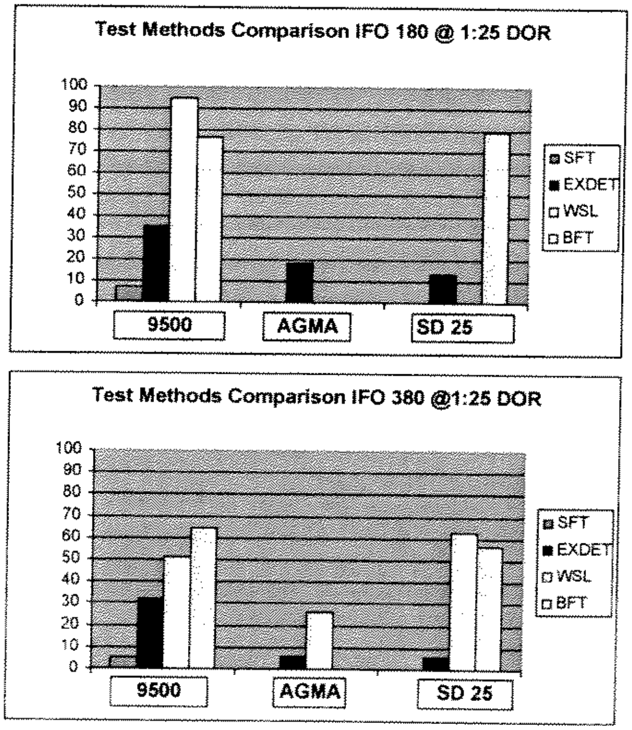

FIGURE 7. DISPERSANT EFFECTIVENESS MEASURED AGAINST IFO 180 (A) AND IFO 380 (B) USING STANDARD 1:25 DOR FOR COREXIT 9500, AGMA DR 379, AND SUPERDIPSERSANT 25.

As shown in Figure 7, no single dispersant preformed with the highest effectiveness under all test methods, similar to the findings of Clayton et al. (1993), MSRC (1993), and Fiocco et al, 1999a,b.). Overall, the results do show that mixing energy appears to be the predominant factor affecting dispersant effectiveness. The higher mixing energy in the BFT, compared to the SFT, produces effectiveness values that are similar to those produced in the WSL. The authors agreed that although lacking quantitative measures of mixing energy to compare the test methods, the BFT and WSL tests were somewhat comparable in mixing energy, and considerably more energetic than the SFT method, while the EXDET is at an intermediate level of mixing energy. Figure 7 shows that results from the EXDET method fall between those produced by the lower energy SFT and the higher energy BFT and WSL methods.

What is not yet known is how the mixing energy levels in these small-scale tests can be related to wave conditions at sea. It would be useful to be able to provide some level of correspondence between dispersant performance in simple laboratory tests and expectations of dispersant performance when applied to oil spills at sea. Because mixing energy is seen as a key factor in generating dispersed oil droplets, it is a variable of continuing interest. In these proceedings, Trudel et al. (2005) attempt to relate the performance of these dispersants against the two IFOs for laboratory, wave basin, and field trials. They showed that the best level of correspondence comes from using fairly generic assessments of mixing energy. Wave basin tests and field trials conducted with lower energy waves provide results closer to the intermediate mixing energy of the EXDET test, while higher energy test conditions in large systems generate data closer to the WSL and BFT data. Research by Kaku et al. (2004) and Venosa et al. (2005) is continuing in an attempt to address quantitatively the correspondence in mixing regimes between lab tests and wave tank tests.

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