Large Scale Comparative Testing of Corexit EC9500A, Finasol OSR 52, Accell Clean DWD, Marine D-Blue Clean, and ZI 400 at Ohmsett

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In October of 2015, the U.S. Department of Interior's Bureau of Safety and Environmental Enforcement (BSEE) conducted independent dispersant effectiveness testing to compare available formulations. Several products were tested at the Ohmsett facility. The study was conducted to better understand and compare the effectiveness of various dispersants under large scale test conditions. Five dispersants were selected from the EPA's NCP Product Schedule and tested on a Gulf of Mexico crude oil: Corexit® EC9500A, Finasol® OSR 52, Accell® Clean DWD, Marine D-Blue Clean™ and ZI 400. To capture operational effectiveness, the dispersants were applied to a surface slick using Ohmsett's spray bar, which simulated a boat spraying system. Data collected included droplet size distribution of the dispersed oil, measured at one and a half meters below the water's surface and using two LISST-100x instruments from Sequoia Scientific. Dispersant Effectiveness (DE) was measured using the volume of the oil, which remained on the surface after the test as compared to the total volume dispensed onto the surface for the test. The performance of the products was quantified and compared to each other based on DE and the droplet size of dispersed oil. Overall, Finasol and Corexit demonstrated the

best performance of the group of dispersants. Both dispersants were among the easiest to work with. Finasol and Corexit did not entrain any air while being pumped and maintained consistency throughout the tests. Accell, which demonstrated significant improvements when compared to the untreated oil, did exhibit operational difficulties during testing. Marine D and ZI 400 performed poorly relative to the other products tested.

INTRODUCTION

One of the major technologies available to planners and responders for oil spills is the use of dispersants. There has been over 30 years of previous dispersant effectiveness data collected through laboratory, wave basin, and field studies. The majority of these studies involved the use of one or more of the Corexit™ family of dispersant formulations. Recently, dispersant formulations, such as Finasol OSR 52 produced by Total Fluides of France and Accell® Clean DWD by Advanced BioCatalytics Corp., have seen increased domestic interest and are included in the Environmental Protection Agency's (EPA) National Contingency Plan (NCP) Product Schedule of approved technologies for oil spill response and mitigation. Accordingly, a need was identified to conduct comparative studies in dispersant effectiveness using multiple dispersant products.

This study compared the performance of five commercially available dispersant formulations, as measured by Dispersant Efficiency (DE) and the size distribution of dispersed oil droplets in the water column. These tests build on previous large scale tests conducted under simulated arctic conditions (Steffek, Bittler, & Guarino, 2016). The goal was to conduct repeatable, large scale tests to obtain performance data about each product. These tests were not meant to fully replicate any specific environmental or operational conditions. The results will aid BSEE and other federal agencies in their decision making regarding dispersant use in U.S.

waters. In addition to providing up-to-date performance data of the products, operational performance was also captured as a general discussion in relation to the ease of use, limitations, and concerns about the products witnessed during testing.

METHODS

Five dispersants were selected from the EPA's NCP Product Schedule and tested on a Gulf of Mexico crude oil. They include Corexit® EC9500A, Finasol® OSR 52, Accell® Clean DWD, Marine D-Blue Clean™ and ZI 400. Two of the products used in this study, Corexit and Finasol, represent large portions of dispersant stockpiles in the United States and Europe. These products have been used in actual spill events and have been studied extensively. As listed on the NCP Product Schedule, Corexit and Finasol have a reported effectiveness on South Louisiana Crude of 54.7% and 71.6% respectively. Accell is a product which BSEE felt was important to include it in this test program because a U.S. oil spill removal organizations (OSRO) now has a 5,000 gallon stockpile of it. As listed on the NCP Product Schedule, of the products tested, Accell has the highest effectiveness on South Louisiana Crude with 96.03%.

ZI 400 has a reported effectiveness on South Louisiana Crude of 89.8% and was chosen for consistency with a previous large scale test at Ohmsett (Steffek, Bittler, & Guarino, 2016). Marine D is one of the newest products listed on the NCP Product Schedule, it was first listed in 2012, and is reported as being among the least toxic dispersants when mixed with No. 2 Fuel Oil at a 1:10 dispersant-to-oil-ratio (DOR). On South Louisiana Crude, Marine D has a reported effectiveness of 55.6% on the NCP Product Schedule. All of the products used in this series of tests were purchased new, or were from the existing supply at Ohmsett and were less than two years old.

The oil used for this testing was a blend from the Hoover Offshore Oil Pipeline System (HOOPS). The constituent fields of HOOPS are Diana, South Diana, Hoover, Marshall, and Madison, and are located approximately 150 miles offshore Galveston in the western portion of the Gulf of Mexico (Exxon Mobil Corporation). The properties of the oil are shown in Figures 1 and 2.

Parameters	Method	Results
API Gravity	ASTM D287	34.0°
Flash Point, Closed Cup	ASTM D93	23.3°C (74°F)
Pour Point	ASTM D97	-30°C (-22°F)
Paraffin – wt% (percent by weight)	---	<0.01
Sulfur – wt%	ASTM D4294	1.36
Saturates – wt%	ASTM D2007	29.49
Aromatics – wt%	ASTM D2007	60.36
Asphaltenes – wt%	ASTM D2007	0.14
Polar Compounds (Resins) – wt%	ASTM D2007	10.0

Figure 1 - Test Oil Properties

Region	API Gravity	Sulfur Content
HOOPS	34°	1.66%
Gulf of Mexico, Gulf Coast Refinery Input	29-34°	1.2 – 1.8%

Figure 2 - API Gravity and Sulfur Content of the test oil as compared to the Gulf of Mexico. (U.S. Energy Information Administration, 2014)

All testing was conducted in the Ohmsett testing facility in Leonardo, NJ. Oil was applied through a manifold roughly 0.25 meters above the water's surface and dispersants were applied approximately 15 seconds later by a spray bar utilizing 8001 nozzles which produce a fan pattern. Dispersants were applied in their neat for with a target dose of 1:20 dispersant to oil ratio. The wave generator was set so that waves had a height of about one meter and every fourth to sixth wave was a breaking wave. The air temperature for these tests was 15.8°C with a standard deviation of 4.1, and the water temperature for these tests was 14°C with a standard deviation of 2.2.

Data collected included droplet size distribution of the dispersed oil, captured at one and a half meters below the water's surface using two LISST-100x instruments, as well as the volume of the oil which remained on the surface after the test as compared to the total volume dispensed onto the surface. LISST instruments, or Laser In-Situ Scattering and Transmissometry instruments, are used to measure the concentration of various particle sizes of a sample in a fluid medium. As the fluid carries the sample past the window of the instrument, the particles are hit with a laser. Depending on the size of the particles, the laser will scatter at specific angles, which the instrument then uses to determine the size of the particles and concentration of the particles in the sample being measured. For dispersant testing, these instruments allowed researchers to quantify the performance of each individual dispersant by quantifying the droplet size distributions of the dispersed oil into the tank water. For this test program, droplets sizes of 70µm or smaller are considered to be fully dispersed because they are assumed to stay suspended in the water column, whereas the larger droplets may resurface and coalesce into a new slick (National Research Council, 2005) (Lunel, 1993) (Neff, 1990).

Test Procedures

The test procedure was adapted from the Ohmsett dispersant effectiveness test protocol developed between 2000 and 2003 by MAR Inc. and SL Ross and documented in "Dispersant Effectiveness Testing on Alaskan Oils in Cold Water" (SL Ross Environmental Research & MAR Incorporated, 2003). Each dispersant was tested on the oil in three separate replicates, and three controls of untreated oil were distributed throughout the test schedule. The replications were intended to avoid confounding effects of weather changes, human error, operational variations, and property changes of the tank water. These items were controlled for in the analysis, if significant. Control runs were used for calculating the volume of oil lost to natural dispersion and the operation of the test itself. The same instrumentation used during the control runs was also used for the dispersant runs to establish a baseline oil concentration and droplet size distribution at the instrument depths. Additionally, the controls were used to determine trends affecting the test results, such as tank condition, weather, and operational changes.

Data Analysis

The LISST data, and measurements taken manually, were then analyzed using a program coded in R (R Core Team, 2014). For this study, the R program's options were set to treat the data in the following way:

- Raw LISST data is imported,
- The total measured concentration is calculated for each sample,
- A background value is established by taking the mean concentration of the first 30 samples for each test,
- All samples with a concentration less than twice the background value are removed to establish the lower limit of the oil plume data,
- The plume data from the two LISST devices are combined since they are run as redundant measurements,
- Based on the sample's concentration, a Grubb's t-test is used to remove statistical outliers,
- The mean and standard deviation values are calculated for the total concentration of oil, the d50 droplet sizes, and droplet size distribution for each test,

- The program then determines which tests are replicates based on user inputs and calculates the mean and standard error of all data captured by the LISST and measured manually.

All statistical analyses were also conducted in R. An Analysis of Variance (ANOVA) was performed to determine if there were significant differences between any of the treatments when considering other factors, followed by the Tukey Honestly Significant Difference (HSD) test to determine which pairwise comparisons were significant between different dispersant products and the control.

RESULTS

For dispersant effectiveness, a linear model was created using the treatment type and oil viscosity. It was found that treatment significantly impacted DE (ANOVA, F=2.5, df=5, p=0.084). This best-fit model explained 55.6% of the variation in DE. The influence of dispersant treatment alone explained 47.4% of the variation in DE in this study.

As reflected in Figure 3, Corexit and Finasol dispersed the highest percentage of the oil based on the average of three tests. As compared to the untreated control (DE=61.6%), the oil treated with Finasol demonstrated a 55.4% improvement for dispersing the surface slick into the water column (DE=95.8%). Finasol was the only dispersant which demonstrated a difference which was statistically significant to the control (Tukey HSD test, p=0.0975). Based on DE calculations, Corexit performed almost identically to Finasol with a DE=91.7%, which was a 48.8% improvement over the untreated. This difference was not statistically significant (Tukey HSD test, p=0.1707).

Accell demonstrated an improvement of 22.5% over the untreated control with DE=75.5% while ZI 400 demonstrated an improvement of 24.7% over the untreated control with

DE=76.89%. Lastly, Marine D averaged DE=73.4%, which is an improvement of 19.1% over the untreated oil. The Tukey HSD test showed that none of these differences were statistically significant to the control (p-values > 0.5). It is also worth mentioning that none of the dispersant treatments were statistically significant to another treatment in regards to DE.

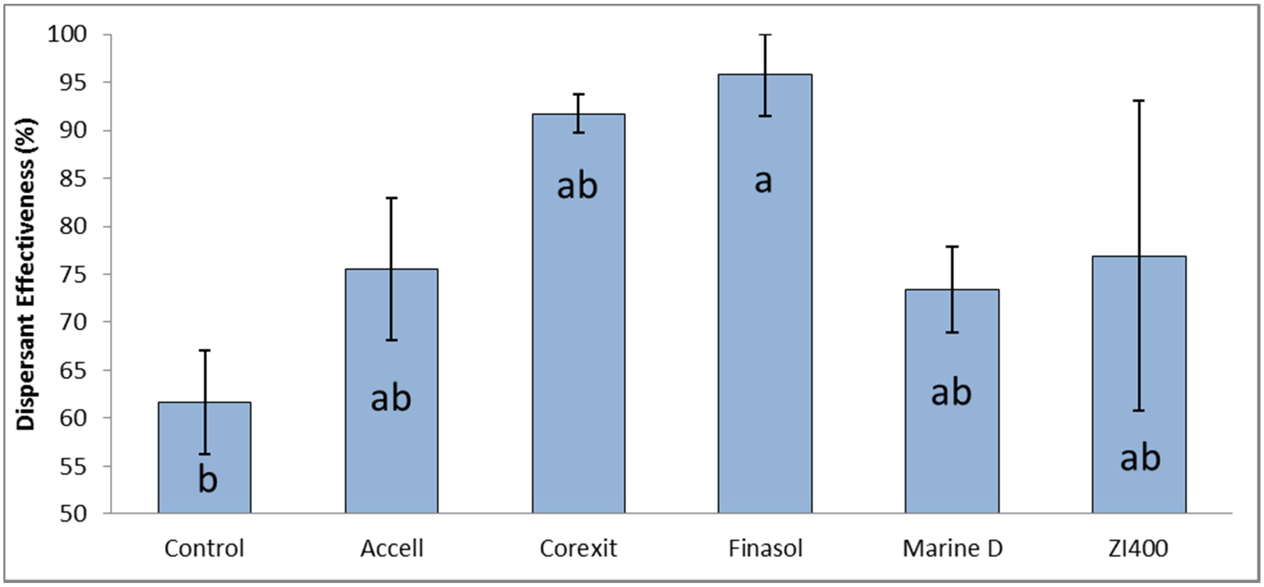

Figure 3 - Mean Dispersant Effectiveness (DE, %) of each dispersant treatment. Letters delineate statistically significant differences as measured with the Tukey HSD test (n = 3, α = 0.10). Group "ab" is not significantly different from groups "a" or "b".

Droplet size distribution (DSD) data was collected during each test using the LISSTs. This data allowed for the calculation of median droplets sizes, as well as determined what percentage of measured droplets fell below ≤ 70µm. For the distribution of oil droplets below 70µm, it was found that treatment and oil viscosity significantly impacted the distribution (Treatment - ANOVA, F = 8.6, df = 5, p = 0.001)(Oil Viscosity - ANOVA, F = 3.6, df = 1, p = 0.082). The best-fit linear model explained 79.5% of the variation in distribution data for these tests. The influence of dispersant treatment alone explained 73.3% of the variation while oil viscosity was 6.1% of the variation.

As shown in Figure 4, Finasol had a higher distribution of small droplet sizes (<70µm) over the other products. A Tukey HSD test found that Finasol produced a significantly higher percentage of droplets below 70µm than the control (p=0.005), Marine D (p=0.051) and ZI400 (p=0.070). Corexit, which had effectiveness similar to that of Finasol, also had a similar droplet size distribution. Corexit produced a significantly higher percent of droplets below 70 µm than the control (p=0.017). Accell Clean DWD was not as effective as Corexit or Finasol, but the droplet size distribution reveals that the oil that was dispersed consisted of a large percentage of very small droplets. Accell produced significantly higher percentage of droplets below 70 µm than the control (p=0.010). However, both Accell and Corexit were not significantly different than any of the other products.

Marine D and ZI 400, which demonstrated no improvement over natural dispersion as measured by DE, demonstrated cumulative distribution curves similar to the untreated oil and did not have significantly higher percentage of droplets below 70µm than the control (p=0.746 and p=0.641), nor were they significantly significant from Accell and Corexit.

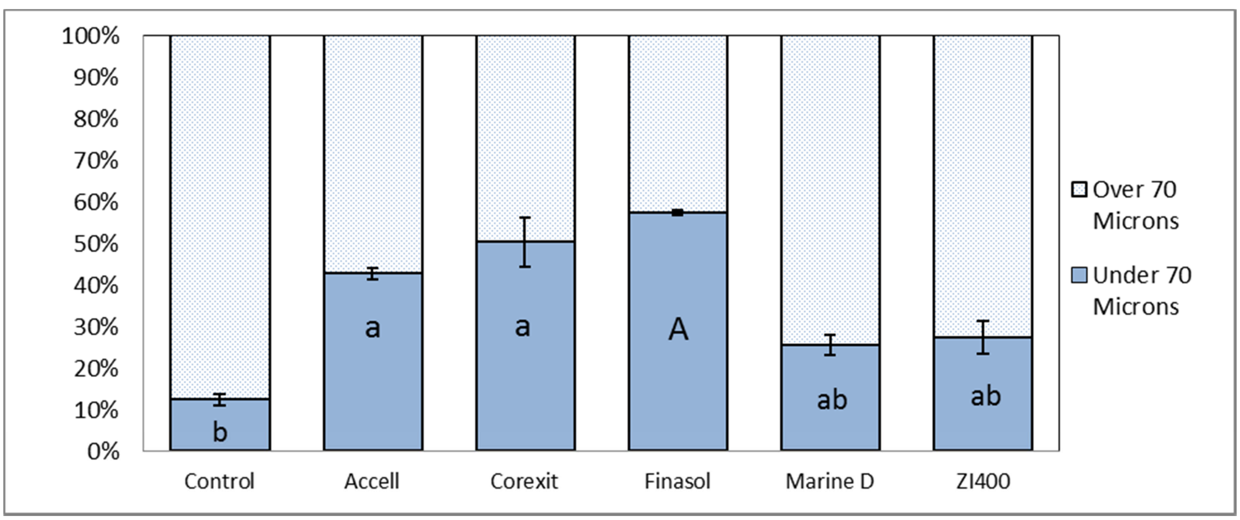

Figure 4 - - Simplified droplet size distribution with two particle size ranges, 2.5-70µm and 70-500µm. . Letters delineate statistically significant differences as measured with the Tukey HSD test (n = 3, α = 0.10). Group "ab" is not significantly different from group "A".

The R program used to analyze the raw LISST output files is able to calculate the median droplet size (d50) for each data sample (based of the range of droplet measured by the LISST).

This can be used to calculate the mean d50 for each test and therefore each treatment. This is summarized in Figure 5. The average median droplet size for the control tests was 200.2±40.8µm. ZI 400 was essentially equivalent with a median droplet size of 203.1±99.7µm. Corexit, the largest reduction in median droplet size with 74.7±19.3µm. None of these results were found to be significant (p<0.100) by the Tukey HSD test.

Product	Median Droplet Size, d50 (µm)	Standard Error
Control	200.2	40.8
Accell	100.8	21.4
Corexit	74.7	19.3
Finasol	111.2	24.3
Marine D	141.3	41.0
ZI 400	203.1	99.7

Figure 5 - Median Droplet Sizes

In addition to the summarized relative DSD presented in Figure 4, the concentration data reported by the LISSTs was summarized into a droplet size bin (2.5-70 µm). As a performance metric, this provides a more comprehensive representation of dispersant performance than DE or relative DSD alone. This single bin represents the mean concentration of oil (measured as volumetric parts per million, ppmV) within the measured population of droplets below 70µm. These values are shown in Figure 6.

For the concentration of oil within the population of droplets below 70µm, it was found that only treatment significantly impacted the concentration data (ANOVA, F = 7.8, df = 5, p = 0.002). The best-fit linear model explained 77.4% of the variation in distribution data for these tests. The influence of dispersant treatment alone explained 73.5% of the variation.

The control tests generated a concentration of oil below 70µm of 1.3ppmV. Of the dispersants tested, Finasol and Corexit generated the highest concentration of oil below 70µm (Finasol=16.9ppmV, Corexit=16.6ppm). The increase in concentration from Finasol and Corexit was significantly different from the control (Finasol-Control, p=0.004)(Corexit-Control, p=0.005), and was significantly different from Marine D and ZI 400 (p<0.1).

Accell generated a concentration of oil below 70µm of 10.5ppmV, which was significantly different than the untreated oil (p=0.085) but was not significantly different than any of the other dispersant products. Marine D and ZI 400 generated the lowest concentration of the dispersants (Marine D=6.2ppmV, ZI 400=6.6ppm), which was not significantly different from results from the control tests.

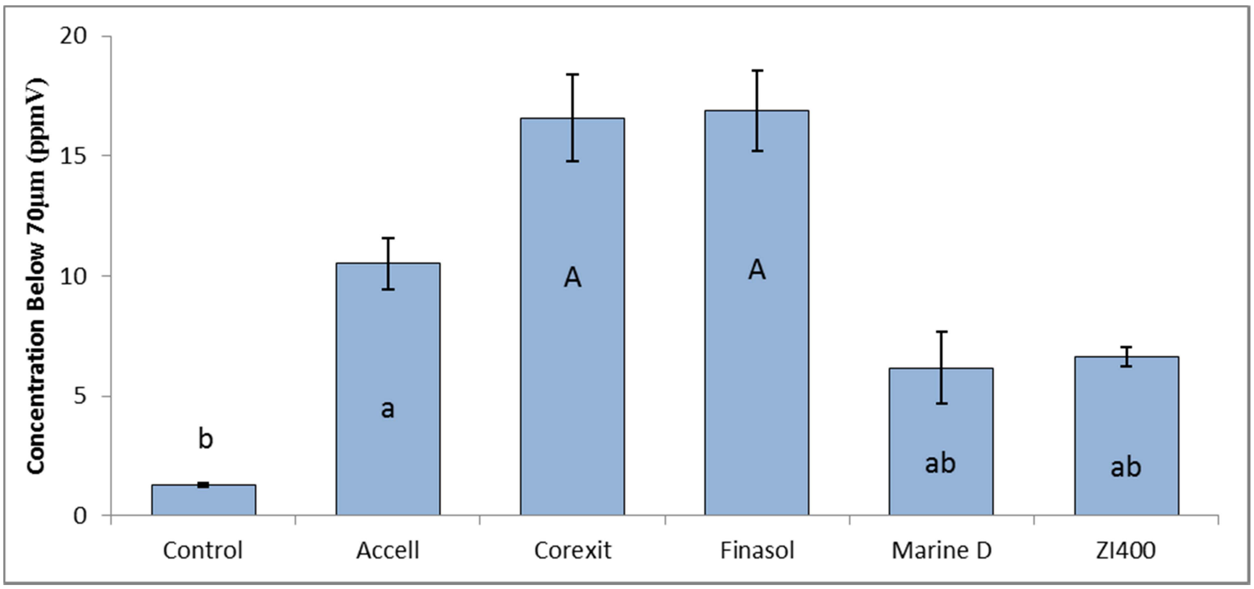

Figure 6 - The mean concentration of oil droplets less than 70 µm in size (ppm volume) as a function of dispersant treatment. Letters delineate statistically significant differences as measured with the Tukey HSD test (n = 3, α = 0.10). Group "ab" is not significantly different from groups "a" or "b" but is significantly different from group "A".

General Observations about Each Product

Separate from the quantitative data collected, observations were made about each products usability and behavior. While circulating Corexit and Finasol through the Ohmsett pumping system, they produced no foam and sprayed evenly for all replicates. Visually, the resulting oil droplets dispersed deep into the tank and amount of oil that initially resurfaced after the waves were turned off was minimal compared to the other products. Two of the Finasol tests resulted in too small a volume of undispersed oil to be reasonably collected.

Accell entrained air while circulating through the pumping system. This proved to be problematic due to the increased pumping pressure required to spray the product through the nozzles. Additionally, one of the tests was cancelled when the product began to gel and become too viscous to flow. The temperature of the dispersant at this time was 13-14°C. This was interesting because there were no flow issues with this product during a previous test program conducted in freezing conditions (Steffek, Bittler, & Guarino, 2016).

Marine D and ZI 400 created a large amount of foam on the surface of the liquid in the reservoir. This foam was very stable and continued to grow without intervention. This foam did not affect the liquid product in the reservoir or the performance of the product. This created handling and metering problems throughout the test program. Also, both of these products had either small bubbles or mist which would rise above the application system rather than fall onto the oil slick. It is worth noting that these two products are also the least viscous of the dispersants tested and this may have led to a much finer droplet when passing through the nozzles. The dispersions created by Marine D and ZI 400 appeared to be much more superficial than those of Corexit and Finasol. The oil would break up and spread along the surface, but did not appear to disperse deep into to the water. There was also much more oil resurfacing after the test was completed as compared to the other products.

The control tests demonstrated higher than expected natural dispersion. At the same time, the LISST data shows that the created plume was made up of very large droplets. These results are captured in the same way as tests which included dispersant application and are reported as such.

CONCLUSIONS

The goal of this test program was to conduct comparative dispersant effectiveness testing at the Ohmsett facility in an effort to capture both qualitative and quantitative data for multiple commercially available dispersant products. Based on the metrics captured, the following conclusions can be made:

Corexit and Finasol produced the highest average DE, but only Finasol was significantly higher than the control ($p = 0.0975$). While Corexit did not perform at a level statistically significant from the Control treatment, the improvement in performance over the control was strong. Accell, Corexit and Finasol all produced significantly greater proportion of droplets under 70 µm compared to the Control (Accell: $p=0.010$, Corexit: $p=0.017$, Finasol: $p=0.005$)

Overall, Finasol and Corexit demonstrated the best performance of the group of dispersants. Both dispersants were among the easiest to work with. Finasol and Corexit did not entrain any air while being pumped and maintained consistency throughout the tests. Accell, which demonstrated significant improvements when compared to the untreated oil, did exhibit operational difficulties during testing.

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