Corexit 9500 DISPERSANT EFFECTIVENESS TESTING IN COLD WATER ON FOUR ALASKAN CRUDE OILS

For

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By

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Disclaimer

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Executive Summary

The objective of the study was to complete effectiveness tests on Alaskan crude oils using Corexit 9500 dispersant and to compare the results to earlier experiments where Corexit 9527 dispersant was used.

The test equipment and test procedures used in the testing were the same as those used in 2006 and documented in the 2006 report available at www.mms.gov/tarprojects/568.htm.

Four Alaskan crude oils were used in the test program. They were Alaskan North Slope (ANS), Endicott (End), Pt. McIntyre (PtMc), and Northstar (NS) and crude oils. ANS is a blend of crude oils from the various Alaska North Slope fields, whereas the other oils are specific to their production areas. Oils were tested fresh and weathered by the removal of light ends using air sparging. The viscosities of the test oils ranged from a low of 6 cP for fresh Northstar crude to 520 cP for the weathered Endicott oil.

The target dispersant-to-oil (DOR) ratio for all experiments was 1:20. Due to oil spreading differences this was not always achieved. DOR estimates ranged from as high as 1:16 to as low as 1:25.

A total of 9 control (no dispersant applied), 10 Corexit 9500 experiments and 2 Corexit 9527 experiments were completed in the test program. Thirteen of the experiments were conducted between January 30 and February 6, 2007 and the remaining eight experiments were completed between March 13 and March 15, 2007.

Dispersed oil drop size distributions were measured using a LISST 100 particle size analyzer. In-water oil concentrations were estimated using a LISST 100 particle size analyzer and a Turner Designs TD3100 oil-in-water analyzer. The LISST 100 device and water sampling pump were positioned at 1.5 meters below the calm water level.

Dispersant effectiveness was estimated by collecting the surface oil remaining on the tank surface immediately after the completion of the experiment and comparing the amount collected to that discharged at the beginning of the experiment.

The Corexit 9500 dispersant was effective in all of the experiments and resulted in very high oil removal in all experiments. In all of the chemically treated experiments the %Dispersed/Lost estimates exceeded 93%.

For all of the successful dispersion experiments the average of the LISST oil particle size volume median diameter measurements (D50s) were below 75 microns. The control experiments all had D50s that were greater than 150 microns. The average oil concentrations in the chemically treated experiments were consistently higher than the control experiments and the drop sizes in the high concentration regions were always smaller in the treated experiments. The peak oil concentrations in the treated experiments also were consistently higher than the control experiments. The LISST 100 oil concentration estimates agreed well with those measured using the Turner TD3100 oil-in-water analyzer.

A Sontek Horizon ADV velocity probe was deployed at 1.5 meters below the calm water surface and used to measure X-Y-Z water velocity fluctuations during each experiment. The velocity data from all experiments was processed by removing single spikes from the records based on a threshold of two standard deviations and then calculating the average kinetic energy (TKE). The TKE value was determined for up to 4 measurements or data collection bursts in each experiment and these values were then averaged to determine a final representative TKE for each experiment. The average TKE for the test series was 205 with Standard Deviation of 39.

The estimates of non-control corrected dispersant effectiveness (DE) for all crude oils were very similar in the 2006 and 2007 test programs with both Corexit 9500 and 9527 achieving greater than 90% dispersion in all experiments. Two experiments were completed in 2007 with Corexit 9527 to address previous in-consistent results in 2003 and 2006 on the

weathered Endicott and Northstar oils. The low dispersion estimates measured for these two oils in 2003 appear to be erroneous based on the 2006 and 2007 results.

The averaged volume median drop diameters (D50) of the oil drops in the dispersions generated for similar oils by Corexit 9527 (from 2006 test program) and by Corexit 9500 (from the 2007 testing) do not show any trend of smaller oil drop sizes generated by either of the two dispersants.

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1.0 Background

Five Alaskan crude oils including Alaskan North Slope (ANS), Endicott, Pt. McIntyre, Northstar and Middleground Shoals were tested at Ohmsett for dispersant effectiveness in cold-water conditions in the winter of 2003 (SL Ross 2003). Corexit 9527 dispersant was used in all of the experiments as this is the dispersant that is currently stockpiled in Alaska. The National Research Council (NRC 2005) reviewed the methods used and the results of this test program and reported that the results should be used with caution because in two of the twelve experiments the oil had to be warmed in order to reduce its viscosity for pumping in the cold conditions. The NRC recommended repeating the work with an improved oil distribution system so the oil could be released without warming. To address the NRC concerns, additional effectiveness testing was completed at Ohmsett in February and March of 2006 using improved testing methods and equipment that have been put in place since the 2003 testing. The results of this testing and descriptions of the improved methodologies and equipment can be found in the full report (SL Ross 2006) that is available online at www.mms.gov/tarprojects/568.htm. Corexit 9527 was used in both the 2003 and 2006 test programs. The objective of the present study was to complete effectiveness experiments on Alaskan crude oils using Corexit 9500 dispersant. If the current Alaskan dispersant stockpiles were depleted during a large spill Corexit 9500 would be brought into service since the Corexit 9527 product is no longer produced. The performance of Corexit 9500 on the Alaskan crude oils is therefore of interest to the spill response community.

2.0 Ohmsett Dispersant Effectiveness Test Methods

The test equipment, instrumentation and test procedures used in the testing were the same as those used in 2006 and documented in the report (<u>SL Ross 2006</u>) available at <u>www.mms.gov/tarprojects/568.htm</u>.

3.0 Oils and Dispersant Used in Test Program

Four Alaskan crude oils were used in the 2007 test program. They were Alaskan North Slope (ANS), Endicott (End), Pt. McIntyre (PtMc), and Northstar (NS) and crude oils. ANS is a blend of crude oils from the various Alaska North Slope fields, whereas the other oils are specific to their production areas. Oils were tested fresh and weathered by the removal of light ends using air sparging. Air sparging is a standard procedure to weather crude oils that is used by researchers worldwide. In this test program, sparging was accomplished by attaching an air hose to a perforated pipe that was submerged in the oil through the bung of the drum of oil to be weathered. An exhaust line was fitted to the drum's vent hole and routed to the outdoors. Compressed air was then pumped through the air hose into the oil and allowed to escape through the vent hose. A drum band heater was used to heat the oil to speed the evaporation process. The weight of the oil was recorded prior to the start of the weathering and checked periodically to establish the status of the weathering. The target evaporative loss for the oils used was 15% by mass for the ANS, Endicott and Pt. McIntrye oils and 30% for the Northstar crude. The basic physical properties of the oils used in the testing are provided in Table 1.

Table 1. Physical Properties of Test Oils

	2003	2006	200	7 Test Oils
	Test Oils	Test Oils		
Oil	Density	Density	Density	Viscosity (cP)
	(mg/l) 25	(mg/l)	(mg/l)	100s ⁻¹ , 1°C
	@20°C	@20°C	@20°C	1008,10
Alaska North Slope				
Fresh	0.873	0.863	0.862	65
Air sparged 15%	0.912	0.887	0.893	200
Air sparged 22%			0.900	300
Endicott				
Fresh	0.878	0.902	0.901	350
Air sparged	0.914	0.917	0.916	520
Northstar				
Fresh	0.812	0.803	0.814	6
Air sparged	0.864	0.839	0.842	30
Pt. McIntyre				
Fresh	0.890	0.861	0.862	45
Air sparged	0.902	0.880	0.898	400

Corexit 9500 dispersant was used in all but two experiments where dispersant was applied. Two experiments were completed using Corexit 9527 to address inconsistent results in the two previous test series.

3.1 Test Matrix Completed

A total of 9 control (no dispersant applied), 10 Corexit 9500 experiments and two Corexit 9527 experiments were completed in the test program. Thirteen of the experiments were conducted between January 30 and February 6, 2007 and the remaining eight experiments were completed between March 13 and March 15, 2007. Experiment number 13 was conducted in frazil ice. The air temperature at the end of the first week of testing dropped dramatically and the tank surface water froze. The ice was broken up using wave action but a layer of frazil ice built up in the tank and the main test program had to be suspended until warmer weather. One experiment was completed in the frazil ice conditions to investigate the use of dispersants in these conditions while the opportunity presented itself. A summary of the experiments completed and their test numbers is provided in Table 2.

Table 2. Test Matrix

Oil	Control Test Number	Corexit 9500 Applied Test Number	Corexit 9527 Applied Test Number
Alaska North Slope			
Fresh	1	19	
Air sparged (15%)	4	5	
Air sparged (22%)	17	18	
Endicott			
Fresh	3	21	
Air sparged (18%)	14	16	15
Northstar			
Fresh	9	10	
Fresh (in frazil ice)		13	
Air sparged (30%)	6	7	8
Pt. McIntyre			
Fresh	2	20	
Air sparged (15%)	11	12	

4.0 Test Results

Dispersed oil drop size distributions were measured using the LISST 100 particle size analyzer. In-water oil concentrations were estimated using a LISST 100 particle size analyzer and a Turner Designs TD3100 oil-in-water analyzer. The LISST 100 device and water sampling pump were positioned at 1.5 meters below the calm water level.

Dispersant effectiveness was estimated by collecting the surface oil remaining on the tank surface immediately after the completion of the experiment and comparing the amount collected to that discharged at the beginning of the experiment.

4.1 Test Conditions and Dispersant Effectiveness Estimates

The test conditions and estimated Dispersant Effectiveness (DE) for all of the large-scale tank experiments are summarized in <u>Table 3</u>. The test results are grouped based on oil type (column 1 in <u>Table 3</u>) rather than the order of test completion. The viscosities of the initial oils ranged from a low of 6 cP for fresh Northstar crude to 520 cP for the weathered Endicott oil. These viscosities were measured at 1 °C and a shear rate of 100 s⁻¹.

The surface water temperatures during the late January and early February portion of the test program (experiments 1 through 13) were between -1 and -5°C. The oil temperatures prior to discharge during these initial experiments were between 4 and -8°C. Testing had to be postponed after experiment 13 because the tank surface froze and open water testing could not be completed. When testing resumed in mid-March, air temperatures had increased considerably (8 to 21°C) and the chiller was no longer available to cool the tank water. The surface water temperatures in experiments 14 through 21 varied between 3 and 9°C and the oil temperatures prior to discharge were between 1 and 20°C.

Seventy to eighty liters of oil was discharged in most of the experiments. The estimated oil thickness at the point where the dispersant spray contacted the oil ranged from 0.9 to 1.63 mm.

Table 3. Ohmsett Tank Dispersant Effectiveness (DE) Test Results Summary

Oil	Initial Oil Viscosity (cP)	Air Temp °C	Water Temp °C	Oil Temp °C	Dispersant Temp °C	Oil Volume (liters)	Oil Thickness (mm)	DOR	% Collected	% Evaporated	% Dispersed / Lost	DE (Control Adjusted)	Links to Video Segments	Test#
Alaska North Slope														
Fresh		-6.1	-4.4	-7.2		80	1.06	0	41	13	46		<u>Test1</u>	1
Fresh		19.2	7.2	15.6	16.7	69	1.63	25	2	0	98	52	<u>Test19</u>	19
Air sparged 15%		-2.2	-4.4	0.0		78	0.90	0	77	5	18		<u>Test4</u>	4
Air sparged 15%		0.9	-3.3	0.0	12.8	77	1.04	17	1	0	99	81	<u>Test5</u>	5
Air sparged 22%		14.2	5.6	13.3		78	1.39	0	41	8	51		<u>Test17</u>	17
Air sparged 22%	300	14.6	5.6	13.9	15.0	71	1.46	24	3	0	97	46	<u>Test18</u>	18
Endicott														
Fresh	350	1.7	-2.2	1.7		75	1.12	0	76	5	19		<u>Test3</u>	3
Fresh		20.7	9.4	19.4	18.3	76	1.62	24	2	0	98	79	<u>Test21</u>	21
Air sparged 18%		8.1	2.8	7.8		76	1.59	0	69	10	24		<u>Test14</u>	14
Air sparged 18%	520	10.1	3.9	7.8	11.7	74	1.12	18	6	0	94	70	<u>Test16</u>	16
Air sparged 18%	520	12.1	4.4	11.1	10.6	71	1.38	21 (9527)	7	0	93	69	<u>Test15</u>	15
Northstar														
Fresh	6	1.1	-1.1	-0.6		78	0.95	0	52	36	11		<u>Test9</u>	9
Fresh	6	3.2	-0.6	3.9	10.0	78	0.97	18	1	0	99	88	<u>Test10</u>	10
Fresh (frazil ice)	6	-5.0	-5.0	0.6	8.9	53	1.10	nm	nm	nm	nm	nm	Test13	13
Air sparged 30%	30	-1.7	-2.2	-2.2		85	1.04	0	49	11	38		<u>Test6</u>	6
Air sparged 30%	30	1.1	-2.8	-0.6	10.0	77	1.15	20	1	0	99	61	<u>Test7</u>	7
Air sparged 30%	30	1.7	-2.2	-0.6	8.9	73	1.15	19 (9527)	1	0	99	61	<u>Test8</u>	8
Pt. McIntyre														
Fresh	45	-1.7	-4.4	1.1		77	0.95	0	62	8	31		<u>Test2</u>	2
Fresh	45	16.0	7.2	14.4	15.0	78	1.62	19	1	0	99	68	Test20	20
Air sparged 15%	400	-7.7	-5.0	-3.3		67	1.10	0	68	9	23		<u>Test11</u>	11
Air sparged 15%	400	-7.9	-6.1	-8.3	4.4	69	1.34	23	1	0	99	76	<u>Test12</u>	12

Note: DE is the dispersant effectiveness estimate after accounting for oil not accounted for in the control experiment for the same oil.

nm - not measured

The target dispersant-to-oil (DOR) ratio for all experiments was 1:20. Due to oil spreading differences this was not always achieved. DOR estimates ranged from as high as 1:16 to as low as 1:25. Several applications of dispersant were made to the oil in the frazil ice test #13 and an accurate estimate of DOR cannot be determined.

The "% Collected" data in Table 3 is the volume percentage of the oil spilled that was collected from the surface after each experiment.

The percentage of oil evaporated over the duration of the experiment was determined only for the control experiments. This value was determined based on the densities of the discharged and collected oils and the density/volume loss relationships shown in <u>Appendix A</u>. In the dispersant applied experiments the oil dispersed within a few minutes of spraying so little time was available for oil evaporation. Use of the collected oil density to determine the percent of oil evaporation would not be valid in these cases since most of the oil dispersed before evaporation could occur.

The "% Dispersed/Lost" data are the percentages of oil not accounted for by collection or evaporation estimates. This oil, not accounted for directly, could be on the tank side-walls or end booms (although these surfaces are swept by the fire monitors during the collection of the oil at the end of each experiment) or dispersed or dissolved into the water column. In "successful" dispersant applied cases the oil has less of an opportunity to evaporate or adhere to side-walls or booms as the oil is seen to quickly disperse into the water and so these losses can more confidently attributed to dispersion of oil. In the "dispersant applied" experiments the "% Dispersed / Lost" estimates were all very high (93% to 99%). The control experiments resulted in "Losses" other than evaporation from about 20% to as high as 50%.

The dispersant effectiveness (DE) "control adjusted" data column is the "% Dispersed / Lost" estimate for each dispersant applied experiment minus the "% Dispersed / Lost" estimate for the control experiment using the same oil. This number can be regarded as the minimal incremental benefit (dispersion) achieved through the application of chemical dispersant to the oil slick after the control experiment results are taken into account. The calculated DE

values should be viewed as the minimal benefit derived from the use of dispersants in these experiments. The actual dispersant effectiveness could easily be as high as the %D/L results reported for those experiments where immediate and complete dispersion of the oil occurs before any oil has the opportunity to reach the tank side walls or end booms or evaporate. The DE (control adjusted) values for the dispersant applied experiments indicate that the application of dispersant improved the dispersion of the oils by 46% to 88%.

Hypertext links are provided in <u>Table 3</u> to composite video clip segments of each of the experiments. The video records can be viewed by double-clicking on a link when accessing this document through MS Word or Adobe Acrobat. The video record for each experiment includes short video segments that have been merged together into one file to show the progression of the experiment from the beginning to the end. The video clips provide a good record of the behavior of the oil in each of the experiments and it is highly recommended that they be viewed to get a full appreciation of the test program.

In summary, the Corexit 9500 dispersant was effective in all of the experiments and resulted in very high oil removal in all experiments. In all of the chemically treated experiments the %Dispersed/Lost estimates exceeded 93%.

4.2 Dispersed Oil Concentrations and Drop Size Distributions

Up to four passes were made down the length of the test tank after the oil was discharged to measure in-water oil concentrations and drop size distributions. A LISST 100 particle size analyzer recorded data on oil drop sizes and in-water oil concentrations. A Turner TD3100 fluorometer was used to measure in-water oil concentrations from water grab samples that were pumped from a depth of 1.5 meters from the calm water surface. Graphs of the oil drop size distributions and concentrations are provided in <u>Appendix B</u>. Hypertext links to these graphs are provided in <u>Table 4</u>.

Table 4. In-Water Oil Characterization Graph Hypertext Links

Oil	DOR	Links to Oil Characterization Graphs	Test #	D50)	Ave. Elevated Oil Conc. by LISST	Peak Oil Conc. (ppm)	TD3100 Data Collected	% Dispersed /Lost
Alaska North Slope				(microns)	(microns)			
Fresh	0	lisstr1	1	177	10	58	yes	46
Fresh		lisstr19	19	10	46	205	no	98
Air sparged 15%		lisstr4	4	150	12	73		18
Air sparged 15%	·	lisstr5	5	49	24	162	yes	99
Air sparged 13% Air sparged 22%	-	lisstr17	17	147	18	33	yes no	51
Air sparged 22%		lisstr18	18	7	37	110		97
Endicott	24	<u>11880 1 0</u>	10	/	31	110	no	91
Fresh	0	lisstr3	3	177	8	47	VAC	19
Fresh	24	lisstr21	21	19	42	178	yes no	98
Air sparged 18%		lisstr14	14	208	24	48	ves	24
Air sparged 18%		lisstr16	16	72	23	166	ves	94
Air sparged 18%		lisstr15	15	60	28	239		93
Northstar	21 (9321)	<u>11880 1 3</u>	13	00	26	239	yes	73
Fresh	0	lisstr9	9	166	34	69	no	11
Fresh	18	lisstr10	10	32	39	65		99
Fresh (frazil ice)		lisstr13	13	286	19	20	yes no	nm
Air sparged 30%		lisstr6	6	224	21	69		38
Air sparged 30%		lisstr7	7	24	40	157	yes	99
Air sparged 30%		lisstr8	8	36	70	198	yes	99
Pt. McIntyre	17 (7341)	<u>11880 o</u>	0	30	/0	170	yes	77
Fresh	0	lisstr2	2	206	9	47	VAC	31
Fresh	16	lisstr20	20	25	37	186	yes	99
Air sparged 15%		lisstr11	11	250	22	47	no	23
Air sparged 15%			12	47	45	58	yes	99
All sparged 1370	23	<u>lisstr12</u>	12	4/	43	30	yes	99

The D50 (volume median diameter) values shown in <u>Table 4</u>, and plotted in <u>Figure 1</u>, are the averages of the volume median diameters measured in each experiment when the oil concentrations were elevated at least 1.5 times above the tank background concentration. For all of the successful dispersion experiments the average of the D50 measurements were below 75 microns. This is consistent with other research (<u>Lunel 1993</u>) that has stated that oil drops distributions with D50'S less than 75 microns are required for permanent dispersion. The control experiments all had D50s that were greater than 150 microns. The average oil concentrations in these elevated concentration regions and the peak oil concentrations were also calculated and are shown in <u>Table 4</u>. The average oil concentrations in the chemically treated experiments were consistently higher than the control experiments and, as described above, the drop sizes in the high concentration regions were always smaller in the treated

experiments. The peak oil concentrations in the treated experiments were consistently higher than the control experiments.

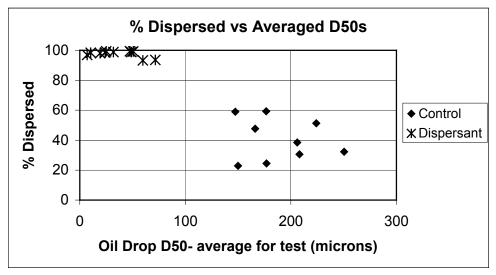


Figure 1. Dispersant Effectiveness versus Average Volume Median Diameter

The LISST 100 concentration estimates compared favorably to those of the TD3100 results with the exception of a few samples where the oil concentrations were high and a precipitate formed in the solvent extract. In these samples (<u>LISST 10</u>, <u>15</u>, <u>16</u>) the TPH measurement by the TD3100 was significantly higher than that measured by the LISST. It is likely that the discrepancy is due to the presence of the precipitate in the sample.

4.3 Wave Turbulence Measurement

A Sontek Horizon ADV velocity probe was deployed at 1.5 meters below the calm water surface and used to measure X-Y-Z water velocity fluctuations during each experiment. The probe was set to record 30-second bursts of data at 25 khz frequency. Measurements were made prior to each instrument pass with the bridge stationary. Since all of the dispersant effectiveness and control experiments were completed using the same wave paddle settings (3.0-inch stroke and 34 cycles per minute) only one of the data sets captured (Test 5, burst 1) is provided as an example of the water velocities recorded. This trace is shown in Figure 2.

The velocity data from all experiments has been processed by first removing single spikes from the records based on a threshold of two standard deviations and then calculating the average kinetic energy (TKE) as determined by the sum of the velocity variances in x, y, and z divided by 2 (Bradshaw 1971). The TKE value was determined for up to 4 measurements or data collection bursts in each experiment and these values were then averaged to determine a final representative TKE for each experiment. These data are provided in Table 5. The average TKE for the test series was 205 with Standard Deviation of 39.

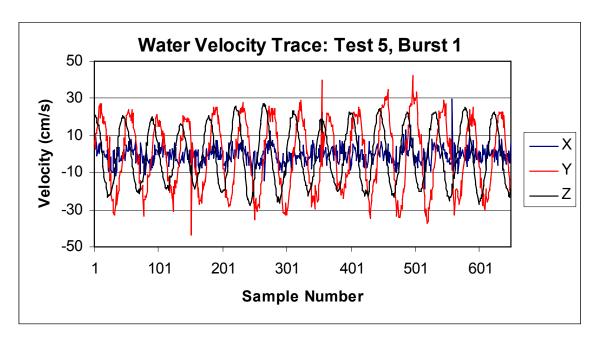


Figure 2. Sample Sontek Horizon ADV Water Velocity Trace

Table 5. Average Kinetic Energy at 1.5 Meter Depth

Test	Burst 1	Burst 2	Burst 3	Burst 4	Averag	4	
	TKE	TKE	TKE	TKE	TKE		
1	349	394	186	0	310		
2	259	223	161	273	229		
3	153	166	426	0	248		
4	191	332	145	213	220		
5	302	200	337	354	298		
6	175	290	252	348	241		
7	195	194	226	260	219		
8	225	194	198	289	226		
9	10	236	184	221	163		
10	166	179	221	0	188		
11	144	269	168	0	193		
12	102	182	201	244	182		
13	91	60	259	0	137		
14	157	0	0	0	157		
15	130	192	232	178	183		
16	256	199	153	199	202		
17	137	149	245	377	227		
19	173	115	174	152	154		
20	177	166	189	140	168		
21	140	158	216	122	159		
					Ave	205	
					StdDev	39	

5.0 Comparison of Results to 2003, 2006 and 2007 Test Results

As outlined in section 1.0, a series of similar dispersant effectiveness experiments were completed in 2003 and again in 2006 using the same oils but with Corexit 9527 dispersant. A comparison of the final dispersant effectiveness estimates from the 2003, 2006 and 2007 test programs is provided in <u>Table 6</u> for those cases where similar experiments were completed in all years.

Table 6. Comparison of 2003, 2006 and 2007 Dispersant Effectiveness Results

	2003	2006	2007
Oil	Corexit 9527	Corexit 9527	Corexit 9500
	% Dispersed/Lost	% Dispersed/Lost	% Dispersed/Lost
Alaska North Slope			
Fresh	98	95	98
Air sparged	85 & 86	97	99
Endicott			
Fresh	74	99	98
Air sparged	3	85 & 91	94 (93 w C9527)
Northstar			
Fresh	100	96	99
Air sparged	8	91	99 (99 w C9527)
Pt. McIntyre			
Fresh	77	99	99
Air sparged	nt	99	99

nt – not tested

The estimates of non-control corrected dispersant effectiveness (DE) for all oils were very similar in the 2006 and 2007 test programs with both Corexit 9500 and 9527 achieving greater than 90% dispersion in all experiments. Two experiments were completed in 2007 with Corexit 9527 to address previous in-consistent results in 2003 and 2006 on the weathered Endicott and Northstar oils. The low dispersion estimates measured for these two oils in 2003 appear to be erroneous based on the 2006 and 2007 results. The fresh oil dispersion experiments in 2007 for ANS, Endicott and Pt. McIntyre were all completed in water that had warmed to greater than 5 °C. Since these oils all completely dispersed at cold temperatures when they were weathered, it is likely that the fresh oils also would have completely dispersed had the water been colder.

The averaged volume median drop diameters (D50) of the oil drops in the dispersions generated for similar oils by Corexit 9527 (from 2006 test program) and by Corexit 9500 (from the 2007 testing) have been plotted in <u>Figure 3</u>. The results do not show any trend of smaller oil drop sizes generated by either of the two dispersants.

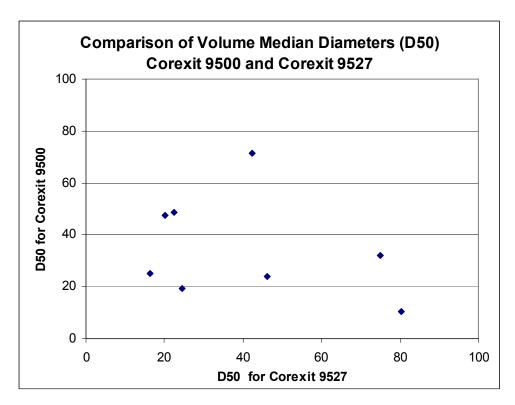


Figure 3. Comparison of Oil Drop Sizes Generated by Corexit 9527 and Corexit 9500

6.0 References

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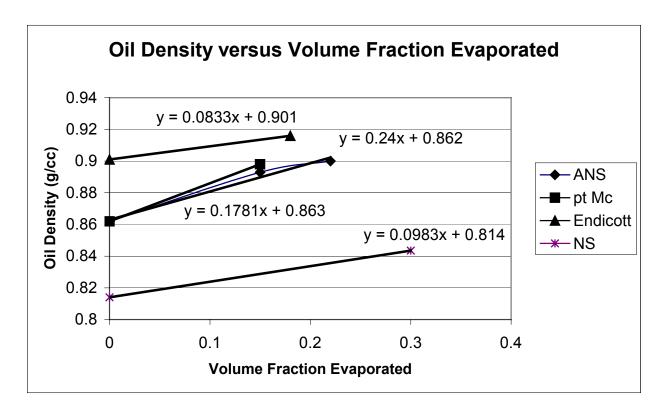
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Appendix A. Evaporative Loss Data from Oil Air Sparging



Appendix B. In-Water Oil Characterization

