

# **CALM SEAS APPLICATION AND DISPERSANT WASH-OUT**

**For**

**U.S. Department of the Interior  
Minerals Management Service  
Herndon, VA**

**By**

**SL Ross Environmental Research Limited  
200-717 Belfast Road  
Ottawa, Canada K1G 0Z4**

**A. Lewis Oil Spill Consultancy  
121 Laleham Road  
Staines, United Kingdom TW18 2EG**

**MAR Incorporated  
P.O. Box 473  
Atlantic Highlands, NJ 07716**

**December 2008**



## **Acknowledgements**

The authors wish to thank the U.S. Minerals Management Service Technology Assessment and Research Branch for funding this study and Joseph Mullin for his guidance in the work. We gratefully acknowledge the support of Dr. Jim Clark of ExxonMobil, who provided the supplies of Corexit 9500 dispersant used in this testing.

## **Disclaimer**

The U.S. Minerals Management Service staff reviewed this report for technical adequacy according to contractual specifications. The opinions, conclusions, and recommendations contained in the report are those of the author and do not necessarily reflect the views and policies of the U.S. Minerals Management Service. The mention of a trade name or any commercial product in the report does not constitute an endorsement or recommendation for use by the U.S. Minerals Management Service. Finally, this report does not contain any commercially sensitive, classified or proprietary data release restrictions and may be freely copied and widely distributed

## Executive Summary

Oil spill dispersants can be applied to spilled oil in calm sea conditions, but will not cause rapid dispersion of the oil if there are no breaking waves. The oil will be dispersed if the sea conditions become rougher with breaking waves soon after dispersant application. If there is a prolonged period of time before breaking waves occur the surfactants in the dispersant will partition (or 'leach') out of the dispersant-treated oil and be lost into the sea. The oil would then have lost a significant amount of dispersant and would not be so effectively dispersed by breaking waves when they occur.

The previous work conducted at the National Oil Spill Response Test Facility (Ohmsett) found that dispersant-treated test oils were almost totally dispersed when breaking waves were applied after the oil had been on the still water surface for periods of up to 6 days ([SL Ross, 2006a](#)), but this time period was reduced to 2 to 4 days if there was a water current of between 5 and 13 cm/s passing under the oil slick ([SL Ross, 2007](#)). The testing completed in the summer of 2005 used IFO 30 fuel oil, Ewing Bank 873 crude oil and GA 209 crude oil. The work in 2007 was conducted with only an artificially weathered Oseberg crude oil.

The experiments described in this report investigated the effect of water currents passing under two different volumes (80 litres and 38 litres) of dispersant-treated oil slicks contained in stationary rings on the water surface of the tank at Ohmsett. Intermediate Fuels Oils (IFO) IFO-180 and IFO-30 and an artificially weathered Alaska North Slope (ANS) crude oil were used in these tests. Oils containing Corexit 9500 at a treatment rate of 1:20 (Dispersant to Oil Ratio, DOR) were contained in two 4.6 m diameter circular rings on the water surface in the Ohmsett tank and subjected to water currents, created by an air bubble barrier, with speeds of 4.0 to 6.3 cm/s for periods of up to 4 days.

The potential for dispersion of these oils was monitored by withdrawing small samples during the period that the oils were on the water and subjecting them to WSL testing. The amount of dispersant remaining in the oil was calculated by comparison with the Warren Spring Laboratory (WSL) result achieved with different amounts of dispersant.

There was an initial period of time when the WSL result from the oil samples taken from the tank increased due to an increase in oil density caused by the loss of the more volatile components by evaporation. The WSL result then started to decrease as due to the loss of dispersant from the oil and into the tank water.

The time for the WSL result to decrease to a value equivalent to a dispersant treatment half of that originally mixed into the oil, a DOR of 1:40 compared to the original DOR of 1:20, depended on the amount of oil in the test ring:

- With 80 litres of oil and a mean 4.0 cm/s water current the period was 56 hours for the ANS oil and 55 hours for the IFO-30 oil.
- With 38 litres of oil and a mean 5.7 cm/s water current the period was 16 hours for the ANS oil and 19 hours for the IFO-30 oil.

The rate of loss of dispersant during the period of most rapid dispersant loss was estimated to be approximately the same for the ANS and IFO-30 oils; 2% to 3% per hour, expressed as a percentage of the original dispersant treatment rate. This compared to approximately 1% to 1.5% per hour for samples of dispersant-treated oil on still water. The dispersant loss rate was slightly higher at the higher current speed and with tests using the lesser volume of oil.

Breaking waves were put through the slicks of test oil on the tank at Ohmsett after various periods of time.

The effectiveness of dispersion was assessed visually and by measurements made with a LISST particle size analyser. The LISST measured the oil droplet size distribution and dispersed oil concentrations in the plume of dispersed oil in the water below the slick.

An IFO-30 oil slick was treated with dispersant and immediately subjected to breaking waves to provide a benchmark for the LISST measurements and visual observations for a successful dispersion with no opportunity for dispersant leaching.

## Table of Contents

1. Objective.....	1
2. Background.....	1
3. Study Approach .....	3
4. Large-Scale Tank Testing at Ohmsett.....	4
4.1 Oil Tested.....	4
4.1.1 Oil Weathering.....	5
4.2 Test Methods and Equipment .....	6
4.2.1 WSL Dispersant Effectiveness Results.....	6
4.2.2 Ohmsett tank test set-up.....	6
4.2.3 Test procedure.....	9
4.3 Tests conducted.....	15
5. Results .....	16
5.1 Test Series 1 .....	16
5.1.1 Test Series 1, ANS.....	16
5.1.2 Test Series 1, IFO-180 .....	20
5.2 Test Series 2.....	24
5.2.1 Test Series 2, ANS.....	24
5.2.2 Test Series 2, IFO-30 .....	27
5.3 Test 2a.....	30
5.4 Test Series 3.....	32
5.4.1 Test Series 3, ANS.....	33
5.4.2 Test Series 3, IFO-30 .....	35
6. Discussion of Results .....	38
6.1 Results obtained with ANS oil.....	38
6.1.1 WSL results.....	39
6.1.2 LISST results .....	44
6.1.3 Visual observation results .....	45
6.2 Results obtained with IFO-180 oil.....	46
6.2.1 WSL results.....	46
6.2.2 LISST results .....	47
6.2.3 Visual observation results .....	47
6.3 Results obtained with IFO-30 oil.....	47
6.3.1 WSL results.....	48
6.3.2 LISST results .....	51
6.3.2 Visual observation results .....	52
6.4 Indicators of dispersion in the tank and WSL results .....	52
6.4.1 The significance of the WSL result .....	52
6.4.2 The significance of the results from the LISST .....	54
6.4.3 The significance of the visual observations .....	58
6.4.4 Relating these indicators together.....	60
6.5 Summary of results and the effect of variables.....	61
6.5.1 Effect of oil type on dispersant loss .....	62
7. Conclusions.....	64
8. References .....	67

9. Appendix 1: Review of PERF Study .....	68
1. Purpose of review .....	1
2. Experimental procedures .....	2
2.1 Test oils used.....	2
2.1.1 Comparison of oil used at Ohmsett in 2007 and oil used in this study.....	5
2.2 Dispersants tested.....	6
2.3 Test methods used.....	6
2.3.1 Dispersant tests with extended contact time without freezing.....	6
3. Comparison of IFP results with 2007 Ohmsett tests .....	8
4. Surfactant leaching with extended contact time.....	14
4.1 Discussion of the surfactant leaching results .....	19
5. IFP results with extended contact time .....	22
5.1 IFP result as a function of DOR and temperature.....	26
5.1.1 IFP Results at 25°C .....	26
5.1.2 IFP Results at 15°C .....	26
5.1.3 IFP Results at 0°C .....	27
5.2 Discussion of results .....	27
5.2.1 Inherent dispersibility of the oil.....	28
5.2.2 Loss of dispersant by extended contact with water .....	30
5.2.3 Flow properties of the oil residues.....	30
6. Discussion of all results.....	32
6.1 Surfactant leaching from dispersant-treated oil .....	32
6.2 IFP result obtained with reduced DOR.....	33
6.2 The onset of a limiting viscosity (rheology) for dispersion.....	34
7. Conclusions .....	35
8. Implications for further testing at Ohmsett.....	37
10. Appendix 2: LISST Plots for Calm Seas Application And Dispersant Wash-Out.....	1

## 1. Objective

The objective of this research project was to continue to investigate the conditions that might lead to loss of surfactant from dispersant-treated oil, so that the subsequent application of breaking waves will not result in dispersion. This project is an extension of two previous studies ([SL Ross, 2006a](#) and [SL Ross, 2007](#)). In this project, the effects of the presence of water currents under the oil, slick thickness and oil type were investigated.

## 2. Background

The use of dispersants to cause spilled oil to disperse at sea, or to enhance the rate of natural dispersion of spilled oil from a very low level to a much higher value, is known to be related to the prevailing ‘mixing energy’. Many laboratory studies have concluded that higher ‘mixing energy’ causes greater levels of dispersion than lower ‘mixing energy’, but this has yet to be well defined or rigorously correlated with conditions that cause dispersion of spilled oil at sea.

The prevailing wind speed, and the wave conditions that it helps to produce, have a large influence on the dispersion of oil at sea. Wind speeds in excess of 7 – 10 knots (3.5 - 5 m/s, equivalent to Beaufort Force 3) create cresting or breaking waves at sea and these waves are necessary for the rapid dispersion of dispersant-treated oil ([SL Ross, 2006b](#)).

At wind speeds below 7 – 10 knots, the spilled oil will drift on the sea surface with the wind and, in the absence of breaking waves in the open sea, the dispersant-treated oil will not be dispersed. Spilled oil drifts under the influence of the prevailing water currents and wind. A slick of spilled oil will drift with 100% of the water current speed, plus a contribution to drift velocity approximately equivalent to 3% of the prevailing wind speed. For Beaufort Force 1 and 2 winds (1 – 3 knots and 4 – 6 knots, respectively,

equivalent to 0.5 – 1.5 m/s and 2 – 3 m/s) the drift velocity contribution from the wind will be 2 – 5 cm/s and 6 – 9 cm/s.

Previous studies have shown that the surfactants that are the active ingredients in dispersants will partition, or leach, from dispersant-treated oil and will be lost to the water. This was first explored in the report “Calm Sea Application of Dispersants” (S L Ross, 2006a) and subsequently investigated further in the report “Changes in Dispersant Effectiveness with Extended Exposure in Calms Seas” (S L Ross, 2007). The first study using absolutely still water in the Ohmsett tank found that the test oils dispersed after 6 days when breaking waves were applied to the slick. In the second study, it was found that under conditions with significant water movement under a slick, the dispersant was lost from the Oseberg crude oil tested to the water phase within a day or two and was no longer effective.

A Petroleum Environmental Research Forum (PERF) funded study by SINTEF and Cedre has looked at the same issue of dispersant leaching, but at the laboratory bench scale using the Institute Français du Pétrole (IFP) dispersant effectiveness test method, and the results were presented in “Effects of Time on the Effectiveness of Dispersants” ([SINTEF, 2007](#)). Four artificially weathered crude oils and four commercial dispersant, plus a model dispersant, were used. This study found that the individual surfactants within a model oil spill dispersant (formulated to be similar to Corexit 9500) did not leach out at different rates; instead, the loss of surfactants to the water was equivalent to a proportional reduction in the dispersant concentration in the dispersant-treated oil. The rate of partitioning of the dispersant was found to be temperature dependent (being more rapid at higher temperatures) and dependent on the test oil rheology (high viscosity caused by wax precipitation near the Pour Point of the oil residue reduced the surfactant loss). A detailed technical review of this PERF funded study was completed as part of this project and the full review can be found in Appendix 1.



### **3. Study Approach**

This research project examined the effect of water currents flowing underneath an oil slick contained in a boom, and in the absence of waves, on the subsequent dispersibility of the dispersant-treated oil.

Localized surface water currents were induced across the Ohmsett tank using a submerged air-bubble barrier. The test oils were retained in two stationary rings and the water flowed beneath it for an extended period.

Samples of the oil were withdrawn at regular intervals and the Warren Spring Laboratory (WSL) effectiveness result was determined in the laboratory. The dispersibility of the oil in the ring was also roughly assessed by the simple technique of dropping a small quantity of the oil into the tank water and stirring with a spoon.

At the end of each test the oil containment rings were lifted and breaking waves were introduced. As these waves passed through the slicks a LISST particle size analyser was deployed and used to measure the droplet size distribution and oil concentrations in the plume of dispersed oil in the water below the slick. Visual observations were also recorded.

## 4. Large-Scale Tank Testing at Ohmsett

Large-scale dispersant effectiveness tests were conducted at the National Oil Spill Response Test Facility (Ohmsett), located in Leonardo New Jersey, in May of 2008.

### 4.1 Oil Tested

The oils used in these experiments were IFO-180 and IFO-30 residual fuel oils and artificially weathered Alaska North Slope (ANS) crude oil. The properties of the oils are contained in Table 1.

Test Oil	Density gm/ml at 23°C	Viscosity at 15°C cP
ANS (Artificially weathered Alaska North Slope crude oil – 25% loss by volume)	0.892	60
IFO-180 (Custom blended)	0.962	1800
IFO-30 (Custom blended)	0.935	260

*Table 1. Summary of properties of oils tested*

The two IFO (Intermediate Fuel Oil) grades, IFO-180 and IFO-30, were blended from a stock of IFO-380 and Marine Gas Oil (MGO) to have viscosities at 50°C of 180 cP and 30 cP, respectively.

The ANS crude oil was artificially weathered by air-sparging and heating at Ohmsett prior to the tests to produce a 25% volume loss. This is equivalent to the oil being on the sea surface for one or two days (dependent on temperature and wind conditions). The intention of doing this was to produce test oil with constant properties that would not change too much during the test period and thus influence the results obtained.

### 4.1.1 Oil Weathering

Despite the ANS oil being “pre-weathered” to a 25% weight loss, some further evaporation of volatile oil components occurred during the test periods. The weight loss from the IFO-30 and ANS oils when stored in trays in 5 mm thick layers, outside and under shelter, during the test period is shown in Figure 1.

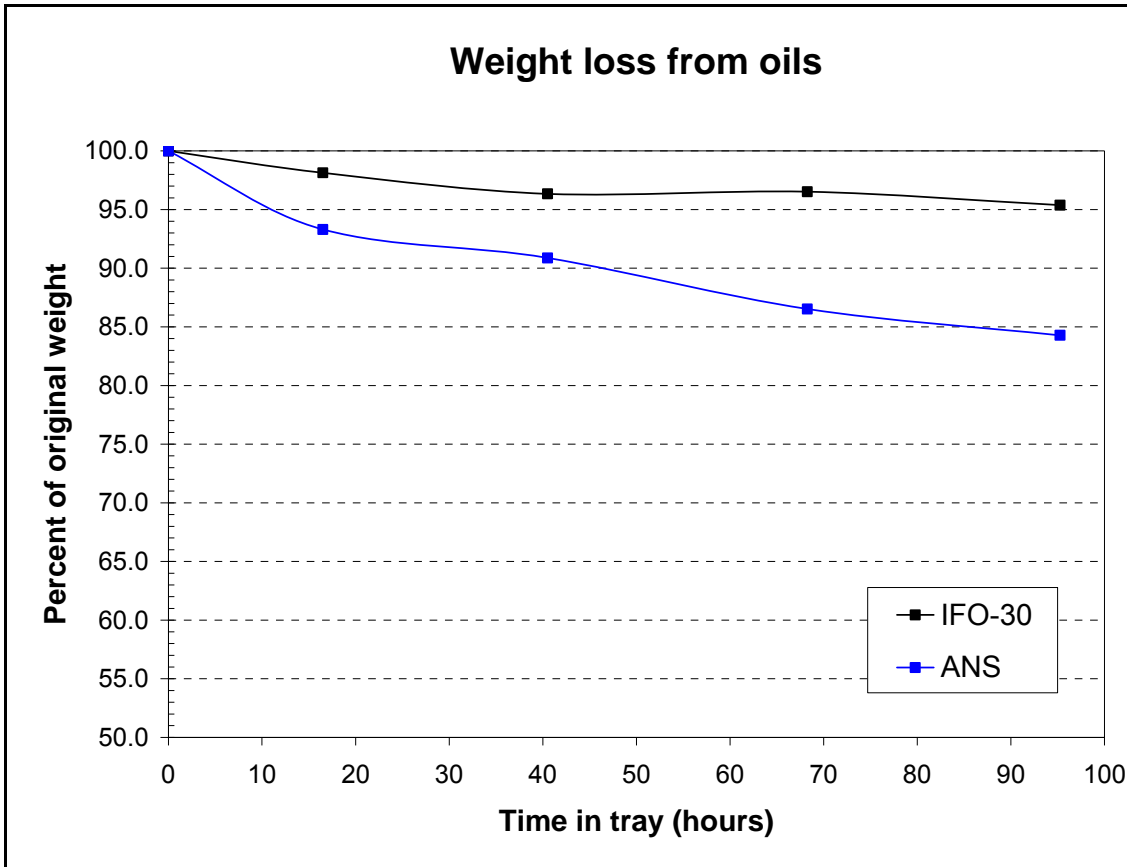


Figure 1. *Evaporative loss from test oils with time*

The density of the ANS oil increased from 0.8922 to 0.9106 gm/ml over 96 hours. The IFO 30 density increased from 0.935 to 0.944 gm/ml.

## **4.2 Test Methods and Equipment**

### **4.2.1 WSL Dispersant Effectiveness Results**

The WSL test was conducted in accordance with the WSL LR 448 (OP) specifications and this was described in detail in Annex A of [SL Ross, 2007](#), “Changes in Dispersant Effectiveness with Extended Exposure in Calm Seas”.

Several different data sets were generated on samples from the experiments of this study:

- **“On tank” samples**

Samples of the test oils taken at regular intervals from the rings on the water surface of the tank.

- **“No Flow” samples**

Samples of the test oils taken at regular intervals from the surface of drums of static salt water (from the Ohmsett tank) stored outside and under cover near the tank.

- **“Weathering Control” sample**

Samples of the test oils taken from trays stored outside and under cover near the tank (no water present in the trays).

### **4.2.2 Ohmsett tank test set-up**

A photograph of the set-up for the work is shown in Figure 2.



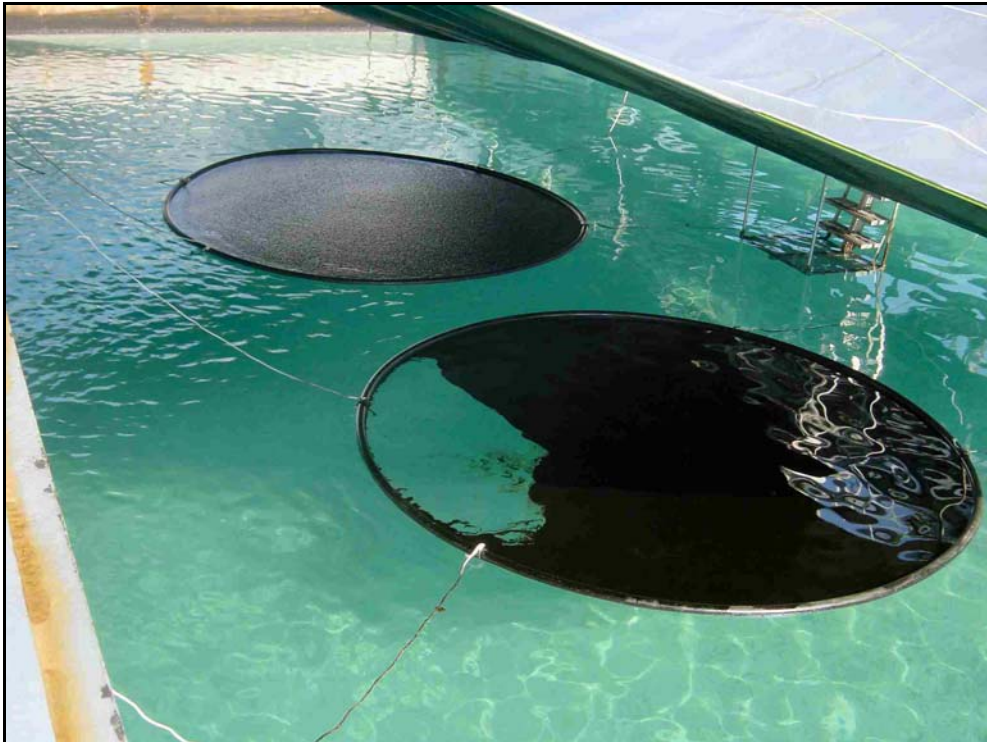
*Figure 2. Photograph of the set-up for the work*

Two oils were to be tested in each test. A boom was placed down the length of the tank between the rings to divide it into two sections, East and West (Figure 3).



*Figure 3. Boom was placed down the water surface*

Two 4.6-meter diameter rings of 7.6 cm diameter plastic pipe were used to contain the test oils (Figure 4). The two rings were placed in the tank, one in the East section and one in the West section, positioned and tethered between the Main Bridge and the Auxiliary Bridge that had been fixed 8.5 meters apart. The area over the rings between the two bridges was covered with a tarpaulin to prevent the test oils from being affected by any rain that might fall during the tests.



*Figure 4. Two rings of plastic tubing were used to contain the test oils*

Compressed air was pumped into perforated pipes (bubble barrier) placed at the bottom of the tank south of the containment rings to produce a surface water current flow towards the rings. The water current speed was greatest near the bubble flow and decreased with distance from the barrier.

The air to the bubble barrier was set to a constant pressure and flow and monitored during the tests. The distance between the bridge and the rings was fixed. The water current

velocity was therefore expected to be constant and the same in all tests, except for uncontrollable wind influence.

The water current velocity flowing under the oil slicks was monitored for periods of several hours each day. These measurements appeared to show a cyclical pattern to fluctuations in the measured current speed. There was apparently a short cycle of fluctuation of about 4 minutes superimposed of a larger cycle of fluctuation of approximately 30 minutes. The effect was to cause the current speed to fluctuate about a mean current speed from nearly 0 cm/sec up to a value approaching double the mean current speed. The reason for these fluctuations has not been identified.

### **4.2.3 Test procedure**

The airflow through the bubble barrier and the distance of the bridge from the bubble barrier were adjusted to produce a current speed of approximately 4 to 6 cm/s. At this current speed small amounts of oil were occasionally stripped away from the containment rings so it was not possible to increase the flow beyond this level without significant oil loss from the rings. There was a gradient of surface water current speed with distance from the bubble barrier. The current speed was measured at the edge of the test rings nearest the bridge and across the width of the rings using both a propeller-based current meter and by timing the movements of small fishing floats.

### **Oil-on-water phase of test**

A pre-determined quantity of oil, either 80 or 38 litres of test oil, pre-mixed with the appropriate quantity of Corexit 9500 to achieve a DOR (Dispersant to Oil Ratio) of 1:20, was carefully placed in each of the rings on the tank (Figure 5).

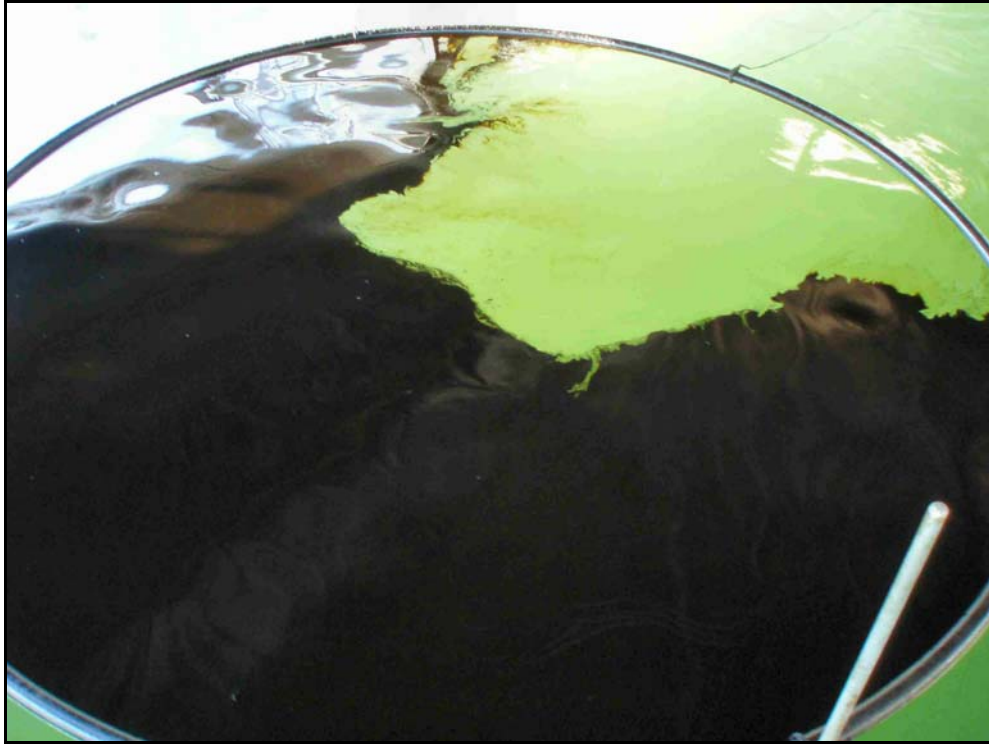




*Figure 5. Oil being placed in ring*

The oil was not static in the ring; surface circulation caused the oil to be slowly moved within the ring and the oil surface presented to the water was being constantly renewed as the internal circulation occurred. Occasional ‘streamers’ of oil broke away from the thin leading edge of the test slick (Figure 6).





*Figure 6. Distribution of oil in ring*

Small samples of the oil were carefully withdrawn each day and these were tested using the WSL dispersant effectiveness test method, except that no additional dispersant was added to the test oil. The opportunity was taken during sampling to conduct a very simple experiment on the visual appearance of any dispersion that might occur. A spoonful of the oil was lifted away from the ring and dropped into the tank water beside the ring (Figure 7). The oil was then stirred into the water and the visual appearance noted.



Figure 7. Spoon test

### Application of breaking waves

At the completion of each test, the circular booms surrounding both test oils were carefully raised on ropes, to minimize disturbance of the oil, to a position on the underside of the bridge. The waves were then started. The wave paddle settings used in these tests were a 7.6 cm stroke and 35 strokes per minute for 30 minutes. This creates the wave characteristics shown in Table 2.

Paddle Frequency, cpm	Breaking/non-breaking	Significant Wave Height, $H_{1/3}$ , m	Wave Length, m	Wave Frequency $\text{min}^{-1}$
35	Breaking	.403	5.1	33.3
Stroke length = 3.0 inches Based on Asher 2005				

Table 2. Breaking wave characteristics

## **Use of the LISST particle size analyzer**

An in-situ laser particle-size (LISST) analyzer was used to monitor in-water oil concentrations and dispersed oil droplet size distributions during tests.

Measurements were made on along-tank transects at a depth of 1.5 m in the water column, with the detector position adjusted from the bridge deck to pass through the center of the dispersing oil slick, through the centre of the visible cloud of dispersed oil. It should be noted that the LISST was not necessarily consistently passed through the portions of the dispersed cloud with highest dispersed oil concentrations from test to test.

The LISST output from all tests is shown in figures in Appendix 2.

The following data were obtained in each pass in these Test Series:

- Volume Median Diameter (VMD) in microns
- Average Oil Concentration in ppm
- Peak Oil Concentration in ppm
- Percentage of total dispersed oil volume contained in oil droplets with diameters of less than 75 microns.

Each of these parameters is an indicator of the degree of dispersion of the oil, but cannot be an accurate quantitative measurement of the degree of dispersion.

### **Volume Median Diameter (VMD)**

Lower VMD of the dispersed oil distribution is an indicator of a higher the degree of dispersion. VMD is the oil droplet size at which one-half the sampled dispersed oil volume consists of larger droplets and one-half consists of smaller droplets. Since it takes many more small droplets to make up one-half the volume, there always will be many more small oil droplets than larger oil droplets. The VMD represents only one

characteristic of the droplet size distribution. Measurements made of dispersed oil at sea ([Lunel, 1993](#)) have indicated that oil droplets with diameters less than 70 microns are permanently retained in the water column, under the prevailing wave conditions of a moderate sea state. If the VMD of the dispersed oil cloud is 70 microns or less then at least half of the oil in the dispersion can be considered permanently dispersed.

### **Average oil concentration**

A high average dispersed oil concentration (at 1.5 metres water depth) is an indicator of a higher degree of dispersion for a given quantity of oil; the average dispersed oil concentration in the water will be higher if a larger quantity of oil had been totally dispersed and lower for smaller quantities of oil. However, the dispersed oil concentration at any point can change rapidly as the dispersed oil is diluted into the water column and the size of the dispersed oil cloud increases. The size of the oil drops in the dispersion also affects the amount of oil that remains in the water column. Average dispersed oil concentration therefore cannot be an absolute indicator of the degree of dispersion.

### **Peak oil concentration**

A higher peak dispersed oil concentration (at 1.5 metres water depth) is an indicator of a higher degree of dispersion for a given quantity of treated oil. Similar to the average dispersed oil concentration, the peak oil concentration measured will vary rapidly with time and location as the dispersed oil is diluted into the water column or large oil drops rise to the surface and cannot be regarded as an absolute indicator of the degree of dispersion. As noted earlier the size of the oil drops in the dispersion also plays an important role in the final dispersion.

### **Percentage of dispersed oil volume in droplets less than 75 microns in diameter**

Measurements made of dispersed oil at sea ([Lunel, 1993](#)) have indicated that oil droplets with diameters less than 70 microns are permanently retained in the water column, under the prevailing wave conditions of a moderate sea state. A high percentage of the dispersed oil volume being present as oil droplets with diameters less than 75 microns is

an indicator of a high degree of dispersion, but it needs to be combined with the dispersed oil concentration (either average or peak) to be an approximate measurement of the amount of dispersed oil that will be retained in the water column. Although the combination of high oil concentration and small drop sizes is an indicator of good dispersion, it cannot be a quantitative measure because of the reasons described above; the possibility that the dispersed oil concentration (average or peak) was not at a maximum at the locations in the dispersed oil cloud where the measurements were made.

### **4.3 Tests conducted**

Three test series (numbered Tests 1 to 3) were conducted, each with two test oils, for a period of between 49.5 and 90.5 hours. In addition, a calibration test (Test 2a) with only IFO-30 was conducted where the dispersant-treated oil was exposed to breaking waves shortly after being placed on the tank. The volumes of oil used in each test and the exposure time on the water are shown in Table 3.

	<b>Oil in East ring</b>	<b>Oil in West ring</b>	<b>Time on water (hours)</b>
<b>Test Series 1</b>	ANS 80 litres	IFO-180 80 litres	71
<b>Test Series 2</b>	ANS 80 litres	IFO-30 80 litres	90.5
<b>Test 2a</b>	IFO-30 80 litres	None	0.5
<b>Test Series 3</b>	ANS 38 litres	IFO-30 38 litres	49.5

*Table 3. Test series conducted in this work*

## **5. Results**

### **5.1 Test Series 1**

Test Series 1 began with the test slicks being placed in the two test rings on the water in the tank at 12:00 on Tuesday, 20<sup>th</sup> May and was completed when breaking waves were applied to the test slicks at 11:00 on Friday 23<sup>rd</sup> May; a total of 71 hours on the water surface.

This test series used 80 litres of each of IFO-180 and ANS, each pre-mixed with Corexit 9500 at a DOR of 1:20. The bubble barrier was fed with air at 20 cubic feet per minute (cfm) at 75 psi. This rate of air flow from the bubble barrier, which was 25 feet from nearest edge of the rings, created an average water current flow of 6.33 cm/s (Standard Deviation 4.00 cm/s) beneath the test oil slicks over the three days of the test. The temperature of the water in the tank varied between 16.1°C (61°F) and 17.2°C (63°F) during the test period.

#### **5.1.1 Test Series 1, ANS**

##### **WSL Results**

Samples of oil (the “On-tank” samples) were taken from the rings in the tank at regular intervals and transferred to the laboratory where the WSL test was undertaken. Samples were also taken from the drum of stationary water (the “No-Flow” samples) for testing.

The WSL results for Test Series 1 with ANS oil are contained in Table 4 and illustrated in Figure 8.

Samples taken			WSL test result (%)	
Date	Time	Time on water (hours)	ANS On-Tank	ANS No-Flow
20/05/2008	12:00	0	60.0	60.0
21/05/2008	08:00	20	51.7	65.5
22/05/2008	08:00	44	14.4	29.5
23/05/2008	08:00	68	2.1	1.9

*Table 4. WSL Results from Test Series 1, ANS*

It can be seen in Figure 8 that there was a slight increase in WSL result with the “No flow” sample from the stationary water in the drum over the first 24 hours. This is due to an increase in the density of the oil due to evaporative loss that in turn creates a higher WSL effectiveness result because the oil is less buoyant. Because of this density effect it is impossible to differentiate the effects of dispersant loss and oil density on the WSL result in the early stages of the test. Dispersant may be leaching away but the density change can mask the effect of dispersant loss. This anomaly with the WSL test has been observed in other studies ([Martinelli.& Lynch, 1980](#)).

The ANS “Weathering Control” sample was tested after 72 hours in a tray and produced a WSL result of 54.9% Another WSL test conducted with no added dispersant to the ANS oil produced a result of 1.2%. This indicates that the evaporative loss from the oil over the 3 days of the test, and the consequent viscosity and density increase, had only a minimal influence on the WSL result obtained, only decreasing from 60.0% to 54.9% over three days. It is important to restate that the WSL effectiveness result actually increased for ANS weathered less than 3 days where the density increase effect (increase in WSL value) was more pronounced than both a viscosity increase and a dispersant leaching effect. The decrease in the WSL results obtained from both the “On tank” and “No flow” samples is therefore almost entirely due to the loss of dispersant from the oil into the water.

The WSL result obtained with the On-tank samples with the 6.3 cm/s water current decreased with time slightly faster than it declined with the “No flow” oil samples. The WSL results declined to 30%, half of the initial value of 60%, in 34 hours on the water in the tank and 44 hours on the stationary water in the drum. These results indicate that the 6.3 cm/s water current flow under the test oil slick caused slightly more rapid dispersant removal from the ANS oil than when it was in contact with stationary water.

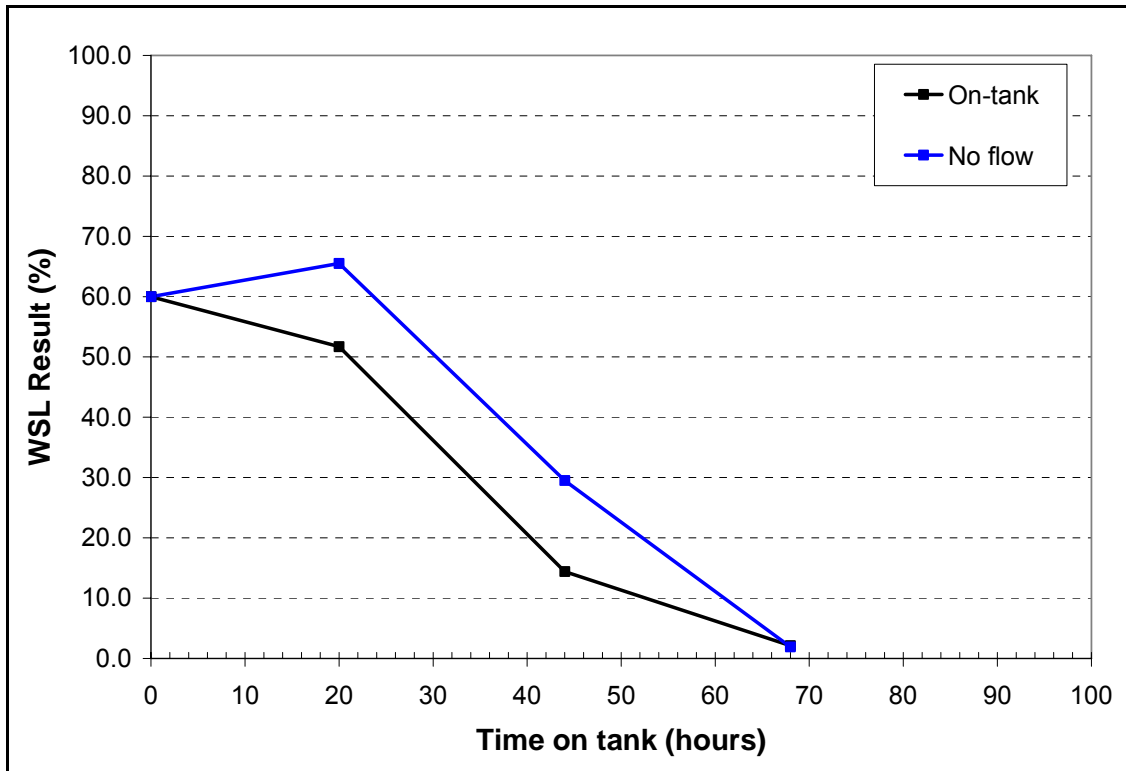


Figure 8. WSL Results from Test Series 1, ANS

### LISST Results

A large amount of oil had been lost from the ring in this test before the breaking waves were applied. This significantly reduced the amount of dispersant-treated oil from the original 80 litres to a much lower, but unknown, volume available for dispersion by the breaking waves. There was not a large amount of oil left in this ring at the end of the test so the in-water dispersed oil cloud was small and difficult to both visually observe and measure.



Measurements were made by the LISST on along-tank transects at a depth of 1.5 m in the water column, with the detector passing beneath the center of the oil slick. The first pass was made as soon as possible after breaking waves had passed through the slick, normally within 5 to 10 minutes.

Only one pass was made with the LISST in this test and the results are presented in Table 5.

<b>Test Series 1 ANS</b>	<b>Volume Median Diameter (<math>\mu\text{m}</math>)</b>	<b>Average Oil Conc (ppm)</b>	<b>Peak Oil Conc (ppm)</b>	<b>Vol % Oil in Drops &lt; 75 <math>\mu\text{m}</math></b>
pass #1	163	4.5	7.9	31.5

*Table 5. LISST results from Test Series 1, ANS*

The initial VMD of the oil drop distribution was relatively large at 163 microns. The average and peak oil concentrations were low, probably because the quantity of oil available for dispersion by the waves was much less than the 80 litres originally placed in the ring and thus available for dispersion at the end of this test. The percentage volume of the dispersed oil present as droplets with diameters below 75 microns, at 31.5% is relatively high indicating that a significant proportion of the oil remaining in the ring at the time that the waves were applied was dispersed into a fine-drop oil dispersion, but the amount of dispersed oil was low because of earlier losses of oil out of the ring.

### **Visual observations**

When samples of the ANS oil in the ring were removed for WSL testing at the intervals described in Table 4 the opportunity was taken to conduct a very simple on-tank experiment. A spoonful of the oil was lifted from the ring and dropped into the tank water. The oil was then stirred into the water adjacent to the ring and the dispersion observed.

The ANS oil sample taken after 20 hours on the water in the tank dispersed easily into a brown cloud, but the samples taken after 44 and 68 hours did not disperse as well; the oil

was temporarily dispersed into the water as black droplets, but these re-surfaced quite quickly.

Visual observations were also made when the breaking waves were put through the slick. The small amount of ANS oil was broken up by the passage of the breaking wave. Large oil droplets could clearly be seen in the water and there was the formation of a small black cloud of oil in the water, but there was no prolonged dispersion of oil visible in the water. The small amount of oil present in the ring at the end of this test and the small dispersed oil cloud generated by the breaking waves made it difficult to observe the characteristics of the dispersion over an extended period of time.

### 5.1.2 Test Series 1, IFO-180

#### WSL Results

Samples of oil (the “On-tank” samples) were taken from the rings in the tank at regular intervals and transferred to the laboratory where the WSL test was undertaken. Samples were also taken from the drum of stationary water (the “No-Flow” samples) for testing. The WSL results for Test Series 1 with IFO-180 oil are contained in Table 6 and illustrated in Figure 9.

Samples taken			WSL test result (%)	
Date	Time	Time on water (hours)	IFO-180 On-Tank	IFO-180 No-Flow
20/05/2008	12:00	0	58.6	58.6
21/05/2008	08:00	20	9.8	57.1
22/05/2008	08:00	44	10.8	23.2
23/05/2008	08:00	68	5.3	9.3

Table 6. WSL Results from Test Series 1, IFO-180

It can be seen in Figure 9 that the WSL result decreased with the time that the dispersant-treated IFO-180 oil was on the water in the tank (“On tank” samples) at a much faster

rate than it declined with the oil samples taken from the stationary water in the drum (“No flow” samples). The WSL result decreased to half of the initial value in 12 hours with samples from the tank with the 6.3 cm/s water current, but this took 45 hours with the samples taken from the drum of stationary water.

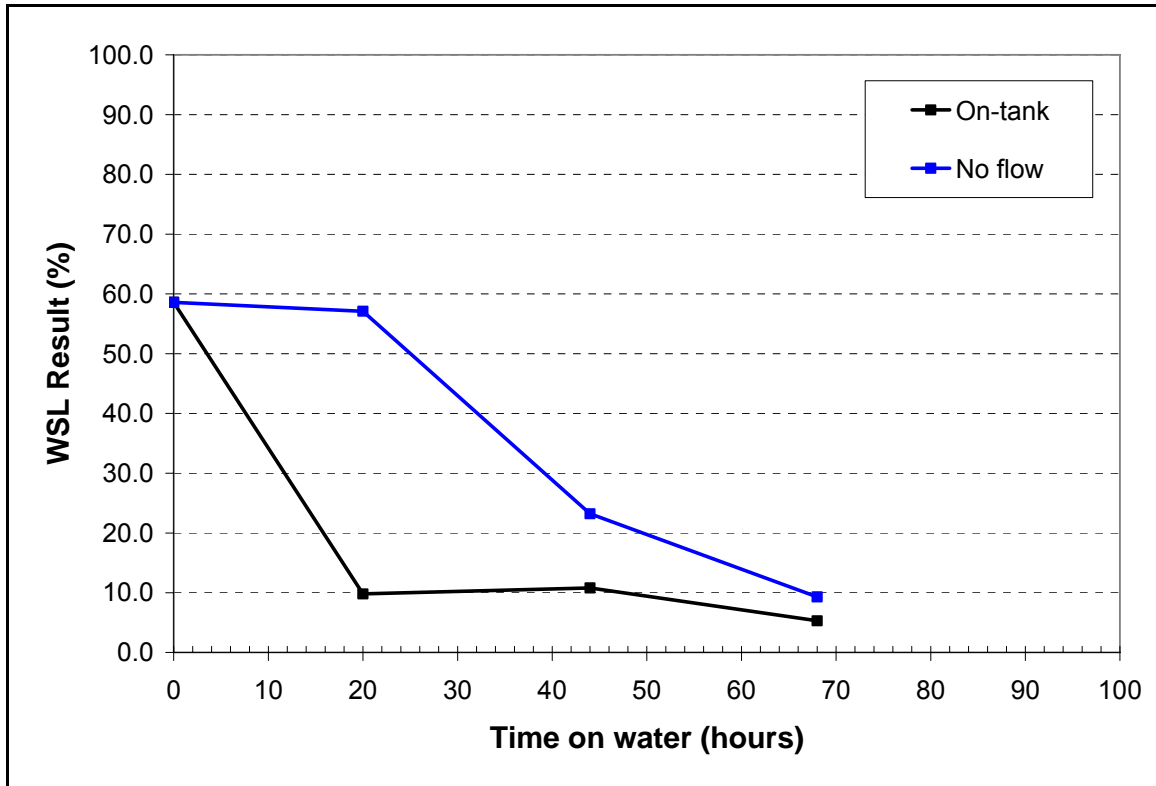


Figure 9. WSL Results from Test Series 1, IFO-180

### LISST Results

Eight LISST runs were conducted on the dispersed oil plume created by the application of breaking waves in the 30 minutes after the waves were applied. The parameters measured are contained in Table 7 and displayed in Figure 10.

The VMD of the dispersed oil was large at 220 microns and decreased with time. The average and peak dispersed oil concentrations were much higher than those measured in the Test 1 with ANS oil. This was most probably due to there being much more of the IFO-180 oil to be dispersed as there had only been slight losses of this oil from the ring before the breaking waves were applied. The higher density of the IFO-180 oil, compared to the ANS oil, would have also permitted a higher proportion of it to be dispersed by the

waves. However, the proportion of the volume of oil dispersed as small droplets (those with diameters less than 75 microns) was initially quite small (10 to 15%) although it increased with time as the average dispersed oil concentration increased up until Pass #4, this proportion then subsequently decreased. When the highest average and peak oil concentrations were measured in pass #4 the percent of oil present in small drops was still relatively small (only 19%). These are indicators that although a significant quantity of the IFO-180 oil was initially dispersed as relatively large oil droplets, these large drops floated out over a period of time and only a small percentage of the dispersed oil was in small enough drops to be considered permanently dispersed. The LISST data indicate that this was not a particularly effective dispersion.

<b>Test Series 1 IFO 180</b>	<b>Volume Median Diameter (<math>\mu\text{m}</math>)</b>	<b>Average Oil Conc (ppm)</b>	<b>Peak Oil Conc (ppm)</b>	<b>Vol % Oil in Drops &lt; 75 <math>\mu\text{m}</math></b>
pass #1	220	25	55	10
pass #2	222	26	51	14
pass #3	216	39	89	17
pass #4	189	67	320	19
pass #5	147	47	145	26
pass #6	152	68	182	22
pass #7	105	25	43	41
pass #8	119	34	47	34

*Table 7. LISST results from Test Series 1, IFO-180*

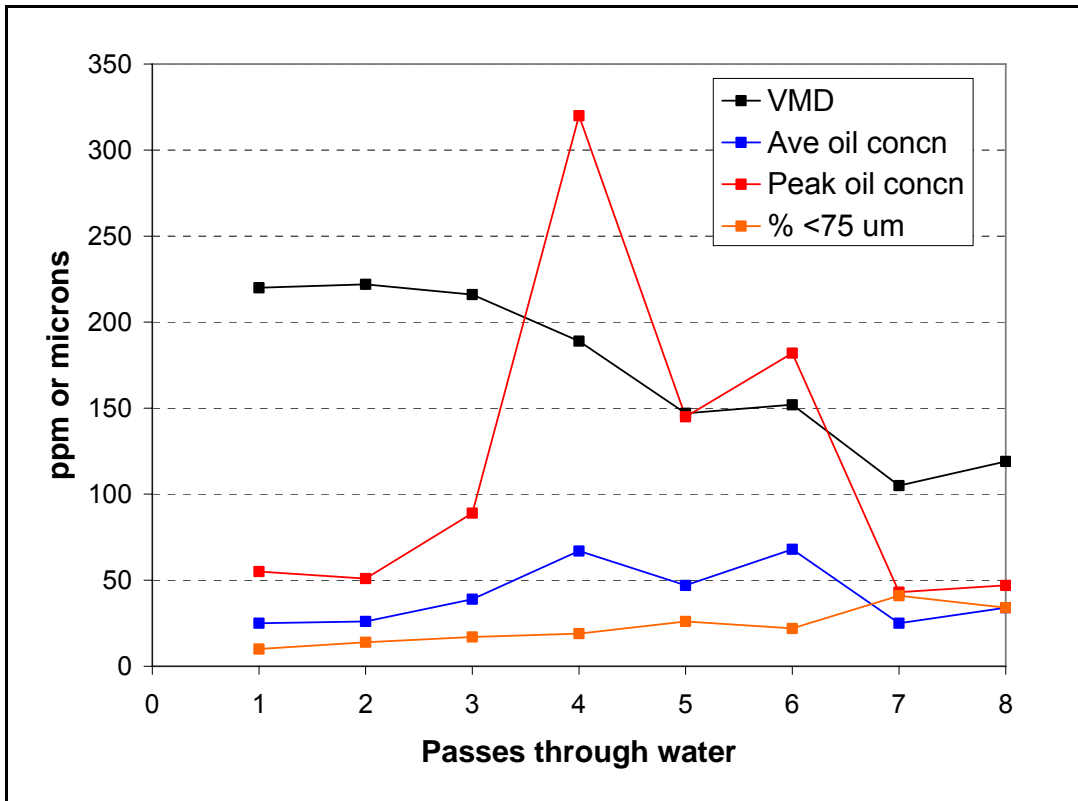


Figure 10. LISST results from Test Series 1, IFO-180 by pass

### Visual observations

When samples of the IFO-180 oil in the ring were removed for WSL testing at the intervals described in Table 6 the opportunity was taken to conduct a very simple on-tank experiment. A spoonful of the oil was lifted from the ring and dropped into the tank water. The oil was then stirred into the water and the dispersion observed.

The IFO-180 oil on the water in the tank had taken on a very grainy appearance by the time that the 20-hour sample was taken. The oil did not disperse very well when stirred into the water with a spoon; the IFO-180 oil was temporarily dispersed into the water as black droplets, but these re-surfaced quite quickly. Similar visual observations were made when the samples were taken at 44 and 68 hours. Visual observations were also made when the breaking waves were put through the slick. As the breaking waves passed through the slick of the IFO-180 oil a coarse, black dispersion of oil in the water was formed.

## **5.2 Test Series 2**

Test Series 2 was similar to Test Series 1 except that IFO-30 was substituted for IFO-180, which had a Pour Point very similar to the prevailing water temperature. It was believed that this factor could be controlling the apparent loss of dispersant.

Test Series 2 began with the test slicks being placed in the two test rings on the water in the tank at 15:00 on Friday, 23<sup>rd</sup> May and was completed when breaking waves were applied to the test slicks at 11:00 on Tuesday 27<sup>th</sup> May; a total of 90.5 hours on the water surface. This test series used 80 litres of each of ANS and IFO-30, each pre-mixed with Corexit 9500 at a DOR of 1:20, in the two rings in the tank. The bubble barrier was fed with air at 20 cubic feet per minute (cfm) at 75 psi. This rate of air flow from the bubble barrier, which was 23 feet from the rings, created an mean water current flow of 4.0 cm/s (Standard Deviation 3.04 cm/s) beneath the test oil slicks over the nearly four days of the test. The temperature of the water in the tank varied between 17.8°C (64°F) and 19.9°C (67.8°F) during the test period.

### **5.2.1 Test Series 2, ANS**

#### **WSL Results**

Samples of oil (the “On-tank” samples) were taken from the rings in the tank at regular intervals and transferred to the laboratory where the WSL test was undertaken. Samples were also taken from the drum of stationary water (the “No-Flow” samples) for testing.

The WSL results for Test Series 2 with ANS oil are contained in Table 8 and illustrated in Figure 11.

Samples taken			WSL test result (%)	
Date	Time	Time (hours)	ANS On-Tank	ANS No-Flow
23/05/2008	15:00	0	60.0	60.0
24/05/2008	07:45	15	74.6	66.1
25/05/2008	07:50	39	57.6	53.6
26/05/2008	11:30	68	5.4	22.3
27/05/2008	08:00	87	5.9	10.6

Table 8. WSL Results from Test Series 2, ANS

After the initial rise in the WSL result due to density increase caused by further evaporative loss from the ANS test oil the WSL result decreased with time for both the “On-tank” and “No flow” samples. The WSL results of samples from the tank with the 4.0 cm/s water current declined to 30%, half of the initial value of 60%, in 54 hours, and in 60 hours with the samples from the stationary water in the drum. Given the known repeatability of the WSL test method this difference may not be significant.

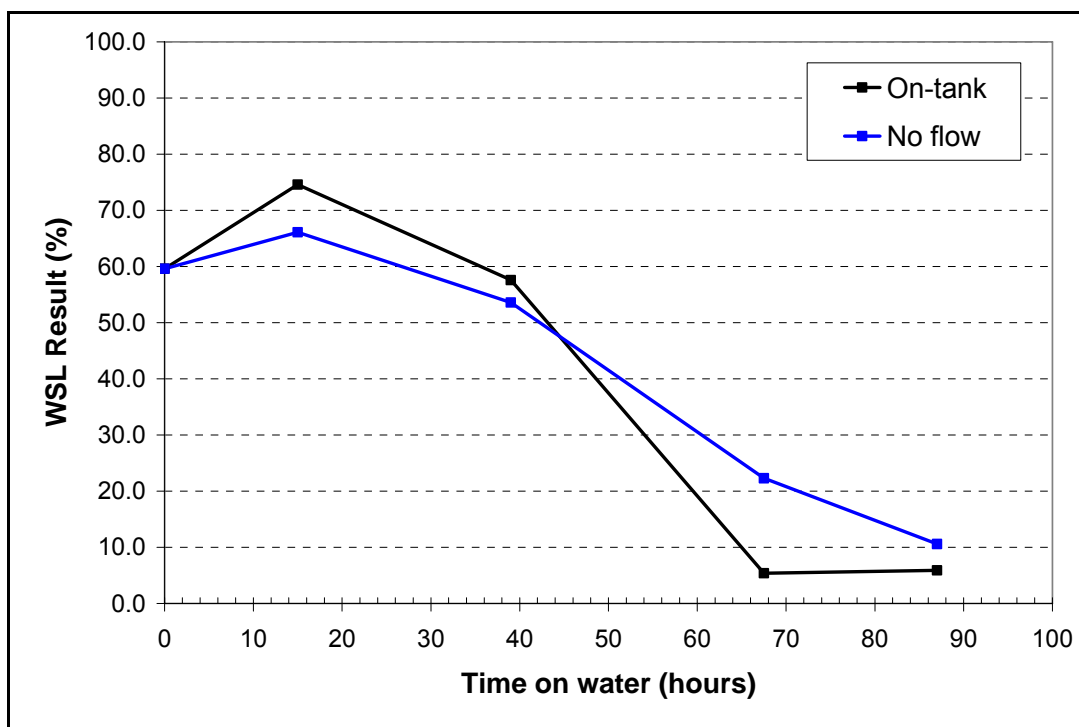


Figure 11. WSL Results from Test Series 2, ANS

## LISST Results

The parameters measured by the LISST instrument in three passes are presented in Table 9. The initial VMD was large but decreased with time. The average and peak oil concentrations were higher than those obtained in test 1 with the ANS oil, most probably because there was much more oil available for dispersion by the breaking waves, and decreased slightly with time. Taken together, the change in these two parameters indicates that larger droplets of oil initially dispersed by the action of the breaking waves were slowly floating out after the breaking waves had passed. The percentage of the volume of dispersed oil present as droplets with diameters less than 75 microns increased with time to 56% by the third pass and the average oil concentration remained relatively constant. This suggests that there was a significant quantity of oil in the oil plume in the form of small drops that could be considered permanently dispersed and the dispersion was somewhat successful.

Test Series 2 ANS	Volume Median Diameter ( $\mu\text{m}$ )	Average Oil Conc (ppm)	Peak Oil Conc (ppm)	Vol % Oil in Drops < 75 $\mu\text{m}$
pass #1	255	19	52	12
pass #2	105	19	34	40
pass #3	72	17	33	56

Table 9. LISST results from Test Series 2, ANS

## Visual observations

When samples of the ANS oil in the ring were removed for WSL testing at the intervals described in Table 8 the opportunity was taken to conduct the simple on-tank experiment with a spoon on the visual appearance of any dispersion that might occur.

The sample of ANS oil taken from the water in the tank after 15 hours on the water surface dispersed well; the oil immediately formed a brown ‘cloud’ when stirred into the water. The sample taken after 39 hours on the water also dispersed into a brown ‘cloud’,



but the samples taken after 68 and 87 hours on the water only dispersed into a black ‘cloud’ of large oil droplets that rapidly re-surfaced.

Visual observations were also made when the breaking waves were put through the slick. The slick of ANS oil was broken up by the passage of the breaking waves. Large oil droplets could clearly be seen in the water and there was the formation of a black cloud of coarsely dispersed oil in the water.

### 5.2.2 Test Series 2, IFO-30

#### WSL Results

Samples of oil (the “On-tank” samples) were taken from the rings in the tank at regular intervals and transferred to the laboratory where the WSL test was undertaken. Samples were also taken from the drum of stationary water (the “No-Flow” samples) for testing. The WSL results for Test Series 2 with IFO-30 oil are contained in Table 10 and illustrated in Figure 12.

Samples taken			WSL test result (%)	
Date	Time	Time (hours)	IFO-30 On-Tank	IFO-30 No-Flow
23/05/2008	15:00	0	58.6	58.6
24/05/2008	07:45	15	66.2	64.7
25/05/2008	07:50	39	18.7	39.9
26/05/2008	11:30	68	12.2	24.8
27/05/2008	08:00	87	5.2	15.0

Table 10. WSL Results from Test Series 2, IFO-30

It can be seen in Figure 12 that the WSL results from both the “On tank” and “No flow” samples decreased with time on the water.

A “Weathered Control” sample of IFO-30 (a sample of the oil in a 5 mm thick layer in a tray and kept under cover near the tank) produced a WSL result of over 70%. This indicates that the overwhelmingly most important reason for the reduction in WSL result from both the “On Tank” and “No flow” samples was their exposure to water; flowing at 4/0 cm/s in the tank and static in the drum. The increase in WSL effectiveness on weathered oil when compared to the fresh oil result of 59% is due to the density increase effect discussed earlier.

The WSL result obtained with the On-tank samples with the 4.0 cm/s water current decreased with the time at a slightly faster rate than it declined with the “No flow” oil samples. The WSL results declined to 30%, half of the initial value of 60%, in 34 hours on the water in the tank and 58 hours on the stationary water in the drum. The increase in effectiveness at the 15-hour mark may again be attributed to the effect of the increased density of the IFO-30 oil as it weathers on the WSL test outcome.

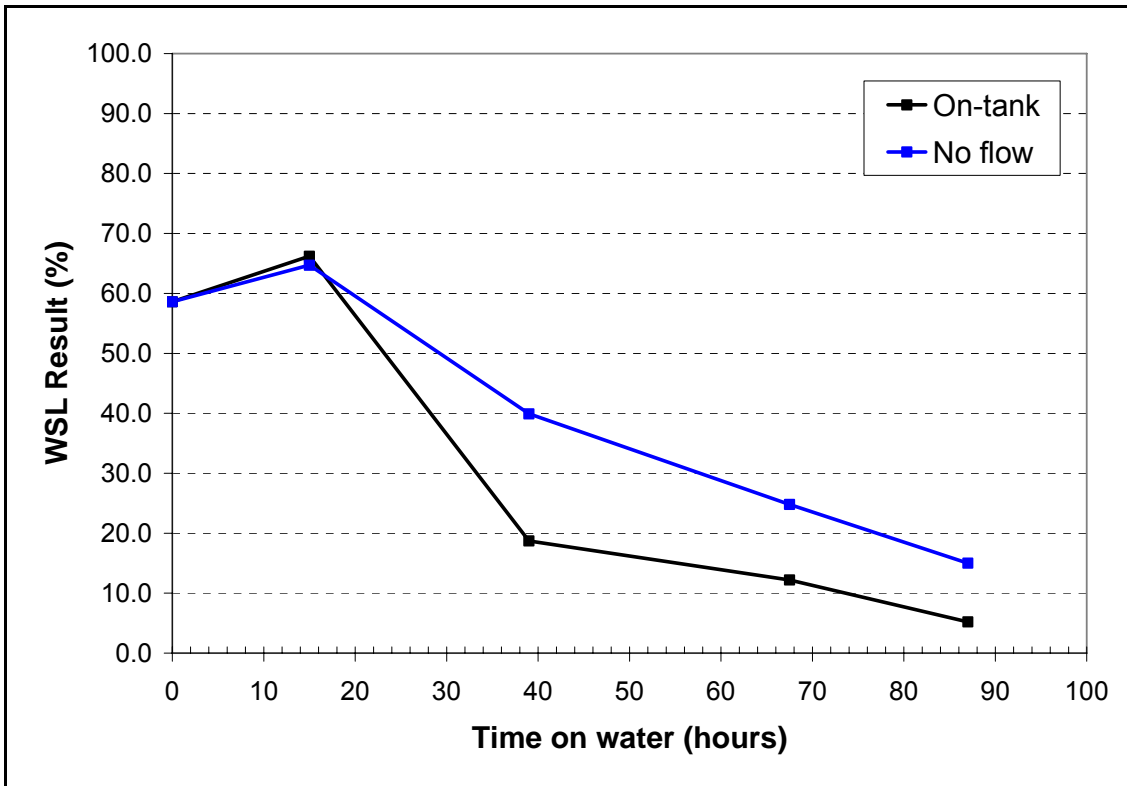


Figure 12. WSL Results from Test Series 2, IFO-30

## LISST Results

The VMD of the dispersed oil plume after the passage of the breaking waves was initially large (228 microns), the peak oil concentration high and the percentage of oil in drops less than 75 microns small (13%). This indicates that the oil was initially being dispersed primarily in the form of large oil droplets. The subsequent decreases in VMD and oil concentrations indicate that the larger oil droplets were floating out of the water and back to the surface leaving the smaller dispersed droplets to form a higher proportion of the lesser quantity of dispersed oil remaining in the water column.

<b>Test Series 2 IFO-30</b>	<b>Volume Median Diameter (<math>\mu\text{m}</math>)</b>	<b>Average Oil Conc (ppm)</b>	<b>Peak Oil Conc (ppm)</b>	<b>Vol % Oil in Drops &lt; 75 <math>\mu\text{m}</math></b>
pass #1	228	28	120	13
pass #2	112	22	47	37
pass #3	75	15	26	55

Table 11. LISST results from Test Series 2, IFO-30

## Visual observations

When samples of the IFO-30 oil in the ring were removed for WSL testing at the intervals described in Table 10 the same simple experiment with a spoon was conducted to assess the visual appearance of any dispersion that might occur.

The sample of IFO-30 oil taken from the water in the tank after 15 hours on the water surface dispersed well; the oil immediately formed a brown ‘cloud’ when stirred into the water. The sample taken after 39 hours on the water did not disperse as well; the ‘cloud’ of small drops of dispersed oil in the water was generally black, rather than brown, and individual droplets of dispersed oil could easily be seen. The samples taken after 68 and 87 hours on the water only dispersed into a black ‘cloud’ of large oil droplets that rapidly re-surfaced.

Visual observations were also made when the breaking waves were put through the slick. A coarse, black dispersion of IFO-30 oil in the water was observed.

### **5.3 Test 2a**

This test was conducted to provide a ‘base-line’ against which the results from the other tests could be compared. There was effectively no time for the Corexit 9500 dispersant to leach out from the oil and it would therefore be present in the oil at the initial treatment rate of a DOR of 1:20.

Test 2a was conducted on the afternoon of Tuesday 27<sup>th</sup> May. 80 litres of IFO-30, pre-mixed with Corexit 9500 at a DOR of 1:20 was placed in the ring on the tank at 13:40. Breaking waves were applied to the slick at 14:15, 35 minutes later. The temperature of the water in the tank was 16 °C (61°F) during this test.

#### **WSL Results**

The WSL result on the sample of IFO-30 oil pre-mixed with Corexit 9500 at a DOR of 1:20 was 60.0%. As there was no soaking period for the loss of dispersant to occur, this is the only WSL result for this test.

#### **LISST Results**

Three LISST passes were made after the oil had been dispersed by the breaking waves and the measured parameters are given in Table 12. Average oil concentrations in the plume ranged from 47 to 70 ppm, with spikes to 134 to 170 ppm, the highest of any test in this series. The VMD of the dispersed oil was very small at 14 to 11 microns and the proportion of dispersed oil present as droplets with diameters of less than 75 microns was very high (92 to 97%) of the total dispersed oil volume. Combined together, these results indicate that a very high level of dispersion of the oil into the water column occurred in the form of oil drops that would be permanently dispersed.

Test 2a IFO-30	Volume Median Diameter ( $\mu\text{m}$ )	Average Oil Conc (ppm)	Peak Oil Conc (ppm)	Vol % Oil in Drops < 75 $\mu\text{m}$
pass #1	14	47	134	92
pass #2	14	60	152	94
pass #3	11	70	170	97

Table 12. LISST results from Test 2a with IFO-30

### Visual observations

The most striking visual observation of the dispersion of the dispersant-treated IFO-30 oil in Test 2a was the creation of a light brown, opaque plume of dispersed oil as soon as the breaking waves passed through the slick (Figure 13).



Figure 13. Photo of brown plume of dispersed oil

The plume of dispersed oil was visibly brown, even though the IFO-30 is a black oil. Individual oil droplets were not visible in the plume and it had a very optically dense appearance, like a brown pigment or ink having been added to the water.

### **5.4 Test Series 3**

The purpose of this test series was to investigate the effect of lower test oil volume; 38 litres compared to 80 litres in each test ring. While this had originally been intended to produce oil layers that were half the thickness of those used in Test Series 1 and 2, previous work had shown that these oils do not spread out to cover the full containment throughout the duration of the test. Rather, the smaller quantity of oil was more dynamic in the ring and spread to cover most of the ring area on occasion, but was herded by winds and/or currents to cover about half of the containment rings at other times. The oil was thinning and thickening and moving over the water surface constantly in these tests with the smaller oil quantities.

Test Series 3 began with the test slicks being placed in the two test rings on the water in the tank at 10:00 on Wednesday, 28<sup>th</sup> May and was completed when breaking waves were applied to the test slicks at 10:00 on Friday, 30<sup>th</sup> May; a total of 49.5 hours on the water surface. The same test series was originally started on the afternoon of Tuesday, 27<sup>th</sup> May, but high winds and a rainstorm overnight caused a very significant proportion of the test oils to escape from the rings, so the test series was re-started on Wednesday morning.

This test series used 38 litres of each of ANS and IFO-30, each pre-mixed with Corexit 9500 at a DOR of 1:20, in the two rings in the tank. The bubble barrier was fed with air at 20 cubic feet per minute (cfm) at 75 psi. This rate of airflow from the bubble barrier, which was 25 feet from the edge of the rings, created an average water current flow of 5.72 cm/s (Standard Deviation 3.76 cm/s) beneath the test oil slicks. The temperature of the water in the tank varied between 21.4°C (70.5°F) and 20.8°C (69.5°F) during the test period.

### 5.4.1 Test Series 3, ANS

#### WSL Results

Samples of oil (the “On-tank” samples) were taken from the rings in the tank at regular intervals and transferred to the laboratory where the WSL test was undertaken. Samples were also taken from the drum of stationary water (the “No-Flow” samples) for testing. The same nominal oil thickness was used in the static drum tests as in the on-tank slick and the oil spread to the entire surface of the drum. The thickness of the oil on the drum in this test series was half that of the Series 1 and 2 tests.

The WSL results for Test Series 3 with ANS oil are contained in Table 13 and illustrated in Figure 14.

Samples taken			WSL test result (%)	
Date	Time	Time (hours)	ANS On-Tank	ANS No-Flow
28/05/2008	10:00	0	60.0	60.0
29/05/2008	08:00	22	10.4	43.1
30/05/2008	08:00	46	9.2	35.2

Table 13. WSL Results from Test Series 3, ANS

It can be seen that the WSL result obtained with the ANS oil samples taken from the water in the tank declined with time at a rate that was much faster than that of the samples taken from the stationary water in the drum. The WSL results of ANS samples from the tank with the 5.7 cm/s water current rapidly declined to 30%, half of the initial value of nearly 60%, in 14 hours. The WSL result obtained with the “No flow” sample was above 30% after 46 hours.

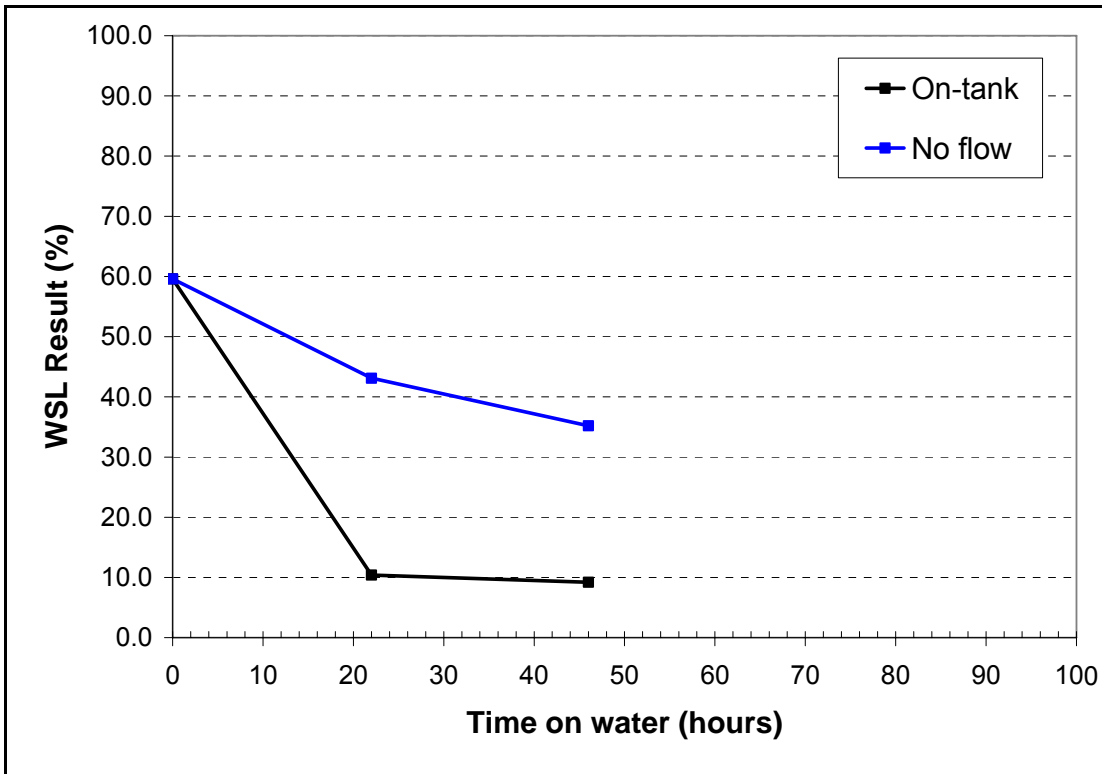


Figure 14. WSL Results from Test Series 3, ANS

### LISST Results

Three LISST passes were made after the oil had been dispersed by the breaking waves and the measured parameters are given in Table 14.

Test Series 3 ANS	Volume Median Diameter (µm)	Average Oil Conc (ppm)	Peak Oil Conc (ppm)	Vol % Oil in Drops < 75 µm
pass #1	139	11	69	38
pass #2	96	14	34	45
pass #3	86	14	27	48

Table 14. LISST results from Test Series 3, ANS

The VMD of the dispersed oil on the first pass at 139 microns was smaller than that measured in the Series 1 and 2 tests (163 and 255 microns, respectively). The average oil concentration at 11 - 14 ppm was lower than in test 2 where the average oil concentration



was 17 - 19 ppm, but this was most probably be due to the reduced initial quantity of oil used in this test (38 litres compared to 80 litres in test 2). The percentage of oil in the form of drops less than 75 microns was relatively high (38%). The VMD decreased in the subsequent two passes but the average oil concentration did not. Combined together, these results indicate a moderate level of dispersion of the oil into the water column in the form of oil that could be considered permanently dispersed.

### **Visual observations**

When samples of the ANS oil in the ring were removed for WSL testing at the intervals described in Table 13 the same simple experiment with a spoon was conducted to assess the visual appearance of any dispersion that might occur.

The sample of ANS oil taken from the water in the tank after 22 hours on the water surface dispersed as a proportion of brown ‘cloud’, but also with a black cloud of oil droplets. The sample taken after 46 hours dispersed as only a black ‘cloud’; no brown colour was apparent.

Visual observations were also made when the breaking waves were put through the slick. The slick of ANS oil was broken up by the passage of the breaking wave. Individual large oil droplets could be seen in the water and a black cloud of dispersed oil was visible.

## **5.4.2 Test Series 3, IFO-30**

### **WSL Results**

Samples of oil (the “On-tank” samples) were taken from the rings in the tank at regular intervals and transferred to the laboratory where the WSL test was undertaken. Samples were also taken from the drum of stationary water (the “No-Flow” samples) for testing.

The WSL results for Test Series 3 with IFO-30 oil are contained in Table 15 and illustrated in Figure 15.

Samples taken			WSL test result (%)	
Date	Time	Time (hours)	IFO-30 On-Tank	IFO-30 No-Flow
28/05/2008	10:00	0	58.6	58.6
29/05/2008	08:00	22	18.6	31.9
30/05/2008	08:00	46	20.4	17.8

*Table 15. WSL Results from Test Series 3, IFO-30*

It can be seen that the WSL result obtained with the IFO-30 oil samples taken from the water in the tank declined with time at a rapid rate. The WSL results for the samples taken from the stationary water in the drum also declined rapidly but at a slightly slower rate. The WSL results obtained with IFO-30 samples from the tank with the 5.7 cm/s water current rapidly declined to 30%, half of the initial value of nearly 60%, in 16 hours. The WSL result obtained with the “No flow” sample declined to the same value in 25 hours.

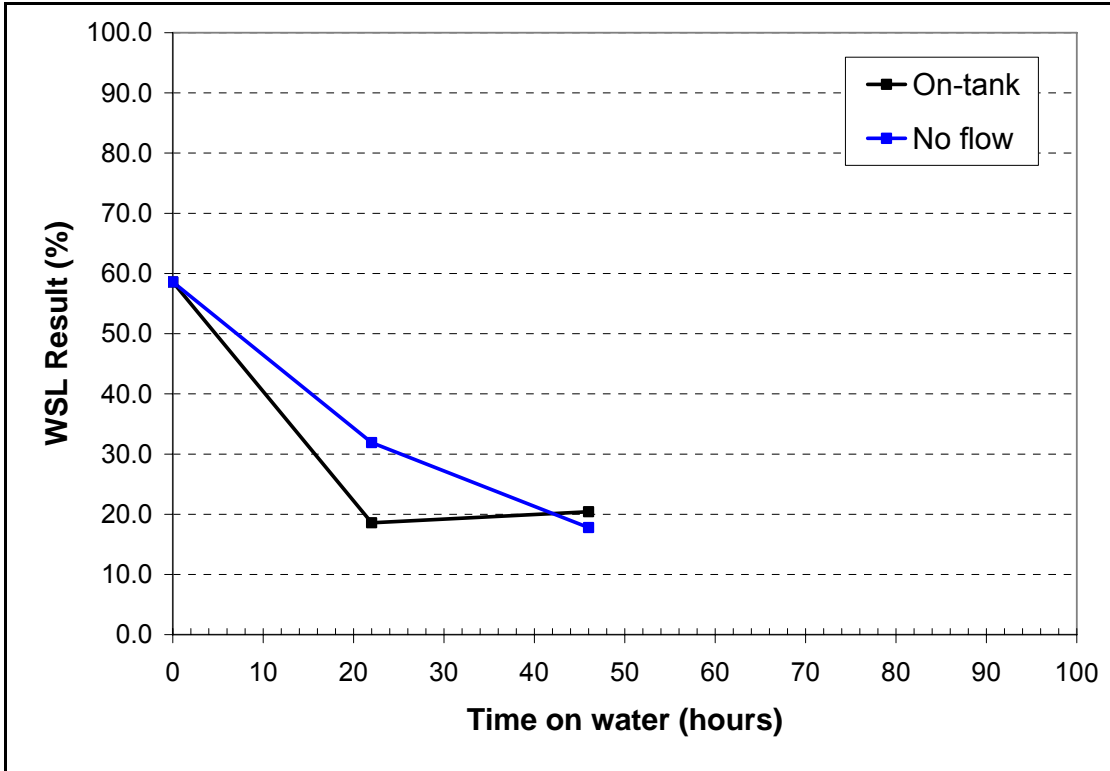


Figure 15. WSL Results from Test Series 3, IFO-30

### LISST Results

Three LISST passes were made after the oil had been dispersed by the breaking waves and the measured parameters are given in Table 16.

Test Series 3 IFO-30	Volume Median Diameter (µm)	Average Oil Conc (ppm)	Peak Oil Conc (ppm)	Vol % Oil in Drops < 75 µm
pass #1	118	26	142	34
pass #2	107	37	59	36
pass #3	80	23	40	51

Table 16. LISST results from Test Series 3, IFO-30

The VMD of the dispersed oil on the first pass was again smaller than in the previous two test series at 118 microns and the volume percentage of oil in the form of small drops was relatively high at 34%. The VMD decreased in the subsequent two passes but the average oil concentrations remained fairly constant. The percentage of oil in the form of drops

less than 75 microns was also high throughout the test. Combined together, these results indicate a moderate level of dispersion of the oil into the water column in the form of oil that would be considered permanently dispersed.

### **Visual observations**

When samples of the IFO-30 oil in the ring were removed for WSL testing at the intervals described in Table 15 the same simple experiment with a spoon was conducted to assess the visual appearance of any dispersion that might occur.

The sample of IFO-30 oil taken from the water in the tank after 22 hours on the water surface did not appear to disperse well; the oil dispersed in the form of a small amount of brown ‘cloud’, but most was in the form of a ‘black’ cloud of oil droplets. The sample taken after 46 hours behaved in a similar manner, except that there was no brown colouration and the dispersion of oil was in the form of oil droplets, both fine and coarse.

Visual observations were also made when the breaking waves were put through the slick. A coarse, black dispersion of IFO-30 oil in the water was observed.

## **6. Discussion of Results**

### **6.1 Results obtained with ANS oil**

The ANS oil was tested in all three Test Series; 1, 2 and 3. The major differences between the Test Series are contained in Table 17.

	<b>Mean current speed under oil (cm/s)</b>	<b>Amount of oil in ring (litres)</b>	<b>Time on tank water before breaking waves passed through the slick (hours)</b>
<b>Test Series 1</b>	6.3	80	68
<b>Test Series 2</b>	4.0	80	87
<b>Test Series 3</b>	5.7	38	46

*Table 17. Current speed, amount of oil and time on water for tests with ANS oil*

### 6.1.1 WSL results

The WSL test results relate to samples taken before the breaking waves were applied to the test oils. They therefore show the potential for dispersion of the oil at the time that the samples were taken.

The rate of decrease of the WSL results obtained with the “On tank” and “No flow” samples were related to the presence of currents and the amount of oil in the test. The results are shown in Table 18. The length of time taken for the WSL result to decrease to half the initial value was longer in the No-Flow tests where there were no currents under the oil. Also the length of time taken for for the WSL result to decrease to half the original value was much shorter in Test #3 where the slicks were thinner and less mobile than in Test #2.

	<b>Mean current speed under oil in On-Tank Tests (cm/s)</b>	<b>Amount of oil in ring (litres)</b>	<b>Time for WSL result to decrease to half the initial value On-Tank (hours)</b>	<b>Time for WSL result to decrease to half the initial value No-Flow On-Drum (hours)</b>
Test Series1	6.3	80 <sup>a</sup>	34	45
Test Series 2	4.0	80	54	60
Test Series 3	5.7	38	14	45
a. Some of the oil in the ring in the “On Tank”ANS Test #1 was lost, so that the actual amount through the test was <<80 L.				

Table 18. Time for WSL result to decrease to half original value with ANS oil

### WSL result and amount of dispersant in the oil

WSL results were obtained with different amounts of Corexit 9500 dispersant premixed into fresh ANS oil. The dispersant treatment rates used were from 0.25% volume of dispersant in oil, equivalent to a DOR (Dispersant to Oil Ratio) of 1:400, up to 5%

volume of dispersant in oil, equivalent to a DOR of 1:20. The results are presented in Figure 16.

The WSL result obtained with the ANS oil is proportional to the amount of dispersant pre-mixed into the oil. The WSL result obtained with samples withdrawn from the water on the tank after the different time periods is therefore proportional to the amount of dispersant that remained within the oil, provided that there were no effects due to oil weathering.

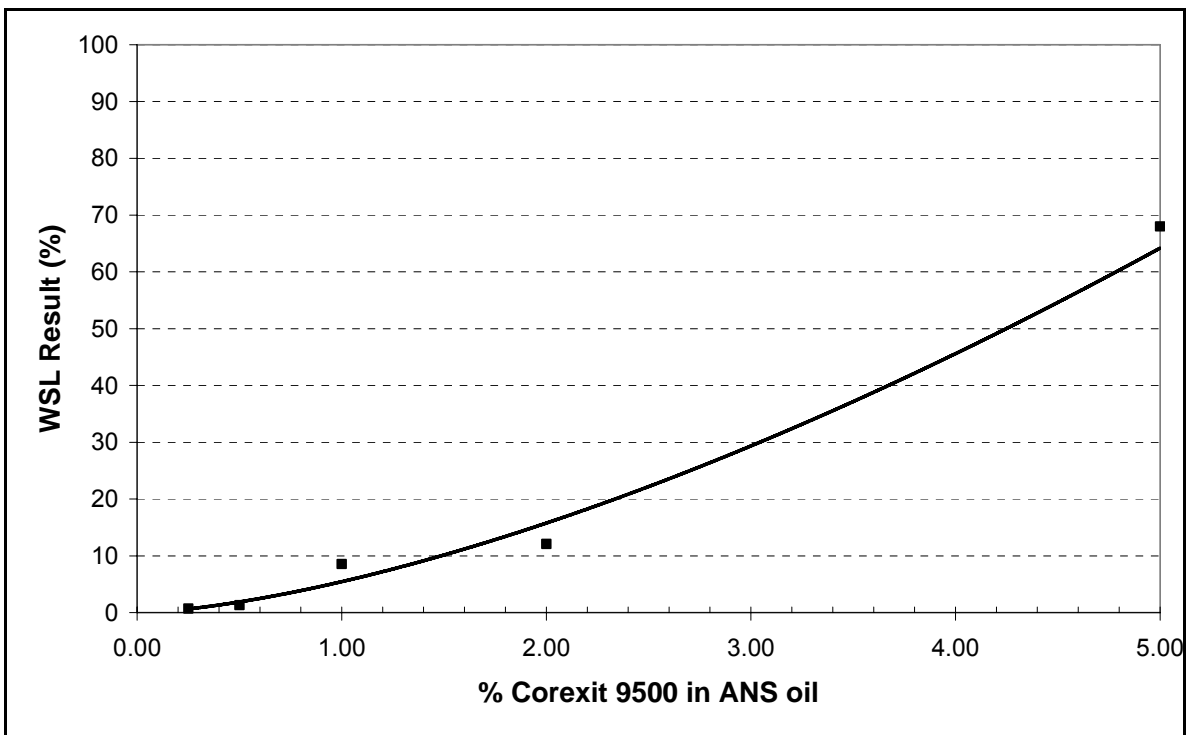


Figure 16. Effect of dispersant treatment rate on WSL result with ANS oil

The ANS oil had been artificially weathered to remove the oil components that would have evaporated if 'fresh' ANS crude oil had been used. There was a slight increase in oil density due to the evaporation of some oil components and this affected the WSL results in the early stages of the tests. There was no wave action during the 'soaking' time when the oil remained on the tank prior to being dispersed by breaking waves, so there was no water-in-oil emulsification that would cause an increase in viscosity, and therefore a decrease in dispersibility as reflected by a reduced WSL result.

The primary cause of a decrease in WSL result obtained with samples taken after time on the water surface was therefore a loss of dispersant into the underlying water. The decrease in WSL result with time is thus proportional to the amount of dispersant lost from the oil with the following two important caveats: the WSL measured effectiveness increases with an increase in oil density and the WSL effectiveness may not drop until excess dispersant leaches from the oil. To expand upon this second point, all tests were completed with an initial DOR of 1:20, a commonly recommended field dosage. This is likely more dispersant than is needed to achieve maximum dispersion in the WSL test but this was not investigated in this study. Ideally the data in Figure 16 should include WSL results for 3% and 4 % dispersant concentrations to identify the minimum concentration of dispersant necessary to achieve the maximum WSL result.

The loss of dispersant from the ANS oil, as the percentage of the original treatment rate of a DOR of 1:20 (5% volume), is shown in Figure 17 for the three Test Series. These numbers are based on the on-tank WSL effectiveness results determined in each test series and their corresponding dispersant percentages from Figure 16.

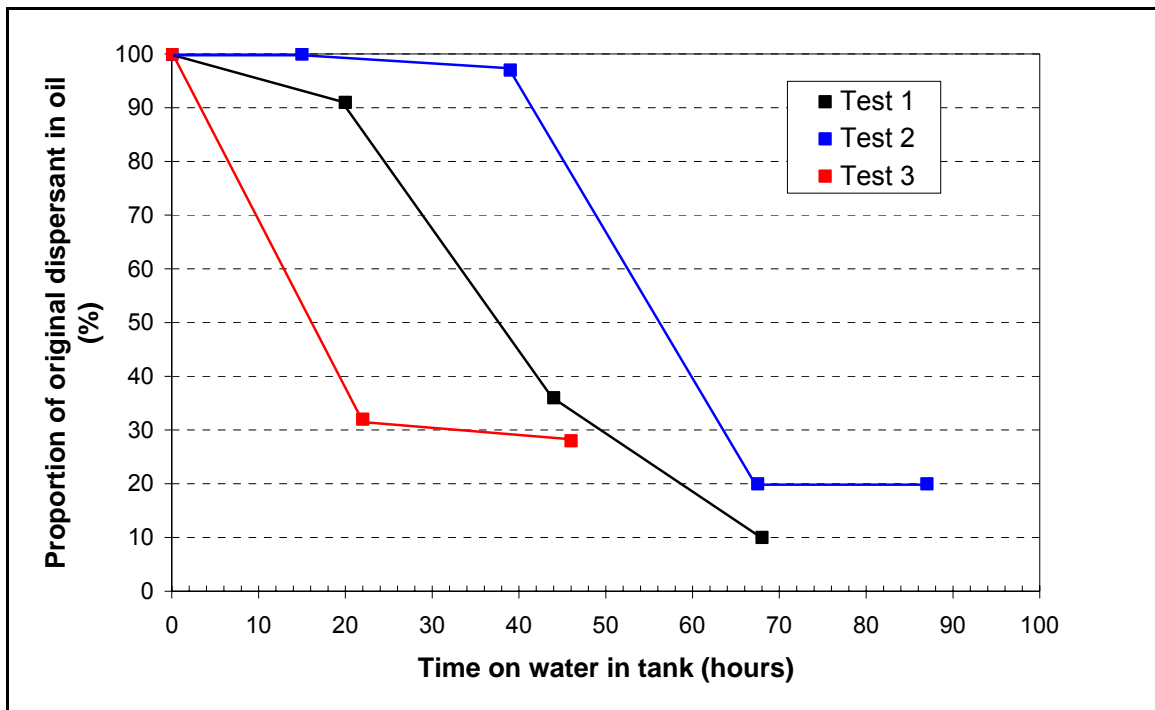


Figure 17. Dispersant decrease with time on tank from ANS oil

There appeared to be a period when dispersant loss to produce a reduced WSL value was countered by the increased oil density that caused an increase in the WSL result. This produced a period when the WSL result rose despite the fact that dispersant was probably being removed from the oil and transferred into the water. We are unable to accurately define the rate of dispersant loss in the early stages of these tests by comparison with the effect of treatment rate of WSL result (Figure 16).

In the Test Series 1 there was a significant loss of oil from the ANS ring over the test duration. The reduced oil volume may be the reason for the shorter period of time prior to the onset of the loss of WSL effectiveness in Series 1 results when compared to the Series 2 results.

Another way of considering dispersant loss is to estimate the rate of loss after the initial plateau period. The early estimates of dispersant in the oil have been ignored in series 1 and 2 and the rate of loss of dispersant has been calculated only for the steep loss periods of all test series. The dispersant loss rates are shown in Table 19.

	<b>Mean current speed under oil (cm/s)</b>	<b>Amount of oil in ring (litres)</b>	<b>Time for dispersant concentration in ANS oil to decrease to half of original value (hours)</b>	<b>Maximum Estimated Dispersant Leach Rate On-Tank (%/hour)</b>	<b>Estimated Dispersant Leach Rate No-Flow On-Drum (%/hour)</b>
Test Series 1	6.3	80	37	2.1	1.8
Test Series 2	4.0	80	56	2.6	1.4
Test Series 3	5.7	38	16	3.1	0.9

*Table 19. Time for dispersant concentration to decrease to half of original amount*



The highest rate of dispersant loss recorded for each on-tank test series was 2.1% per hour for Series 1, 2.6% per hour for Series 2 and 3.1% per hour for Series 3. The higher rate of loss for test series 3 would be expected due to the smaller quantity of oil and its more dynamic behaviour in the ring. The time taken for the dispersant concentration to apparently reach half its original value was only 16 hours in Test Series 3 compared to 37 hours in Test Series 1. And dispersant was being lost at a more rapid rate (3.1%/hr) in Test Series 3 than in Test Series 1 (2.1%/hr) during the period of steepest decline.

The loss rates for Test Series 1 should be higher than in Test Series 2 for the same reason; since a lot of oil was lost from the ANS ring in the first test. This loss of oil may explain the fact that the loss rate in Series 1 was lower than in Series 2. The methods used to identify the rate losses were not precise so it likely best not to try to infer too much from the results other than to say that the dispersant loss was in the 2 to 3% per hour range.

Similar calculations were completed to determine the rate of loss of dispersant from the static on-drum tests during the same time periods as the maximum rate loss recorded in the on-tank tests. The results are also presented in Table 19. The rate of loss in the static tests were consistently lower than in the on-tank tests but were significantly lower only for Test Series 3 for an unknown reason.

### **WSL result and dispersion in the tank**

WSL tests were performed on samples taken just before the breaking waves were put through the test oil slicks. The test results were of low values (Table 20). However, it is possible to estimate the amount of dispersant that remained in the oil (on the basis of the WSL results and Figure 16) and therefore the DOR at the time the oils were dispersed by breaking waves in the tank (Table 20).

	<b>Time on water before breaking waves (hours)</b>	<b>WSL result just before dispersion (%)</b>	<b>Calculated amount of dispersant present in oil (%)</b>	<b>Inferred DOR at time of dispersion</b>
<b>Test Series 1</b>	68	2.1	0.55	1:180
<b>Test Series 2</b>	87	5.9	1.09	1:90
<b>Test Series 3</b>	38	9.2	1.44	1:70

Table 20. *Effective DOR at time of dispersion by breaking waves with ANS oil*

### 6.1.2 LISST results

The LISST results relate to the dispersion of oil that occurred when breaking waves were passed through the slicks of test oils. The four parameters from the LISST results for the first pass of each of the three tests with the ANS oil, plus the WSL results obtained with samples taken just before the breaking waves were applied in the tank, are presented in Table 21.

	<b>Volume Median Diameter (µm)</b>	<b>Average oil concn. (ppm)</b>	<b>Peak oil concn. (ppm)</b>	<b>Oil in Drops &lt; 75 µm (% vol)</b>	<b>WSL result just before dispersion (%)</b>
<b>Test Series 1</b>	163	4.5	7.9	31.5	2.1
<b>Test Series 2</b>	255	19	52	12	5.9
<b>Test Series 3</b>	139	11	69	38	9.2

Table 21. *Measured LISST parameters with ANS oil*

The LISST results cannot be viewed independent of each other. If the VMD, average oil concentrations and percentage of oil present in the form of small droplets are considered together the dispersion can be characterized by the LISST results. For example, the series 3 LISST data has the smallest VMD, a high percentage of oil less than 75 microns and a significant average oil concentration (equivalent to series 2 since only half as much oil

was dispersed in the series 3 test). Series 2 had a much higher VMD, and much lower percentage of oil present in drops less than 75 microns when compared to series 3 so the dispersion in this test would be expected to be poorer than test 3. This is consistent with the WSL results. The series 1 test had a moderate VMD, relatively high volume percentage of oil less than 75 microns and a very low average oil concentration. However, the low average oil concentration was undoubtedly due to the small volume of oil present in the ring at the end of the test. These results taken together would indicate that based on the LISST data the dispersion in Test 1 was of a similar quality as the test 3 series dispersion. This is not reflected in the WSL test result.

Comparison with the WSL results obtained with samples taken just before the breaking waves were applied in the tank appears to show that the degree of dispersion of ANS oil was greatest in Test 3 and least in Test 1.

### **6.1.3 Visual observation results**

The visual observations of dispersion made during the sampling of the ANS oil in the period prior to dispersion by the breaking waves indicated a change from a relatively easily dispersible oil where stirring the oil into the water caused a brown “cloud” of dispersed oil, to a less dispersible oil where stirring only caused a black “cloud” of dispersed oil of larger oil droplets. Given the rough and ready nature of the test, it is not possible to correlate the visual observations with the WSL results obtained with the samples, but an apparent change seems to have occurred at around a WSL value of 30% to 50%.

On each of the three occasions that the ANS was dispersed into the water in the tank by breaking waves a black dispersion of coarse dispersed oil droplets was observed, but there was no light brown “cloud” of very fine dispersed oil formed in the water. This was consistent with the results of the WSL test that showed that after two to four days of dispersant leaching into the water, much of the dispersant had leached out of the slicks, but a small amount remained. The small amount appears to have been sufficient to

facilitate the break up into a coarse dispersion of relatively large oil droplets in the water, but not enough for a permanent dispersion of very fine droplets.

## **6.2 Results obtained with IFO-180 oil**

Only one test was conducted with the IFO-180 in Test Series 1 when it was left on the tank for 68 hours before the breaking waves were put through the oil slick.

### **6.2.1 WSL results**

As described in Section 5.1.2, the WSL results decreased with the time that the dispersant-treated IFO-180 oil was on the water in the tank (“On tank” samples) at a much faster rate than it declined with the oil samples taken from the stationary water in the drum (“No flow” samples). The WSL result decreased to half of the initial value in 12 hours with samples from the tank with the 5.5 cm/s water current, but this took 40 hours with the samples taken from the drum of stationary water.

Visual examination of the oil on the tank (being subjected to an underflow of water at 5.5 cm/s) and oil in the drum (with no water flow) indicated the probable reason for this difference in behaviour.

The average temperature of the water in the tank was 15°C during Test Series 1. The average air temperature was also 15°C, falling to 12°C at night and rising by approximately 1°C during the day.

The Pour Point of the IFO-180 was determined to be 15°C. The oil in the drum had set to a gel, while the oil on the tank was maintained as a grainy slurry of oil and precipitated wax by the gentle movement caused by the water current and the motion of the oil within the ring. Dispersant loss from the slurry of oil on the tank was possible, but slower from the gelled oil in the drum.

### 6.2.2 LISST results

The average oil concentrations and peak concentrations in the water were high, but based on high VMD values and low values for % of oil < 75µm, the dispersed oil droplets generally were large with only a small proportion being small enough to remain permanently dispersed.

### 6.2.3 Visual observation results

The IFO-180 oil on the water in the tank had taken on a very grainy appearance before it was subjected to breaking waves. The oil did not disperse very well when stirred into the water with a spoon; the IFO-180 oil was temporarily dispersed into the water as black droplets, but these re-surfaced quite quickly. As the breaking waves passed through the slick of the IFO-180 oil a coarse, black dispersion of oil in the water was formed.

## 6.3 Results obtained with IFO-30 oil

The IFO-30 oil was tested in calibration Test 2a, Test Series 2 and 3. The major differences between the Test Series are contained in Table 22.

	<b>Average current speed under oil (cm/s)</b>	<b>Amount of oil in ring (litres)</b>	<b>Time on tank water before breaking waves passed through the slick (hours)</b>
<b>Test 2a</b>	not applicable	80	0.5
<b>Test Series 2</b>	4.0	80	87
<b>Test Series 3</b>	5.7	38	46

Table 22. Tests with IFO-30 oil

The most marked difference between these tests and the tests conducted with IFO-180 and the ANS oil was the inclusion of a test with minimal soaking time before the

breaking waves were passed through the test oil slick on the tank. This provided a calibration for the results obtained in the more prolonged tests.

### 6.3.1 WSL results

The WSL result from the sample taken in Test 2a just before the oil was dispersed that was 58.8%. No dispersant had been lost from this oil. The WSL results from the samples taken just before dispersion on the tank in Test Series 2 and 3 were much lower, 5.2% and 20.4% respectively, indicating that there had been a substantial loss of dispersant (Table 23).

	<b>Time on tank water before breaking waves passed through the slick (hours)</b>	<b>WSL result just before dispersion (%)</b>
<b>Test 2a</b>	0.5	58.6
<b>Test Series 2</b>	87	5.2
<b>Test Series 3</b>	46	20.4

*Table 23. Tests with IFO-30 oil*

A curve of dispersant treatment rate, expressed as percentage of Corexit 9500 in the IFO-30 versus WSL result was produced (Figure 18).

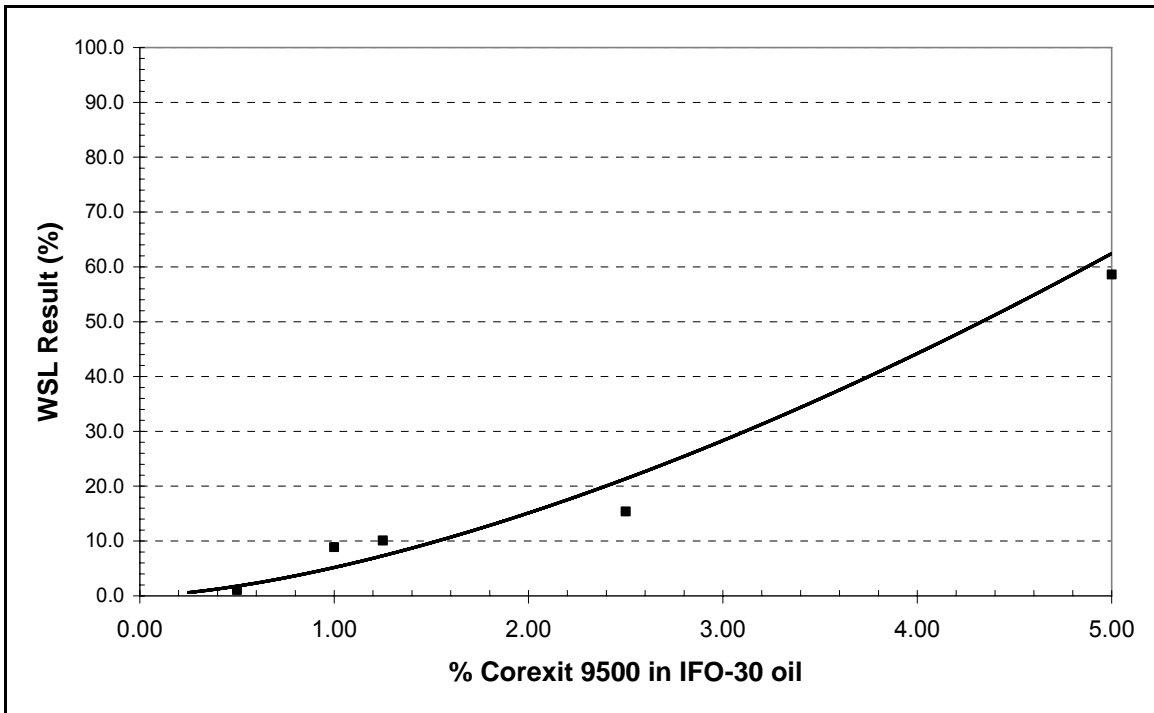


Figure 18. Effect of dispersant treatment rate on WSL result with IFO-30 oil

The effective treatment rates of Corexit 9500 in the IFO-30 slicks of Test Series 2 and 3 over the duration of the soaking period were determined using the data in Figure 18 and the WSL results measured for the oils sampled during each test. The same density and excess dispersant issues discussed in the ANS results apply in the IFO-30 analysis, although to a lesser degree because the evaporative loss and density increase would not have been as great for the IFO-30 oil as it was for the ANS oil.

As can be seen from Figure 19, the rate of dispersant loss from the IFO-30 oil was similar to that from the ANS oil (see Figure 17) with half the amount of dispersant being lost in 55 hours for Test 2 and 19 hours in Test 3 for the IFO-30 oil, compared to 56 hours and 16 hours for the ANS oil.

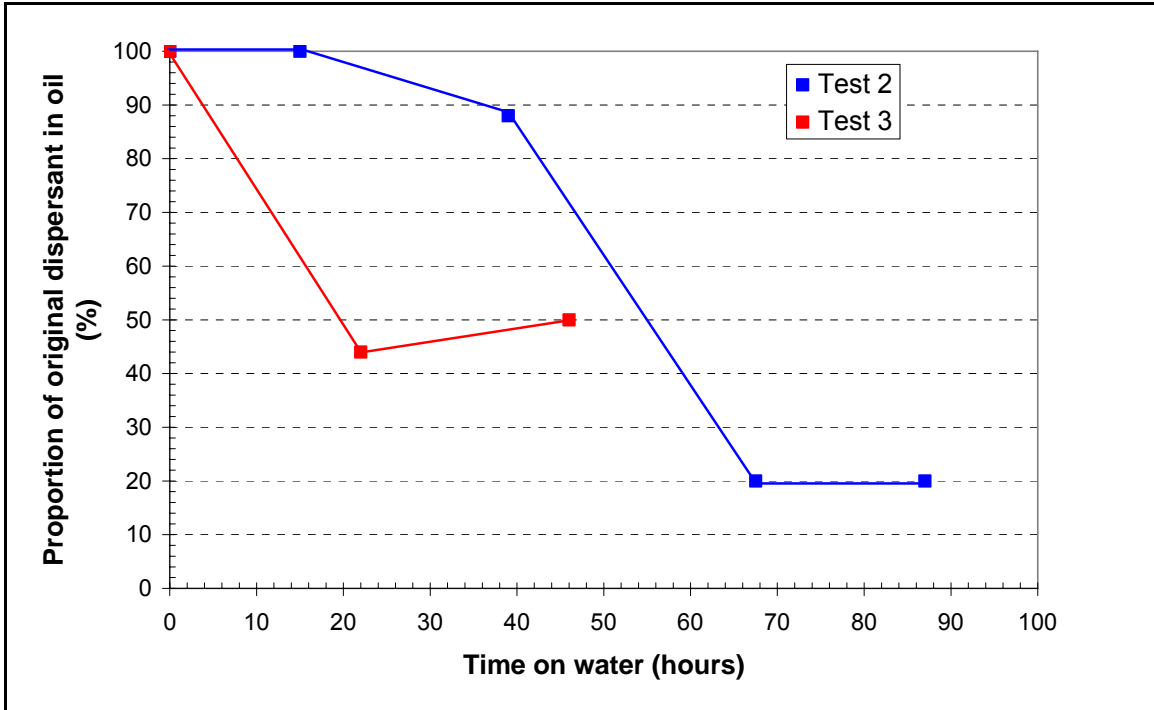


Figure 19. Decrease of dispersant concentration with time in IFO-30 oil

Although the time taken for the IFO-30 oil to apparently lose half the original amount of dispersant, and therefore have a much reduced WSL result, were very different; 55 hours for Test Series 2 and only 19 hours for Test Series 3 (Table 24), the maximum rate of loss of dispersant during the period of steepest decline were very similar at 2.4% and 2.3% per hour (see Table 24).

The rate of loss of dispersant in the static drum tests were about half that of the on tank tests (1.1% to 1.4% pr hour). These are similar to the corresponding rates with ANS.



	Mean current speed under oil (cm/s)	Amount of oil in ring (litres)	Time for dispersant concentration in IFO-30 oil to decrease to half of original value (hours)	Maximum Estimated Dispersant Leach Rate On-Tank (%/hour)	Estimated Dispersant Leach Rate No-Flow On-Drum (%/hour)
Test Series 2	4.0	80	55	2.4	1.1
Test Series 3	5.7	38	19	2.3	1.4

Table 24. Time for dispersant concentration to decrease to half original amount

### 6.3.2 LISST results

The LISST results from the first pass of each test are presented in Table 25, together with the WSL results from samples taken just before the oil was dispersed by the breaking waves.

	Volume Median Diameter ( $\mu\text{m}$ )	Average oil concn. (ppm)	Peak oil concn. (ppm)	Oil in Drops < 75 $\mu\text{m}$ (% vol)	WSL result just before dispersion (%)
Test 2a	14	47	134	92	58.6
Test Series 2	228	28	120	13	5.2
Test Series 3	118	26	142	34	20.4

Table 25. LISST Results for IFO-30 Test Series

The significant dispersion observed in Test 2a, was confirmed by all of the in-water oil measurements. The high WSL result, the very small VMD of 14 microns, the high average dispersed oil concentration of 47 ppm and the proportion of dispersed oil measured as droplets smaller than 75 microns in diameter (92%) are all indicators of a high level of dispersion in this test. For test series 2 and 3 the LISST measurement indicate:

- A lesser degree of dispersion in Test Series 3 due to the higher VMD, lower average oil concentration and smaller percentage of oil in drops less than 75 microns.
- A low level of dispersion in Test Series 2 which had the highest VMD, and the lowest percentage of oil in the form of drops less than 75 microns.

### **6.3.2 Visual observation results**

The production of a very visible brown plume of dispersed oil in the water in Test 2a was indicative of a very high level of dispersion. The absence of a substantial brown plume in the water after dispersion by the breaking waves in both Test Series 2 and 3 and the formation of a black plume of large oil droplets dispersed in the water were indicative of a lower level of dispersion in these tests.

## **6.4 *Indicators of dispersion in the tank and WSL results***

Several different indicators of dispersion were used in the study;

- WSL results,
- Measurements made by the LISST
- Visual observation.

### **6.4.1 The significance of the WSL result**

The WSL result is an indicator of the potential for dispersion, not a predictor of the precise amount of oil that will be dispersed in any particular wave environment, since many possible wave conditions are possible at sea (or in the tank at Ohmsett). The WSL results are measurements of the amount of the test oils dispersed under the specific conditions of the WSL test method, not a measurement of dispersed oil concentration or dispersed oil droplet size distribution produced by breaking waves in the tank at Ohmsett or of the oil droplet size that can be maintained in the water in the tank by the prevailing wave conditions.

In the WSL test method all of the test oil (5 ml) and the water (250 ml) are mixed together during the 2 minutes rotation at 33 rpm. This does not represent the passage of a single breaking wave, but the rapid sequence of 66 end-over-end rotations that provide a very high level of mixing of the oil into the water. This mixing will produce a particular oil droplet size distribution, dependent on the rheology of the oil and the reduction in interfacial tension produced at the oil/water interface.

This initial 'high energy' mixing is then offset by a 1-minute standing period. Only the oil droplets that are retained within the bottom 50 ml of the 255 ml of oil and water mixture in the flask are sampled, the largest oil droplets are allowed to float out of the sampling zone during the 1-minute standing period. Because of the specified shape of the WSL test flask, an oil droplet at the very bottom of the flask will have to float 8.74 cm in 1 minute (0.146 cm/s) to escape the sampling zone.

This will be the largest oil droplet that can be 'captured' – all oil droplets of the same size, or larger, will have floated clear during the one minute because they are higher up in the water column. The oil droplet diameter that would float out at a rise velocity of 0.146 cm depends on the density of the oil. These can be calculated using Stokes Law (and corrected for induced turbulence at higher rise velocities) and are presented in Figure 20.

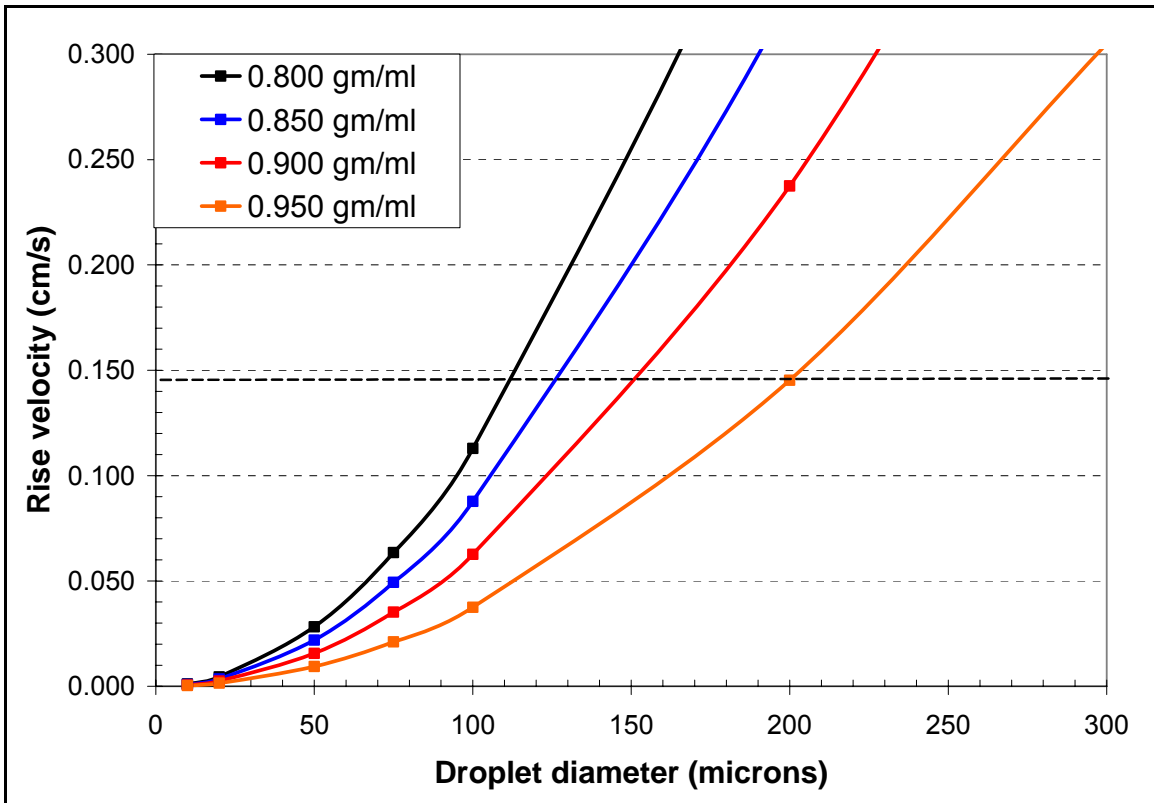


Figure 20. Rise velocity in seawater and droplet size

The maximum diameters of droplet that would be captured in the WSL method are:

- Oil density 0.800 gm/ml; 112 microns
- Oil density 0.850 gm/ml; 127 microns
- Oil density 0.900 gm/ml; 150 microns
- Oil density 0.950 gm/ml; 200 microns

The oil droplet size distribution sampled in the WSL method is that created by intense mixing and then ‘truncated’ by allowing the largest oil droplets to escape from the sampling zone in the test.

#### 6.4.2 The significance of the results from the LISST

The LISST measurements made in the tank at Ohmsett are of the actual dispersion of the test oils caused by the breaking waves and of the oil droplets maintained in the water column by the turbulence produced by the subsequent passage of waves (both non-

breaking and breaking) in the tank, not a dispersion of oil produced in some standardised laboratory method such as the WSL test.

A disadvantage of the LISST (in common with all other currently available instrumentation) is that it cannot measure the dispersed oil concentration and dispersed oil distribution at all locations in the water under the oil simultaneously; the measuring head has to be towed along transects after dispersion of the oil has occurred. Since the precise location or timing of the onset of the dispersion of oil caused by a breaking wave in the tank cannot be known, measurements cannot be made at the precise onset of dispersion.

Once a plume of dispersed oil has been rapidly propelled into the water column by the passage of a breaking wave, the smaller oil droplets immediately begin to be dispersed (horizontally and vertically) by the turbulence in the water column and this causes a decrease in dispersed oil concentration in the water column. The larger oil droplets begin to slowly drift upwards through the water, due to their inherent buoyancy and this also decreases the dispersed oil concentration. These tendencies will continue until another breaking wave passes through the same location. Further oil might be dispersed from the water surface and the oil droplets that are already in the water column will be, once again propelled into the water.

Over time, the situation might approach an average 'steady state', but in the short-term it is a sequence of the rapid dispersion of surface oil into oil droplets in the water column, being caused by breaking waves, and a much slower process of diffusion of the smaller oil droplets and float-out of the larger oil droplets under the influence of a fluctuating level of turbulence caused by the subsequent non-breaking waves.

The VMDs of the dispersed oils in all but Test 2a were initially very high, over 100 microns or even 200 microns, but slowly decreased to less than 80 microns in the 30 minutes after initial dispersion. This decrease in VMD was accompanied by a decrease in average oil concentration to 10 or 20 ppm in the water. These were clear indications that

the oils had been dispersed as a wide range of oil droplet size by the breaking wave, but that the subsequent turbulence was insufficient to maintain them as a dispersion in the water. In contrast, the VMD of the dispersion of oil produced in Test 2a was 14 microns and this did not increase with time and the average dispersed oil concentration increased from 47 ppm to 70 ppm in subsequent passes.

The VMD of the oil dispersion that could be maintained in the tank by the prevailing turbulence from waves (both breaking and non-breaking) was therefore less than 80 microns and higher than 14 microns.

The relationship between the parameters measured by the LISST for all tests is displayed in Figure 21. There is a broad correlation, but there is insufficient data to produce any reasonable fit for most of the parameters. A high WSL result in the laboratory was correlated with a low VMD, increased average and peak oil concentrations and a higher proportion of the volume of dispersed oil present as droplets with diameters less than 75 microns. On the other hand, a very low WSL result correlated with a much higher VMD (100 microns for a 20 - 25% WSL result and 200 microns for a 5% WSL result) of the dispersed oil and lower average and peak dispersed oil concentrations. For clarity Figure 22 contains only the VMD of the dispersed oil obtained when the breaking wave was put through the slick on the tank is related to the WSL result obtained with samples taken just before dispersion. The only data set where a wide range of results were obtained is for IFO-30 and the relationship between VMD in tank and the WSL result can be expected to change with oil density.

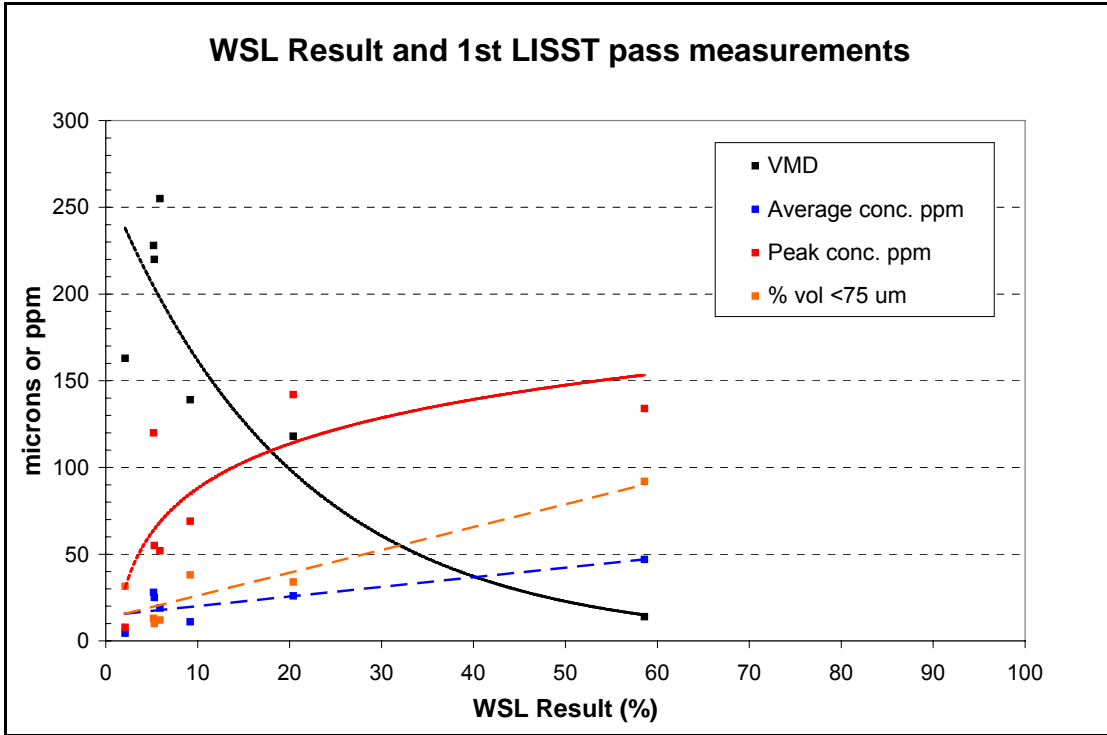


Figure 21. Relationship between parameters measured by LISST and WSL result

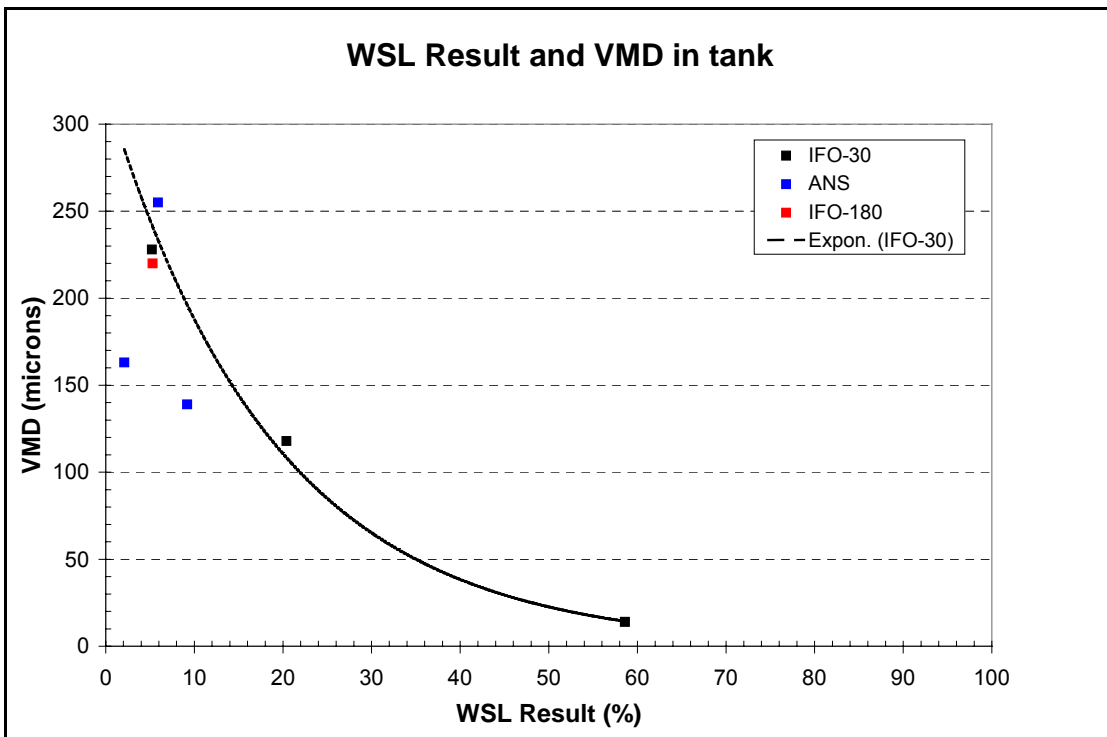


Figure 22. Relationship between initial VMD and WSL result

### 6.4.3 The significance of the visual observations

Previous work at sea ([Lewis, 2004](#)) and at Ohmsett has used a four-point scale (Table 26) to try and relate easily-made visual observations of the dispersion of oil to quantitative measurements of the amount of dispersed oil at sea, in the tank at Ohmsett or in laboratory test methods ([Trudel et al., 2005](#)).

Rank	Standard Phrase	Description
1	No obvious dispersion	<ul style="list-style-type: none"> <li>• Dispersant being washed off the black oil as white, watery solution leaving oil on surface.</li> <li>• Quantity of oil on sea surface not altered by dispersant</li> </ul>
2	Slow or partial dispersion	<ul style="list-style-type: none"> <li>• Some surface activity (oil appearance altered).</li> <li>• Spreading out of oil.</li> <li>• Larger droplets of oil (1 mm in diameter or greater) seen rapidly rising back to sea surface, but overall quantity appears to be similar to that before dispersant spraying</li> </ul>
3	Moderately rapid dispersion	<ul style="list-style-type: none"> <li>• Quantity of oil visibly less than before spraying.</li> <li>• Oil in some areas being dispersed to leave only sheen on sea surface, but in other areas still some oil present.</li> </ul>
4	Very rapid and total dispersion	<ul style="list-style-type: none"> <li>• Oil rapidly disappearing from surface.</li> <li>• Light brown plume of dispersed oil visible in water under the oil and drifting away from it</li> </ul>

Table 26. Visual Scale Descriptors

Some of the characteristics in this ranking scale are subjective or descriptive and therefore difficult to be used in an unambiguous manner, especially by observers who have not witnessed oil being dispersed at sea. The major feature of this visual observation ranking of 4, for what is described as “Very rapid and total dispersion”, is the observation of a light brown (“*café au lait*”) plume in the water.



Although this ranking of visual observations with other measurements made at sea ([Lewis, 2004](#)), in the tank at Ohmsett in previous studies ([SL Ross, 2006b](#)) and in laboratory test methods ([Lewis, 2006](#)) has produced a broad level of agreement with the other indicators of the degree of dispersion of oil, no absolute correlation has been made.

The case of the opaque appearance of the brown plume of dispersed oil is light scattering by the small oil droplets. In a similar way, light scattering by fat globules and casein micelles in cow's milk cause it to appear turbid and opaque. Both the fat globules and the smaller casein micelles, which are just large enough to deflect light, contribute to the opaque white color of milk. The fat globules in cow's milk have a VMD of around 3 to 5 microns ([Walstra et al., 1969](#)). The smaller oil droplets in dispersed oil will contribute to the opacity of the brown plume, provided that they are small enough and are present in sufficient concentration in the water.

The VMD of the dispersed IFO-30 oil in Test 2a was 14 microns and the average dispersed oil concentration was approximately 50 ppm. As smaller oil droplets contain less proportion of the volume than larger oil droplets, there would have been a much higher numerical proportion of oil droplets smaller than 14 microns in the dispersed oil plume. The NMD (Number Median Diameter) of a distribution is the diameter which divides the numerical distribution in half; half the number of droplets present in the distribution would be smaller than the NMD and half would be larger. A VMD of 14 microns would be equivalent to an NMD of approximately 4 or 5 microns. This numerical concentration of small oil droplets would be sufficient to cause the opaque appearance of the dispersed oil, provided that the dispersed oil concentration is high enough.

The presence of an opaque brown plume of dispersed oil is therefore indicative that a substantial proportion, both numerical and volume, of the dispersed oil is present as very small oil droplets that are from 3 to 5 microns in diameter. The absence of such a brown plume indicates that the oil is dispersed as larger oil droplets, not that no oil is dispersed.

#### **6.4.4 Relating these indicators together**

The different indicators of the degree of oil dispersion used in the study (WSL results, LISST measurements and visual observation) are all indirect or direct assessments of a combination of two relevant parameters:

- (i) Dispersed oil droplet size.
- (ii) Dispersed oil concentration in the water.

The conversion of only a small proportion of surface oil into small oil droplets would only result in a low level of dispersion, as would the conversion of a much larger proportion of the surface oil into larger oil droplets, which subsequently float out and re-surface. In both cases, such occurrences would result in a lower dispersant effectiveness result being obtained than if a substantial proportion of the surface oil were converted into small oil droplets. The concentration of dispersed oil droplets in the water column after the initial dispersion of the oil will not be constant because smaller droplets will be dispersed into the water column and larger droplets will float out.

The immediate removal of the oil from the water surface in the tank by the action of a breaking wave is not necessarily an indicator of long-term dispersion; the oil may have been temporarily dispersed at large oil droplets which have sufficient buoyancy to float out and re-surface under the influence of the less energetic mixing provided by the subsequent non-breaking waves.

The appearance of a brown, opaque cloud of dispersed oil is an indicator that a substantial proportion of the oil has been converted into very small oil droplets. This is therefore a good indicator of very high levels of oil dispersion. The absence of a brown plume is not an indicator that no dispersion has occurred; the oil droplets will be of larger size, but may still be maintained in the water column by the prevailing turbulence. On the other hand, a portion of the oil may have been dispersed as small droplets, but their concentration may not be great enough to be visible as a light brown cloud.

The most direct measurement of dispersed droplet size and concentration were those obtained with the LISST instrument. It appears that a VMD of below 20 microns and an average dispersed oil concentration of above 40 or 50 ppm in the water column is an unambiguous indicator of a very high level of dispersion in the Ohmsett tank. A VMD in excess of 80 microns and an average oil concentration of below 20 ppm in the water column is an indicator of lower levels of oil dispersion.

## **6.5 Summary of results and the effect of variables**

It is clear from the results presented in this report that there was substantial loss of dispersant from the oil retained in the rings with time on the water surface in the tank at Ohmsett, leading to a significant reduction in the level of dispersion caused by breaking waves from all of the test oils in all of the tests, except for Test 2a with IFO-30. Test 2a provides the benchmark for the other tests. The high level of dispersant in the IFO-30 in Test 2a, the original treatment rate of 5% volume of Corexit 9500 in the oil – equivalent to a DOR of 1:20 – produced very high levels of dispersion, as evidenced by:

- A relatively high WSL result.
- A small VMD, relatively high average and peak dispersed oil concentrations and a very large proportion of this being in the form of droplets with diameters less than 75 microns.
- The presence of a visible brown plume of very small dispersed oil droplets in the water.

The extent and rate of dispersant loss from the test oils was reflected by changes in these measurements and observations:

- Decreasing WSL results.
- Larger VMDs, lower average and peak dispersed oil concentrations with a smaller proportion of the dispersed oil being in the form of droplets with diameters less than 75 microns.

- The presence of a black cloud of larger dispersed oil droplets in the water.

The reduction in the WSL result with time on the water has been used to determine the loss of dispersant from the oil into the water. This was possible following the findings of the SINTEF report that shows, through the use of analytical chemistry techniques, that the surfactant losses to water were in proportion to the original composition of the dispersant.

### **6.5.1 Effect of oil type on dispersant loss**

The rates of loss of dispersant from both ANS and IFO-30 oils were inferred from the reduction in WSL result achieved by samples of the dispersant-treated oils taken from the water after various time intervals. These WSL results were then related to a calibration curve of WSL result obtained with treatment rate in the relevant oil to estimate the amount of dispersant remaining in the oil.

Due to increases in the densities of both of these test oils in the initial stages of the testing, caused by the evaporation of the more volatile components of the oils, the WSL results initially increased with time before declining, as dispersant loss became the dominant factor. This produced an ‘onset period’ of apparently no dispersant loss (or dispersant loss countered by an increase in WSL result due to oil density increase) before a period of time when a steep rate of dispersant loss could be determined. Two indicators were used to assess the rate of dispersant loss:

- The time taken for the WSL result to be equivalent to a decrease of dispersant treatment rate to half of its original value. This period started as soon as the oil was placed on the tank.
- The maximum rate of dispersant loss during the period of steepest decline. This period started after the ‘onset period’.

Both the ANS and IFO-30 oils showed similar behaviour. The times taken for the dispersant concentration to decrease to half of the original value in Test Series 2 (80 litres of oil and a mean 4.0 cm/s water current) were 56 hours for the ANS oil and 55 hours for the IFO-30 oil.

The times taken for the dispersant concentration to decrease to half of the original value in Test Series 3 with reduced quantities of oil (38 litres and a mean 5.7 cm/s current) were 16 hours for the ANS oil and 19 hours for the IFO-30 oil. The test oils would have produced an average oil layer thickness of 5 mm (Test Series 1 and 2) or 2.5 mm (Test Series 3). However, the oils did not spread out to form layers of an even thickness and the oil layer did not occupy the entire water surface within the rings. The area of free water surface within the rings fluctuated as the current created by the air bubble barrier caused the oil layer to thin and thicken. The lower amount of oil generally occupied less of the water surface area within the ring and was subject to more extensive fluctuations in size (and therefore oil layer thickness).

Both the ANS and IFO-30 oils lost dispersant at similar rates ranging from 2.1% to 3.1% of the original treatment rate per hour during the periods when dispersant rate loss could be quantified. The treatment rate, as DOR, dropped from the original 1:20 to 1:40 in 55 to 65 hours and to 1:100 in 65 to 67 hours. The ANS and IFO-30 oils lost dispersant at a slower rate when kept on stationary water ranging from 0.9% to 1.8% of the original treatment rate per hour, for equivalent periods of time.

The loss of dispersant from IFO-180 oil (as evidenced by the decreased WSL result) was much slower when kept on static water. This was because the IFO-180 had a Pour Point of 15°C, the test temperature, and was a solid gel on static water, but a grainy semi-solid composed of oil and precipitated wax when maintained on the tank with a water current flow.

## 7. Conclusions

1. The rate of loss of Corexit 9500 dispersant from ANS and IFO-30 oils contained in rings on the water surface in the tank at Ohmsett was similar. The rate of loss of dispersant from an IFO-180 oil was affected by the oil having a Pour Point of 15°C, identical to the test temperature. The IFO-180 oil was present as a grainy 'slush' of precipitated wax and oil on the water surface in the tank, prevented from totally gelling by the effect of the low velocity water current.
2. The loss of dispersant from the oils into the water with time caused a reduction in the level of oil dispersion caused by breaking waves. The potential reduction in the level of oil dispersion was reflected in the WSL results obtained with oil samples withdrawn from the tank.

During the extended period on the water surface the WSL results for both the ANS and the IFO-30 oils initially increased due to evaporative loss from the oils leading to increased oil densities. The WSL result then decreased as dispersant was lost from the oil into the tank water. This led to an 'onset period' of increasing WSL result with time followed by a decreasing WSL result as dispersant was lost to the tank water.

The time for the WSL result to decrease to a value equivalent to a dispersant treatment half of that originally mixed into the oil, a DOR of 1:40 compared to the original DOR of 1:20, depended on the amount of oil in the test ring:

- With 80 litres of oil and flowing water conditions (mean flow rate 4-6cm/sec) the period was 56 hours for the ANS oil and 55 hours for the IFO-30 oil.
- With 38 litres of oil and flowing water conditions (mean flow rate 4-6cm/sec) the period was 16 hours for the ANS oil and 19 hours for the IFO-30 oil.

The lower amount of oil (38 litres compared to 80 litres) generally occupied less of the water surface area within the ring and was subject to more extensive fluctuations in size, and therefore oil layer thickness that was in contact with the water. This appeared to be the mechanism resulting in faster dispersant loss and the much shorter time required for the WSL result to drop to a value equivalent to have the original dispersant treatment rate.

3. Both the ANS and IFO-30 oils lost dispersant at similar rates ranging from 2.1% to 3.1% of the original treatment rate per hour during the periods of the evident high loss rate of dispersant, when dispersant rate loss could be quantified. The treatment rate, as DOR, dropped from the original 1:20 to 1:40 in 55 to 65 hours and to 1:100 in 65 to 67 hours. The ANS and IFO-30 oils lost dispersant at a slower rate when kept on stationary water, compared to the current flow tests, for equivalent periods of time.
4. The actual levels of oil dispersion achieved by breaking waves were revealed by parameters measured using a LISST particle size analyser. The concentration of dispersed oil in the water column, VMD (Volume Median Diameter), and proportion of droplets <75 microns in the dispersed oil plume taken shortly after dispersion is a good indicator of dispersion, but more information could be gained by measuring longer-term changes in VMD and average dispersed oil concentrations.
5. A test conducted with dispersant-treated IFO-30 oil and with only 30 minutes on the water surface before breaking waves were applied provided a benchmark for the measurements made in the other tests. A very high level of dispersion, appearing to be almost total and equivalent to a 60% WSL result, produced a cloud of very small oil droplets (a VMD of 14 microns) which were of high average dispersed oil concentration (50 - 70 ppm) in the water, with a very high proportion (92 – 97% volume) of these droplets having a diameters less than 75

microns. The cloud of dispersed oil was light brown in colour and opaque due to a high numerical concentration of very small (4 to 5 micron diameter) oil droplets.

6. All the other tests with the dispersant-treated test oils being on the water for extended periods of time (from 2 to 4 days), produced lower levels of dispersion. The WSL results on the samples taken just prior to dispersion in the tank by breaking waves ranged from 2.1 % (Test 1 with ANS) to 20.4% (Test 3 with IFO-30). The dispersed oil clouds produced were visually black in colour and consisted of larger oil droplets (initial VMDs ranging from 100 to over 200 microns), but the VMD decreased with time as the larger oil droplets floated out. The average dispersed oil concentrations varied from 5 to 30 ppm in water and the proportion of droplets with diameters less than 75 microns varied from 10 to 40% volume.

These results cannot be directly translated into quantitative measurements of the amount of dispersed oil because the quantities of oils used were not identical in all tests. The measurements made by the LISST instrument would not necessarily have been made at the precise location and time of the maximum dispersed oil concentration. Nevertheless, taken in combination, these measurements are important quantitative indicators of the level of dispersion.



## 8. References

Lewis, A. 2006. UK 2003 Oil Spill Dispersant Sea Trials: Overview of Work Done and Results Achieved. Proceedings of Interspill 2006 Conference held at London ExCel, Docklands, London, UK.

Lewis, A. 2004. Determination of the Limiting Oil Viscosity for Chemical Dispersion At Sea. (MCA Project MSA 10/9/180). Final Report for DEFRA, ITOPF, MCA and OSRL. April 2004.

Lunel, T, 1993: Dispersion: Oil droplet Size Measurements at Sea. Proceedings of the 16<sup>th</sup> Arctic and Marine Oil Spill Program (AMOP) Technical Seminar. Environment Canada, pp. 1023 – 1055.

Martinelli, F.N., and B.W.J. Lynch. 1980. Factors affecting the efficiency of dispersants. Warren Spring Laboratory Report LR 363 (OP) 1980.

Trudel, B.K, R.C. Belore, A. Lewis, A. Guarino and J. Mullin. 2005. Determining the Viscosity Limits for Effective Chemical Dispersion: Relating Ohmsett Results to those from Tests At-Sea. Proceedings of 2005 International Oil Spill Conference.

SINTEF, 2007. Review of Effects of Time on the Effectiveness of Dispersants. SINTEF Report STF80MK A07143, dated 15<sup>th</sup> December 2007

SL Ross Environmental Research Limited, A. Lewis and MAR Incorporated. 2006a. Chemical Dispersibility in Calms Sea Conditions. Report. August 2006.

SL Ross Environmental Research Limited, A. Lewis and MAR Incorporated. 2006b. Chemical Dispersibility of U.S. Outer Continental Shelf Crude Oils in Non-Breaking Waves. August 2006.

SL Ross Environmental Research Limited, A. Lewis and MAR Incorporated. 2007. Changes in Dispersant Effectiveness with Extended Exposure in Calm Seas. December 2007.

Walstra, P., H. Oortwijn. and J. J. de Graaf., 1969. Studies on milk fat dispersions. I. Methods of determining globule-size distribution. Neth. Milk Dairy J. 23:12.

## **9. Appendix 1: Review of PERF Study**

### **Review of**

**SINTEF Report STF80MK A07143  
dated 15<sup>th</sup> December 2007**

**“Effects of Time  
on the  
Effectiveness of Dispersants”**

## Executive Summary

The purpose of this review was to determine whether the results obtained in the SINTEF report “Review of Effects of Time on the Effectiveness of Dispersants, SINTEF Report STF80MK A07143, dated 15<sup>th</sup> December 2007” were of relevance to further work to be conducted at Ohmsett in May 2008. Another task was to review the results obtained with combinations of test oils and dispersants that were not to be used at Ohmsett to determine whether any consistent trends are evident.

The SINTEF study investigated two processes:

- (i) Surfactant depletion from the test oil residues into the underlying water in the Institute Français du Pétrole (IFP) dispersant effectiveness test with extended contact time.
- (ii) The IFP dispersibility of the test oil residues as a function of oil residue rheology (high viscosity caused by wax precipitation near the Pour Point of the oil residue).

Due to the experimental design and number of variables (4 oil types and 3 test temperatures) the influence of these two underlying processes had not been clearly distinguished. With hindsight, it might have been better to have fewer variables so that the separate significant effects could be more clearly discriminated.

The study of the depletion of surfactants with time established that the dispersant formulation was not greatly changed due to surfactant leaching and the overall effect was of dispersant loss with time; the DOR (Dispersant to Oil Ratio) was reduced. The extent of dispersant loss from the oil residue was proportional to temperature being highest at 25°C and lowest at 0°C. The oil type had a very marked effect on the rate and extent of dispersant loss. The reason for the different susceptibility of the oil residues to dispersant loss is not evident from the study.

It is well known that the IFP result is not proportional to DOR and that this varies with oil type. Some of the oil residues tested were inherently more dispersible than others and therefore required less dispersant (a lower DOR) to achieve high IFP results. The significance of

The use of three test temperatures; 25°C, 15°C and 0°C, that spanned – or were close to – the Pour Points of the oil residues tested, makes the results difficult to interpret. Most of the IFP results obtained at 25°C were mainly influenced by the effect of dispersant depletion, while the IFP results obtained at 0°C were often due to the effects of oil residue viscosity and Pour Point of the oil residues.

The study implies that the IFP results obtained are indicative of dispersant performance at sea with relatively high IFP results ‘predicting’ good dispersant performance at sea and relatively low IFP results ‘predicting’ poor performance at sea. This is not in agreement with observations made at Ohmsett with cresting / breaking waves and indications given by results from the WSL test method.

The SINTEF report confirms the observations made at Ohmsett that surfactant leaching will lead to dispersant loss from oils left for an extended period on the water. The work in the SINTEF report was conducted under the very slow sub-surface water current that prevails in the IFP test method. The work conducted at Ohmsett in 2006 (‘static’ water tests) and in 2007 has already indicated that the water current velocity under the oil is an important factor in controlling the rate of surfactant leaching.

The work at Ohmsett in 2007 used the same Oseberg crude oil as used by SINTEF and CEDRE. A residue equivalent to the Oseberg 200°C+ residue used by SINTEF and CEDRE while the oil used at Ohmsett underwent further evaporation under the prevailing conditions to become equivalent to an Oseberg 240°C+ residue (in SINTEF’s terminology). This slight difference in oil properties did not influence the results obtained in the two sets of tests. The dispersion of the Oseberg residue by breaking waves in the Ohmsett tank was conducted at 25°C. The Pour Point of oil residue would have little

influence on the dispersion process at this temperature. Many of the effects reported in the SINTEF report are due to the different oil residues being tested close to, or below, the Pour Point of the oil residues. In fact, this aspect of the oil residue dominated the results obtained, almost to the exclusion of the stated objective of the study that was to investigate the effect of surfactant leaching.

The work conducted in the SINTEF / CEDRE study used the standardised conditions of the IFP test method. While this ensured a certain consistency of results, it did not allow for a systematic study of the variables that are most likely to influence the leaching of surfactants and therefore dispersant loss. Oil layer thickness is likely to be an important variable. An oil layer thickness of 5 mm was used in the 2007 Ohmsett studies, although the oil was observed to circulate within the circular boom. Oil layers that are both thicker and thinner than an average 5 mm should be used in further Ohmsett tests to determine if this is an important variable.

Overall, there are no inconsistencies between the results reported by SINTEF and the results obtained from previous tests at Ohmsett. The results from the SINTEF study were greatly influenced by the properties of the test oil residues and the test temperatures used. The Ohmsett results were obtained with only one oil – the residue of Oseberg crude oil – and at a temperature where the ‘complications’ caused by the Pour Point of the oil residue could be avoided. The flexibility of experimental design available at Ohmsett will allow the relevant variables to be systematically explored in a way that is not possible when conducted using a standardised laboratory test method.

## Table of Contents

1.	Purpose of review.....	1
2.	Experimental procedures.....	2
2.1	Test oils used.....	2
2.1.1	Comparison of oil used at Ohmsett in 2007 and oil used in this study.....	5
2.2.	Dispersants tested.....	6
2.3.	Test methods used.....	6
2.3.1	Dispersant tests with extended contact time without freezing.....	6
3.	Comparison of IFP results with 2007 Ohmsett tests .....	8
4.	Surfactant leaching with extended contact time.....	14
4.1	Discussion of the surfactant leaching results .....	19
5.	IFP results with extended contact time.....	22
5.1	IFP result as a function of DOR and temperature.....	26
5.1.1	IFP Results at 25°C .....	26
5.1.2	IFP Results at 15°C .....	26
5.1.3	IFP Results at 0°C .....	27
5.2	Discussion of results .....	27
5.2.1	Inherent dispersibility of the oil.....	28
5.2.2	Loss of dispersant by extended contact with water .....	30
5.2.3	Flow properties of the oil residues.....	30
6.	Discussion of all results.....	32
6.1	Surfactant leaching from dispersant-treated oil .....	32
6.2	IFP result obtained with reduced DOR.....	33
6.2	The onset of a limiting viscosity (rheology) for dispersion.....	34
7.	Conclusions .....	35
8.	Implications for further testing at Ohmsett.....	37

## **1. Purpose of review**

The purpose of this review was to determine whether the results obtained in the SINTEF and CEDRE study and reported in “Review of Effects of Time on the Effectiveness of Dispersants, SINTEF Report STF80MK A07143, dated 15<sup>th</sup> December 2007” were of relevance to further work on a similar topic planned to be conducted at Ohmsett in May 2008.

Another task was to review the results obtained with combinations of test oils and dispersants that were not to be used at Ohmsett to determine whether any consistent trends are evident.

Since the tests planned to be conducted at Ohmsett were not to involve ice, this review is only on those sections of the SINTEF report that are concerned with experiments and tests without ice.

## **2. Experimental procedures**

### **2.1 Test oils used**

The work carried out by SINTEF and CEDRE used four crude oils selected as being representative of four different crude oil types:

1. Troll B crude oil (naphthenic)
2. Balder crude oil (asphaltenic)
3. New Oseberg crude oil (paraffinic)
4. Ringhorne crude oil (waxy)

The designation of crude oils into the four classifications (naphthenic, asphaltenic, paraffinic and waxy) is not particularly useful in the context of the project. An oil that is “waxy”, i.e. has a high wax content, exhibits this characteristic by having a high Pour Point, close to or higher than the test temperature. The classification “waxy” is therefore a combination of crude oil properties and the prevailing temperature. A crude oil classified as “paraffinic” also contains a relatively high proportion of wax, since waxes are solid paraffins, and do precipitate out at low temperatures.

It should be noted that Pour Point - which is a very important oil property in this study - is not the temperature at which the oil becomes solid, it is the temperature at which it just flows when cooled at a specific rate under conditions specified in the Pour Point test method (IP 15/61 / ASTM D97-66). The Pour Point is 3°C (or 5°F) above the temperature at which the oil fails to flow in the test method, because the cooling oil is only examined at 3°C (or 5°F) intervals. The Pour Point of an oil can be the result of wax precipitation or, less usually, viscosity increase with lower temperature, or a combination of the two. Wax starts to precipitate at a higher temperature (determined as the Cloud Point for transparent distillate fuels such as diesel fuel) and the amount precipitated increases with decreasing temperature. Precipitated wax forms a lattice within the oil that turns it into a gel that prevents flow under the very low-shear conditions of the test.



The work described in the report was carried out with simulated weathered residues that had been produced by distillation to simulate evaporation of the most volatile oil components. These test oils were:

1. Troll 200°C+
2. Balder 200°C+
3. Oseberg 200°C+
4. Ringhorne 150°C+

The properties of these oil residues are described in Table 1.

Crude oil	Residue	Evap, (vol. %)	Density (gm/ml)	Pour Point (°C)	Visc. at 13°C (cP)	Wax (% wt.)
<b>Troll</b>	200°C+	17	0.908	-9	55	1.6
<b>Balder</b>	200°C+	11	0.929	0	990	0.5
<b>Oseberg</b>	200°C+	30	0.884	+9	260	2.9
<b>Ringhorne</b>	150°C+	20	0.860	+12	1270	5.9

*Table 1. Properties of oil residues used in the testing at SINTEF and CEDRE*

The IFP testing conducted at SINTEF and CEDRE was conducted at three temperatures; 25°C, 15°C and 0°C.

The Pour Points of three of the four test oil residues (Balder 200°C+, Oseberg 200°C+ and Ringhorne 150°C+) were within the test temperature range of 0°C to 25°C. The viscosities of these oils would be non-Newtonian (i.e. not be proportional to applied shear stress) in this temperature range and this is evident from Figure 5.1 in the report. Only the Troll residue would be expected to have a viscosity directly proportional to temperature.

As can be seen from Figure 5.1, copied from the Sintef report and reproduced below in Figure 1, two oils (Oseberg 200°C+ and Ringhorne 150°C+) have a very non-linear viscosity temperature relationship at a temperature 14°C above their Pour Points. The relevant measured viscosities at test temperatures are given below in Table 2.

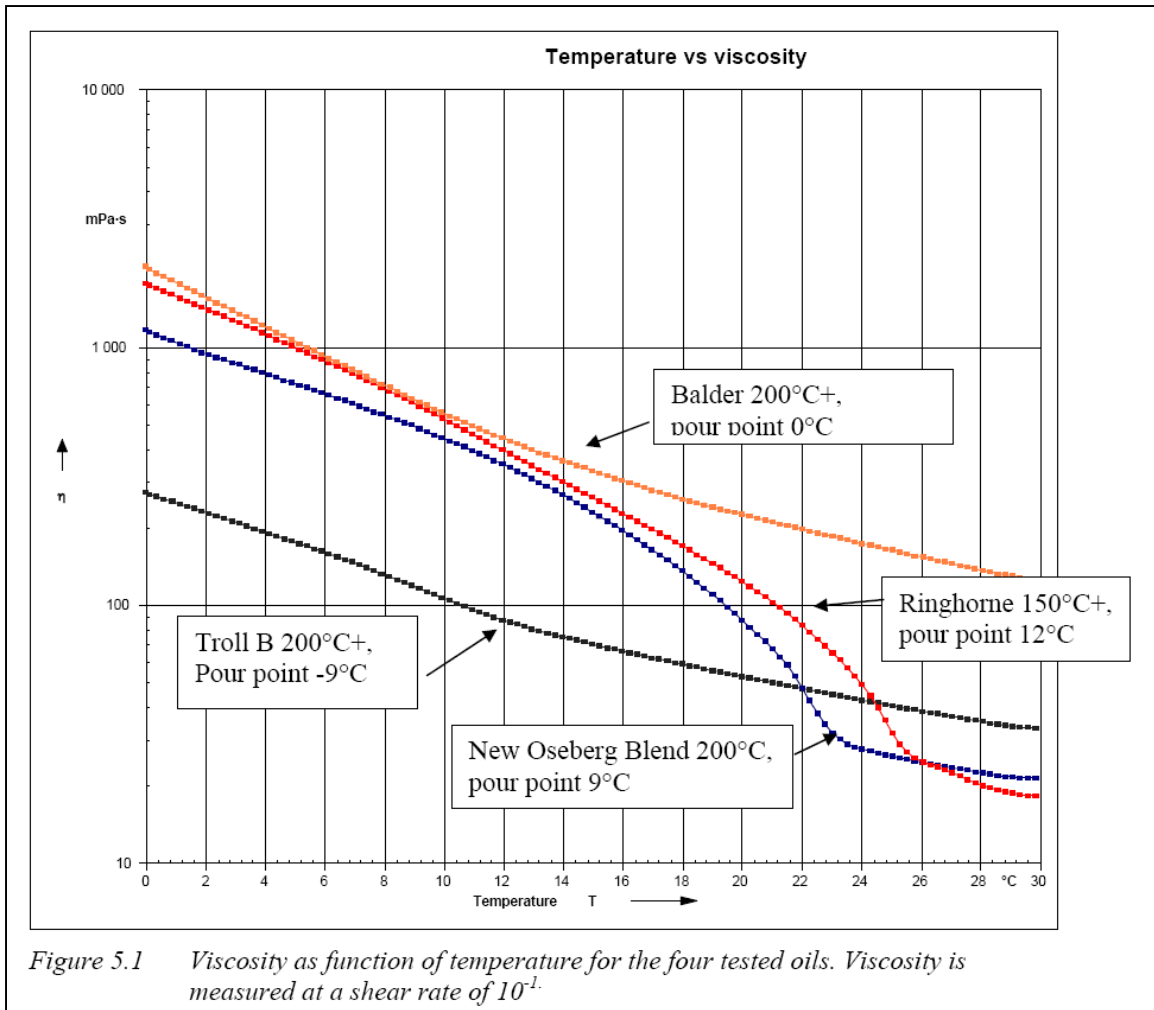


Figure 1 Sintef Report Figure 5.1

	Pour Point (°C)	Viscosity at $10s^{-1}$ (cP)		
		0°C	15°C	25°C
Troll B 200°C+	-9	280	70	41
Balder 200°C+	0	2000	360	160
New Oseberg 200°C+	+9	1200	220	27
Ringhorne 150°C+	+12	1700	270	32

Table 2. Apparent viscosities of test oils at test temperatures

Determining the viscosity of an oil residue below its Pour Point is clearly not impossible because the results are presented. However, it does call into question the significance of the viscosity value obtained because the oil is nominally 'solid' at temperature below its Pour Point. If the viscosity of an oil were determined in precisely the same conditions as

those used in the test to determine the Pour Point it would become a very high value (many thousands of cP) because the viscosity would be effectively infinite (the oil would be solid) at 3°C below the Pour Point.

The oils in the IFP dispersant test method were allowed to remain on the water surface without significant disturbance for very long periods before the application of agitation. They would certainly been exposed to considerably less shearing action than in the viscometer used to produce the viscosity values in Figure 5.1 and the ‘true’ viscosity (the resistance to flow) of the oil in the IFP test apparatus was probably significantly higher than the values indicated in Figure 5.1 (and Table 2). Correlations between IFP test effectiveness and measured oil viscosity should be treated with caution.

### **2.1.1 Comparison of oil used at Ohmsett in 2007 and oil used in this study**

The ‘topped’ Oseberg Blend crude oil used at Ohmsett in the 2007 experiments had been ‘pre-weathered’ by heating and air-sparging to a nominal loss of 27% by weight and had a density at 23.5°C of 0.8810 gm/ml, equivalent to a density of 0.8860 gm/ml at 15°C. Compared to the density of the Oseberg crude oil at 15°C of 0.8355 gm/ml given in the crude oil assay, this indicated that the original Oseberg Blend crude oil supplied from Norway had already lost some of the ‘light ends’ by the time that it arrived in the USA, as a density of 0.8860 gm/ml at 15°C represents a loss of 32% by weight from the original crude oil and is equivalent to distillation to approximately 200°C.

The artificially weathered Oseberg oil residue on the water in Ohmsett tank continued to lose volatile oil components during the time that it was on the water surface. The test temperatures at Ohmsett were 78°F (25.5°C) during the day - when dispersion occurred – and 68°F (20.0°C) during the night. The density increased to 0.8980 gm/ml at 15°C due to further evaporation during the 49 hours on the tank.

The Ohmsett experiments therefore used a more highly ‘weathered’ (evaporated) Oseberg oil than that used by SINTEF and CEDRE in their laboratory tests. The test oil dispersed at Ohmsett was equivalent to an Oseberg 240°C+ residue (in SINTEF’s terminology).

## **2.2. Dispersants tested**

Corexit 9500, Dasic Slickgone NS, Superdispersant 25, Finasol OSR 52 and a model dispersant were used by SINTEF and CEDRE in their laboratory tests. Only Corexit 9500 was used in the Ohmsett tests.

## **2.3. Test methods used**

SINTEF and CEDRE used a modified IFP test method in their laboratory studies, while the work at Ohmsett used the wave action produced in the tank to cause dispersion, with the WSL (or Labofina) test method used to give an indication of probable dispersant performance. In the event, the indications obtained from the WSL results about performance in the Ohmsett tank were ambiguous and this will be discussed later in this report.

### **2.3.1 Dispersant tests with extended contact time without freezing**

The objective of the Task 2 work was to evaluate the change in dispersant effectiveness over time in open water conditions with no ice present. The work involved dispersant effectiveness testing using the IFP test and parallel surfactant leaching tests using the IFP apparatus. Two sets of parallel effectiveness and leaching tests were conducted at each contact time. The IFP test was modified by:

1. Extending the contact times between dispersant and oil by up to 2 weeks, and;
2. For tests with the model dispersant only, premixing of oil and dispersant before application of oil in the containment ring

All tests with commercial dispersants used the standard drop-wise addition of dispersant. The model dispersant was pre-mixed into the oils. The contract times were 1 min

(standard), 6hr, 12 hr, 24 hr, 72 hr, 168 hr and 336 hr depending on effectiveness and temperature. Test temperatures were 0, 15 and 25°C. The model dispersant, Corexit 9500 and Finasol OSR 52 were all tested at 15°C.

All IFP tests were conducted with the standard continuous dilution of 2.5 l/hr of fresh (3.3%) seawater during the entire test period. The IFP is a French standard (AFNOR 90-345) method. The test oils were not in contact with perfectly still water. A very slight current flow under the test oil 'slicks' in the IFP apparatus is generated by the water flow in and out of the test vessel. Given the volume of water in the IFP apparatus (4 litres), the size of the test vessel (depth 19 cm with a surface diameter of water of 16.5 cm) and the water exchange rate (2500 cm<sup>3</sup>/hr), the water flow would induce a current of approximately 0.002 cm/sec under the water surface in the test vessel. This is a very slow current compared to the current values measured at Ohmsett in 2007 and is probably more equivalent to the static water work conducted at Ohmsett in 2006.

In the IFP test, 5 ml of test oil is contained within a 10 cm diameter vertical ring. This would produce an average oil thickness of 0.64 mm thick, but the oil forms a 'lens' that is thicker in the middle and thinner at the edges. SINTEF and CEDRE therefore used much thinner oil layers in their IFP tests than the nominal 5 mm thick layer were used at Ohmsett.

### **3. Comparison of IFP results with 2007 Ohmsett tests**

The only direct comparison between the SINTEF/CEDRE IFP tests and the work done at Ohmsett can be for Oseberg residue treated with Corexit 9500. However, even then there are differences:

- The dispersion tests at Ohmsett were conducted at 25°C, rather than at 15°C in the SINTEF / CEDRE IFP tests.
- The Oseberg oil at Ohmsett was started as an Oseberg 200°C+ residue, but then weathered further to produce an “Oseberg 240°C+ residue”, rather than a Oseberg 200°C+ residue in the SINTEF / CEDRE IFP tests.
- A range of sub-surface water current velocities were used in the Ohmsett tests, all of which were apparently much higher than that produced in the IFP test method.

The results obtained in the IFP test at SINTEF for Oseberg 200°C+ treated with Corexit 9500 at a DOR of 1:20 are presented in Figure 2 and the WSL results obtained during the Ohmsett 2007 results are presented in Figure 3.

Figure 2 shows a steady decrease in the IFP result with contact time for both Corexit 9500 and the model dispersant treated Oseberg 200°C+ residue. The IFP results drops to approximately half the initial value achieved by Corexit 9500 in about 240 hours (10 days), but longer – about 14 days – with the model dispersant. Since the Corexit 9500 was added drop-wise and the model dispersant was pre-mixed with the test oil, the significance of this difference is not known, but is probably due to the difference in dispersant addition method.

The decrease in the WSL results in the Ohmsett tests was more rapid and accompanied by an initial increase due to evaporation of oil on the water surface that caused an

increase in oil density (and therefore WSL result – see report for details). The WSL effectiveness dropped from approximately 40% to approximately 10% in 48 hours.

The underlying decrease in both the IFP and WSL results can be attributed to the progressive loss of surfactants into the water. The apparently slower rate of surfactant loss in the IFP tests (as reflected by the decreasing IFP results), compared to that in the Ohmsett tank (as reflected by the decreasing WSL results), could be due to the higher sub-surface current flow in the Ohmsett tests compared to that in the IFP test.

However, the relevance of both the IFP and WSL test results to the dispersion of the dispersant-treated oil by breaking waves in the Ohmsett tank needs to be considered.

The work at Ohmsett in 2007 found that:

- The application of breaking waves to the oil after exposure to an average water current speed of 13 cm/s for 43 hours (indicated by \* in Figure 3), and which produced a WSL result of only 11%, caused a very coarse dispersion of the oil.
- The application of breaking waves to the oil after exposures to an average water current speed of 5 to 6 cm/s for 91 hours (indicated by \*\* in Figure 3), and which produced a WSL result of only 7%, caused fine dispersion of the oil as a brown plume of small oil droplets in the water.

### Oseberg 200°C+ residue tests at 15°C

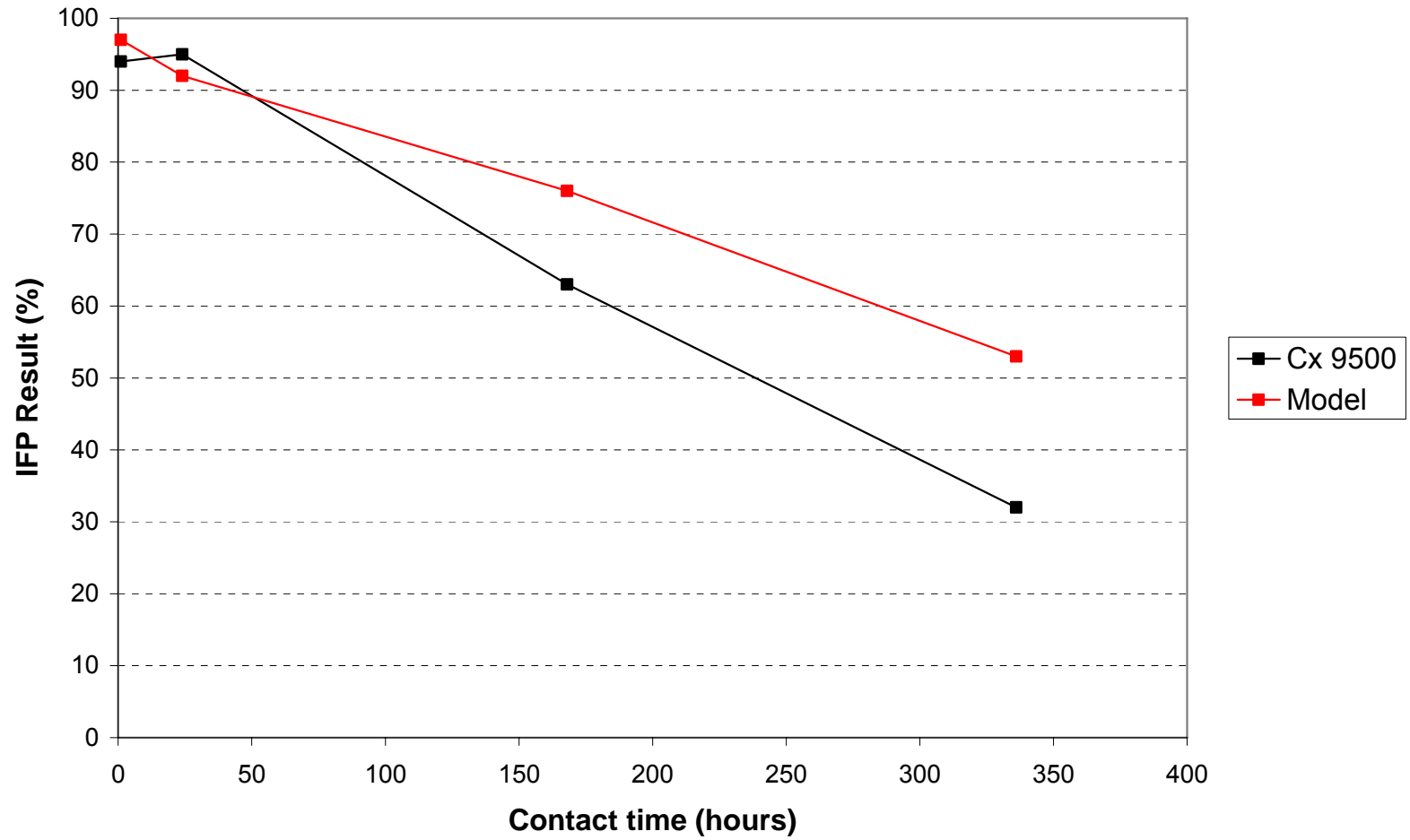


Figure 2. IFP results obtained by SINTEF and CEDRE



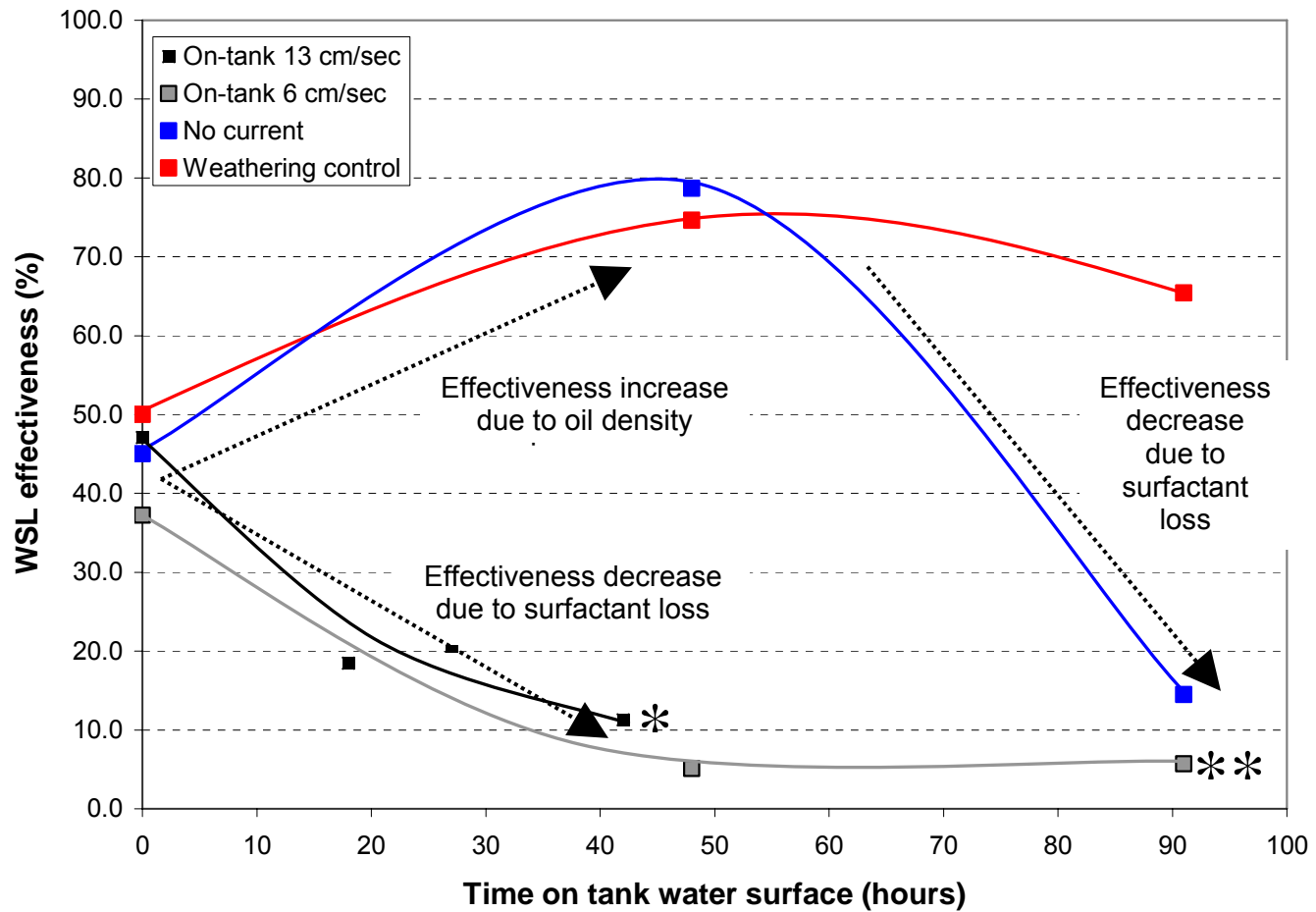


Figure 3. WSL results obtained at Ohmsett in 2007

It should therefore not be assumed that a relatively low WSL (or IFP) result is indicative of a low level of dispersion when the oil is exposed to breaking waves. In fact, it is known from the 2007 work at Ohmsett that an oil / dispersant combination that produces a low WSL result of approximately 10% will be effectively dispersed when exposed to breaking waves in the tank.

This observation underscores the lack of proven relationship between the results obtained in the IFP test (and the WSL test) with dispersant performance in breaking waves. The very high IFP results of around 95% in the SINTEF / CEDRE report are presumed to indicate a high level of dispersant performance at sea (this is implied, but not stated), and this may be true. However, the SINTEF report suggests, or implies, that a relatively low IFP result value of 32% (for example) would indicate poor performance at sea. In the case of a sea condition where breaking waves are present, this suggestion is not borne out by the available evidence.

It has often been stated that the IFP test method is relatively “low energy” compared to the “high energy” WSL test and the implication is that the IFP test method is simulating a calmer sea state, perhaps without breaking waves, than the WSL test method which simulates energetic breaking wave conditions at sea.

Previous work at Ohmsett has indicated that substantial and rapid dispersion does not happen with many oils in the absence of cresting / breaking waves, but does occur as soon as such waves are applied. A “lower energy” wave regime – without cresting / breaking waves – that causes substantial dispersion of oil has not been identified at Ohmsett and the significance of the IFP result to dispersant performance in the Ohmsett tank has not been obtained.

The significance of the IFP results to the probable performance of a dispersant / oil residue combination at Ohmsett – or at sea in a particular sea state - has not been established. It is therefore not possible to determine what a relatively low IFP result

would mean if the oil and dispersant were subjected to testing at Ohmsett. The indications are that an IFP result would probably be lower than the WSL result determined for the same oil / dispersant combination. However, even a low WSL result of 10% is **not** an indication that dispersion will not occur at Ohmsett when breaking waves are applied.

#### **4. Surfactant leaching with extended contact time**

Surfactant leaching is described in Section 5.4.2 of the SINTEF report and the results are given in Appendix 3 of that report. These surfactant studies were only conducted with the model dispersant. However, the model dispersant formulation is similar to that of Corexit 9500 and it is reasonable to expect that it probably behaved in a very similar way to Corexit 9500. The surfactant leaching and IFP tests were conducted with two different treatment rates; a DOR of 1:20 at SINTEF and 1:25 at CEDRE. This difference probably had no significant effect on the results obtained.

The major finding of the work described in the SINTEF report about surfactant leaching is that the formulation (the relative proportions of individual surfactants) of the model dispersant did not change very significantly with time; the individual surfactants leached out 'in proportion' and the overall effect was of a reduction in dispersant concentration in the test oils. This greatly simplifies the analysis of the results because the dispersant can be considered to be an unchanging blend of the individual surfactants.

The values presented in the Tables below are taken from Appendix 3 (pages 109 to 112) and have been normalised so that the original dispersant concentration is 100%. The values given at each time is the proportion, as a percentage, of the original dispersant concentration in the oil.

<b>% original dispersant</b>	<b>0</b>	<b>1 min</b>	<b>1 hr</b>	<b>24 hr</b>	<b>168 hr</b>	<b>336 hr</b>
<b>15°C</b>	100	110	110	100	50	53
<b>0°C</b>	100	113	90		90	50

Table 3. Dispersant concentration with time in Troll 200°C+ residue

<b>% original dispersant</b>	<b>0</b>	<b>1 min</b>	<b>1 hr</b>	<b>24 hr</b>	<b>168 hr</b>	<b>336 hr</b>
<b>25°C</b>	100	80	80	54	26	2
<b>15°C</b>	100	92	86	78	40	16
<b>0°C</b>	100	100	98		38	86

Table 4. Dispersant concentration with time in Balder 200°C+ residue

<b>% original dispersant</b>	<b>0</b>	<b>1 min</b>	<b>1 hr</b>	<b>24 hr</b>	<b>168 hr</b>	<b>336 hr</b>
<b>25°C</b>	100	108	85		35	43
<b>15°C</b>	100	103	90	88	90	80
<b>0°C</b>	100	55	80		95	85

Table 5. Dispersant concentration with time in Oseberg 200°C+ residue

<b>% original dispersant</b>	<b>0</b>	<b>1 min</b>	<b>1 hr</b>	<b>6 hr</b>	<b>24 hr</b>	<b>72 hr</b>	<b>168 hr</b>	<b>336 hr</b>
<b>25°C</b>	100	106	94		100		78	12
<b>15°C</b>	100	108	56	56	110	84	90	54

Table 6. Dispersant concentration with time in Ringhorne 150°C+ residue

These results are also presented in Figure 4, 5 and 6.

### 3 OILS at 25 deg

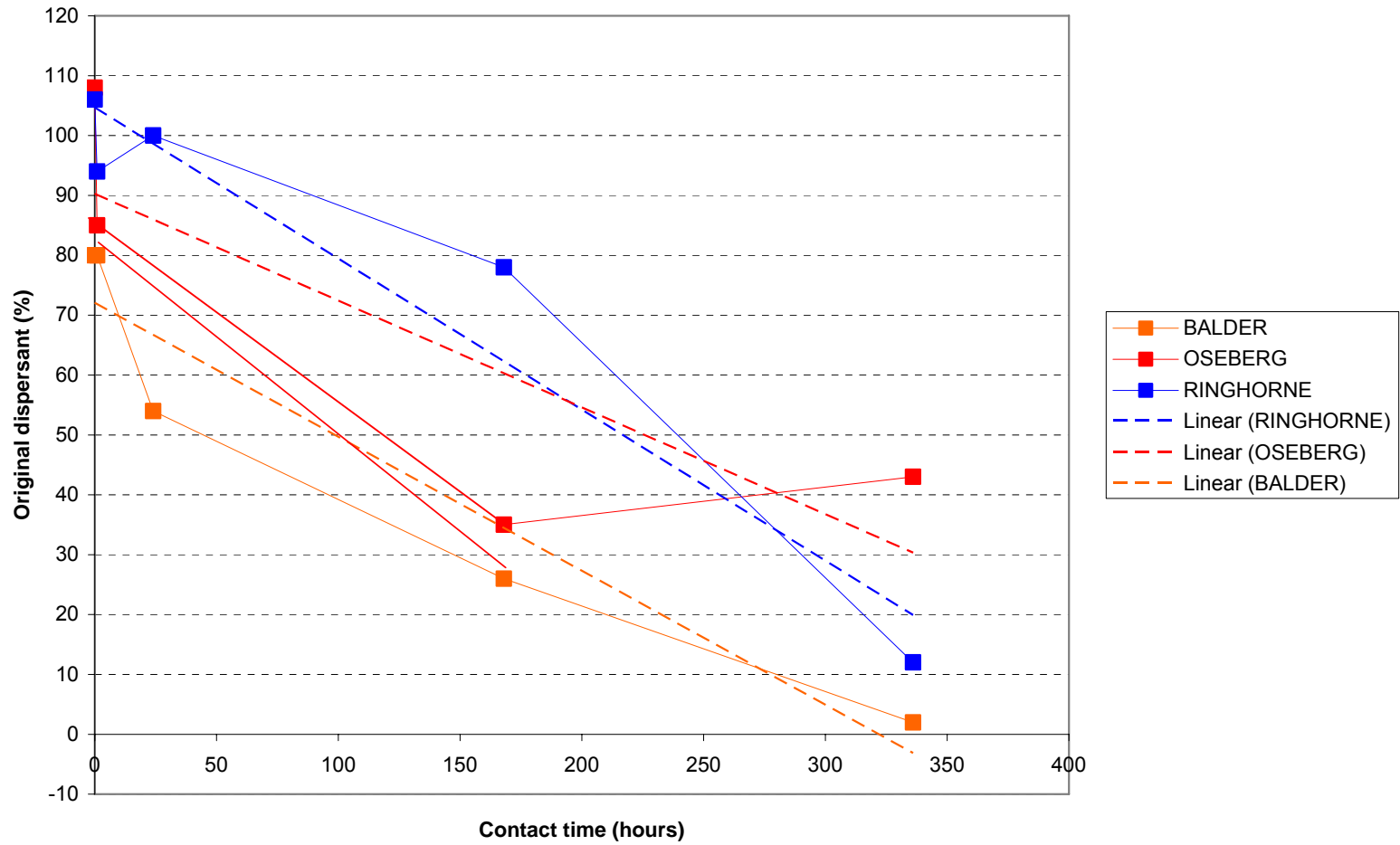


Figure 4. Decrease of dispersant concentration in oil residues at 25°C

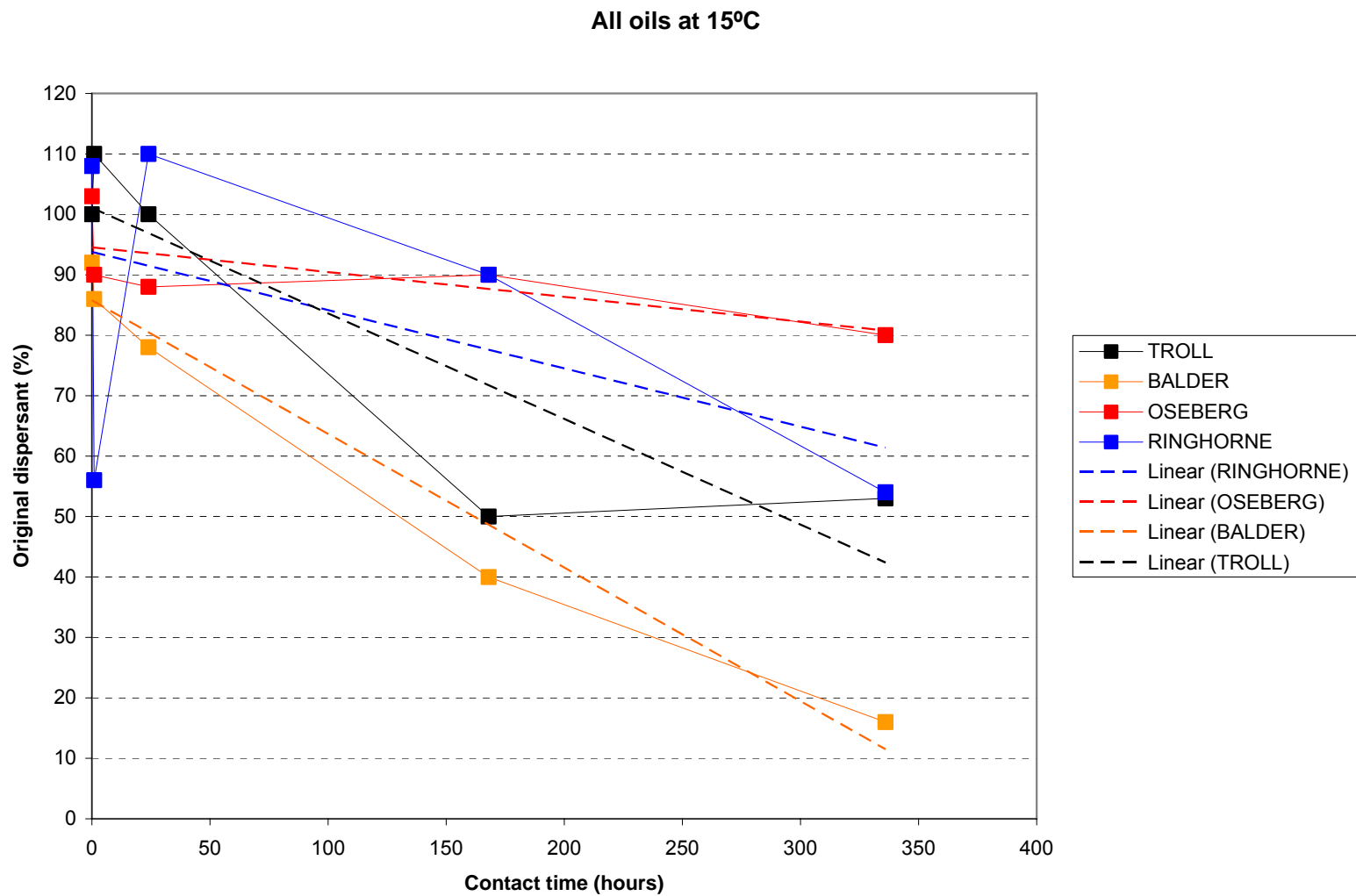


Figure 5. *Decrease of dispersant concentration in oil residues at 15°C*

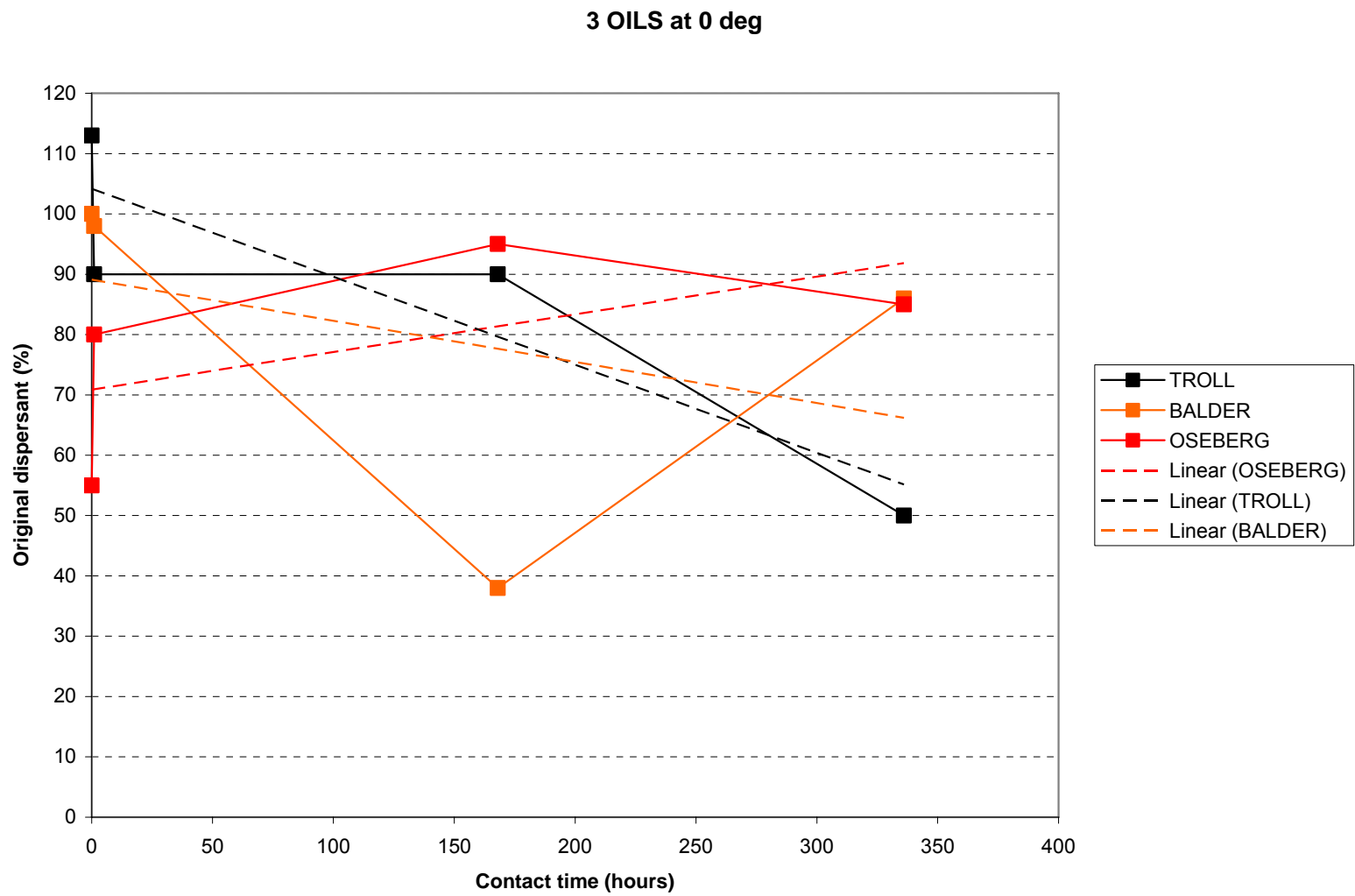


Figure 6. *Decrease of dispersant concentration in oil residues at 0°C*



#### **4.1 Discussion of the surfactant leaching results**

There is quite a wide scatter in these results, but it is also obvious that there are some consistent trends:

- The first trend to note is that the dispersant loss is most rapid at the highest test temperature of 25° and least rapid at the lowest test temperature of 0°C.
- The second trend to note is that the extent of dispersant loss after two weeks varies with the oil residue type:
  - The Balder 200°C+ residue lost the highest proportion of dispersant. At 25°C the Balder 200°C+ residue lost almost all the surfactants (98% loss and only 2% remained) from the oil.
  - The Oseberg 200°C+ residue lost the lowest proportion of dispersant. At 25°C the Oseberg 200°C+ residue retained 43% of the dispersant.
  - The Troll 200°C+ and Ringhorne 150°C+ residues lost an intermediate proportion of dispersant.

The same trends are evident at 15 °C, but at 0 °C the scatter in the results is too large to reveal an obvious trend.

The reason for this very marked difference in surfactant leaching behaviour from the different oils is not obvious:

- **Influence of viscosity**

The Balder 200°C+ residue had the highest viscosity at 25°C (160 cP), while the Oseberg 200°C+ residue had the lowest viscosity (27 cP). It therefore seems very unlikely that the influence of oil viscosity on oil spreading, and therefore oil layer thickness, was the cause of this difference. The lower viscosity oil – the Oseberg 200°C+ residue – would have been likely to spread to a greater extent (albeit constrained by the ring in the IFP apparatus) and therefore form a thinner oil layer than that of Balder 200°C+ residue. If oil / water contact area was the cause of this behaviour, the Oseberg residue would have lost more dispersant, more rapidly than the Balder residue and this was **not** the case.

- **Influence of Pour Point**

At 25°C all the oils were above their Pour Points, but some wax precipitation would have occurred. The Balder 200°C+ residue had a Pour Point of 0°C while the Oseberg 200°C+ residue had a Pour Point of +9°C, but the Ringhorne 150°C+ residue had a Pour Point of +12°C. The rate or extent of dispersant loss is not directly related to Pour Point in the tests at 25°C.

At the lower test temperature of 15°C, the dispersant loss was not quite as fast or extensive as at 25°C, but the Balder residue (Pour Point 0°C) lost the most, the Oseberg (Pour Point +9°C) residue the least, with intermediate losses being recorded for the Ringhorne residue (Pour Point +12°C) and Troll residue (Pour Point -9°C). SINTEF suggest that the oil residue rheology controls the dispersant loss process, but it is not apparent from these results precisely what combination of apparent viscosity and Pour Point cause this effect.

There appears to be no obvious compositional differences in the oils (see Table 5.1 in the SINTEF report) that would easily explain this difference in surfactant loss behaviour. The Balder residue has the highest level of asphaltenes and lowest level of waxes, but no consistent trend among the other residues is obvious. Whatever the reason, the Balder 200°C+ residue showed the greatest propensity to lose dispersant, while the Oseberg 200°C+ residue showed to greatest propensity to retain dispersant.

## 5. IFP results with extended contact time

The IFP results for the same combinations of oil residues and temperatures using the model dispersant are presented in Tables 7 to 9.

<b>Contact time (hours)</b>	<b>BALDER 200°C+</b>	<b>OSEBERG 200°C+</b>	<b>RINGHORNE 150°C+</b>
0	95	100	90
1	94	100	97
24	91		76
168	90	84	37
336	59	83	24

Table 7. IFP Results at 25°C

<b>Contact time (hours)</b>	<b>TROLL 200°C+</b>	<b>BALDER 200°C+</b>	<b>OSEBERG 200°C+</b>	<b>RINGHORNE 150°C+</b>
0	97	96	97	58
24	97	97	92	24
168	91	83	75	0
336	86	76	53	0

Table 8. IFP Results at 15°C

<b>Contact time (hours)</b>	<b>TROLL 200°C+</b>	<b>BALDER 200°C+</b>	<b>OSEBERG 200°C+</b>
0	97	100	38
1	97	98	38
168	91	77	27
336	86	88	15

Table 9. IFP Results at 0°C

These results are also presented in Figures 7 to 9.

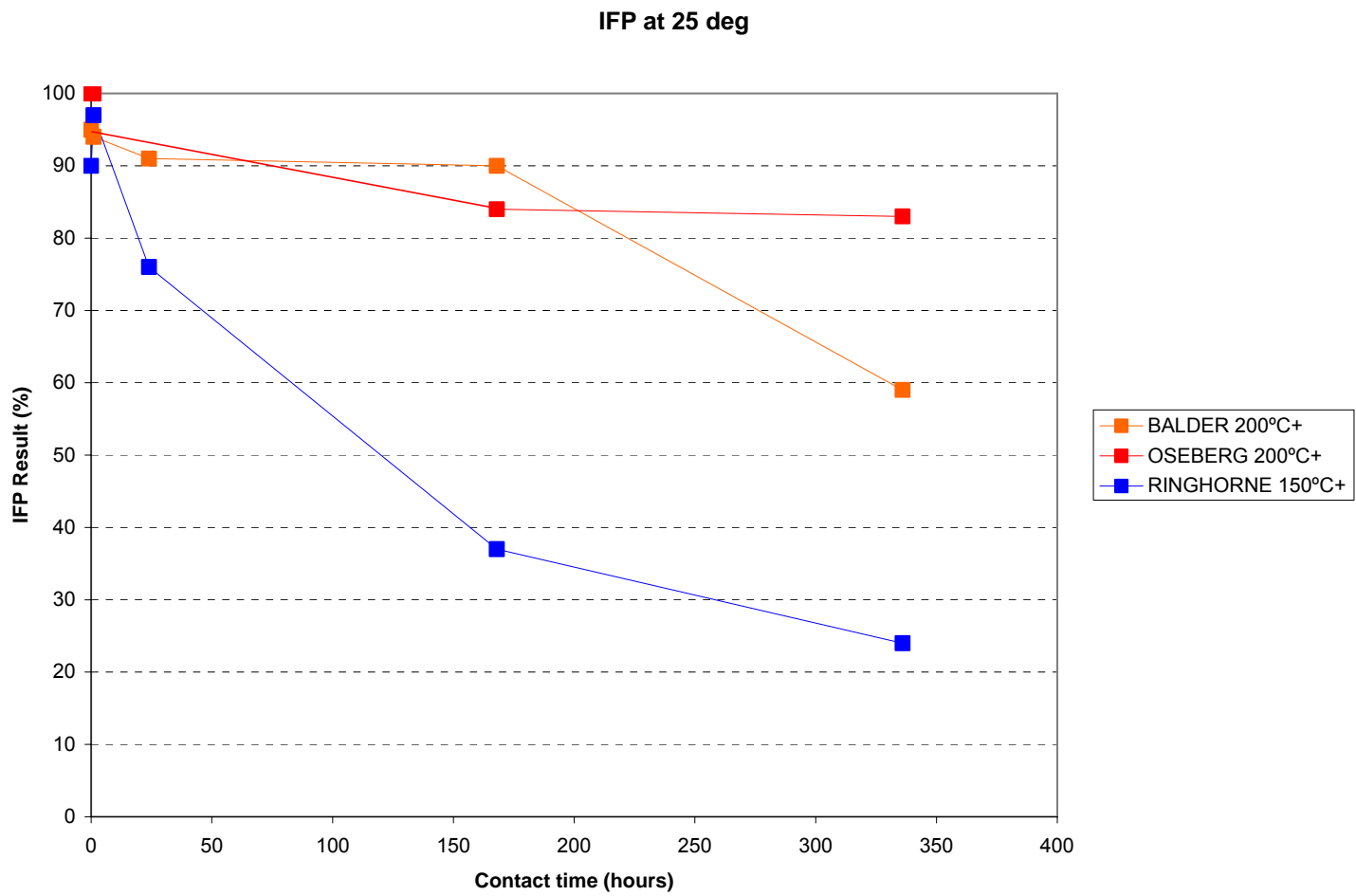


Figure 7. Decrease of IFP result with contact time at 25°C

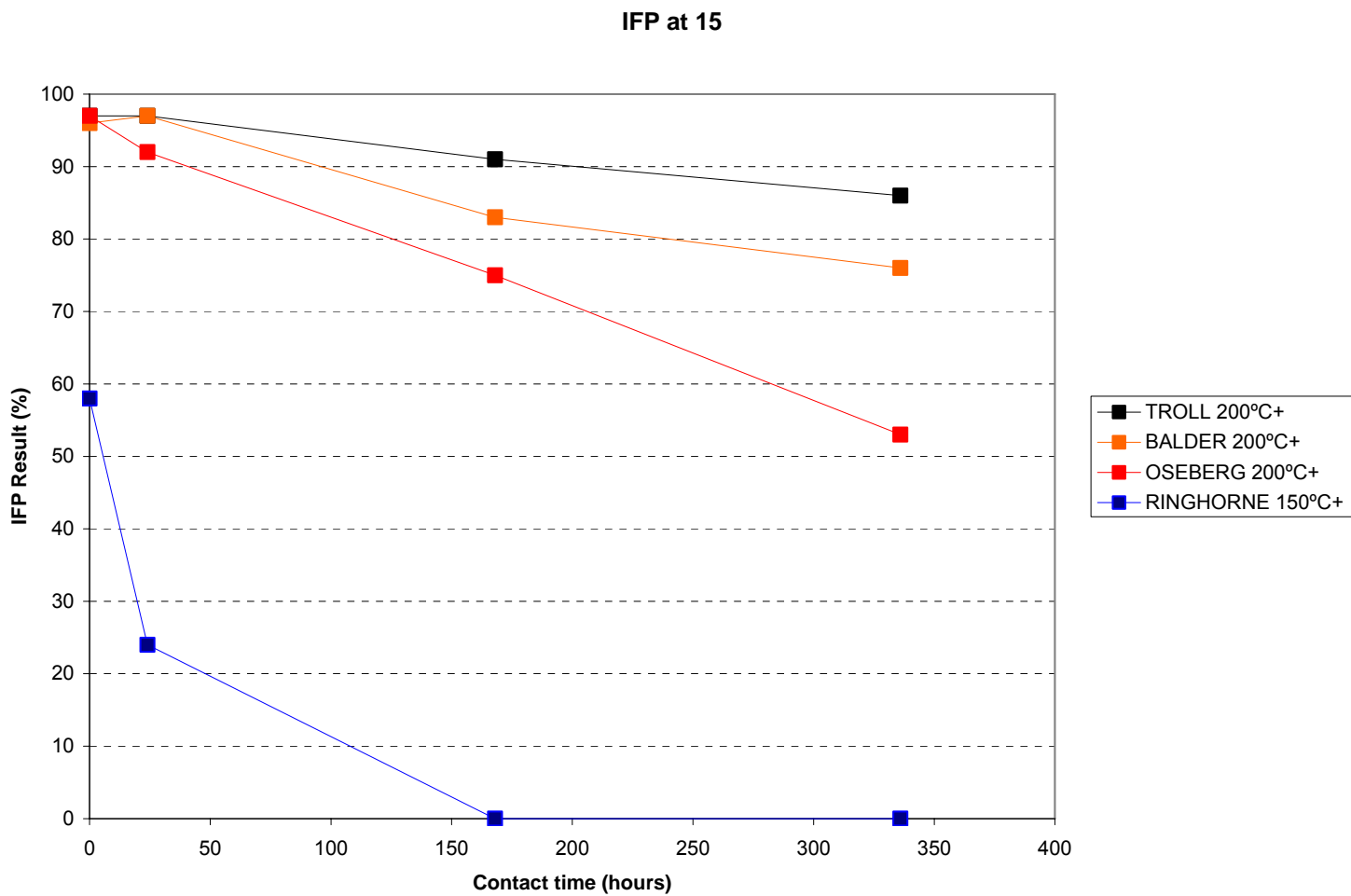


Figure 8. Decrease of IFP result with contact time at 15°C

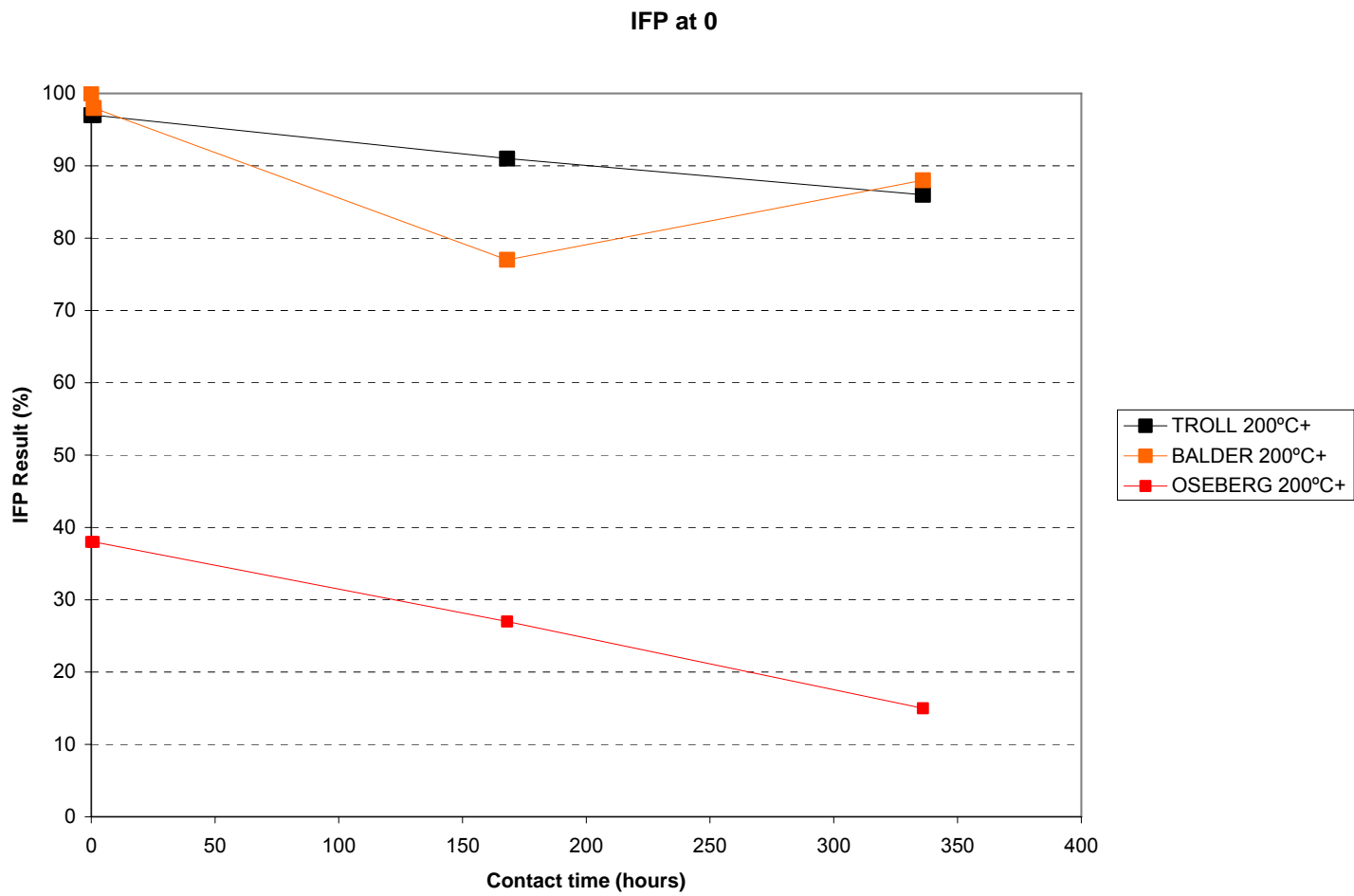


Figure 9. Decrease of IFP result with contact time at 0°C

## **5.1 IFP result as a function of DOR and temperature**

### **5.1.1 IFP Results at 25°C**

- The Balder 200°C+ residue lost almost all of the dispersant (from a DOR of 1:20 to a DOR of 1:1000) and the reduction in IFP result was from 95% to 60% after two weeks.
- The Oseberg 200°C+ residue lost approximately half the dispersant concentration (from a DOR of 1:25 to 1:58) and there was only a slight drop in the IFP result, from 95% to 83%, after two weeks.
- The Ringhorne 150°C+ residue lost a substantial proportion of the dispersant (DOR decrease from 1:20 to 1:167) and there is a very marked drop in IFP result from 95% to 24% after two weeks.

### **5.1.2 IFP Results at 15°C**

- The Troll 200°C+ residue lost about half of the dispersant (DOR decreased from 1:25 to 1:48) and the IFP result decreased only slightly from 97% to 86% after two weeks.
- The Balder 200°C+ residue lost a lot of the dispersant (DOR decreased from 1:20 to 1:125) and the IFP result decreased from 97% to 76% after two weeks.
- The Oseberg 200°C+ residue lost only a little dispersant (DOR decreased from 1:25 to 1:31) and the IFP result decreased from 97% to 53% after two weeks.
- The Ringhorne 150°C+ residue lost only a minor proportion of dispersant (DOR decrease from 1:20 to 1:22) and the IFP result decreased from 58% to 0% after one week.



### 5.1.3 IFP Results at 0°C

- The Troll 200°C+ residue lost half of the dispersant (DOR decreased from 1:25 to 1:50) and the IFP result decreased from 97% to 86% after 2 weeks. The loss of dispersant had relatively little effect on the IFP result. The residue was well above its Pour Point of -9°C and the oil was dispersible.
- The Balder 200°C+ residue lost relatively little dispersant (DOR was reduced from 1:20 to 1:23). The IFP result remained high, dropping from 100% to 88% after 2 weeks. The residue was at its Pour Point (0°C), but was dispersible and (probably due to the low wax content of 0.5% wt.)
- The Oseberg 200°C+ residue apparently lost little dispersant during two weeks. (There is an inconsistency in the reported results; the dispersant concentration for the 1 minute test is given as 2.2% wt (DOR 1:45), but at the 336 hour test is given as 3.4% wt. (DOR 1:29)). The IFP result was initially low, 38%, and decreased to 15% after two weeks

## 5.2 *Discussion of results*

The IFP results obtained with the oil residues appear to be a function of several factors:

1. The inherent dispersibility of the oil, i.e. the amount of dispersant (DOR) required to cause a high level of dispersion of the oil residue
2. The loss of dispersant (reduction of DOR) on extended contact time with water.
3. The flow properties of the oil residue at the test temperature, as indicated by the Pour Point and apparent viscosity of the oil residue

### 5.2.1 Inherent dispersibility of the oil

The standard DOR of 1:20 or 1:25 produced initial IFP results that were close to 100% for most of the tests. It is therefore not easy to discriminate trends of the IFP results between the different oil residues. However, the decrease in DOR caused by the dispersant being lost to the water on extended contact time. As can be seen from the IFP results and DORs contained in Table 10 and presented in a slightly different format in Figure 10:

- The Troll 200°C+ residue produced an IFP result of 86% when the DOR dropped to 1:50 at 15°C and 0°C.
- The Balder 200°C+ residue produced IFP results of 76% when the DOR dropped to 1:125 at 15°C and 60% when the DOR dropped to 1:1000 at 25°C
- The Oseberg 200°C+ residue produced an IFP result of 83% when the DOR dropped to 1:58 at 25°C and 53% when the DOR dropped to 1:31 at 15°C.
- The Ringhorne 150°C+ residue produced an IFP result of 24% when the DOR dropped to 1:167 at 25°C

On the basis of these limited results the Balder residue was the most dispersible oil; the highest IFP results were obtained at the lowest DOR of dispersant. The Troll and Oseberg residues were both less dispersible than the Balder residue and required more dispersant (a higher DOR) to achieve a similar IFP result. The Ringhorne 150°C+ residue was the least dispersible oil at 25°C.

	25°C		15°C		0°C	
	IFP %	DOR	IFP %	DOR	IFP %	DOR
Troll 200°C+ residue	-	-	97	1:25	97	1:25
After 2 weeks	-	-	86	1:48	86	1:50
Balder 200°C+ residue	95	1:20	97	1:20	100	1:20
After 2 weeks	60	1:1000	76	1:125	88	1:23
Oseberg 200°C+ residue	95	1:25	97	1:25	38	1:45?
After 2 weeks	83	1:58	53	1:31	15	1:29
Ringhorne 150°C+ residue	95	1:20	58	1:20	-	-
After 2 and 1 weeks	24	1:167	0	1:22	-	-

Table 10. IFP results and DORs

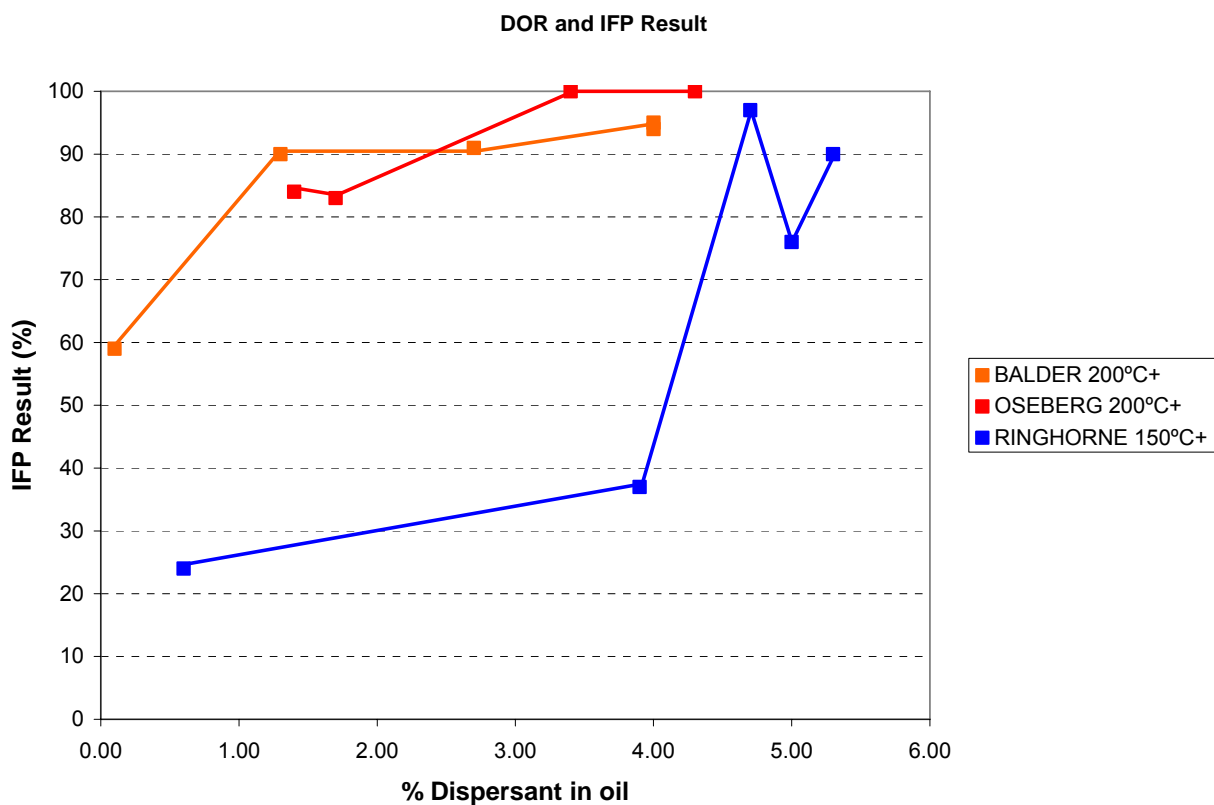


Figure 10. Effect of DOR on IFP result

## 5.2.2 Loss of dispersant by extended contact with water

As discussed in Section 4.1, the Balder 200°C+ residue showed the greatest propensity to lose dispersant and the Oseberg 200°C+ residue showed the least propensity to lose dispersant at 25°C. The Ringhorne 150°C+ residue showed intermediate behaviour.

Reducing the temperature reduced the extent of dispersant loss. At 15°C, the Balder 200°C+ residue again showed the greatest propensity to lose dispersant, the Troll 200°C+ residue exhibited the next greatest tendency to lose dispersant and the Oseberg 200°C+ and Ringhorne 150°C+ residues retained almost all of the dispersant.

## 5.2.3 Flow properties of the oil residues

The flow properties of the oil residues – as indicated by the Pour Point and apparent viscosities of the oil residues at the test temperatures (Table 11) – begin to affect the IFP results at the test temperature was reduced.

	Pour Point (°C)	Viscosity at 10s <sup>-1</sup> (cP)		
		0°C	15°C	25°C
Troll 200°C+	-9	280	70	41
Balder 200°C+	0	2000	360	160
Oseberg 200°C+	+9	1200	220	27
Ringhorne 150°C+	+12	1700	270	32

Table 11. Pour Points and viscosities of oil residues

At 25°C the IFP results are primarily affected by the inherent dispersibility of the oil and the subsequent loss of dispersant to the water on extended contact.

The behaviour of the Ringhorne 150°C+ residues tested at 15°C begins to be mainly affected by the Pour Point of +12°C. The other residues show similar levels of initial IFP result as they did when tested at 25°C, but the 2-week contact time IFP result of only 53% (at a DOR of 1:31) for the Oseberg 200°C+ residue indicates that the Pour Point of +9°C

is starting to influence the result. These two oil residues were becoming less dispersible, irrespective of dispersant treatment rate, because wax precipitation was causing an increase in residue viscosity and this was limiting dispersion. Although the apparent viscosity is also a factor, as discussed in Section 2.1, the viscosity values quoted in the report are – to some extent – an artefact of the method used to determine them. The IFP results obtained (Figure 9) are a direct reflection of the proximity of the oil residue Pour Point to the test temperature of 0°C.

- The Troll 200°C+ residue was well above its Pour Point of -9°C and the oil was dispersible. The loss of dispersant reduced the treatment rate from 1:25 to 1:50 and this had relatively little effect on the IFP result.
- The Balder 200°C+ residue was at its Pour Point (0°C), but was dispersible and (probably due to the low wax content of 0.5% wt.) and there was little loss of dispersant; the DOR was reduced from 1:20 to 1:23. The IFP result remained high.
- The IFP results for the Oseberg 200°C+ residue were initially low at 38% because the oil residue was 9°C below its Pour Point (+9°C) and therefore had a high viscosity (probably much higher than the 1200 cP reported). The IFP result decreased from 38% to 15% after two weeks, but the dispersant concentration was not greatly reduced by leaching. (There is an inconsistency in the reported results; the dispersant concentration for the 1 minute test is given as 2.2% wt (DOR 1:45), but at the 336 hour test is given as 3.4% wt. (DOR 1:29).

The precipitation of wax caused the oil residues to become progressively less dispersible as the test temperature was reduced. This is similar to the ‘limiting viscosity’ effect caused by increased oil viscosity, or emulsified oil viscosity, caused by the ‘weathering’ of spilled oil on the sea surface. The oil residue with the highest Pour Point, Ringhorne 150°C+, was the least dispersible oil and this became more marked at the lower

temperatures. The oil with the lowest Pour Point, Troll 200°C+, was the most dispersible oil and was least affected by the reduction in test temperature.

## **6. Discussion of all results**

The work conducted by SINTEF and CEDRE and the results described in the report revealed two separate effects caused by the test conditions and oil residues employed:

1. Surfactant leaching from dispersant-treated oil residue into the underlying water.
2. The onset of a limiting viscosity (rheology) to dispersion for each oil residue as the test temperature was reduced

The use of four different crude oil types, simulated weathered residues with Pour Points within, or close to, the three test temperatures used, and contact times of up to 2 weeks produced a wide range of IFP results in a matrix that is difficult to interpret. With hindsight, it might have been better to have fewer variables so that the separate significant effects could be clearly distinguished.

### **6.1 *Surfactant leaching from dispersant-treated oil***

During the extended contact time of up to 336 hours (two weeks) the individual surfactants from a model dispersant formulation leached out ‘in proportion’; the relative proportions of the individual surfactants were not significantly altered by the leaching. The overall effect was to deplete the dispersant concentration in the oil residue with extended contact time. The rate and extent of dispersant depletion was:

- (i) Temperature dependant; occurring most rapidly at 25°C, but more slowly and to a lesser extent at 0°C.
- (ii) Dependant on oil residue type; the dispersant was depleted from the Balder 200°C+ residue to a much greater extent than it was depleted from the

Oseberg 200°C+ residue. The dispersant depletion from the Troll and Ringhorne residues happened to an extent that was intermediate to that from the Balder and Oseberg residues.

## **6.2 IFP result obtained with reduced DOR**

The reduction in IFP result obtained by the depletion of dispersant, equivalent to a reduction in the dispersant treatment rate (DOR – Dispersant to Oil Ratio), was not proportional to the extent of dispersant depletion and varied with oil type and temperature.

The different oil residues were of different inherent dispersibility. The fact that all the initial IFP results, conducted with a DOR of 1:20 or 1:25 were all close to 100% (except with the Ringhorne 150°C+ residue at 15°C and the Oseberg 200°C+ residue at 0°C) is not an indication that the oils have similar dispersibility. It indicates that with the DOR used the IFP test method is not capable of discriminating between the different dispersibilities of the oil residues.

It is well known that the reduction in dispersant treatment rate does not produce a linear change in laboratory dispersant effectiveness test results and that this effect varies with different oils. When dispersant is used at the standard treatment rate (a DOR of 1:20 or 1:25) with low viscosity, non-emulsified oils (such as the oil residues used in this work) it is effectively an ‘over-treatment’. Reducing the DOR by a factor of two to a DOR of 1:50 may cause little change in the IFP result obtained with many oils. It may therefore have been better to reduce the initial DOR so that an IFP result significantly less than 100% was obtained. The differences in the inherent dispersibility of the test oils would then have been more apparent.

The Balder 200°C+ residue appeared to be very ‘tolerant’ of DOR reduction; high IFP results were obtained with very low DORs. The Oseberg 200°C+ residue was markedly less tolerant to DOR reduction; the IFP result decreased more as the DOR was reduced.

## **6.2 The onset of a limiting viscosity (rheology) for dispersion**

The main elements of the work, IFP tests and leaching experiments, were conducted at 25°C, 15°C and 0°C. The Pour Points of the four oil residues used varied between -9°C and +12°C, with three of the Pour Points (Balder 200°C+ residue; 0°C, Oseberg 200°C+ residue; +9°C and Ringhorne 150°C+ residue; +12°C) being at temperatures within the test matrix temperature range of 0°C to 25°C.

The apparent viscosities of the four oil residues used in the study were determined at 10 sec<sup>-1</sup> across a temperature range of +30°C to 0°C. Deviations from a log-linear plot of viscosity versus temperature indicated that wax precipitation was interfering with the flow process and this typically happened at approximately 14°C degrees above the Pour Point. All of the four oil residues had some wax precipitated when tested within the test matrix temperature range of 0°C to 25°C. The amount of wax precipitated at the test temperatures of 25°C, 15°C or 0°C would have been proportional to the wax content and Pour Point of the oil residue.

The precipitation of wax caused the oil residues to become progressively less dispersible as the test temperature was reduced. This is similar to the 'limiting viscosity' effect caused by increased oil viscosity, or emulsified oil viscosity, caused by the 'weathering' of spilled oil on the sea surface. The oil residue with the highest Pour Point, Ringhorne 150°C+, was the least dispersible oil and this became more marked at the lower temperatures. The oil with the lowest Pour Point, Troll 200°C+, was the most dispersible oil and was least affected by the reduction in test temperature.

At the test temperature of 25°C, the dominant effect of extended contact time was surfactant leaching leading to dispersant depletion to reduced DOR and therefore reduced IFP result, except for the Ringhorne 150°C+ residue which was becoming less dispersible due to wax precipitation. Observation of the effect is complicated by the fact that the oil residue that lost most dispersant, Balder 200°C+, is also the oil residue that can be effectively dispersed with very low treatment rates of dispersant.



## 7. Conclusions

1. The SINTEF study investigated two processes:

- (iii) Surfactant depletion from the test oil residues into the underlying water in the IFP test with extended contact time.
- (iv) The IFP dispersibility of the test oil residues as a function of oil residue rheology (high viscosity caused by wax precipitation near the Pour Point of the oil residue).

Due to the experimental design and number of variables (4 oil types and 3 test temperatures that were similar to the Pour Points of the oil residues) the influence of these underlying processes has not been clearly distinguished.

2. The study of the depletion of surfactants with time established that the dispersant formulation was not greatly changed due to surfactant leaching. The overall effect was of dispersant loss with time, rather than that of individual surfactants. The extent of dispersant loss from the oil residue was proportional to temperature being highest at 25°C and lowest at 0°C. Dispersant loss at 0°C was not very significant.

3. The oil type had a very marked effect on the rate and extent of dispersant loss at 25°C and 15°C. Dispersant was most rapidly lost from the Balder 200°C+ residue to very low levels within the two week time period, but dispersant loss was to a much lesser extent from the Oseberg 200°C+ residue and intermediate for Troll 200°C+ and Ringhorne 150°C+ residues. The reason for the different susceptibility of the oil residues to dispersant loss is not evident from the study. There appears to be no relation with oil residue viscosity, Pour Point or chemical composition from the data presented, but it is suspected that oil composition is probably the key.

4. The IFP result obtained after extended contact with water is not proportional to the extent of dispersant loss and varied with oil type. Dispersion of the Balder 200°C+

residue produced high IFP results at 25°C and 15°C even when most of the dispersant had been lost (equivalent to DORs of 1:1000 or 1:125) from the oil. The Oseberg 200°C+ residue was inherently less dispersible than the Balder 200°C+ residue and required more dispersant to achieve a high IFP result. The effect of dispersant loss could have been easily studied by using reduced DORs in the IFP test. Conducting IFP tests with the oil residues and DORs of 1:25, 1:50 and 1:100 would probably reveal the cause of the trends that were observed.

5. The use of three test temperatures; 25°C, 15°C and 0°C, that spanned – or was close to – the Pour Points of the oil residues tested, makes the results difficult to interpret. Most of the IFP results obtained at 25°C were mainly influenced by the effect of dispersant depletion, while the IFP results obtained at 0°C were often due to the effects of oil residue viscosity and Pour Point of the oil residues. The IFP results obtained at 15°C were influenced by both effects; dispersant depletion **and** the effects of viscosity / Pour Point. The relative influence of the two effects (dispersant loss and Pour Point) were different for the different oil residues used.

The conclusions of the report offer little insight into the relative importance of the two effects. The conclusions suggest that all the results could be explained in terms of oil residue rheology that requires further investigation. A more focused experimental design could have revealed more.

6. The study implies that the IFP results obtained are indicative of dispersant performance at sea with relatively high IFP results ‘predicting’ good dispersant performance at sea and relatively low IFP results ‘predicting’ poor performance at sea. This is not in agreement with observations made at Ohmsett with cresting / breaking waves and indications given by results from the WSL test method.

## **8. Implications for further testing at Ohmsett**

1. The work reported in the SINTEF report confirms that surfactant leaching will lead to dispersant depletion in oils left for an extended period on the water in the Ohmsett tank. The report shows that the loss of surfactants is proportional for all the surfactants in the dispersant; the dispersant formulation is not ‘unbalanced’ by the loss on an individual surfactant. This is useful information since it means that there is no necessity to conduct expensive analytical chemistry techniques to track the depletion of individual surfactants. The effects of surfactant leaching can be easily simulated by the simple process of using reduced DOR in the WSL laboratory test method. This will be most usefully done at Ohmsett so that the appropriate temperatures and degree of oil ‘weathering’ can be used.
2. The work in the SINTEF report was conducted under the very slow sub-surface water current that prevails in the IFP test method. The work conducted at Ohmsett in 2006 (‘static’ water tests) and in 2007 with higher sub-surface water current flows has already indicated that current flow is an important factor in controlling the rate of surfactant leaching. The SINTEF report contributes little insight on this important aspect. The range of sub-surface water current velocities used at Ohmsett in 2007 cover the most likely range that would be experienced at sea; faster wind-induced currents would be associated with breaking wave regimes. Some consideration should be given to better ways of measuring the low sub-surface water current velocities.
3. The work at Ohmsett in 2007 used the same Oseberg crude oil (“New Oseberg” in the SINTEF report). A residue equivalent to the Oseberg 200°C+ residue used by SINTEF and CEDRE for the reported work was placed on the tank at Ohmsett, but under the prevailing conditions (day time water temperature of 25°C) lost further volatile components to become equivalent to an Oseberg 240°C+ residue

(in SINTEF's terminology). The oil used at Ohmsett was therefore slightly different to that used in the laboratory work at SINTEF and CEDRE, but this is justifiable because the prevailing conditions caused the evaporation to happen.

4. Many of the effects reported in the SINTEF report are due to the different oil residues being tested close to, or below, the Pour Point of the oil residues. In fact, this aspect of the oil residue dominated the results obtained, almost to the exclusion of the stated objective of the study that was to investigate the effect of surfactant leaching.
5. The work conducted in the SINTEF / CEDRE study used the standardised conditions of the IFP test method. While this ensured a certain consistency of results, it did not allow for a systematic study of the variables that probably influence the leaching of surfactants and therefore dispersant depletion. Oil layer thickness is likely to be an important variable. An oil layer thickness of 5 mm was used in the 2007 Ohmsett studies, although the oil was observed to circulate within the circular boom. Oil layers that are both thicker and thinner than an average 5 mm should be used in further Ohmsett tests to determine if this is an important variable.
6. One aspect of the 'calm sea' tests of the previous work at Ohmsett and the work in the SINTEF report is that the test oil is not emulsified. Since the viscosity increase caused by emulsification of spilled oil (in rougher seas) is the most likely reason to limit the dispersant effectiveness at sea, the observations and results obtained in these current studies should be interpreted with care. In particular, the time "window of opportunity" for dispersant use is likely – in the absence of emulsification – to be much longer than when emulsification occurs. It might also be that very low treatment rates of dispersant might be found to be effective on the un-emulsified oil. As such, an end-point at Ohmsett with dispersion limited by the depletion of dispersant might be difficult to obtain in the time allowed if the standard dispersant treatment rate of DOR of 1:20 or 1:25 is the only starting

point. It is suggested that some Ohmsett tests be conducted with lower initial dispersant treatment rates, e.g. DOR 1:50 or 1:100.

7. There is an inference in the SINTEF report that a relationship between IFP result and performance at sea exists; a relatively high IFP result is implied to mean that dispersant performance would be 'good' at sea, while a relatively low IFP result is implied to be an indication that dispersant performance would be 'poor'. These terms are not clarified, nor are the IFP / performance at sea relationships elucidated; only implied. The results from the Ohmsett testing in 2007 showed that a low (~10%) result in the WSL test method is **not** an indication that dispersion will not occur if the oil is exposed to cresting / breaking waves at Ohmsett. Since the WSL test is often said to be of 'higher' energy than the relatively low 'energy' IFP test, further testing at Ohmsett will be able to better establish a relationship between WSL result and dispersant performance in the tank.

## **10. Appendix 2: LISST Plots for Calm Seas Application And Dispersant Wash-Out**

Oil drop sizes were measured during the breaking wave application phase of each test using the LISST 100X particle size analyzer. The oil concentrations, volume median diameters ( $D_{50}$ ) and  $D_{90}$  data collected for each test have been plotted in Figures A2.1 through A2.4. These data have been processed further to provide the average volume median drop diameter ( $D_{50}$ ), average and peak oil concentration and percentage of oil present in drops of diameter less than 75 microns (oil that would likely be permanently dispersed in an offshore environment) during periods of high measured oil concentration. The results of this analysis are provided in Table A2.1.

These oil drop size measurements only provide single point measurements in space and time and do not provide a complete record of the spatial and temporal characteristics of the oil in the water column. As such, these measurements must be interpreted and used carefully.

Table A2.1 Oil Drop Size Distribution Summary Data from LISST Particle Size Analyzer

Run & Pass #	Volume Median Drop Diameter (μm)	Average Oil Conc (ppm)	Peak Oil Conc. (ppm)	Volume % of Oil in Drops < 75 μm
Run #1				
ANS				
pass #1	163	4.5	7.9	31.5
IFO 180				
pass #1	220	25	55	10
pass #2	222	26	51	14
pass #3	216	39	89	17
pass #4	189	67	320	19
pass #5	147	47	145	26
pass #6	152	68	182	22
pass #7	105	25	43	41
pass #8	119	34	47	34
Run #2a				
IFO 30				
pass #1	14	47	134	92
pass #2	14	60	152	94
pass #3	11	70	170	97
Run #2				
ANS				
pass #1	255	19	52	12
pass #2	105	19	34	40
pass #3	72	17	33	56
IFO 30				
pass #1	228	28	120	13
pass #2	112	22	47	37
pass #3	75	15	26	55
Run #3				
ANS				
pass #1	139	11	69	38
pass #2	96	14	34	45
pass #3	86	14	27	48
IFO 30				
pass #1	118	26	142	34
pass #2	107	37	59	36
pass #3	80	23	40	51

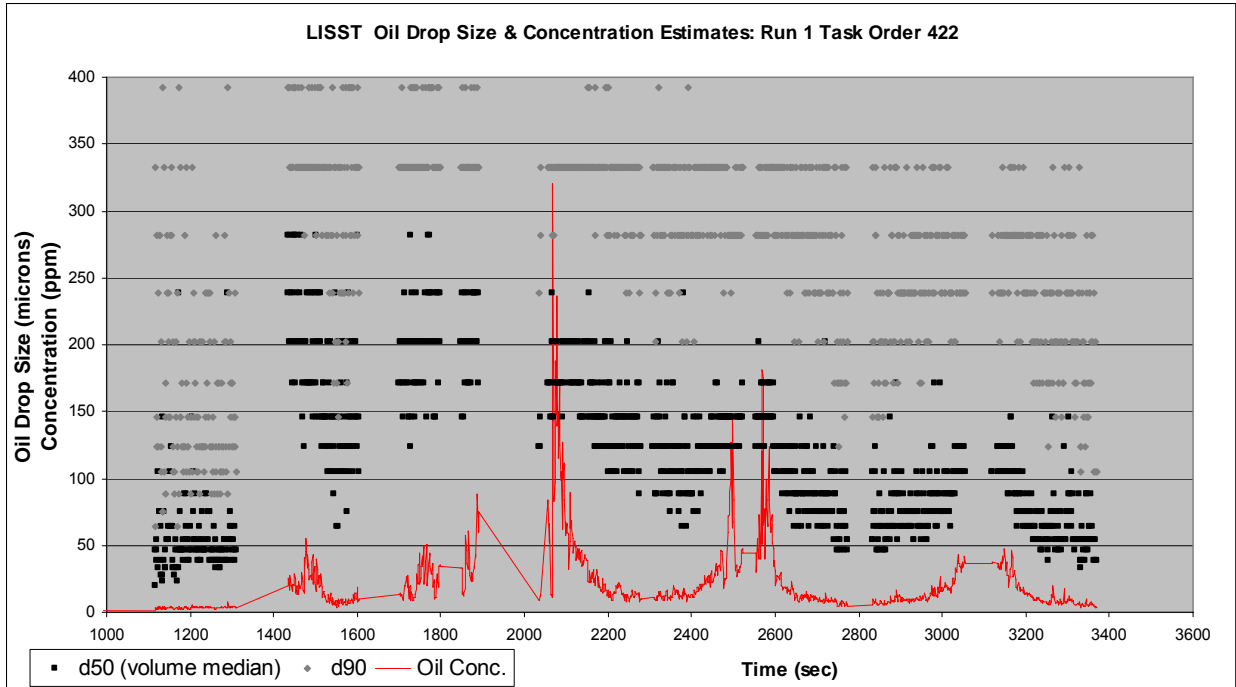


Figure A2.1 Run 1 LISST plot

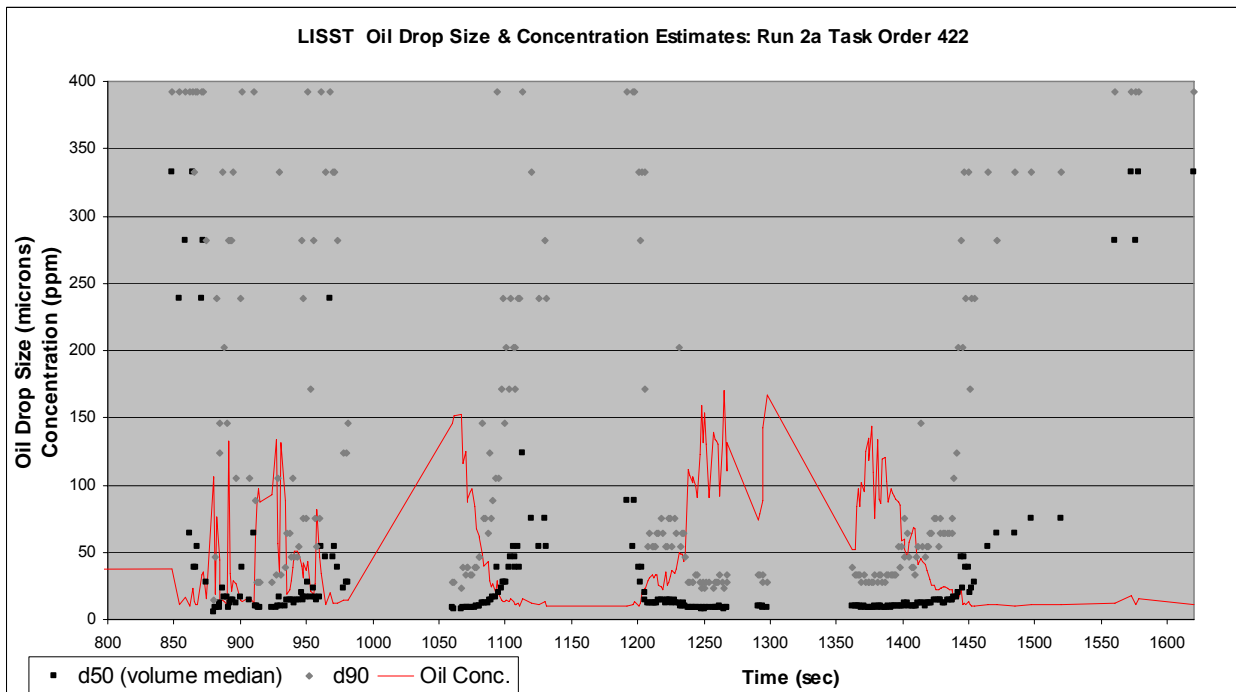


Figure A2.2 Run 2a LISST plot



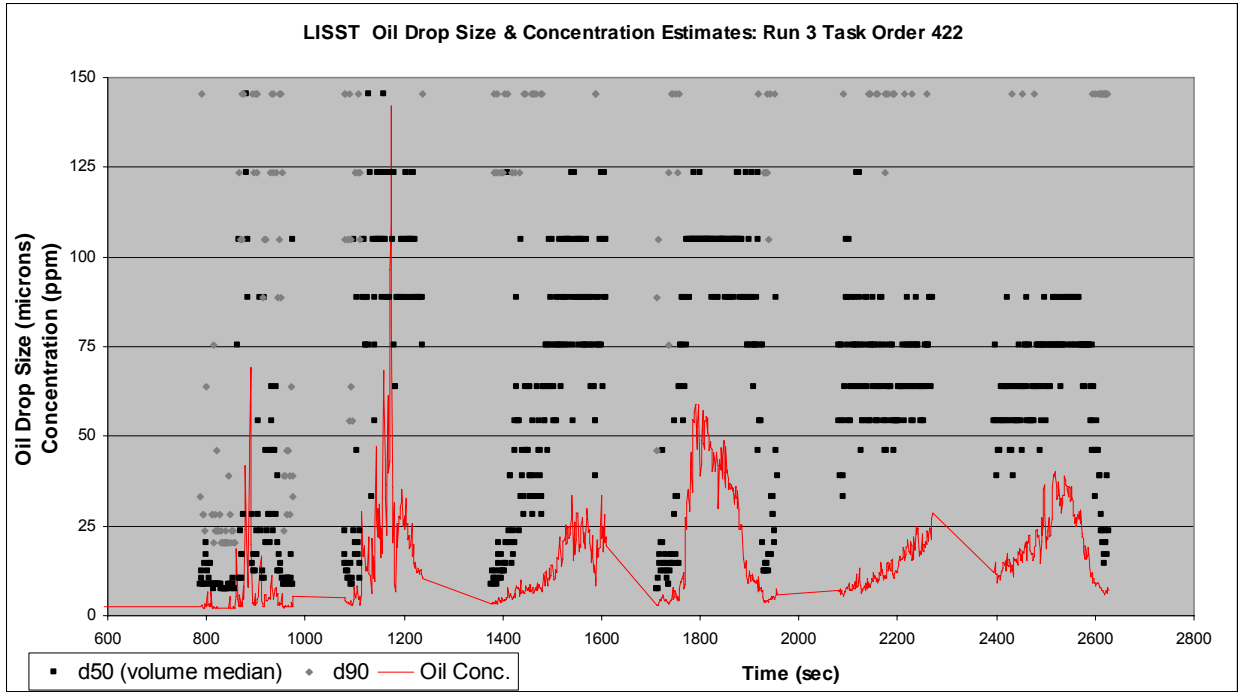


Figure A2.3 Run 3 LISST plot

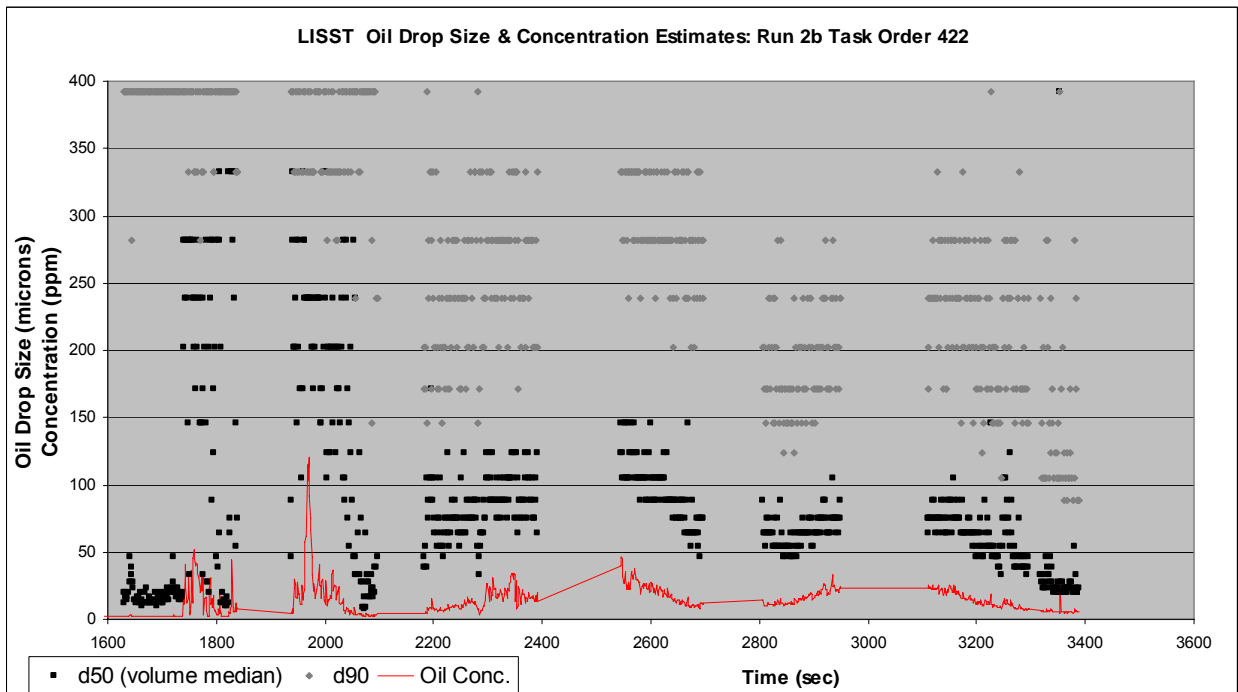


Figure A2.4 Run 2b LISST plot