# CHANGES IN DISPERSANT EFFECTIVENESS WITH EXTENDED EXPOSURE IN CALM SEAS

For

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By

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# Executive Summary

Oil spill dispersants can be applied to spilled oil in calm sea conditions, but may not cause immediate rapid dispersion of the oil if there is insufficient wave energy. If the oil does not disperse shortly after the application of a dispersant, the surfactants might partition (or 'leach') out of the dispersant-treated oil and into the sea over a period of time. The previous work carried out at the National Oil Spill Response Test Facility in Leonardo, New Jersey (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, indicating that the rate of loss of surfactants from the oil had been very low (S L Ross, 2006a).

The experiments described in this report investigated the effect of water currents passing under a dispersant-treated oil slick contained in a stationary ring on the water surface. 'Topped' Oseberg Blend crude oil was used as the test oil in these experiments. Oil containing Corexit 9500 at a treatment rate of 1:20 (Dispersant to Oil Ratio, DOR) was contained in a layer 5 mm thick in a 4.6 meter diameter circular ring on the water surface in the Ohmsett tank. Water current speeds of 13 cm/s and 5-6 cm/s were created under the contained oil by a air bubbler system positioned in the tank. The oil remained on the water in the tank for nearly two days in the first experiment (exposed to 13 cm/s current speed) and for nearly four days in the second experiment (exposed to 5 to 6 cm/s current speed). Samples of the oil were removed at regular intervals and subjected to dispersant effectiveness testing using the Warren Spring Laboratory (WSL) dispersant effectiveness test method.

It was found that further evaporation of the more volatile oil components from the oil continued while the oil was on the water surface. The nominal 27% weight loss from the 'fresh' Oseberg Blend crude oil achieved by the 'topping' increased to approximately 40% weight loss after 48 hours on the water.

There was a decrease from an initial value of approximately 45% in WSL effectiveness with time for the samples of dispersant-treated oil on the water surface in the tank. The WSL effectiveness dropped to approximately 10% after 43 hours with the 13 cm/s current and to approximately 5% after 91 hours with the 5 to 6 cm/s current. No significant differences in WSL effectiveness were observed between the samples exposed to the two different water current speeds. This is consistent with surfactants being removed from the dispersant-treated oil by the water currents. In contrast, there was an initial increase in the WSL effectiveness from approximately 45% to approximately 75% over the first 48 hours for the samples not in contact with water, or in contact with static water. This increase in WSL effectiveness was apparently due to the increase in oil density that accompanied the further evaporation of volatile oil components.

The visual observations made when breaking waves were passed through the dispersant-treated ‘topped’ Oseberg Blend crude oil slicks in the Ohmsett tank were clear:

- The application of breaking waves to the oil after exposure to an average water current speed of 13 cm/s for 43 hours resulted in only very coarse dispersion.
- 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 caused fine dispersion of the oil, visible as a light-brown plume of small oil droplets in the water.

It therefore seems that exposure to the higher water current speed of 13 cm/s, equivalent to 3% of a mean wind speed of 16.7 km/hr (Beaufort Force 3, a gentle breeze) for 43 hours removed more surfactant than exposure to a water current speed of 5 to 6 cm/s, equivalent to 3% of a mean wind speed of 7.4 km/hr (Beaufort Force 2, a light breeze) for 91 hours.

Although the WSL effectiveness results gave a good indication of the surfactant depletion process that was occurring in the tank tests, the relationship between WSL effectiveness result and behavior caused by exposure to breaking waves in the tank is not direct. A low WSL effectiveness result is not a reliable indicator that dispersion will not occur.

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## 1. Objective

The objective of this research was to continue to investigate the conditions, first explored in the report “Calm Sea Application of Dispersants” (S L Ross, 2006a), that might lead to loss of surfactant from dispersant-treated oil, so that the subsequent application of breaking waves will not result in dispersion. The previous study using absolutely still water in the Ohmsett tank found that the oils dispersed after 6 days when breaking waves were applied to the slick. In this study, the effects of water currents of different speeds passing under a slick of dispersant-treated ‘topped’ Oseberg Blend crude oil were investigated.

## 2. Background

Previous research conducted at Ohmsett with IFO-30 fuel oil and Ewing Bank 873 crude oil (S L Ross, 2006a) found that dispersant-treated oil was almost totally dispersed when breaking waves were applied after the oil had been on still water for periods of up to 6 days. In still water conditions, the surfactants remained in the dispersant-treated oil. There was an exceptional experimental result with each oil, when oil was not dispersed, but the general finding was that surfactants did not partition (or ‘leach’) out of the dispersant-treated oil.

Associated research experiments conducted at Ohmsett (S L Ross et al. 2006b) showed that dispersion did not commonly occur in non-breaking waves, but occurred rapidly once breaking waves were applied. No intermediate condition of wave energy or water motion that caused rapid ‘leaching’ of the surfactants, but did not cause dispersion of the oil, were identified at Ohmsett; oil that had been ‘primed’ for dispersion by the addition of dispersant would generally disperse when breaking waves eventually passed through it. Any loss of surfactants from the dispersant applied at the normally recommended rate to the seawater underlying dispersant-treated oil in quiescent conditions must have been partial or slow and did not measurably affect the dispersant’s performance after several days. The general conclusion from that study was that the oils tested and treated with dispersant at the recommended treatment rate in very calm sea conditions will remain dispersible for several days and would subsequently disperse when the sea becomes rougher.

Smaller-scale experiments in the S L Ross wave-tank as part of the Calm Seas project (S L Ross et al. 2006a) gave slightly different indications. Dispersion of test slicks of ANS (Alaska North Slope) crude oil treated at 1:10 or 1:20 (DOR – Dispersant to Oil Ratio) showed no significant drop in effectiveness when allowed to soak for a period of 15 to 45 hours, but the same oil treated with only 1:50 DOR of dispersant showed a significant drop in dispersant effectiveness. The effect was not so marked with IFO-30 fuel oil. These results from the lower-dose experiments suggest that dispersant may be slowly leaching from the oil and enough dispersant was lost from the under-treated slicks to affect the final dispersion.

Conditions where the surfactants could be slowly removed from the oil and into the water without substantial dispersion may exist for certain combinations of oil viscosity, oil layer thickness, dispersant treatment rate and prevailing water current. An oil slick driven across a reasonably calm sea with no significant breaking waves by a slight wind might experience sufficient water exchange at the oil / water interface to strip the surfactants out of the oil, without causing dispersion of the oil. There are generally no significant breaking waves below a wind speed of 7.4 to 11.1 km/hr, yet the oil slick will still drift with the wind due to the windage at approximately 3% of wind speed. A 5.6km/hr wind will cause a slick to drift at 4.4 cm / sec and the underlying oil / water interface will be continuously ‘washed’ by the induced current caused by this differential movement. In order that surfactants would be lost from the oil / water interface they would have to be mobile within the oil and low oil viscosity would facilitate an easier transfer. Prolonged drifting of low-viscosity, dispersant-treated oil in such conditions might result in significant surfactant loss.

Attempts were made at Ohmsett in 2005 to maintain a ‘captive’ slick in a boom and expose it to a constant sub-surface current firstly by towing the ‘captive’ slick up and down the tank and then with the use of a small, electrically-driven outboard motor. There were a number of practical difficulties that were only partially overcome and the limited number of tests completed were not very successful. Some indications that surfactant loss could be occurring were found; the test slick exposed to a continuous sub-surface current from the motor for a prolonged period while in the boom, appeared to be more reluctant to disperse in subsequently applied breaking waves than similar slicks allowed to drift freely on the surface of the tank. However, accurate determination of Dispersant Effectiveness (DE) was not possible in many of the tests due to various boom failures during the long-term tests and difficulties experienced in collecting dispersant-laden oil at the end of some of the tests.

## 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 oil.

Localized surface water currents were induced across the Ohmsett tank using a submerged air-bubble barrier. The test oil was retained in a stationary ring and the water flowed beneath it.

At sea, the wind induces a current in the surface water. High wind speeds result in cresting or breaking waves that cause dispersion of oil. This study used average surface water current speeds of 13 cm/s and 6 cm/s to ‘bracket’ the likely maximum surface water current speed of 10 cm/s caused by 13 km/hr wind, the highest wind speed that would not create a significant frequency of small breaking waves and thus lead to dispersion (Table1).

| Description | Beaufort Force | Mean wind speed (knots) | Mean wind speed (km/hr) | Mean wind speed (m/s) | Water current at 3% of wind speed (cm/s) |
|---|---|---|---|---|---|
| Calm | 0 | 0 | 0 | 0.00 | 0 |
| Light air | 1 | 2 | 3.7 | 0.80 | 2.4 |
| Light breeze | 2 | 5 | 9.3 | 2.40 | 7.2 |
| Gentle breeze | 3 | 9 | 16.7 | 4.30 | 12.9 |

*Table 1. Wind speed and current speed*

## 4. Large-Scale Tank Testing at Ohmsett

### *4.1 Oil Tested*

The oil used in these experiments was Oseberg Blend crude oil that had 27% by weight evaporated prior to the tests. The original sample of crude oil was supplied from Norway. The 27% weight evaporative loss was achieved by air-sparging and heating the crude oil in a barrel. This oil is subsequently referred to as ‘topped’ Oseberg crude oil.

Oseberg Blend crude oil is a blend of crude oils from several oilfields in the Norwegian sector of the North Sea. Crude oils from the Oseberg, Huldra, Veslefrikk, Brage, Frøy and Lille-Frigg fields are transported through a 115 kilometres-long, 71-cm diameter sub-sea pipeline to the Sture terminal near Bergen. A 2007 crude oil assay of Oseberg Blend crude oil (Statoil PKS 2007) gives the density of the crude oil at 15ºC of 0.8355 gm/ml. The TBP (Total Boiling Point) curve is also given in this assay.

## 4.2 Test Methods and Equipment

### 4.2.1 Ohmsett tank test set-up

A photograph of the set-up for the work is shown in Figure 1.

A 4.6 meter diameter ring of 7.6 cm diameter plastic tubing was used to contain the test oil. The ring was placed in the tank, positioned and tethered between the Main Bridge and the Auxiliary Bridge that had been fixed 8.5 meters apart. The area over the water between the two bridges was covered with a tarpaulin to prevent the oil being affected by rain.

*Figure 1 Ohmsett tank set up showing 4.6 meter diameter ring to contain oil under tarpaulin*

A 9 meter long bubble barrier was placed on the bottom of the tank to the South of the bridge position (Figure 2). Compressed air was pumped into this bubble barrier and produced a surface water current flow away from the barrier and towards the ring. The water current speed was greatest near the bubble barrier and decreased with distance from the barrier.

*Figure 2.* *Bubble barrier*

### 4.2.2 Test procedure

The air flow through the bubble barrier and the distance of the bridge from the bubble barrier were adjusted to produce a current speed of approximately 13 cm/sec (for On tank Test # 1), or 6 cm/sec (for On tank Test # 2) across the width of the ring.

There was a gradient of surface water current speed with distance from the bubble barrier. The current speed was measured at various points with the Sontek velocity probe and additional average surface current measurements were also made by using a propeller-based current meter and the use of small fishing floats.

Eighty liters of test oil, pre-mixed with the appropriate quantity of Corexit 9500 to achieve a DOR (Dispersant to Oil Ratio) of 1:20, were carefully placed in a circular boom on the tank (Figure 3).

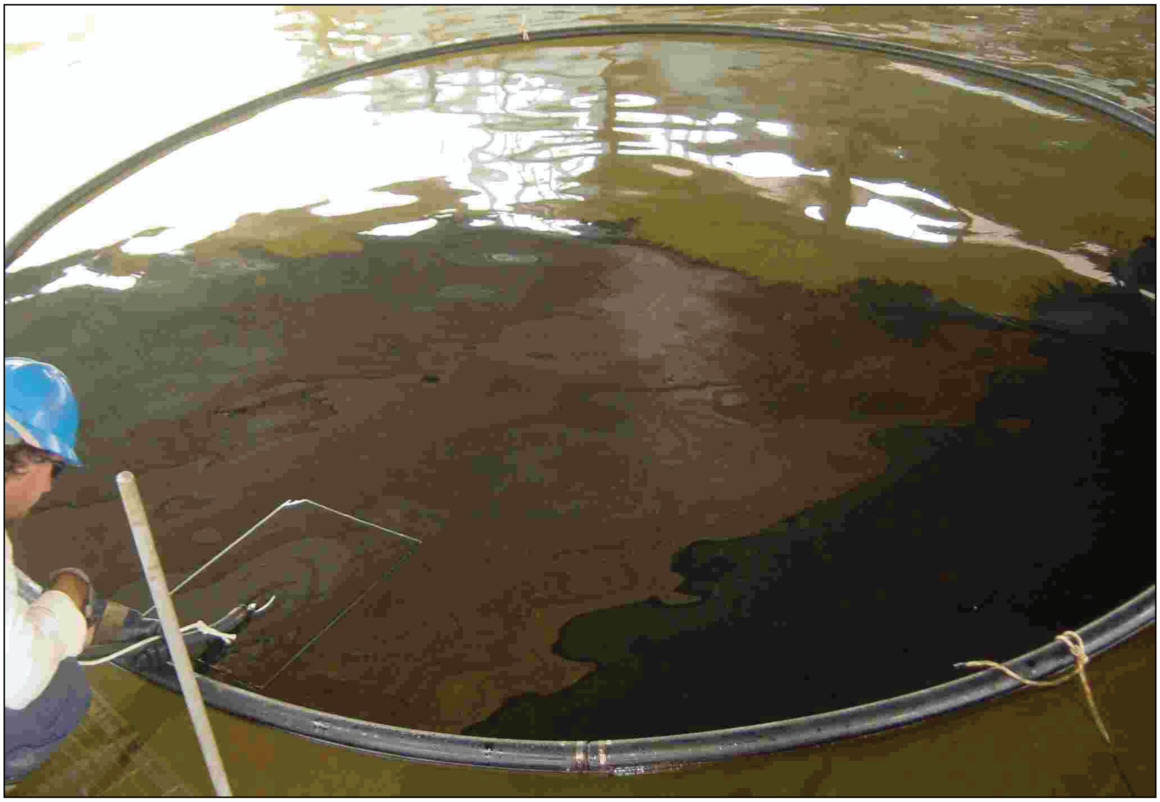

*Figure 3. Dispersant-treated oil addition*

The current flow in the water under the oil in the ring caused the oil on the water surface to be concentrated in the 'down-current' portion of the ring with a small area of open water (Figure 4).

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.

Small samples of the oil were carefully withdrawn each day and these were tested using the WSL dispersant effectiveness test method (Appendix A), except that no additional dispersant was added to the test oil.

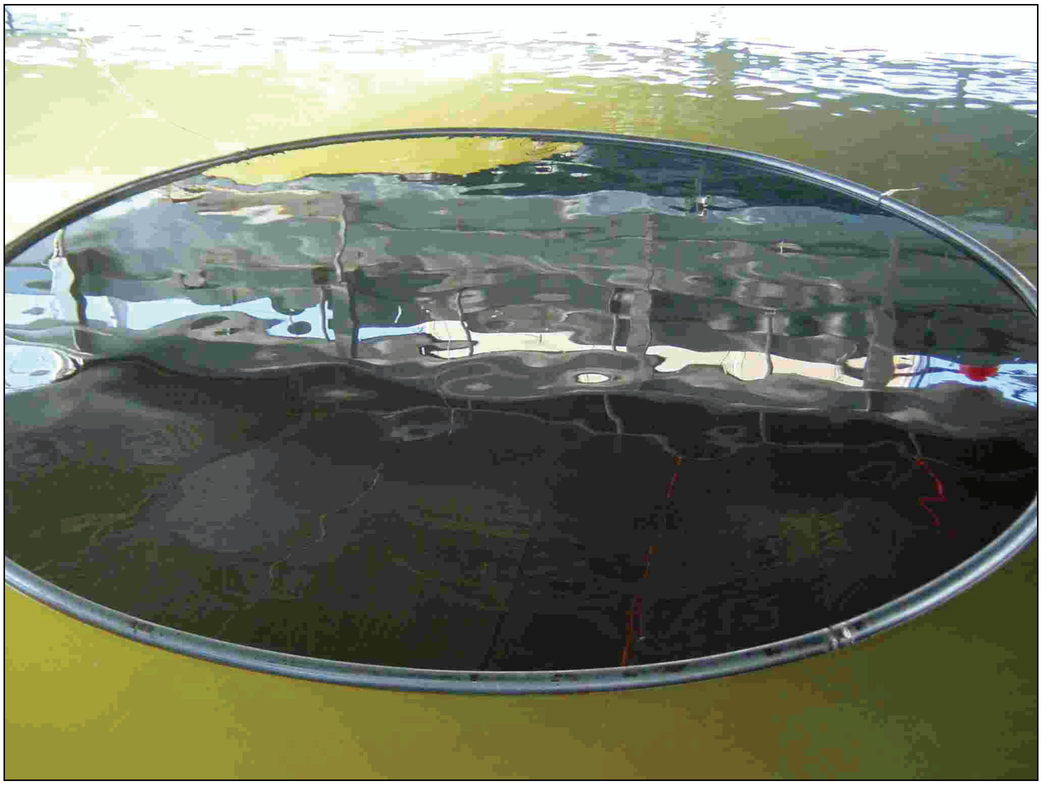

*Figure 4. Oil in the ring*

The prevailing surface water temperatures during the tests varied between 20ºC at night and 25ºC during the day.

At the end of the test, the circular boom was 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 33 to 34 strokes per minute for 30 minutes. During the period of wave activity the behavior of the oil was assessed visually. The LISST particle size analyzer was towed at a 1.5-metre depth through any visible dispersed oil cloud or under the surface oil slick if a cloud was not visible.

# 5. Results

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

- **“Weathering Control” samples**
  “Topped” Oseberg Blend crude oil was placed in a tray in a layer 5 mm thick. The tray was shielded from the rain underneath the deck of Ohmsett.

- **“No current” samples**
  A 5 mm layer of “topped” Oseberg Blend crude oil was placed on the water in a drum filled from the Ohmsett tank.

- **“On tank Test” samples**
  On tank Test # 1 was carried out with an average surface water current speed across the ring of 13 cm/sec. The average surface water current speed for On tank Test #2 was 6 cm/sec.

## *5.1 Oil Weathering*

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

The addition of a DOR of 1:20 of Corexit 9500 increased the overall density to 0.8830 gm/ml at 22.7ºC (0.8880 gm/ml at 15ºC).

### 5.1.1 “Weathering control” samples

Two samples, each of 215 gms of the ‘topped’ Oseberg Blend crude oil, were weighed into aluminium trays (26 cm x 19.5 cm) to produce an oil layer 5 mm thick (Figure 5). These trays were placed, protected from rain, under the deck of the tank and left for a total of 49 hours. The weight of the oil decreased by 9.96% due to the evaporation of the more volatile oil components.

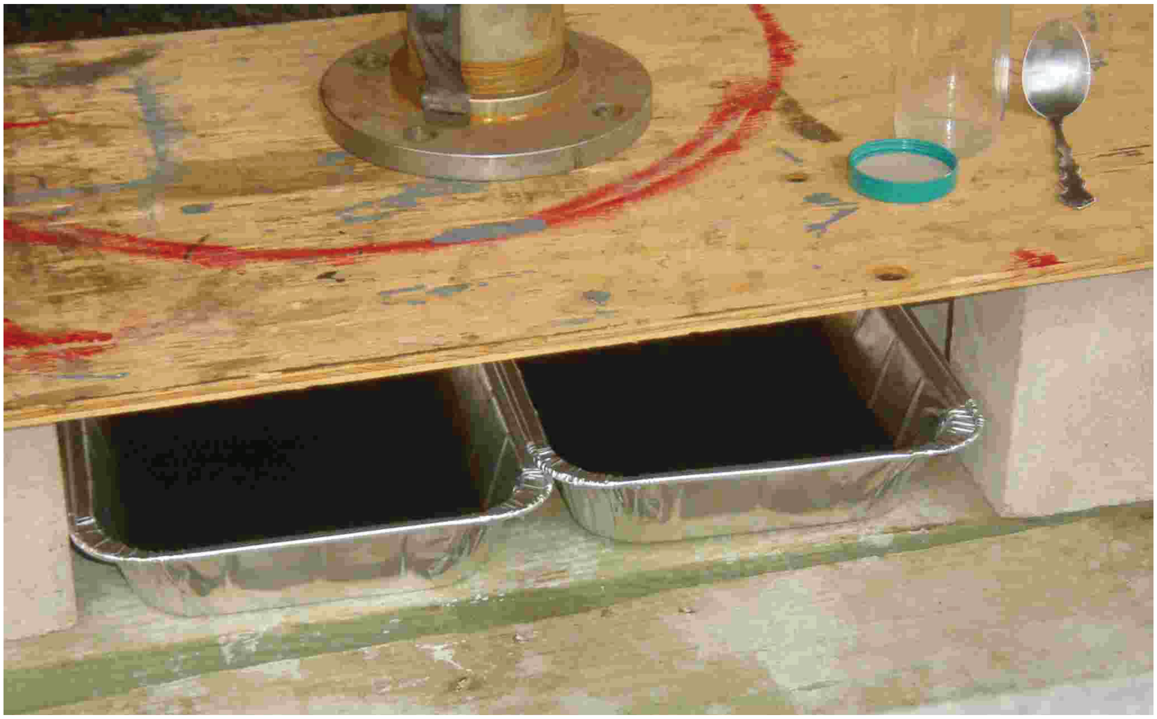

*Figure 5. “Weathering control” samples in trays*

The nominal 27% weight loss of the ‘topped’ Oseberg Blend crude oil sample was equivalent to a 32% weight loss from the ‘fresh’ crude oil. The loss of a further 9.96% weight after 49 hours in the aluminium trays indicates that the fresh crude oil would have lost a total of 38.8% weight. This is equivalent to a distillation temperature of 240ºC. The density of the oil increased from 0.8810 gm/ml at 23.5ºC to 0.8930 gm/ml at 22.7ºC, equivalent to an increase from 0.8860 gm/ml to 0.8980 gm/ml at 15ºC.

### 5.1.2 “On tank” test samples

The density of the ‘topped’ Oseberg Blend crude oil on the water surface in the tank increased with time, indicating that further evaporation of volatile components had taken place from the oil.

The increase in oil density with time on the tank water surface is shown in Figure 6. Although there is some scatter in the results, the overall trend of oil density increase is clear; a relatively rapid increase in oil density over the first 48 hours, followed by a much slower increase in oil density.

The intention to use a ‘pre-weathered’ oil to prevent or minimise changes in oil properties during the course of the experiment was not fully fulfilled; the crude oil lost additional volatile components and the oil density and oil viscosity therefore increased with time on the water surface of the tank.

This increasing oil density had a marked affect on the WSL effectiveness results obtained (see Section 5.3).

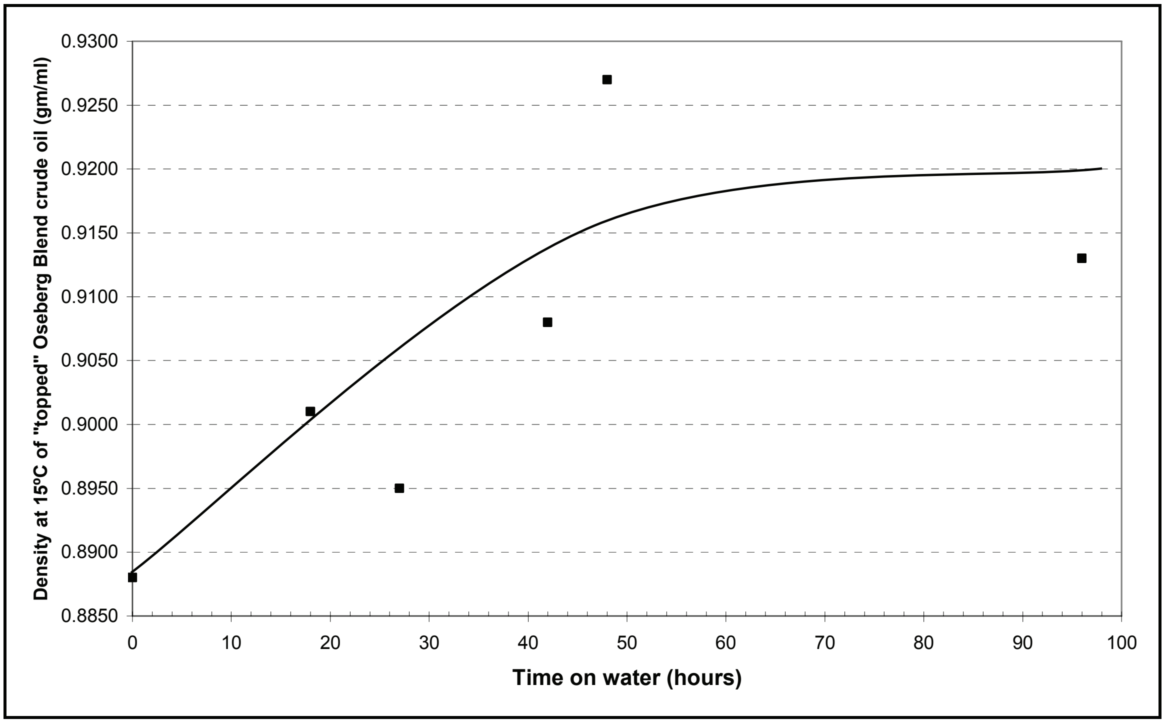

*Figure 6. Increase in density of 'topped' Oseberg Blend crude oil with time on water surface in Ohmsett tank*

## 5.2 Dispersion in the tank

**On tank Test # 1**

The dispersant-treated, 'topped' Oseberg crude oil was placed in the boomed area on the tank at 14:45 on Tuesday, 19th June. The bubble barrier air-flow and distance to the boomed area was set to produce an average water surface current of 13 cm/s underneath the oil. At 09:45 on Thursday, 21st June the air-flow through the bubble barrier was turned off and the ring was lifted out. The dispersant-treated, 'topped' Oseberg Blend crude oil had been on the water surface in the tank for 43 hours exposed to a constant average surface water current of 13 cm/s.

The wave generator was then started. The wave paddle settings used in these tests were a 3-inch stroke and 33 to 34 strokes per minute for 30 minutes. Within a few minutes breaking waves were passing through the oil slick. Based on visual observations the breaking waves caused only a very coarse dispersion of the oil. This resembled tea leaves, with individual small black specks easily visible from the viewing distance of about 3 meters. No light-brown dispersed oil plume was visible.

The LISST particle size analyzer was towed at a 1.5-metre depth along the length of the slick. Some larger oil droplets were found, but there was no extensive dispersed oil at depth in the tank. The in-water oil concentrations and oil drop size volume median diameters (VMDs) measured by the LISST are shown in Figure 7. The oil concentration data show frequent spikes in concentrations as high as 100 to 200 ppm. However, the oil drops were large (100 to 200 micron VMD) in these zones of high oil concentration and this oil was quickly rising back to the surface.

A video clip of the dispersion can be viewed by clicking on the following link: On tank test #1 Dispersion.

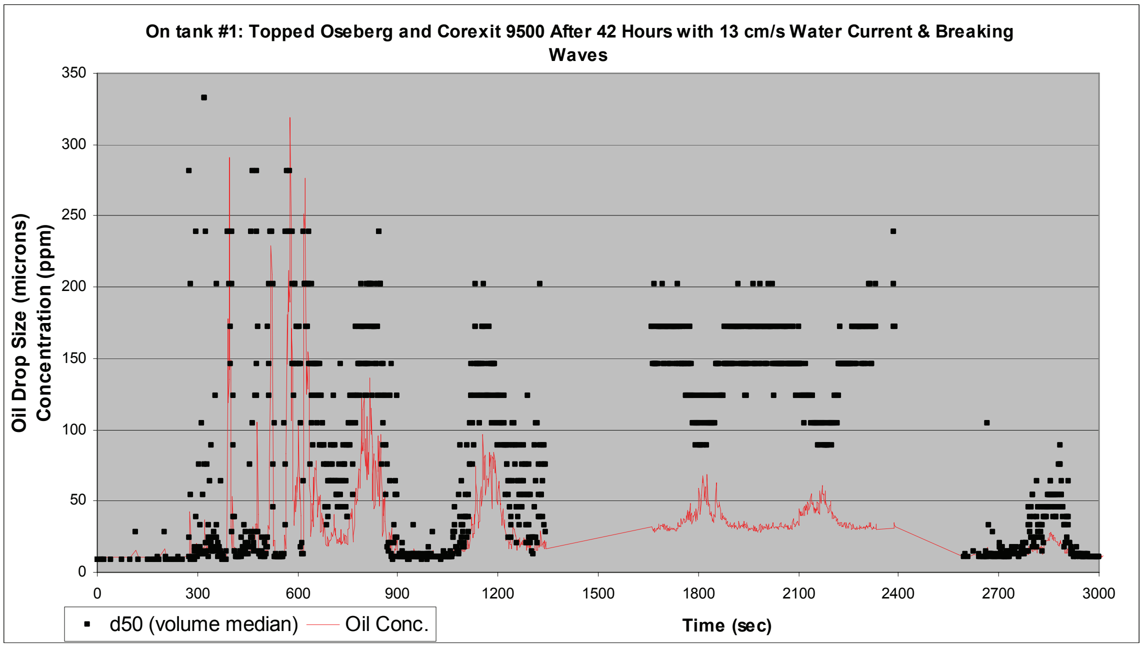

*Figure 7. In-water oil concentrations and drop size volume median diameters: On tank test #1*

**On tank Test # 2**

The dispersant-treated, 'topped' Oseberg crude oil was placed on the tank at 14:30 on Thursday, 21st June. The bubble barrier air-flow and distance to the boomed area was set to produce an average water surface current of 5 to 6 cm/s underneath the oil. At 09:30 on Monday, 25th of June the air-flow through the bubble barrier was turned off and the ring was lifted out. The oil had been on the water surface in the tank for 91 hours and exposed to a constant average surface water current of 5 to 6 cm/s.

The wave generator was then started. The wave paddle settings used in these tests were a 3-inch stroke and 33 to 34 strokes per minute for 30 minutes. Within a few minutes breaking waves were passing through the oil slick. The breaking waves caused all of the oil to disperse as a brown plume in the water. A video clip of the dispersion can be viewed by clicking on the following link: On tank test #2 Dispersion.

## 5.2 WSL Dispersant Effectiveness Results

Samples of the 'topped' Oseberg Blend crude oil were taken from the tank (both "On tank" Tests #1 and #2), the trays ("Weathering control") and the water-filled drum ("No current") at intervals and subjected to WSL testing by the method described in Appendix 1. The results are contained in Table 2.

| Hours | WSL dispersant effectiveness results (%) | | | |
|---|---|---|---|---|
| | On-tank 13 cm/sec | On-tank 6 cm/sec | No current | Weathering control |
| 0 | 47.1 | 37.2 | 45.0 | 50.0 |
| 18 | 18.5 | | | |
| 27 | 20.6 | | | |
| 42 | 11.3 | | | |
| 48 | | 5.1 | 78.7 | 74.6 |
| 91 | | 5.7 | 14.5 | 65.4 |

*Table 2 WSL dispersant effectiveness results*

These results are also illustrated in Figure 8. Several trends are evident.

- Initial increase in effectiveness with time for "Weathering control" and "No current" samples

  The dispersant effectiveness, as measured in the WSL method, increased from 40 or 50% to approximately 70% during the first 48 hours. The dispersant effectiveness of the "Weathering control" samples was maintained at this level, but that of the "No current" samples sharply decreased with prolonged exposure.

- Gradual decrease in effectiveness for "On tank" samples

  The dispersant effectiveness, as measured in the WSL method, gradually decreased with time on the water surface for samples from both of the "On tank" tests.

The reason for the apparent increase in WSL dispersant effectiveness with time during the first 48 hours for the "Weathering control" and "No current" samples is the increase in oil density. The WSL test method is very sensitive to the oil density; higher density oils cause higher effectiveness results than oils with lower density.

This effect is best illustrated by further 'weathering' of the 0 hours sample for "On tank" test #2. (Table 3). As collected and tested during the work at Ohmsett, the WSL effectiveness result was determined to be 37.0%. The same sample was subjected to further evaporation to raise the oil density from 0.8830 gm/ml to 0.9000 gm/ml. The dispersant effectiveness on the sample was then determined to be 62.1%.

| **"On tank" test #2.** | **Oil density (gm/ml)** | **WSL dispersant effectiveness (%)** |
|---|---|---|
| Zero hours on water | 0.8830 | 37.0 |
| After further evaporation | 0.9000 | 62.1 |

*Table 3. Effect of further 'weathering' (i.e. evaporation) on "On Tank" Test # 2 initial sample*

The samples that were not exposed to any water surface, and thus suffered no surfactant loss, were the "Weathering control" samples (the red squares and line in Figure 8). These samples exhibited an initial increase in WSL effectiveness as the oil density increased due to evaporation of the more volatile components. The WSL effectiveness rose from 50% to 75%. This higher level of WSL effectiveness was broadly maintained with increased time.

The samples that were exposed to a static water surface, and had very slow surfactant loss, were the "No current" samples (the blue squares and line in Figure 8). These samples also exhibited an initial increase in WSL effectiveness as the oil density increased due to evaporation of the more volatile components, but after 48 hours there was a very significant drop in WSL effectiveness, from nearly 80% to 15%. This appears to have been due to the slow loss of surfactants from the dispersant-treated Oseberg Blend crude oil into the tank water in the drum.

Samples from the two "On tank" tests exhibited no initial increase in WSL effectiveness. In both cases, the WSL effectiveness declined with time. The WSL effectiveness dropped from approximately 40% to approximately 10% in 48 hours. No significant differences in the rate of decline of WSL effectiveness with time are evident from the water current speeds of 13 cm/s in test #1 and 5 to 6 cm/s in test #2.

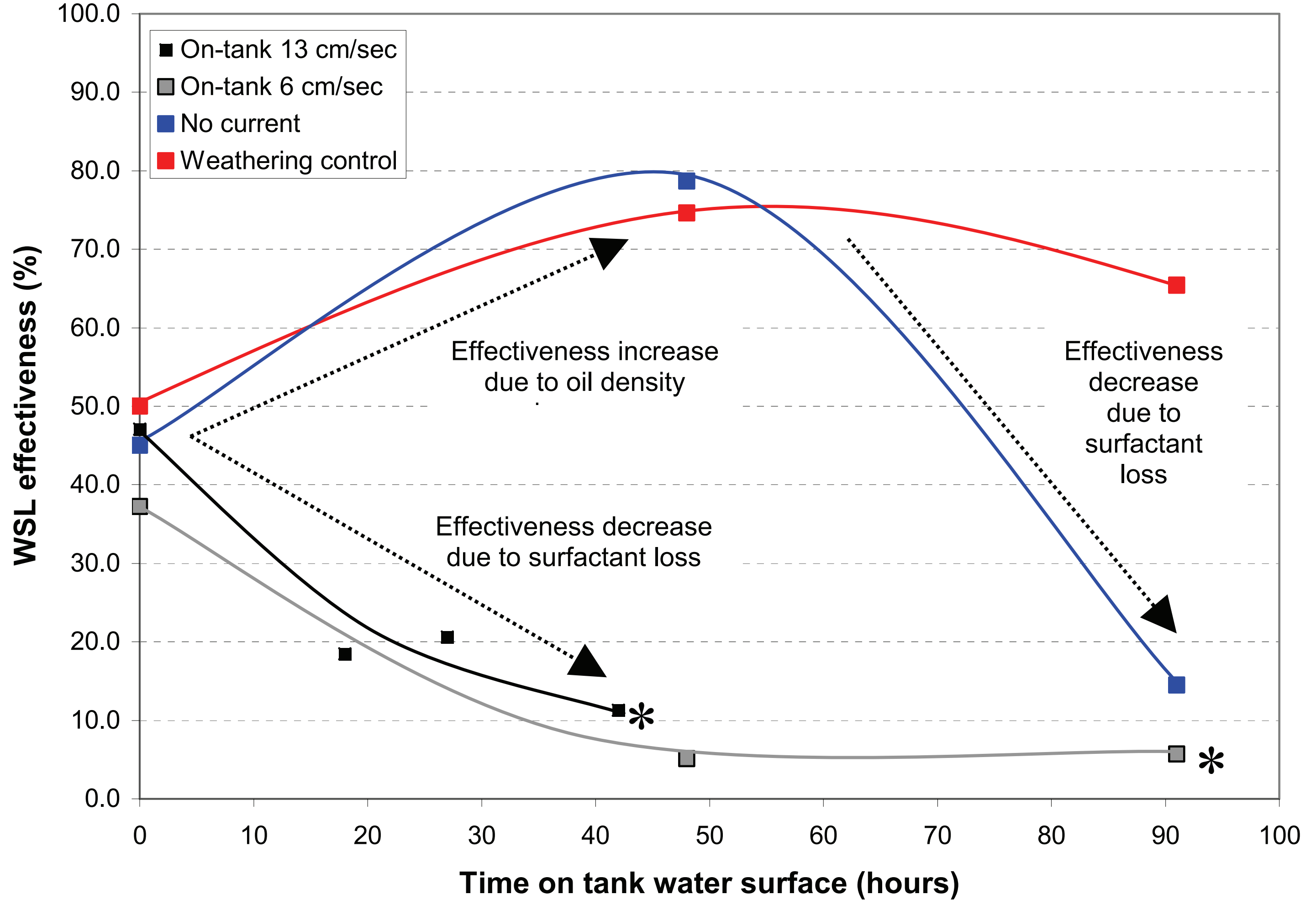

*Figure 8.* *Effect of time on WSL dispersant effectiveness result*

## 6. Discussion of Results

The intention to use a 'pre-weathered' crude oil to avoid changes in oil properties during the course of the experiment was not fully fulfilled. Although the Oseberg Blend crude oil was subject to heating and air-sparging in a barrel prior to the tank tests and the crude oil lost a nominal 27% by weight (32% weight on the 'fresh' Oseberg Blend crude oil), further evaporation of more volatile components caused a weight loss of approximately 40% weight after 48 hours. The oil density and oil viscosity therefore increased with time on the water surface of the tank.

The visual observations made when breaking waves were passed through the 'topped' Oseberg Blend crude oil in the Ohmsett tank were clear:

- The application of breaking waves to the oil after exposure to an average water current speed of 13 cm/s for 43 hours caused only very coarse dispersion.
- 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 caused fine dispersion of the oil as a brown plume of small oil droplets in the water.

There was clearly a difference in the dispersion of the oil caused by the different water current speeds. The higher current speed for the shorter duration caused the oil to be poorly dispersed, while after the lower current speed for a more prolonged period allowed to oil to be well dispersed by the breaking waves. This is consistent with the higher current speed causing more extensive removal of the surfactants from the dispersant-treated oil. The more extensive oil 'weathering' caused by the longer period on the water surface did not prevent dispersion from happening and therefore was not the cause of the failure of the oil to disperse after 43 hours.

The results from the WSL effectiveness testing are internally consistent. The trends observed were:

- A marked initial increase for the first 48 hours in WSL effectiveness with both the "Weathering control" samples and the "No current" samples, apparently due to the increase in oil density caused by evaporative loss of the more volatile oil components.
- A subsequent decrease in WSL effectiveness with the "No current" samples, apparently due to slow surfactant ‘leaching’ into the static water from the dispersant-treated oil.
- A gradual decrease of WSL effectiveness with time for both the "On tank" samples with no initial increase, apparently due to relatively rapid surfactant depletion from the dispersant-treated oil. No significant differences in WSL effectiveness were observed between the samples exposed to the two different water current speeds.

The information from these WSL effectiveness results was used to determine when the tests in the tank should be stopped and the breaking waves applied to the tests slick. When the WSL effectiveness had dropped to approximately 10% after 43 hours in Test #1 (13 cm/s current speed) it was decided that sufficient surfactant had probably been removed by the water current and that good dispersion was unlikely to occur. The visual observations and LISST measurements made at the termination of Test #1 appeared to confirm this interpretation of the WSL effectiveness result; the oil was only poorly dispersed.

However, the relevance of the WSL effectiveness results on the likely performance in the tank tests was not borne out by the conclusion of Test #2. For operational reasons, the WSL tests could not be conducted until after the conclusion of the tank test. The oil was left on the tank test for the longest possible time (over a weekend) and dispersed on the Monday morning.

The dispersant-treated oil had been on the water surface for 91 hours being exposed to a 5 to 6 cm/s water current. Breaking waves caused a fine dispersion of the oil with a light-brown plume being visible in the water, despite the subsequent determination of the WSL effectiveness as being only 5.7%. The relevant WSL effectiveness results are compared with the visual observations of dispersant effectiveness in Table 4.

| Sample | WSL effectiveness (%) | Link to Video of Dispersion | Visual observation |
|---|---|---|---|
| "On tank" test #1 after 42 hours | 11.3 | Video 1 | Very coarse dispersion with individual small black specks easily visible from the viewing distance of about 3 meters. |
| "On tank" test #2 after 91 hours | 5.7 | Video 2 | Fine dispersion of the oil as a brown plume of small oil droplets in the water. |

*Table 4. Comparison of WSL effectiveness results and visual observations of the effect of breaking waves in the tank*

The WSL effectiveness results gave a clear indication of the surfactant depletion process that was occurring from the dispersant-treated oil slick exposed to the water current in the tank. However, the relationship between the WSL effectiveness results and the effects of breaking waves on the dispersant-treated oil is clearly not direct; a low WSL effectiveness result does not indicate that no, or poor, dispersion will occur.

## 7. Conclusions

1. The previous work carried out at Ohmsett (S L Ross, 2006a) found that dispersant-treated oil was almost totally dispersed when breaking waves were applied after the oil had been on absolutely still water for periods of up to 6 days. There appeared to be no substantial removal of surfactants from the dispersant in the oils tested.

   The visual observations of the dispersion of the dispersant-treated 'topped' Oseberg Blend crude oil caused by breaking waves being applied in the tank after a period of exposure to water currents underneath a contained slick showed that:

- The application of breaking waves to the oil after exposure to an average water current speed of 13 cm/s for 43 hours caused only very coarse dispersion.

- 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 caused fine dispersion of the oil as a brown plume of small oil droplets in the water.

The higher water current speed (13 cm/s) for 43 hours appeared to cause substantial removal of surfactants from the dispersant-treated oil, but exposure to the lower water current speed (5 to 6 cm/s) for the longer period of 91 hours caused far less surfactant removal. These water current speeds are equivalent to an oil slick drifting at 3% of wind speed in a "gentle breeze" (Beaufort Force 3, mean wind speed of 16.7 km/hr) and a "light breeze" (Beaufort Force 2, mean wind speed of 7.5 to 9.3 km/hr) with no cresting or breaking waves.

2. The visual observations of the dispersion of dispersant-treated oil in the Ohmsett tank made in these experiments are consistent with the earlier work. The time taken to remove surfactants from dispersant-treated oil is proportional to the water current speed flowing under the oil (Table 5).

| **Description** | **Beaufort Force** | **Mean wind speed (knots)** | **Mean wind speed (km/hr)** | **Water current (cm/s)** | **Time taken to remove surfactants and thus cause poor dispersion** |
|---|---|---|---|---|---|
| Calm | 0 | 0 | 0 | 0 | More than 6 days |
| Light air | 1 | 2 | 3.7 | 2.4 | |
| Light breeze | 2 | 5 | 9.3 | 7.2 | More than 91 hours |
| Gentle breeze | 3 | 9 | 16.7 | 12.9 | Less than 43 hours |

*Table 5. Relationship between wind speed, water current speed and dispersion*

3. The WSL dispersant effectiveness results gave a clear indication of the surfactant depletion process that was occurring from the dispersant-treated oil slick exposed to the water current in the tank. However, the relationship between the WSL effectiveness results and the effects of breaking waves on the dispersant-treated oil is clearly not direct; a low WSL effectiveness result does not indicate that no, or poor, dispersion will occur.

## 8. Recommendations

The findings of this study; that exposure to water currents beneath a dispersant-treated oil slick can cause poor subsequent dispersion by breaking waves (and that this effect is proportional to current speed), are strictly applicable to only the oil tested (‘topped’ Oseberg crude oil), the oil layer thickness (5 mm) and the dispersant (Corexit 9500) and treatment rate (DOR of 1:20) used in the experiments. The results from this study have resolved some of the ambiguities from the previous tests and confirmed that the water current speed beneath a dispersant-treated oil slick is an important mechanism that determines whether or not dispersant use will be effective.

Further work could be undertaken to investigate the effects of variables such as:

**Oil type and oil layer thickness**

The test oil used in this work, the ‘topped’ Oseberg Blend crude oil, was selected to be the same as that used in a parallel PERF study. This oil is not necessarily typical of oils that might be spilled in US waters. It is likely that the surfactant depletion process depends on oil layer thickness and this is related to the physical properties of the oil. The relatively high incidence of spills of Heavy Fuel Oils of various grades, plus the potential difficulties associated with dispersant treatment of such oils, may make these oils suitable candidates for further work.

**Correlation between laboratory test DE results and field / Ohmsett results**

Further experimentation needs be conducted to improve the understanding of laboratory-scale DE test results with respect to likely DE results achieved at full scale. Existing laboratory tests such as the WSL, Exdet and Baffled Flask Test need to be evaluated in conjunction with Ohmsett test results to identify laboratory scale tests that are scalable to large tank test and field results.

# 9. References

SL Ross Environmental Research Limited, A. Lewis and MAR Incorporated. 2006a. Chemical Dispersibility in Clams 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.

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# Appendix A. Warren Spring Laboratory Dispersant Effectiveness Test Method

## INTRODUCTION

The method for the determination of the Efficiency Index of oil spill dispersants is defined in the report LR 448 (OP). This revision expands on that method and incorporates the analytical procedures currently in use.

## DEFINITION

The Efficiency Index of an oil spill dispersant is defined as the percentage, by weight of the test oil which has been transferred, as small droplets into the water phase under the conditions of the test, assuming complete and even distribution at the time of sampling.

## SUMMARY OF THE METHOD

The oil spill dispersant is added, dropwise, to a measured volume, (by weight) of the test oil on the surface of seawater at 10°C in a conical separating funnel. The separating funnel is rotated about its horizontal axis, at right angles to its longitudinal axis, for a period of 2 minutes at 33 ±1 rpm. After rotation has ceased, the stopper is removed and after 1 minute standing time, 50ml of oily water are run off through the bottom tap. The quantity of oil present in the sample is then determined spectrophotometrically after extraction into dichloromethane.

## APPARATUS

### SEPARATING FUNNELS

(1) A conical separating funnel of nominal capacity 250ml, (Fig 1). After use the funnel should be rinsed thoroughly with dichloromethane to remove any oil remaining inside, then washed in a laboratory glasswasher. The washing programme should include a thorough rinse with distilled water to ensure that all traces of detergent are removed. The funnel should then be allowed to drain and cool before being placed in the temperature controlled cabinet ready for use.

(2) A separating funnel to BS 2021 with a nominal capacity of 100ml.

### MOTOR DRIVEN RACK

A motor driven rack, into which can be fitted and clamped the 250ml separating funnel. The rack should rotate about a horizontal axis approximately 15-20 mm below the level of the seawater in the separating funnel.

### SYRINGES

(1) A glass syringe, fitted with a needle, capable of accurately dispensing 0.2ml of dispersant in drops of 5 to 10 microlitres.
(2) A glass syringe capable of accurately dispensing 5.0ml of the test oil.

(3) A glass syringe, fitted with a needle, capable of accurately dispensing 2.0ml of Type 1 dispersant, and 2.0ml of Type 2 dispersant in drops of 5 to 10 microlitres

**SPECTROPHOTOMETER**
A spectrophotometer capable of measuring absorbance at 580nm, and equipped with glass cells of 10mm path length.

Stopclock

Measuring cylinders-, 250ml and 50ml

## REAGENTS

**SEAWATER**
Seawater taken from the sea and having a total solids content of 3.3 - 3.5% Synthetic seawater is also permissible.

Sodium sulphate, anhydrous

Dichloromethane

## METHOD

**CALIBRATION**
Transfer 0.1, 0.2, 0.3, 0.4 and 0.5g of the test oil, accurately weighed, into separate 100ml volumetric flasks. Dissolve the oil in dichloromethane and make each flask up to volume.

Measure the absorbance of each solution at 580nm in glass cells of 10mm path length, using the dichloromethane as a reference solution.

A graph may be plotted of absorbance against concentration of oil in the dichloromethane solution. Alternatively the line of best fit of the calibration points may be calculated to give linear regression coefficients.

## PROCEDURE

The test procedure is carried out in a temperature controlled cabinet maintained at 10°C. All reagents, test materials and apparatus should be kept in the cabinet for 24 hours before conducting the test.

Place the unstoppered separating funnel in the motor driven rack. In a measuring cylinder, measure 250ml of seawater and transfer to the separating funnel.

Using the syringe, transfer 5ml, by weight, of the test oil to the surface of the seawater and start the stopclock. Weigh the syringe before and after use to calculate the weight (± 0.001g) of the 5ml of the oil.
Using the appropriate syringe, take the required volume of the dispersant to be tested, (0.2ml of type 3 dispersant). 1 minute after completing the addition of the test oil to the seawater, transfer the dispersant to the oil. The addition of the dispersant to the oil should be done dropwise, starting from the centre of the oil lens and working radially

outwards so that the dispersant is distributed as evenly as possible. Place the stopper in the separating funnel and clip on the retaining cap of the motor driven rack. Close the door of the temperature controlled cabinet.

When the time of the stopclock shows 2.5 minutes from the addition of the oil to the seawater, start the rotation of the separating funnel, and continue for 2 minutes.

After 2 minutes switch off the motor driven rack and allow the separating funnel to stand, undisturbed for exactly 1 minute. Remove the stopper, and run off from the bottom tap, 50ml of oily water into a measuring cylinder. The taking of this sample should take no longer than 10 seconds.

The remainder of this determination may be done outside the temperature controlled cabinet.

Transfer the 50ml sample from the measuring cylinder to a 100ml separating funnel. Wash the measuring cylinder twice with 10ml of chloroform and add to the 100ml separating funnel. Stopper the funnel and shake for 1 minute. Allow the phases to separate completely and run off the chloroform layer into a 100ml volumetric flask through a 75mm glass filter funnel fitted with a 9.0cm Whatman No 1 filter paper and into which has been placed no more than 1.5g anhydrous sodium sulphate. Repeat the chloroform extraction twice more, using 20ml chloroform on each occasion. Thoroughly wash the filter paper and sodium sulphate, with chloroform and then dilute to the mark on the volumetric flask. Stopper the flask and shake well.

Measure the absorbance of the sample solution using glass cells of 10mm path length and a spectrophotometer set to a wavelength of 580nm. The calibration standards prepared from the test oil should be measured at the same time as the sample solution.

Using either the graph or the calculated regression coefficients convert the absorbance measurement from the sample solution into concentration figures expressed as 'grams of oil per 100ml of chloroform'. This is equivalent to the weight of oil contained in the 50ml sample of oily water taken from the 250ml separating funnel.

## CALCULATION

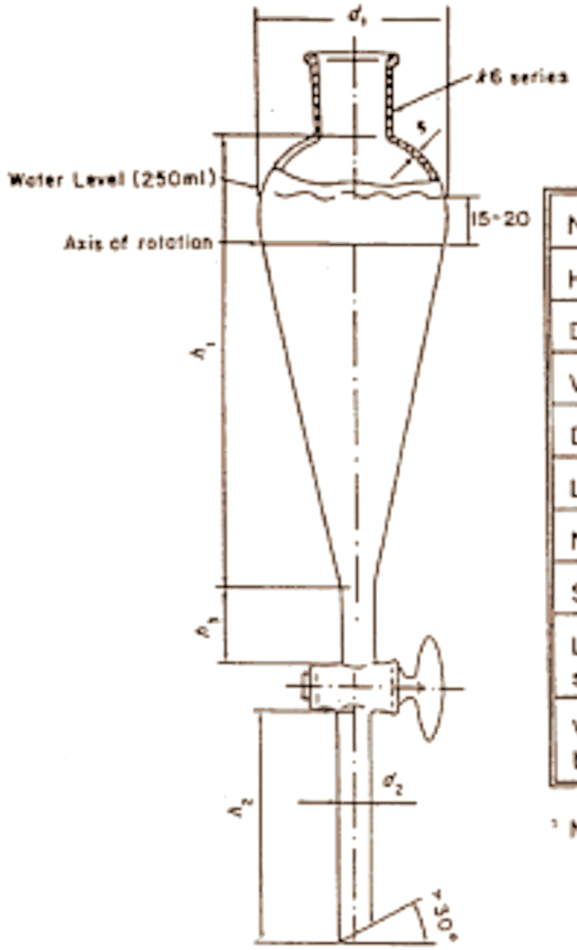
Calculate the efficiency index as follows:

$$\%\ \text{Efficiency} = \frac{\text{weight of oil in 50ml sample of oily water} \times 500}{\text{weight of test oil added to the 250ml separating funnel}}$$

## REPORT

The Efficiency Index is the average of three separate determinations. The calculated average is reported to one decimal place for each of the two reference fuel oils.

## ANNEX 1, FIGURE 1



| | |
|---|---|
| Nominal capacity | 250ml |
| Height of body, h1 | 185mm |
| Diameter of body, d1 max | 83mm |
| Wall thickness of body, s min | 1.2mm |
| Diameter of stem[1], d2 ± 0.5 | 12.5mm |
| Length of stem, h2 ± 10 | 70mm |
| Nominal bore of stopcock min | 3mm |
| Size of stopper (see ISO 383) | k6 series |
| Length of tube between bulb and stopcock, h3 max | 20mm |
| Wall thickness of tube between bulb and stopcock min | 1.5mm |

[1] Medium walled tubing (see ISO 4803)

STANDARD CONICAL SEPARATING FUNNEL 250ml CAPACITY

NB. The distance between the seawater level when filled with 250ml seawater at 10°C and the axis of rotation of the flask should be between 15mm and 20mm.