

# DETERMINATION OF THE LIMITING OIL VISCOSITY FOR CHEMICAL DISPERSION AT SEA

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## ABSTRACT

Many previous studies using laboratory test methods have shown that the ability to disperse spilled oils depends on several factors including: spilled oil properties (and how these change with oil weathering), the mixing energy, and the dispersant-to-oil ratio (DOR). There appears to be a 'limiting oil viscosity' value that, when exceeded, causes a sharp reduction in the effectiveness of a dispersant. The results obtained in laboratory tests are relative and not absolute, and it has therefore proved very difficult to correlate dispersant effectiveness results from these laboratory tests with dispersant performance at sea. A series of small-scale dispersant tests were conducted at sea in the English Channel in June 2003. Several small test slicks of residual fuel oils of different viscosity grades were laid on the sea and immediately sprayed with different dispersants at different DORs. Observers used a simple ranking system to visually assess the degree of dispersion that occurred when a cresting wave passed through an area of the dispersant-treated oil. Collation of the results showed that there were obvious and consistent differences in the degree of effectiveness observed with different combinations of oil viscosity, dispersant and treatment rate.

## BACKGROUND

The initial stage of dispersion, the creation of small oil droplets, of low viscosity oils can be the result of breaking wave action without the addition of oil spill dispersants; this is often called natural dispersion. The addition of chemical dispersants to a slick of spilled oil can cause a very sharp but temporary drop in the oil / water interfacial tension (IFT) and this greatly reduces the degree of agitation required to cause a much higher proportion of the spilled oil being dispersed by the prevailing wave action, than would be the case if dispersant was not added. The successful use of a dispersant will cause the spilled oil to be rapidly transferred from the surface of the sea into the water column as very small oil droplets, but this will not happen evenly across the oil slick area; dispersion will be most rapid in the localised areas where the dispersant-treated oil is exposed to the more intense shearing caused by breaking, or cresting, wave action.

## MEASURING THE PERFORMANCE OF DISPERSANTS AT SEA

There are two apparently obvious ways of quantitatively determining the effectiveness of dispersant treatment on test oil slicks at sea:

- (i) Measure the total amount of oil that remains on the sea surface, and how this reduces with time.
- (ii) Measure the amount of oil dispersed into the water column, and how this increases with time.

Unfortunately, it is impossible to accurately conduct these quantifications with currently available techniques, or attempting to do so will unduly influence the dispersion process. There are no current methods using visual observation or remote-sensing techniques that can accurately quantify the amount of oil on the sea surface by determining the oil layer thickness and hence calculating the oil volume in a measured oil slick area. Ultraviolet Fluorometry (UVF) can be used to measure the dispersed oil concentration in water (Hurford et al., 1989). This is an extremely useful technique for assessing whether dispersion is happening (Barnea and Laferrier, 1999 and Henry, 1999), but cannot be conducted with sufficient spatial and temporal resolution to produce an accurate quantification of the amount of dispersed oil at any time. Attempts to relate the results of continuous release experiments with results obtained in the WSL (Warren Spring Laboratory) laboratory test method (Lunel, 1995) have so far proved unsuccessful. It is therefore not currently possible to measure the effectiveness of dispersants when used at sea in the same way that is easily achievable in laboratory tests.

### Visual estimation of dispersant performance

The visual effects of dispersants on spilled oil can be confusing; not all visible effects of dispersant addition to spilled oil are indicators of subsequent dispersion. The significant visible difference appears to be in the initial phase of the dispersion process; the action of a breaking or cresting wave passing through the dispersant-treated oil either does, or does not, create a wide distribution of oil droplet sizes. Without the creation of small oil droplets, the subsequent stage of dispersion involving dilution of the dispersed oil will not occur.

Visual estimation of the effectiveness of dispersants was used to approve dispersants in the UK before the WSL (Warren Spring Laboratory) test method was adopted in 1979 as the UK dispersant approval test procedure. The 'harbour test' method (pp 102–103 in Cormack, 1983) used a simple rig to spray a 'carpet' of test oil onto the sea that was sprayed with the dispersant under test at several different treatment rates. An agitation board—an arrangement of wooden bars—was towed behind the vessel to add mixing energy to disperse the oil. A team of observers followed in another vessel and visually assessed the effectiveness of the dispersant. Results from repeated tests using a variety of observers confirmed that the apparently subjective test produced reliable and repeatable results, even with observers who had little previous experience. Testing with this method was discontinued in the mid-1980s when the correspondence between the results and those from WSL method testing was felt to be sufficient. This visual observation approach was used to construct the test matrix for the UK 2003 sea trials.

### THE 2003 UK SEA TRIALS

The primary objective of the 2003 UK sea trials was to define the limiting oil viscosity for the use of oil spill dispersants (Lewis, 2004). The approach used was to construct a "3-dimensional" matrix of oil viscosity, dispersant brand and dispersant treatment rate that would reveal the 'break point' between dispersants not working at all (or to any significant degree) and dispersants working to some appreciable degree. This is not a smooth, graduated quantification in dispersant performance that might be easily achieved by a laboratory test method, but since this is currently impossible to achieve at sea, the approach would provide an operationally useful indication of dispersant performance. Previous sea trials had used a limited number (from 2 to 5) of slicks of relatively large amounts (10 to 50 tonnes) of test oils (for example Lichtenthaler and Daling, 1985 and Lewis et al., 1998). In contrast, the UK 2003 sea trials had the potential to use combinations of four oils, three dispersants and three dispersant treatment rates to produce 36 test oil slicks. Very small oil slicks were used with a volume of only 10 or 20 litres. This approach substantially reduced the environmental risk, complexity and cost of the project.

The small-scale sea trials were conducted at a location approximately 10 nautical miles to the south of the Isle of Wight at the end of June 2003. The sea trial was intended to be held over 3 days; 23rd to 25th June, 2003. However, the sea was too rough for testing on the 23rd, too calm for testing on the 24th and while testing began on the 25th it was abandoned for safety reasons by midday. Testing took place on Thursday 26th and Friday 27th June with wind speeds varying between 8 and 14 knots.

### Test oils used

IFOs (Intermediate Fuel Oils) were used in this work for several reasons; unlike crude oils, the properties of IFOs do not rapidly change when spilled at sea, IFOs are readily available and IFO-180 and IFO-380 are the typical HFOs (Heavy Fuel Oils) that might be spilled by large ships because they are the most-used bunker fuel

oil grades. Due to operational reasons, only two grades of IFO oils were used in the majority of the tests and the properties of these two test oils used in the sea trials are contained in Table 1.

### Dispersants used

Three oil spill dispersants, all of which have been approved by Defra for use in UK waters in recent years and are in the MCA dispersant stockpile, were used in this work. In order not to provide any commercial advantage, or disadvantage, to the dispersant manufacturers the brand identity of these dispersants in this paper has been concealed by using Dispersants A, B and C in place of the brand names.

### Dispersant treatment rates

The three dispersant treatment rates used in this work were nominal DORs (Dispersant to Oil Ratios) of 1:25, 1:50 and 1:100. A DOR of 1:25 is the typically recommended dispersant treatment rate, but some laboratory studies had indicated that dispersants could still be effective when used at the lower treatment rates. It should be noted that these are 'nominal' treatment rates.

### Sea trial procedure

The test oils were pumped from the deck of *Wilcarry* and laid down onto the sea as a 20-metre long strip or 'carpet' through a Manta Ray' skimmer head as the barge sailed directly into the wind at approximately 2 knots. The test oils produced an irregular width 'carpet' on the sea surface with the oil width ranging from 0.5 m or even less wide to a maximum of 1 m wide when it was sprayed with dispersant. Dispersant was sprayed at the required rate onto the oil layer from the modified 'Boatspray' system shortly after the oil was deposited on the sea (Photograph 1). Three single nozzles, nominally 5.0, 2.5 and 1.25 L/min, were used and changed as required. The average actual DOR achieved depended on how wide the oil 'carpet' was when sprayed and is shown in Table 2.



PHOTOGRAPH 1. DISPERSANT SPRAYING OF TEST SLICK

Table 1. Physical properties of test oils

	Density @ 20°C (gm/ml)	Viscosity (mPa.s or cP centiPoise)			
		15°C		50°C	
		@10s <sup>-1</sup>	100s <sup>-1</sup>	100s <sup>-1</sup>	@10s <sup>-1</sup>
IFO-180	0.970	2,075	1925	134	146
IFO-380	0.983	7,100	n/a	314	324

Table 2. Effect of oil carpet width on actual treatment rate

Nominal DOR	1.0 metre wide oil	0.7 metre wide oil	0.5 metre wide oil	0.3 metre wide oil
1:25	1:20	1:29	1:41	1:58
1:50	1:55	1:79	1:111	1:158
1:100	1:90	1:128	1:180	1:257

### Visual observations made during dispersant use

It is not possible to quantify the amount of oil that has been dispersed at any particular time by visual observation. However, it is possible to use visual observation to assess whether or not the dispersion process is, or is not, proceeding. The most visible signs of dispersion are most evident in the localised, cresting wave locations. When a cresting wave passes through a dispersant-treated slick of an oil that will disperse, the visual appearance is of a plume or 'cloud' of small oil droplets is formed as the crest passes through, and this produces brown or black colours in the cresting wave. The plume of dispersing oil droplets can often be seen trailing in the wake of the cresting wave, below the surface in the upper layers of the water column. The dispersed oil plume may or may not be easy to see depending on the observation conditions. Polarized sunglasses proved to be a very useful aid to observation. In view of the possibilities of confusion caused by visible effects that are not indicators of dispersion, a panel of experts composed of individuals who have extensive experience of dispersant use at previous sea-trials and at real oil spill incidents was used to conduct this important element of the sea-trial. This expert team included representatives from CEFAS (The Centre for Environment, Fisheries and Aquaculture Science), CEDRE (Centre de Documentation de Recherche et d'Experimentations sur les pollutions accidentelles des eaux), ITOPF (International Tanker Owners pollution Federation Ltd., the MCA (Maritime and Coastguard Agency), and OSRL (Oil Spill Response Limited). The expert observers were based on the MCA *Osprey* (Photograph 2) and filled in their observations on a standardised reporting form as shown as Table 3. It should be noted that the classification categories are not linear and that there is no zero classification. The visual observations only apply to the initial stage of dispersion; the almost immediate effects of a cresting wave passing part of the test oil slick or those made within a few minutes after this. The observations only apply to that small portion of the test oil slick that was observed when a cresting wave passed through it. No attempt was made to study the eventual fate of the entire slick.



PHOTOGRAPH 3. MCA OSPREY WITH EXPERT OBSERVER TEAM ONBOARD

### Tests conducted

The tests conducted are shown in Table 4. The test runs were coded and randomised so that the precise combination of oil, dispersant and treatment rate was unknown to the experts and other observers. The expert observers did not discuss their individual observations and the completed forms were collected after each test.

### RESULTS

The results obtained, expressed as average visual rankings for the different test oil / dispersant / dispersant treatment rate combinations, plus the range of the individual observations made, are shown in Table 5. These results show that the observers independently, and without discussion, recorded very similar observations; all observations were within one category or within two consecutive categories. The nominal dispersant treatment rates are given alongside the actual applied dispersant treatment rates which were calculated on the basis of the width of the oil 'carpet' and the width of the dispersant spray photographically recorded at the time of the experiment.

### Effect of dispersant brand, wind speed and dispersant treatment rate

The IFO-180 fuel oil used in these tests appeared to be totally and rapidly dispersed by Dispersant C used at a nominal DOR of 1:25 at 12 knots wind speed. The other two dispersants appeared to be somewhat less effective, but they still appeared to cause moderate dispersion when used at a nominal DOR of 1:25 (actual DOR an average of 1:30, varying between 1:40 and 1:20). The effects of the higher dispersant treatment rate and the higher wind speed in producing higher dispersant performance were more noticeable for the higher viscosity oil (IFO-380, with a viscosity of 7,000–8,000 cP at the sea temperature of 15°C) than for the lower viscosity oil (IFO-180, with a viscosity of approximately 2,000 cP at sea temperature of 15°C), although the general level of dispersant performance with IFO-380 was low. At a lower wind speed of 7–8 knots, Dispersant C at a DOR of 1:25 still caused moderately rapid dispersion of IFO-180 and at a DOR of 1:100 (average actual treatment rate of 1:130, varying between 1:180 and 1:90) caused an appreciably lower level of slow and partial dispersion similar to that achieved by Dispersant B and Dispersant A at a nominal DOR of 1:25. Dispersant B at a nominal DOR of 1:50 caused no significant dispersion of IFO-180.

### CONCLUSIONS

The 2003 UK sea-trials investigated the initial part of the dispersion of heavy fuel oils that is easily visible to a trained observer. This is the initial stage of dispersion when the dispersant-treated oil slick is broken up into oil droplets by breaking or cresting waves. This effect was observed to occur with some but not all test oil and dispersant combinations. This effect was taken as an indicator of subsequent dispersion of the oil on the basis that if it happened, then the subsequent stages of dispersion would occur, but that if it did not occur, then any further dispersion would probably not take place. It should be noted that the different grades of

Table 3. Visual observation ranking scheme used by expert observers

Rank	Standard Phrase	Description	2 mins	5 mins	10 mins
1	No obvious dispersion	Dispersant being washed off the black oil as white, watery solution leaving oil on surface. Quantity of oil on sea surface not altered by dispersant			
2	Slow or partial dispersion	Some surface activity (oil appearance altered). Spreading out of oil. 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			
3	Moderately rapid dispersion	Quantity of oil visibly less than before spraying. Oil in some areas being dispersed to leave only sheen on sea surface, but in other areas still some oil present.			
4	Very rapid and total dispersion	Oil rapidly disappearing from surface. Light brown plume of dispersed oil visible in water under the oil and drifting away from it			

IFO fuel oils used in the sea-trials were not taken as being typical or representative of all fuel oils of these IFO grades, since Heavy Fuels Oils (HFOs) vary very widely in properties such as Pour Point. It is perfectly possible for an IFO-180 or IFO-380 to have a Pour Point of +20°C (the grade maximum limit is +30°C) and therefore to be solid (effectively with infinite viscosity) at 15°C and yet still conform to the grade viscosity maxima of 180 cP and 380 cP at 50°C. This could occur with IFOs of any grade produced from waxy crude oils. However, the IFO-180 and IFO-380 fuel oils used in these sea trials were chosen to act as oil viscosity standards; they are representative of any oils that would have an oil viscosity of approximately 2,000 cP and 7,000–8,000 cP, respectively, at the prevailing sea temperature. Under the prevailing conditions of the sea trial (with a sea temperature of 15°C and wind speeds varying between 7 and 14 knots), it was found that the IFO-180 grade test oil could be rapidly and apparently totally dispersed by some dispersants at some treatment rates. It was much more difficult to disperse the IFO-380 grade fuel oil under the same conditions and only slow and partial dispersion was observed in some cases. There were visibly evident differences in the rate and degree of dispersion caused by:

#### Oil viscosity

The 2,000 cP at 15°C IFO-180 grade fuel oil appeared to be reasonably rapidly dispersed by two out of three dispersants, but the 7,000 cP at 15°C IFO-380 grade fuel oil could not be rapidly dispersed by any of the three dispersants.

#### Wind speed

The IFO-180 grade fuel oil appeared to be rapidly dispersed by a treatment with Dispersant C at a nominal DOR of 1:25 at a wind speed of 12 knots, but more slowly at a wind speed of 8 knots. There was similar, but lesser, effect with the IFO-380 grade fuel oil; it appeared to be dispersed to a greater degree at a wind speed of 14 knots than at 8 knots, but in both cases there was only an apparently slow and partial dispersion evident by visual observation.

#### DOR

Dispersants applied at a nominal DOR of 1:25 appeared more effective than when applied at a nominal DOR of 1:50 or 1:100.

Only Dispersant C exhibited some low level of dispersion of the IFO-180 grade fuel oil when used at a nominal DOR of 1:100 (applied average DOR of 1:130, varying between 1:180 and 1:90). The application of dispersants to the IFO-380 grade fuel oil resulted in actual dispersant rates that were approximately half of the intended nominal treatment rates because the oil floated in a thicker layer than anticipated. Nominal DORs of 1:25, 1:50 and 1:100 produced actually applied average DORs of 1:40, 1:110 and 1:180.

The results suggest that IFO-180 grade fuel oils with similar properties to that tested could be readily dispersed in summer sea temperatures around the UK provided that the prevailing wind speed is at least 5 to 8 knots. The marked effect of wind speed on the ability of dispersants to disperse these grades of fuel oils suggests that IFO-380 grade fuel oil may be dispersible at higher wind speeds than those under which it was tested. The precise effect is not known because the sea trials could not proceed with 20 knot winds for safety reasons. However, some dispersion of the IFO-380 grade fuel oil did appear to take place with both Dispersant C and Dispersant B when used at a nominal DOR of 1:25 (average actual DOR of 1:40) of at 13 knot and 14 knot wind speeds.

The physical state of spilled IFO-380 fuel oil on the sea surface will influence the potential effectiveness of dispersant use. The maximum permitted Pour Point for IFO-380 grade fuel oil is +30°C. Some IFO-380 fuel oils could therefore be solid at typical UK sea temperatures. Even if they are not solid, many IFO-380 fuel oils will float as lumps and patches of oil that are many centimetres thick. In some circumstances, dispersant spraying will be incapable of delivering sufficient dispersant to cause effective dispersion, or it will be washed off before it can penetrate into the oil.

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Table 4. Tests conducted in UK 2003 sea-trials

Wednesday 25th June 2003				
Test No.	Time	Oil	Dispersant	Nominal DOR
1	09:40	IFO-80	Dispersant A	1:25
2	10:20	IFO-80	Dispersant A	1:50
3	10:50	IFO-80	Dispersant C	1:50
Thursday 26th June 2003				
Test No.	Time	Oil	Dispersant	Nominal DOR
10	10:10	IFO-180	Dispersant C	1:25
11	10:25	IFO-180	Dispersant C	1:50
12	10:40	IFO-180	Dispersant C	1:100
14	11:00	IFO-180	Dispersant A	1:25
17	11:30	IFO-180	Dispersant B	1:25
15	11:50	IFO-180	Dispersant B	1:50
10A	12:15	IFO-180	Dispersant C	1:25
18	12:55	IFO-380	Dispersant B	1:25
50	13:30	IFO-380	Control (no dispersant)	
24	13:40	IFO-380	Dispersant C	1:25
24A	13:55	IFO-380	Dispersant C	1:25
18A	14:20	IFO-380	Dispersant B	1:25
19	14:40	IFO-380	Dispersant B	1:50
23	15:00	IFO-380	Dispersant A	1:25
25	15:20	IFO-380	Dispersant C	1:50
60	15:45	IFO-380	Control (no dispersant)	
Friday 27th June 2003				
Test No.	Time	Oil	Dispersant	Nominal DOR
10F	09:40	IFO-180	Dispersant C	1:25
14F	09:55	IFO-180	Dispersant A	1:25
17F	10:15	IFO-180	Dispersant B	1:25
18F	11:05	IFO-380	Dispersant B	1:25
23F	11:30	IFO-380	Dispersant A	1:25
24F	11:50	IFO-380	Dispersant C	1:25
18FA	12:10	IFO-380	Dispersant B	1:25

for the sea trials. Francois Xavier Merlin attended as an expert observer as an in-kind contribution from CEDRE. External observers included Joe Mullin from the U.S. MMS (Minerals Management Service) and Ken Trudel from S L Ross Environmental Research.

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Table 5. Results of tests conducted at UK 2003 sea-trials

IFO-180 Tests						
Test	Dispersant and nominal treatment rate used	Actual applied DOR (Min.) Average (Max.)	Average observation ranking (range of individual visual observations) at time after dispersant added in minutes			Wind speed (knots)
			2 minutes	5 minutes	10 minutes	
10	C at 1:25	(1:40) 1: 30 (1:20)	4 (4)	4 (4)	4 (4)	12
10A	C at 1:25	(1:40) 1: 30 (1:20)	3 (2-4)	3.2 (3-4)	3 (3-4)	7
10F	C at 1:25	(1:40) 1: 30 (1:20)	3 (3)	3 (3)	3 (3)	8
11	C at 1:50	(1:110) 1: 80 (1:55)	3.2 (2-3)	2.7 (2-3)	2.3 (2-3)	12
12	C at 1:100	(1:180) 1: 130 (1:90)	2.3 (2-3)	2.2 (2-3)	1.8 (1-2)	11
17	B at 1:25	(1:40) 1: 30 (1:20)	1.7 (1-2)	2 (2)	1.8 (1-2)	9
17F	B at 1:25	(1:40) 1: 30 (1:20)	2 (2)	2 (2)	2 (2)	8
15	B at 1:50	(1:110) 1: 80 (1:55)	1 (1)	1 (1)	1 (1)	8
14	A at 1:25	(1:40) 1: 30 (1:20)	1.5 (1-2)	1.8 (1-2)	1.4 (1-2)	10
14F	A at 1:25	(1:40) 1: 30 (1:20)	2.2 (2-3)	2.8 (2-3)	2.5 (2-3)	10
IFO-380 Tests						
24	C at 1:25	(1:60) 1:40 (1: 30)	1 (1)	1 (1)	1 (1)	8.5
24A	C at 1:25	(1:60) 1:40 (1: 30)	1.1 (1-2)	1.2 (1-2)	1.2 (1-2)	8
24F	C at 1:25	(1:60) 1:40 (1: 30)	3 (3)	2 (2)	2 (2)	14
25	C at 1:50	(1:160) 1:110 (1: 80)	1.7 (1-2)	1.7 (1-2)	1.7 (1-2)	8
18	B at 1:25	(1:60) 1:40 (1: 30)	2 (2)	2 (2)	2.3 (2-3)	7.5
18A	B at 1:25	(1:60) 1:40 (1: 30)	2 (2)	2 (2)	2 (2)	7.5
18F	B at 1:25	(1:60) 1:40 (1: 30)	2.5 (2-3)	2.2 (2-3)	2 (2)	12
18FA	B at 1:25	(1:60) 1:40 (1: 30)	2.7 (2-3)	1.2 (1-2)	1.2 (1-2)	13
19	B at 1:50	(1:160) 1:110 (1: 80)	1.4 (1-2)	1.6 (1-2)	1.4 (1-2)	8
23	A at 1:25	(1:60) 1:40 (1: 30)	1.6 (1-2)	1.6 (1-2)	1.5 (1-2)	9
23F	A at 1:25	(1:60) 1:40 (1: 30)	1.7 (1-2)	1.2 (1-2)	1.2 (1-2)	11

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