Study of the Feasibility of Chemical Dispersion of Viscous Oils and Water-in-Oil Emulsions

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Abstract

Investigations have been undertaken to review the possibilities of chemically dispersing high viscosity oils and water-in-oil emulsions with recently developed modern dispersants. This study was conducted in two steps, in the laboratory using standard dispersibility tests, the WSL (Warren Spring Laboratory) method and the IFP (Institut Français du Pétrole) dilution method, which are both used to assess the efficacy of dispersants, and at a larger scale, in the Polludrome. The laboratory methods produced high efficiency results for high viscosity oils; the WSL method produced of up to 50% efficiency for oils with viscosities of up to 10,000 to 20,000 cSt, depending on the dispersant used. However, for emulsified oils, the efficiency was much lower, <15% for similar viscosities. In the Polludrome, which simulates somewhat more realistic sea conditions, the dispersion efficiency measured with viscous oils was lower, which suggested the laboratory tests over-estimate dispersion. In tests in the Polludrome, it was necessary to adopt special treatment strategies such as double dispersant applications to get significant dispersion of emulsions. Such strategies are very difficult to reproduce realistically in the laboratory tests. Moreover, laboratory tests, especially the IFP test, seem not to be suitable for testing oils with viscosities over 15,000 cSt and unrealistic results have been observed. Laboratory tests, which were originally developed for dispersant approval purposes, are not very reliable methods for studying the dispersion of high viscosity oils. This can be overcome by using larger testing facilities, such as the Polludrome, in which the environmental conditions can be more realistically simulated. Tests with the Polludrome showed that the oil viscosity limits for dispersion, which had been defined in the eighties, can be upgraded to reflect the improvements made in the formulations of the modern dispersants. For dispersing emulsions, multiple application strategies can be carried out, possibly using demulsifiers and dispersants. However, care should be taken to choose the products as the study proved that, under some conditions, not all products are compatible.

1.0 Introduction

In recent years, dispersant formulations have been improved by the manufacturers. Some products have proved to be effective even on weathered and emulsified oils (Fiocco and Lessard, 1997). The previously considered oil viscosity limits for dispersants should be reconsidered in light of these developments. In

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addition, it seems possible to use demulsifiers to reduce the water content and the viscosity of emulsified oils, which can then be dispersed by a regular dispersant application. Many experimental studies have been carried out with these products to assess their efficiency and to optimise their use at sea. Laboratory tests, which were originally developed for dispersant approval purposes (to rank dispersants on their effectiveness with medium viscosity oils), have been performed to study the limits of dispersion, such as with very high viscosity oils. However, the ability of these laboratory test procedures to simulate the effectivenss of dispersants at sea has yet to be determined. Moreover, the study of the emulsified oils requires the preparation of water-in-oil emulsions in the laboratory. Emulsion preparation has proved to be difficult to reproduce and the emulsions produced were partially unstable even at low temperature for high water contents. In addition, they have revealed structures different from those of naturally formed emulsion.

In the present study, several laboratory dispersibility tests have been conducted on emulsified and non-emulsified oils. The results were then compared with those obtained at a larger scale in the Polludrome, a dedicated hydraulic canal which simulates open sea conditions and enables emulsion formation, their treatment and the optimisation of applications strategies to be studied under more realistic conditions.

2.0 Laboratory Test Methods

2.1 Dispersion of High Viscosity Oils by the WSL(or Labofina) Test Method

The first step was to identify the best dispersants from a selection using a high viscosity oil with the WSL test method (Martinelli, 1984).

These nine dispersants used were selected from those approved for use in France; Corexit 9500, Dasic Slickgone NS, Disperep 8, Dispolene 36 S, Finasol OSR 52, Gamlen OD 4000, Inipol IP 80, Inipol IP 90 and Oceania 1000. The testing was performed on mixtures of BAL 110 (an Arabian Light crude oil artificially weathered by topping at 110°C to remove the most volatile components) and Heavy Fuel Oil (HFO) in various proportions. This resulted in oil blends with viscosities varying from 2500 to 42000 cP at 10°C. The dispersibility tests were conducted at 10 C°. The results are shown in Figure 1.

The WSL efficiency was a function of oil viscosity for all the dispersants tested. The efficiency tended towards zero for an oil viscosity of approximately 40,000 cP, while a 50% WSL efficiency was obtained for oil viscosity ranging from 10,000 to 20,000 cP (Figure 2). The three most efficient dispersants were Inipol IP 90, Corexit 9500 and Dasic Slickgone NS. The differences in the performance of these products were slight, for example the efficiencies obtained with an oil viscosity of 18,000 cP ranged from 50% to 56%. These slight differences are not significant in this test method because of oil losses onto the wall of the flask. The standard deviation was below 5% only for viscosities between 8,000 and 17,000 cP. Consequently, this ranking could be slightly different in other test conditions and cannot be considered definitive.

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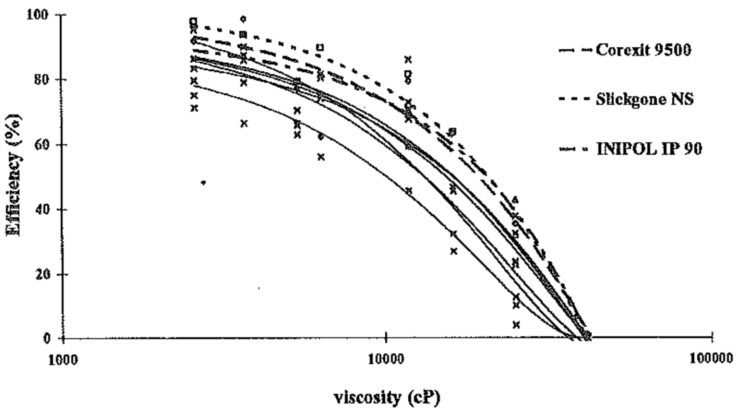

Figure 1. WSL Test Dispersibility Efficiency Versus Oil Viscosity

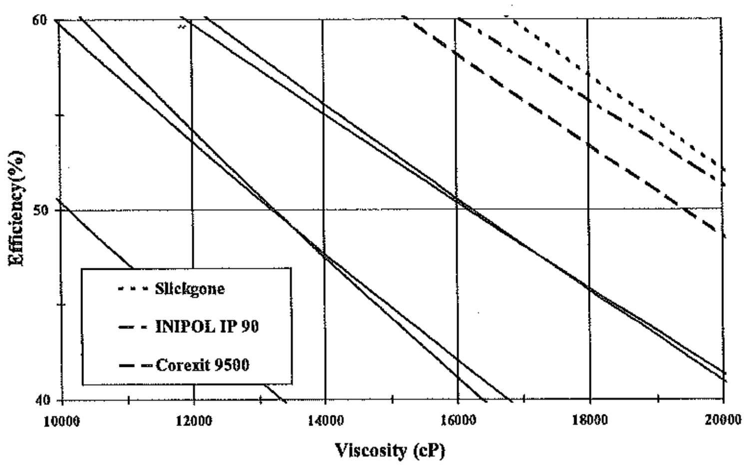

Figure 2. 50% Efficiency of Various Dispersants

2.2 Dispersion of High Viscosity Oils by the IFP Test Method

These tests were performed according to the protocol of the IFP test currently used for approving the dispersants in France (NFT 90 345, French standard). Four dispersants, (the three dispersants which gave the highest results on the WSL test plus an additional one, representative of the performance of the other dispersants) were tested with BAL 110 and Heavy Fuel Oil (HFO) blends with viscosities varying from 3,500 to 28,000 cP at 15°C. The results are shown in Figure 3 and illustrate a limitation of this test. For oil viscosity increasing from 5,000 to 15,000 cP, the efficiency gradually decreased as expected, but for viscosities above

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20,000 cP, an increase of efficiency was observed.

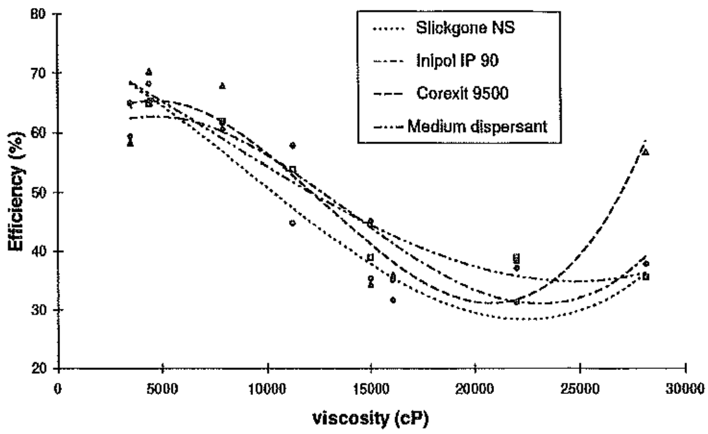

Figure 3. IFP Dispersibility Efficiency Versus Oil Viscosity

2.3 Dispersion of Water-in-Oil Emulsions by the WSL Test Method

2.3.1 Preparation of the Emulsions

Emulsions were prepared in the laboratory. The mixing energy was provided by a rotating stirrer and the sea water was added progressively to the oil as it was being stirred. The test oil was a mixture of HFO/BAL 110 (70/30). The water content of the emulsion was determined by the Dean & Stark method (NFT 60 113, French standard) and the viscosity measured using Haake VT 550 at 15°C with a 10 s^{-1} shear rate. The emulsions with a water content close to saturation proved to be unstable; a decrease in the viscosity was observed above 60% (Figure 4). Consequently, for all the following dispersibility tests, the maximum water content was set at 50%.

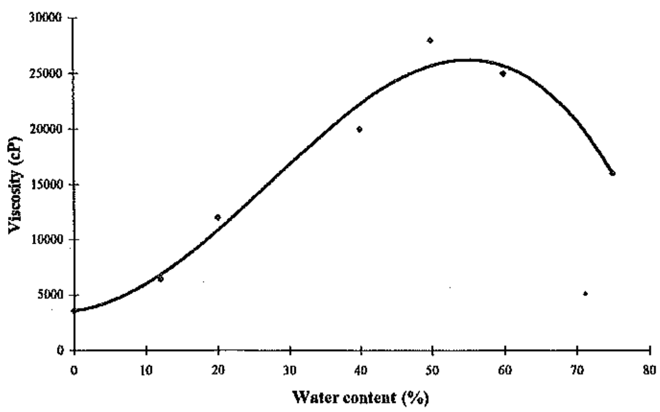

Figure 4. Viscosity Versus Water Content

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2.3.2 One Single Dispersant Application

These tests were performed to study the dispersibility of the emulsified oils with the selected dispersants using the standard WSL method. One single application of 0.2 ml dispersant to 5 ml of emulsified oil was used. The efficiencies obtained were all very low and the performance of the dispersants could not be differentiated. The test protocol was modified by progressively increasing the test duration up to 30 minutes. Even in these conditions, the emulsified oil remained poorly dispersible.

2.3.3 Two Dispersant Applications and Combined Demulsifier/Dispersant Applications

Different treatment strategies were assessed by using a selected dispersant and a demulsifier (Demulsip), two dispersant applications and combinations of demulsifier and dispersant. The WSL method was modified to accommodate these changes; the duration of rotation was 5 minutes for the first application and 2 minutes for the second. The dosage rate was 2% w/w on oil for the demulsifier and 5 % for dispersants. The results obtained with 30% water content emulsions are illustrated Figure 5.

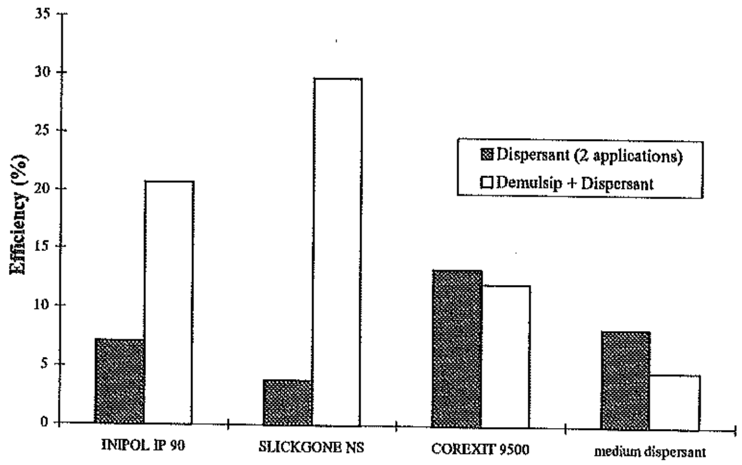

Figure 5. WSL Dispersibility of 50% Water-in-Oil Emulsions

The efficiency result was lower for two dispersants when they were used in combination with the demulsifier. These incompatibilities have been observed in previous laboratory studies (Lewis *et al.*, 1993).

Tests were also performed on several emulsions of increasing water content with one dispersant, Corexit 9500. The results are presented in Figure 6. The curves show that, in these tests conditions, the demulsifier exerted a negative effect on the performance of the dispersant.

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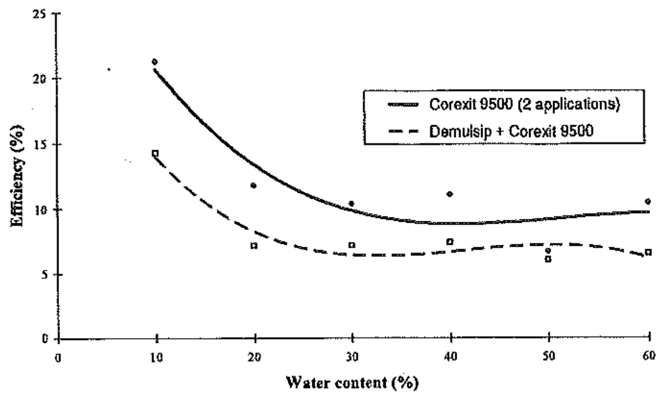

Figure 6. WSL Dispersibility Efficiency Versus Water Content

The degree of apparent incompatibility between the dispersant and the demulsifier (Demulsip) varied with dispersant. The very low efficiencies obtained by testing of these emulsions led to additional tests being performed at a larger scale in the Polludrome with emulsions that were formed by oils as they weathered.

3.0 Polludrome Testing

Two series of tests were conducted in the Polludrome to assess two treatment strategies; two dispersant applications and a combination of demulsifier and dispersant application. The test procedure was the same for these two experiments. For this study, simulating with open sea conditions, the Polludrome (Figure 7), was used in the loop configuration with the water being continuously circulated. The test conditions were; wave height of 40 cm, a current speed of 20 cm/s, a water depth of 0.90 m, the volume of seawater was 9.5 m^3 and the test temperature was 20°C.

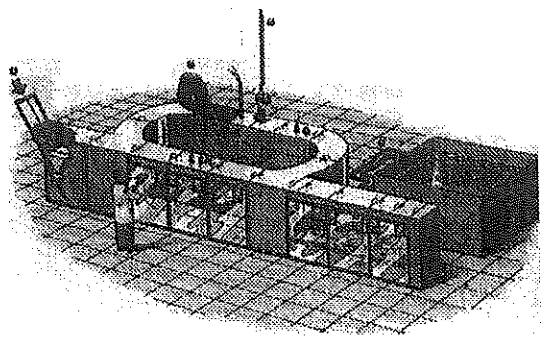

Figure 7. The Polludrome

The test oil was a mixture of BAL 110 ('topped' Arabian Light crude oil) and Heavy Fuel Oil (HFO) at a 30/70 volume ratio. At the beginning of a test, 10 litres of the test oil were poured onto the water surface and allowed to weather (evaporate and emulsify) for three hours under the prevailing conditions.The emulsified oil was then sampled before being sprayed with dispersant or demulsifier. After about one hour, the oil slick was treated again with dispersant. The dispersant was applied as a fine spray and some of the sprayed chemical missed the target, but these losses could not be measured. However, all tests were carried out according to the same procedure. The relative progress of the rate of oil dispersion was followed using a turbidimeter and water samples were taken to measure the actual oil concentrations in the water. The emulsified oil remaining on the water surface was sampled at various times and the water content and viscosity of these samples were measured. The water content was determined by the Dean & Stark method (NFT 60 113, French standard) and the emulsion viscosity was measured using Haake VT 550 ($10s^{-1}$ shear rate) and Brookfield viscometers. The oil in water concentration was determined by solvent extraction with dichloromethane, filtration through anhydrous sodium sulfate and spectrophotometry at 580 nm. Tests were carried out with Corexit 9500, Dasic Slickgone NS and Inipol IP 90 dispersants, plus an additional dispersant with a performance that was representative of the other dispersants, as determined by the WSL testing. The demulsifier used was the Demulsip.

3.1 Two Dispersant Applications

The emulsified oil was sprayed with dispersant at a treatment rate of 5% weight dispersant of the original oil weight. When the oil concentration in the water column had stabilised, the oil remaining on the water surface was treated again with dispersant at 10% weight of the estimated residual floating oil. The effect of demulsifier application, instead of the first dispersant application, was also assessed for one dispersant (demulsifier : 2%, dispersant : 5%).

Figure 8 illustrates the efficiencies for all the products and Figure 9 shows the respective effect of a dispersant and a demulsifier concerning oil viscosity and water content. The first dispersant application after three hours weathering was found to act as a demulsifier in each case. The dispersant 'broke' the emulsion and this led to a drop in emulsion viscosity and water content (Figure 9). The dispersion of the remaining oil was achieved by the second application of dispersant (Figure 8).

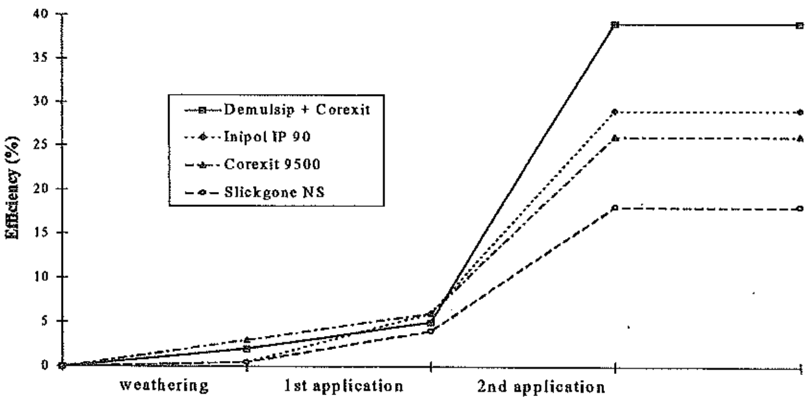

Figure 8. Efficiency in Polludrome Tests

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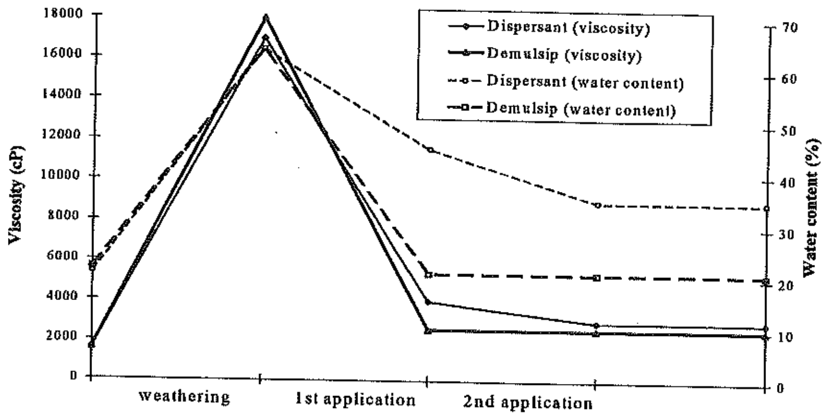

Figure 9. Viscosity and Water Content for the First Application

3.2 Combination of Demulsifier and Dispersant Applications

An additional series of tests was performed using a demulsifier application at 2% weight followed by a dispersant application to study the efficiency of such combinations and to reveal possible incompatibilities as suggested by the WSL results. The experimental procedure was changed slightly; the oil volume was reduced to 5 litres and the temperature was 15°C. The results are shown in Figure 10.

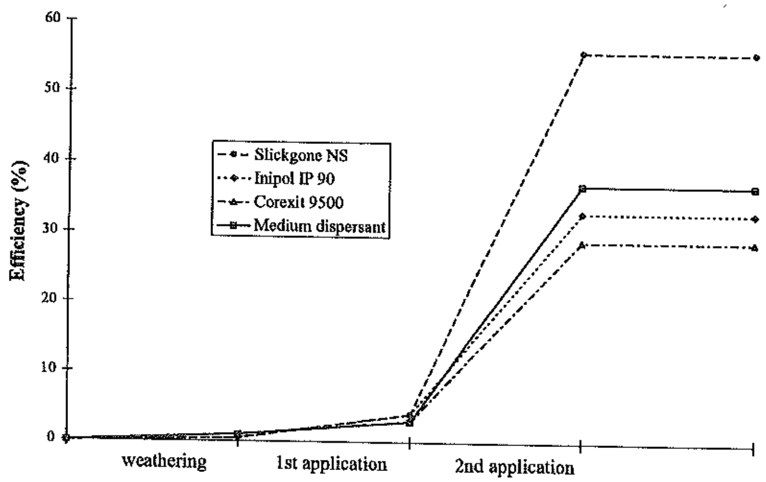

Figure 10. Effectiveness of Combinations of Demulsip and Dispersant in Polludrome Tests

The results obtained show that an application of demulsifier is more effective at breaking the emulsion than an application of dispersant. Compared to two dispersant applications, the combination of Demulsip and Corexit 9500 was the most effective dispersant/demulsifier combination.

3.3 Non-Emulsified Oils

A series of tests was conducted using one of the four dispersants to treat mixtures of HFO/BAL 110 of increasing viscosity. The test conditions were the same as described previously concerning the parameters of the open sea simulation.

The oil volume was 2 liters, which corresponds to a maximum oil-in-water concentration in the Polludrome of 210 ppm. The oil slick was treated with a single dispersant application (at a treatment of 5% weight). The temperature was 15°C. Results were then compared with those obtained by the IFP and WSL test methods (Figure 11).

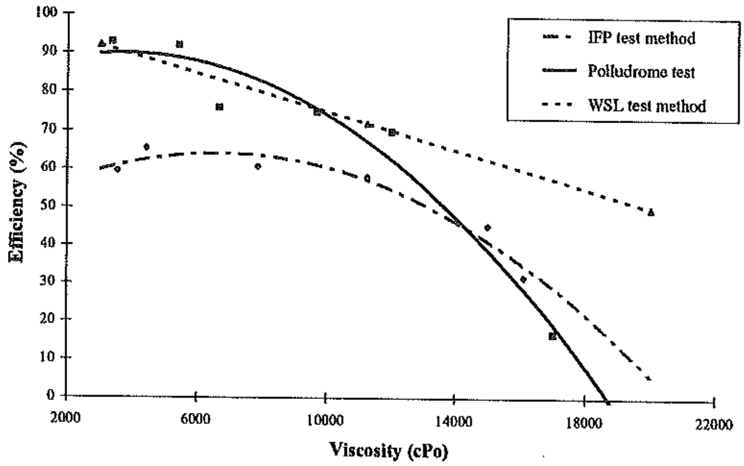

Figure 11. Efficiency Versus Oil Viscosity for WSL, IFP and Polludrome Dispersibility Tests

4.0 Discussion

4.1 Non-Emulsified Oils

The results of the laboratory dispersant testing methods appear to show that the laboratory tests cannot accurately assess the feasibility of a dispersion of some oils at sea.

The WSL method indicates that high efficiency can be obtained up to an oil viscosity of 20,000 cP. This is unrealistic when compared to practical experience acquired at sea trials (Lewis *et al.*, 1998) and at real oil spills. However, the WSL test seems to rank dispersants reliably, especially in the range of oil viscosities between 8,000 and 17,000 cP, a viscosity range characterized by a low variability of the results.

The IFP test method, which is characterised by a lower energy of mixing, should be more representative of the behaviour at sea. For relatively low viscosity oils (less than 17 000 cP), the results are coherent and generally agree with the indication of dispersibility from the WSL method, but in extreme conditions, particularly for very high oil viscosity, there can be unexpectedly high efficiency results. The test method used might explain these unexpected results. High viscosity oils (which also have a high density) need time to get dispersed. Subjected to the wave beater agitation, lumps break off of the main body of the oil and are submerged. Dispersion results from a violent contact with the beater itself and not from the much lower mixing energy created by the turbulence of beater at the water surface.

Testing in the Polludrome seemed to produce more reliable results, with a clear decrease of efficiencies with increasing oil viscosity which was not observed with the laboratory tests. However, this trend was obtained with only one dispersant and without replicates.

Comparison between the three test methods (WSL, IFP and Polludrome) shows that the Polludrome results correlated with those from the WSL method for low viscosities (up to 12,000 cP) and with those produced by the IFP test for higher values (between 12,000 and 17,000 cP). For the highest viscosity oils, only tests performed in the Polludrome led to low efficiency results. However, tests have been performed only on mixtures HFO/BAL 110 and these observations have to be completed with other types of oil.

4.2 Emulsified Oils

The results from the WSL and IFP laboratory tests were insufficient to assess the effectiveness of a dispersant, in combination with a demulsifier or not, because of the very low effectiveness results obtained with emulsified oil. The different treatment strategies revealed possible incompatibilities between some products, but the differences in results are not significantly different to enable form conclusions to be made.

The tests performed in the Polludrome lead to different conclusions, particularly concerning the benefit of using a combination of demulsifier and dispersant. Two dispersants applications acted in a similar way to a combination of demulsifier and dispersant; the first dispersant application reduces the viscosity and the water content of the oil, thus improving the efficiency of the dispersion achieved by the second application. However, the use of a specifically designed demulsifier proved to be more efficient in combination with any of the dispersants assessed in this study. In addition, a 5% dispersant application was more efficient in the Polludrome than the 10% application used in the laboratory test methods. These encouraging results should be further investigated. The weathering time was only three hours and it would be interesting to form more stable emulsions by extended weathering. Treatments with demulsifiers and dispersants could reveal quite different results with more stable emulsions. Moreover, the chemicals were applied in ideal conditions in the Polludrome; there was no dilution process and the oil slick was homogeneous and not subjected to current and waves. It is likely that the application process would be less efficient at sea.

5.0 Conclusions

In the light of these studies, it appears that the laboratory tests do not accurately simulate the dispersion process at sea. Efficiencies are generally

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overestimated and the test protocol needs to be adapted to the viscosity range. In addition, emulsions prepared in the laboratory are poorly dispersible, even when subjected to a strong mixing energy. The laboratory tests were developed to rank dispersants, with some limitations for some viscosity ranges, and the simulation of sea conditions is poor.

Dispersibility tests conducted in the Polludrome seem to produce more reliable results and allow the assessment of alternative treatment strategies. The experiments described showed that the oil viscosity limit for successful dispersion is higher than the 2000 cSt oil viscosity limit which has been included in the French operational guidelines since the eighties. The improvements in dispersant formulation have led to increased efficiency with high viscosity oils. This indicates that the oil viscosity limit should be reconsidered and increased. Additional tests should be performed with other types of oils to complete the study and to devise new practical limits for emulsion and oil dispersibility.

In addition, these tests showed that dispersants can be used as demulsifiers. The implications for response strategies are clear; there is a possibility of a pre-treatment at low dosage with dispersant to extend the time window for dispersant use. In addition to dispersants which have an emulsion breaking capability, there are specific products, demulsifiers, that possess the primary ability to break emulsions. The combined use of demulsifier followed by a subsequent dispersant application promises the capability to produce high dispersion rates of emulsified oils. So far, the Polludrome tests showed that the demulsifier had no negative effects on the dispersant performance. However, the relatively high toxicity of some demulsifiers, compared to dispersants, must be borne in mind (Peigné, 1993). The relative merits of using dedicated demulsifiers or emulsion-breaking dispersants needs to be addressed. In addition, as demulsifiers efficiencies are oil-specific in their effect (Lewis and Walker, 1993), a wider range of oil types should be studied in a further step.

In conclusion, it appears that all these results presented in this paper could lead to new strategies for oil spill treatment. These options should be taken into account in the oil spill contingency plans and in the operational procedures for oil spill response.

6.0 Acknowledgements

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7.0 References

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