DISPERSANTS AND DEMULSIFIERS: STUDIES IN THE LABORATORY, HARBOR, AND POLLUDROME

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ABSTRACT: *When spilled at sea, many oils are known to form emulsions. These emulsions are often of high-water content and viscosity, poorly dispersible, hard to recover and pump, and likely to remain as a persistent pollutant that may come ashore. To avoid these difficulties, demulsifiers have been used, either to inhibit emulsion formation or to break emulsions that have already been created. CEDRE (Centre de Documentation de Recherche et d'Experimentations sur les Pollutions Accidentelles des Eaux) has studied the efficiency of several demulsifiers on the rate of emulsion formation and on the dispersability of emulsified oils of different types. This study was conducted in three stages. First, a study of the rate and extent of emulsification was conducted in the laboratory. Second, the effect of demulsifiers was studied in floating mesocosms placed in a harbor. The demulsifiers did not succeed in totally preventing emulsion formation, but they inhibited the degree of emulsification of the oils for some time. Third, the dispersability of weathered oils was studied in laboratory using the IFP and WSL test methods and then in the Polludrome, where the effects of different treatment strategies combining demulsifiers and dispersants applications were assessed.*

Introduction

When spilled at sea, many oils are known to form emulsions with sea water. These emulsions are often of high-water content and viscosity, poorly dispersible, hard to recover and pump, and remain as a persistent pollutant that can come ashore. The water content can be very high (up to 75% volume or more), thus leading to the increase of the pollutant volume, which complicates cleanup operations.

To avoid these difficulties, different treating agents can be used to inhibit or prevent the emulsion formation and cause more rapid natural dispersion of oil, thus reducing the overall impact of the oil pollution. Demulsifiers—emulsion inhibitors or emulsion breakers—can be used to stop or limit the emulsion formation while dispersants are designed to promote rapid dispersion of the oil. Both demulsifiers and dispersants are surfactant mixtures; therefore, both contribute to complementary objectives: reduction of the persistence of oil residues on the sea surface and enhancement of the natural dispersion process. Demulsifiers, by preventing emulsion formation, can help oil to naturally disperse, while dispersants are known to limit emulsion formation even at a very low dosage. In recent years, dispersant formulations have been improved by manufacturers, and some dispersants have proved to be efficient even on weathered and emulsified oils (Fiocco and Lessard, 1997). The operational limits for dispersants that have been set in the past should be reconsidered in light of these developments. Many experimental studies have been devoted to these products to assess their efficiency and to optimize their use at sea. Different response strategies have been considered, such as the combined use of demulsifiers or dispersants at low dosage to promote natural dispersion. A first application of demulsifier at low treatment rate can be used to slow down the emulsification of the oil and enlarge the "time window" for the dispersant application (Walker and Lunel, 1995). The extensive use of dispersants at low overall treatment rates during the *Sea Empress* incident was reported to have exerted an emulsion-breaking and subsequent dispersion effect (Lunel *et al.*, 1995). To address these questions, CEDRE conducted experimental studies in three stages:

- In the first stage, the effects of demulsifiers—emulsion breakers or emulsion inhibitors—were studied in the laboratory by measuring the rate (or kinetics) of emulsification with two different oils. The studies were conducted with the oils alone and when treated with demulsifiers. The purpose was to assess the capacity of these products to prevent or limit the emulsification process.
- The second stage was to conduct a series of field trials performed in floating mesocosms, areas of sea surface confined by booms in a harbor.
- The third stage was to assess the dispersability of weathered oils. After an initial laboratory screening of nine dispersants using the WSL test method (Martinelli, 1984), three dispersants were selected for further testing using the IFP test method (NFT 90 345, French standard). Certain oil and dispersant combinations (and demulsifier and dispersant combinations) were then subjected to more extensive testing in the Polludrome.

The Polludrome, illustrated in Figure 1, is a new testing facility at CEDRE and is equipped with wave, current, and wind generators. The main characteristics of the Polludrome are flume width of 0.60 m, a water depth of 1.20 m, and a water surface area of 10.5 m^2. The Polludrome enables many investigations of oil combating techniques and strategies to be simulated in conditions of open sea, shoreline, or rivers.

Stage 1: Laboratory studies of the rate of emulsification

The laboratory emulsification studies were performed using the modified Mackay-Zagorski method developed by IKU (Hokstad *et al.*, 1993). The method is to place oil and sea water

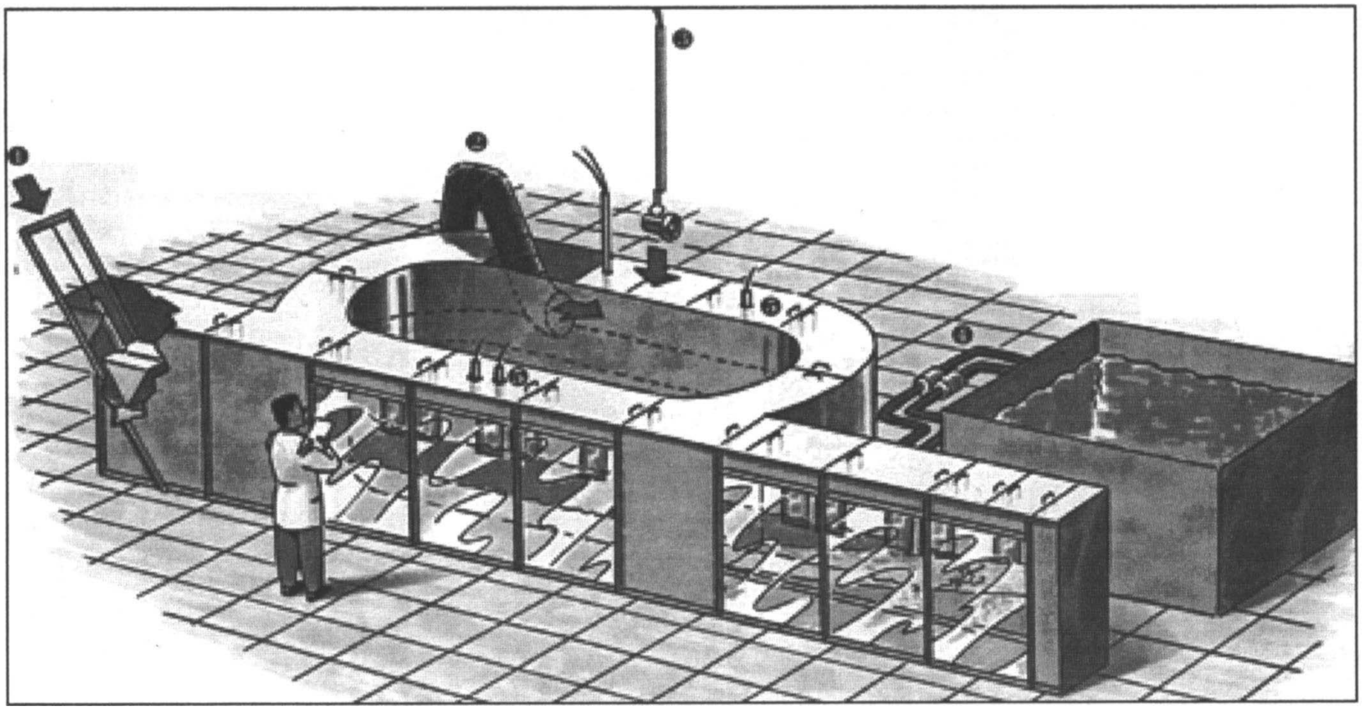

Figure 1. The Polludrome: a testing canal for oil spill research. To conduct its research programs on oil spill countermeasures, CEDRE recently equipped its facilities with a new experimental tool—a hydraulic canal in which various marine and inland water environmental conditions can be simulated. This canal is set in an air-conditioned room and is equipped with waves, current, UV light, wind generators, and a pumping system to re-create the natural dilution process through tidal movements (from a water storage tank). The canal consists of a loop in which the water can be circulated and a straight part in which a shoreline can be re-created with materials of varied granulometry. Large windows are dispatched on the canal to allow useful observations. This equipment allows investigations in realistic environmental conditions as can be met at sea, on the shoreline, and in rivers. Currently, different studies are planned that are relative to "oil and chemicals' weathering and behaviour at sea, dispersion of viscous oils, oil fine mineral interactions in estuarian conditions, performance of sorbent pads and booms on river" and technical evaluation of pollutant detectors. ❶ wave generator (adjustable frequency), ❷ wind generator (a large fan which rotating speed can be controlled), ❸ current generator(s) (one or two little propellers which rotating speed can be adjusted), ❹ pumps to circulate the water between the canal and the additional tank to create tides, ❺ sensors to control wind and current speed. Canal dimension: width, 0.6m; wall height, 1.6 m ; average water depth, 1 m. Tides : tidal range, up to 0.6 m (±0.3 m); period, from 4 to 12 hours. Climate room: 0 to 30°C.

(75 ml oil and 225 ml sea water) in a cylindrical separating flask that is rotated, end-over-end, at 30 revolutions per minute for 150 minutes. The level of the oil/water interface is measured at regular intervals, and the water content of the emulsion is calculated. These tests were conducted with two oils: BAL 110 (an Arabian Light crude oil distilled to 110ºC to remove the most volatile components) and Mazout 50/50 (an IFO-50 grade residual fuel oil). Three demulsifiers—Demoussifier, Gamabreak, and Demulsip—were tested. Different treatment rates of demulsifiers in oil were assessed at temperature of 15°C.

The kinetics of emulsification (*A*, the maximum water content, and *k*, the first order rate constant) were calculated by linear regression in the following way:

$$\% H_2O = A \times e^{-\frac{k}{t}} \tag{1}$$

where *A* equals maximum water content (% volume), *k* equals rate constant (minutes^{-1}), and *t* equals time (minutes). The results obtained and the curves of the above equation are shown in Figures 2 and 3. Both the maximum water content (*A*) and the rate of water uptake (*k*) were dependent on oil type and the demulsifiers used (Table 1), but the effect of the demulsifier was to cause the maximum water content to vary much more than the rate of water uptake. The maximum water content was therefore used to rank the effectiveness of the demulsifiers.

Table 1. Water uptake rate and kinetics of emulsification in the rotating flask laboratory test method.

		BAL 110	Mazout 50/50
Without demulsifier	k (min)	4.2	5.3
	A (% H_2O)	80.9	78.6
Demoussifier 100 ppm	k	17.9	
	A	86.4	
Demoussifier 500 ppm	k	13.8	12.0
	A	44.3	38.5
Demoussifier 1,000 ppm	k	11.6	
	A	22.6	
Gamabreak 500 ppm	k	21.2	11.1
	A	41.2	65.5
Demulsip 500 ppm	k		11.0
	A		67.8

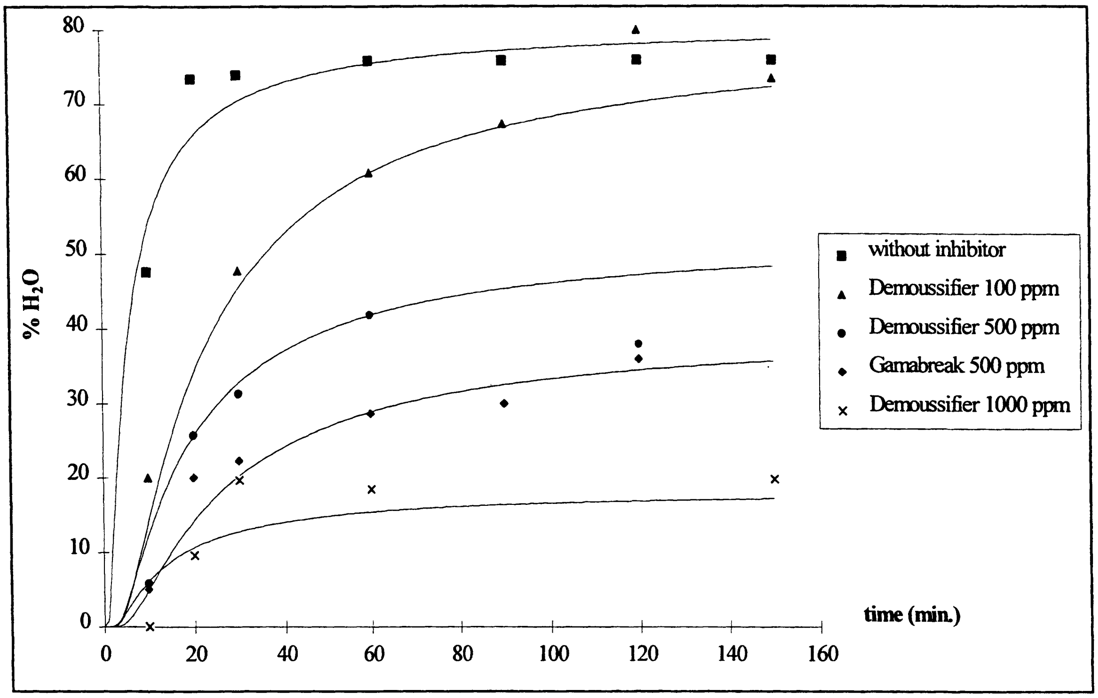

Figure 2. Water content of distilled Arabian Light crude oil (BAL 110) in the rotating flask laboratory test method.

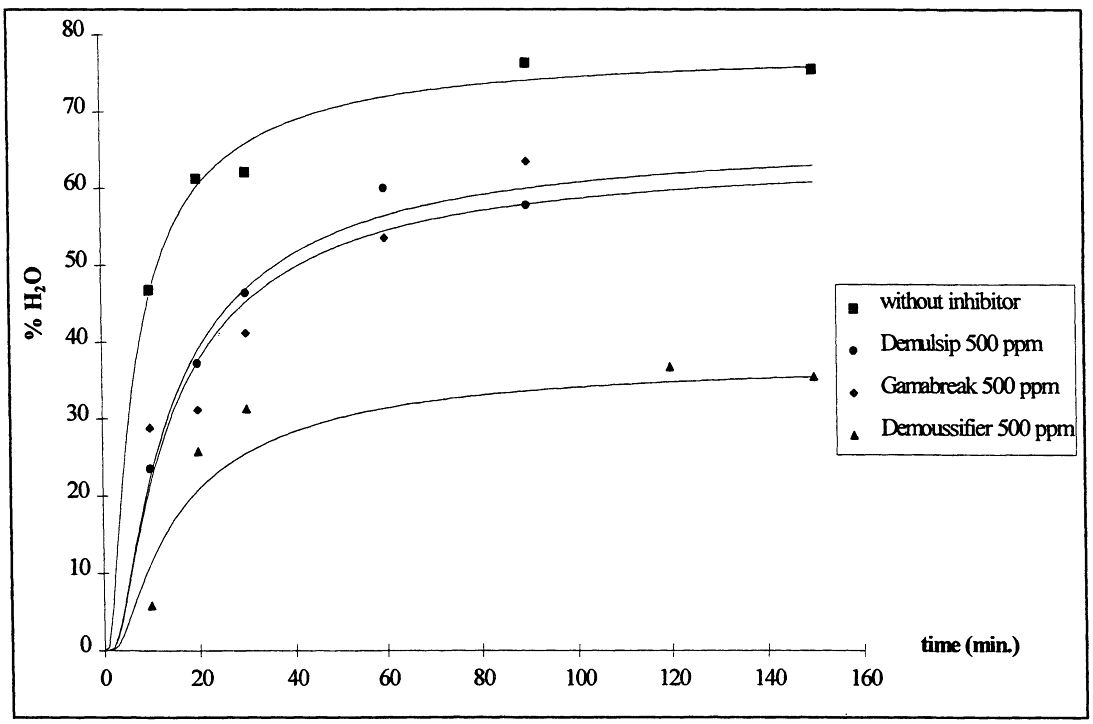

Figure 3. Water content of IFO-50 residual fuel oil (Mazout 50/50) in the rotating flask laboratory test method.

Stage 2: Small-scale field tests of demulsification in a harbor

These tests were conducted in four floating mesocosms, each consisting of an area of 9 m^2 contained within a flexible boom set in a sheltered harbor. The walls of the booms were flexible, and the surface of the water was subjected to agitation caused by the wake created by passing ships. Three demulsifiers—Demoussifier, Gamabreak, and Demulsip—were tested at a demulsifier to oil treatment rate of 1,000 ppm on Mazout 50/50 (IFO-50 fuel oil) and at 2,000 ppm on BAL 110 ("topped" Arabian Light crude oil). Thirty liters of oil were placed in three of the mesocosms, while the fourth was used as a control without demulsifier addition. The water temperature was 9°C. The emulsification of the oil in the mesocosm was followed up by measuring the evolution of the water content, determined by the Dean & Stark method (NFT 60 113, French standard).

Observations showed that the effect of the different demulsifiers on the emulsification of the BAL 110 crude oil was found to be temporary. Emulsification was slowed down for approximately 24 hours after application of the demulsifier, although no differences between treated and untreated oils were observed. The model previously assessed with success in laboratory could be applied only during the first hours, after which the coefficient *A* lost its significance. The speed of emulsification was still significant, and it was observed that the best products according to the laboratory ranking (Table 2) were also the more efficient to slow down the emulsification process in natural conditions. These observations demonstrate that the laboratory test can rank the products for one oil according to their efficiency, but it is not able to predict their real efficiency at sea.

The laboratory test conducted in close flasks cannot simulate the progressive dilution of the demulsifier in an open-water body, which is responsible for the loss of efficiency after around 1 day.

Stage 3: Dispersability in the laboratory and in the Polludrome

Two laboratory methods—WSL and IFP—and the Polludrome were used for this stage of the studies.

WSL test method dispersability testing. WSL dispersability tests were performed on mixtures of BAL 110 and heavy fuel oil in various proportions resulting in oil blends with viscosities varying from 2,500 to 42,000 cP at 10°C. WSL tests were conducted at 10 C°. These tests were conducted on nine dispersants selected from the list of dispersants approved for use in France: Corexit 9500, Disperep 8, Dispolene 36 S, Finasol OSR 52, Gamlen OD 4000, Inipol IP 80, Inipol IP 90, Oceania 1000, and Dasic Slickgone NS. The WSL dispersability test results are shown in Figure 4. WSL efficiency was a function of oil viscosity for all the dispersants tested. The efficiency tended toward 0% for 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 4). As assessed by the WSL method with these oils, the most efficient dispersants were Inipol IP 90, Corexit 9500, and Dasic Slickgone NS.

IFP test method dispersability testing. These tests were performed according to the protocol of the IFP test currently used for approving dispersants in France. Four dispersants (the three dispersants that gave the best results on the WSL test plus an additional dispersant representative of the performance of the other dispersants) were tested against a BAL 110 and heavy fuel oil mixture with a viscosity of 8,000 cP at 15°C. The results are shown in Table 3. High IFP efficiencies were obtained with this test oil with all the selected dispersants.

Table 2. Water uptake rate and kinetics of emulsification in the rotating flask laboratory test method.

		BAL	Mazout 50/50
Without demulsifier	k	2.6	
	(min)		30.8
Demoussifier			
2,000 ppm (BAL)	k	5	
1,000 ppm (Mazout 50/50)			29
Gamabreak			
2,000 ppm (BAL)	k	12	
1,000 ppm (Mazout 50/50)			50
Demulsip			
2,000 ppm (BAL)	k	13	
1,000 ppm (Mazout 50/50)			52

Polludrome testing. For this study dealing with open-sea conditions, the Polludrome was used in the loop configuration with the water being circulated continuously. The test conditions were wave height of 40 cm, current speed of 20 cm/s, water depth of 0.90 m, volume of sea water of 9.5 m^3, and test temperature of 20°C. The test oil was a mixture of BAL 110 ("topped" Arabian Light crude oil) and heavy fuel oil at 30/70 volume ratio. At the beginning of a test, a volume of 10 liters of this test oil was poured onto the water surface and allowed to weather (evaporate and emulsify) under the prevailing conditions. After 3 hours, the emulsified oil was sampled and then 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 stabilized, the oil remaining on the water surface was treated again with dispersant at 10% weight of the estimated residual floating oil. The dispersant was applied as a fine spray thus inducing some loses of chemical that missed the target, but these losses could not be measured. All tests, however, were conducted 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 oil remaining on the water surface was sampled at various times to determine its water content and viscosity. 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 and Brookfield viscometers. The oil in water concentration was determined by solvent extraction with dichloromethane, filtration through anhydrous sodium sulfate, and spectrophotometery at 580 nm. The Polludrome tests were conducted with Corexit 9500, Dasic Slickgone NS, and Inipol IP 90, plus an additional dispersant with a performance that was representative of the other dispersants, as determined by the WSL testing. In addition, a series of tests was performed using a demulsifier application at 2% weight demulsifier on oil treatment rate instead of the first dispersant application.

The results of the Polludrome testing are shown in Figures 5, 6, and 7. As the oil emulsified, the viscosity increased from less than 2,000 cP (measured at 20°C and 10 s^{-1}) to 16,000 cP to 18,000 cP after 3 hours (Figure 5), and the water content increased to between 55% and 70% after 3 hours (Figure 6). The viscosity of the emulsified oil had increased to approximately 12,000 cP.

The first dispersant application after 3 hours weathering was found to act as a demulsifier in each case. Addition of the dispersants caused a substantial decrease of emulsion viscosity to between 4,000 and 8,000 cP (Figure 5) and a slight decrease in water content to between 40% and 55% volume (Figure 6) 1 hour after they were applied. The concentration of dispersed oil in the

Table 3. Efficiency of dispersants according to the IFP test.

	Corexit 9500	Inipol IP 90	Slickgone NS	Average dispersant
Raw efficiency	78	71	72	68
Adjusted value	63	56	57	53

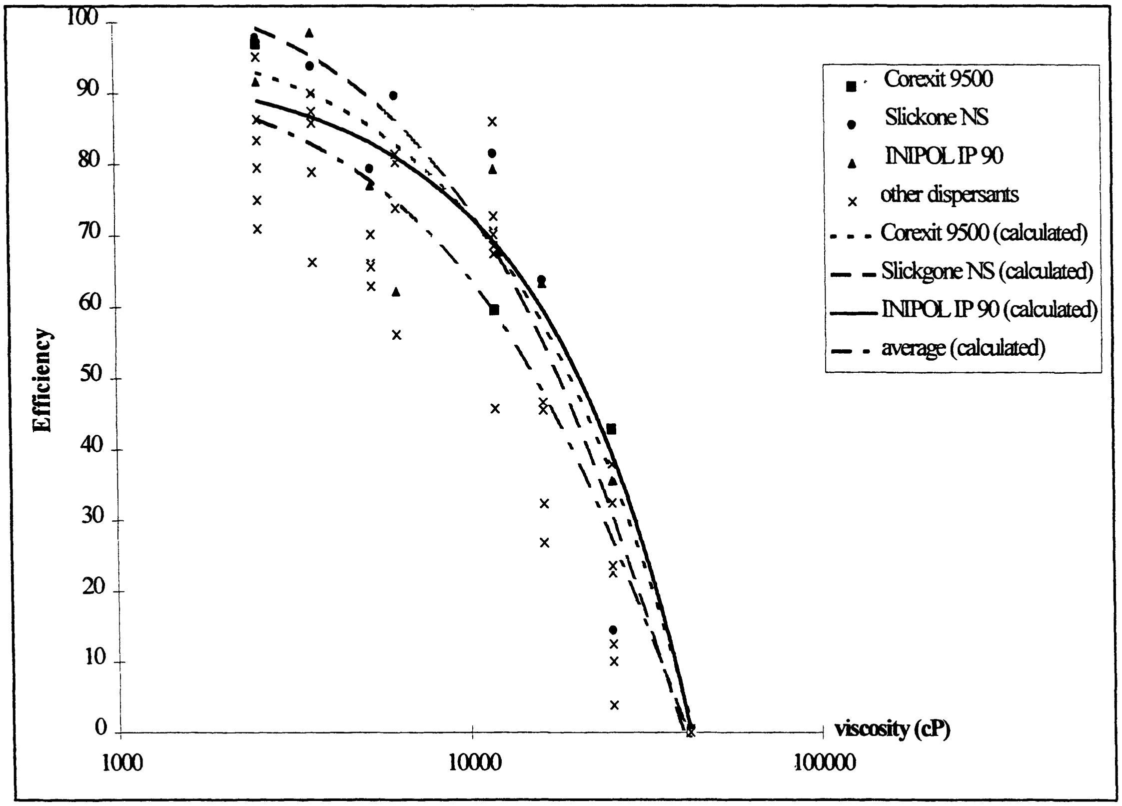

Figure 4. WSL dispersability efficiency versus oil viscosity.

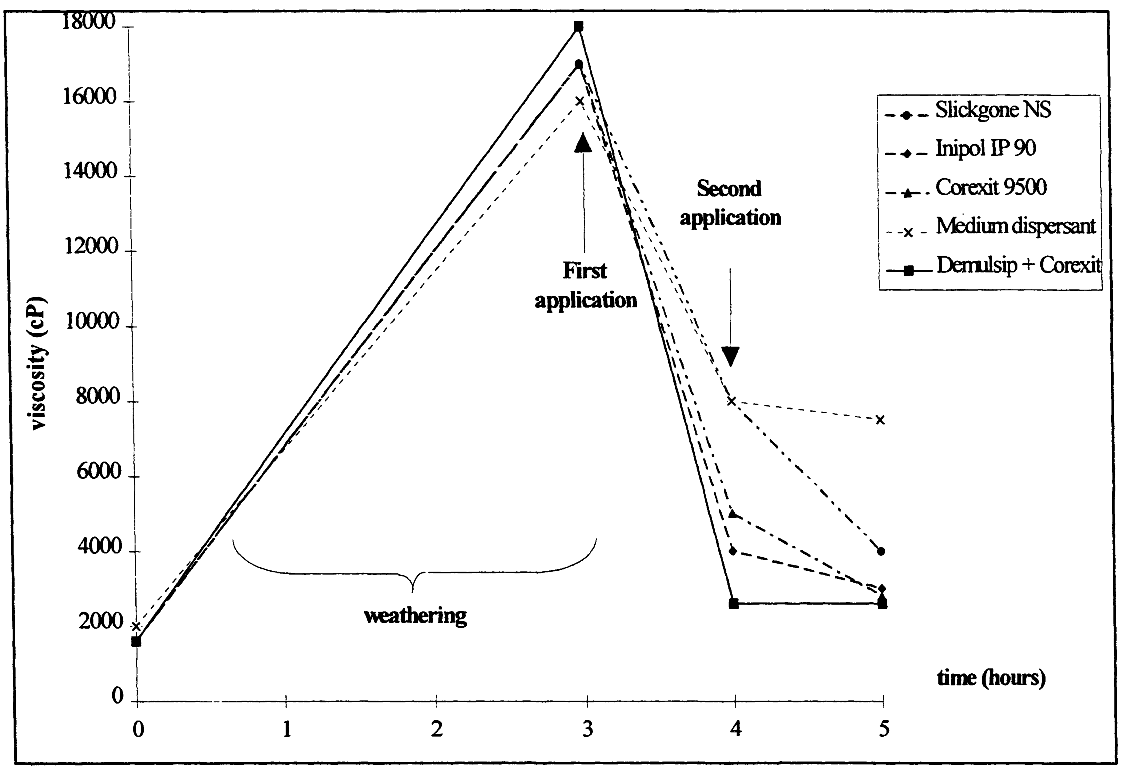

Figure 5. Viscosity versus time of BAL 110/heavy fuel oil mixture (30/70 volume blend) in Polludrome tests.

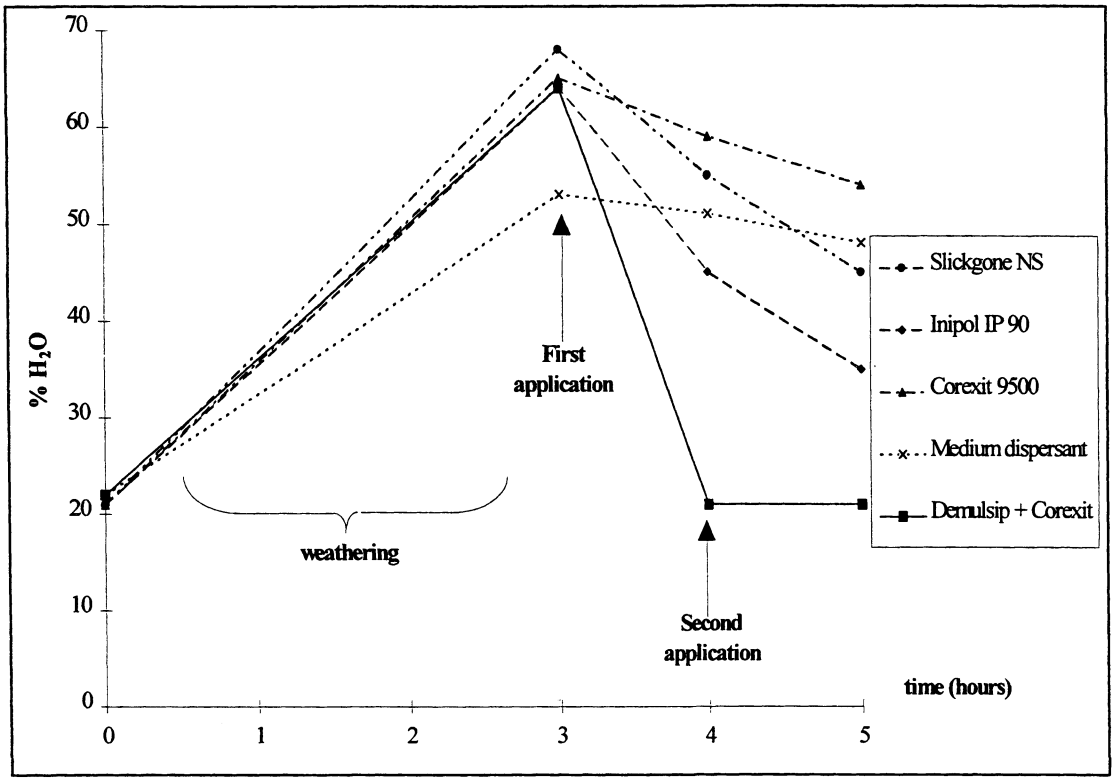

Figure 6. Water content versus time of BAL 110/heavy fuel oil mixture (30/70 volume blend) in Polludrome tests.

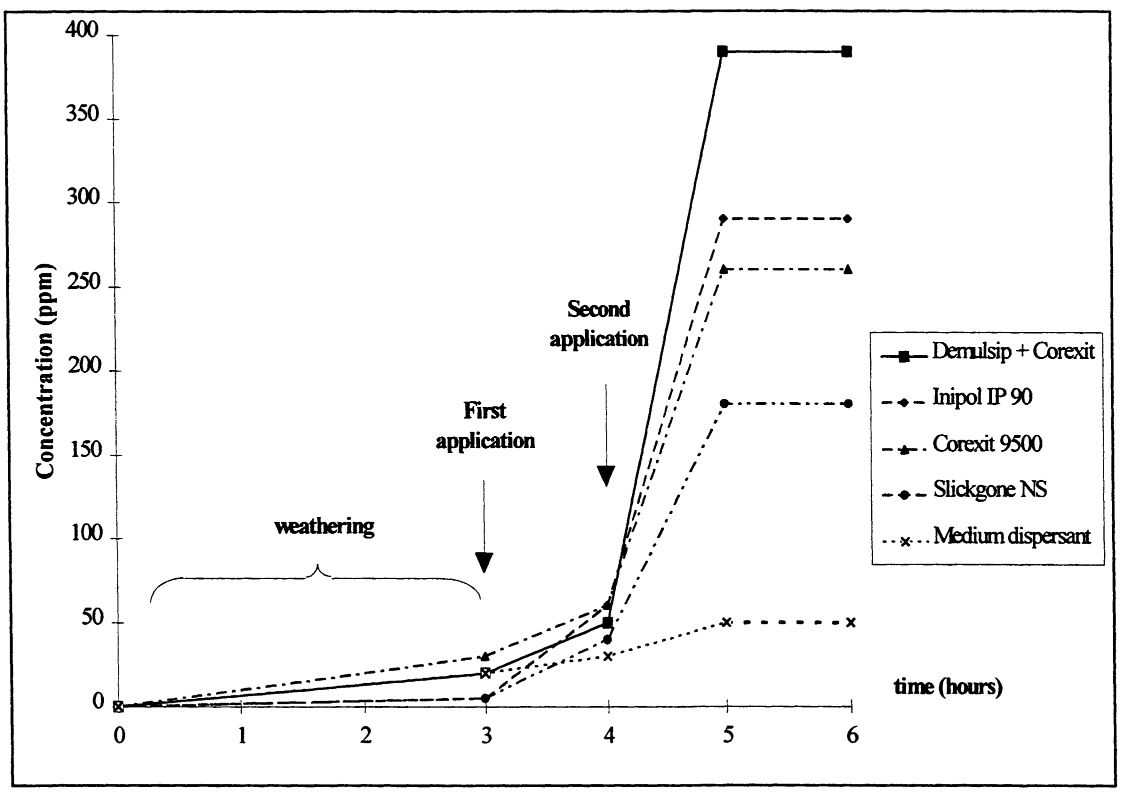

Figure 7. Dispersed oil concentration versus time of BAL 110/heavy fuel oil mixture (30/70 volume blend) in Polludrome tests.

water rose slightly after the first application of dispersant (Figure 7). Using Demulsip demulsifier at 2% addition was just as effective at reducing the emulsion viscosity and increasing the dispersed oil concentration as using 5% dispersant. The demulsifier was much more effective at reducing the emulsion water content than the dispersants (Figure 6), even though less was added. The relative effects of the four dispersants (Corexit 9500, Dasic Slickgone NS, Inipol IP90, and the "medium" performing dispersant) differed in each case: the three most effective dispersants were similarly effective at causing the significant emulsion viscosity decrease (Figure 5) and slight increase in dispersed oil concentration (Figure 7), but there were differences in the reduction in water content of the emulsion (Figure 6).

The second application of dispersant was more efficient in increasing the dispersed oil concentration (Figure 7), but had a lesser effect on emulsion viscosity and water content. The combination of first adding demulsifier and then dispersant was the most effective at breaking the emulsion and dispersing the oil, as shown by the decrease of water content and the increase of the concentration of dispersed oil.

Discussion of results

Demulsifier testing results. The results of the laboratory testing of demulsifiers are not completely in agreement with the observations made in floating mesocosms. The ranking of the products according to their effectiveness is different:

- Laboratory test results: Demoussifier > Gamabreak ≈ Demulsip > untreated oil
- Floating mesocosm results: Demulsip ≈ Gamabreak > Demoussifier ≈ untreated oil

It appears that the laboratory test, performed in a closed system, does not simulate all of the processes that occur at sea, particularly the dilution of the demulsifier into the sea. The laboratory test method was developed from methods originally designed to classify crude oil production demulsifiers. Other factors appear to be important in oil slick treatment. More relevant laboratory test methods may need to be developed to test oil spill demulsifiers intended for use at sea.

Dispersant testing results. The results of dispersant testing show that the laboratory tests (WSL and IFP methods), as well as the tests in the Polludrome, are in good general agreement; the more effective dispersants differ in performance from the "medium" performing dispersant in a generally comparable way. This is a confirmation that the WSL and IFP laboratory methods for testing dispersants are well adapted for ranking the products according to their relative efficiency. The laboratory test methods are simplifications of complex mixing and dilution processes that occur at sea, and more comprehensive studies, such as the optimization of a treatment strategy (number of dispersant applications, treatment rates, combinations of different agents, etc.), require a flume test like the Polludrome to simulate, in a more realistic way, the various situations that can occur. In terms of simulating open-sea conditions, however, the high concentrations of dispersed oil that have been measured in the Polludrome show that there is still room for improvement. In the future, it will be necessary to increase the dilution in the Polludrome system by partial and continuous renewal of water to better simulate conditions at sea.

Several operational implications can be deduced from these results. Some dispersants are now capable of dispersing emulsified oils of relatively high viscosity (10,000 cP and more), which indicates that dispersant formulations have improved and that the operational limits for dispersant use devised many years ago could be raised. The current recommendation in France is not to use dispersants on oils or emulsions with a viscosity higher than 2,000 cP, while some other countries use higher limits, such as 5,000 cP. The tests performed in the Polludrome show that it is possible to treat high-viscosity emulsified oils by operating in two steps: a first treatment at low dosage to break the emulsion, thus reducing the viscosity, followed by a regular dispersant application. These tests confirm that dispersants applied at low dosage act initially as demulsifiers. Dispersants have not been specifically formulated to break the emulsions, however, and it may be preferable to use an efficient demulsifier to prepare the emulsified oil for dispersion. The Demulsip demulsifier followed by the Corexit 9500 dispersant proved to be the most efficient demulsifier/dispersant combination tested.

From an operational point of view, a first treatment at low treatment rate of a dedicated demulsifier or a dispersant can enlarge the "time window" for dispersant use and thus win the necessary time to organize the regular dispersion. In a real case, one could imagine that the first aircraft arriving at an oil spill could apply a first treatment at low treatment rate on large areas of an oil slick to slow down oil weathering. This would permit subsequent dispersant spraying by other means. In light of the test results obtained in the floating mesocosms with demulsifiers, this gain of time might not be longer than about 24 hours. All these considerations need to be confirmed by performing more tests on different oils. In these studies, all the oils had a relatively similar composition because they were made from mixtures of a light crude oil (Arabian Light) and a heavy fuel. It is required to run studies on other oils, particularly waxy ones. A larger number of products, notably demulsifiers, must be assessed, and further studies of treatment strategies involving demulsifiers and dispersants on high-viscosity emulsified oils are required.

Conclusions

Because of the results of these studies, it has become evident that the oil viscosity limit for successful dispersion of oil, set in France as 2,000 cP 15 years ago, is no longer realistic. The improvements in dispersant efficiency with high-viscosity emulsified oils indicate that this limit should be reconsidered and increased. More tests should be performed with other types of oils to complete the study and devise new emulsion and oil viscosity limits. In addition, it now seems possible to use some dispersants as demulsifiers, which has implications for operational response techniques. There is the possibility of a pre-treatment at low dosage of dispersant to prolong the "time window" for dispersant use. Although some dispersants have an emulsion-breaking capability, it is specially developed 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. The relatively high toxicity of some demulsifiers compared to dispersants, however, must be remembered (Peigné, 1993). The relative merits of using dedicated demulsifiers or emulsion-breaking dispersants must be addressed. The dosage can be a key parameter: is a demulsifier at very low dosage more efficient than a dispersant used at a higher concentration? Further studies should be conducted to answer this question. It is known that demulsifiers are oil-specific in their effect (Lewis and Walker, 1993). A wide range of oil types should be studied.

In conclusion, it appears that the results presented in this paper could lead to new strategies for treating oil spills. These options should be considered in the oil spill contingency plans and operational procedures of oil spill response.

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