Dispersant Effectiveness after Extended Low-energy Soak Times

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Abstract

A net environmental benefit can often be achieved by applying dispersants to an oil spill. Currently, dispersants are considered ineffective when applied to a spill in calm or near calm conditions. This is often the case for oil spills in ice, but calm conditions occur in temperate regions as well. If dispersant application is postponed until wave-energy increases, the oil may have weathered to the point that effectiveness is reduced because the dispersant cannot effectively penetrate the oil phase.

A joint group of industry, oil-spill response organizations, and government agencies is sponsoring a project to study the fate and effectiveness of chemical dispersants after prolonged contact with oil in a marine environment under calm conditions. The goal is to provide oil-spill responders with data supporting the decision for early application of dispersants in low-energy environments with the expectation that wave energy will increase within days after the spill.

SINTEF and CEDRE are currently conducting lab-scale experiments to determine the effectiveness of dispersants on a waxy oil, a napthenic oil, an asphaltenic oil, and a parrafinic oil after extended contact in calm conditions. This paper will present preliminary findings of this ongoing study.

Introduction

Application of chemical dispersants to marine oil spills is an important response option that can yield net environmental benefits. From the perspective of the spilled oil, chemical dispersion is a two-step process (see **Figure 1**). The active surfactant compounds within chemical dispersants must first penetrate into the oil phase, and then sufficient ambient mixing energy is needed to produce dispersed oil droplets. Dispersion will not occur in calm conditions and effectiveness is reduced in very low sea states.

Penetration of surfactants into an oil film is a time-dependent step. It is most effective when dispersants are applied before the oil has weathered to become highly viscous from evaporation or emulsification. Depending on the characteristics of the spilled oil and the ambient conditions, the time window for effective dispersant application can be as small as 24 to 48 hours. The dispersant window may close if dispersant application is postponed because existing sea states are too low.

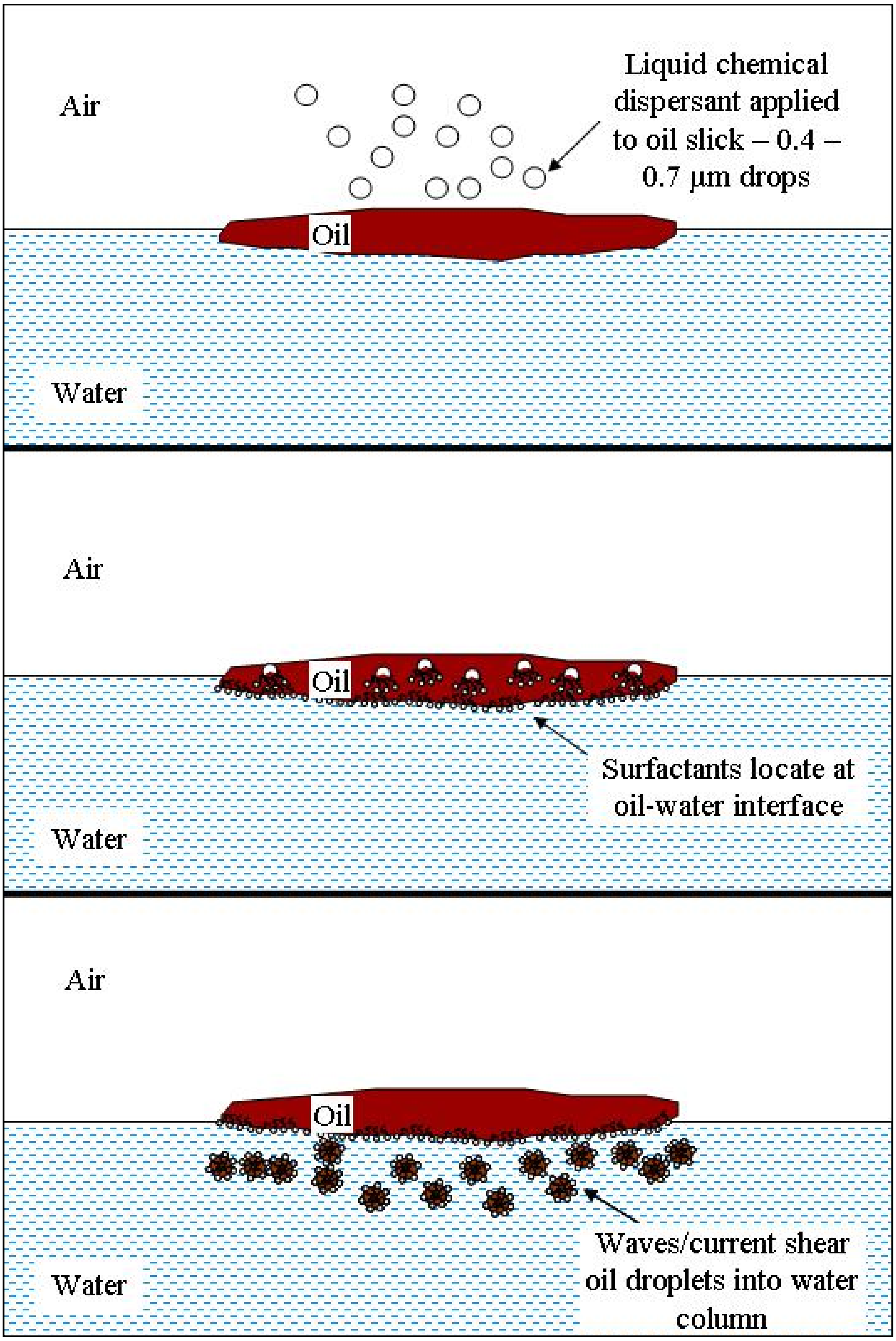

Figure 1. Conceptual drawing of simplified chemical dispersion mechanism.

Calm seas can occur in temperate climates but they typically don't persist for long. In arctic regions, ice conditions act to dampen ambient wave energy for significant periods. Natural movement of ice to the edge of ice zones or strong storms can produce mixing conditions needed for dispersion even in high concentrations of ice.

A joint group of industry, oil-spill response organizations, and government agencies is sponsoring a project to study the fate and effectiveness of chemical dispersants after prolonged contact with oil in a calm marine environment. The goal is to provide data that allow oil-spill responders to make science-based decisions on whether or not to apply dispersants to oil spills even if sea states are low.

The Norwegian research institute SINTEF and the French Centre of Documentation, Research and Experimentation on Accidental Water Pollution (CEDRE) are currently conducting joint lab-scale experiments to determine the effectiveness of dispersants after extended contact in calm conditions. The study is evaluating four crude oils representing four broad categories: a napthenic oil (Troll B), an asphaltenic oil (Balder), a parrafinic oil (New Oseberg Blend), and a waxy oil (Ringhorne). This paper presents preliminary findings of this ongoing study.

Test Plan and Methods

The study includes a series of dispersant effectiveness tests on the four crude oils mentioned above after extended dispersant and oil contact on seawater. The two main goals of the study are to measure changes in dispersant effectiveness over time and to analytically determine the leaching rate of the surfactants from the oil phase to the seawater over time.

SINTEF and CEDRE are using a modified version of the IFP dilution dispersant effectiveness test method to carry out experiments for this study. This method was chosen because it is a dilution test; it uses a low oil to seawater ratio; the mixing energy used in the test is well characterized; and the precision and accuracy of the test is well known because both SINTEF and CEDRE have long-term experience with the method. The mixing of the IFP test has been characterized as low-to-mid energy in comparison to marine conditions. Figure 2 shows a drawing of the test apparatus.

The primary modification made to the IFP test method was extending the time between application of dispersant to the oil and start of the energy generating mechanism. Dispersant-free seawater was continuously circulated through the IFP dispersion vessel during the oil-dispersant contact periods to ensure that buildup of surfactant in the water phase did not affect leaching. Duplicate tests were used with a third replicate performed if the discrepancy between duplicates exceeded a predetermined threshold.

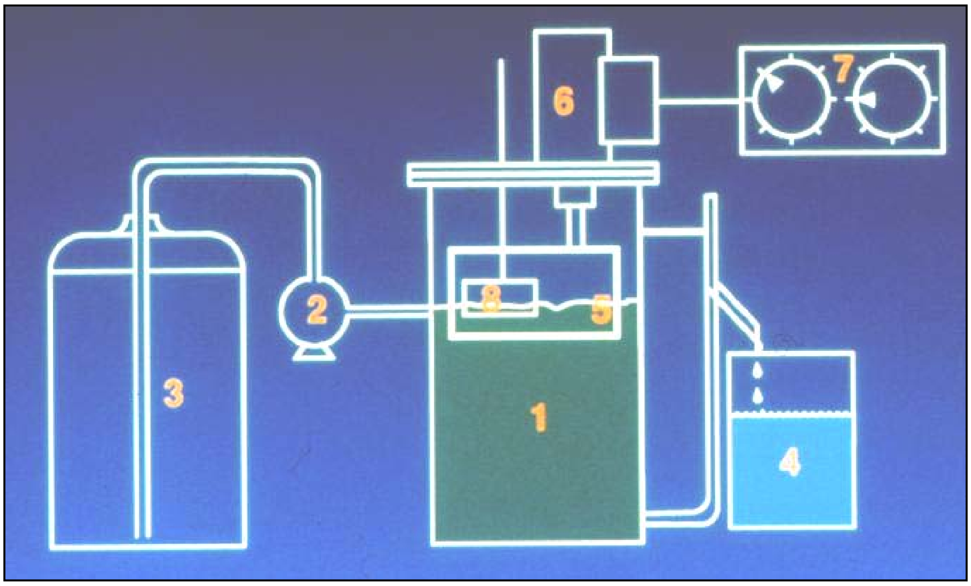

Figure 2. Schematic drawing of IFP test apparatus. 1-dispersion vessel, 2-peristaltic pump, 3-seawater storage, 4-dispersed oil collection vessel, 5-oscillating hoop, 6-oscillating hoop motor, 7-motor controller, 8-oil containment ring.

The study includes evaluation of four commercial dispersants in screening tests and a model dispersant. Two of the four commercial dispersants will be tested in the full program. For the commercial dispersants, the standard IFP test drop-wise application of the dispersant to the oil is being used. This will allow evaluation—to the extent practical in this lab-scale test—of the important step of dispersant penetration into the oil phase.

A model dispersant was included in the test program to study the leaching characteristics of the common surfactants used for many commercial dispersants (Tween 80, Span 80, Tween 85, and Aerosol OT). The proprietary nature of commercial dispersant formulations means that exact concentrations of the various components are unknown. The model dispersant, however, was mixed by the researchers using a specified formulation.

The model dispersant will be premixed with the oils before placing the mixture in the IFP test apparatus. This combined with the known surfactant concentrations will facilitate determination of the leaching rates. A novel method for the chemical fingerprinting of oil based on liquid chromatography-mass spectrometry (LC-MS) developed by Statoil (Eide and Zahlsen, 2005) will be used to measure the concentration of surfactants in the oil phase over time. For the model dispersant, each test condition will include measurement of dispersant effectiveness and LC-MS analysis to determine surfactant leaching rates.

Prior to testing, the napthenic, asphaltenic, and parrafinic crudes were heated until the vapor temperature reached 200°C to simulate 12 – 24 hours of natural weathering, depending on ambient conditions. Because preliminary testing found very limited dispersion of the 200°C weathered sample of the waxy crude (Ringhorne), a 150°C weathered Ringhorne sample was substituted. Preliminary characterization data on the four crude oils is shown in Table 1.

Table 1. Preliminary Physical Properties of the Study Oils

Oil type	Evaporation (vol.%)	Residue (wt. %)	Density (g/mL) at 15.5°C	Pour Point* (°C)	Viscosity (cP) at 13°C	Interfacial tension (mN/m)	Asphaltenes** (wt. %)	Wax*** (wt. %)
Fresh Troll B	0	100	0.891	-18	-	-	0.06	1.38
200°C+	12.9	88.9	0.908	-9	-	-	0.07	1.55
Fresh Balder	0	100	0.914	-6	219	-	0.79	2.21
200°C+	11	89	0.929	-	985	-	0.89	2.48
Fresh New Oseberg	0	100	0.859	-12	-	13.2	0.46	2.09
200°C+	29.5	72.5	0.884	9	-	12.7	0.64	2.88
Fresh Ringhorne	0	100	0.83	6	66	15	0.17	4.84
150°C+	20	82	0.86	12	1270	14	0.21	5.9
200°C+	32.3	70.7	0.875	24	3510	14	0.25	6.84

- indicates that the data is pending.
* Pour point determined using ASTM D97-77
**Asphaltenes determined using IP 143/90
***Waxes determined by extracting with 2-butanone/DCM at –10ºC (Bridie *et al*. 1980)

Screening IFP tests at 15°C using four commercial dispersants to determine their effectiveness on the napthenic oil after contact times of 1 minute and 24 hours were completed. Additional screening tests were performed on the other three oils using the same four dispersants. The objective of the screening tests was to provide data to choose two commercial dispersants to use for the bulk of the study.

After completing the screening tests, additional 15°C IFP tests with longer contact times will be completed on the four oils using the two selected commercial dispersants and the model dispersant. Testing will include dispersant-oil contact times ranging from 1 minute to 2 weeks. This testing was partially completed at the time of this writing.

Further tests will be completed at 0°C without ice and at 25°C using the same 1 minute to 2 week contact times and three oil-dispersant pairs that resulted in effective dispersion at 15°C.

Test plans include evaluation of the effects of freezing. For these tests the IFP-test apparatus will be modified to allow freezing of seawater from the water surface after application of oil and dispersant. Because ice and cold temperatures are expected to reduce the leaching of surfactants from oil, the tests with ice will extend to 1.5 months. After the desired contact time, the ice will be melted within the IFP test apparatus followed by completion of the standard test procedure. Two oil types will be studied.

Preliminary Findings

This paper provides only preliminary results as this study was roughly 50% complete at the time of this writing. For reporting these preliminary results, the commercial dispersants will be identified as Dispersant A, Dispersant B, Dispersant C, and Dispersant D.

Figure 3 shows the results of initial screening tests completed to identify the two commercial dispersants to use for the bulk of the study. The plan was to evaluate the effectiveness of four commercially available dispersants on the napthenic (Troll B) oil at contact times of 1 minute and 24 hours. The initial screening tests, however, showed insignificant differences between the commercial dispersants. Because of this, additional IFP tests with 1 minute of contact time were completed for all four study oils (**Figure 4**).

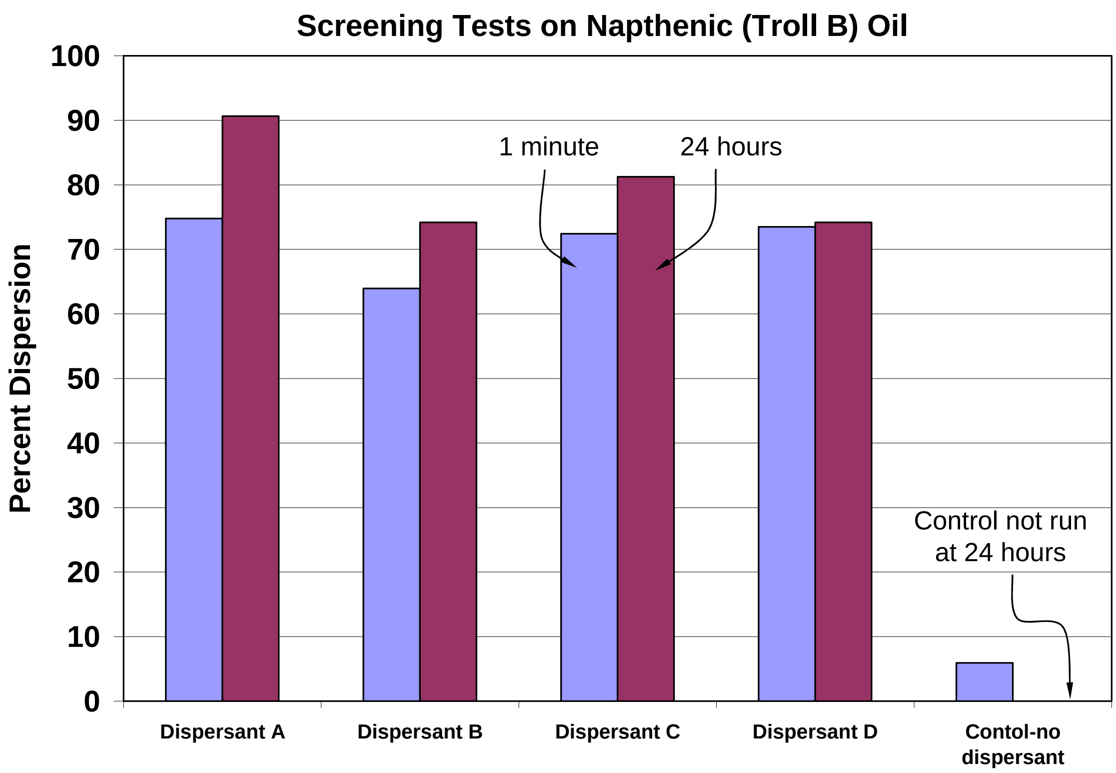

Figure 3. Results of screening tests on the napthenic oil to evaluate four commercial dispersants at 15°C.

In the screening tests, Dispersant A, Dispersant B, and Dispersant C performed approximately the same for the napthenic oil, asphaltenic oil (Balder), and paraffinic oil (New Oseberg Blend). Dispersant D was consistently less effective than the others on the asphaltenic, paraffinic, and waxy (Ringhorne 150°C) oils. As mentioned, the 200°C weathered waxy oil had little dispersion with all dispersants in the screening tests with 1 minute of contact time. To allow some testing of this oil, a 150°C weathered sample was substituted. The 150°C weathering is equivalent to 0.5 – 3 hours of weathering for a spill at sea.

The screening results indicated that Dispersant A, Dispersant B, and Dispersant C had roughly equivalent effectiveness on all four study oils. Dispersant A and Dispersant B were chosen for further study because these two are maintained in greater stockpiles around the world by oil spill response organizations.

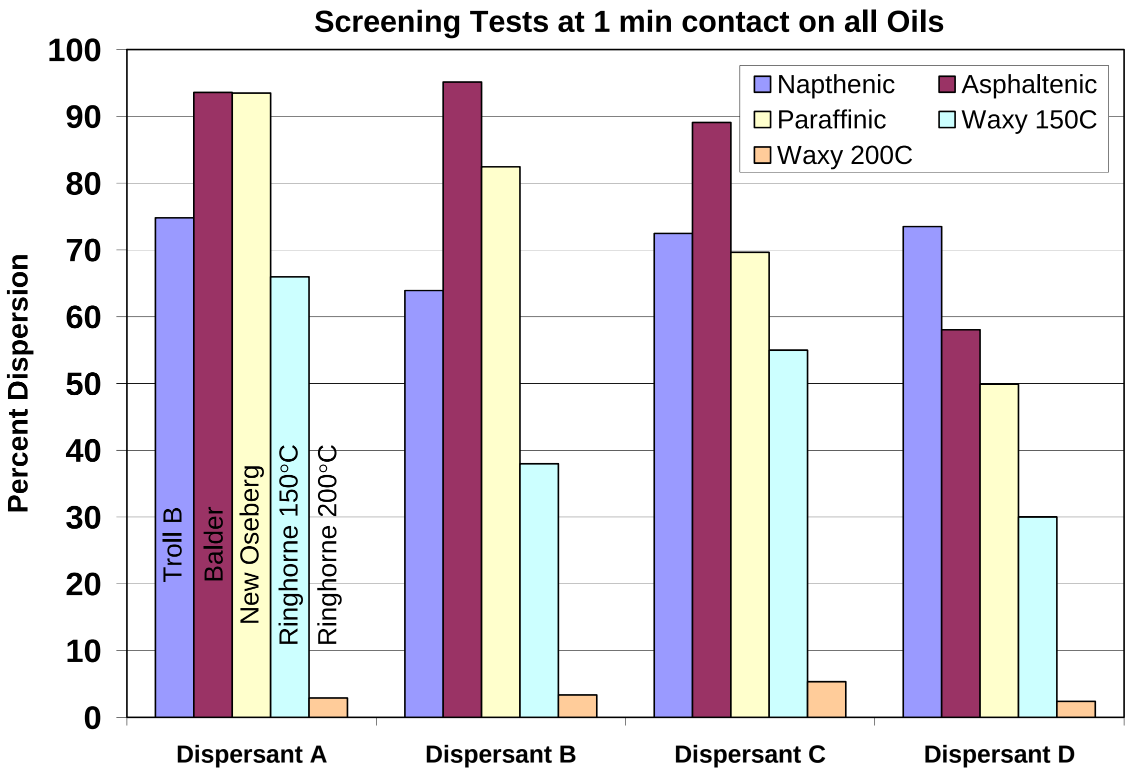

Figure 4. Results of screening tests on all oils to evaluate four commercial dispersants at 15°C.

Figure 5 shows the available data from tests performed at 15°C using Dispersant A and Dispersant B on all oils with contact times from 1 minute to 2 weeks. This figure is not complete. The absence of a bar means results are pending test completion and some results are based on a single test. A 1-hour test of the napthenic oil and Dispersant A is not shown in the figure but results are consistent with the trend seen (79% dispersion).

For the napthenic and asphaltenic oils, some testing out to 2 weeks of contact time are complete. The results indicate that for these oils the surfactants maintain their activity over this time period. For the napthenic oil, more effective dispersion was observed as contact time increased.

The paraffinic oil was readily dispersed out to 1 week of contact. Only Dispersant A has been evaluated at 2 weeks on the paraffinic oil. The dispersion of the paraffinic oil using Dispersant A reduced to 32% at 2 weeks.

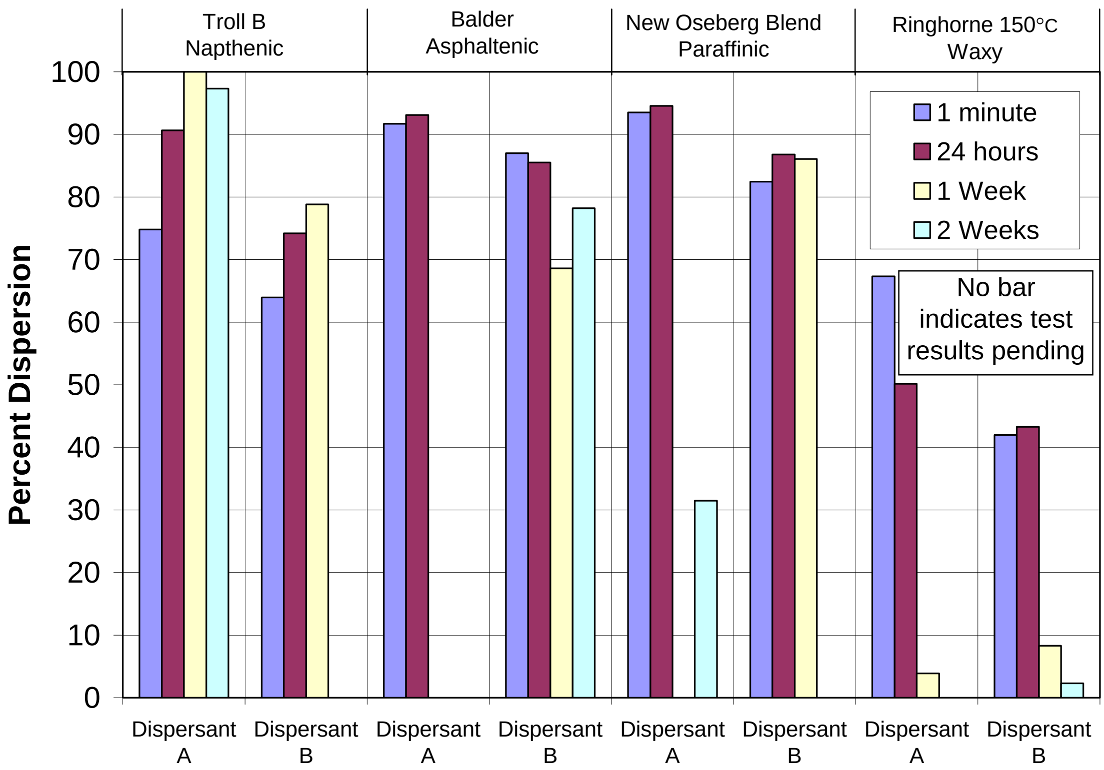

Figure 5. Preliminary results from testing performed using Dispersant A and Dispersant B with extended contact times at 15°C.

The test program includes a dispersant with a known formulation (the model dispersant) to facilitate analysis of the leaching of surfactants from the oil phase to the seawater over time. The model dispersant was premixed with the oils prior to performing the IFP tests. Some dispersant effectiveness testing is complete, however, the LC-MS testing to evaluate the leaching of the model dispersant from the study oils is not completed and no data are presented here.

Figure 6 shows the preliminary results evaluating the effectiveness of the model dispersant on the four study oils. The model dispersant performed somewhat better than the commercial dispersants for most runs most likely because of the premixing. The only exception so far is that the model dispersant effectiveness dropped below 20% after 24 hours of contact with the waxy crude. The asphaltenic oil remained dispersible after 1 week of contact. The 2 week data wasn't completed. For the paraffinic oil, the 1 week data wasn't completed, however, the 1 minute, 24 hours, and 2 week results are consistent with the commercial dispersants.

Comparing the model dispersant to the commercial dispersant indicates that, for these tests, penetration of dispersant into the oil phase may not have limited dispersion because the drop-wise addition of commercial dispersants to the oils resulted in findings equivalent to the premixing tests with the model dispersant. For both the model and commercial dispersants, the reduction in effectiveness seen for the paraffinic oil after 1 week and the waxy oil after 24 hours is possibly the result of a physical change in the oil that limited the formation and transfer to the water column of dispersed oil droplets. More testing is needed to confirm.

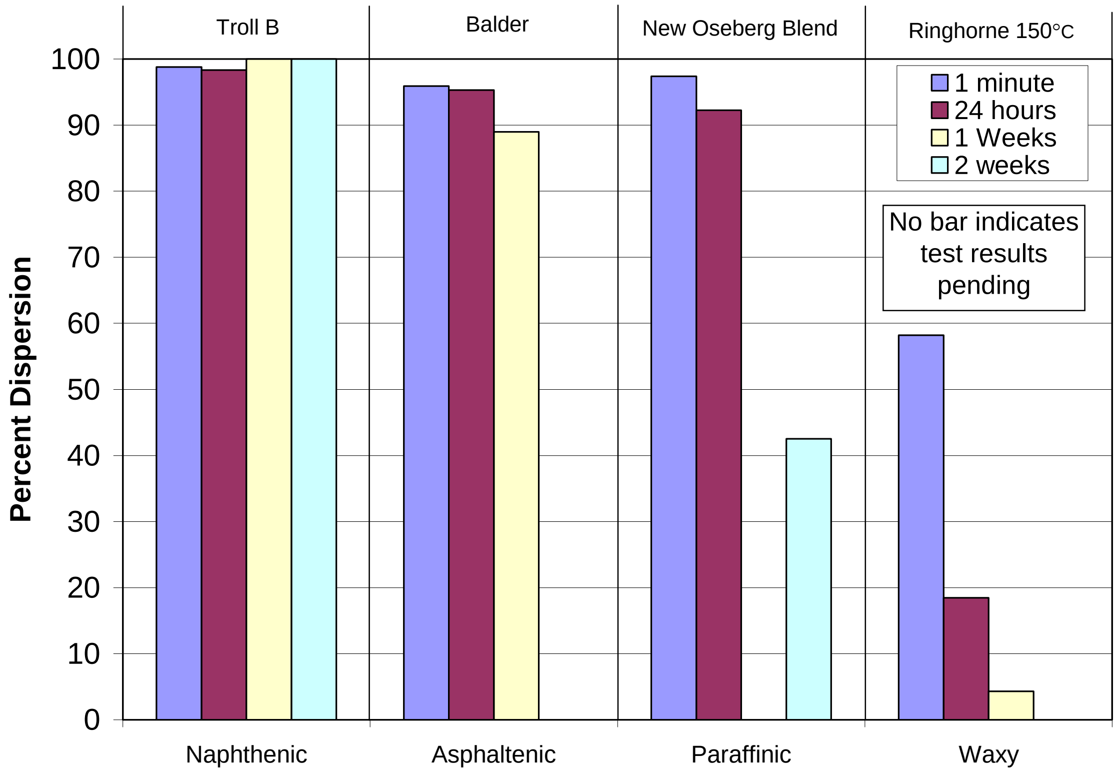

Figure 6. Preliminary results from testing performed using the model dispersant with extended contact times at 15°C.

Considering that the low-to-medium mixing energy of the IFP test may not simulate the energetic conditions possible with breaking waves, those oil and contact time combinations that resulted in dispersion below 20% but above 5% will be retested at some point using a higher energy dispersion-effectiveness test—the Mackay-Nadeau-Steelman (MNS) test (Mackay et al., 1978). These additional tests will simulate periods of calm followed by a high-energy event such as a storm.

Although the quality of the dispersion, i.e., the size and stability of the dispersed oil droplets, will not be measured in this study, the IFP test itself requires the generation of relatively small oil droplets. This is because the dispersed oil flows out of the bottom of the dispersion vessel to the collection chamber (see **Figure 2**). Fast rising coarse oil droplets are unlikely to flow out of the dispersion vessel.

Preliminary Conclusions

The primary goal of this study is to provide data for oil-spill responders that allow science-based decisions on whether to apply dispersants to spills in low sea states. This is an ongoing project that was roughly 50% complete at the time of this writing. The project is scheduled to be completed by year-end 2006.

The results for IFP dispersant effectiveness tests performed at 15°C indicate that both napthenic and asphaltenic oils can be effectively dispersed if dispersant is applied within 24 hours after a spill even if calm conditions persist for 2 weeks. A paraffinic oil remained dispersible 1 week after application. A waxy oil became significantly less dispersible sometime between 24 hours and 1 week after application.

The preliminary conclusion from this study is that dispersants should be considered for spills in calm conditions if applied early when the oil is still amenable to dispersant penetration.

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