Recent Results from Dispersant Testing

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Abstract
Recent results of dispersant testing are reviewed, including slight revision in the dispersant analytical procedures, testing of new products, testing of long-term stored dispersants, and a comparison of Corexit 9527 and 9500 dispersant formulations.

The procedure for the Swirling Flask Test has not altered appreciably since its inception, however the analysis of the quantity of oil dispersed has undergone significant changes. The originally-developed procedure made use of colorimetric analysis, but has since advanced to gas chromatographic analysis. With the change in analysis method, however, a host of subtle changes have been required that were not considered when first changing from colorimetry to gas chromatography. A number of minor improvements have been made to the procedure to correct and upgrade facets of the analysis.

Several new dispersant products have been tested, results of this testing will be summarized.

A test series was conducted on the dispersant Corexit 9527 that had been stored for more than 20 years in a tank truck. The tests show that the effectiveness, toxicity and colour of the product did vary somewhat between the three levels, however this might not be significant in terms of field effectiveness.

A comparison of the laboratory effectiveness of Corexit 9527 and 9500 was completed. Results show that the effectiveness of 9500 is generally greater than that of 9527, however, this is not related to the amount of effectiveness. Generally, the higher the effectiveness, the greater the effectiveness of 9500 and vice versa. Statistically, about 1/4 of the time, 9527 is more effective than 9500.

1.0 Introduction
Studies on various facets of dispersants continue at Environment Canada's laboratories. This paper reports on several smaller studies related to dispersant effectiveness. During the years from 1985 to 1990, Environment Canada and the United States Minerals Management Service endeavoured to develop new laboratory dispersant effectiveness tests that provided repeatable results with systems that have relation to the open waters where dispersants are actually used to combat oil spills. During this time, five tests were examined out of a total suite of about 20 possibilities. Initial work was done on the possible test concepts to assess potential for further study. The tests that were selected for detailed comparative testing were
now begins at 10% effectiveness for heavy oils. As a result, the detection limit on the Swirling Flask Test is now 10%; all oils dispersing less than 10% fall below the range of calibration standards, and are reported as <10% effectiveness. The limitation in not being able to quantify effectiveness of dispersed mixtures that are below this threshold, is not considered significant, as the error and standard deviation below 10% is nearly as great.

The revised procedure is now simplified, with a single analytical method to apply to all oil types, and a detection limit of 10% dispersant effectiveness. Appendix A contains the newly revised procedures. This is also the procedure used in the following sections.

3.0 Results of Testing of New Products

Several new products were tested for both dispersant effectiveness and for effectiveness as a surface washing agent. The dispersant test procedure followed that in the appendix and was implemented using the standard ASME oil. The properties of this oil are given in Jokaty et al. (1999). The surface washing test results followed procedures given in the literature (Fingas et al., 1995b). This test is simply a measure of the removal of Bunker C on a trough by water flushing, after the oil is treated with a ratio of 1:5 of the agent.

Test results are given in Table 1.

Table 1 shows that the products, Dasic Stickgone and Dispiston showed a moderate dispersant effectiveness and that the products, Z1-800 and Z1-808 show a high dispersant effectiveness. As surface washing agents only the Dasic Stickgone showed a moderate dispersant effectiveness and only in fresh water. This is actually an interesting result because most dispersants show little or no effectiveness as a surface washing agent.

<table>
<thead>
<tr>
<th>Product</th>
<th>Dispersant Effectiveness</th>
<th>Surface Washing Result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Std. Dev.</td>
</tr>
<tr>
<td>Dasic Stickgone N5</td>
<td>31.8</td>
<td>3.7</td>
</tr>
<tr>
<td>Dispersant SPC 1000</td>
<td>32.2</td>
<td>3.0</td>
</tr>
<tr>
<td>SuperDisperton 25</td>
<td>18.1</td>
<td>1.6</td>
</tr>
<tr>
<td>SX-100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Vynac DSP 2823</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Z1-800</td>
<td>54.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Z1-808</td>
<td>58.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>

4.0 Storage of Dispersants over Time

One of the problems with dispersant use is that dispersants are often stored for many years and then the question of their efficacy arises. Over the years ESD has tested old stock dispersants, mostly from the Canadian Coast Guard, to assess their efficacy. The Coast Guard stock in Newfoundland is about 20 years old and is maintained in a tank trailer. Before the most recent test, the trailer had not moved for about 6 years. Sampling at three layers (top, middle and bottom; and a mixed sample)
Table 2 Long Term Storage of Corexit 9527

<table>
<thead>
<tr>
<th>Layer</th>
<th>Average</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>38.4</td>
<td>5.0</td>
</tr>
<tr>
<td>Centre</td>
<td>34.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Bottom</td>
<td>48.3</td>
<td>7.3</td>
</tr>
<tr>
<td>Stirred</td>
<td>42.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Average</td>
<td>40.4</td>
<td>5.4</td>
</tr>
</tbody>
</table>

The results show that there is a small differential in effectiveness between the top and bottom layers, within the standard deviation noted. This difference is about twice as when the top, centre and bottom layer effectiveness values are averaged.

The difference also matches the colouration differences noted in the material as placed by darker colours in the lower layer of the tank. There appears to be a 

settling of the heavier surfactants. The colouration differences, however, may be due to rust or dirt particles collecting on the bottom. The variation in colour was measured using a Perkin-Elmer Model 552A

spectrophotometer. The stirred sample was used as the reference, with changes in absorbance being recorded for the other three - a positive number indicates greater absorbance, and a negative number indicates lower absorbance. The wavelengths used were arbitrarily assigned, based on limits of response, covering the widest range possible. The results are in Table 3.

Table 3 Colour Variations in the Long-Term Stored Dispersant

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Top Sample</th>
<th>Centre Sample</th>
<th>Bottom Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.008</td>
<td>0.012</td>
<td>0.125</td>
<td>0.012</td>
</tr>
<tr>
<td>0.012</td>
<td>0.006</td>
<td>0.159</td>
<td>0.012</td>
</tr>
<tr>
<td>0.008</td>
<td>-0.001</td>
<td>0.049</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Absorbance readings for the top and centre samples indicates that there is no significant difference between the top, centre and mixed samples. The higher absorbance of the bottom sample is consistent with a visually darker colour noted. It was debris in the sample, possibly rust, which may be imparting the colouration to the surrounding solution.

These data indicate that there is no significant effects as a result of the long term storage of this particular batch of Corexit 9527.

Comparison of the Effectiveness of Corexit 9527 and Corexit 9500

Several theories on the comparative effectiveness of Corexit 9527 and 9500 have been proposed. For example, some speculation was that 9500 was much more active on heavy oils and that Corexit 9527 was more effective on certain specific oils. Sufficient data now exist to compare these two products over a wide range of oils.

Table 4 gives the numerical summary of the test data. These data are taken from the oil properties database (Jokuty et al., 1999) and values were measured by the methods given in the appendix with the exception that the published version that was current during the year, would have been used. Figure 1 shows the same data graphically, with the best fit line through the data.
This comparison shows that generally Corexit 9500 is slightly more effective than Corexit 9527. There does not seem to be a heavy oil effect. This comparison is somewhat less effective because of the broad spectrum of data used, some of the older data may be less accurate. Furthermore, the Corexit 9527 data is older and was rounded down to steps of 5. However, the trend is still clear that the effectiveness of 9500 is higher for those oils where effectiveness is very good and only slightly more effective on the heavier, less dispersible oils. In about 1/4 of the cases, Corexit 9527 is more effective.

6.0 References


Appendix A  Swirling Flask Test Method

A.1 Summary of Test Method
Dispersant is pre-mixed with oil, placed on water in a test vessel. The test vessel is agitated on a moving table shaker. At the end of the shaking period, a settling period is specified and then a sample of water taken. The oil in the water column is extracted from the water using a pentane/dichloromethane mixture and analyzed using gas chromatography. The extract is analyzed for oil using a gas chromatograph equipped with a flame ionization detector (GC-FID). Quantification is by means of comparison to an internal standard. Effectiveness values are derived by calibration at fixed effectiveness values.

A.2 Reagents and Equipment

Reagents
Water purified by reverse osmosis or equivalent means is used for the test water. Dichloromethane is distilled in glass grade. Pentane is distilled in glass grade. Fine granular salt, non-iodized, is used for making the salt water. The chemical dispersant is used as supplied by the manufacturer. Oil is used as received.

Apparatus
A modified 120 ml Erlenmeyer flask is used as the test vessel. A side spout is added to enable taking the water sample with minimal disturbance of re-surfaced oil. These are illustrated in Figure 2. Modified vessels are available from Pro Science Inc., Toronto (416-699-9901).

The shaker is a moving table shaker with an orbital motion of 1 inch and fitted with flask holders. Ideally, such shakers should be constructed in enclosed environmentally-controlled chambers, thereby increasing temperature control. If such an enclosed chamber is not used, the measurement should be conducted inside temperature-controlled rooms. (The New Brunswick Environmental Shaker model G27 (New Brunswick Scientific, Edison, NJ) is one enclosed shaker that meets specifications.)

Analysis is accomplished using a gas chromatograph equipped with a flame ionization detector. The Hewlett Packard 5890 GC/FID with Chemstation software package is an equivalent unit. The column is a fused silica DB5ms column (J & W Scientific, Folsom, CA or equivalent).

The following is a list of other necessary supplies. Suppliers of suitable units are given in brackets. Equivalent supplies are acceptable in every case.

- 15 - 12mm x 32mm crimp style vials with aluminium/Teflon seals (Supelco or equivalent)
- 12 - 125 mL glass, Erlenmeyer flasks, modified with the addition of a drain spout attached to base (available from Pro Science Inc., Toronto, Ontario, phone 416-699-9901)
- 6 - 25 mL glass, graduated mixing cylinders and stoppers
- 6 - 125 mL glass, separatory funnels and stoppers
- 6 - 100 mL glass, graduated mixing cylinders and stoppers
- 250 ml. glass, separatory funnels and stoppers
- 50 ml. glass, graduated cylinders
- 5 to 25 ml. dispenser or glass graduated cylinders
- 10 μl. to 100 μl. positive displacement pipette (Mandel Scientific Co. or equivalent)
- 1 ml. positive displacement pipette - variable volume (Mandel Scientific Co. or equivalent)
- 1 - digital timers
- 20 ml. to 100 ml. dispensor or graduated cylinders
- 1 - 20 L. plastic carboy

1. Interferences and Sources of Error

Interferences can be caused by contaminants, particularly residual oil or sludges in solvents, on glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All glassware must be thoroughly cleaned. The cleaning process includes rinsing with dichloromethane to remove the oil, followed by rinsing three times each with tap water, purified water, acetone and then acetone. Once cleaned, precautions must be taken to minimize interferences that glassware with surfactants to prevent unwanted interferences.

Dispersant effectiveness is very susceptible to energy levels. Table top shakers generally start and stop slowly. Shakers that start motion rapidly and stop quickly impart a high energy to the system and thus cause more dispersion than would be the case with a normal shaker. Furthermore, this variation would not be controllable. The shaker table used should be observed for rapid movements or stops to ensure that it is usable for these tests. The rotational speed of the shaker should be checked with a tachometer every week.

The Erlenmeyer flasks used in this test are taped and the energy level varies with the amount of oil. The dispenser is used to fill the vessels with water should be properly checked by weighing the amount of water delivered.

The output is highly sensitive to the volume of oil, water and extractant used. All pipettes and dispensers should be calibrated on a weekly basis using water and a balance with an accuracy consistent with the weights being measured.

The use of positive displacement pipettes is mandatory for all controlled losses of microtire quantities. Use of volume displacement pipettes will result in incorrect results due to the viscosity of the dispersants and oils, the variable costs of the oils to be tested (some semi-solid) and the density of dichloromethane.

The order of addition of the dispersant and oil has effects on the accuracy of mixtures. As the dispersant may interact with the vessel walls if added first, thereby altering the quantity available in the premix. It is therefore important to add oil to vessel first, and add the dispersant directly to the oil. The second addition of oil is added simply because it is easier to control a large volume of oil than a minute volume of dispersant when attempting to achieve a specific ratio of 25:1.

Following surfactant addition, vigorous mixing is required to thoroughly disperse the sample. Sharp, manual strokes are suggested for light oils, while some oils may require stirring with a glass rod or spatula.

There are indications that the results for some premixed dispersant/oil combinations change over time. It is necessary to take precautions against this potential source of variation. The testing should be concluded as soon after the premix is prepared as possible, generally within a few hours. Results from samples stored for periods as long as a week should not be considered reliable.

Since the performance of the dispersant is affected by salinity, thorough mixing of the salt water is required. Care should also be observed to avoid evaporation from open containers of salt water. Over a period of days and weeks, the loss of water can significantly increase the salinity. An airtight closure is recommended to maintain salinity levels at 3.3%.

Temperature is a factor in dispersion, so it is important that all components (salt water, premix and temperature controlled chamber) are stable at 20°C before starting.

Extreme care should be taken when applying the oil to the surface such that mixing does not occur. The oil should gently glide across the water to form a sheen. If the oil streams out into the water, the agitation can disperse the oil, increasing the amount of oil dispersed and erroneously raising the final dispersion result.

Water in the spout attached to the swirling flask may contain more or less oil than the water in the flask itself. Therefore, it is important to drain the contents of the spout (about 3 ml.) before sampling. Oil sometimes migrates into the spout and may form plug. This is especially true for heavy oils. It is important that the plug does not enter the sample.

The performance of the test can be verified and compared using standard oil and dispersant samples. These are available at no charge, but in limited quantities, from the Emergencies Science Division, Environment Canada, Ottawa, Ontario. Phone: 613-998-9622.

A.4 Procedures

A.4.1 Crude Oil and Dispersant Sample Collection and Storage

The bulk oil is mechanically mixed for 24 hours prior to obtaining a working sample. Working samples are stored in 2 L high-density polyethylene bottles with polypropylene screw closures. The working sample is mechanically shaken for 30 minutes prior to removing a sub-sample for testing. When not in use, all samples should be stored in a temperature controlled room at 5°C. The dispersant is manually shaken, vigorously, prior to sampling.

A.4.2 Premix Sample Preparation

A small amount of oil is weighed into a 5 ml. amber vial with Teflon lined cap (approx. 1.0 ml). Approximately 100 mg of dispersant is added to the oil. Oil is added until a 1.25 ratio of dispersant to oil is achieved (approx. 2.5 ml oil is added). The sample is well mixed by manual shaking or stirring.

A.4.3 Salt-Water Preparation

Grain salt is weighed added to water from reverse osmosis (RO) filtration to obtain a 3.3% (w/v) solution. The water temperature is brought to 20°C before use.

A.4.4 Swirling Flask Preparation

The 120 ml of salt water is placed into a 125 ml modified Erlenmeyer flask. The flask is inserted into the flask holders on the oscillating table of the shaker.
A 4.8 Calibration Standards

A series of 6 oil in solvent standards are prepared for evaluating the efficiency of the dispersant for each dispersant/oil combination. The volume of premixed dispersant/oil solution for each standard is selected to represent a percentage efficiency of the dispersed oil, e.g., $50 \mu L = 50\%$ efficiency (see Step 4.10 below for method of choosing calibration standard volumes). The dispersant/oil mixture is then accurately measured and applied to the water surface, and treated in the same manner as the samples (see Step 4.4 and 4.5 above). At this point, the entire volume of water is transferred to a 250 mL separatory funnel and extracted with 3 portions of 20 mL of a solvent mixture of 70:30 dichloromethane:petroleum ether. All oil is extracted, including the oil slick and oil on the walls of the swirling flask test vessel, using the volume of extraction solvent to rinse the flask of remaining oil before adding to the separatory funnel. The extracts are combined in a graduated cylinder and topped up to a total volume of 60 mL. Chromatographic analysis is then performed to determine the petroleum content by integrating the resolved peak area by the following equations:

$$RPH = \frac{A_{total}}{A_{int}} \times \frac{1}{RRF} \times 20 (\mu g) \times \frac{60}{0.9} \times 120/120$$

which simplifies to:

$$RPH = \frac{A_{total}}{A_{int}} \times 1330/RRF (\mu g)$$

Where:

- $RPH$ is the Resolved Petroleum Hydrocarbon amount in $\mu g$
- $A_{total}$ is the total integrated area
- $A_{int}$ is the area of the internal standard
- $RRF$ is the Relative Response Factor which in turn is given by $RRF = \frac{A}{A_{std}} \times \frac{C_{std}}{C}$, where $A$ is the area, $C$ is the concentration of the compound of interest.

A 4.9 Selecting the Volume Range of the Calibration Standards

The volumes of the six calibration standards are chosen such that the $RPH$ determined for each of the six samples of each dispersant/oil combination fall within the $RPH$ range of the standards. The following guide is used to determine the range of standards for each type of oil being dispersed:

- **Heavy Oil**: 10, 15, 20, 25, 30, 35%
- **Medium Oil**: 10, 20, 30, 40, 50, 60%
- **Light Oil**: 30, 40, 50, 60, 70, 80%

A 4.10 Gas Chromatograph Parameters and Sequencing

Resolved Petroleum Hydrocarbon (RPH) analysis for $C_{4}$ through $C_{30}$ n-alkanes of the dispersed oil-in-water is carried out by high resolution capillary GC/FID under the following conditions:

- **Column**: 30 M X 0.25 mm id HP-5 fused silica column (0.10 $\mu m$ film thickness)
- **Detector**: flame ionization detector
- **Autosampler**: Hewlett Packard 7673 or equivalent
- **Inlet**: Splitless
Carrier: helium, 1.6 mL/min, nominal
Make up: helium, 28.4 mL/min
Detector air: 400 mL/min
Detector hydrogen: 30 mL/min
Injection volume: 1 μL
Injection temperature: 290 °C
Detector temperature: 320 °C
Temperature program: 50 °C for 1 minute, then 15 °C/min to 310 °C, hold 5 minutes. The total run time is 23.33 minutes.

Daily calibration: Alkane standard mixture of 20 ppm (containing 5-α-Androstan, selected alkanes, and α-Terphenyl in hexane) is measured before and following each sample set.

Cleaning Glassware
A rigorous cleaning program is undertaken throughout the experiment to prevent possible cross contamination and accumulation of surfactants on the glass. Glassware is thoroughly rinsed with tap and purified (RO) water and then dried between each experimental run. At weekly intervals, the lab ware is immersed in a 1% (v/v) solution of detergent or equivalent for 24 hours, followed by a final rinsing with tap and purified (RO) water and dried.

Calculation and Reporting
The percentage of dispersion is calculated by creating a calibration curve of the standard versus RPH and then taking the RPH of the unknown sample and setting the appropriate effectiveness value.

At least six measurements of the RPH and effectiveness should be measured. A standard deviation of more than double the average indicates poor reproducibility and the experiments should be repeated. RPH values that fall below the range of the lowest calibration value should be reported as less than the value of that calibration standard. This last known standard is also the detection limit of the test.

Figure 2 - The Swirling Flask Vessel