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Environmental Protection
Agency

Hazardous Waste Engineering
Research Laboratory
Cincinnati OH 45268

Research and Development

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Project Summary

A Field Dispersant Effectiveness Test

Anibal Diaz

The EPA's Releases Control Branch of the Hazardous Waste Engineering Research Laboratory has developed a rapid field test to evaluate the dispersibility of various commonly-transported oils to provide a data base for dispersant selection and application.

The Field Dispersant Effectiveness Test (FDET) is designed to generate droplet sizes that closely resemble the dispersion of oil occurring at sea. A fixed mixing intensity and time induces the effects necessary to produce the dispersion and reveal the effectiveness of the dispersant and dispersibility of the oil.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research report that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

This project was conducted to develop a Field Dispersant Effectiveness Test (FDET) and determine the dispersibility of various commonly transported oils (mostly crude). The test is required to be economical, simple enough for use in the field, and able to provide realistic results. In addition, the test was used to generate a data base that has much of the information necessary to determine the feasibility of dispersing a specific spilled oil and the chemical agent(s) best suited for the job.

Initial steps in this study included evaluating the theoretical implications of shaking a sealed container to generate the desired oil droplets. The primary constraint was to make the droplets small enough (i.e., 10-20 μm) to approach the values encountered with ocean induced dispersion. Various methods were considered for the mixing process and demonstrated that moving the mixture of oil, dispersant and water in a sealed tube along its longitudinal axis at a set frequency, stroke length and time would provide the necessary energy level to produce an acceptable dispersion.

The practical constraints of time saving and simplicity were met by utilizing an apparatus that was readily available from any hardware store or laboratory (see Figure 1). A standard half-inch test tube was used for mixing the dispersant, oil and water, and a flashlight, ruler, and stopwatch, for determining the separation of the oil from the water. The height of the clear water space under the dispersed oil layer provided the basis for calculating the Percent Dispersion. The entire test procedure requires less than fifteen minutes.

Finally, the FDET was used to evaluate various oils and dispersants and to develop a data base of oil dispersibility. Eighteen commonly transported crude oils and six dispersants were selected for the test (see Table 1). Nine of the oils were also sparged and six were emulsified with water to make them comparable to the oil at a spill site. Three different dispersant-to-oil ratios were used to determine the best combination and each test was performed in triplicate to meet data quality objectives. The results were put into a dBase III program for future reference.

Description of the Technique

The FDET has been designed to produce an oil dispersion that closely resembles

the product of wave action at sea. The turbulent flow theory was followed to arrive at the mixing required. Various manual methods were considered to obtain the necessary small scale turbulence. A ½-inch test tube to hold the mixture and a regulated hand shake for the mixing process proved successful.

The FDET relies on a specific mixing pattern. The mixture of dispersant oil and water is shaken in the stoppered test tube. The oil disperses as the tube is moved along the longitudinal axis at 120 cycles per minute with a 4-inch stroke length for one minute. Stronger mixing produces a smaller droplet size but fails to provide greater resolution between a good and a poor dispersion. Weaker mixing fails to provide sufficient stability to the dispersion.

The determination of percent dispersion requires a measurement of the visible water space in the tube after settling for 10 minutes. As expected, the oil droplets rise out of the water column leaving a clear space underneath a dark oil layer. A good dispersion allows a slower separation rate and a smaller distance between the tip of the tube and the opaque oil dispersion in the given time while a poor dispersion gives a faster separation rate and a larger clear water space under the oil dispersion in the same amount of time. The difference between the clear space, L, and the initial water height (i.e., 5 cm) provides a measure of the amount of oil dispersion left in the tube at that point. The dispersibility or effectiveness values are derived by substitution into the equation:

$$D = \frac{5\text{-}L}{5} \times 100\%$$

Where,
D = percent dispersed
5 = initial water height in test tube
L = height from tip of tube to opaque layer

Procedures

Test Fluids

The oils and dispersants considered in this study are listed in Table 1. Each oil was analyzed for various physical properties as a quality measure for future comparative studies of their dispersibility. Several samples were sparged with air and heated on a steam bath or emulsified with water to make them more similar to the oils found at a spill site. The treatment promotes the loss of the most volatile components of the oils and changes their viscosity, specific gravity and flash point.

Table 1. *List of Test Fluids*

Oils	*Source*
Arabian Light	*API/EPA SROP*
Prudhoe Bay	*API/EPA SROP*
South Louisiana	*API/EPA SROP*
No. 2 Fuel	*API/EPA SROP*
Bunker C	*API/EPA SROP*
Bunker C	*API*
Bachequero	*API — Exxon*
Laqunillas	*API — Exxon*
Mississippi Heavy	*API — Texaco*
BCF-17	*API — Texaco*
Topped Lago Medio	*API — Texaco*
Minas Crude	*API — Texaco*
Murban	*OHMSETT stock*
La Rosa	*OHMSETT stock*
Gabon	*OHMSETT stock*
Hybernia	*OHMSETT stock*
Amauligak	*OHMSETT stock*
Alberta	*OHMSETT stock*
DFM	*OHMSETT stock*

Dispersants	*Source*
D — 609	*Arco Chemical Co.*
1100WD	*British Petroleum*
1100X	*British Petroleum*
Corexit 9527	*Exxon Chemical Co.*
Magnotox	*Magnus Maritec Int'l, Inc.*
ECO Atlantol AT7	*ASPRA, Inc.*

These are the same changes that occur in the field.

Synthetic seawater was used for the tests to avoid the influence of variation in seawater composition. The test water was prepared by mixing salts with tap water in accord with the instructions given by ASTM D 1145-75.

Test Methods

The test procedure consists of four preparatory steps and the eight major steps illustrated in Figure 1.

The preparation for testing includes filling a test tube to 5 cm with the synthetic seawater, filling one dropper with oil and another with dispersant and custom fitting opaque shield over a flashlight to direct the illumination through a centrally located aperture.

The major steps include the shaking, settling, and measurement of a water/oil interface to determine the oil dispersion. Ten drops of oil and one drop of dispersant were mixed into the water in a stoppered test tube. The preferred mixing pattern involved moving the tube for 1 minute at 120 cpm with a 4-inch stroke length. The mixture was allowed to settle for 10 minutes, set the tube over the hole in the shield covering the beam of the flashlight and adjust an O-ring around the tube at the point light no longer penetrates through the mixture. The positioning of the O-ring indicates the highest point of translucence. The determination of the interface for clear oils may require lateral illumination of the tube and gradually moving the tips of two pens held in parallel between the light and the tube to the point that they fuse into one shadow. Subsequently, we measure the height of this interface, L, from the tip of the test tube to the O-ring and use that number to calculate the Percent Dispersion, D.

Results and Conclusions

It is possible to obtain a rapid evaluation of oil dispersibility, at the site of an oil spill, using readily available hardware from the laboratory and proper application of dispersants. A person responding to an oil spill would only need a copy of the FDET method, some dispersant, a couple of droppers, a ruler, and a test tube to determine the dispersibility of the oil. The test could be performed on a beach or a rolling ship without prior training and provide a report of good, fair, or poor dispersion that is comparable to laboratory test results.

The FDET relies on mixing variables that have been selected as a practical extension of the turbulence theory to generate droplet sizes that closely resemble the dispersion of oil occuring at sea. This study determined that a stroke length of 4 inches, a frequency of 120 cpm, and a shake time of one minute permitted adequate dispersion of the oil. A faster or longer stroke raised the stability of the dispersion, but made the test physically exhausting. A shorter or slower shake time made a less stable dispersion. The shake selected makes the test easier to perform, more precise and a better representation of dispersion at sea.

The settling time also affects the determination of the dispersion. Measurements after settling for 5 and 15 minutes do not allow differentiation between a good and a poor dispersion. The 5-minute measurement demonstrates insufficient equilibration of the droplet motion. The 15-minute measurement suffers from the restriction imposed by the height of the test tube. The tests showed that only the 10-minute measurement provides a clear differentiation between good and poor dispersion.

The FDET results obtained compare well with the results obtained with the EPA Revised Standard Dispersant Effectiveness Test (see Figure 2). Prudhoe Bay oil was tested with fifteen dispersants using both methods and the effectiveness values overlapped for eleven out of the

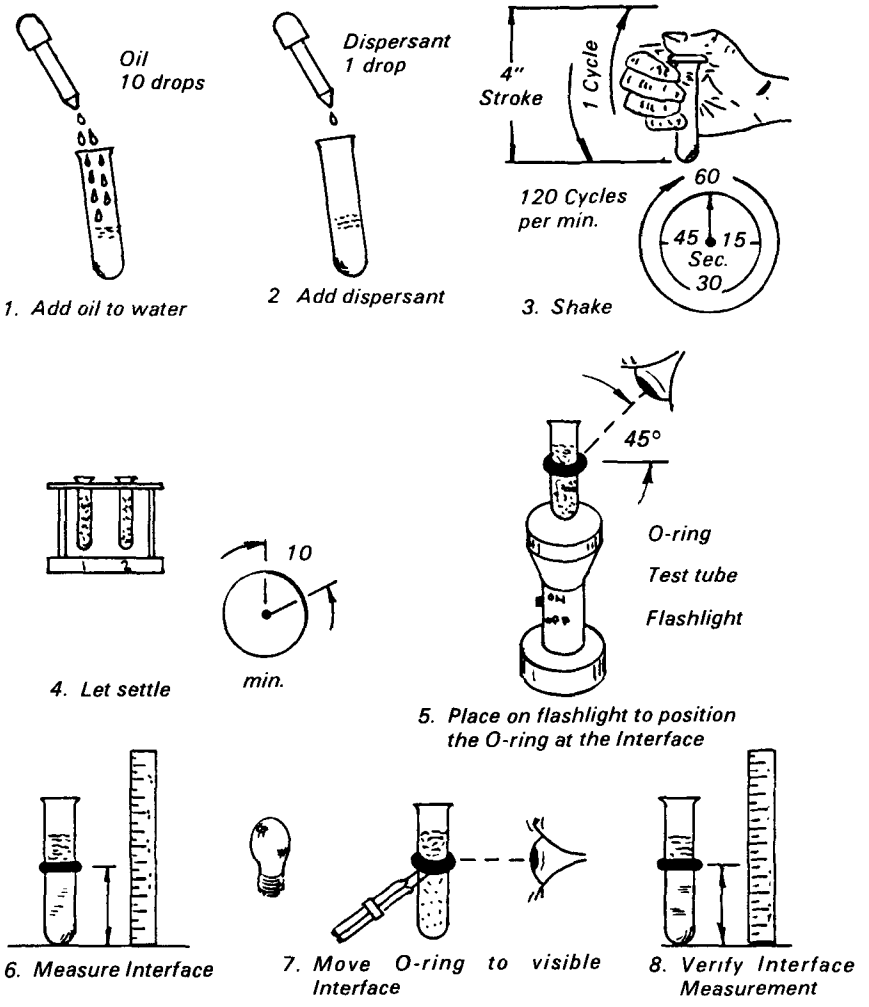

Figure 1. *The FDET Procedure.*

fifteen cases. Both methods agreed in classification of a good dispersion (60-100%), fair dispersion (20-59%) and poor dispersion (<20%).

All of the oils tested dispersed with four out of six dispersants considered. Eighteen oils were tested for dispersibility using up to six dispersants. Most of the oils dispersed more than 70% by volume with a good dispersant but failed to disperse by more than 40% with a poor dispersant. Removal of the most volatile components of the oil and emulsification with up to 30% water did not change the dispersibility of the oil.

The FDET has been used to establish a data base of information on oil dispersibility and dispersant effectiveness. The dBase III file covers the physical properties of the 18 oils tested and their dispersibility using up to 6 different dispersants. The data in this file will facilitate proper selection and application of dispersants in the field.

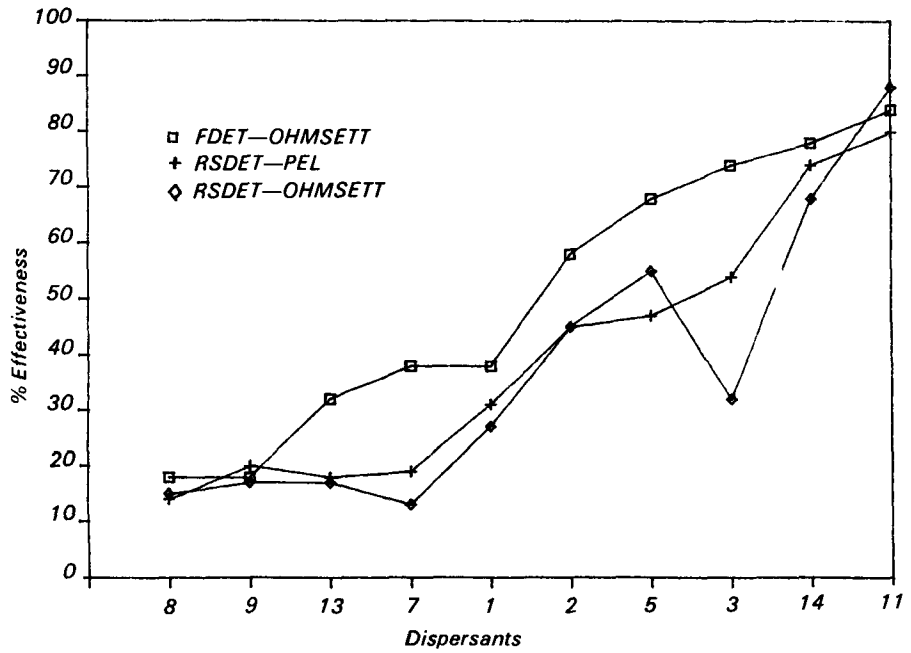

Figure 2. *Comparison of dispersibility of Prudhoe Bay crude oil effectiveness by FDET and RSDET.*

Anibal Diaz is with Mason & Hanger-Silas Mason Co., Inc., Leonardo, NJ 07737.
Richard A. Griffiths *is the EPA Project Officer (see below).*
The complete report, entitled "A Field Dispersant Effectiveness Test," (Order No. PB 87-234 886/AS; Cost: $13.95, subject to change) will be available only from:

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Project Summary

Sampling Oil-Water Mixtures at OHMSETT

Michael Borst

This report describes procedures developed for sampling oil and water mixtures.

Two procedures for sampling in containers are discussed: grab and stratified sampling. Both of these techniques require stripping free-standing water from the container bottom. The grab sample technique requires that the remaining fluids be thoroughly mixed before immersing a bottle through the resulting homogeneous emulsion. The stratified sampling procedure uses a sample thief to capture a segmented cross-section of the remaining fluids.

Two procedures for sampling flowing fluids were tested. The two sampling tubes tested were installed immediately downstream of a series of static mixers and a centrifugal pump. The sampling ports were a simple slotted tube and a pilot-shaped tube.

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Discussion

In the documentation of oil spill skimmer performance, a measure of the relative oil/water makeup of collected fluids is essential. The U.S. Environmental Protection Agency (EPA) conducted tests at the Oil & Hazardous Materials Simulated Environmental Test Tank (OHMSETT) in Leonardo, New Jersey to determine the usefulness of several techniques to obtain and analyze representative samples of oil/water mixtures. Two methods of sampling containers holding the mixed fluids and two methods of sampling flowing streams of the mixed fluids were tested.

Complete statistical studies were not conducted, but the tests indicate that the two methods for sampling containers of the fluids would give a precision of 3% oil. The first method entailed thoroughly mixing the oil and water to form a homogeneous emulsion. The sample was then taken by lowering a bottle through the emulsion to obtain a 100 ml sample for later analysis. The second method used a stratified sampling thief to capture a representative cross-sectional core of the fluids. The entire sampler was then sent to the laboratory for analysis. Tests were conducted using the stratified sampler to determine if the complete analysis could be abbreviated for field application, where speed rather than accuracy may be the prime consideration. These tests showed that, while order-of-magnitude results could be obtained, significant deterioration of precision should be expected. The selection of the method used in the field would depend on the use of the sample and support facilities available as well as the shape of the container sampled.

Two methods of sampling flowing streams were investigated. One method used a slotted sampling port; the second method used a pitot-shaped tube for the sampling port. In both cases, the sampling port was located immediately downstream of an in-line static mixer. The analysis of samples taken through the two ports each gave results within the precision of the comparison technique. The use of the static mixer to eliminate radial nonsymmetry in the flowing liquid appears to make the selection of samples purely arbitrary.

These tests were performed using only OHMSETT Circo X medium oil and salt

water as the immiscible fluids. Highly viscous mixtures may affect the results of future application of either of the stationary techniques. When sampling materials other than oil and water, chemical compatibility of the materials with the sampling device must be considered.

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***Richard A. Griffiths** is the EPA Project Officer (see below).*
The complete report, entitled "Sampling Oil-Water Mixtures at OHMSETT," (Order No. PB 88-102 892/AS; Cost: $11.95, subject to change) will be available only from:
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