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THE EFFECTIVENESS OF DISPERSANTS: VARIATION WITH ENERGY

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ABSTRACT: *A study of the relationship of dispersant effectiveness and mixing energy was performed. Energy was varied by changing the rotational speed of a specially designed apparatus. The effects of dispersant type and oil type were also measured. The stability of the resulting emulsions was gauged by measuring the amount of oil that remained in the water column over time.*

The findings are that each oil-dispersant combination shows a unique threshold or onset of dispersion. The effectiveness goes up linearly with energy, expressed as flask rotational speed. Natural dispersion was also measured and shows behavior similar to that of chemical dispersion, except that the thresholds occur at a higher energy and effectiveness rises more slowly with increasing energy. Effectiveness (defined as the percentage of oil in the water column) rises rapidly to 80 to 90 percent with increasing energy for light oils treated with chemical dispersants. Heavier oils will disperse, but to lesser effectiveness values.

Differences in energy have been cited often as the reasons for the varying results of dispersant effectiveness tests in both field and laboratory. Difficulties in varying and measuring energy have left the variation of dispersion and mixing energy largely unstudied. Energy, as it relates to the sea and oil spills, is a complex topic.[21] Descriptions of what is meant by energy relevant to oil dispersion vary. One way to describe energy is by measuring the wavelength and amount of turbulence near the surface.[4] Another definition describes sea energy in terms of steepness of waves and period.[14].

Several papers discuss the relationship between dispersion and energy, but little experimental work has been published.[3,5,10,13,15,23] Fundamental literature on surfactants does not deal with energy and effectiveness.[1,18]

Many different types of dispersant test procedures and apparatus are described in the literature.[8,19,20,22] Some work has been done on determining the reason for the poor correlation among test results. Most of the investigators cite energy as the most significant factor. The general conclusion has been that the differences in energy levels, and the way these have been applied to the oil-water mixture, result in effectiveness values that are unique. This paper presents results from a series of experiments, spanning two years, in which the energy applied to the system was varied over a wide range. Results show that energy is a very important factor in determining oil spill dispersant efficiency.

Experiments

Several rounds of experiments were conducted to determine the effect of varying energy. Several oils were used in these tests. Table 1 lists these oils and gives their basic physical properties.[2] The dispersants used in this study are the Exxon product Corexit 9527 (abbreviated "C9527" in some tables in this paper) and the Dasic product Dasic Slickgone LTD (abbreviated "Dasic" in this paper). All runs in which dispersant was used were performed with dispersant already mixed in the oil at a ratio of 1 to 25 by volume. This practice was adopted to achieve more repeatable results, as determined in earlier experiments in which both premixed and dropwise addition were used.[8] Salt water was prepared with sodium chloride to 33 ‰ or degrees salinity. All tests were done at a temperature of 20° C. Apparatus, oil, and water were left at these temperatures for at least 20 minutes before the beginning of each test to ensure thermal equilibrium. All tests were done in thermally controlled chambers.

An apparatus, called simply "the high-energy test," was developed to measure dispersion at very high energy levels. This vessel is square, with sides 30 cm long. The effect of the corners is to create high levels of turbulence. The volumes of oil and water used are 0.25 mL and 5 L, to yield an oil-to-water ratio of 1:20,000. This ratio was shown in a previous paper to yield repeatable results.[11] The mixing time is 20 minutes, and the settling time is 10 minutes before samples are taken. The mixing energy is supplied by a Brunswick shaker, a moving table apparatus. This shaker is capable of rotational speed variations from 50 to 450 rpm, with relatively good repeatability. The revolutions meter on the shaker is calibrated periodically with a tachometer to ensure accuracy.

A pipette is used to remove a 30-mL sample from the apparatus after the settling time. Analysis is performed by taking a sample of water from the test vessel after the run is complete, extracting the water with a solvent, and measuring the absorbance at three visible wavelengths (370, 340, and 400 nm), then assigning effectiveness on the basis of a calibration curve. Calibration curves are prepared in a manner similar to the actual runs. Water is used in these calibration runs to ensure that extraction efficiency is compensated for and to compensate for the coloration caused by small water droplets alone.

The high-energy apparatus was tested for validity by constructing two other apparatuses with different vessels. Tests were done with all three apparatuses, to ensure that the data showed no artifacts associ-

Table 1. Test oil properties

Oil	Description	Kinematic viscosity (*m^2/s at 15° C*)	Density (*g/mL at 15° C*)
ASMB	Alberta sweet mixed blend	8	0.84
Arabian light	Arab blend	40	0.87
Arabian heavy	Arabian blend	45	0.89
Bunker C light	Less viscous bunker C	200	0.93
Endicott	Cook inlet crude	85	0.91
Malongo	Angolan crude oil	100	0.88
North Slope	Prudhoe Bay Crude	55	0.88

ated with the type of vessel employed, the volume of water, the oil-to-water ratio, and the type of agitation. These results have already been reported in the literature.[11,12] All three test apparatuses yielded similar data.

Experimental results

Results are summarized in Table 2 and Figure 1. This figure illustrates the results of dozens of experiments. (A table of all results is given in the appendix.) The lines on the graph show the overall tendency of the data. Dispersion increases very rapidly from a low value to nearly 80 or 90 percent, and natural dispersion onset occurs at an energy level similar to or higher than that for chemical dispersion. Finally, the natural dispersion curve has a smaller slope than the chemical dispersion curve.

The energy is sufficient in the high-energy apparatus to disperse bunker C light. Tests on regular bunker C did not yield dispersion chemically or naturally. Bunker C grouped into large droplets on the surface during the natural dispersion runs, and partially during the chemical runs. This result indicates that the energy in the apparatus is insufficient to disperse this oil or that this oil is undispersable under test conditions. Onsets of natural dispersion are difficult to assign, but are the same as or lag those of chemical dispersion. The curves of natural dispersion have a smaller slope than those of chemical dispersion. In addition, the heavier oils tested are not dispersed to the same degree as other oils. The effect of chemical dispersant is to increase the dispersion amount by a large factor for the same level of mixing energy.

High-energy dispersion of oil is difficult to measure because of the high noise level in the data. As the average energy increases, so too does the amount of different energy levels, producing noise in the data. Table 3 shows the results of the application of linear regression to the natural dispersion data. The r^2 is low for a number of the oils, indicating the high noise level. Despite this, the slopes of the lines are very similar and are all 0.05 or similar values. The natural and chemical curves were tested for fit with a variety of functions in a previous paper.[11] The conclusion of this paper was that both were best fit with linear functions. The chemically dispersed oil data was addressed by applying linear regression to the onset portion and then standard statistics to the top or "saturated" portion of the graph. Effectiveness values taken at 50 to 100 rpm were used to calculate the onset of dispersion, and values above 100 rpm were used to calculate the "saturated" portion. Statistics on these manipulations are shown in Table 4. The r^2 values for the linear regression on the onset portions are very high, because typically only 2 to 4 data points are available. The initial slopes are again similar and are about 2.0. The effectiveness limits were calculated by taking an average of the high values. These values range from 64 to 90 percent.

Table 2. Summary results of the high-energy experiments (effectiveness values in percent for oil type and condition)

	Alberta sweet mixed blend			Arabian light			North slope		Arabian medium		Bunker C light		Malongo		Endicott	
rpm	Natural	With C9527	Dasic	Natural	With C9527	Dasic	Natural	With C9527	Natural	With C9527	Natural	With C9527	Natural	With C9527	Natural	With C9527
440	36	88	60	11	73	69	49	81	36	93	30	66	41	61	36	73
420	33	89	69	15	71	—	25	75	—	—	20	—	—	—	—	—
400	39	89	71	20	67	67	20	80	16	—	17	61	25	64	—	—
380	35	88	78	22	65	—	25	82	—	—	27	—	—	—	—	—
360	—	87	70	19	68	—	26	84	—	—	—	—	—	—	—	—
350	13	—	—	—	—	60	—	—	25	—	32	61	48	67	33	78
340	31	89	80	17	69	—	28	86	—	—	—	—	—	—	—	—
320	26	91	78	16	69	—	29	88	—	—	16	—	—	—	—	—
300	26	82	81	24	71	61	28	87	29	—	15	64	44	59	33	87
280	26	89	81	25	69	—	22	83	—	—	26	—	—	—	—	—
260	31	83	79	—	71	—	19	84	—	—	—	—	—	—	—	—
250	13	98	—	—	—	74	—	—	33	90	23	74	46	69	36	83
240	18	77	80	—	71	—	20	88	—	—	—	—	—	—	—	—
220	25	89	80	—	73	—	19	88	—	—	21	—	—	—	—	—
200	26	79	84	20	66	—	17	89	16	94	23	74	30	69	27	90
180	20	84	77	21	71	74	26	90	—	—	23	—	—	—	—	—
160	16	82	82	20	71	—	20	90	—	—	—	—	—	—	—	—
150	14	93	—	—	—	66	—	—	15	89	0	71	29	65	16	83
140	1	82	62	9	61	—	0	76	—	—	—	—	—	—	—	—
125	10	87	—	—	—	—	—	—	—	—	0	—	—	—	—	—
120	4	79	85	13	23	—	0	83	—	—	—	—	—	—	—	—
100	14	79	83	18	72	73	7	87	12	82	10	64	18	58	23	82
90	13	82	—	—	—	—	—	—	—	—	—	—	—	—	—	—
80	10	89	85	21	72	—	24	90	—	—	—	—	—	—	—	—
75	10	80	—	—	—	—	28	—	—	—	14	—	—	—	—	85
60	0	53	26	8	35	—	0	46	3	—	—	—	—	—	—	—
50	0	7	—	—	—	7	0	—	9	5	0	0	2	0	0	1

Note: C9527 = Corexit 9527

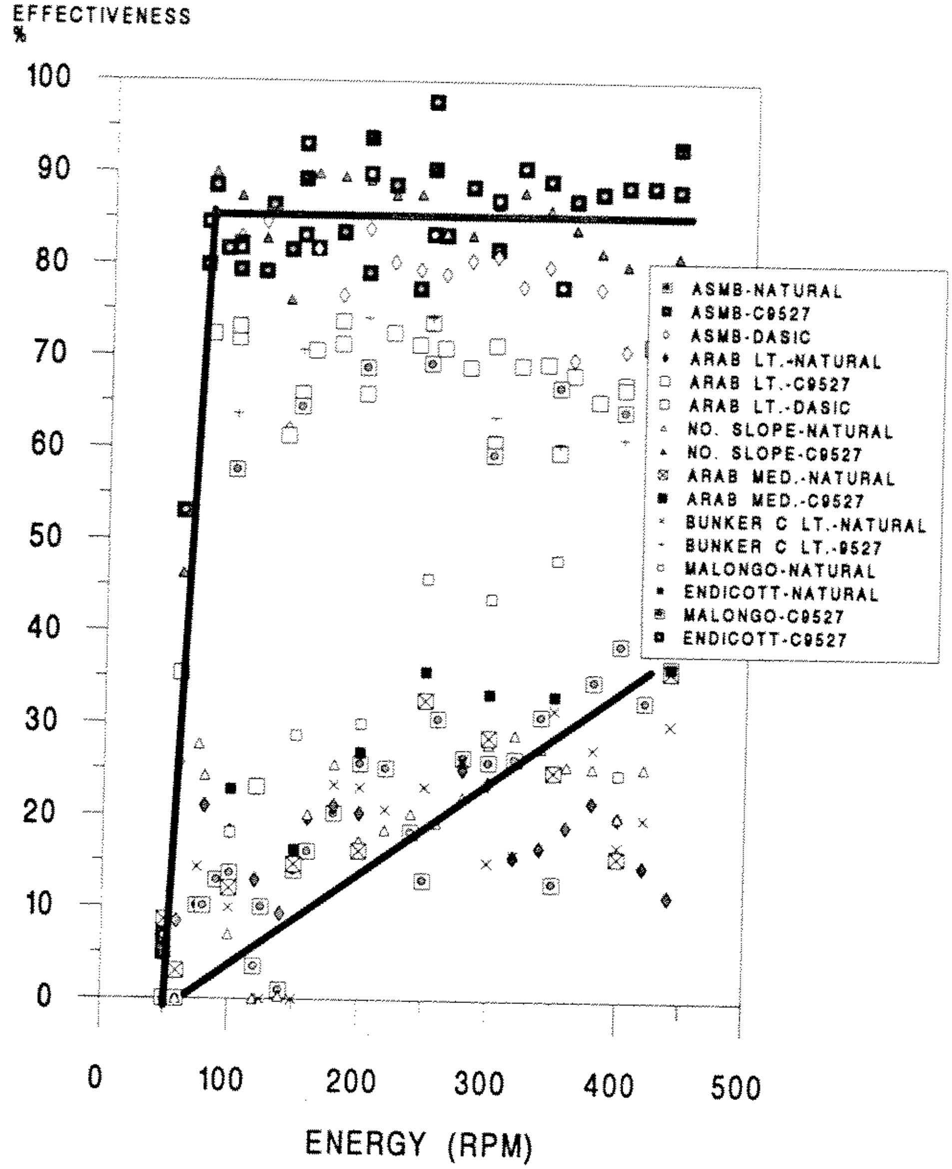

Figure 1. Composite data from the high-energy experiments

The standard deviations are generally within 10 percent of these values.

The high-energy dispersion curves of the oils are plotted separately, as shown in Figures 2 through 8. The chemically dispersed curves are added by approximating the initial slope calculations and maximum calculations, as given in Table 3. The natural dispersion curves were fit by using linear regression, as described earlier.

Table 3. Statistical data on the natural curves

Oil type	Slope	r^2
Alberta mixed blend	0.08	0.72
Arabian light	0.01	0.3
North Slope	0.06	0.41
Arabian medium	0.06	0.6
Bunker C light	0.05	0.37
Malongo	0.05	0.26
Endicott	0.05	0.66

Figures 2 through 8 show the same trend for each oil. Chemical dispersion shows rapid onset with energy to a high value, and then remains relatively constant with increasing energy. Natural dispersion onsets are difficult to establish, but appear to be close to or perhaps higher than their chemical equivalents. The slope of the natural dispersion curve is much smaller than that of the chemical dispersion curve. The natural dispersion curve is approximately linear.

Summary and conclusions

Chemical dispersion increases with energy (measured in these experiments as revolutions of the experimental apparatus in a given time period) in a linear fashion until a maximum is reached. For light oils this maximum is about 80 percent. For heavier oils the maximum is about 65 percent. The dispersion curve is very steep; that is, only a small amount of energy causes a large amount of change in dispersion. There exists an energy threshold below which little dispersion occurs. Chemical dispersion curves for different oils appear to be parallel (have similar slopes). This result may indicate that the mechanism is fixed and only the threshold varies.

Table 4. Statistical data on the dispersion curves

Oil type	Dispersant	Initial slope	r^2	Effectiveness limit	SD
Alberta mixed blend	Corexit 9527	2.6	0.94	86	5
Alberta mixed blend	Dasic	3	1	76	7
Arabian light	Corexit 9527	1.9	1	67	11
Arabian light	Dasic	2.2	1	68	6
North Slope	Corexit 9527	2.2	1	84	4
Arabian medium	Corexit 9527	2.6	1	90	5
Bunker C light	Corexit 9527	2.2	1	67	6
Malongo	Corexit 9527	1.9	1	64	4
Endicott	Corexit 9527	2.9	0.97	82	6

Note: SD = standard deviation

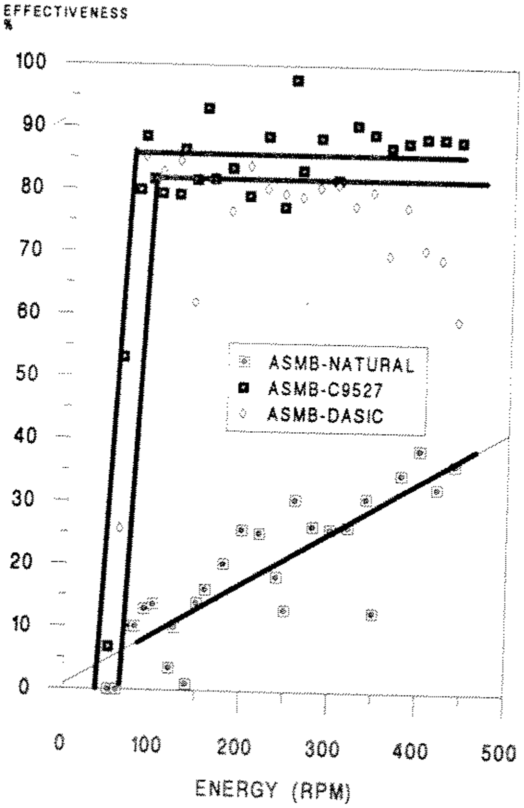

Figure 2. High-energy effectiveness for Alberta sweet mixed blend

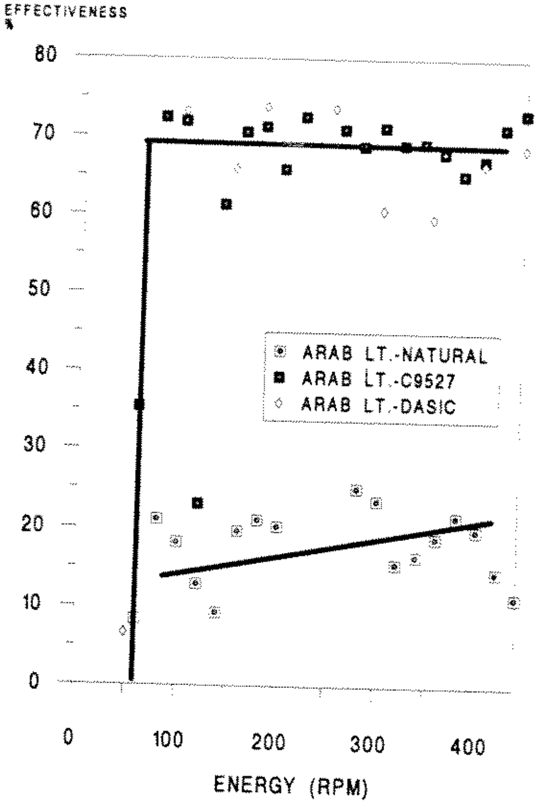

Figure 3. High-energy effectiveness for Arabian light crude oil

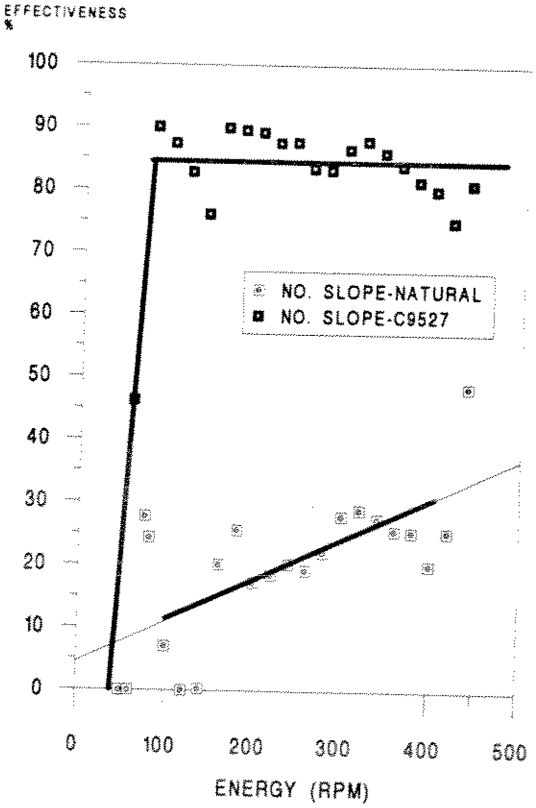

Figure 4. High-energy effectiveness for North Slope crude oil

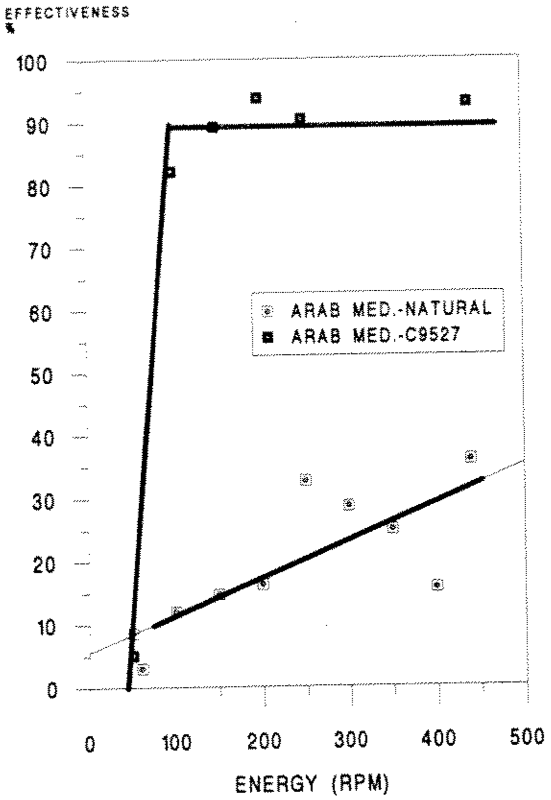

Figure 5. High-energy effectiveness for Arabian medium crude oil

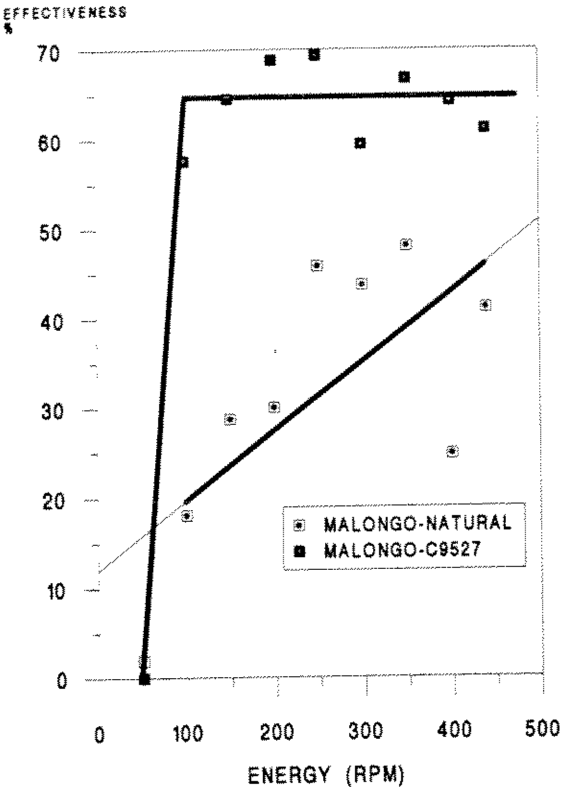

Figure 7. High-energy effectiveness for Malongo crude oil

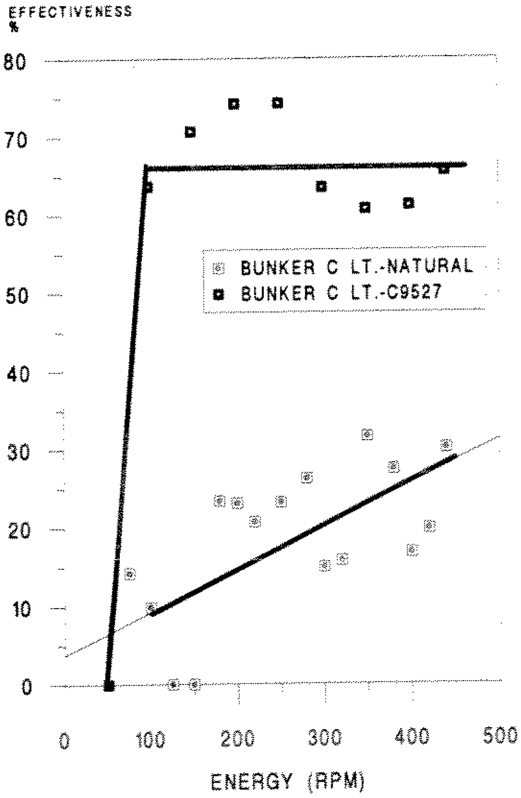

Figure 6. High-energy effectiveness for bunker C light

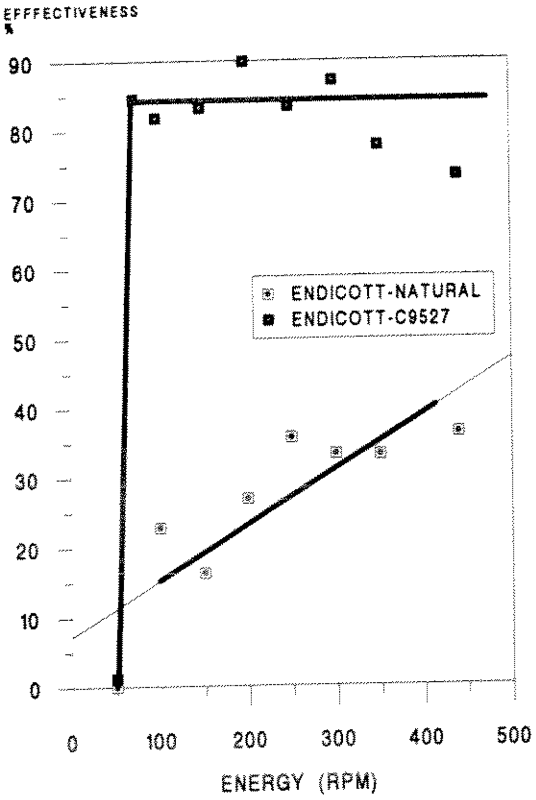

Figure 8. High-energy effectiveness for Endicott crude oil

Natural dispersion is analogous to chemical dispersion, except that the increase with energy is much less. The onset of natural dispersion is difficult to assign, but is similar to or higher than that of chemical dispersion.

The major question these experiments raise is how the energy in these tests relates to that at sea. There are a few observations that indicate that most typical sea energies actually occur at the low end of the energy range shown in the test data presented here. In one test at sea, Alberta sweet mixed blend and bunker C light were observed to start dispersing naturally at a sea state of Beaufort 6.[6] The *Ekofisk Bravo* oil was observed to disperse naturally at sea states around Beaufort 5 or 6.[7] It is recognized that turbulent energy is the important factor for dispersion. Technology does not exist at this time to measure this type of energy at sea and in the laboratory.

There may be potential for energy measurement in the future with laser doppler or hot wire instruments. This development would ensure that the findings reported in this study could be applied directly to sea surface observations.

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