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PHYSICAL AND CHEMICAL STUDIES ON DISPERSANTS: THE EFFECT OF DISPERSANT AMOUNT AND ENERGY

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SUMMARY

A study of the relationship of dispersant effectiveness with the factors of dispersant amount and mixing energy was performed. Energy was varied by changing the rotational speed of a specially-designed apparatus. .

The findings are that effectiveness goes up linearly with energy, expressed as flask rotational speed. Natural dispersion was also measured and shows similar behaviour to chemical dispersion except that the thresholds occur at a higher energy and effectiveness rises more slowly with increasing energy. The effect of dispersant amount at higher energies is that same as was found in previous studies for lower energies. The effectiveness increases exponentially with increasing dispersant amount. Although there exists a tradeoff between dispersant amount and energy to achieve high effectiveness values, energy is the more important factor.

INTRODUCTION

In a previous paper, the present authors have reviewed the effect of energy on dispersant effectiveness (Fingas et. al 1993). Energy has been often cited as the reason for the varying results of dispersant effectiveness tests in both the 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 (Robbins and Domenico, 1984; Donelan, 1978; Kitaigorodskii, 1983). Descriptions vary of what is meant by energy relevant to oil dispersion. Several papers discuss the relationship between dispersion and energy, but little experimental work outside of this laboratory has been published (Mackay et. al., 1983; Fingas, 1988a, 1989a, 1989b; Chau et. al. 1987; Wilson et. al., 1981). Fundamental literature on surfactants does not deal with energy and effectiveness (Mittal, 1976; Becher, 1977). Some work has been done on determining the reason for the poor correlation between test results. Most of the investigators cite energy as being 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 and with other parameters, dispersant amount in this case, being varied as well.

EXPERIMENTAL

This round of experiments builds on previous test results where only the energy level was varied. These results will be reviewed briefly. Similar test methods and apparatus were used in the new round of experiments.

The energy-only tests were performed using various oil types. Table 1 lists these oils and gives their basic physical properties (Bobra and Callaghan, 1990). The dispersants used in the energy study are the Exxon product Corexit 9527 (abbreviated "C9527" in some tables in this paper) and the Dasic product Dasic Slickgone LTS (abbreviated "Dasic" in this paper). All runs where dispersant was used, were performed with dispersant already mixed in the oil at a ratio of 1 to 25 by weight. This practice was adopted to achieve more repeatable results as determined in earlier experiments where both premixed and drop-wise addition were used (Fingas, 1991a). Saltwater was prepared with sodium chloride to 33 oo/o 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.

TABLE 1	**TEST OIL PROPERTIES**		
OIL	**DESCRIPTION**	**KINEMATIC VISCOSITY** (mm/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

An apparatus, called simply "the high energy test" in our laboratories, was developed to measure dispersion at very high energy levels. This vessel is square and of dimensions 30 cm. on all sides. 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 (Fingas et. al., 1991b). 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 100 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), and 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 apparatus with different vessels. Tests were done in all three apparatus to ensure that the data showed no artifacts associated 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 (Fingas et. al., 1991b, 1992). All three test apparatus yielded similar data.

For this paper the high energy apparatus was employed and only ASMB oil with the properties shown above, was used. The dispersant used for the dispersant variance was Corexit 9527.

HIGH ENERGY RESULTS FROM PREVIOUS WORK

A table of the high energy results is given in Table 2. Figure 1 illustrates the results of dozens of experiments. The lines on the graph are applied to show the overall tendency of the data. The findings are as follows: that dispersion increases very rapidly from a low value to nearly 80 or 90% and that natural dispersion onset occurs at an energy level similar to or higher than that for chemical dispersion, and finally that the natural dispersion curve has a lesser slope than that for chemical dispersion.

The energy is sufficient in the high energy apparatus to disperse light Bunker C. Tests on regular Bunker C did not yield dispersion chemically or naturally. During the natural dispersion runs and partially during the chemical runs, the Bunker C grouped into large droplets on the surface. This is indicative 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 or lag the chemical dispersion. The curves of natural dispersion have a lesser slope than those for chemical dispersion. In addition, the heavier oils tested are not dispersed to the same degree as other oils. The effect of

TABLE 2

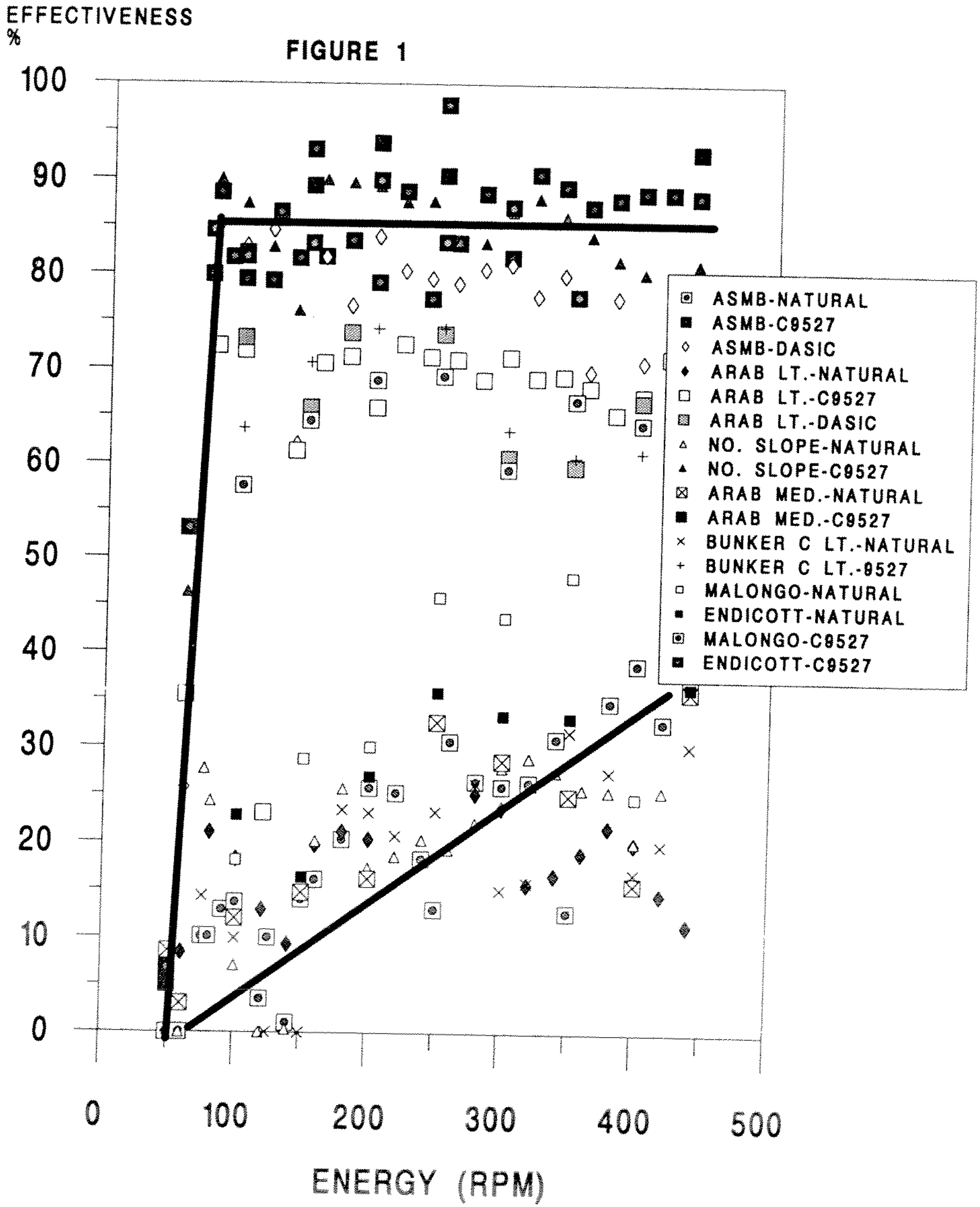
SUMMARY RESULTS OF THE HIGH ENERGY EXPERIMENTS

EFFECTIVENESS VALUES IN PERCENT FOR OIL TYPE AND CONDITION

	ALBERTA MIXED BLEND			ARABIAN LIGHT			NORTH SLOPE		ARABIAN MEDIUM		BUNKER C LIGHT		MALONGO		ENDICOTT	
RPM	NATURAL	W/C9527	DASIC	NATURAL	W/C9527	DASIC	NATURAL	W/C9527	NATURAL	W/9527	NATURAL	W/C9527	NATURAL	W/C9527	NATURAL	W/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

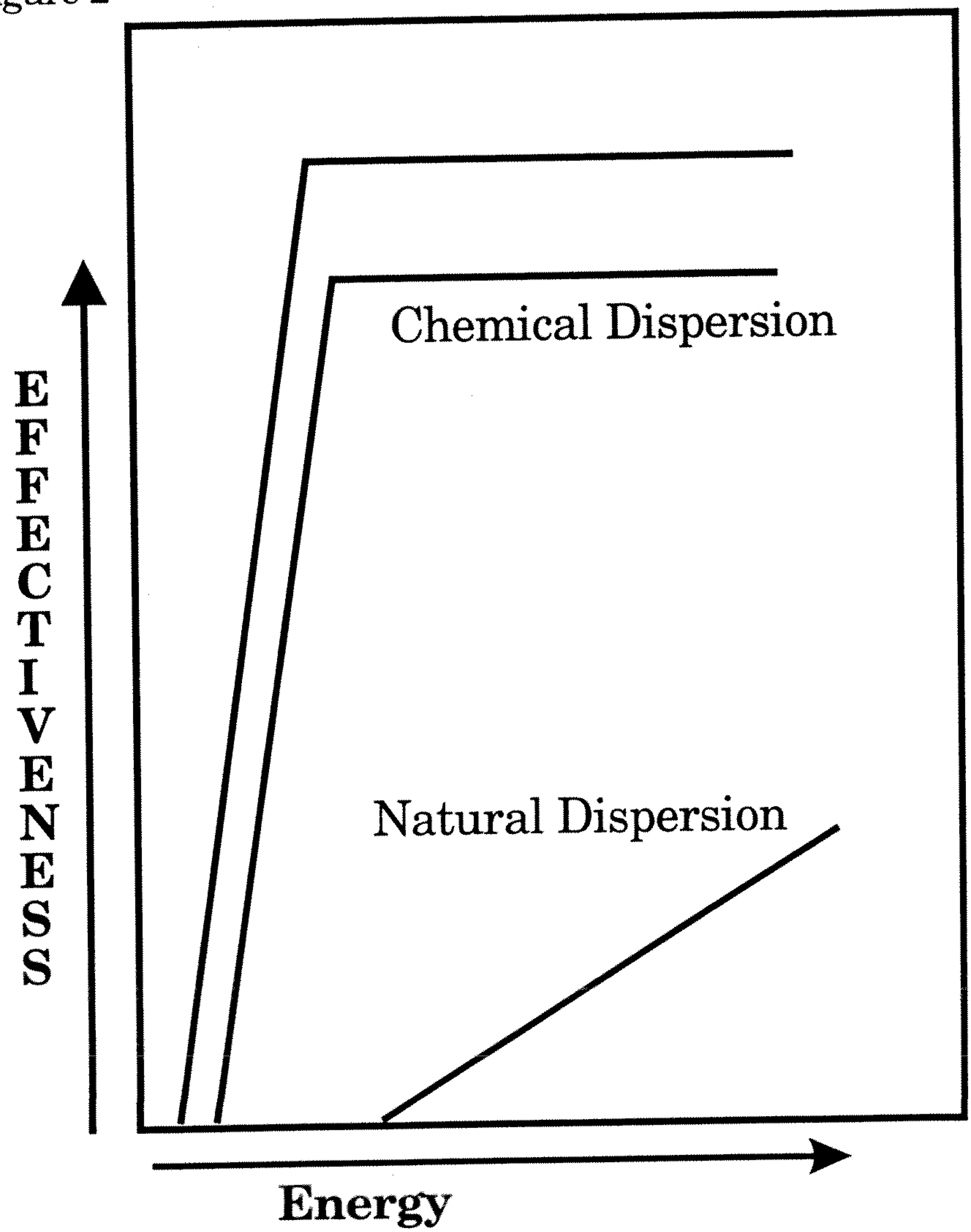
LEGEND C9527 = COREXIT 9527

COMPOSITE DATA FROM THE HIGH ENERGY EXPERIMENTS



Schematic High Energy Results

Figure 2



chemical dispersant is to increase the dispersion amount by a large factor for the same level of mixing energy. These findings are illustrated graphically in Figure 2.

The 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, thus causing noise in the data. This is particularly evident in the case of natural dispersion where the onset is obscured by noise. This is been drawn as a linear function in Figure 2 simply because the exact form is unknown, however, linear regression provides the best fit.

RESULTS OF THE ENERGY AND DISPERSANT QUANTITY WORK

Numerical results are given in detail in Table 3 and summarized in Table 4. Methodology was the same as in the previous studies, however, because of improved techniques and equipment, the standard deviation of the results is lower by about a factor of two. This is an improvement, however, it has revealed another small problem with the experiment. The system has several resonances. At several points there are standing waves in the vessel and at other time higher turbulence. This is most observable at 100 rpm, where the visible turbulence (and the resulting numbers) is much higher than at subsequent points. This causes a major problem with natural and low dispersant amounts because the effects are much more noticeable at low effectiveness values. The values at 100 rpm were taken from interpolation for curve fitting to avoid skewing the mathematical results.

Table 4 **SUMMARY ENERGY AND DISPERSANT QUANTITY RESULTS**

	Ratio of Dispersant to Oil						
Energy (rpm)	**0**	**1/400**	**1/200**	**1/100**	**1/50**	**1/25**	**1/12.5**
400	13.8	27.2	44	54.7	71.1	78.3	90.8
350	11.2	26.7	33.3	54.3	77.3	87.3	95.4
300	15	28.9	40.7	68.9	86.4	93.6	97.5
250	28.9	30.6	43.6	78.2	94.4	96.5	99.3
200	21.2	25.4	41.6	83.8	94.5	93.9	99.1
150	6.1	16.7	42.6	85.9	81.9	89.5	88.9
100	3.6	8.4	25	45	47	48.2	57.5
50	1.6	0	7.4	4.5	5.8	6.7	26
0	0	0	0	0	0	0	0

Another difficulty is the drop-off in effectiveness at high energies. This is caused by the loss of oil to the walls of the test apparatus. Studies of the latter phenomenon have confirmed this observation. This is unavoidable in this type of experiment. As the energy is increased, so too is the amount of surface area of the

Table 3

Experimental Values for Alberta Sweet Mixed Blend Oil

	Natural Dispersability					12.5:1 Ratio					25:1 Ratio				
RPM	Run #1	Run #2	Run #3	Ave	SD	Run #1	Run #2	Run #3	Ave	SD	Run #1	Run #2	Run #3	Ave	SD
400	17.8	10.5	13.1	13.8	3.7	89.6	93.8	89.0	90.8	2.6	84.1	79.3	73.1	78.8	5.5
350	11.2	6.6	15.8	11.2	4.6	92.9	101.5	91.8	95.4	5.3	85.3	88.8	88.0	87.3	1.8
300	18.6	6.7	19.6	15.0	7.1	96.6	99.1	96.8	97.5	1.4	91.6	92.3	96.8	93.6	2.8
250	23.2	25.4	38.0	28.9	7.9	100.9	97.0	100.0	99.3	2.1	94.3	94.6	100.6	96.5	3.6
200	20.3	12.8	30.3	21.2	8.8	97.2	99.8	100.2	99.1	1.6	94.4	93.2	94.1	93.9	0.6
150	8.1	2.3	8.0	6.1	3.3	82.9	92.3	91.5	88.9	5.2	90.2	90.8	87.4	89.5	1.9
100	33.4	43.2	56.1	44.3	11.4	100.0	100.0	100.0	100.0	0	100.0	96.8	100.0	98.9	1.9
50	4.5	0.1	0.1	1.6	2.5	20.1	26.5	31.3	26.0	5.6	5.3	8.1	6.8	6.7	1.4

	50:1 Ratio				
RPM	Run #1	Run #2	Run #3	Ave	SD
400	73.7	69.6	70.1	71.1	2.2
350	77.5	75.1	79.5	77.3	2.2
300	85.5	86.5	87.4	86.4	0.9
250	90.7	94.8	97.7	94.4	3.5
200	91.8	98.7	93.1	94.5	3.7
150	81.7	80.4	83.6	81.9	1.6
100	100.0	100.0	100.0	100.0	0
50	5.5	6.0	5.8	5.8	0.3

	100:1 Ratio					200:1 Ratio					400:1 Ratio				
RPM	Run #1	Run #2	Run #3	Ave	SD	Run #1	Run #2	Run #3	Ave	SD	Run #1	Run #2	Run #3	Ave	SD
400	50.8	60.4	53.1	54.7	5	28.9	55.3	47.7	44.0	13.6	28.2	27.0	26.4	27.2	0.9
350	52.8	59.8	50.3	54.3	4.9	28.9	36.3	34.7	33.3	3.9	26.8	28.0	25.3	26.7	1.4
300	73.5	70.4	62.7	68.9	5.6	45.3	39.3	37.6	40.7	4	25.6	32.2	28.9	28.9	3.3
250	80.6	78.4	75.6	78.2	2.5	46.8	42.7	41.3	43.6	2.9	29.8	37.5	30.6	32.6	4.3
200	83.1	78.8	89.6	83.8	5.4	42.0	41.4	41.5	41.6	0.3	23.8	25.7	25.4	24.9	1
150	79.9	77.9	100.0	85.9	12.2	40.2	47.4	40.2	42.6	4.2	17.1	17.8	16.7	17.2	0.5
100	95.6	93.1	102.2	97.0	4.7	75.8	83.3	81.2	80.1	3.9	73.4	64.3	67.1	68.3	4.7
50	4.2	5.8	3.6	4.5	1.1	13.6	1.9	6.8	7.4	5.9	0.9	16.6	0.0	5.9	9.3

vessel exposed to the oil. Because the oil-to-water ratio is 1:20,000, even a small amount of loss is observed. It should be noted that in the previous study, this is not observed in all cases because some oil/dispersant combinations do not adhere to the walls to the same extent as others (Fingas et. al. 1993).

The results are shown graphically in Figure 3 and 4. The curves in Figure 3 were made using interpolation. The form of curve is that which was found to be best for these functions in previous studies (Fingas et. al. 1993). The software, Table Curve, was used in this study to reconfirm that two-lines fit the data the best. The curves for the no-dispersant case are hard to fit, as was also noted in previous studies, because of noise in the data. In this paper, they were fit with an interpolated step function rather than a straight line as previous. This does result in a slightly better fit in the new study. In either case, the R^2 or regression coefficient is about 0.6.

The maximum values of dispersion occur at 250 rpm. When these values are plotted versus the dispersant ratio, a smooth exponential curve is obtained. These values are given in Table 5 and shown graphically in Figure 5. This finding is in accordance with previous findings that dispersion amount is exponential with dispersant dosage (Fingas et. al., 1990). In Figure 5 these values are also compared to the dispersabilities at 50 rpm, a considerably lower energy. The effect of energy can also be seen to be much greater than that of dispersant amount. The equations and correlation curves for the logarithmic curves fit to the data are given in Figure 5.

Table 5

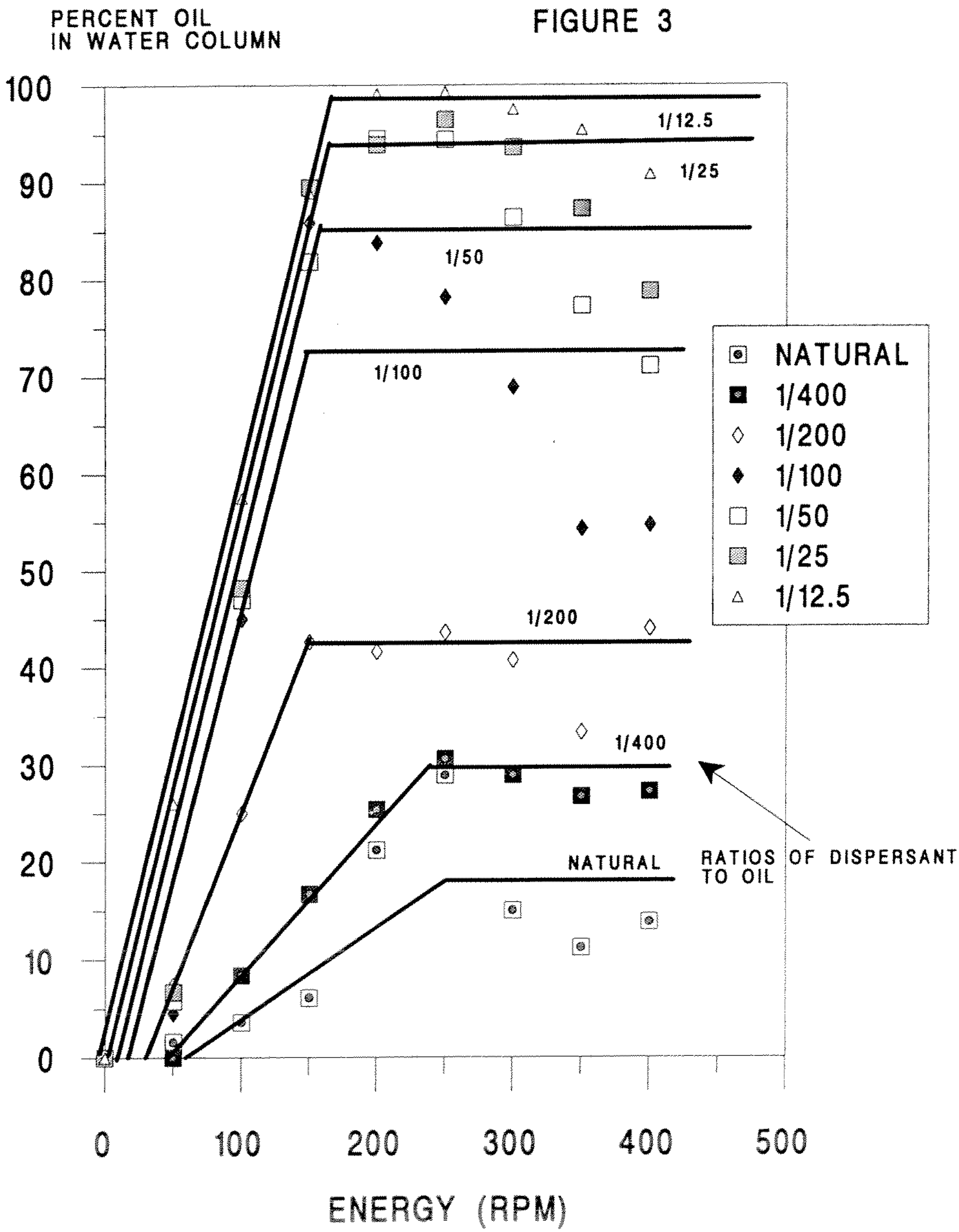
Maximum Dispersabilities at Each Ratio

Ratio	Dispersability (%)
0	28.9
0.0025	30.6
0.005	43.6
0.01	78.2
0.02	94.4
0.04	96.5
0.08	99.3

Curve fitting was done on each of the series of data and using the best-fit curve in each series, the X-intercept or the dispersant threshold was found. The table of these thresholds is given in Table 6 and illustrated graphically in Figure 6. A linear curve is the simplest one to fit this data and provides a relatively high correlation coefficient of 0.8. Curve-fitting showed that more complex equations such as square functions provide only a slightly better correlation coefficient.

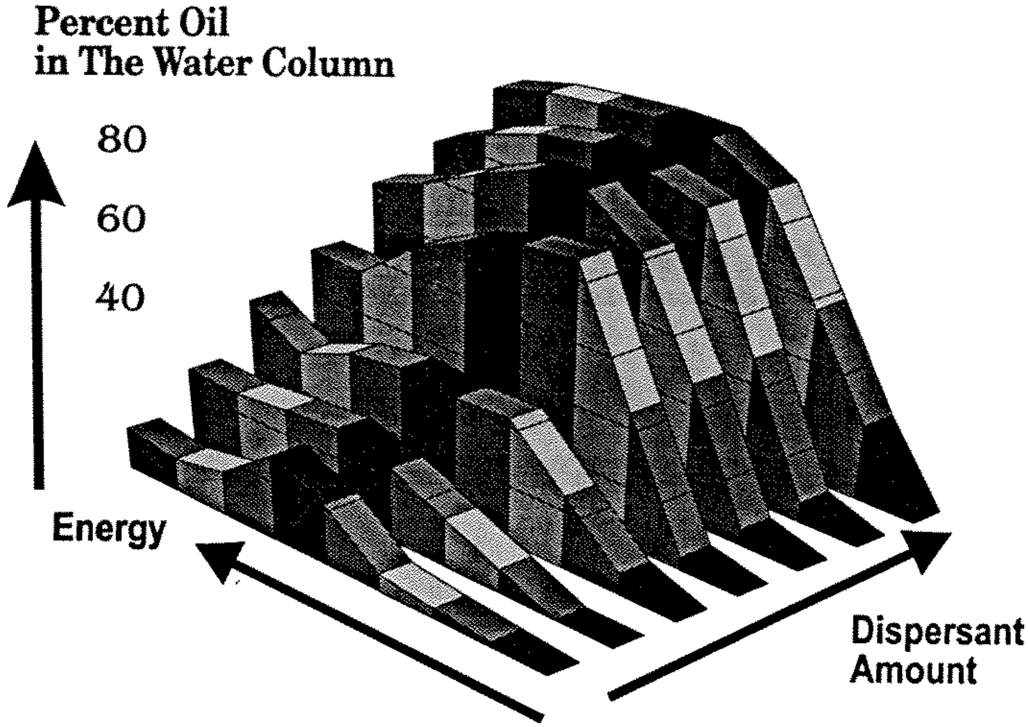
DISPERSION WITH VARYING ENERGY

FIGURE 3



Three-Dimensional View of Results

Figure 4



EFFECT OF INCREASING DISPERSANT AMOUNT

FIGURE 5

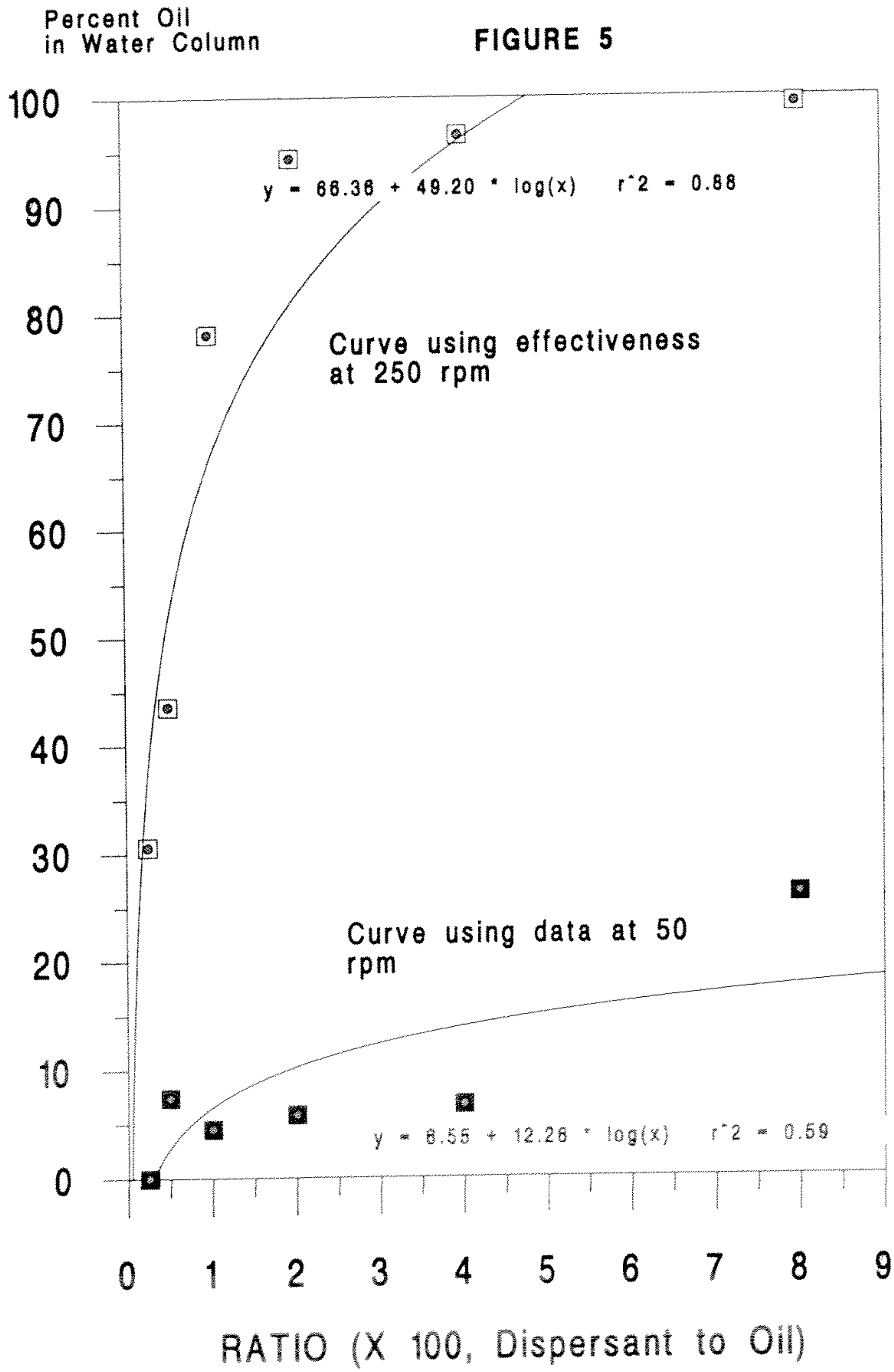


Table 6

Onset To Dispersion

Dispersant Ratio	Onset Energy (rpm)
0	52
0.0025	50
0.005	43
0.01	47
0.02	44
0.04	44
0.08	31

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. 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.

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 shape of the energy dispersion curve is unclear, but may be linear or may be a step function similar to that for chemical dispersion.

The effect of dispersant amount at high energies is the same as at low energies (Fingas et. al., 1990). The finding of this and previous studies is that the amount of dispersion or effectiveness increases exponentially (or equivalently logarithmically) with dispersant amount. The effect of dispersant amount on effectiveness is similar to but less than energy.

The onset energy at which dispersion occurs decreases with increasing dispersant amount. The effect of increasing dispersant amount is then to both increase amount of oil put into the water column, but also to decrease the threshold level of energy required to perform this function.

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