

# A REVIEW OF OIL SPILL DISPERSANTS AND THEIR EFFECTIVENESS

A Summary of Work Done by Environment Canada and The United States Minerals Management Service

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## INTRODUCTION

Dispersants still generate much discussion and many studies since the birth of the oil spill industry twenty years ago after the TORREY CANYON incident. There still exists a strong polarization between dispersant proponents and opponents. Documentation on actual field use is poor. Interviews with operators having used dispersants often results in contradictory opinions on whether the dispersant worked in that situation or not. Large scale biological experiments have failed to convince environmentalists that the use of dispersants is safe in all conditions, although the evidence is becoming increasingly clear that dispersants cause little, if any ecological damage above that by un-treated oil.

## WHAT ARE DISPERSANTS ?

The active ingredients in dispersants are surface active agents or surfactants. Surfactants have varying solubility in water and have varying actions toward oil and water. One parameter that has been used to characterize surfactants is the HLB or the hydrophilic-lipophilic balance.<sup>1</sup> A surfactant with an HLB of about 1 to 8 promotes the formation of water-in-oil emulsions and one with an HLB between 12 and 20 promotes the formation of oil-in-water emulsions. Dispersants have HLB's between 9 to 11. The HLB range as defined is only applicable to non-ionic surfactants, however ionic surfactants can be rated using an expanded scale and often have HLB's ranging from 25 to 40. They are strong water-in-oil emulsifiers, very soluble in water, relatively insoluble in oil, and generally work from the water to any oil present. Such products have little applicability to oil on water because they rapidly disappear in the water column, having little effect on oil. However, because of their commonality and cheapness many ionic-surfactants are proposed as dispersants. It is these agents, that should be better classed as surface-washing agents.

Surface-washing agents then are surfactant-containing mixtures with high HLB's and are best suited to removing oil from solid surfaces such as shorelines, roads and parking lots. Environment Canada with the Minerals Management Service have developed an effectiveness test for such agents and results of these tests are reported in the literature. Many such agents come onto the market each year, many are repackaged industrial cleaners and have little utility in spills.

### **DISPERSANTS - FIELD EFFECTIVENESS TRIALS**

Over a ten year period bridging the last decade, 106 test spills were laid out to test the effectiveness of oil spill dispersants.<sup>2</sup> These spills are summarized in Table 1. A number of smaller tests or other tests which were not documented have taken place but are not included here. Of the 107 slicks documented, 23 are controls used to establish a comparison. Percentage effectiveness is reported in 25 spills and the average for these is 30%. Values range from 0 to 100%. Most experimenters have not assigned effectiveness values because, as will be demonstrated in more depth later, effectiveness values are difficult to assign.

The test results show clearly that dispersants will not remove all of the slick, even under highly controlled experimental situations. Of greater concern than this is the methodology used to estimate effectiveness. Some experimenters simply estimated effectiveness, but most based their measure on integrations of water column concentrations relative to surface slick dimensions. This is not a correct means to perform the measure because the underwater concentrations have little positional relationship to the surface slick. Underwater dynamics of the ocean are very different from surface dynamics. Extreme cases of the positional variances between surface and sub-surface slicks have been illustrated by Brown and Goodman in controlled tank testing.<sup>3</sup> Their work has shown that the underwater plumes move in highly random fashions with respect to the surface slick and even two trials conducted on the same day will not have similar movement patterns.

Many experimenters used underwater concentrations to estimate field effectiveness. They generally used the method of dividing the water into different compartments and averaging concentrations. Mathematically this is not appropriate when the compartments do not have the same dimensions in all three axes. Furthermore averaging concentrations of oil over large quantity of water results in effectiveness values that are much larger than by using other methods. In fact because dispersion only occurs from the thicker portions of the slick and because these only constitute about 10% of the slick surface area, only these portions should be used. Other errors in the opposite direction compensate for this somewhat, but the net result is an absence of defined techniques for measuring effectiveness using underwater oil concentrations.

Surface measures are also inadequate. Remote sensing does not provide a thickness measure and thus calculating volume is impossible. Many surface phenomena also interfere with the process of estimating slick volume. These have been detailed in a recent paper by Goodman and Fingas.<sup>24</sup> A new technique for measuring surface thickness is currently in development by Esso Resources Canada, Minerals Management Service, Environment Canada and the American Petroleum Institute. This instrument offers potential to measure effectiveness on the open ocean.

In summary, field trials of dispersant effectiveness have not shown any quantitative proof of high (>70%) dispersant effectiveness. Analytical means do not exist at this time to accurately quantify dispersant effectiveness at field trial situations.

Table 1 - DISPERSANT FIELD TRIALS

Location/ Identifier	Reference	Year	Number	Oil Type	Amount, M3	Dispersant	Application Method	Rate, D: O	Sea State	Effectiveness Claimed			
North Sea	Cormack and Nichols [1,2]	1976	1	Ekofisk	0.5	10% conc.	ship, WSL	...	I	...			
			2	Kuwait		10% conc.	ship, WSL	1:20	2-3	100			
			3	Murban	1.7	Corexit 9627	helicopter	1:5	1	...			
Wallops Island	McAuliffe et. al. al. [1,3]	1978	4	La Rosa	1.7	Corexit 9627	helicopter	1:5	1	...			
			5	Murban	1.7	Corexit 9627	helicopter	1:11	I	100			
			6	La Rosa	1.7	Corexit 9627	helicopter	1:11	1	50			
			7	North Slope	1.7	Control later Corexit 9627	control then helicopter	> 1:5	0-1	...			
			8	North Slope	3.2	Corexit 9627	airplane, Cessna	> 1:5	0-1	...			
South California	Smith et al. [4]	1978	9	North Slope	1.7	Recovery + Corexit 9627	helicopter	> 1:5	0-1	...			
			10	North Slope	0.8	BPI IOOWD	ship, WSL	> 1:5	0-1	...			
			11	North Slope	0.8	Corexit 9627	ship	> 1:5	0-1	...			
			12	North Slope	3.2	Corexit 9627	airplane, Cessna	> 1:5	1-2	...			
			13	North Slope	0.8	Corexit 9627	ship	> 1:5	1-2	...			
			14	North Slope	0.8	BPI IOOWD	ship, WSL	> 1:5	1-2	...			
			15	North Slope	0.6	Several, demonstration	several, demonstration	...	1-2	...			
			16	North Slope	0.2	10%, 9627	ship, WSL	1:1	2	...			
			Victoria	Green et al. [1,6]	1978	17	North Slope	0.4	10%, 9627	ship, WSL	1:1	1	...
						18	North Slope	0.2	10%, 9627	ship, WSL	1:1	I	...
19	Prudhoe Bay	1.6				control	control	...	2-3	0.5			
Long Beach	McAuliffe et. al. [1,5]	1979	20	Prudhoe Bay	1.6	2% conc.	ship	1:67	2-3	8			
			21	Prudhoe Bay	1.6	2% conc.	ship	1:67	2-3	5			
			22	Prudhoe Bay	3.2	conc.	airplane, DC-4	1:20	2-3	78			
			23	Prudhoe Bay	1.6	conc.	airplane, DC-4	1:25	2-3	45			
			24	Prudhoe Bay	1.6	control	control	...	2-3	1			
			25	Prudhoe Bay	3.2	conc.	airplane, DC-4	1:27	2-3	60			
			26	Prudhoe Bay	1.6	2%	ship	1:11	2-3	11			
			27	Prudhoe Bay	1.6	2%	ship	1:11	2-3	62			
Mediterranean, Protecmar	Bocard et al. [7]	1979	28-41	light fuel	3 each	BPHOOX BPHOOWD Finasol OSR- 5 Corexit 9627	ship, helicopter, various and airplane CL215	...	1-3	...			
			Mediterranean, Protecmar 11	1980	42-49	light fuel	1-5.5	BPHOOX BPHOOWD Finasol OSR- 5 Corexit 9627	ship, helicopter, various and airplane CL215	...	1-3	...	
Mediterranean Protecmar III	Bocard and Gatellier [1,7,8]	1981	50	light fuel	6.5	Dispolene 325	airplane, CL215	1:3	1-2	50			
			51	light fuel	6.5	Shell	airplane, CL215	1:3	2-3	...			
			52	light fuel	6.5	control	control	...	1-2	...			
Newfoundland	Gill et al. [9]	1981	53	ASMB	2.5	control	control	...	1	...			
			54	ASMB	2.5	Corexit 9627	airplane, DC-8	1:10	1	...			
Norway	Lichtenthaler and Daling [1,10]	1982	55	Statford	0.2	control	control	...	2-3	0.8			
			56	Statford	0.2	10% conc.	ship	1:10	2-3	6			
			57	Statford	0.2	10% conc.	ship	1:10	2-3	1.7			
			58	Statford	0.2	control	control	...	2-3	2.6			
			59	Statford	0.2	1 0% conc.	ship	1:17	2-3	1.9			
			60	Statford	0.2	1 0% conc.	ship	1:18	2-3	22			
			61	Statford	0.2	1 0% conc.	ship	1:18	2-3	2			
North Sea	Cormack [1,11]	1982	62	Arabian	20	control	control	...	1	...			
			63	Arabian	20	Corexit 9627	airplane, Islander	1:2	1	...			
			64	Arabian	20	Corexit 9627	airplane, Islander	1:4	1	...			

Table 1 - DISPERSANT FIELD TRIALS

Location/ Identifier	Reference	Year	Number	Oil Type	Amount, M3	Dispersant	Application Method	Rate, D: O	Sea State	Effectiveness Claimed	
Mediterranean Protecmar V	Bocard et al. [1,12]	1982	65	light fuel	3	10% Dispolene	ship	1:2	3	...	
			66	light fuel	5	Dispolene 325	airplane, CL215	1:2.4	3	...	
			67	light fuel	5	Dispolene 325	ship	1:2.8	2	...	
			68	light fuel	5	Dispolene 325	airplane, CL215	1:2.8	2	...	
			69	light fuel	3.5	Dispolene 325	ship	1:2.8	1.2	...	
			70	light fuel	4	Dispolene 325	helicopter	1:2.9	1.2	...	
			71	light fuel	2	premixed	premixed	1:20	1.2	40-50	
			72	light fuel	5	control	control	...	2	...	
Holland	Delvigne [1,13]	1983	73	Statfjord	2	control	control	...	1.2	2	
			74	light fuel	2	control	control	...	1.2	2	
			75	Statfjord	2	control	control	...	1	2	
			76	Statfjord	2	Finasol	OSR-5	airplane	1:10-30	1	2
			77	light fuel	2	Finasol	OSR-5	airplane	1:10-30	1	2
			78	Statfjord	2	Finasol	OSR-5	premixed	1:20	2-3	100
			79	light fuel	2	control	control	...	2-3	2	
			80	Statfjord	2	Finasol	OSR-5	airplane	1:10-30	1.2	2
			81	Statfjord	2	Finasol	OSR-5	airplane	1:10-30	1.2	2
Halifax	Swiss and Gill [1,14,15]	1983	82	ASMB	2.5	Corexit 9527	helicopter	1:20	1	2.5	
			83	ASMB	2.5	control	control	...	1	1	
			84	ASMB	2.5	Corexit 9550	helicopter	1:10	1	1.3	
			85	ASMB	2.5	control	control	...	1	1	
			86	ASMB	2.5	BP MA700	helicopter	1:10	2-3	10-41	
			87	ASMB	2.5	control	control	...	2-3	7	
Norway	Lichtenthaler and Daling [16]	1984	88	Statfjord	10	control	control	...	1	...	
			89	Statfjord	10	Corexit 9527	airplane, Islander	1:75	1	...	
			90	Statfjord	10	control	control	...	2	...	
			91	Statfjord	10	Corexit 9527	airplane	1:80	2	...	
			92	Statfjord	12	Corexit 9527	premixed	1:33	2	...	
			93	Statfjord	10	Corexit 9527	airplane	1:50	-	-	
Brest, Protecmar VI	Bocard [7,17]	1985	94	fuel oil	5	control	control	...	1	...	
			95	fuel oil	28	Dispolene 355	helicopter	1:9	1	...	
			96	fuel oil	part of above	Dispolene 355	ship-spray	1:9	1	...	
			97	fuel oil	part of above	Dispolene 355	ship-aerosol	1:9	1	...	
Haltenbanken	Sorstrom [19]	1985	98	topped Statfjord crude	12.5	control	...	...	1.2	...	
			99	topped Statfjord crude	12.5	Finasol	premixed, injected 3 m below surface	1:50	1.2	...	
			100	topped Statfjord crude	12.5	control	...	...	1.2	...	
			101	topped Statfjord crude	12.5	Alcopol (demulsifier)	premixed	250 ppm	1.2	...	
									1.2	...	
Beaufort Sea	Swiss et al. [20]	1986	101 (CA)	topped Federated crude	2.5	control	...	...	1.2	...	
			102 (CB)	topped Federated crude	2.5	control	...	...	1.2	...	
			103 (CI)	topped Federated crude	2.5	BP MA700	helicopter	1:10	2-3	...	
			104 (TI)	topped Federated crude	2.5	BP MA700	helicopter	1:1	2-3	...	
			105 (T2)	topped Federated crude	2.5	Corexit CRX-8	helicopter	1:1	2-3	...	
			106 (C2)	topped Federated crude	2.5	control	...	...	1.2	...	
									1.2	...	

**DISPERSANTS - ACTUAL USAGE**

Table 2 lists dispersant usage during some notable large spills.<sup>25,26</sup> Results are summarized from the noted references and recent presentations. The problem with actual spill data is that some observers may have reported seeing evidence of effectiveness and others directly the opposite. In few of the cases were any analytical means tried to quantify effectiveness or even to provide better estimates. Dispersants are used more frequently in countries like Great Britain and in many Eastern countries. Again no quantitative results are available to show effectiveness nor lack of such.

TABLE 2 **HISTORICAL USE OF DISPERSANTS**

SPILL EVENT	YEAR	COUNTRY	AMOUNT SPILLED (t)	DISPERSANT AMOUNT (t)	RESULTS
TORREY CANYON	1967	ENGLAND	119000	10000	ADVERSE ECOLOGICAL
OCEAN EAGLE	1968	PUERTO RICO	12000	60	MIXED
SANTA BARBARA	1969	USA	1000	32	MIXED
ARROW	1970	CANADA	5000	12	MIXED
PACIFIC GLORY	1970	ENGLAND	6300	?	MIXED
SHOWA MARU	1975	SINGAPORE	15000	500	MIXED
JAKOB MAERSK	1975	PORTUGAL	88000	110	MIXED
OLYMPIC ALLIANCE	1975	ENGLAND	2000	220	MIXED
URQUIOLA	1976	SPAIN	100000	2400	MIXED
AMOCO CADIZ	1978	FRANCE	220000	2500	MIXED
ELENI V	1978	ENGLAND	7500	900	MIXED
CHRISTOS BITAS	1978	ENGLAND	3000	280	MIXED
BETELGEUSE	1979	IRELAND	1000	35	MIXED
IHTOC I	1979	MEXICO	500000	5000	MIXED
SIVAND	1983	ENGLAND	6000	113	MIXED
PUERTO RICAN	1984	USA	7000	10	NOT MEASURABLE
EXXON VALDEZ	1989	USA	50000	8	MIXED , TESTS ONLY
MEGA BORG	1990	USA	10000	40	MIXED

**LABORATORY EFFECTIVENESS TESTS**

Many different types of dispersant test procedures and apparatus are described in the literature. One estimate places this at 50 different tests or procedures. Of these only a handful are in common use. These include the Labofina or rotating flask test, the Mackay or MNS test, the swirling flask test, and the SET (Simulated Environmental Test Tank)

Several investigators have reported results of apparatus comparison tests.<sup>27-37</sup> In the eleven papers reported here, all authors have concluded that the results of the different tests do not correlate well, but some conclude that some of the rankings are preserved in different tests. Generally, the more different types of oil tested, the less the results correlate. It is painfully obvious that there exists some difficulty in laboratory testing of dispersants or that commonality in test design is needed. This section will summarize studies of laboratory tests and show that laboratory tests can be designed to give a reasonable value of oil dispersion given that the parameters of turbulent energy, oil-to-water ratio, and settling time are set at realistic values.

The most common laboratory apparatus are listed in Table 3. In some cases different protocols have been described in the literature for the same apparatus. There is no reason why different protocols cannot be used on the same apparatus.

Previous comparisons of the different apparatus have been limited. Byford and Green compared the Labofina and Mackay tests on a series of 2 oils and 5 dispersant combinations.<sup>28</sup> They concluded that the ranking of effectiveness between the two tests correlated well, although the numerical values had significant variation. Meeks compared EPA, Russian, Warren Springs, and French dispersant effectiveness results for two oils and three dispersants.<sup>31</sup> He concluded that the results of the tests are sufficiently different that even the rank of effectiveness is not preserved. Daling and Ness compared the Mackay and Labofina Apparatus using 2 oils and 7 dispersants.<sup>29</sup> They concluded that numerical correlation among results is poor, but that the rank of effectiveness is consistent between the results generated using the two apparatus. Daling compared the Mackay, Labofina and IFP devices for three different oils, with three different water contents and one dispersant.<sup>38</sup> This comparison showed that the numerical results were not correlatable, and the ranking of effectiveness also varied significantly. The present author and co-workers compared the Labofina, Mackay, oscillating hoop and swirling flask apparatus for 10 oils and three dispersants.<sup>27</sup> We concluded that the correlation among the numerical results was poor and that rank of effectiveness correlated only weakly. The oscillating hoop test results, in particular, correlated poorly with other results.

Little work has been done on determining the reason for the poor correlation between test results. All of the above 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. The investigators followed the specified test procedure when using an apparatus and did not vary any of the conditions. The only exception to this was the study by Daling and Ness, in which the dynamic sampling normally specified for the Labofina and Mackay apparatus was varied up to 10 minutes.<sup>29</sup> This factor was found to be very important in improving correlation between the effectiveness values yielded by the two apparatus.

### **EFFECT OF OIL-TO-WATER RATIO AND SETTLING TIME**

This section will focus on two of the variables important to laboratory dispersant tests, the oil-to-water ratio and the settling time, that time between the taking of the sample for analysis and the time that the energy is no longer applied to the apparatus. Increased settling time allows large, unstable oil droplets to rise to the surface before the sample is taken and thus reduces the effectiveness values to represent only the more stable dispersions. The oil-to-water ratio varies dramatically in the various test protocol.

#### **Experimental**

Apparatus were operated according to standard procedures except as noted in this paper. The oil-to-water ratio was changed by varying the amount of oil added to the system and the water amount was kept constant at the normal specified level. The settling time was varied by sampling water from the apparatus after the specified time. In the flowing cylinder, analysis of dispersion is performed by trapping oil in a filter and analyzing oil in this filter. Settling time can not be varied in this apparatus.

TABLE 3

## COMPARISON OF LABORATORY TEST APPARATUS

	TEST NAME	ALTERNATE NAME (S)	ENERGY SOURCE	WATER VOLUME (L)	PRIME USE
<b>1</b>	LABOFINA	WARREN SPRINGS ROTATING FLASK	VESSEL ROTATION	0.25	REGULATORY GENERAL
<b>2</b>	MACKAY	MNS MACKAY-NADEAU- STEELMAN	AIR STREAM	6	REGULATORY GENERAL
<b>3</b>	SWIRLING FLASK		VESSEL MOVEMENT	0.12	REGULATORY GENERAL
<b>4</b>	SET	SIMULATED ENVIRONMENTAL TEST TANK	CIRCULATING PUMP	119	REGULATORY
<b>5</b>	IFP	DILUTION TEST FRENCH STANDARD	OSCILLATING HOOP	16	REGULATORY GENERAL
<b>6</b>	CASCADING WEIR	MACKAY FLUME	FALL OVER WEIR	CONSTANT FLOW 0.5 L/s	EXPERIMENTAL
<b>7</b>	FLOWING COLUMN		FALL DOWN TUBE	1 (FLOWING)	EXPERIMENTAL
<b>8</b>	CONCENTRIC TUBE	BOBRA	WATER FLOW	CONSTANT FLOW (~0.05 L/s)	EXPERIMENTAL
<b>9</b>	OSCILLATING HOOP		OSCILLATING HOOP	35	EXPERIMENTAL
<b>10</b>	WAVE-PLATE TANK	SOUTH AFRICAN BP SUNBURY	MOVING PLATES	30	REGULATORY GENERAL
<b>1 1</b>	HIGH-ENERGY		MOVING VESSEL	5	EXPERIMENTAL
<b>1 2</b>	SPINNING DROP	INTERFACIAL	WATER MOVEMENT	<0.05	EXPERIMENTAL
<b>1 3</b>	BLENDER		PROPELLER	1.5	EXPERIMENTAL

The oscillating hoop apparatus employs a hoop which is moved up and down at the surface of 35 litres water. Detailed protocols for operating this apparatus have been described previously.<sup>39</sup> The swirling flask apparatus uses a 125 mL Erlenmeyer flask with a standard laboratory shaker to induce a swirling motion to the contents. Procedures for this device are also detailed in the literature.<sup>40</sup> A revised newer procedure is also included in the Appendix of this paper. The Mackay apparatus uses a high-velocity stream of air to energize 6 L water and both operating procedures and construction details are documented.<sup>41</sup> The labofina test employs a 250 mL separatory funnel which is rotated at 33 rpm.<sup>42</sup> Analysis for all four apparatus 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, and then assigning effectiveness on the basis of a calibration curve. All runs 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 where both premixed and drop-wise addition were used.<sup>39</sup>

Physical properties of the oils used in these tests are given in Table 4. The dispersants used include the Exxon products Corexit 9527 (abbreviated C9527 in some tables in this paper) and Corexit CRX-8 (abbreviated CRX-8), and the British Petroleum product, Enersperse 700 (abbreviated EN 700). In two tests, experimental dispersants were used and were designated "test product" and "experimental dispersant".

The flowing cylinder test was developed at Environment Canada's laboratory in Ottawa and no operating procedures have been previously published. The basic operating principal is that water is continuously removed from the bottom of a cylinder and replaced at the top of the cylinder. This circulation draws dispersed oil into the water column and ultimately into a filter which removes the oil and the clean water returns to the top of the cylinder where its drop down the cylinder wall provides energy for dispersion. The length of the cylinder is sufficiently long that only small (1 to 30 micron diameter) particles enter the hose. Any larger particles formed resurface, as confirmed by particle size analysis and visual inspection.

The procedures for operating the apparatus are summarized below. The system is assembled and three-stage filter loaded. The lower stage (last to encounter flow) is a standard back-up pad, the next is a 0.22 micron filter and the first or uppermost is 5 microns. The filter holder is reassembled. The vessel is filled with 1000 mL salt water (33 ppt). The peristaltic pump which has previously been calibrated to pump at 100 mL/min, is started and the hoses filled. Once equilibrium flow is achieved the specified volume of oil with dispersant premixed, is carefully placed on the centre of the water surface. The apparatus is allowed to operate for the specified period of time; 10 circulations lasting 100 minutes was the standard for the data presented here.

At the end of the run, the 0.22 and 5.0 micron filters are removed and placed into a separatory funnel, 30 mL of methylene chloride are added and the separatory funnel is shaken for 30 minutes in a wrist action shaker set for a 1.5 degree deflection. A portion of the methylene chloride is taken and its absorbance measured at 340, 370 and 400 nanometres. The percentage dispersion is taken from calibration curves prepared at each wavelength and the value reported is the average percentage at the three wavelengths. The standard curves are prepared in similar manner as the normal runs, except that the

prescribed amount of oil to represent a given percentage is injected at the septum placed in the hose line before the particulate filters. The filters are processed as before and the resulting values are used to prepare the calibration curve. This method of calibration is used to compensate for oil loss in the hoses, pump and filter assemblies.

For every value presented here, at least two independent experiments were run. If values did not agree within the normal repeatability values for a particular device, repeat runs were performed until at least three values were within the repeatability percentage. The repeatability of results for each device was taken as the mean difference between duplicate runs before performing repeat runs. It can also represent the standard error or the plus and minus value noted behind many measurements. The standard error for each device is as follows: swirling flask - 3%, flowing cylinder - 5%, Mackay - 9%, Labofina - 7%, and oscillating hoop - 9%. Maximum errors can be as much as 40% for the Mackay and Labofina tests and as much as 20% for the other tests.

### **The Role of Oil-To-Water Ratio and Settling Time**

The effects of oil-to-water ratio were first evaluated by changing the ratios in experiments using the oscillating hoop and swirling flask apparatus. These results are shown in Figure 1. The effect of changing the oil-to-water ratio in the oscillating hoop is surprisingly large and results in a sharp peak at an oil-to-water ratio of 1:500. For two apparatus and for the different oil-dispersant combinations, the overall effect is the same. The effectiveness drops down at ratios below 1:200 and dramatically so at ratios as low as 1:20. The maximum effectiveness is seen at ratios around 1:500 and from 1:1000 becomes relatively stable up to 1:3000. It is suggested that this variation is the result of different mechanisms of dispersant action. At low oil-to-water ratios, there is a large amount of surfactant present and this surfactant interacts forming micelles rather than interacting with the oil. At low ratios, there are sufficient numbers of micelles to solubilize portions of the oil. At high oil-to-water ratios the primary interaction between oil and surfactant is the formation of dispersed particles. At ratios close to 1:500, both mechanisms come into play and apparent dispersion is increased.

The flowing cylinder was used to test the effect of increasing the oil-to-water ratio from 1:4000 up to 1:120,000. This was achieved by placing incrementally smaller amounts of oil and dispersant mixture into the apparatus. The oil-to-water ratio noted here does not take into account the recirculated water. Ten recirculations were performed per run increasing the oil-to-water ratio from a nominal 1:40,000 up to 1:1,200,000 (This form of calculation will not be used again in this paper.) To ensure that recirculation had no effect on the results, a series of experiments were performed in which clean water was pumped into the system rather than water from the filter. This series of experiments resulted in the same values as the experiments where the water was recirculated.

Figure 2 shows the results of these experiments graphically. The effectiveness values are relatively constant over the oil-to-water ratio measured. In summary, the oil-to-water ratio shows little or no effect on dispersion results when the ratio is 1:1000 or higher, but shows large effects when the ratio is at 1:500 or smaller. At 1:500 effectiveness results are the highest measured and below 1:200 effectiveness values decrease significantly.

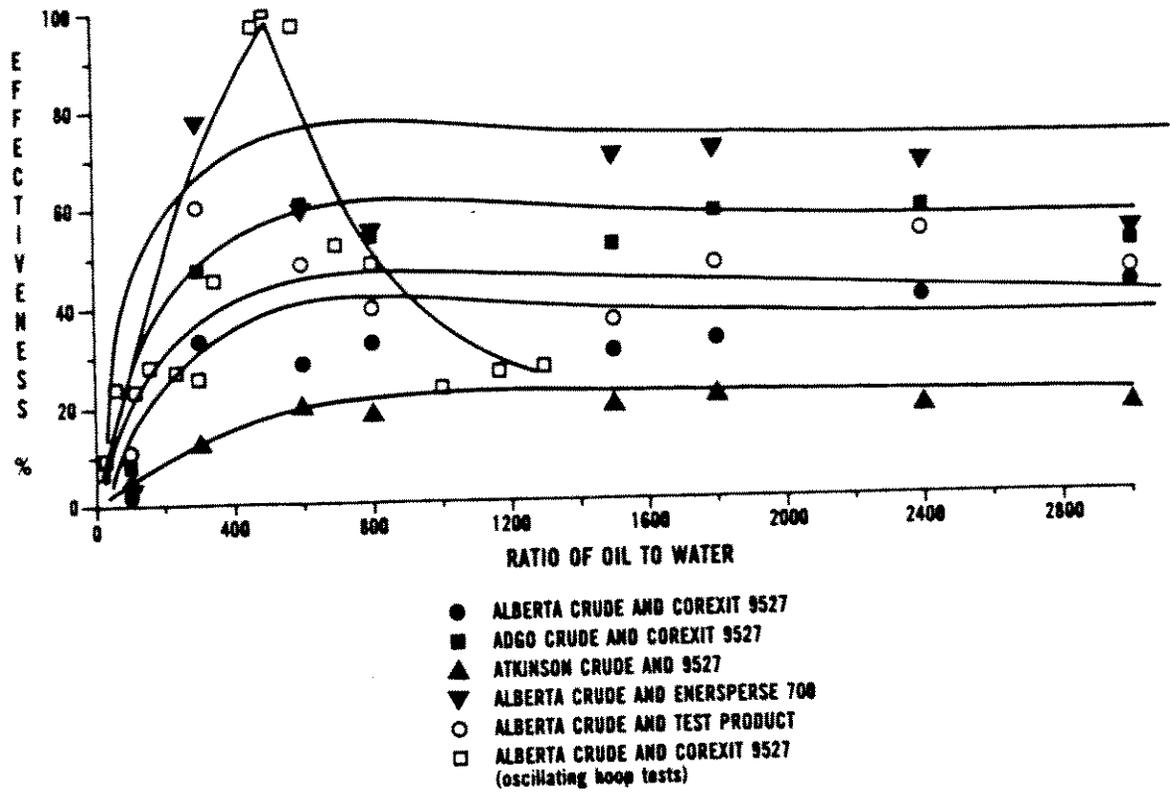


Figure 1 Effectiveness and Oil-to-Water Ratio in Two Apparatus

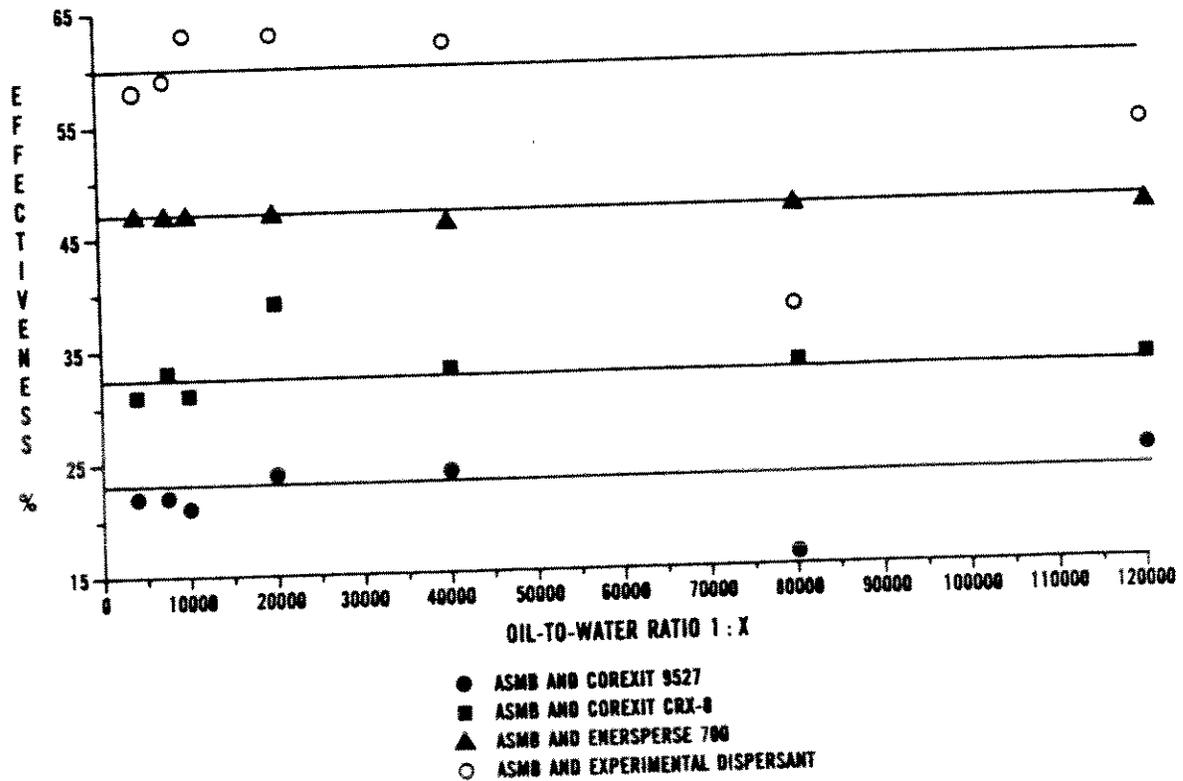


Figure 2 Effectiveness and Oil-to-Water Ratio In The Flowing Column Apparatus

TABLE 4 TEST OIL PROPERTIES

OIL	DESCRIPTION	KINEMATIC VISCOSITY	DENSITY
		(mm <sup>2</sup> /s at 15 C)	(g/mL at 15 C)
ADGO	BEAUFORT SEA CRUDE	68	0.95
AMAULIGAK	BEAUFORT SEA CRUDE	16	0.89
ASMB	ALBERTA SWEET MIXED BLEND CRUDE	8	0.84
ATKINSON	BEAUFORT SEA CRUDE	52	0.91
AVALON	NORTH ATLANTIC CRUDE	14	0.84
BENT HORN	HIGH ARCTIC CRUDE	15	0.82
FEDERATED	ALBERTA MIXED CRUDE	5	0.83
GEAR OIL	AUTOMOTIVE GEAR OIL	1700	0.88
HIBERNIA	NORTH ATLANTIC CRUDE	91	0.88
ISSUNGNAK	BEAUFORT SEA CRUDE	4	0.83
LAGO MEDIO	VENEZUELAN CRUDE	47	0.87
LUBE OIL	AUTOMOTIVE CRANKCASE OIL	255	0.88
MOUSSE MIX	BUNKER C AND ASMB MIXED	140	0.91
NORMAN WELLS	NORTHERN CANADIAN CRUDE	7	0.83
PANUK	EAST COAST LIGHT CRUDE	1	0.78
PRUDHOE BAY	ALASKAN BEAUFORT CRUDE	55	0.88
SYNTHETIC CRUDE	PROCESSED HEAVY OIL	5	0.86
TRANSMOUNTAIN	MIXED ALBERTA CRUDE	12	0.86
UVILUK	BEAUFORT SEA CRUDE	16	0.88

TABLE 5 EFFECT OF SETTLING TIME  
IN THE SWIRLING FLASK

OIL	DISPERSANT	PERCENT DISPERSION AFTER SETTLING TIME IN MINUTES							
		0	2.5	5	7.5	10	12.5	15	20
ASMB	C9527	68	43	37	33	30	30	29	29
	CRX-8	76	53	44	43	34	33	33	31
	EN 700	81	74	74	71	63	61	60	58
ATKINSON	C9527	86	62	55	47	47	41	42	41
NORMAN WELLS	EN 700	98	83	85	69	71	71	70	69
		<b>60</b>	<b>120</b>	<b>240</b>	<b>420</b>				
ASMB	C9527	22	20	12	14				
	CRX-8	28	11	13	10				
	EN 700	43	24	18	16				

The effect of settling time has been investigated with 3 apparatus. The results for these experiments with the swirling flask are shown in Table 5, with the Mackay apparatus in Table 6 and with the oscillating hoop in Table 7. In all cases, the effect of settling time is highly dependent on the oil-dispersant combination but the effect is the same with each apparatus. An oil-dispersant combination which shows a rapid fall-off in effectiveness with time does so in all three tests. The opposite case is also true. The fact that a number of oils (for example Atkinson, Hibernia and Lago Medio) do show this decrease in effectiveness with increasing settling time indicates that they produce dispersions with larger droplets and are thus unstable. The increase in settling time beyond 10 minutes does not yield significantly different results, as can be seen in Table 5. It is suggested that the 10-minute settling time is optimal for the apparatus tested here.

The effect of settling time is the single most-important factor in the operating protocol of the various effectiveness experiments. The effect can be as much as one order of magnitude for a particular oil-dispersant combination and is repeatable. Furthermore the effect is consistent among different apparatus.

#### **Testing of Dispersant/Oil Combinations Using Similar Protocols**

A series of tests was conducted to test the hypothesis that the settling time and oil-to water ratio is very important to the outcome of the dispersion effectiveness. Four devices were used, the swirling flask, the flowing column, the Labofina and the Mackay apparatus. Published protocols were adhered to with three exceptions. The oil-to-water ratio was set to 1:1200 in each apparatus except in the case of the flowing cylinder where because of the ability to analyze the samples, the minimum is 1:4000. The settling time was set to 10 minutes in all cases except again in the case of the flowing cylinder where this parameter is not relevant. Thirdly, the analysis was performed using the procedure of exacting with methylene chloride, analyzing at three wave lengths and averaging the results. This procedure results in greater accuracy than published procedures where only one wavelength is used.

The results of this comparison testing procedure are shown in Table 8. The tests were conducted using 16 different oils and three different dispersants, the Exxon products Corexit 9527, CRX-8, and the British Petroleum product Enersperse 700 (formerly known as BP MA-700). As Table 8 shows, the dispersant effectiveness values are nearly identical for the four tests. Oils that are very readily dispersed naturally, that is without the use of dispersant, were measured by a blank run and correcting the dispersion for this effect. Table 8 shows that virtually identical dispersant effectiveness results are produced by all four apparatus when the oil-to-water ratio is the same at 1:1200, when the settling time is 10 minutes, and when the results from the two energetic devices, the Labofina and Mackay are corrected for natural dispersion.

The results indicate that laboratory dispersant effectiveness results can be similar even if measured in very different apparatus. The most important factor in achieving the same results is the settling time allowed before taking the sample. The oil-to-water ratio is the next most important factor and finally correction for natural dispersion is necessary in the more energetic apparatus.

These findings have far-reaching implications; first, energy is not the prime only factor as was once thought. Secondly the fact that effectiveness values tend to one value for

TABLE 6

**EFFECT OF SETTLING TIME  
IN THE MACKAY APPARATUS**

OIL	DISPERSANT	PERCENT DISPERSED AFTER SETTLING		
		NO TIME	5-MINUTE	10-MINUTE
ASMB	C9527	99	88	83
	CRX-8	69	26	21
	EN 700	94	93	91
ATKINSON	C9527	99	31	24
	CRX-8	99	30	23
	EN 700	85	23	16
AVALON	C9527	92	28	22
	CRX-8	85	16	12
	EN 700	74	22	21
FEDERATED	C9527	73	12	7
	CRX-8	91	70	66
	EN 700	95	83	81
HIBERNIA	C9527	100	64	52
	CRX-8	94	30	25
	EN 700	92	38	31
ISSUNGNAK	C9527	100	88	81
	CRX-8	100	92	83
	EN 700	100	93	86
LAGO MEDIO	C9527	20	0	0
	CRX-8	78	22	18
	EN 700	95	28	12
NORMAN WELLS	C9527	100	65	55
	CRX-8	98	77	74
	EN 700	100	90	81
PRUDHOE BAY	C9527	95	43	30
	CRX-8	90	27	22
	EN 700	90	69	67
TRANSMOUNTAIN	C9527	99	82	81
	CRX-8	100	30	23
	EN 700	95	77	70
UVILUK	C9527	94	80	77
	CRX-8	82	45	44
	EN 700	93	91	87

TABLE 7

**EFFECT OF SETTLING TIME  
IN THE OSCILLATING HOOP  
APPARATUS**

OIL	DISPERSANT	PERCENT DISPERSION	
		NO TIME	5-MINUTE
AMAULIGAK	C9527	100	90
	CRX-8	100	56
	EN 700	92	64
ASMB	C9527	51	26
	CRX-8	82	21
	EN 700	91	82
ATKINSON	C9527	92	52
	CRX-8	86	48
	EN 700	86	78
AVALON	C9527	84	40
	CRX-8	87	18
	EN 700	52	16
FEDERATED	C9527	93	33
	CRX-8	62	23
	EN 700	92	54
HIBERNIA	C9527	94	50
	CRX-8	76	65
	EN 700	81	54
ISSUNGNAC	C9527	100	51
	CRX-8	85	7
	EN 700	98	91
LAGO MEDIO	C9527	86	10
	CRX-8	89	64
	EN 700	86	64
NORMAN WELLS	C9527	62	29
	CRX-8	67	17
	EN 700	67	57
PRUDHOE BAY	C9527	92	65
	CRX-8	88	37
	EN 700	84	73
TRANSMOUNTAIN	C9527	84	76
	CRX-8	84	37
	EN 700	84	78
UVILUK	C9527	84	76
	CRX-8	83	45
	EN 700	78	72

TABLE 8 EFFECTIVENESS IN FOUR APPARATUS

OIL	DISPERSANT	DISPERSABILITY IN PERCENT			
		SWIRLING FLASK	FLOWING CYLINDER	LABOFINA	MNS
ADGO	9527	61	52	78	64
	CRX-8	42	40	77	87
	EN 700	67	59	76	93
AMAULIGAK	9527	48	38	86	44
	CRX-8	56	46	73	85
	EN 700	54	39	59	73
ASMB	9527	22	21	31	39
	CRX-8	28	31	34	61
	EN 700	43	43	62	76
ATKINSON	9527	7	18	57	17
	CRX-8	9	10	47	19
	EN 700	8	18	55	22
BENT HORN	9527	29	46	29	29
	CRX-8	27	37	27	51
	EN 700	44	51	19	42
FEDERATED	9527	39	35	51	35
	CRX-8	23	31	35	76
	EN 700	38	42	70	76
GEAR OIL	9527	29	18	18	12
	CRX-8	40	25	27	10
	EN 700	10	6	15	30
HIBERNIA	9527	6	12	23	6
	CRX-8	9	10	19	9
	EN 700	7	8	23	14
ISSUNGNAC	9527	24	22	61	41
	CRX-8	42	76	35	100
	EN 700	42	60	75	100
LAGO MEDIO	9527	7	8	29	16
	CRX-8	11	15	19	19
	EN 700	10	23	24	27
LUBE OIL	9527	13	19	40	44
	CRX-8	14	24	40	53
	EN 700	13	23	40	80
MOUSSE MIX	9527	9	15	27	30
	CRX-8	11	25	18	26
	EN 700	24	32	23	43
NORMAN WELLS	9527	41	55	65	47
	CRX-8	60	47	70	65
	EN 700	63	53	74	89
PANUK	9527	100	100	89	100
	CRX-8	93	100	85	100
	EN 700	100	100	87	100
PRUDHOE BAY	9527	7	13	47	27
	CRX-8	5	16	38	23
	EN 700	17	14	48	37
SYNTHETIC CRUDE	9527	57	50	78	83
	CRX-8	69	55	40	91
	EN 700	61	39	76	88

LEGEND 9527 = COREXIT 9527, CRX-8 = COREXIT CRX-8, EN 700 = ENERSPERSE 700

a given oil/dispersant combination suggests that this value may have physical implications or meaning, and thirdly there will be impact on the selection of testing apparatus.

Energy has long been thought to be the most important factor in laboratory dispersant effectiveness testing.<sup>1,43</sup> It was felt that results could only be correlated with the energy level and that this would have to be measured at sea to give true indication of dispersant effectiveness there. For example, one thought that if one could have an energy measuring device appropriate to oil spill dispersion, one could measure the energy at sea and subsequently in a laboratory device and assign a sea-state equivalent value to this laboratory device, Beaufort 3 as an example. The laboratory measure would then represent dispersion only at that energy level. The four devices used in this study have, by visual examination, widely varying energy levels. The energy level of the Labofina and Mackay are much higher than that of the swirling flask and the flowing cylinder devices. This is borne out by the fact the one cannot measure natural dispersabilities in either of the latter two devices, irrespective of operating conditions. The observation in this study that the apparent energy differences in the apparatus, did not lead to major differences, leads one to conclude that energy does not have a major role in determining effectiveness other than a contribution which correlates with natural dispersability.

The hypothesis to explain these results is given later in this paper. The energy to initiate chemical dispersion is low and stays relatively constant until thresholds for the natural dispersion are reached. The threshold at which an oil is naturally dispersed is a function of oil composition and is relatively unique to an oil.

The second impact of the finding that all effectiveness values tend to one value, implies that the values may have some meaning in physical or chemical terms. Perhaps these values represent the maximum dispersion under normal conditions in the laboratory or at sea. Recent work has shown that the major losses associated with effectiveness at sea are physical losses of dispersant and because these tests were performed with dispersants pre-mixed with the oil, they may indeed reflect a maximum value.<sup>1,43</sup>

Finally, because laboratory effectiveness values tend to one value, selection of apparatus can be made on the basis of simplicity, ease of use, and best repeatability. The swirling flask test is the most repeatable, easiest to use, simplest and permits the most tests to be performed in one day. The Labofina is the second apparatus in terms of ease of use and speed, but is the third in terms of repeatability. The flowing cylinder is third in terms of complexity, is the fourth in terms of numbers of runs performed per day, but is second in terms of repeatability.

#### **MECHANISM STUDIES CONDUCTED PRIOR TO 1990**

Initial studies by this group of researchers focused on changing variables in the laboratory tests and observing the effect on dispersant effectiveness. Long-term settling (or rising, depending on the point of view) experiments using the swirling flask apparatus were the first round of experiments to be conducted. It was found that there were about 3 classes of dispersants, those that showed good stability over 48 hours (effectiveness only went down about 20%), those that showed medium stability over the same time period (effectiveness went down about 50%) and those that had poor stability (effectiveness went down about

75%). Most commercial products showed good stability. The tests showed that dispersed oil could be relatively stable in water over a 48-hour period.

Tests conducted on the oscillating hoop, Labofina, Mackay and the Swirling Flask test showed one very disturbing finding. All of the first three tests were insensitive to whether the dispersant was placed in the water or on the oil. Only the swirling flask test showed no trace of this tendency. This finding would imply at first glance, that in the case of the first 3 apparatus, the dispersant can work from the water to the oil rather than vice versa which is the way it would be in real situations or in the swirling flask apparatus. This was the first strong indication that the protocols or apparatus were deficient in measuring dispersant effectiveness.

Because the dispersant worked as well from the water to the oil in these apparatus, experiments were conducted to see the effect of two main differences between the four dispersant-effectiveness apparatus, oil-to-water ratio and settling time. As the oil-to-water ratio was increased, the effectiveness went down in all the tests, however became more similar to that of the swirling flask. Similar results were observed as the settling time was increased. When the four apparatus were run using an oil-to-water ratio of about 1:1000 and a settling time of ten minutes, nearly identical results were produced for many oils, but not for all. Examination of the properties of the errant oils showed that all were naturally dispersible. Blanks (samples without dispersants) were run in the respective apparatus and values subtracted from those runs with dispersant. In other words, dispersant effectiveness values were corrected for natural dispersion. This finding is very significant in that all tests can be related and furthermore, the constant result produced by these tests would appear to be a universal effectiveness value. These test results are detailed in the literature.<sup>64</sup>

A new test was developed to confirm the effect of oil-to-water ratio. This test is different in concept than any of the other tests. The test, known in Environment Canada labs as the flowing-cylinder test, employs a measuring cylinder with a top and bottom side-spout. Water is circulated from the bottom side-spout through a filter to catch dispersed oil and returned to the cylinder via the top spout. The only dispersing energy supplied to the system is the small amount of energy resulting from the fall of the water from the top spout to the oil layer (a distance of about 3 cm). Dispersed oil is continuously removed from the system so that there is no interference of dispersed oil with any processes that may be ongoing. The height between the surface of the oil and the withdrawal spout is about 30 cm. This ensures that only small, stable droplets which do not resurface are withdrawn from the system. Other droplets will rise to re-form a slick. The test was developed for two reasons, to have a system which could measure oil-to-water ratios to very high values (as large as 1:1,000,000) and to have a system which was not analogous to those others tested in terms of energy addition. The flowing cylinder apparatus yielded the same results as the other four tests when they are operated at high oil-to-water ratios and 10 minute settling times. This confirms that the previous findings were independent of apparatus mode of operation. The device was used to measure the effect of oil-to-water ratio on dispersant effectiveness. It was found that effectiveness was constant with oil-to-water ratio from about 1:800 up to 1:1,000,000 and that effectiveness peaked at 1:600 then slowly fell as the ratio decreased to 1:100. This was confirmed by performing the same experiment in the other three apparatus. It was concluded that this effectiveness was due to a change in mechanism of dispersant

action from high oil-to-water ratios to the low ones. In the case of low ratios, the surfactant may interact to form agglomerates and micelles, thus interfering with the main process by removing surfactant. This would account for the lower effectiveness at the lower ratios. Because dispersion at sea would involve high ratios, laboratory equipment should mimic these conditions as much as is possible.

The next round of experiments focused on the measurement of dispersed oil droplet sizes produced in the different apparatus. The apparatus were operated at the optimal settling time and oil-to-water ratio, as noted above. After several dozen measurements, it was found that in all apparatus, all oils with all dispersants resulted in the same droplet size of 30 microns VMD. In performing particle analysis, two measurements are obtained, particle size and number of particles at this size. The distribution may change from one sample to another. A distribution is a very difficult way to understand test results. For this reason scientists developed the concept of VMD, or volume mean diameter, which is a single number and is the only way to simplify the interpretation of a complex distribution. It is calculated by summing the volume of particles until the mid-point of the total volume is reached. It is the size at which half the volume of the particles are represented. Because the volume of particles goes up as the cube of particle diameter, averages or numbers of particles are meaningless. One 50 micron diameter oil particle contains more oil than 100,000 - 1 micron droplets.

The significance of the droplet-size finding is that there exists a distribution size of oil droplet sizes, 30 microns VMD as found in the experiments, which are stable and to which all oil spill dispersions will tend. The significance of this finding is two-fold. First, further measurement of sizes is meaningless since the value of 30 microns is found and second, most oil dispersions, once formed, are relatively stable.

Investigations into the basics of surfactant technology has brought some revelations into the whole issue of dispersants and their effectiveness. Existing dispersants consist of three active ingredients or surfactants - a high HLB one typically around 15, a low HLB one, typically around 5 HLB, and an ionic surfactant whose HLB would be about 40. All the commercial dispersants produced since 1968 have had a very similar formulation, only the solvents and specific choices of these surfactants vary. The formulation is sometimes even provided in general terms by surfactant suppliers. The formulation was first developed as a low-toxicity domestic degreasing or oil-removing formula. The logic behind choosing the two surfactants with HLB of 5 and 15 was that the different geometric configurations would cause tighter packing than would occur by using one surfactant alone. The second presumption is that mixing surfactants of high and low HLB can be done to produce a stable product with an average HLB of around 10. The ionic surfactant is present to give even tighter packing but its HLB is difficult to consider in designing a formulation. As later studies show, each of these assumptions may be incorrect in open systems such as at sea.

One problem examined by several researchers was the herding, or pushing aside, of the oil by the dispersant. This was observed at many field trials and during actual applications. Before 1980 or so, most people believed that this phenomena was actually dispersants working very rapidly. Unfortunately, some people still cling to the belief. The only research on herding on open systems was done by Brown of Esso Resources who was able to quantify herding rates and velocities. Tests in the Environment Canada laboratory

showed that herding occurred at all times on thin slicks with most dispersants. Once waves were increased from 2 to 3 cm. herding ceased. Literature on the phenomenon is scarce, however early work by Environment Canada has shown that tests of herding agents showed similar limitations.<sup>44</sup> The finding has basis in physics because the spreading force of a chemical is weak compared to gravity and that the two forces would be equal at a gravitational difference of 2 to 5 cm. This also explains why herding is not universally observed at spill scenes. Work done by Becher on herding has shown that surfactants with HLB's greater than 10 cause herding and that this effect increases as the HLB increases.<sup>45</sup> This shows that either the dispersant has high HLB's or that the surfactants are separating to cause herding. The latter is largely confirmed by analysis of remote sensing data at the Beaufort Sea trials which show surfactant on the sea surface slowly separating from the slick. To confirm this hypothesis, the formulator of a major dispersant recently revealed that their herding agent has an identical surfactant as the high HLB one in the dispersant!

Investigation into dispersant formulation continued with work on simple mixtures. Rendering the existing mixtures more oleophilic resulted in only slightly improved performance for lighter oils. Significant lessons were learned about dispersant action mechanisms. First, surfactant HLB is much more critical than originally thought. As an example, one surfactant family showed a high effectiveness with an HLB of 10.2, whereas the member with one more methylene group showed no effectiveness and caused the oil to form emulsion. Second, only surfactants with HLB of 10 showed promise. Third, mixtures of surfactants to yield an average HLB of 10 using high and low HLB products were not as effective as single surfactants but were more effective than either surfactant alone. Fourth, ionic surfactants by themselves lacked effectiveness and simply went into the water. Finally, most solid surfactants did not work, probably because they would not mix with the oil.

In 1989, a joint study with the United States Minerals Management Service was initiated to examine another phenomenon, that of the accelerated weathering caused by dispersants.<sup>46</sup> It was known that dispersants causes accelerated weathering of the oil, but the extent to which this might occur was not. Two series of experiments were run, the first phase using standard dispersant laboratory effectiveness apparatus, the Mackay, the Labofina and the Swirling Flask test. The method of performing the experiment was to measure oil in the water column and left on the surface so that a mass balance could be achieved. In experiments where oils were not treated with dispersant, all mass could be accounted for within the experimental error of about 5%. For dispersant-treated oils the loss of mass was taken as the amount lost due to accelerated weathering. This round of experiments showed that the amount of weathering was dependent on the oil type. The amount lost from the treated oil was about half of the maximum amount lost through normal weathering on exposure for long periods of time. For a series of common crude oils, this averaged about 10%, but could be as much as 20% for a very light oil.

The second phase of the experiment involved analysis of both the oil in the water and the oil remaining on top by gas chromatography and comparison to the starting oil. It was found that accelerated weathering again occurred to about the same percentage as found before. Besides this, a very important discovery was made, that the composition of the oil in the water column and on the surface had changes other than those caused by weathering alone. It was found that more n-alkanes of those chain lengths corresponding to the same

chain length of the oleophilic portion of the surfactant, were taken into the water column. Surface oil was deficient in these same compounds, confirming the hypothesis that this was the result of absorption to the oleophilic portion of the surfactant. The oil on the surface contained a higher proportion of n-alkanes of longer chain lengths than did the starting oil, showing that separation of the oil does occur to a certain extent and that certain portions, eg. longer molecules, are less dispersible. These findings are significant, showing that longer-chain surfactants may be necessary to achieve greater dispersion, that surface means of measuring dispersant effectiveness at sea must compensate for the accelerated weathering and that there are oil components which are not readily dispersible.

The findings of the mechanism studies conducted up to 1990, can be summarized as follows:

1. That separation of mixed surfactant systems occurs,
2. That herding is limited to low wave heights, <2 to 3 cm,
3. Herding in existing dispersants is largely due to the high HLB fractions of mixed surfactant systems currently in use,
4. Dispersant use results in accelerated weathering of the oil,
5. Dispersants draw more of the oils compounds that correspond to their oleophilic chain lengths into the water,
6. That long chain lengths and perhaps other components of the oil, are dispersed less than shorter chain lengths, and
7. That the droplet sizes produced by most dispersants and most oils in most apparatus may have the same size distribution.

#### **CHANGES IN CHEMICAL COMPOSITION WITH DISPERSION AND WEATHERING**

Few studies have been conducted to investigate the changes in oil composition associated with chemical dispersion. Some workers have investigated the accelerated weathering or evaporation attributed to dispersant action, but did not attempt to quantify the effect. Two specific phenomena were investigated; the accelerated weathering caused by dispersants, and secondly the change in the composition of the n-alkanes (the normal or straight-chain aliphatic compounds) which often constitute a large part of the oil's volume. These compounds are relatively easy to study by gas chromatography, being easy to identify and quantify.

Dispersant-accelerated weathering (evaporation) has been noted in the past by a number of workers. McAuliffe was the first to publish information on this topic.<sup>50-52</sup> This phenomenon was further defined by McAuliffe in subsequent laboratory experiments where it was found that the C<sub>2</sub> to C<sub>10</sub> hydrocarbons under a chemically-dispersed slick were of a lower concentration than under mechanically-dispersed slicks.<sup>53</sup> McAuliffe subsequently reviewed a number of experiments, both field and laboratory, in which the accelerated weathering of C<sub>2</sub> to C<sub>10</sub> hydrocarbons was measured.<sup>54</sup> Wilson and co-workers conducted extensive tank experiments and noted a slightly-faster evaporation rate for chemically-treated oil.<sup>55</sup> Anderson and co-workers noted major differences in the toxicity of mechanically and chemically-dispersed oil to shrimp.<sup>56,57</sup> Further studies showed that the

lower toxicity of chemically-dispersed oil was due to accelerated evaporation of toxic monoaromatics.<sup>58</sup> Bowler and co-workers conducted a number of experiments using a laboratory effectiveness apparatus and found that dispersants increased the evaporation rate of oil when comparing treated and untreated oil.<sup>59</sup> Fingas and co-workers found similar accelerated weathering using dispersants on fuel in a model sewer system.<sup>60,61</sup>

No studies dedicated to studying the chemical composition changes after the application of dispersant were found in the literature. Compositional changes in dispersed oil, were however noted by some workers while studying other facets of the dispersion process. Peake and Hodgson noted that water under an oil treated with an undecanoic acid surfactant was enriched in undecane, but attributed the effect to an anomaly which required further study.<sup>62</sup> Wilson and co-workers noted that there was a compositional difference between the starting and dispersed oil, but suggested that the differences may be due to degradation.<sup>55</sup> Shaw and Reidy found compositional changes but correlated these to mixing energy and not presence or absence of a dispersant.<sup>63</sup>

### Experimental

Two forms of experiments were performed. First, evaporative loss was measured in laboratory dispersant effectiveness apparatus. Secondly, dispersant tests were performed in the swirling flask apparatus and the starting oil; surface oil, treated but undispersed; and the oil in the water column were analyzed using a gas chromatograph.

In the first set of experiments, three different apparatus were used. The swirling flask apparatus was operated according to published procedure.<sup>40</sup> The MNS (Mackay-Nadeau-Steelman) or Mackay test was operated according to published procedure except that the oil-to-water ratio was maintained at 1:1200.<sup>41</sup> The Warren Springs, Labofina or alternatively, the rolling flask test, was also operated according to published procedure except for the same oil-to-water ratio as above.<sup>42</sup> The same oil-to-water ratio was maintained in all apparatus to eliminate this as a variable and also for the reason that lower ratios have been shown to effect results.<sup>64</sup>

The full experiments and results are given in the literature.<sup>65</sup>

All experiments were run in the same manner; oil was applied to the water surface, the apparatus energized in its regular manner and after the run was completed, the surface oil was removed using 2.5 cm by 2.5 cm sorbent pads (SPC sorbent). These were in turn extracted using 30 mL methylene chloride. Concentrations were determined colorimetrically using a previously-prepared calibration curve. The calibration curves were prepared in analogous fashion to ensure that losses and sorbent efficiencies were accounted for. Results were repeatable to within 10%. The untreated crude oil was processed in the same manner as above to ensure that evaporation was compensated for. To account for accelerated weathering, experiments were done to measure the oil remaining on the surface and that in the water column. The amount lost to accelerated weathering was obtained by subtracting those amounts from the original amount added. The initial or untreated oil quantity was determined to be that amount left after processing in the apparatus without dispersants. This was done to ensure that losses, evaporation and inefficiencies were accounted for. The oil left on top after dispersion was determined using the sorbent

procedure described above. Oil in the water column was determined by the published procedure for the apparatus and always involved extracting a portion of the oil and analyzing colorimetrically using a pre-determined standard curve. At least two runs were performed for every apparatus, oil and dispersant combination. If values were outside 15% experiments were repeated until the majority of values were within 15% of each other.

Five oils were used in both experiments. Mousse mix is a name given to a mixture of Bunker C and Alberta Sweet Mixed Blend (ASMB) and is frequently used in our laboratory for physical experiments. The name derives from the high tendency of that mixture to form mousse (water-in-oil emulsion).

Gas chromatographic analysis was used in the second set of experiments to examine the composition of the starting oil, the surface oil and the oil dispersed into the water column. Methylene chloride extracts were performed as described above, effectiveness measured colorimetrically to ensure the consistency of results with those of previous experiments, and then a 0.5 microliter portion of the extract was injected into a Hewlett-Packard 5890 chromatograph. The chromatographic conditions were as follows: initial temperature - 40°C, initial time - 5.0 minutes, temperature programming rate - 6.0°/min., final temperature - 300°C, final time - 30 min., and attenuation - 2. The column used was a SPB-1 and with helium as the carrier gas at a flow rate of 2.7 mL/min. The hydrogen flow rate for the FID detector was 30 mL/min and the air flow rate 240 mL/min.

A synthetic oil was made and run through the entire experiment to confirm that enrichment of certain n-alkanes as observed in the regular experiment was not a result of breakdown of the dispersant. No compounds other than those in the synthetic oil were evident in the gas chromatograph resulting from this test.

### **Weathering of Oil**

The results of the experiments using laboratory effectiveness apparatus are summarized in Table 9. The values presented in this table are the amounts of oil unaccounted for after the oil on the surface and in the water column were computed, and thus represents the amount lost through evaporation since other losses were compensated for during the calibration procedure.

The accelerated weathering ranges from 0 to 30 % with an average of 11 %. These values should be taken in context with the error for each of the apparatus used; swirling flask 5%, Labofina 7%, and MNS 10%. All weathering values obtained were positive, thus indicating that despite the measurement error, dispersants always accelerate the weathering of the oil. The accelerated weathering is least in the MNS, as one might expect because the device operates with a high velocity stream of air and this would evaporate the untreated oil to a large extent. If the untreated oil is evaporated to a large extent the loss by accelerated weathering is small, because results are always compared to the weathering of this untreated oil after processing through the entire experiment. These results indicate that an average of 11% of the mass is removed over a short time period by the action of dispersants. Untreated oil would ultimately lose this mass by evaporation over a longer time depending on temperature and wind speed.

The accelerated weathering of oil was also examined in the second round of experiments. The swirling flask apparatus was used and untreated oil, surface oil and oil

dispersed into the water column were examined by GC analysis. A computer program was used to analyze the relative amounts of n-alkanes and then draw comparisons between compositions in the three fractions. The results of this analysis are illustrated in Figure 3 and tabularly in Table 10. The weathering of oils is shown in the  $C_9$  to  $C_{13}$  portion of this figure. The amount of these compounds present in either the undispersed oil remaining on the top or in the water column is on average less than that in the starting oil. Each of the compounds, up to about  $C_{13}$  is about 5% less in abundance than the starting oil. This analysis shows that accelerated weathering is taking place, even of the n-alkane fractions. The gas chromatographs for the same region of GC analysis show a strong decrease in other compounds present in the water or the undispersed oil remaining on the surface, compared to that of the untreated oil. This indicates that these compounds, largely aromatics, are almost totally removed from the oil during the dispersion process.

#### Alkane Composition Changes

Three forms of compositional differences have been found:

1. The  $C_9$  to  $C_{13}$  n-alkanes in both the undispersed oil remaining on the surface and those in the water column are in lower concentrations than in the starting oil. This is the accelerated weathering as described above.
2. The concentration of certain n-alkanes between  $C_{13}$  and  $C_{18}$  is much greater in the water column than in the starting oil and is depleted in the surface oil.
3. The concentration of n-alkanes between  $C_{19}$  and  $C_{26}$  is slightly greater in the undispersed surface oil, than in the untreated oil and the dispersed oil.

These selectivities are illustrated in Figure 3. The figure presents a bargraph of the concentration difference at a particular carbon number, between the untreated oil, the oil left on the surface or oil in the water column. Annotation appears on each graph to show which portion of the oil has a greater concentration. Figure 3 shows the comparison of n-alkane composition between untreated oil with oil left on the top of the water. The alkane selectivity is again evident. The surface oil is depleted in  $C_9$  to  $C_{12}$  n-alkanes by accelerated weathering, is somewhat depleted in some of the  $C_{13}$  to  $C_{19}$  components which are concentrated in the water column and finally the surface oil is enriched in the larger n-alkanes which disperse poorly. These experiments show that the concentrations of n-alkanes in the dispersed oil and oil left on the surface are altered by the use of surfactants. Two areas of alteration are strongly evident, one falling in carbon numbers 12 to 18 and the other above these values. The former is directly indicative of the type of dispersant used, and in fact could be used to identify the specific dispersant. This selectivity is thought to be a result of absorption of n-alkanes to the oleophilic portion of the surfactant. This occurs at the same chain length as the oleophilic portion or 1 or 2 carbon units shorter. Such phenomena has been observed before and actually is used in designing surfactants for solubilizing materials.<sup>66</sup> It has however never been reported or studied in terms of oil spill dispersants.

The concentrations of the higher alkanes ( $C_{19}$  and above) are lower in the dispersed oil than in the starting oil and in the surface oil. This indicates that these components are less dispersible than the shorter alkanes and are concentrated in the undispersed surface layer.

Table 9

**EVAPORATION IN THREE APPARATUS**

OIL	DISPERSANT	PERCENTAGE EVAPORATION IN APPARATUS			
		SWIRLING FLASK	LABOFINA	MNS	AVERAGE
ADGO	COREXIT	4	0	0	1
	ENERSPERSE	0	2	3	2
ASMB	COREXIT	25	31	2	19
	ENERSPERSE	11	25	7	14
MOUSSE MIX	COREXIT	15	6	2	8
	ENERSPERSE	9	8	14	10
HIBERNIA	COREXIT	30	18	10	19
	ENERSPERSE	25	4	14	14
LAGO MEDIO	COREXIT	4	3	12	6
	ENERSPERSE	30	12	2	15
					11

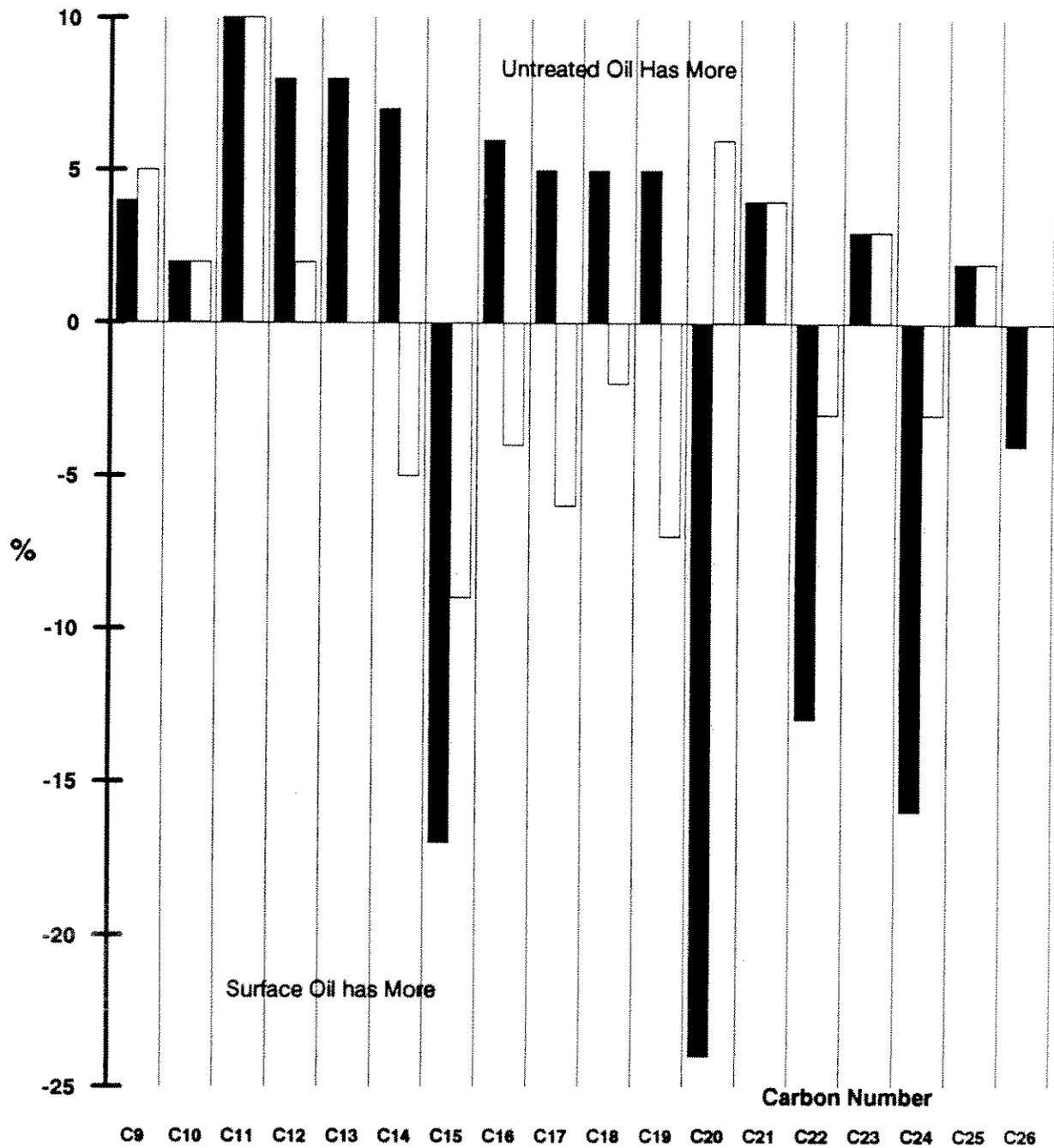
Table 10

**Alkane Content**

(Content Determined by GC Analysis of Weathered Fraction only)

Oil	Dispersant	n-Alkane Content (%)			Alkane Enrichment (%)	
		Oil	Water	Top	Water	Top
Adgo	Corexit	13	13	25	0	-
	Enersperse	13	37	55	184	-
ASMB	Experimental	43	54	44	26	2
	Corexit	43	68	33	58	-23
Hibernia	Enersperse	43	66	45	53	5
	Corexit	48	44	44	-8	-8
Lago Medio	Enersperse	48	60	47	25	-2
	Corexit	40	87	53	118	32
Mousse Mix	Enersperse	40	56	38	40	-5
	Corexit	44	81	44	84	0
					68	23
				Average	59	1

**Figure 3 Alkane Composition Comparison: Experimental Dispersant and Oil Left On Surface**



The overall effect of this selectivity is thought to be significant upon the final dispersion effectiveness, but not dominating. Table 10 shows the approximate concentrations of the n-alkanes in the three studied fractions. There appears to be an n-alkane enrichment overall in the water column caused by dispersants. The average alkane enrichment is 59%. The n-alkane fraction content in the surface oil remains about the same. This is consistent with the previous finding, as the depletion of the  $C_{13}$  to  $C_{19}$  fraction by dispersant action is matched by the increased amount of the larger n-alkanes left on the surface.

In summary, dispersants cause accelerated weathering of oil, removing most of the oil components up to  $C_{12}$ . The acceleration consists of the removal of about 11% of the oil mass on the short term. Most of the aromatics and some of the n-alkanes are removed.

Dispersants absorb some of the n-alkanes corresponding to their surfactant oleophilic chain lengths, this results in an increased concentration of these compounds in the water column and their depletion in the slick remaining on the surface. This selectivity is unique to the dispersant formulation.

Dispersants do not have as much effect on longer chain n-alkanes ( $>C_{19}$ ) as they do on the shorter ones. The surface oil is enriched in these longer chain n-alkanes.

These three effects, although significant, are not major and do not dominate the dispersion process. These findings do however, have implications for dispersant laboratory testing. These effects must be known if the top or remaining portion of the oil is to be analyzed. The application of remote sensing or other surface techniques, to measure oil dispersion on the sea should include consideration of the additional amount removed by accelerated weathering.

## **PARTICLE SIZE**

The particle sizes of dispersant droplets is a highly-discussed topic with little work actually performed on measuring droplet size. Byford measured droplet sizes in the Mackay and Labofina apparatus when operated in the usual protocol. He found droplet sizes of 70 to 110 microns VMD. Daling has found similar results. Both sets of measurement were made using a laser dispersion apparatus. Earlier measurements by Jasper provided data on dispersion droplet sizes using a Coulter counter. VMD measurements were not given. It is important to note that data without conversion to VMD (Volume Mean Diameter) is meaningless. The volume is related to the diameter as a cube function. One 30 micron droplet has more volume than 1000 one-micron droplet particles. The VMD is the diameter at which one half of the volume of the sample is accounted for. It is the only single value that can appropriately describe a droplet size distribution.

Environment Canada has conducted extensive particle size studies using a variety of instruments. A series of studies was conducted using a Hiac-Royco particle size analyzer operating on the principle of light blockage. The instrument has both a laser and photodiode head to give a broad range of coverage from 0.1 microns to 200 microns. This study continues at the present time with a new laser dispersion instrument. Both instrument result will be used and both will be confirmed and have been in the past, using optical microscopy.

A series of tests was conducted to study the droplet size distribution resulting from when a number of factors were varied, including oil type, dispersant, oil-to-water ratio and settling time. Table 11 provides the numerical results from this study. All data are from the Hiac-Royco unit. The data at the bottom of the table the average of two or more determinations. The Labofina apparatus was used for some of the determinations and the swirling flask for others. There was no apparent differentiation between the droplet sizes produced by either apparatus when operated under the same conditions.

Table 11 shows a number of well-defined trends:

1. All droplet sizes tend toward 33 microns VMD under optimal conditions, and in fact, further tests (results not published here) show this to be the case under a large variety of conditions,
2. Low oil-to-water ratios and short settling times show an increase in droplet sizes, and
3. there does appear to be a significant difference between different oils and different dispersants.

Studies on droplet size distributions continue.

#### **METHODS OF PREPARING CALIBRATION CURVES**

The results of some tests conducted in the past year appeared to be in error and the problem was investigated. It was found that some surfactants, in particular an experimental dispersant known as BQ, produced a high degree of coloration in the extraction process. This coloration, because of the methodology used to measure effectiveness, interferes and cause the values to appear quite high. The traditional method of measuring laboratory dispersant effectiveness is to take a small aliquot of the dispersion test water, extract the oil, usually with methylene chloride and then measure the colour at a specific wavelength. This value is compared to a standard curve and an effectiveness assigned. The preparation of the standard curve was traditionally done by injected the appropriate amount of oil directly into the methylene chloride and measuring colour density. When the swirling flask test was developed, it was found that the traditional approach of preparing standard curves was somewhat in error because the simple addition of water to the extraction process produced some coloration in the methylene chloride. This results in inflated effectiveness values. The protocol for the swirling flask effectiveness overcomes this error by using a standardization procedure that is directly analogous to the actual extraction procedure. This cancels the effect that sea water alone can have on the results.<sup>64</sup> Also, the protocol calls for colorimetric measurements at three separate wavelengths (340, 370 and 400 nm) to overcome errors caused by the lack of resolution of the spectrometer.

The effect of the dispersant on the calibration procedure was tested but was not included because the commercial dispersants tested did not show a significant effect. However, the reinvestigation of this in recent times has shown that some surfactant mixtures will result in high colorations of the methylene chloride causing high and incorrect dispersant effectiveness. Table 12 gives summary values of some experiments conducted to investigate calibration procedure.

Table 11

## Effect of Oil-to-water Ratio and Settling Time On Particle Diameter

OIL	DISPERSANT	VMD AT TIME (microns at min)								
		0.5	1	1.5	2	3	4	5	7	10
<b>O/W ratio = 1:50</b>										
MOUSSE MIX	COR. 9527							68	69	53
	EN 700							69	68	57
NORMAN WELLS	COR. 9527									46
	EN 700									48
<b>O/W ratio = 1:125</b>										
MOUSSE MIX	COR. 9527						57	56	56	46
	EN 700						58	56	57	46
NORMAN WELLS	COR. 9527									45
<b>O/W ratio = 1:500</b>										
MOUSE MIX	COR. 9527						33	32	32	33
	EN 700						34	33	32	33
NORMAN WELLS	COR. 9527						44	44	43	42
	EN 700						39	39	37	34
ASMB	COR. 9527						46	45	45	44
	EN 700						45	45	45	42
PRUDHOE BAY	COR. 9527							44	44	34
	EN 700							45	45	33
<b>O/W ratio = 1:1250</b>										
MOUSE MIX	COR. 9527	42	32	32	32	33				
	EN 700	31	32	31	30	29				
ASMB	COR. 9527	33	33	32	33	33				
	EN 700	33	33	33	33	33				
NORMAN WELLS	COR. 9527	33	33	34	33	33				
	EN 700	33	33	33	33	32				
PRUDHOE BAY	COR. 9527	42	38	39	37	33				
	EN 700	31	30	31	31	31				

Table 12 EFFECT OF CALIBRATION PROCEDURES ON EFFECTIVENESS VALUES

Oil/Dispersant Combination	EFFECTIVENESS IN PERCENT AS GIVEN BY EACH CALIBRATION PROCEDURE			
	TRADITIONAL (direct oil)	STANDARD (water corrected)	STANDARD + (water & dispers.)	CORRECTION (dispersant alone)
ASMB + BQ	60	46	29	27
ASMB + Corexit	33	31	33	
Issungnak + BQ	65	46	21	22
Issungnak + Corexit		22	22	
Norman Wells + BQ	75	57	31	33
Syncrude + BQ	40	27	30	

The means for performing each form of calibration is as follows. The "traditional" method, not generally used by Environment Canada, consists of adding the correct amount of oil directly to the extract, usually methylene chloride. The method does not compensate for coloration caused by the sea water or the dispersant. The "standard" method refers to the method published for the swirling flask apparatus in which the standard curves are prepared in a manner analogous to the actual extraction procedure. This method compensates for the coloration caused by the water and losses incurred during the extraction procedure. The next method given in Table 12 is referred to as "standard +" and consists of applying the standard procedure plus adding the dispersant premixed in proportion to the actual test (1:25, dispersant to oil). This method directly compensates for dispersant coloration but would require that a complete calibration curve be prepared for every oil/dispersant combination. The final method is to correct the standard curve by compensating for the dispersant. This is accomplished by running a calibration experiment without oil but with the dispersant. Colorimetric readings are taken and subtracted from the ultimate experimental results. This method has the advantage that a correction is achieved for each dispersant without having to draw up an entire calibration curve. As can be seen from the table, this method yields results similar to the procedure of preparing an entire calibration curve but is much simpler.

The results in Table 12 show that the dispersant BQ yields much higher dispersant effectiveness than is correct. The dispersant BQ requires correction for the coloration it produces by itself. The dispersant Corexit 9527 does not appear to yield such errors. The few values done by the traditional method indicate that this does not yield satisfactory results because large amounts of coloration are not compensated for.

Given that a dispersant itself can be run through the calibration procedure and a correction value derived, this procedure should be followed with all new dispersants to ensure that true effectiveness values are measured.

#### EFFECT OF AMOUNT OF DISPERSANT AND SALINITY

The effects of a number of basic parameters on dispersant effectiveness were tested using the swirling flask apparatus operated in a normal configuration and using standard procedures except for changes in the parameter of interest.<sup>34</sup> Dispersant was pre-mixed with the oil to ensure a higher degree of repeatability. Experiments were performed with Alberta Sweet Mixed Blend (ASMB) crude oil and the dispersant Corexit 9527, except where noted.

The effect of the amount of dispersant was studied by conducting a series of experiments using differing amounts of dispersant in the oil, ASMB, in every case. The ratio

of dispersant to oil was varied from 1:5 to 1:60 in steps of 5. The behaviour of the various dispersants are consistent, the effectiveness rapidly falls off with decreasing dispersant amount. Effectiveness approaches 0 at dispersant-to-oil ratios of about 1:40 to 1:60. Some experimental dispersants display a slightly better performance. The maximum achievable dispersion is about 90% with the Alberta Sweet Mixed Blend crude oil used in the test. The effectiveness falls off rapidly with decreasing surfactant amount and this may explain the variances in observed dispersant effectiveness both in the lab and in the field. A doubling of dispersant can easily result in a doubling of effectiveness and vice versa.

The effect of salinity on dispersant effectiveness was tested in two separate experiments. Alberta Sweet Mixed Blend, Norman Wells and Adgo crude oils were used with the dispersants Corexit 9527 and Enersperse 700 in the first round of experiments. These results are shown in Figure 4. Because of the surprising results obtained, a second round of experiments was performed using Alberta Sweet Mixed Blend crude oil and the dispersants Corexit 9527, Enersperse 700 and Citrikleen. These results are shown in Figure 5. Polynomial curves with two variables were fit to the data using a least-squares procedure. The results are consistent between the different oil/dispersant combinations. Dispersant effectiveness is at a maximum at a salinity of 40 to 45 ‰ (parts-per-thousand or degrees salinity) and falls down very sharply with a decrease or increase in salinity. Freshwater effectiveness is low for all oil/dispersant combinations. Separate experiments were conducted with other dispersants, including those designed for freshwater with similar results. This indicates that ionic interaction is necessary to the dispersion process, at least for the dispersants tested. The decrease in effectiveness with salinity increase above 40 ppt was unexpected, but may be explained by the fact that the main surfactants in the products tested are non-ionic and the HLB of these is strongly dependent on ionic strength.

#### **EFFECT OF OIL PROPERTIES ON DISPERSANT EFFECTIVENESS**

It has been a long-held belief that the high variation in dispersant effectiveness with different oils was the result of the viscosity of the oil. Earlier workers showed that effectiveness correlated with viscosity, however their experiments were conducted by mixing two very different compositions together to yield differing viscosities.<sup>47</sup> It is uncertain whether the change in effectiveness was a result of the changing viscosity, composition or both. Other observations showed that there were several instances where compositional factors were important.<sup>67</sup>

Composition data were found for a number of oils for which dispersant effectiveness was measured.<sup>63</sup> Asphaltene and wax contents were measured for all oils in the series. Dispersant effectiveness using the dispersants Corexit 9527, Enersperse 43 and Dasic Slickgone was measured using the swirling flask test.<sup>40</sup> Least squares methodology was employed to correlate the data and linear, exponential, binomial, and logarithmic curves were fit to each set of data and the best fit chosen. Exponential curves generally provided the best fit between viscosity, dispersant effectiveness and the composition data. Linear equations generally provided the best fit between composition parameters. A high correlation coefficient (over about 0.50) shows a strong relationship between the data and a low correlation coefficient (0.00 to 0.20) shows a very weak relationship between the two sets of data. There is little differentiation found between data sets for the different

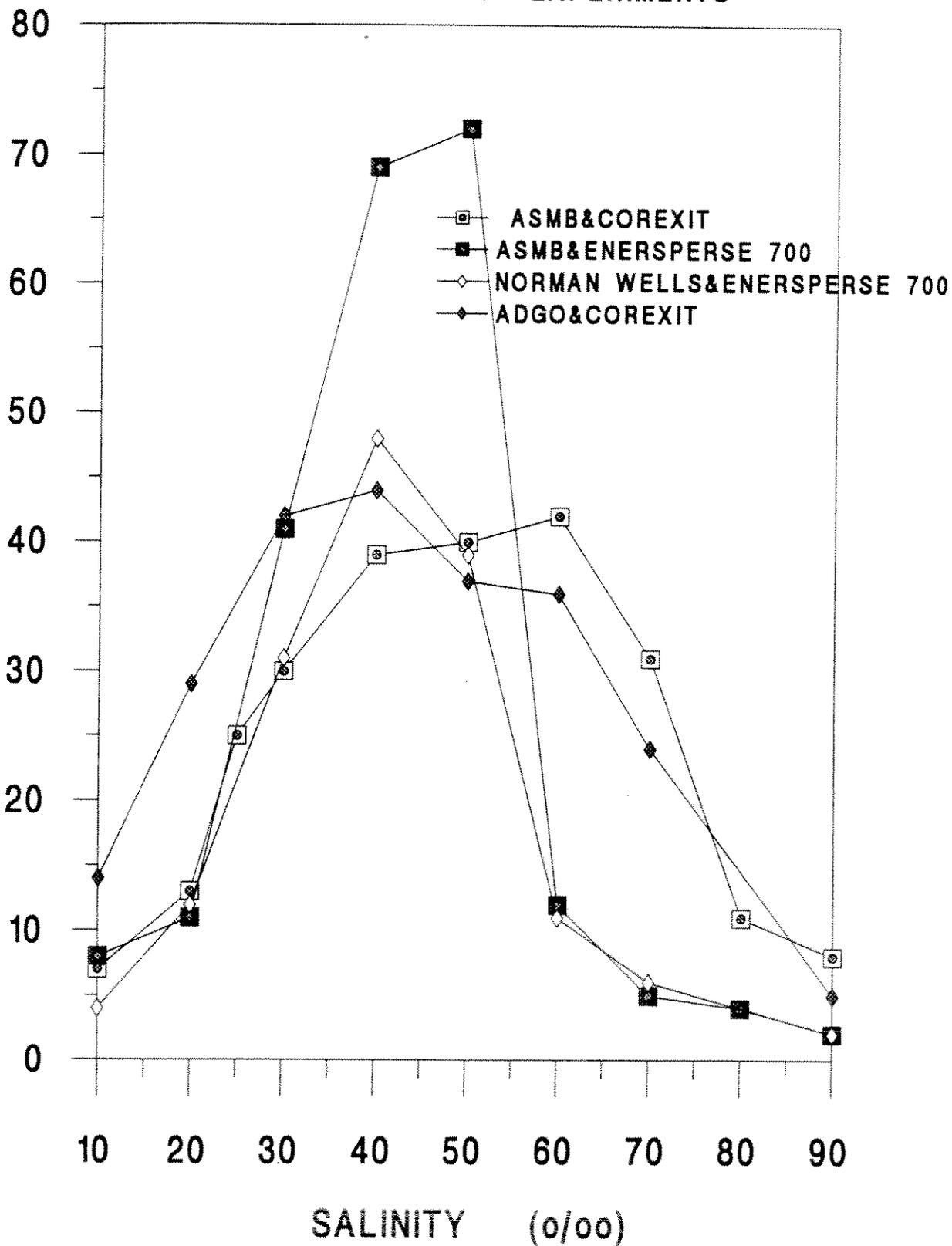
# VARIATION OF EFFECTIVENESS WITH SALINITY

EFFECTIVENESS

%

FIGURE 4

FIRST EXPERIMENTS

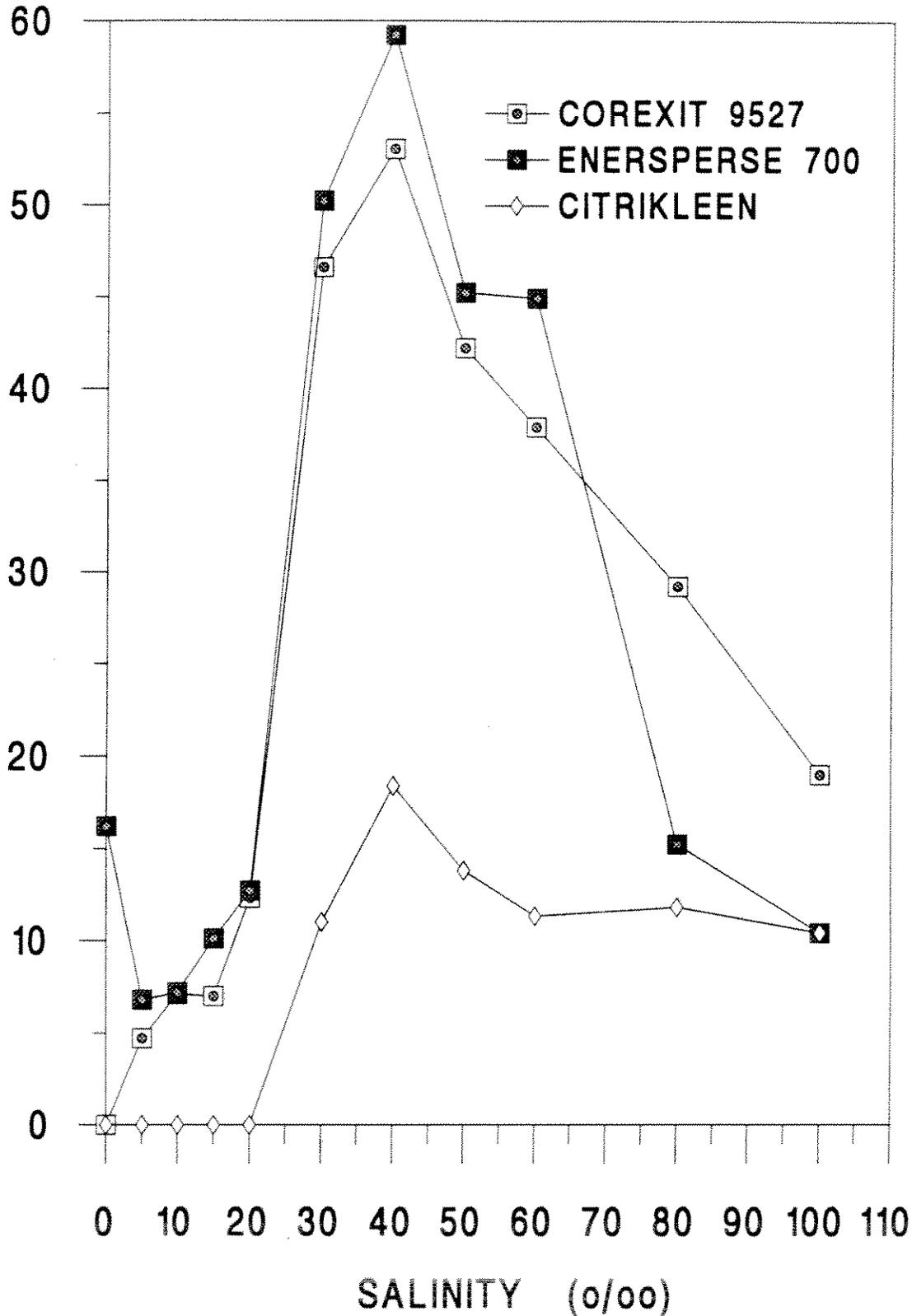


# VARIATION OF EFFECTIVENESS WITH SALINITY

EFFECTIVENESS  
%

FIGURE 5

VERIFICATION RUN



dispersants and thus the average value of these was employed in subsequent analysis to simplify calculations. The agreement among the effectiveness values for the three dispersant data sets is illustrated by correlation of these data with the saturate content in the oil. A correlation coefficient (squared) of 0.76 was achieved with Corexit 9527 effectiveness data, 0.83 with Enersperse 700 data, 0.88 with Dasic data and 0.86 with the average of the 3 data sets. This close correlation also illustrates that the three dispersants are affected in very similar ways by oil composition.

Figure 6 illustrates the correlation between average dispersant effectiveness and the saturate content of the oil. The saturate content is the percentage of the oil which constitutes hydrocarbon compounds with only singly-bonded carbon. As can be seen by this figure, there is a strong correlation between dispersant effectiveness and saturate content. The greater the saturate content, the greater is the effectiveness. Table 13 also shows that effectiveness is strongly correlated with the other oil constituents except for wax content. Figure 7 shows the correlation of average dispersant effectiveness with aromatic content. Dispersant effectiveness goes down as oil aromatic content increases. There is little relationship between wax content and effectiveness. It should be pointed out, however, that wax content is difficult to measure consistently and is a very low value. When measurement difficulties are overcome in the future, a correlation may be found. The correlation of dispersant effectiveness and oil viscosity is poor. This is contrary to expectations and common wisdom. Examination of the data shows that although some high viscosity oils show poor dispersant effectiveness, other oils such as Adgo and Atkinson show high effectiveness. The viscosity of the heavy oil used in this study is very large. A correlation of oil viscosity and dispersant effectiveness was also performed with data from the lighter oils only and is shown in Figure 8. The correlation coefficient (squared) is 0.32, which although low is considerably higher than the correlation in which the heavier oils are included. This does however indicate that viscosity alone is a poor predictor of dispersant effectiveness.

There are two additional trends that are significant. First, there is a strong correlation between viscosity and oil composition. Asphaltene, aromatic and polar components are positively correlated with viscosity and saturate content is negatively correlated. Secondly, the components are correlated strongly with each other in a linear function. This is as expected because an increase in one component requires a decrease in another component.

### **SUMMARY OF THE SALINITY AND COMPOSITION STUDIES**

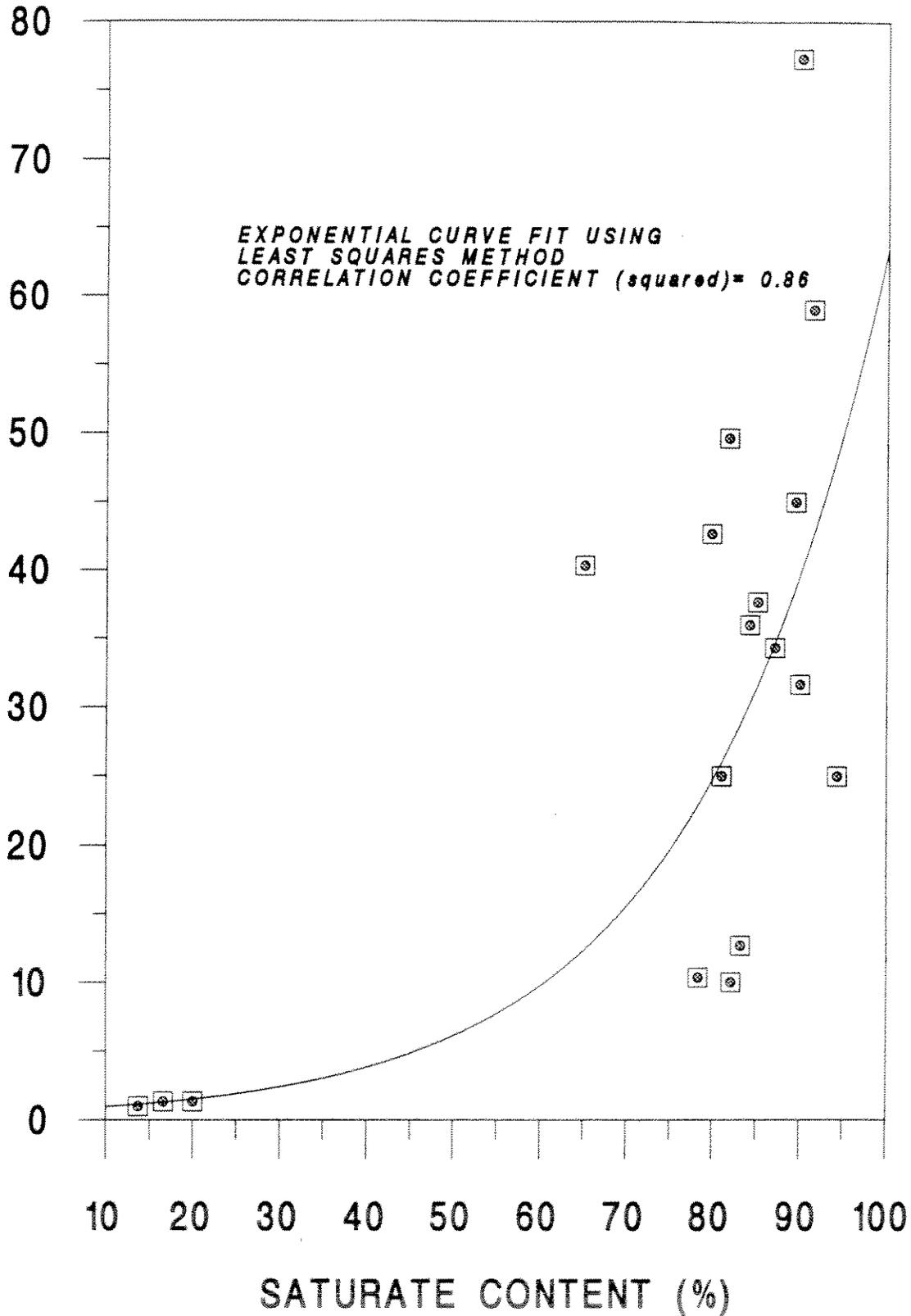
The results of the current studies can be summarized as follows:

1. The Dispersants tested in this study are most effective at a salinity of about 40 ‰ (ppt or degrees salinity). Dispersant effectiveness rapidly decreases when salinity is increased or decreased. Freshwater effectiveness of present-day dispersants is very low,
2. The amount of dispersant is very important to effectiveness. Effectiveness falls to nearly 0 for a light oil at a dispersant-to-oil ratio between 1:40 and 1:60 when premixed and nearly to 0 at a dispersant-to-oil ratio between 1:20 and 1:40 for a dispersant application situation,
3. Dispersant effectiveness is positively correlated with the saturate content of oil

# CORRELATION OF EFFECTIVENESS WITH SATURATE CONTENT

AVERAGE  
DISPERSANT  
EFFECTIVENESS  
%

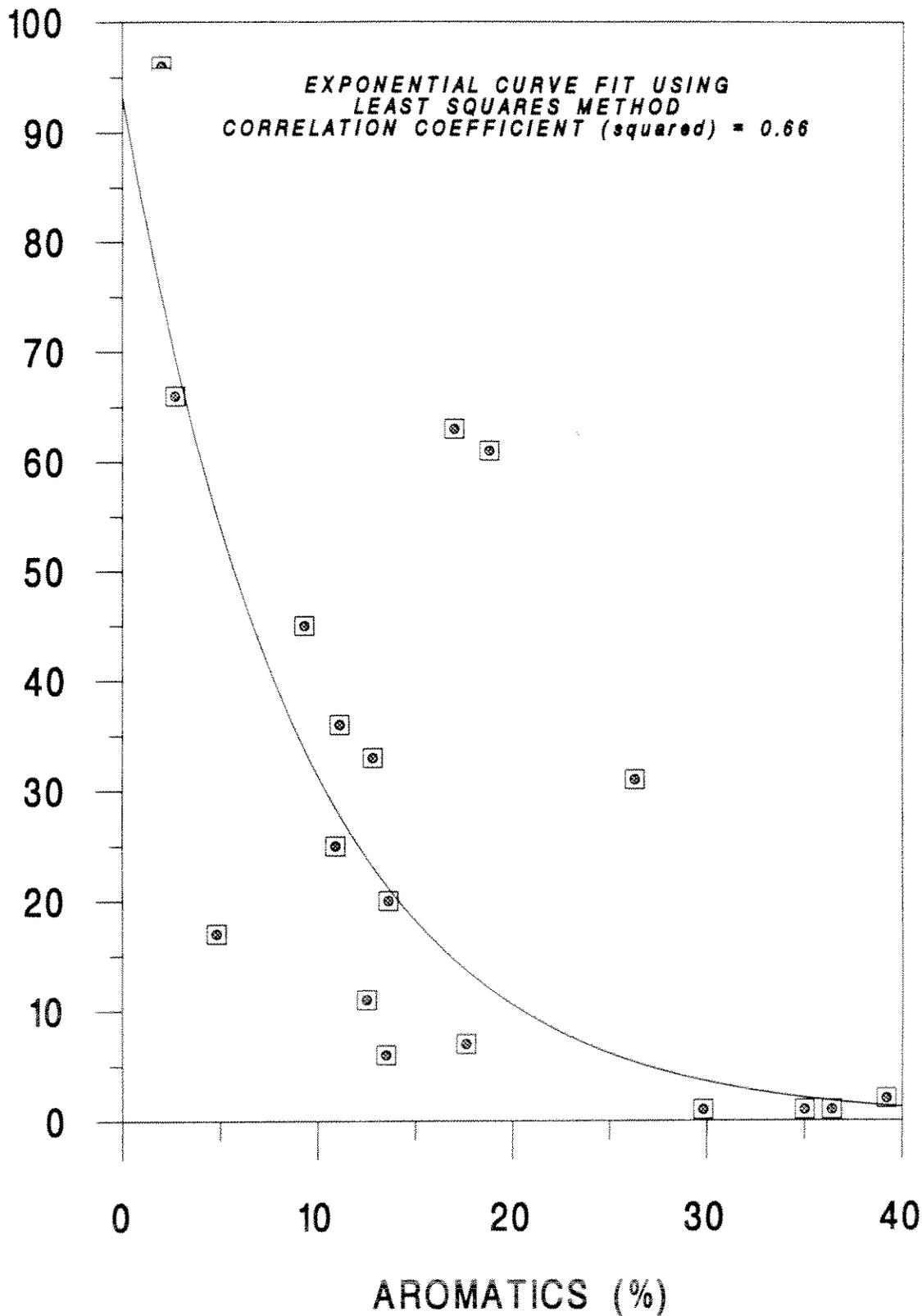
FIGURE 6



# CORRELATION OF EFFECTIVENESS WITH AROMATIC CONTENT

COREXIT 9527  
EFFECTIVENESS  
(%)

FIGURE 7



# CORRELATION OF EFFECTIVENESS AND VISCOSITY OF LIGHTER OILS

EFFECTIVENESS  
% 80

FIGURE 8

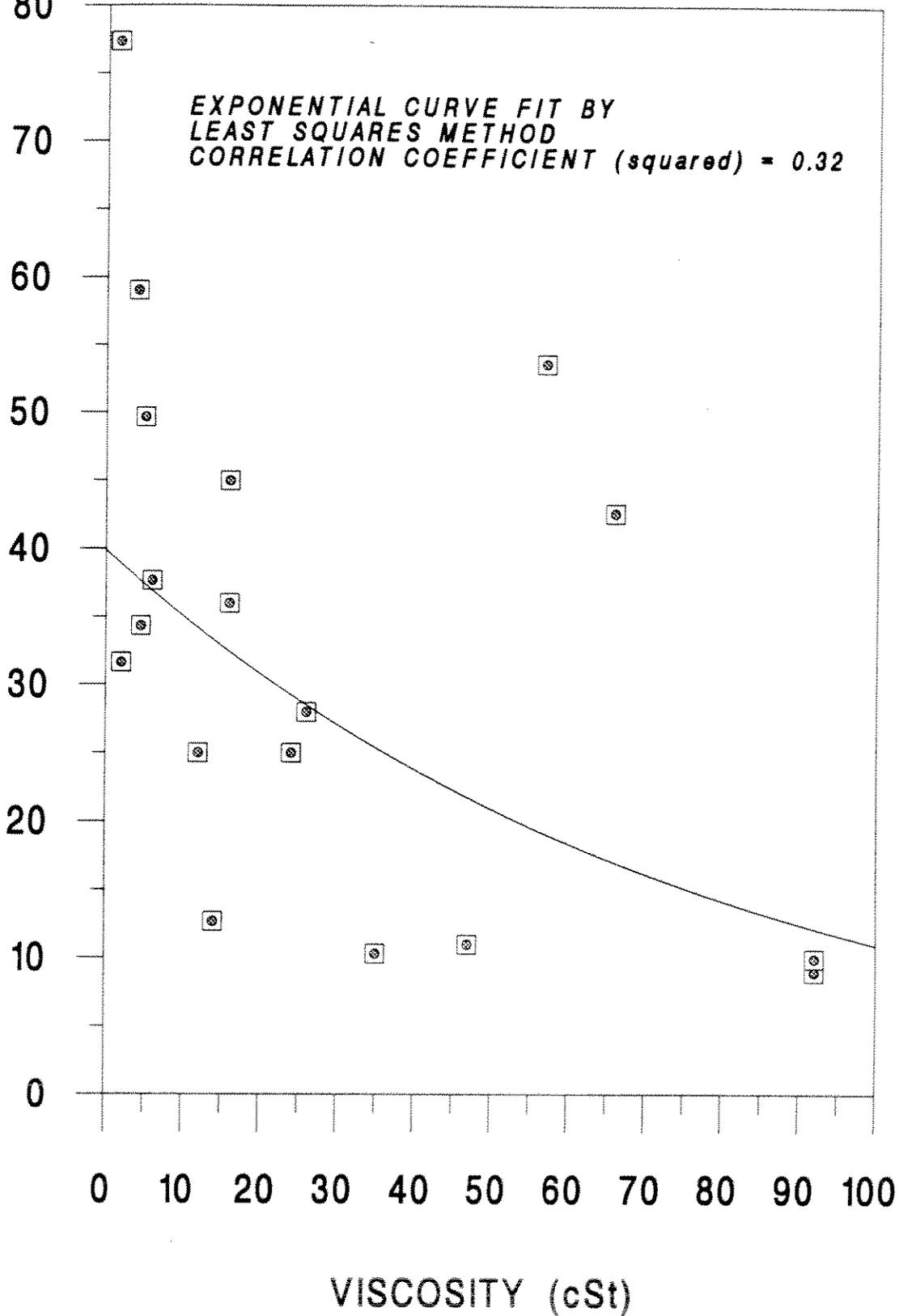


Table 13

## DISPERSANT EFFECTIVENESS AND OIL PROPERTIES

OIL	DISPERSANT EFFECTIVENESS			HYDROCARBON ANALYSIS			ASPHALTENES	WAXES	VISCOSITY
	COREXIT	ENERSPERSE	DASIC	SATURATES	AROMATICS	POLARS			
	Effectiveness in percent			weight percent of total			weight %	%	cSt
ADGO	61	59	8	79.8	18.8	0.9	0.59	0.88	66
AMAULIGAK	45	62	28	89.5	9.3	0.4	0.31	0.87	16
ARABIAN LT.	17	22	33				2.61	1.76	
ASMB	33	51	24	84.2	12.8	1.2	1.55	1.74	16
ATKINSON	39	73	49				2.39	0.72	57
AVALON	11	11	16	83.2	12.5	1.8	2.48	3.22	14
BENT HORN	17	23	35	94.3	4.8	0.3	0.4	2.11	24
BUNKER C	1	1	2	20	35	15	6.73	1.23	48000
CAL. SM 16	1	1	1	13.7	29.8	31.4	18.63	2.37	34000
CAL. SM 11	1	1	1	13.7	36.4	24.1	20.13	1.6	6400
COHASSET	95			90	2		0.35	0.9	2
COLD LAKE	2	1	1	16.6	39.2	19.3	11.87	1.35	235000
ENDICOTT	7	6	14				3.16	0.54	92
FEDERATED	25	40	38	87.1	10.9	1.3	0.9	1.96	4.5
HIBERNIA	6	10	14	82.1	13.5	2	3.62	1.1	92
ISSUNGNAK	66	60	51	91.5	2.7	0.3	0.53	1.2	4
LAGO MEDIO	5	13	15				4.53	1.43	47
N. WELLS	36	51	26	85.1	11.1	1.6	1.15	1.25	6
PANUKE	96	96	40	90	2		0.29	0.83	1.5
PRUDHOE BAY	7	10	14	78.3	17.6	2.5	2.04	0.65	35
S. LOUISIANA	31	48	42	65.1	26.3	8.4	0.2	1.06	
SYNCRUDE	63	61	25	81.8	17	0.9	0.2	1.42	5
TERRA NOVA	16	28	40				0.59	0.89	26
TR. MOUNTAIN	20	28	27	81	13.6	1.9	3.23	1.39	12

and negatively correlated with the asphaltene, aromatic and polar components of the oil. This shows that the current generation of dispersants has little effect on oil components other than the saturates and that dispersant effectiveness is limited by the composition of the oil rather than other factors.

4. Dispersant effectiveness is only poorly correlated with oil viscosity. This correlation appears to be secondary, that is oil viscosity is strongly correlated with the amount of asphaltenes and aromatics in the oil. Dispersant effectiveness is decreased by these components and thus is indirectly affected by the viscosity as an indicator of composition. The direct effect of oil viscosity as it affects mixing of dispersant with oil was not measured in this study, but may be important.

### **DISPERSANTS VERSUS SURFACE-WASHING AGENTS**

Studies conducted in the Environment Canada laboratory show that the effectiveness of a class of surfactant agents known as surface-washing agents and those for dispersants are orthogonal. That is, an agent which is a good dispersant is a poor surface washing agent and vice versa. This has important implications for laboratory testing. Agents should be subjected to both tests if there is uncertainty about which purpose the agent has. Furthermore, surface exposure in tests should be minimized to ensure that the incorrect property is not measured. The orthogonal nature of the two properties is illustrated in Figure 9.

### **HERDING**

Herding is felt to be quite important to the effectiveness at sea. It also plays a role in laboratory testing. Canevari has done some studies on the role of herding.<sup>69</sup> Before these studies, the conventional wisdom was that HLB was the governing factor behind dispersant herding.<sup>45</sup>

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### **THE EFFECT OF ENERGY ON DISPERSANT EFFECTIVENESS**

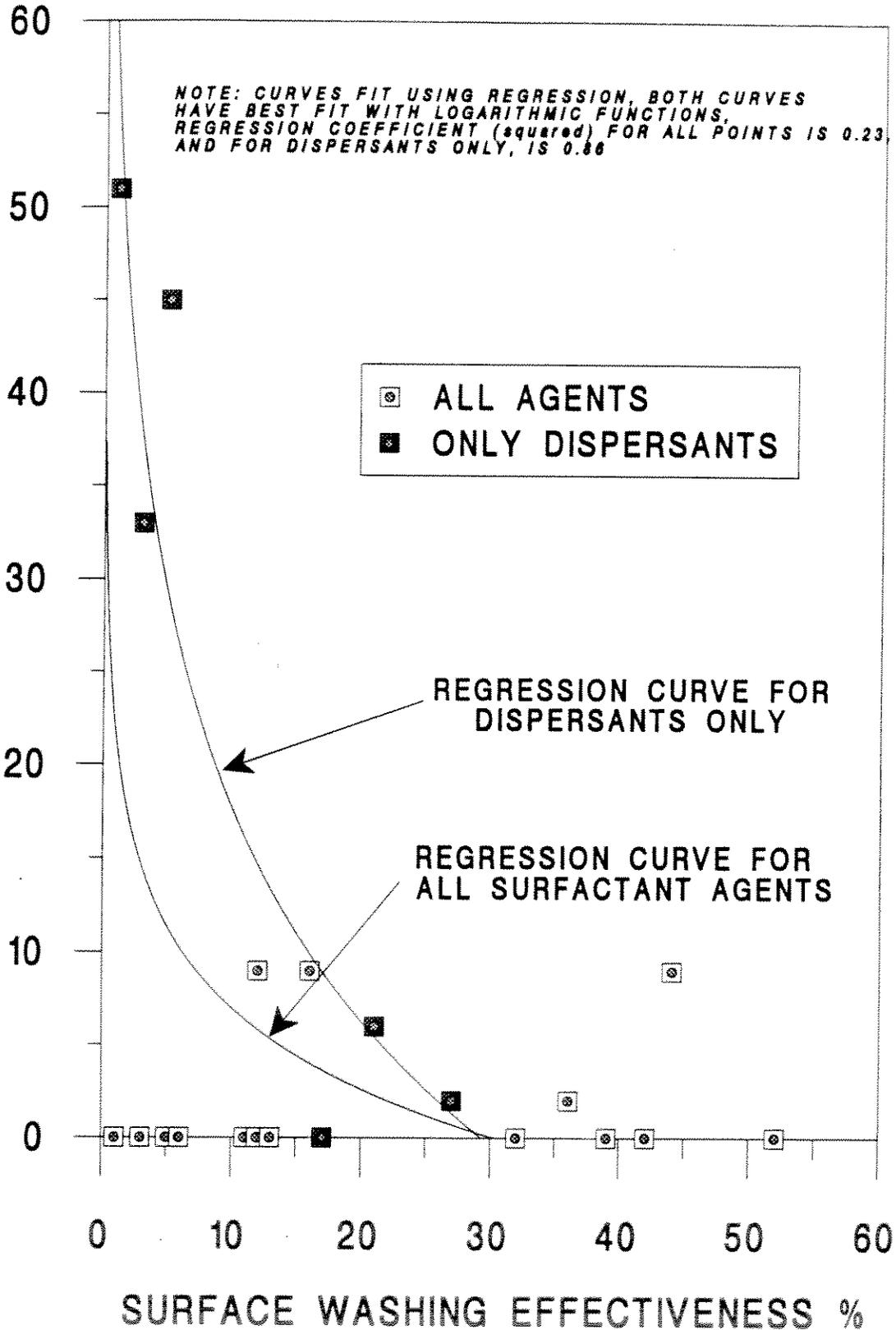
Energy has been ascribed as the principle reason for the varying results of dispersant effectiveness results in the field and in the laboratory. Difficulties in varying or measuring this energy have left the variation of dispersion and energy largely unstudied. Energy is a difficult topic.<sup>70</sup> Descriptions of what is meant by relevant energy to oil dispersion varies. One description of energy is that it is a relative measure of the wavelength and amount of turbulence in the near surface.<sup>71</sup> Another definition is that of steepness of waves and their periods.<sup>72</sup> Several discussions on the relationship between dispersion and energy have taken place, but little experimental work has been published.<sup>73-75</sup> Fundamental literature on surfactants also does not propose energy relationships.<sup>45,66</sup>

Many different types of dispersant test procedures and apparatus are described in the literature. One estimate places this at 50 different tests or procedures.<sup>76-81</sup> Little 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. Usually investigators

# CORRELATION OF DISPERSANT AND SURFACE-WASHING EFFECTIVENESS

DISPERSANT EFFECTIVENESS %

FIGURE 9



followed the specified test procedure when using an apparatus and did not vary any of the conditions.

#### **EFFECT OF OIL-TO-WATER RATIO AND SETTLING TIME**

A previous study by Environment Canada found that a significant portion of the variance of dispersant effectiveness among the various apparatus was due to differing settling times and differing oil-to-water ratios.<sup>64</sup> Energy could be compensated for by doing a blank run in the more energetic apparatus and correcting the chemically-dispersed run by this amount. This was based on the assumption that a similar mechanism prevails between chemical or natural dispersion. It should be noted that the noise level is so great in many of the more energetic apparatus that any correction value within a factor of two could give an appropriate result.

The first two variables studied are important to laboratory dispersant tests, the oil-to-water ratio and the settling time, that time between the taking of the sample for analysis and the time that the energy is no longer applied to the apparatus. Increased settling time allows large, unstable oil droplets to rise to the surface before the sample is taken and thus reduces the effectiveness values to represent only the stable dispersions.<sup>64</sup> The oil-to-water ratio varies in the various test protocol. The effect of changing the oil-to-water ratio in some of the apparatus is large and results in a peak at an oil-to-water ratio of 1:500. For two apparatus and for the different oil-dispersant combinations, the overall effect is the same. The effectiveness drops down at ratios below 1:200 and very much at ratios as low as 1:20. The maximum effectiveness is seen at ratios around 1:500 and from 1:1000 becomes relatively stable up to 1:1,000,000. It is suggested that this variation is the result of different mechanisms of dispersant action.<sup>64</sup> At low oil-to-water ratios, there is a large amount of surfactant present and this surfactant interacts with itself forming micelles rather than interacting with the oil. At low ratios, there are sufficient numbers of micelles to solubilize portions of the oil. At high oil-to-water ratios the primary interaction between oil and surfactant is the formation of stabilized droplets. At ratios close to 1:500, both mechanisms come into play and apparent dispersion is increased. The effect of settling time is an important factor in the operating protocol of the various effectiveness experiments. The effect can be as much as one order of magnitude to the apparent dispersion amount.

Although settling time and oil-to-water ratio are shown to be very important in terms of correlating laboratory data, the role of energy has not been fully understood.

#### **EXPERIMENTAL**

Several rounds of experiments were conducted to determine the effect of varying energy. Several oils were used in these tests. Table 14 lists these oils and gives their basic physical properties. The dispersants used include the Exxon products Corexit 9527 (abbreviated C9527 in some tables in this paper) and Corexit CRX-8 (abbreviated CRX-8), the Dasic Chemicals Product, Dasic Slickgone LTS (abbreviated Dasic) and the British Petroleum product, Enersperse 700 (abbreviated EN 700). All runs where 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 where both premixed and drop-wise addition were used.<sup>79</sup> Saltwater 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.

The standard swirling flask apparatus was used to study the effect of small changes in energy. The swirling flask apparatus uses a 125 mL Erlenmeyer flask with a standard laboratory shaker to induce a swirling motion to the contents. Procedures for this device are detailed in the literature.<sup>40</sup> For the tests here, the rotational speed was varied from 50 to 450 rpm. Another test was developed using a 2 L Erlenmeyer flask. This flask was operated in a very similar manner to the swirling flask. The oil-to-water ratio was fixed at 1:20,000 and the shaking rotation varied from 50 to 200 rpm to study the effect of energy variation.

The labofina test employs a 250 mL separatory funnel which is rotated at 33 rpm.<sup>42</sup> The apparatus was operated with an oil-to-water ratio of 1:1000 to 1:30,000 and samples were taken after a settling time of 10 minutes. Oil-to-water ratio was varied in this apparatus to study the effect of natural dispersion.

A blender (standard Waring laboratory unit) was used to conduct some of the oil-to-water ratio tests. The volume of water used was 1 L. This apparatus was used primarily to confirm results in other apparatus.

A new apparatus was developed to measure the effects of high energy levels. This apparatus, dubbed "Round High Energy Test", consisted of a cylindrical vessel of dimensions 29 cm., diameter, and 30 cm. height. During operation the vessel is covered. Either 4.8 or 5.4 L of water were used in this apparatus and sufficient oil to yield an oil-to-water ratio of 1:20,000. This is the value found to be the ratio at which natural dispersion no longer increases with increasing oil-to-water ratio.

Another new apparatus, called simply "the high energy test" in our laboratories, was developed to measure dispersion at very high energy levels. This vessel is square of dimensions 30 cm. on all sides. The effect of the corners is to create high levels of turbulence. The volume of oil and water were again the same as in the above device. In both apparatus, 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 consisting of a moving table. This shaker is capable of rotational speed variations from 50 to 450 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 for all four apparatus 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), 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 addition of small water droplets.

#### **STUDY OF OPTIMUM OIL-TO-WATER RATIOS FOR NATURAL DISPERSION**

A study of the effect of oil-to-water ratio on amount of oil naturally-dispersed in the water was conducted using 2 different experimental apparatus and procedures. This was

done to ensure that the optimal ratio was used for the high energy tests. The first apparatus used was that of the Labofina, as described in the experimental section above. The apparatus was operated as described and the amount of oil added was adjusted to vary the ratio between 1:1000 and 1:30:000. The results of 164 separate experiments are shown in Figure 10. It can be seen that the amount of oil naturally dispersed increases constantly up to a ratio of about 1:20,000 and then appears to stay relatively constant. Data above a ratio of 1:30,000 are hard to obtain because this is the limit of relatively accurate colorimetric oil-in-water measurements and also because the noise level of measurement rises to a high level as a result of the small amount of oil in the apparatus.

A separate series of experiments was performed to verify these results. These were performed in the blender apparatus as described in the experimental section above. Results from these experiments are shown in Figure 11. These results confirm the previous finding that the natural dispersion rises as the oil-to-water ratio increases. This particular test indicates that the increase is already stable as the oil-to-water ratio increases to 1:20,000.

The percent of oil in the water column (naturally dispersed) increases as the oil-to-water ratio increases up to about 1:20,000. This is very different from the chemical-dispersed situation where the same inflection point is about 1:600.<sup>64</sup> This implies that an important role of chemical dispersants is the stabilization of oil droplets in water. Many more chemically-dispersed droplets can reside in the same volume compared to naturally-dispersed droplets.

### **STUDY OF THE EFFECT OF HIGH ENERGY ON DISPERSION**

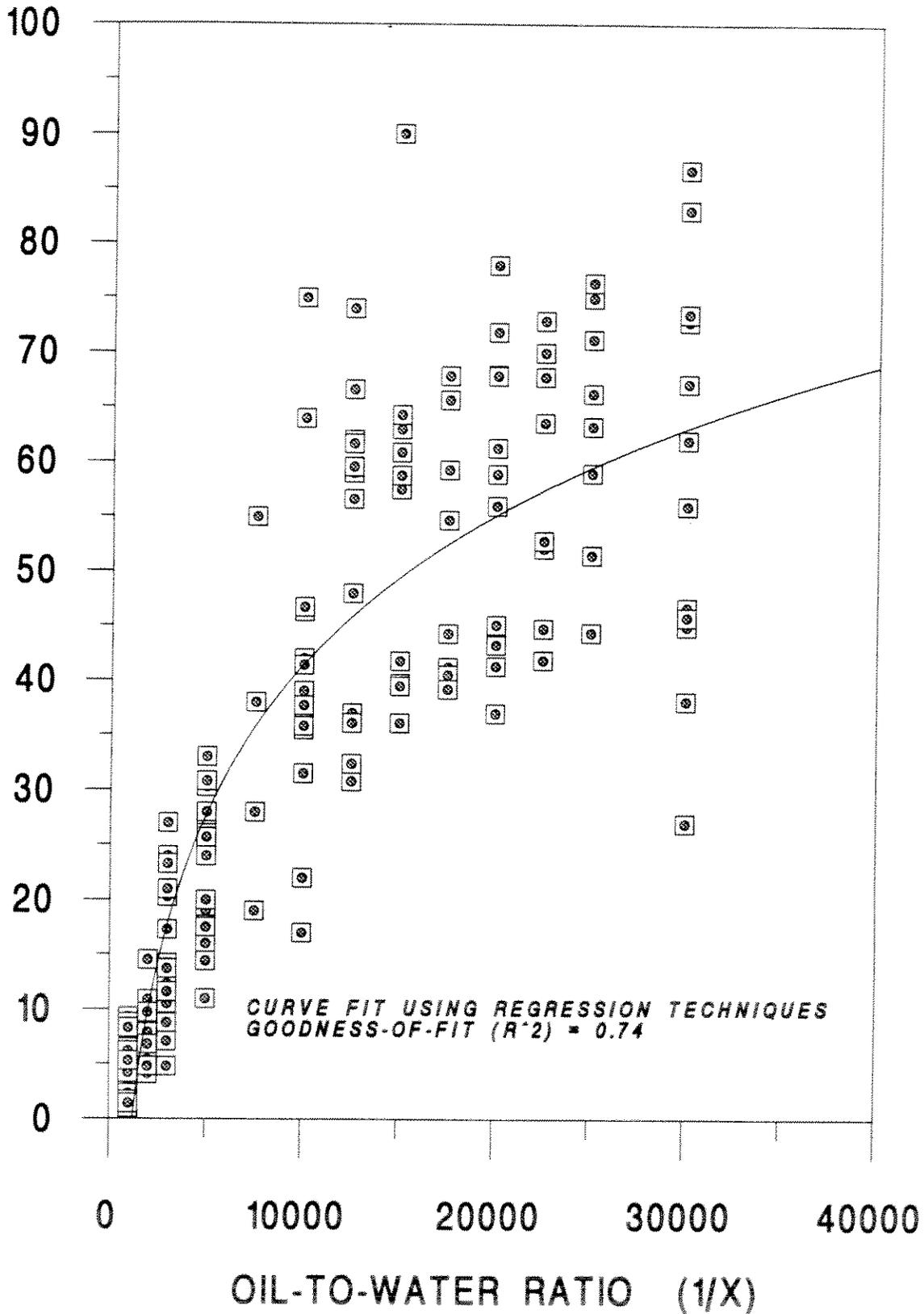
High energy studies were initiated using the round flask. The first test results obtained, using ASMB oil and Corexit 9527, are illustrated in Figure 12. The results show that dispersion is increased as the rotational speed is increased. This can be attributed to the increasing amount of turbulent energy in the apparatus. Figure 13 illustrates data from further runs in the round apparatus at two different water levels. Experiments were conducted using the 2 L Erlenmeyer apparatus to confirm the above results. These data are shown in Figure 13 as well. For these tests ASMB oil and the dispersant Enersperse 700 were used. All data show that dispersion increases as energy is increased and that experimental procedure, apparatus, and dispersant have little effect on the overall trend.

Experiments involving heavier oils (heavier than ASMB) were unsuccessful in that insufficient energy was available to completely disperse the oils or to achieve dispersion without the use of dispersants. The high energy device using a square vessel was developed to address this problem. The square apparatus can generate significant more turbulent energy than the round or 2 L apparatus. This is evidenced by visual appearance, the dispersion of heavier oils and by dispersion of oil without using dispersants. Results of dispersion tests done on ASMB with Corexit 9527 and ASMB without dispersant are shown in Figure 14. This figure illustrates the results of dozens of experiments. The findings are as follows: that dispersion increases very rapidly from a low value to 100% or nearly so and that natural dispersion onset occurs at an energy level higher than that for chemical dispersion, and finally that the natural dispersion curve has a lesser slope than that for chemical dispersion.

# MEASUREMENT OF OIL-TO-WATER RATIO AND NATURAL DISPERSION IN THE LABOFINA

DISPERSION  
%

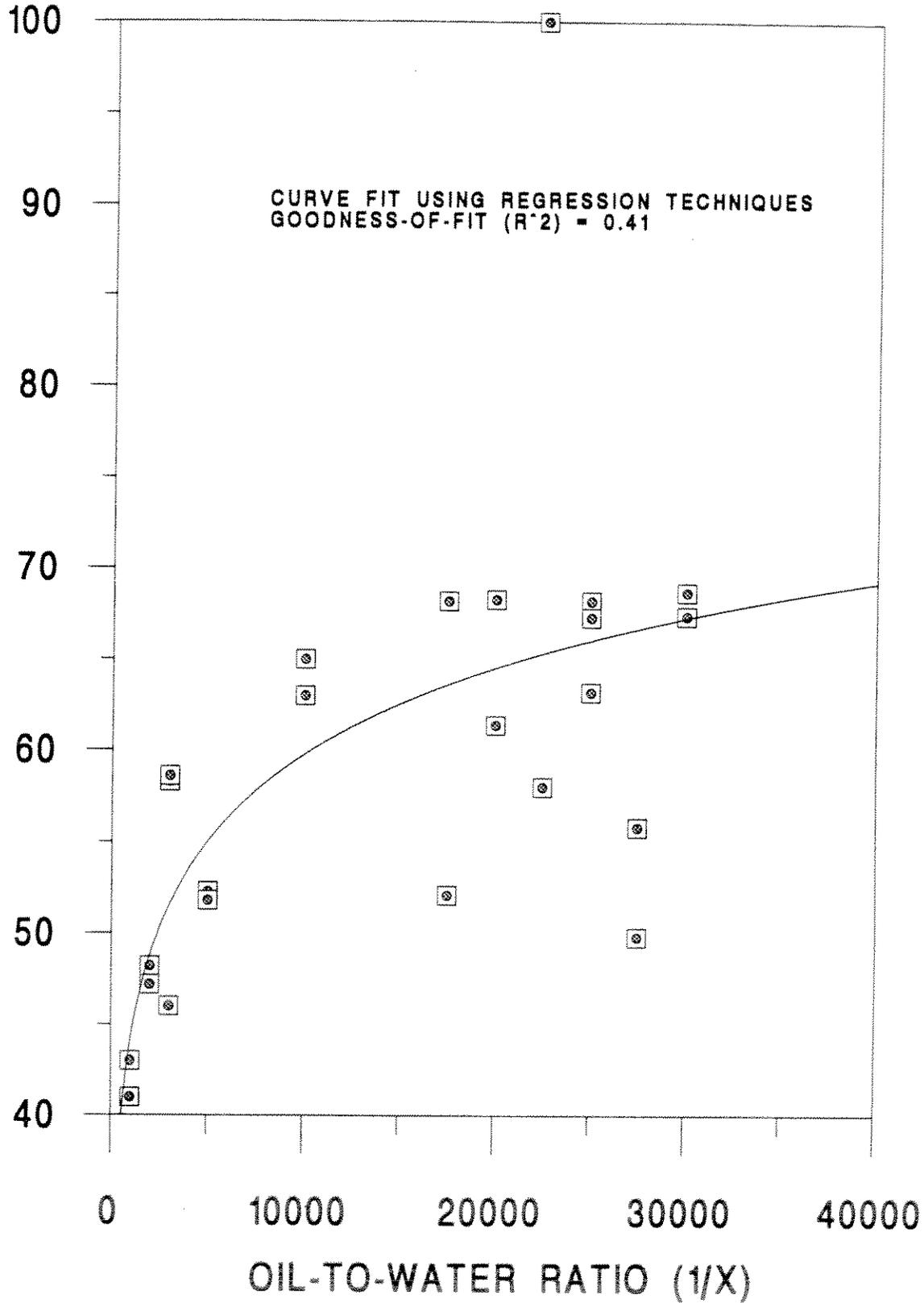
FIGURE 10



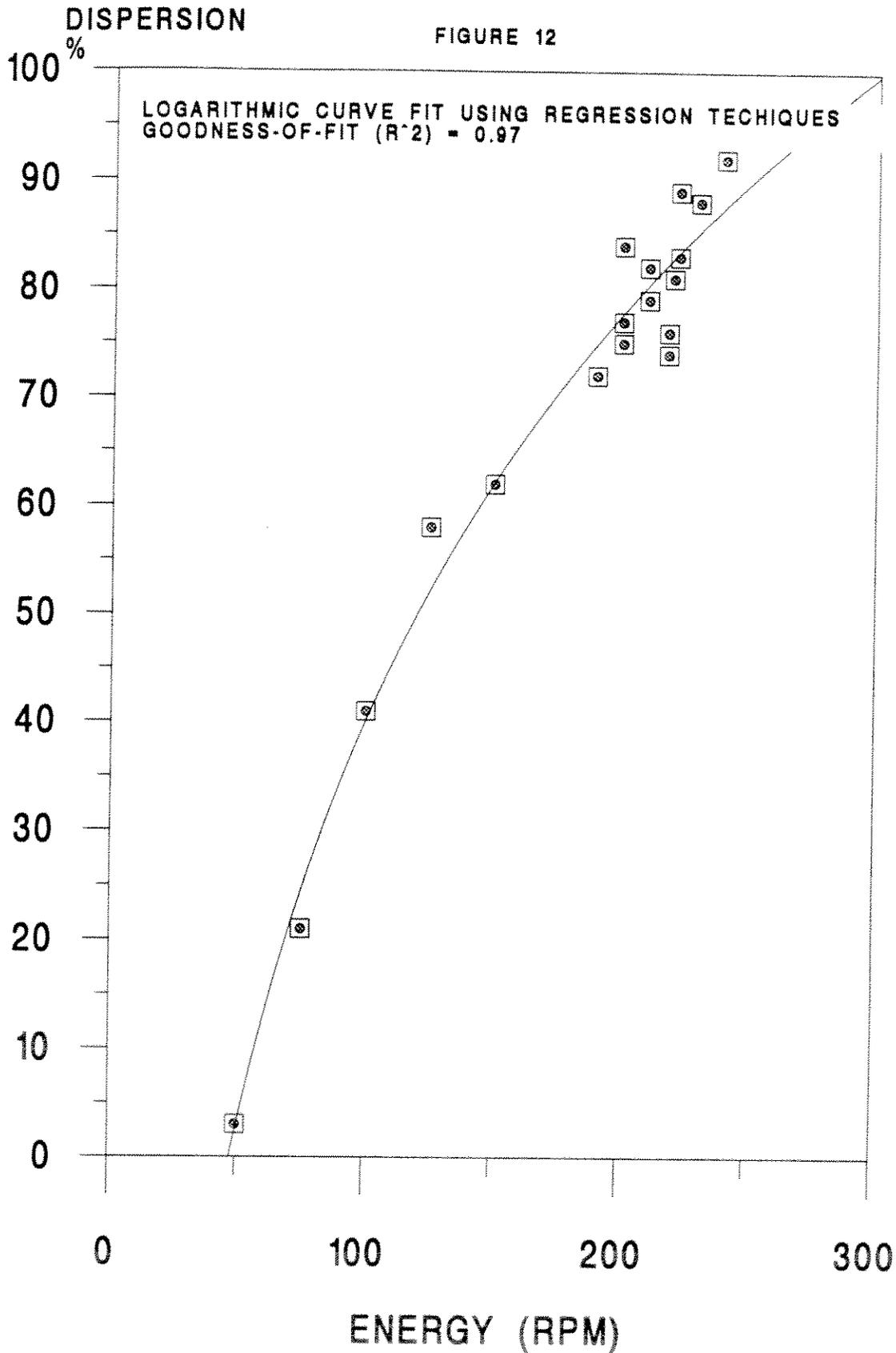
# NATURAL DISPERSION AND OIL-TO-WATER RATIO IN THE BLENDER APPARATUS

DISPERSION  
%

FIGURE 11



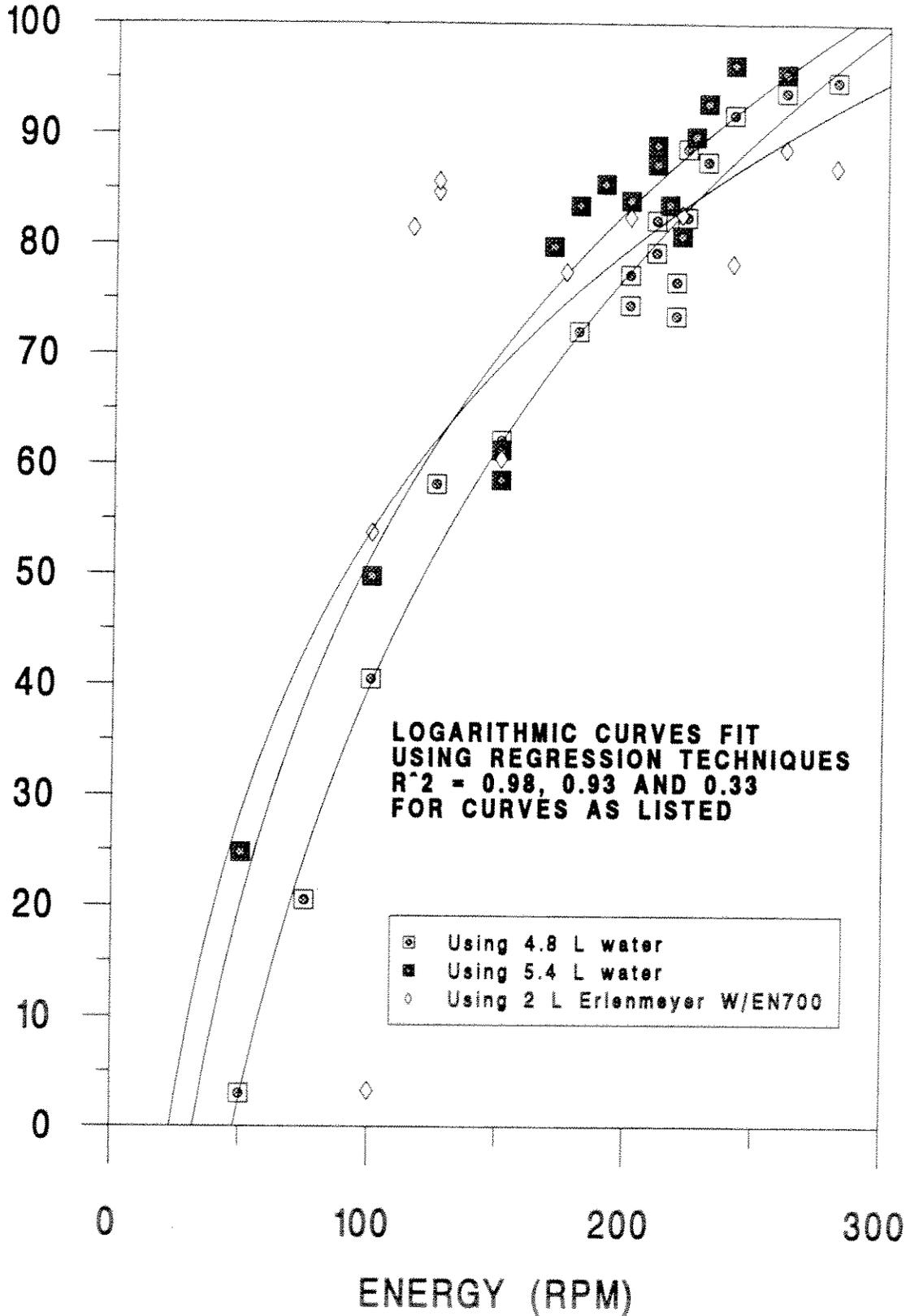
# DISPERSION IN THE ROUND HIGH ENERGY APPARATUS



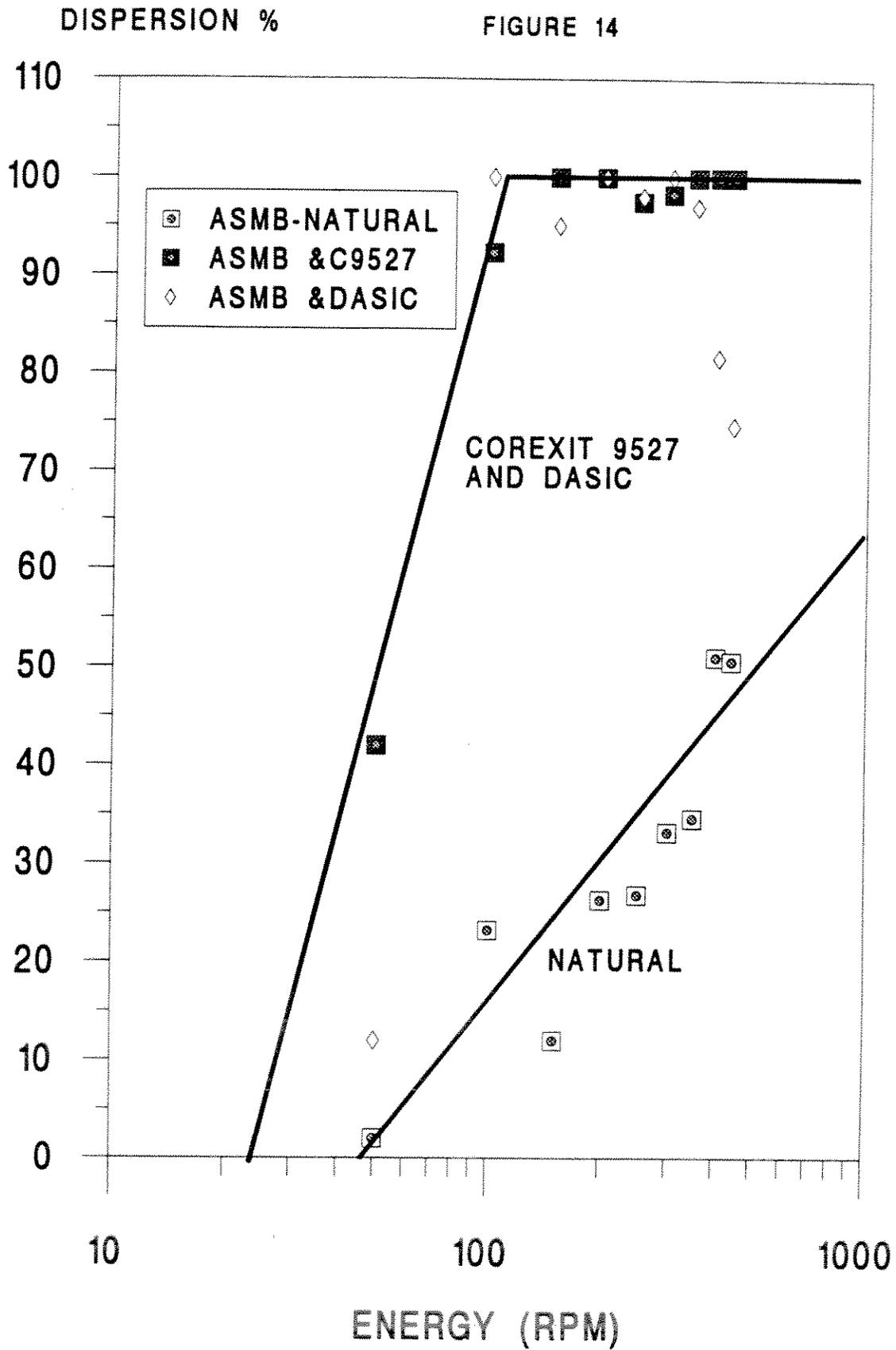
# ENERGY RELATIONSHIP IN THE ROUND AND 2-L HIGH ENERGY APPARATUS

DISPERSION  
%

FIGURE 13



# HIGH ENERGY DISPERSION OF ALBERTA SWEET MIXED BLEND



Many confirmation experiments were conducted. Figure 15 summarizes the results of some of these for different oils and dispersant combinations. 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. 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 normal conditions. Similar trends are seen in the data in Figure 15 as in the previous figure. Onsets of natural dispersion lag the chemical dispersion and the curves of natural dispersion have a lesser slope than those for chemical dispersion. In addition, the two heavier oils tested, North Slope and Bunker C light, do not go to the 100% dispersion level but stay at the 90% level. This is indicative that they are not as readily dispersable as the ASMB and Arabian Light oils. Another trend observed is that the order of chemical and natural dispersion onsets for the oils tested, are the same and are similarly spaced with respect to energy. The effect of chemical dispersant is to decrease the onset of dispersion and increase the amount by a large factor.

Some preliminary work has been done on assessing the difference in dispersion at high and low energies. This work indicates that dispersions formed at lower energies are more stable. Experiments on the amount of oil that remains dispersed in the water column after 24 hours is about 20% for the high energy dispersion and 80% for the low energy dispersion. Interestingly, the amount of dispersed oil remaining in the water column after 24 hours is about the same in both the high and low energy experiments. The difference may well be the amount of dispersant in the droplets. Studies on this aspect continue.

Further investigations were conducted on the dispersion in the region of dispersion onset. This study was done using ASMB, Arabian Light and Norman Wells crude oil. Corexit 9527 was used in the tests and the swirling flask apparatus was used because it is a low energy apparatus and energy variances are much less than in the high energy apparatus. Only one or 2 data values can be obtained on the onset slope with the high energy apparatus. These tests were performed to further investigate the behaviour of dispersion near the onset region and to examine the slope of this region. Results of these tests are illustrated in Figure 16. The best fit curves through these points are linear.

The lower energy portion was studied further using the square high-energy apparatus. Energy was varied by changing the rotation ratio of the shaker in 5 rpm increments. Data are shown in Figure 17. These results again show that dispersion rises rapidly in a linear fashion until complete dispersion is achieved.

Curve fitting on the data from the square apparatus was done and is shown in Table 15. This shows that the best approach is the use of a combination of two linear curves. Similarly curve-fitting techniques were applied to the natural dispersion curves. These data as given in Table 16 and show that the best approach is a linear function.

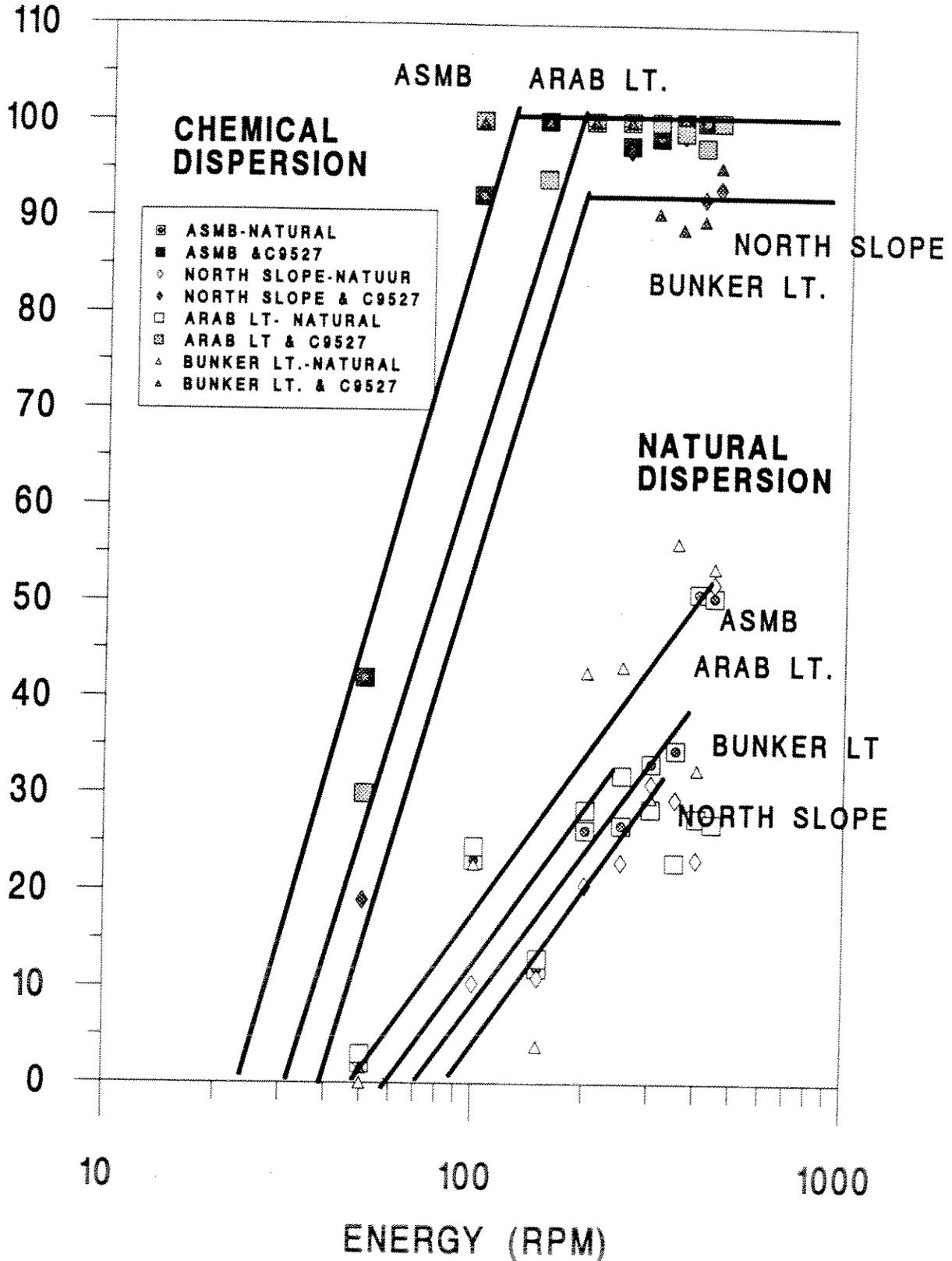
### **SUMMARY OF ENERGY AND RATIO EFFECTS**

The idealized relationships between energy and dispersion are shown in Figure 18, 19 and 20. Chemical dispersion increases with energy in a linear fashion until a maximum is reached. For light oils this maximum is about 100%. For heavier oils this is about 90%. The dispersion curve is very steep, that is only a small amount of energy causes a large

# HIGH ENERGY DISPERSION OF FOUR OIL TYPES

DISPERSION %

FIGURE 15



# CORRELATION OF ENERGY AND DISPERSION IN THE SWIRLING FLASK APPARATUS

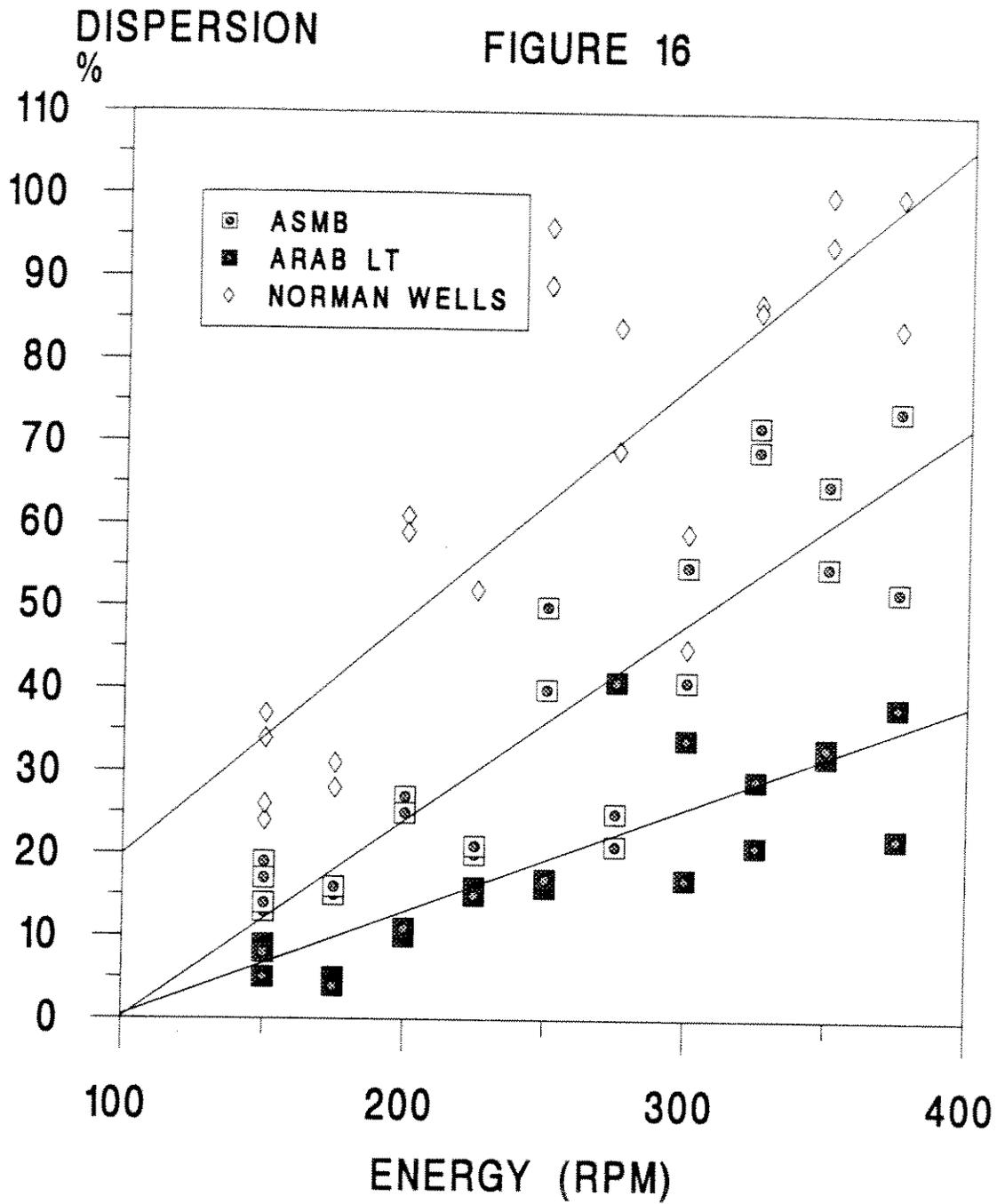


TABLE 14 TEST OIL PROPERTIES

OIL	DESCRIPTION	KINEMATIC	DENSITY
		VISCOSITY (mm <sup>2</sup> /s at 15 C)	(g/mL at 15 C)
ASMB	ALBERTA SWEET MIXED BLEND	8	0.84
ARABIAN LIGHT	LESSER VISCOSITY ARAB BLEND	40	0.87
BUNKER C LIGHT	LESSER VISCOSITY BUNKER C	200	0.93
NORMAN WELLS	NORTHERN CANADIAN CRUDE	7	0.83
NORTH SLOPE	ALASKAN BEAUFORT CRUDE	55	0.88

TABLE 15 CORRELATION MATRIX FOR THE HIGH ENERGY CURVE

CURVE TYPE	FORMULA	GOODNESS OF FIT (R <sup>2</sup> ) FOR OIL/DISPERSANT COMBINATION					
		ASMB	ASMB	NORTH SLOPE	ARAB LT.	ARAB LT.	BUNKER
		C9527	DASIC	C9527	C9527	DASIC	C9527
EXPONENTIAL	$Y = A + B \text{EXP}(X)$	0.35	0.2	0.28	0.31	0.28	0.28
LOGARITHMIC	$Y = A + B \text{LOG}(X)$	0.64	0.32	0.47	0.56	0.44	0.49
3-ORDER POLY	$Y = A + B X \dots DXXX$	0.91	0.82	0.84	0.84	0.84	0.84
4-ORDER POLY	$Y = A + B X \dots EXXXX$	0.99	0.93	0.95	0.92	0.94	0.95
5-ORDER POLY	$Y = A + B X \dots FXXXXX$	1	0.99	0.98	0.98	0.98	0.98
LINEAR	$Y = A + B X$	0.38	0.11	0.22	0.21	0.32	0.21
<i>GOODNESS OF FIT = UNCORRECTED R<sup>2</sup></i>							
STEP - MULTI	$A + BX/(1 + CXX) + D \text{LOG} X$	0.99					
LIN-LOG	$Y = A + BX + C \text{LOG}(X)$	0.98					
INV-BINOMIAL	$Y = AX/1 + BX + CXXX$	0.94					
INV-LINEAR	$Y = AX/1 + BX$	0.94					
LOG	$Y = A + B \text{LOG}(X)$	0.94					
INV-LINEAR	$Y = AX/B + CX$	0.94					
STEP - X/LOG	$Y = A + BX/C \text{LOG}(X)$	0.88					
LINEAR, ALT	$Y = A + B(C + X)$	0.88					
EXPON. MOD.	$Y = A + B \text{EXP}(CX)$	0.88					
STEP - POLY	$Y = AX/1 + BX + CXX$	0.88					
STEP - SQ/LOG	$Y = A + B XX/C \text{LOG}(X)$	0.83					
STEP - LOG/SQ	$Y = A + B(\text{LOG} X)/(CX + DXX)$	0.78					

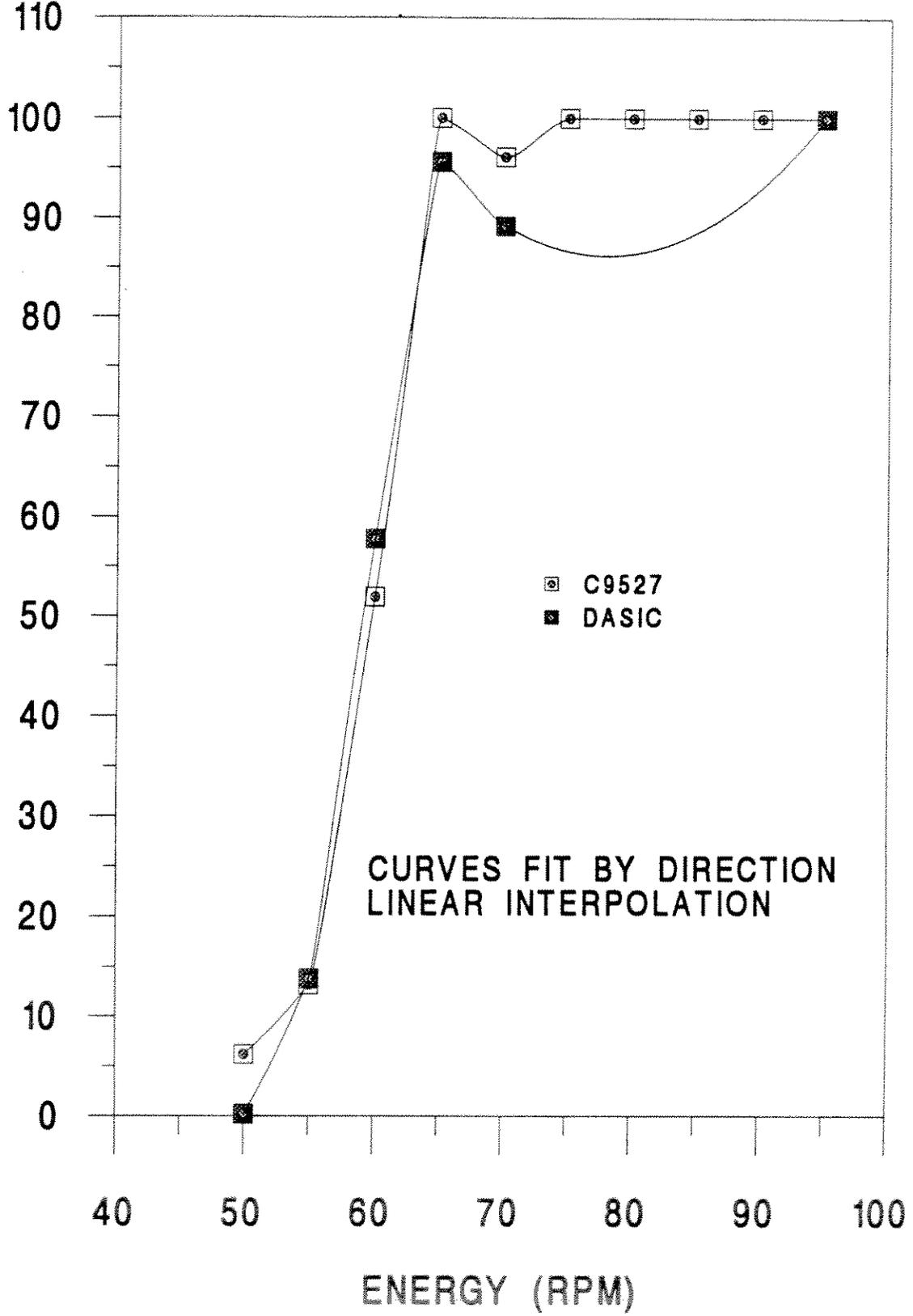
TABLE 16                      **CORRELATION MATRIX FOR NATURAL DISPERSION**

CURVE TYPE	FORMULA	GOODNESS OF FIT (R <sup>2</sup> ) FOR OIL TYPE		
		ASMB	ARAB LIGHT	NORMAN WELLS
LINEAR	$Y=A + BX$	0.77	0.63	0.7
LOG	$Y=A + B \text{ LOG}(X)$	0.73	0.65	0.73
EXPONENTIAL	$Y=A + B \text{ EXP}(X)$	0.81	0.71	0.7

# CORRELATION OF ENERGY AND DISPERSION AT THE INITIAL SLOPE OF THE ENERGY CURVE

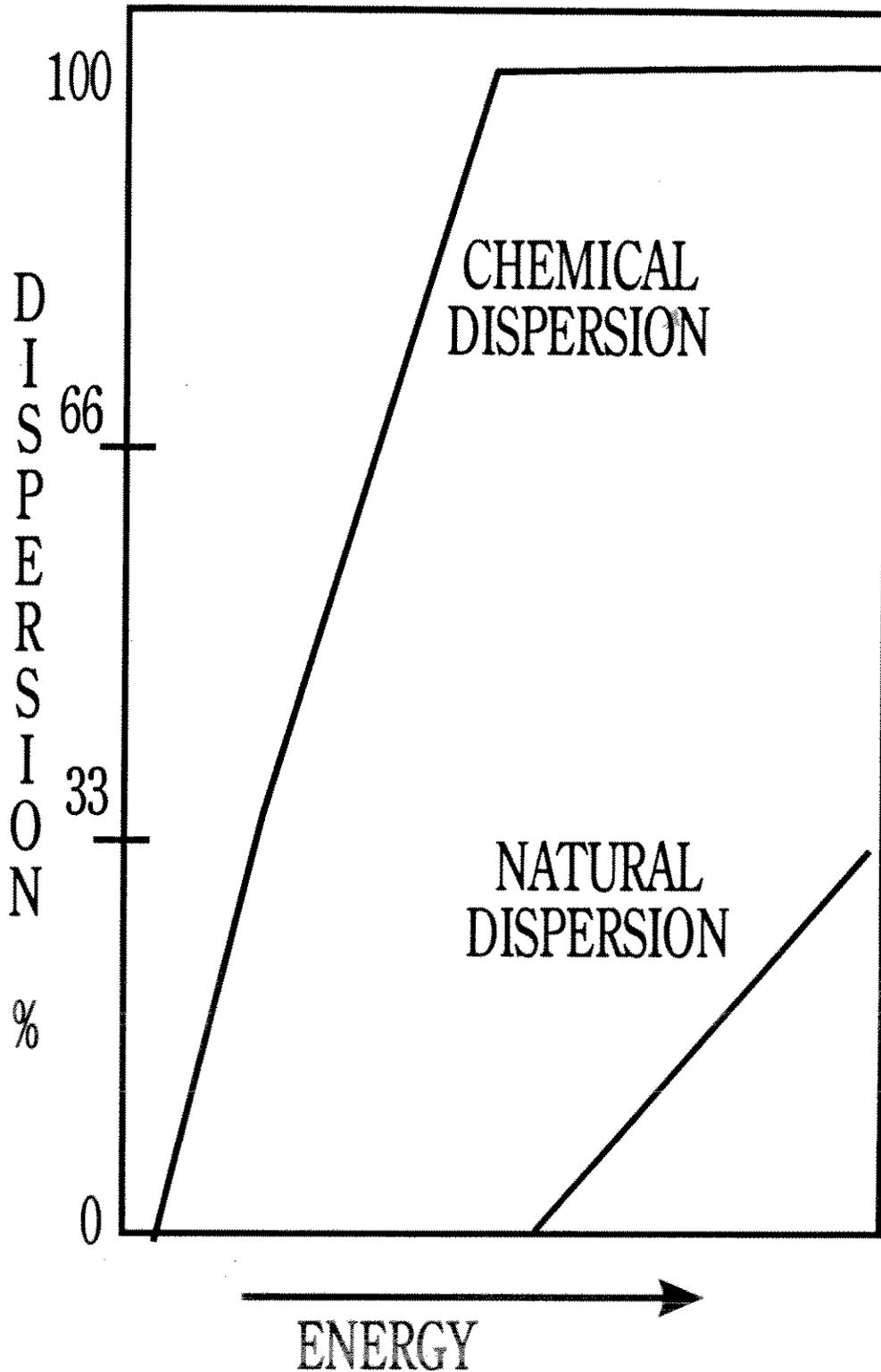
DISPERSION  
%

FIGURE 17



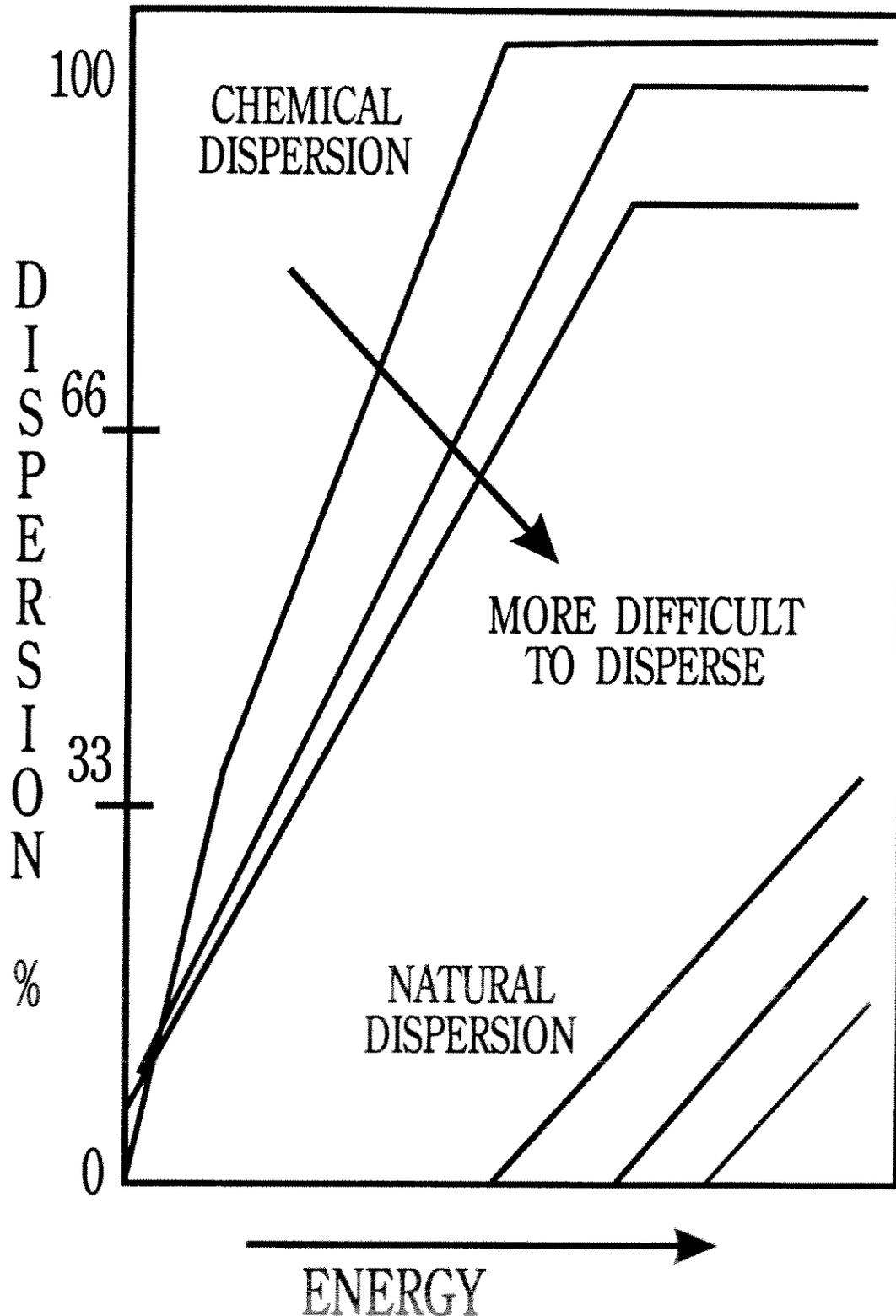
# SCHEMATIC OF THE DISPERSION OF A TYPICAL LIGHT CRUDE OIL

FIGURE 18



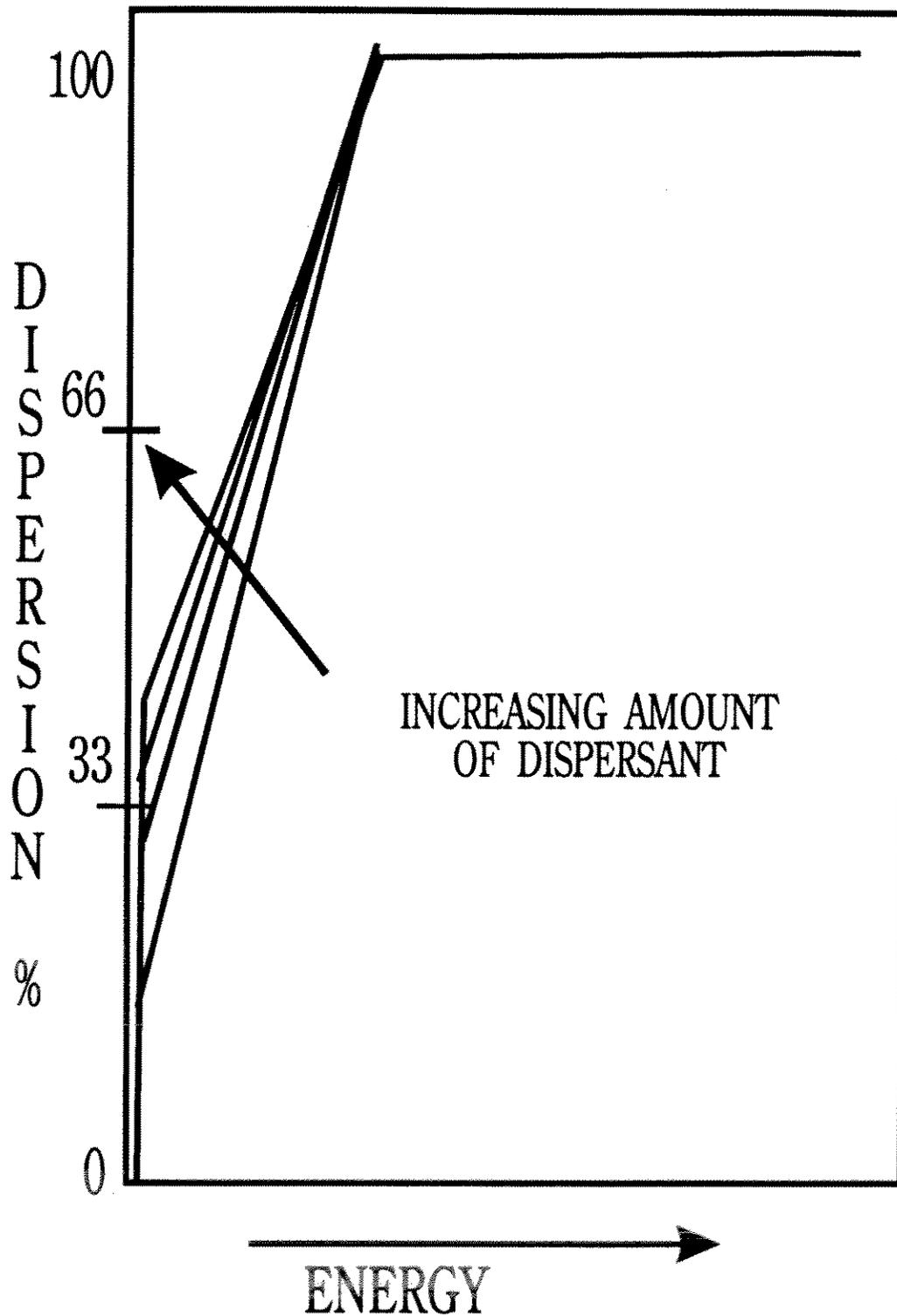
# SCHEMATIC OF ENERGY RELATIONSHIP AND DISPERSION WITH DIFFERENT OILS

FIGURE 19



# SCHEMATIC OF THE VARIATION OF DISPERSION WITH DISPERSANT AMOUNT

FIGURE 20



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. This may be indicative that the mechanism is fixed and only the threshold varies.

Natural dispersion is analogous to chemical dispersion except that the onset occurs at a higher energy and the increase with energy is much less.

Initial work on dispersion quantities show the trend depicted in Figure 20. The effect is to increase the dispersion at low energies, but this has little effect on high energies.

Initial work has also been conducted on particle stability. This shows that there may be significant differences in the stability of dispersions at low and high energies. Tests of stability show that droplets formed at low energy will largely remain in the water column (80% after 24 hours) whereas those formed under high energy do not (20% after 24 hours). The difference does not appear in droplet size, but is probably due to the lesser amount of dispersant in those droplets formed at high energy. This lesser dispersant amount is simply a result of forming many more droplets at high energy with the same amount of dispersant.

The major question these experiments raise is how the energy in these tests relates to that at sea. There are a few observations which indicate that most typical sea energies actually occur at the low end of the energy spectrum shown in the test data presented here. In one test at sea, ASMB and Bunker C light were observed to start dispersing naturally around Beaufort 6.<sup>82</sup> The EKOFISK BRAVO oil was observed to disperse naturally at sea states around Beaufort 5 or 6.<sup>2</sup> It is recognized that turbulent energy is the important factor for dispersion. This energy level correlates with sea state, wave steepness and many other oceanographic factors. Technology does not exist at this time to measure this type of energy at sea and in the laboratory. There may be potential for this in the future with laser doppler or hot wire instruments.

These studies have shed new light on the role of chemical dispersions in the dispersion process. The effect that dispersants have include:

1. lowering of the energy to the onset of dispersion,
2. increasing the amount of dispersion,
3. increasing the amount of oil that a given volume of water can hold, and
4. increasing the dispersant droplet stability in the water column.

## **SUMMARY OF THE PHYSICAL STUDIES**

The results of the current studies can be summarized as follows:

1. The Dispersants tested in this study are most effective at a salinity of about 40 ‰ (ppt or degrees salinity). Dispersant effectiveness rapidly decreases when salinity is increased or decreased. Freshwater effectiveness of present-day dispersants is very low,
2. The amount of dispersant is very important to effectiveness. Effectiveness falls to nearly 0 for a light oil at a dispersant-to-oil ratio between 1:40 and 1:60,
3. Dispersant effectiveness is positively correlated with the saturate content of oil and negatively correlated with the asphaltene, aromatic and polar components of the oil. This indicates that the current generation of dispersants has little effect on oil components other than the saturates and that dispersant effectiveness is limited by the composition of the oil rather than other factors.

6. Dispersant effectiveness is only poorly correlated with oil viscosity. This correlation appears to be secondary, that is oil viscosity is strongly correlated with the amount of asphaltenes and aromatics in the oil. Dispersant effectiveness is decreased by these components and thus is indirectly affected by the viscosity as an indicator of composition. The direct effect of oil viscosity as it affects mixing of dispersant with oil was not measured in this study, but may be important.

7. Energy level is important to dispersant effectiveness results. There exists an energy threshold above which oils are dispersed to a large degree in water. The droplets produced are not as stable as those at low energy levels. The energy levels at which these thresholds occurs is very high and for even light crude oils may exceed the equivalent of a sea state of Beaufort 7.

8. Natural dispersion occurs and appears to have an energy threshold at a similar energy level to that described above. The total percentage of oil removed by natural dispersion is very dependent on oil type, and is comparable to the amount of that removed by the dispersant at low energy levels.

9. The primary role of a chemical dispersant appears to be the stabilization of droplets in the water column, and not the formation of such droplets. This is supported by experiments which show that a given volume of water can hold about 50 times more oil if dispersants are used than when not.

10. The calibration curve procedure is important to achieving reasonable results. The curve must be prepared in a manner analogous to the test itself of values of effectiveness are exaggerated.

#### **NEW DISPERSANT FORMULATIONS**

Work on the development of new dispersant formulations has gone forward at Environment Canada's laboratories. Focus was placed on solving some of the problems noted with the current generation of dispersants as noted above. The first attempt was the done by "doping" current dispersants with more oleophilic surfactants. Results of this effort is shown in the Table at the end of the paper. Dispersant "BQ" is a dispersant that was made in this fashion. The products made using this technique at somewhat more effective than the current generation of products, but are not multiples more effective, a step that is needed.

The next stage of the development was to test any promising surfactant for the application. It was found that several surfactant offered potential well in excess of current mixtures, especially for heavy oils such as Bunker C. Mixtures of these surfactants offer multiples of effectiveness beyond that offered by current generation dispersants. Testing must continue to ensure that these new products show stability and acceptable toxicity. Preliminary Effectiveness data is given in Table 17

Table 17 Effectiveness of New Dispersant Products Developed Under the Joint EC-MMS Program

DISPERSANT	EFFECTIVENESS WITH ALBERTA BLEND (%)	EFFECTIVENESS WITH BUNKER C (%)
best conventional	40	1
experimental "GY"	94	19
experimental "GU"	74	40
experimental "GM"	65	32
experimental "GO"	53	31
experimental "GX"	53	20

### RECENT DISPERSABILITY MEASUREMENTS

Table 18 gives recent dispersability results using the swirling flask test method. Each value is the average of at least 3 determinations. Most results are the average of 6 separate measurements.

### ACKNOWLEDGEMENTS

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## APPENDIX DETAILED TEST METHODS

### SWIRLING FLASK TEST

#### Premixed Method

1. Turn on u.v./visible spectrophotometer.
2. Turn on Brunswick Shaker and set for 20°C.
3. Make artificial seawater with 33 g/L of salt in distilled water.  
( the bucket has a line marking 66 L).
4. Place 120 ml of artificial seawater in a 125 ml spouted erlenmeyer flask ( 6 runs can be performed simultaneously).
5. Place the flask with the seawater in the slot of the shaker (or on the rack) and allow 20 minutes for it to reach thermal equilibrium.
6. With the flask in the slot of the shaker, carefully float 100  $\mu$ l of the 25:1 oil/dispersant mixture ( make sure that it is well shaken) on top of the sea water. The oil should be placed in the middle of the surface.
7. Swirl the flask at 150 rpm for 20 minutes.
8. Remove the flask from the slot, and place on the rack to stand for 10 minutes. It is important not to leave it in the slot for the settling time, as it will have to be disturbed after, providing extra energy to the system.
9. Discard the first 1-2 ml of sample from the spout, then transfer 30 ml from the spout into a graduated cylinder.
10. Transfer the 30 ml into a separatory funnel.
11. Using 5 ml pipette add 5 ml of dichloromethane and stopper tightly. Shake the mixture vigorously for 15 seconds, release the built up pressure into the fumehood, and then allow 2 minutes for the layers to separate.
12. Drain the bottom organic layer to the etched 1 ml mark on the funnel into a small erlenmeyer flask, and keep it stoppered.
13. Repeat the extraction (steps 11 and 12) twice more, for a total of 3 times.

14. Zero the spectrophotometer at 370 nm, by placing dichloromethane in both cuvettes and pressing the auto-zero button.
15. Remove the front cuvette, fill it with the sample. Allow 1 minute for settling and record the absorbance at 370, 340, and 400 nm.
16. Re-zero the spec. for each sample done.
17. Use the calibration curves available for each oil in the binder to determine the percent dispersability of the sample.

## **SWIRLING FLASK TEST**

### **One Drop Method**

1. Turn on u.v./visible spectrophotometer.
2. Turn on Brunswick Shaker and set for 20°C.
3. Make artificial seawater with 33 g/L of salt in distilled water. (the bucket has a line marking 66 L).
4. Place 120 ml of artificial seawater in a 125 ml spouted erlenmeyer flask ( 6 runs can be performed simultaneously).
5. Place the flask with the seawater in the slot of the shaker (or on the rack) and allow 20 minutes for it to reach thermal equilibrium.
6. With the flask in the slot of the shaker, carefully float 100 $\mu$ l of oil in the middle of the surface.
7. Carefully float a 10  $\mu$ l drop of dispersant in the centre of the oil slick.
8. Swirl the flask at 150 rpm for 20 minutes.
9. Remove the flask from the slot, and place on the rack for 10 minutes. It is important

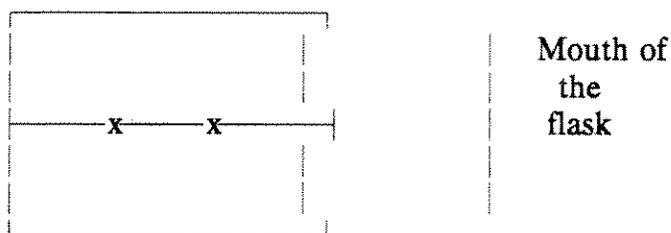
not to leave it in the slot for the settling time, as it will have to be disturbed after, providing extra energy to the system.

10. Discard the first 1-2 ml of sample from the spout, then transfer 30 ml from the spout into a graduated cylinder.
11. Transfer the 30 ml into a separatory funnel.
12. Using a 5 ml pipette add 5 ml of dichloromethane and stopper tightly. Shake the mixture vigorously for 15 seconds, release the built up pressure into the fumehood, and then allow 2 minutes for the layers to separate.
13. Drain the bottom organic layer to the etched 1 ml mark on the funnel and into a small erlenmeyer flask, and keep it stoppered.
14. Repeat the extraction (steps 11 and 12) twice more, for a total of 3 times.
15. Zero the spectrophotometer at 370 nm, by placing dichloromethane in both cuvettes
16. Remove the front cuvette, fill it with the sample. Allow 1 min for settling and measure the absorbance at 370, 340, 400 nm
17. Re-zero the spec. for each sample done
18. Use the calibration curves available for each oil in the binder to determine the percent dispersability of the sample

## SWIRLING FLASK TEST

### Two Drop Method

1. Turn on u.v./visible spectrophotometer.
2. Turn on Brunswick Shaker and set for 20°C
3. Make artificial seawater with 33 g/L of salt in distilled water.  
( the bucket has a line marking 66 L)
4. Place 120 ml of artificial seawater in a 125 ml spouted erlenmeyer flask ( 6 runs can be performed simultaneously).
5. Place the flask with the seawater in the slot of the shaker (or on the rack) and allow 20 minutes for it to reach thermal equilibrium.
6. With the flask in the slot of the shaker, carefully float 100 µl of oil in the middle of the surface.
7. Carefully float a 5 µl drop of dispersant one third of the diameter into the oil slick. As quickly as possible float another 5 µl drop of dispersant one third of the diameter in from the other side. The drops should be placed approximately as depicted:



8. Swirl the flask at 150 rpm for 20 minutes.
9. Remove the flask from the slot, and place on the rack to stand for 10 minutes. It is important not to leave it in the slot for the settling time, as it will have to be disturbed after, providing extra energy to the system.
10. Discard the first 1-2 ml of sample from the spout, then transfer 30 ml from the spout into a graduated cylinder.
11. Transfer the 30 ml into a separatory funnel.

12. Using a 5 ml pipette add 5 ml of dichloromethane and stopper tightly. Shake the mixture vigorously for 15 seconds, release the built up pressure into the fumehood, and then allow 2 minutes for the layers to separate.
13. Drain the bottom organic layer to the etched 1 ml mark on the funnel and into a small erlenmeyer flask, and keep it stoppered.
14. Repeat the extraction (steps 11 and 12) twice more, for a total of 3 times.
15. Zero the spectrophotometer at 370 nm, by placing dichloromethane in both cuvettes.
16. Remove the front cuvette, fill it with the sample. Allow 1 min for settling and measure the absorbance at 370, 340 and 400 nm.
17. Re-zero the spec. for each sample done.
18. Use the calibration curves available for each oil in the binder to determine the percent dispersability of the sample.

## HIGH ENERGY TEST

1. Turn on u.v./visible spectrophotometer.
2. Turn on modified Brunswick Shaker with basket in middle, and set for 20°C.
3. Make artificial seawater with 33 g/L of salt in distilled water.  
(the bucket has a line marking 66 L)
4. Place 5.0 Litres of artificial seawater in the 6 Litre glass vessel.
5. Place the 6 Litre vessel with the seawater in the basket of the shaker and allow 20 minutes for it to reach thermal equilibrium.
6. With the vessel in the basket of the shaker, carefully float 250 µl of the oil-dispersant mixture in the middle of the surface. (This yields a 20000:1 water:oil ratio and can be varied).
7. Place the glass cover on ensuring that the neoprene (w/silicone coating) sealant is covering the complete top surface of the vessel and making a proper seal. Fasten down the glass top with the 4 bungy cords (The shorter one goes from back to front, the others across the width and two diagonally).
8. Swirl the vessel at the desired RPM for 20 minutes.
9. Turn off the shaker, and let stand for 10 minutes.
10. Place a 30 ml pipette into the water (Being careful not to pick up any oil from the top layer) and remove 30 ml from the vessel.
11. Transfer the 30 ml into a separatory funnel.
12. Using 5 ml pipette add 5 ml of dichloromethane and stopper tightly. Shake the mixture vigorously for 15 seconds, release the built up pressure into the fumehood, and then allow 2 minutes for the layers to separate.
13. Drain the bottom organic layer to the etched 1 ml mark on the separatory funnel into a small 25 ml erlenmeyer flask, and keep it stoppered.
14. Repeat the extraction (steps 11 and 12) twice more, for a total of 3 times.
15. Zero the spectrophotometer at 370 nm, by placing dichloromethane in both

cuvettes.

16. Remove the front cuvette, fill it with the sample and measure the absorbance at 370, 340, 400 nm.
17. Re-zero the spec. for each sample done.
18. Use the calibration curves available for each oil in the binder to determine the percent dispersability of the sample.



DISPERSANT EFFECTIVENESS OIL	TABLE 18 DISPERSANT	EFFECTIVENESS PERCENT			
		AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS
A MEDIUM	C 9527	12	13	12	11
A MEDIUM	CRX-8	13	15	7	16
A MEDIUM	ENER 700	13	11	19	8
A MEDIUM	DASIC	16	9	26	13
ADGO	C 9527	61	61	82	41
ADGO	CRX-8	39	61	31	26
ADGO	ENER 700	59	76	53	47
ADGO	DASIC	8	11	7	5
AMAULIGAK	C 9527	45	50	36	49
AMAULIGAK	CRX-8	50	61	51	37
AMAULIGAK	ENER 700	62	65	62	59
AMAULIGAK	DASIC	28	23	40	22
AMAULIGAK	DREW	0	0	0	0
AMAULIGAK	C 9550	0	0	0	0
AMAULIGAK	BQ	60	72	52	57
AMAULIGAK	II	7	22	0	0
ARABIAN LIGHT	C 9527	17	31	16	3.3
ARABIAN LIGHT	CRX-8	9	15	8.6	4.8
ARABIAN LIGHT	ENER 700	22	16	27	23
ARABIAN LIGHT	DASIC	33	24	36	40
ARABIAN LIGHT	BQ	42	28	54	43
ASMB	C 9527	33	42	28	28
ASMB	CRX-8	45	57	43	35
ASMB	ENER 700	51	68	51	35
ASMB	DASIC	24	18	27	28
ASMB	DREW LT	0	0	0	0
ASMB	C 9550	0	0	0	0
ASMB	BQ	79	81	82	73
ASMB	II	18	49	5	0
ASMB	WELLAID 3315	14	8	12	21
ASMB	BP1100WD	12	6	14	17
ASMB	IKU-9	65	65	-	-
ASMB	BP1100X	7	1	10	11
ATKINSON	C 9527	39	59	31	27
ATKINSON	CRX-8	31	67	19	7
ATKINSON	ENER 700	73	79	75	66
ATKINSON	DASIC	49	33	61	53
AVALON J-34	C 9527	11	18	7.5	8
AVALON J-34	CRX-8	5	7.6	5.3	3.3
AVALON J-34	ENER 700	11	15	12	7
AVALON J-34	DASIC	16	8	18	21
AVALON J-34	BQ	10	11	11	7.1
AVALON ZONE 4	C 9527	10	14	10	5.7
AVALON ZONE 4	CRX-8	7	14	4.2	3.1
AVALON ZONE 4	ENER 700	26	25	27	27
AVALON ZONE 4	DASIC	30	12	40	38
AVALON ZONE 4	BQ	13	16	14	10
BCF-24 (VENEZUELA)	C 9527	5	6	5	5
BCF-24 (VENEZUELA)	CRX-8	6	12	3	2
BCF-24 (VENEZUELA)	ENER 700	11	2	16	14
BCF-24 (VENEZUELA)	DASIC	2	0	4	3

DISPERSANT EFFECTIVENESS OIL	TABLE 18 DISPERSANT	EFFECTIVENESS PERCENT			
		AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS
BENT HORN	C 9527	17	12	17	21
BENT HORN	CRX-8	20	15	19	27
BENT HORN	ENER 700	23	10	18	42
BENT HORN	DASIC	35	14	43	48
BETA	C 9527	0	0	0	0
BETA	CRX-8	0	0	0	0
BETA	ENER 700	0	0	0	0
BETA	DASIC	0	0	0	0
BUNKER C	C 9527	1	2.3	1.1	1
BUNKER C	CRX-8	2	3.8	1.3	0.9
BUNKER C	ENER 700	1	0.9	1.9	0.8
BUNKER C	DASIC	2	2.1	2.9	0.6
BUNKER C	BQ	1	1.4	1.4	0.8
BUNKER C LIGHT	C 9527	1	0.6	1	0.4
BUNKER C LIGHT	CRX-8	1	0.7	0.9	0.7
BUNKER C LIGHT	ENER 700	1	0.7	2	1.5
BUNKER C LIGHT	DASIC	1	0.6	1.7	1.3
BUNKER C LIGHT	BQ	2	1.6	2.6	0.8
CARPENTERIA	C 9527	3	2	4	3
CARPENTERIA	CRX-8	1	0	2	2
CARPENTERIA	ENER 700	7	2	11	7
CARPENTERIA	DASIC	5	0	8	7
COHASSET	C 9527	95	88	100	98
COHASSET	CRX-8	44	44		
COHASSET	ENER 700	45	45		
COHASSET	DASIC	9	9		
COHASSET (11.2% W)	C 9527	96	88	99	100
COHASSET (25.6% W)	C 9527	88	75	92	97
COHASSET (28.1% W)	C 9527	90	74	97	100
COLD LAKE BITUMEN	C 9527	2	1.9	2.3	0.4
COLD LAKE BITUMEN	CRX-8	1	1.1	2.1	0.6
COLD LAKE BITUMEN	ENER 700	1	0.9	1.4	0.4
COLD LAKE BITUMEN	DASIC	1	1	1	0.3
COLD LAKE BITUMEN	BQ	1	1.1	1.5	0.3
DOS CUADRAS	C 9527	18	22	20	11
DOS CUADRAS	CRX-8	9	10	9	7
DOS CUADRAS	ENER 700	18	6	28	15
DOS CUADRAS	DASIC	8	1	14	9
EMPIRE	C 9527	4	4		
EMPIRE	CRX-8	5	5		
EMPIRE	ENER 700	2	2		
EMPIRE	DASIC	2	2		
ENDICOTT	C 9527	7	17	2.3	2.8
ENDICOTT	CRX-8	8	20	1.3	2.4
ENDICOTT	ENER 700	6	10	2.4	6.4
ENDICOTT	DASIC	14	8.1	15	18
ENDICOTT	BQ	13	18	6.9	13
ENDICOTT (11.7%W.)	C 9527	2	2	2	2
ENDICOTT (11.7%W.)	CRX-8	2	2	3	2
ENDICOTT (11.7%W.)	ENER 700	6	2	9	6
ENDICOTT (11.7%W.)	DASIC	3	1	3	4
ENDICOTT (11.7%W.)	BQ	4	1	6	6

DISPERSANT EFFECTIVENESS OIL	TABLE 18 DISPERSANT	EFFECTIVENESS PERCENT			
		AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS
ENDICOTT (7.5% W.)	C 9527	3	3	3	3
ENDICOTT (7.5% W.)	CRX-8	4	5	3	3
ENDICOTT (7.5% W.)	ENER 700	6	4	6	9
ENDICOTT (7.5% W.)	DASIC	4	1	1	11
ENDICOTT (7.5% W.)	BQ	6	4	6	7
FEDERATED	C 9527	25	41	24	11
FEDERATED	CRX-8	31	50	26	16
FEDERATED	ENER 700	40	41	56	22
FEDERATED	DASIC	38	23	55	35
FEDERATED	BQ	64	66	85	42
HIBERNIA	C 9527	6	13	1.9	1.8
HIBERNIA	CRX-8	6	14	2.6	2
HIBERNIA	ENER 700	10	7.3	10	14
HIBERNIA	DASIC	14	8.6	18	16
HIBERNIA	BQ	9	7.8	12	6
HIBERNIA	WELLAID 3315	4	3	4	4
HIBERNIA (15.4% W)	C 9527	4	6.1	2.3	2.5
HIBERNIA (15.4% W)	CRX-8	3	5.8	1	2
HIBERNIA (15.4% W)	ENER 700	8	5	11	7.5
HIBERNIA (15.4% W)	DASIC	7	1	8	11
HIBERNIA (15.4% W)	BQ	5	4	6	4
HONDO	C 9527	2	2	2	1
HONDO	CRX-8	1	0	1	2
HONDO	ENER 700	3	1	5	3
HONDO	DASIC	2	0	4	3
ISSUNGAK	C 9527	66	70	93	35
ISSUNGAK	CRX-8	60	58	75	47
ISSUNGAK	ENER 700	62	51	79	57
ISSUNGAK	DASIC	51	31	60	61
ISSUNGAK	BQ	77	77	69	84
LAGO MEDIO	C 9527	5	9.5	3.6	1.5
LAGO MEDIO	CRX-8	5	13	1.8	1.4
LAGO MEDIO	ENER 700	13	11	21	5.9
LAGO MEDIO	DASIC	15	4.1	18	24
LAGO MEDIO	BQ	18	22	25	6.3
MAYAN	C 9527	4	3	5	4
MAYAN	CRX-8	3	1	3	4
MAYAN	ENER 700	7	7	7	6
MAYAN	DASIC	4	0	7	6
MOUSSE MIX	C 9527	6	9	5	3
MOUSSE MIX	CRX-8	9	15	8	5
MOUSSE MIX	ENER 700	14	10	19	13
MOUSSE MIX	DASIC	17	9	22	20
MOUSSE MIX	BQ	18	25	17	12
MOUSSE MIX	II	6	15	3	0
NORMAN WELLS	C 9527	36	51	40	17
NORMAN WELLS	CRX-8	43	60	38	30
NORMAN WELLS	ENER 700	51	73	26	53
NORMAN WELLS	DASIC	26	19	33	27
NORMAN WELLS	DREW LT	0	0	0	0
NORMAN WELLS	C 9550	0	0	0	0
NORMAN WELLS	BQ	77	83	80	68
NORMAN WELLS	II	11	33	0	0

DISPERSANT EFFECTIVENESS	TABLE 18	EFFECTIVENESS PERCENT			
		DISPERSANT	AVERAGE	% PREMIXED	% 1 DROP
NUGUINI	C 9527	50	57	46	48
NUGUINI	CRX-8	57	72	38	61
NUGUINI	ENER 700	55	48	52	66
NUGUINI	DASIC	28	21	31	33
NUGUINI	BP1100X	11	0	16	15
NUGUINI	BP1100WD	20	23	16	21
NUGUINI	C9550	3	0	0	10
OSEBERG	C 9527	29	35	21	30
OSEBERG	CRX-8	26	42	13	24
OSEBERG	ENER 700	29	20	39	29
OSEBERG	DASIC	13	12	14	13
PANUK	C 9527	96	95	95	97
PANUK	CRX-8	78	100	62	71
PANUK	ENER 700	96	93	97	99
PANUK	DASIC	40	44	38	37
PANUK	BQ	100	100	100	99
PANUK (47.4% W)	C 9527	99	96	100	100
PANUK (53.2% W)	C 9527	99	96	100	100
PITAS POINT	C 9527	99	100	99	99
PITAS POINT	CRX-8	99	100	99	99
PITAS POINT	ENER 700	99	100	99	99
PITAS POINT	DASIC	99	100	99	99
PITAS POINT (36% EVAP)	C 9527	99	100	99	99
PITAS POINT (36% EVAP)	CRX-8	99	99	99	99
PITAS POINT (36% EVAP)	ENER 700	99	100	99	99
PITAS POINT (36% EVAP)	DASIC	92	90	95	90
PORT HUENEME	C 9527	1	0	2	2
PORT HUENEME	CRX-8	1	0	2	1
PORT HUENEME	ENER 700	3	1	4	4
PORT HUENEME	DASIC	3	0	4	4
PRUDHOE BAY	C 9527	13	19	13	7
PRUDHOE BAY	CRX-8	13	23	9	6
PRUDHOE BAY	BQ	32	43	29	24
PRUDHOE BAY	ENER 700	35	48	26	31
PRUDHOE BAY	DASIC	11	14		18
PRUDHOE BAY (1989)	C 9527	7	13	5.8	2.5
PRUDHOE BAY (1989)	CRX-8	7	15	3.2	3.9
PRUDHOE BAY (1989)	ENER 700	10	15	3.1	13
PRUDHOE BAY (1989)	DASIC	14	11	18	13
PRUDHOE BAY (1989)	BQ	15	25	4.8	16
PRUDHOE BAY (1989)	WELLAID 3315	4	3	5	3
PRUDHOE BAY (89) (14.5% W)	C 9527	4	5	4	3
PRUDHOE BAY (89) (14.5% W)	CRX-8	4	8	2	3
PRUDHOE BAY (89) (14.5% W)	ENER 700	8	4	6	14
PRUDHOE BAY (89) (14.5% W)	DASIC	10	2	14	13
PRUDHOE BAY (89) (14.5% W)	BQ	9	7	15	5
PRUDHOE BAY (89) (7.6% W)	C 9527	6	9	3	5
PRUDHOE BAY (89) (7.6% W)	CRX-8	6	13	3	3
PRUDHOE BAY (89) (7.6% W)	ENER 700	16	8	25	16
PRUDHOE BAY (89) (7.6% W)	DASIC	16	12	19	18
PRUDHOE BAY (89) (7.6% W)	BQ	19	29	18	10

DISPERSANT EFFECTIVENESS	OIL	DISPERSANT	EFFECTIVENESS PERCENT			
			AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS
	SANTA CLARA	C 9527	2	2	5	0
	SANTA CLARA	CRX-8	2	0	5	0
	SANTA CLARA	ENER 700	3	3	5	0
	SANTA CLARA	DASIC	3	0	3	6
	SANTA MARIA (11.0)	C 9527	1	0.5	1.1	0.9
	SANTA MARIA (11.0)	CRX-8	1	2.3	1.2	0.8
	SANTA MARIA (11.0)	ENER 700	1	0.4	2.7	0.8
	SANTA MARIA (11.0)	DASIC	1	0.2	2.2	0.8
	SANTA MARIA (11.0)	BQ	1	0.4	2.2	1.7
	SANTA MARIA (15.0)	C 9527	1	1.3	0.7	0.3
	SANTA MARIA (15.0)	CRX-8	1	0.4	0.8	0.6
	SANTA MARIA (15.0)	ENER 700	1	0.9	0.9	1
	SANTA MARIA (15.0)	DASIC	2	0.8	3	3.3
	SANTA MARIA (15.0)	BQ	1	1.4	1.3	0.8
	SOCKEYE	C 9527	18	10	24	21
	SOCKEYE	CRX-8	13	13	14	12
	SOCKEYE	ENER 700	20	8	28	24
	SOCKEYE	DASIC	10	2	14	15
	SOUTH LOUISIANA CRUDE	C 9527	31	53	19	21
	SOUTH LOUISIANA CRUDE	CRX-8	36	55	33	19
	SOUTH LOUISIANA CRUDE	ENER 700	48	31	75	37
	SOUTH LOUISIANA CRUDE	DASIC	42	27	50	50
	SOUTH LOUISIANA CRUDE	BQ	62	71	80	35
	SYNTHETIC CRUDE	C 9527	63	77	88	25
	SYNTHETIC CRUDE	CRX-8	41	49	41	34
	SYNTHETIC CRUDE	ENER 700	61	69	69	45
	SYNTHETIC CRUDE	DASIC	25	23	30	21
	SYNTHETIC CRUDE	BQ	55	89	42	34
	TERRA NOVA CRUDE	C 9527	16	29	13	6.5
	TERRA NOVA CRUDE	CRX-8	11	22	5.2	6.5
	TERRA NOVA CRUDE	ENER 700	28	21	38	24
	TERRA NOVA CRUDE	DASIC	40	19	58	44
	TERRA NOVA CRUDE	BQ	40	40	53	27
	TRANSMOUNTAIN BLEND	C 9527	8	14	6	3.1
	TRANSMOUNTAIN BLEND	CRX-8	8	13	5.3	6.6
	TRANSMOUNTAIN BLEND	ENER 700	28	17	43	25
	TRANSMOUNTAIN BLEND	DASIC	27	11	40	31
	TRANSMOUNTAIN BLEND	BQ	19	25	18	15
	USED MOTOR OIL	C 9527	33	42	31	27
	USED MOTOR OIL	CRX-8	31	39	31	23
	USED MOTOR OIL	ENER 700	36	47	32	30
	USED MOTOR OIL	DASIC	29	29	27	31
	USED MOTOR OIL	BQ	36	42	41	24
	WAXY, LIGHT-HEAVY	C 9527	5	5		
	WAXY, LIGHT-HEAVY	CRX-8	6	6		
	WAXY, LIGHT-HEAVY	ENER 700	47	47		
	WAXY, LIGHT-HEAVY	DASIC	0	0		

DISPERSANT EFFECTIVENESS	TABLE 18	EFFECTIVENESS PERCENT			
OIL	DISPERSANT	AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS

**EXPLANATION OF TESTS**

*ALL TEST RESULTS ARE FOR SALT WATER AT 3.3%*

*ALL TEST RESULTS ARE THE AVERAGE OF AT LEAST 6  
EXPERIMENTAL DETERMINATIONS*

*PREMIXED - REFLECTS THE LARGEST AMOUNT DISPERSED  
WHEN DISPERSANT MIXED INTO OIL AT RATIO 1:25*

*1-DROP - REFLECTS LARGEST AMOUNT DISPERSED AT  
A DISPERSANT TO OIL RATIO OF 1:10*

*- TEST MEASURES HOW OIL/DISPERSANT COMBINATION  
FUNCTIONS WITH REAL APPLICATION*

*2-DROP - REFLECTS LARGEST AMOUNT DISPERSED AT  
A DISPERSANT TO OIL RATIO OF 1:10 BUT DELIVERED IN  
TWO DROPS*

*- TEST MEASURES THE HERDING EFFECT OF THE  
OIL/DISPERSANT COMBINATION WHEN COMPARED  
TO THE ONE DROP TEST*

*IKU-9 IS AN EXPERIMENTAL DISPERSANT MADE BY IKU, NORWAY  
BQ AND II ARE EXPERIMENTAL DISPERSANTS MADE BY EETD*