

**STUDY OF OIL SPILL DISPERSANTS
EFFECTIVENESS AND PHYSICAL STUDIES**

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INTRODUCTION

Dispersants continue to be a lively topic of discussion twenty years after the TORREY CANYON incident. Little has changed in the way of documentation. There is still no undisputed documentation on large-scale experiments or use to show whether dispersants are effective or not. Similarly, no large scale biological experiments have convinced all environmentalists that the use of dispersants is safe in all conditions, although the evidence is becoming increasingly clear that dispersants cause little ecological damage above that by untreated oil and that they could, in fact, minimize ecological damage if they were effective. The current focus on dispersants is now more on the effectiveness than on the toxicity. The current emphasis on joint Environment Canada-U.S. Minerals Management Service work is on mechanism studies. These are intended to discover the variables involved in dispersant action so that insights will be found on how effectiveness can be improved.

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.¹ A surfactant with an HLB of about 1 to 8 promotes the formation of water-in-oil emulsions and one with an HLB in the range of 12 to 20 promotes the formation of oil-in-water emulsions. Dispersants have HLB's in the range of 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. Many of these agents would be better classed as surface-washing agents.

Surface-washing agents 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. EETD has developed an

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effectiveness test for such agents and results of these tests are reported in the literature. Many surfactant-containing agents of all types come onto the market each year, many are re-packaged industrial cleaners and have little utility in spills.

DISPERSANTS - FIELD EFFECTIVENESS TRIALS AND ACTUAL USE

Over the past 12 years, 107 test and control spills have been laid out to test the effectiveness of oil spill dispersants.² The results achieved during these tests show clearly that dispersants are not highly effective, 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 than 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.³ 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. Furthermore, all of the experimenters who used underwater concentrations to estimate field effectiveness also used the method of dividing the water into different compartments and averaging concentrations. Mathematically this is not appropriate and can result in effectiveness values that are much larger than the actual values. 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, the error in measurement can be as great as a factor of 10 in two dimensions and as great as 10 times 10 or 100-fold in three dimensions or overall! Other errors in the opposite direction compensate for this somewhat, but the overall result is a large exaggeration of effectiveness.

Surface measures are also inadequate. Remote sensing does not provide a thickness measure and thus calculating volume is impossible. Numerous surface phenomena also interfere with the process of estimating slick volume. These have been detailed in a paper by Goodman and Fingas.⁴ A new technique for measuring surface thickness is currently under 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 or qualitative proof of high (> 50%) dispersant effectiveness. Analytical means do not exist at this time to

accurately quantify dispersant effectiveness in field trial situations.

Dispersant usage during some notable large spills has been reviewed by a number of authors.^{5,6} The problem with actual spill data is that some observers may have reported seeing evidence of effectiveness and others directly the opposite. In none 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 Arabic countries. Again, no quantitative results are available to show effectiveness nor lack of such.

DISPERSANTS - LABORATORY STUDIES OF EFFECTIVENESS

A number of laboratory studies have been performed to compare the test results from different apparatus and procedures. A review of these results shows that there is poor correlation in effectiveness results between the various test methods.⁷ A recent study by the present author has shown that lack of correlation is primarily a function of settling time allowed between the time that the energy is no longer applied and the time that the water sample is taken from the apparatus.⁸ Another important factor is that of the oil-to-water ratio in the apparatus. When these two parameters are adjusted to be the same and to larger values test results from most apparatus are similar. Results from more energetic dispersant effectiveness tests, such as the Mackay test and the Labofina or Warren Springs test, are somewhat higher but, when corrected for natural dispersion, these results are nearly identical to those from less energetic apparatus. Results from a series of tests including corrected results, are shown in Table 1. The effectiveness results from all tests are nearly identical even though the errors for measurement in the Mackay and Labofina tests are 10 percent or more. The fact that these values are nearly identical may imply that they have some meaning. Just the fact that this phenomena occurs also indicates that energy plays a lesser role than was previously thought. The high energy in the Mackay and Labofina tests only increases the dispersant effectiveness for those oils that disperse naturally.

Early studies were used to help to come to an understanding of laboratory effectiveness tests. It had been found that the existing tests yield different results for different dispersant-oil combinations. This was especially true when the oil type was varied, rather than the dispersant type. Dispersants which appeared to be effective on one oil were often quite ineffective on that same oil in another apparatus or test protocol. Additionally, the main test then in the literature, the Labofina (or Warren Springs or Rolling Flask) test and the Mackay (or MNS or Mackay-Nadeau-Steelman) test produced results that were quite different. The former test uses a separatory funnel with 250 mL of water and 5 mL of oil to test the dispersant. The resulting oil-water ratio is 1:50, a factor that shall later be shown to be of

TABLE 1 EFFECTIVENESS IN FOUR APPARATUS

OIL	DISPERSANT	DISPERSABILITY IN PERCENT			
		SWIRLING	FLOWING	LABOFINA	MNS
		FLASK	CYLINDER		
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
ISSUNGNAK	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	36	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 = COREXT 9527, CRX-8 = COREXT CRX-8, EN 700 = ENERSPERSE 700

significance. The separatory funnel is rotated at 33 rpm for 10 minutes and then a sample taken after a settling time of 2 minutes and analyzed colorimetrically. The Mackay apparatus, on the other hand, employs 10 mL of oil and 6 L of water to yield an oil-to-water ratio of 1:600. Energy is supplied by a high velocity stream of air. Sampling is done dynamically - no settling time is allowed. The results of the two tests differ with oils - the Mackay test consistently gave higher numbers for heavier oils and especially for very viscous oils. The Mackay effectiveness numbers were also very noisy and had a tendency to be very high or very low. The Labofina effectiveness values tended to only appear in the mid-range of values - that is around 50%. Attempts to correlate both results with field values were futile. The first effort of EETD was to generate a good data set with both devices to determine what the variances indeed were. The second effort was to test other concepts to see if every device or test yields unique effectiveness values. An oscillating hoop test which employs an oil-to-water ratio of 1:200 using the given protocol was tried. The values produced using this apparatus and test protocol showed values more similar to the Mackay test than to the Labofina, however the data was also noisy like that from the Mackay test. Early conclusions from these study were that lab tests produced unique results based on their protocols and test features. This offered no hope for further understanding of dispersants effectiveness.

EETD continued research despite the pessimistic conclusions noted above. The first effort was the development of a rapid and simple test. The purpose of this was to speed research. About 10 tests per day could be done with the Labofina apparatus then in use and about 6 for the Mackay apparatus. It was obvious that to perform tests for many oils and dispersants in many different conditions, that a faster test was needed. The development resulted in the Swirling Flask test which employs a standard 125 mL flask with a bottom spout for decanting the sample. Depending on the type of test, 30 to 50 runs could be conducted in one day. The protocol chosen for the test was an oil to water ratio of 1:1200 and a settling time of ten minutes. The first results achieved with this new test did not correlate well with either the Mackay or Labofina tests results and there was almost no correlation with the oscillating hoop test results. What was dramatically different from all three tests was that results were repeatable within 5%. Results from other tests were often ten times this value!

Testing continued using the new apparatus. The effectiveness of many oils and several dispersants were measured. Values appeared to be correct but low compared to those for other tests. Variation of effectiveness with settling time was measured extensively and it was found that the effectiveness changes as an exponential function with settling time settling from 0 to 10 minutes and then

only changes a small amount after 10 minutes. This settling time was also measured in the Labofina and Mackay tests and found to be the same. Some of the "noise" in both the latter tests can then be explained by the settling time. In the case of the Labofina, sampling is done at the 2-minute mark, a time at which particles are rapidly rising to the surface. Any small error in timing can result in significant variation in amount of oil sampled and subsequently effectiveness. Test results using the swirling flask apparatus are presented in Table 2.

MECHANISM STUDIES

The first round of mechanism studies 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 characteristics. The tests showed that dispersed oil could be somewhat 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 oil was placed in the water or on the oil. Only the swirling flask tested showed no trace of this tendency. In fact, in the case of the three offending apparatus, it only made a small difference in effectiveness on where the dispersant was placed, with the Labofina showing the least difference, and the Mackay the most. 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 nature 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 almost 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 apparatus mentioned above, 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 for the settling time. 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 deviant oils

Table 2 DISPERSANT EFFECTIVENESS			EFFECTIVENESS PERCENT		
OIL	DISPERSANT	AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS
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	TL	TL	TL
AMAULIGAK	C 9550	0	TL	TL	TL
AMAULIGAK	BQ	60	72	52	57
AMAULIGAK	II	0	22	TL	TL
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	TL	TL	TL
ASMB	C 9550	0	TL	TL	TL
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	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
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
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

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OIL	DISPERSANT EFFECTIVENESS		EFFECTIVENESS PERCENT		
	DISPERSANT	AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS
BUNKER C LIGHT	BQ	2	1.6	2.6	0.8
CALIFORNIA CRUDE (11.0)	C 9527	1	0.5	1.1	0.9
CALIFORNIA CRUDE (11.0)	CRX-8	1	2.3	1.2	0.8
CALIFORNIA CRUDE (11.0)	ENER 700	1	0.4	2.7	0.8
CALIFORNIA CRUDE (11.0)	DASIC	1	0.2	2.2	0.8
CALIFORNIA CRUDE (15)	BQ	1	0.4	2.2	1.7
CALIFORNIA CRUDE (15)	C 9527	1	1.3	0.7	0.3
CALIFORNIA CRUDE (15)	CRX-8	1	0.4	0.8	0.6
CALIFORNIA CRUDE (15)	ENER 700	1	0.9	0.9	1
CALIFORNIA CRUDE (15)	DASIC	2	0.8	3	3.3
COHASSET	BQ	1	1.4	1.3	0.8
COHASSET (11.2% W)	C 9527	95	88	100	98
COHASSET (25.6% W)	C 9527	96	88	99	100
COHASSET (28.1% W)	C 9527	88	75	92	97
COLD LAKE BITUMEN	C 9527	90	74	97	100
COLD LAKE BITUMEN	CRX-8	2	1.9	2.3	0.4
COLD LAKE BITUMEN	ENER 700	1	1.1	2.1	0.6
COLD LAKE BITUMEN	DASIC	1	0.9	1.4	0.4
COLD LAKE BITUMEN	BQ	1	1	1	0.3
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 (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
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
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 (15.4% W)	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
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

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 2 DROPS

Table 2 DISPERSANT EFFECTIVENESS			EFFECTIVENESS PERCENT			
OIL	DISPERSANT	AVERAGE	% PREMIXED	% 1 DROP	% 2 DROPS	
0.8	LAGO MEDIO	C 9527	5	9.5	3.6	1.5
0.9	LAGO MEDIO	CRX-8	5	13	1.8	1.4
0.8	LAGO MEDIO	ENER 700	13	11	21	5.9
0.8	LAGO MEDIO	DASIC	15	4.1	18	24
0.8	LAGO MEDIO	BQ	18	22	25	6.3
1.7	MOUSSE MIX	C 9527	6	9	5	3
0.3	MOUSSE MIX	CRX-8	9	15	8	5
0.6	MOUSSE MIX	ENER 700	14	10	19	13
1	MOUSSE MIX	DASIC	17	9	22	20
3.3	MOUSSE MIX	BQ	18	25	17	12
0.8	MOUSSE MIX	II	6	15	3	0
98	NORMAN WELLS	C 9527	36	51	40	17
100	NORMAN WELLS	CRX-8	43	60	38	30
97	NORMAN WELLS	ENER 700	51	73	25	53
100	NORMAN WELLS	DASIC	26	19	33	27
0.4	NORMAN WELLS	DREW LT	0	TL	TL	TL
0.6	NORMAN WELLS	C 9550	0	TL	TL	TL
0.4	NORMAN WELLS	BQ	77	83	80	68
0.3	NORMAN WELLS	II	0	33	TL	TL
0.3	PANUK	C 9527	96	95	95	97
2.8	PANUK	CRX-8	78	100	62	71
2.4	PANUK	ENER 700	96	93	97	99
6.4	PANUK	DASIC	40	44	38	37
18	PANUK	BQ	100	100	100	99
13	PANUK (47.4% W)	C 9527	99	96	100	100
3	PANUK (53.2% W)	C 9527	99	96	100	100
3	PRUDHOE BAY	C 9527	13	19	13	7
9	PRUDHOE BAY	CRX-8	13	23	9	6
11	PRUDHOE BAY	BQ	32	43	29	24
7	PRUDHOE BAY	ENER 700	35	48	25	31
2	PRUDHOE BAY	DASIC	11	14		18
2	PRUDHOE BAY (1989)	C 9527	7	13	5.8	2.5
6	PRUDHOE BAY (1989)	CRX-8	7	15	3.2	3.9
4	PRUDHOE BAY (1989)	ENER 700	10	15	3.1	13
6	PRUDHOE BAY (1989)	DASIC	14	11	18	13
11	PRUDHOE BAY (1989)	BQ	15	25	4.8	16
16	PRUDHOE BAY (1989)	WELLALD 3315	4	3	5	3
22	PRUDHOE BAY (89) (7.6% W)	C 9527	6	9	3	5
35	PRUDHOE BAY (89) (7.6% W)	CRX-8	6	13	3	3
42	PRUDHOE BAY (89) (7.6% W)	ENER 700	16	8	25	16
8	PRUDHOE BAY (89) (7.6% W)	DASIC	16	12	19	18
2	PRUDHOE BAY (89) (7.6% W)	BQ	19	29	18	10
14	PRUDHOE BAY (89) (14.5% W)	C 9527	4	5	4	3
6	PRUDHOE BAY (89) (14.5% W)	CRX-8	4	8	2	3
3	PRUDHOE BAY (89) (14.5% W)	ENER 700	8	4	6	14
1	PRUDHOE BAY (89) (14.5% W)	DASIC	10	2	14	13
5	PRUDHOE BAY (89) (14.5% W)	BQ	9	7	15	5
5	SOUTH LOUISIANA CRUDE	C 9527	31	53	19	21
1	SOUTH LOUISIANA CRUDE	CRX-8	36	55	33	19
1	SOUTH LOUISIANA CRUDE	ENER 700	48	31	75	37
1	SOUTH LOUISIANA CRUDE	DASIC	42	27	50	50
1	SOUTH LOUISIANA CRUDE	BQ	62	71	80	35
1	SYNTHETIC CRUDE	C 9527	63	77	88	25
1	SYNTHETIC CRUDE	CRX-8	41	49	41	34
1	SYNTHETIC CRUDE	ENER 700	61	69	69	45
1	SYNTHETIC CRUDE	DASIC	25	23	30	21

OIL	DISPERSANT	AVERAGE	EFFECTIVENESS PERCENT		
			% PREMIXED	% 1 DROP	% 2 DROPS
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
TRANSMOUNTAIN BLEND	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

EXPLANATION OF TESTS

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

BQ AND II ARE EXPERIMENTAL DISPERSANTS MADE BY EETD

TL = TO LOW TO MEASURE

revealed that all were naturally dispersible. Blanks (samples without dispersants) were run in the respective apparatus and blank values subtracted from the value run 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. Perhaps this value is the maximum effectiveness which could be expected with the oil-dispersant combination.

At the same time as the above tests were under way, 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 and is unique to tests around the world. The test, known in EETD 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 chemical 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 on-going. The height between the surface of the oil and the withdrawal spout is about 30 cm. This ensures that only more 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 so that variables did not include modes of adding energy or operation. The flowing cylinder apparatus yielded the same results as the other four devices or tests when they are operated at high oil-to-water ratios and 10 minute settling times. This confirms that the previous findings was independent of apparatus mode of operation and that an additional device could produce the same results. 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 between high oil-to-water ratios and low. 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 strive to do the same.

DROPS

34

3.5

24

14

7

1

6

5

1

5

7

3

3

1

1

The next round of experiments focused on the measurement of dispersed oil droplet sizes produced in the different apparatus. After several hundred measurements, it was found that in all apparatus, all oils with all dispersants resulted in the same droplet size of 30 microns VMD. This occurs when the apparatus are operated at the optimal settling time and with the optimal oil-to-water ratio, as noted above. The meaning of VMD should be explained at this point. In performing particle analysis, two measurements are obtained, particle number and 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 same number is the result and second, most oil dispersions are relatively stable. The only variance noted in stability is caused by the dispersant.

Analysis of remote sensing data showed additional problems with dispersants including, herding of the oil and the direct passage of dispersant into the water column. Initial thinking was that rendering dispersants more oleophilic would cure both of these problems. Studies also began in EETD labs to examine possible formulation changes for dispersants. Early work focused on "doping" existing dispersant formulations with surfactants that would render the mixture more oleophilic. This did not result in success because, as can be seen later, dispersant technology is very critical in terms of oil/water solubility.

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 of 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 the use of 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 is incorrect in open systems such as in the use of dispersants at sea.

One of the problems examined by a number of researchers was the herding, or pushing aside, of the oil by the dispersant. This was observed at a number of 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 EETD 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 E. Nagy has also shown that tests of herding agents showed similar limitations. The finding is logical in that the spreading energy 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 was not universally observed at spill scenes. Work done by Betcher on herding has shown that surfactants with HLB's greater than 10 do herd and that this effect increases as the HLB increases. This indicates 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 shows surfactant on the sea surface slowly separating from the slick. To confirm these 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!

The solvents in the old dispersant mixtures were aromatic petroleum solvents and were quite toxic to aquatic life. After the TORREY CANYON incident, this was changed to less toxic petroleum solvents. The generation of "no mix" dispersants saw this change to butyl cellosolve and polyols. Butyl cellosolve is now regarded as a chemical with potential health problems. Improvements in dispersants could also include solvent change because the current solvents have a tendency to move the surfactants into the water rather than accommodate them to the oil.

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: that surfactant HLB is much more critical than originally thought (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); that only surfactants with HLB of 10 showed promise, that mixtures of surfactants to yield an average HLB of 10 using high and low HLB products were not as effective as single surfactants nor did their group effectiveness indicate as high an effectiveness as would be expected; that ionic surfactants by themselves had no effectiveness and simply went into the water; and that most solid surfactants did not work, largely because they would not mix with the oil.

In 1989, a joint study with the U.S. MMS was begun to examine another phenomenon, that of the accelerated weathering caused by dispersants.⁹ It was known that dispersants caused 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 oils 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 resulted in the findings 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 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 compare this to the starting oil. Using chromatographic analysis, it was found that accelerated weathering again occurred to about the same percentage as found before. In addition to this, a very important discovery was made, that the composition of the oil in the water column and on the surface had compositional changes other than those caused by weathering alone. It was found more n-alkanes were taken into the water column for those chain lengths corresponding to the same chain length of the oleophilic portion of the surfactant. Surface oil was deficient in these same compounds, confirming the hypothesis that this was absorption to the oleophilic portion of the surfactant. The oil on the surface contained a higher amount 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 dispersable. These findings are significant, showing that longer-chain surfactants may be necessary to achieve greater dispersion, that surface means of measuring dispersant effectiveness means must compensate for the accelerated weathering and that there are lesser dispersable components of the oil.

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.
7. That the droplet sizes produced by most dispersants and most oils in most apparatus may have the same size distribution

EFFECT OF TEMPERATURE, SALINITY, AMOUNT OF DISPERSANT AND MIXING TIME

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 the variance in the parameter of interest.⁹ Dispersant was pre-mixed with the oil to ensure a higher degree of repeatability. All experiments were performed with Alberta Sweet Mixed Blend (ASMB) crude oil and the dispersant Corexit 9527, except where noted.

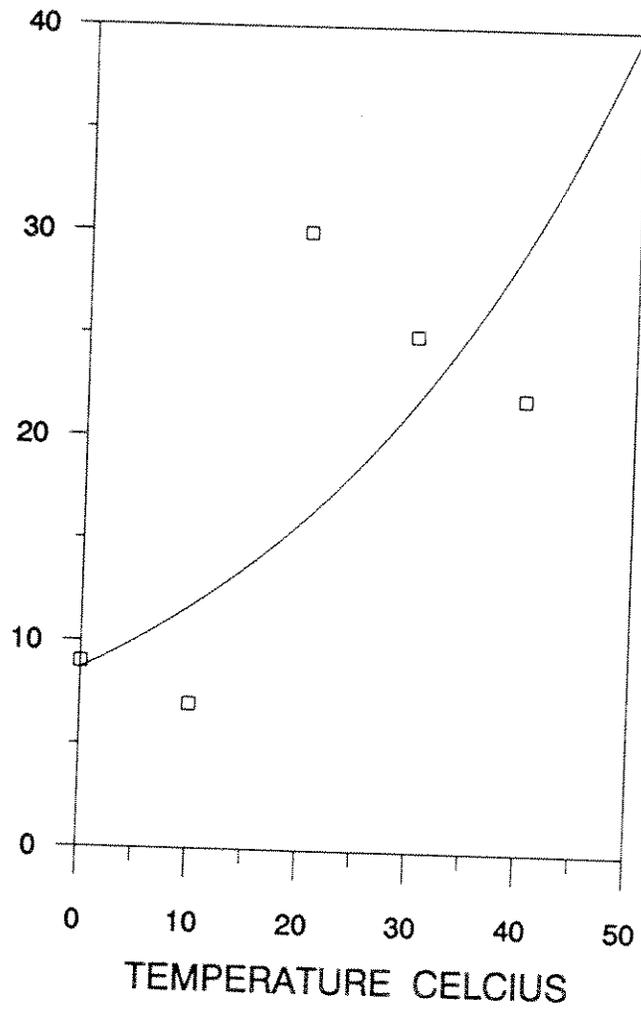
Figure 1 shows the effect of temperature on effectiveness. The temperature refers to both the temperature of the oil and the seawater. The graph shows that effectiveness rises significantly with increasing temperature. There is approximately a two-fold rise in effectiveness with a three-fold rise in temperature. A large part of this variation is due to the decreasing viscosity of the oil with temperature rise.

Figure 2 shows the effect of salinity on dispersant effectiveness. Both ASMB and Norman Wells crude oils were used with Corexit 9527 and Enersperse 700. Polynomial curves with two variables are 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 ppt (parts-per-thousand or degrees salinity) and falls down very sharply with a decrease or increase in salinity. Freshwater effectiveness is nearly 0 for all four 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

VARIATION OF EFFECTIVENESS WITH TEMPERATURE

FIGURE 1

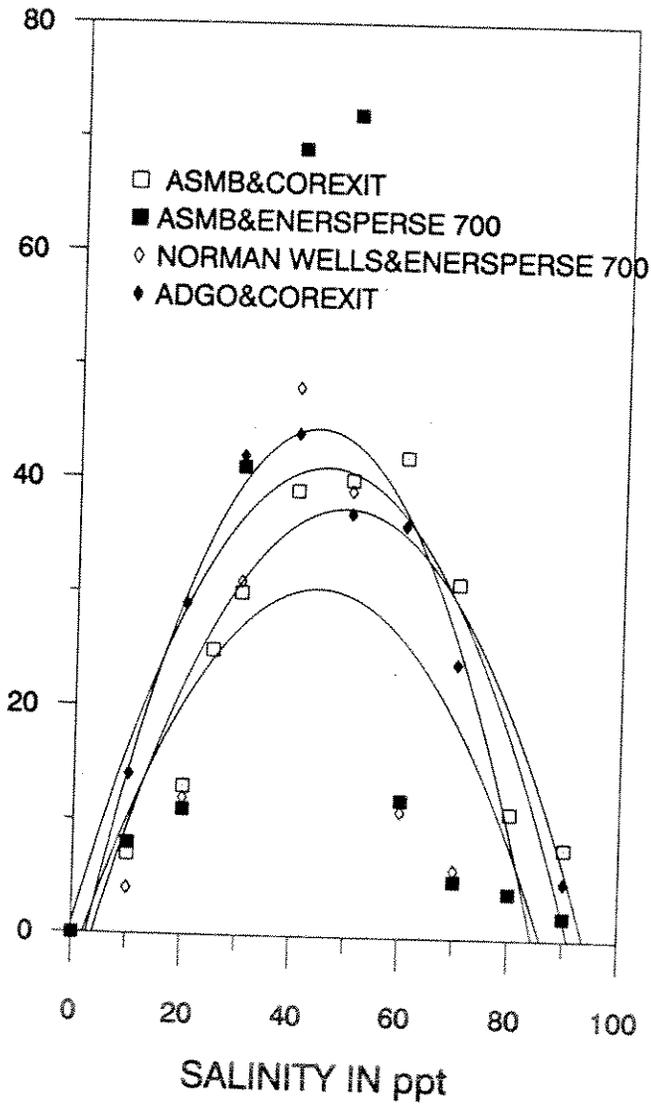
EFFECTIVENESS %



VARIATION OF EFFECTIVENESS WITH SALINITY

FIGURE 2

EFFECTIVENESS %



tested. The decrease in effectiveness with salinity increase above 40 ppt was unexpected, but is easily explained by the fact that the main surfactants in the products tested are non-ionic. These formulations are optimal at a moderate ionic strength.

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 parts of oil. Results of this experiment are shown in Figure 3. The curves are logarithmic and are fitted using a least-squares methodology. The correlation coefficients for the values are very high and range between 0.90 and 0.99. 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 for three commercial dispersants. Some experiment dispersants display a slightly better performance. The sharpness of the curves is somewhat a surprise and can 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. Loss of dispersant in an experiment can result in a very significant difference.

The effect of mixing time was investigated by running the standard swirling flask experiment for times different than the usual 20 minutes. Results of this are shown in Figure 4. Straight lines were fit to the data with high correlation coefficients. The results show that, contrary to expectations, there is no increase in effectiveness but the results are not entirely consistent. The results appear to indicate that there is probably little change in effectiveness, but that increased evaporation over the time period removes some of the oil. The conclusion is that there is little effect with increased mixing time. It is mixing energy, as has been shown by other experiments, that will increase dispersant effectiveness.

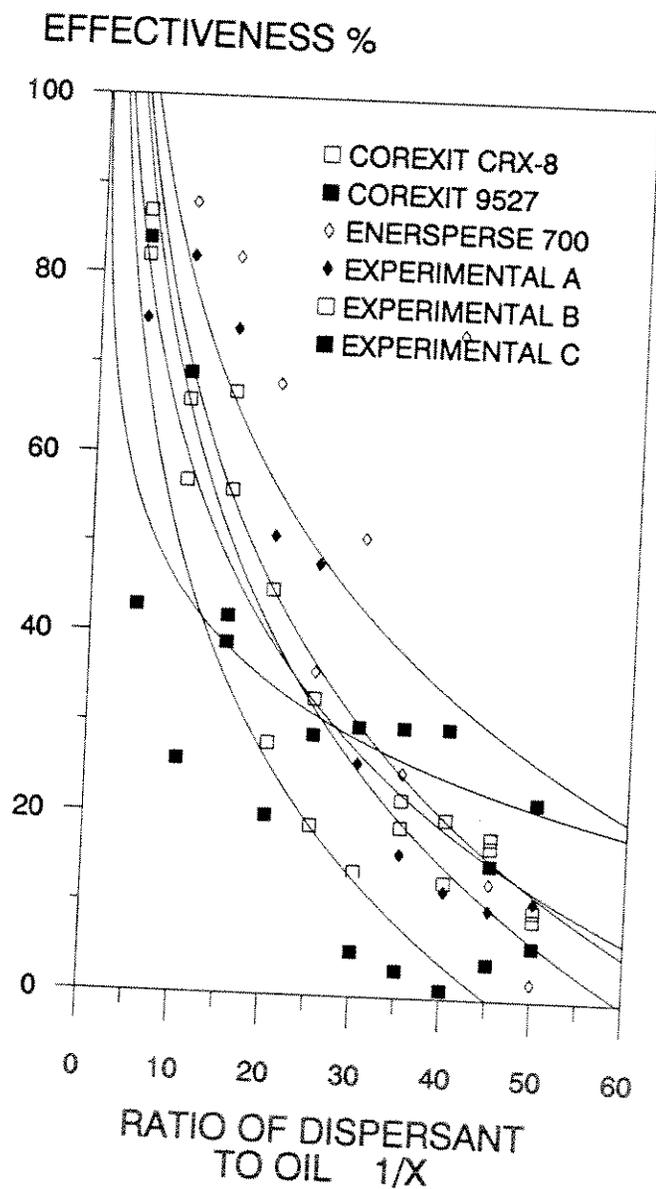
METHODS OF PREPARING CALIBRATION CURVES

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

VARIATION OF EFFECTIVENESS WITH DISPERSANT QUANTITY

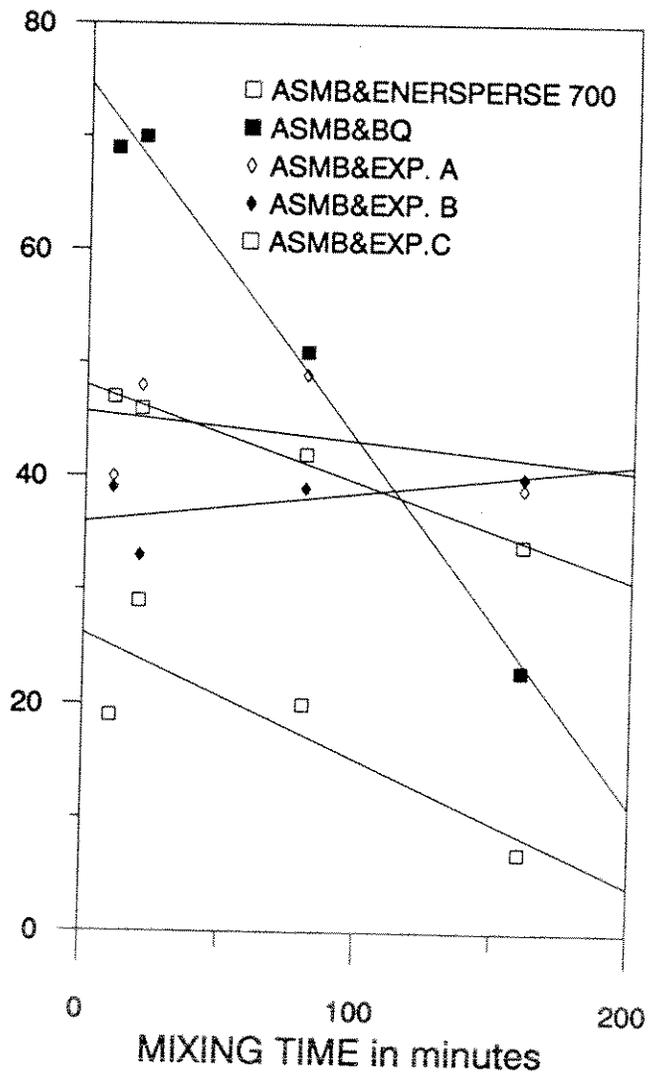
FIGURE 3



VARIATION OF EFFECTIVENESS WITH MIXING TIME

FIGURE 4

EFFECTIVENESS %



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.⁸ 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 3 gives summary values of some experiments conducted to investigate calibration procedure.

Table 3 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
Isaungnak + BQ	65	46	21	22
Isaungnak + 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 3 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 3 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.

SUMMARY RESULTS OF RECENT STUDIES

The recent studies can be summarized as follows:

1. The effect of temperature is largely the result of changing viscosity. The higher the temperature, the greater the effectiveness.
2. Dispersants are most effective at a salinity of about 40 ppt. Dispersant effectiveness rapidly decreases when salinity is increased or decreased. Freshwater effectiveness of present-day dispersants is very low.
3. 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.
4. Mixing time has little effect on effectiveness, and
5. Calibration procedure for laboratory dispersant effectiveness tests is important. Calibration procedure must include contact with water in a manner analogous to the extraction procedure itself. Failure to include this procedure results in inflated effectiveness values. Compensation for the coloration produced by the dispersant alone is important for some dispersants only. A separate calibration curve for each oil/dispersant combination is an accurate way of performing the compensation but is very time-consuming. Compensation can be performed simply by running a dispersant blank through the calibration procedure.

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