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PHYSICAL AND CHEMICAL STUDIES ON OIL SPILL DISPERSANTS: THE EFFECT OF ENERGY

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INTRODUCTION

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.[1] 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. [2] Another definition is that of steepness of waves and their periods. [3] Several discussions on the relationship between dispersion and energy have taken place, but little experimental work has been published.[4-7] Fundamental literature on surfactants also does not propose energy relationships. [8,9]

Many different types of dispersant test procedures and apparatus are described in the literature. One estimate places this at 50 different tests or procedures.[10-15] 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 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.[16] 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.[16] 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.[16] 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 1 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.[13] Saltwater was prepared with sodium chloride to 33 ∞/o or degrees salinity. All tests were done at a temperature of 20°C. Apparatus, oil and water were left at these temperatures for at least 20 minutes before the beginning of each test to ensure thermal equilibrium. All tests were done in thermally-controlled chambers.

TABLE 1 TEST OIL PROPERTIES

OIL	DESCRIPTION	KINEMATIC VISCOSITY (mm /s AT 15 C)	DENSITY (g/mL At 15 C)
ASMB	ALBERTA SWEET MIXED BLEND	8	0.84
ARABIAN LIGHT	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

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.[17] 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.[18] 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 1. 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 2. 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.[16] 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 3. 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 4 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 4 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.

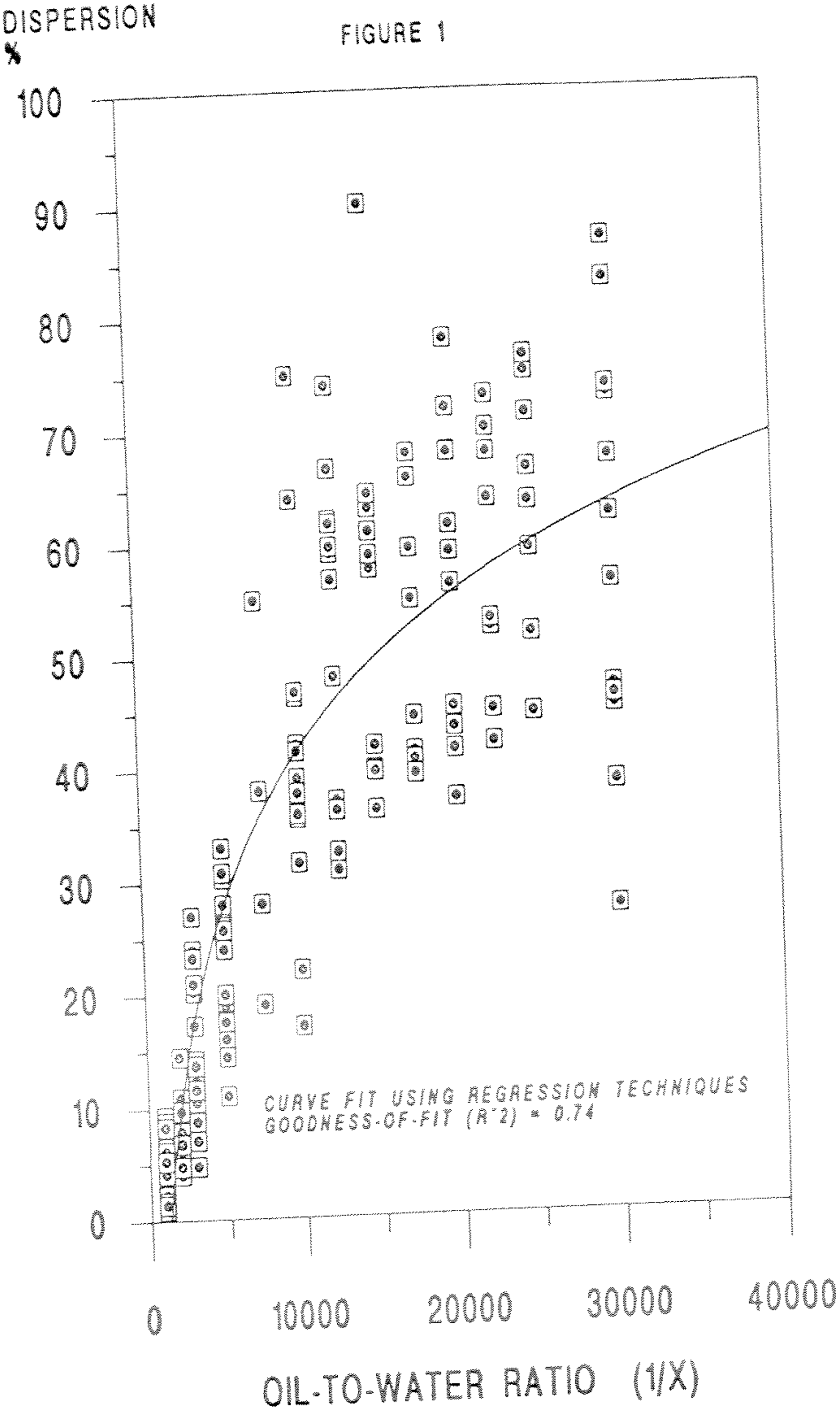
Experiments involving heavier oils (heavier than ASMB) were unsuccessful in that insufficient energy was available to completely disperse the oils or to achieve dispersion without the use of dispersants. The high energy device using a square vessel was developed to address this problem. The square apparatus 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 5. 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.

Many confirmation experiments were conducted. Figure 6 summarizes

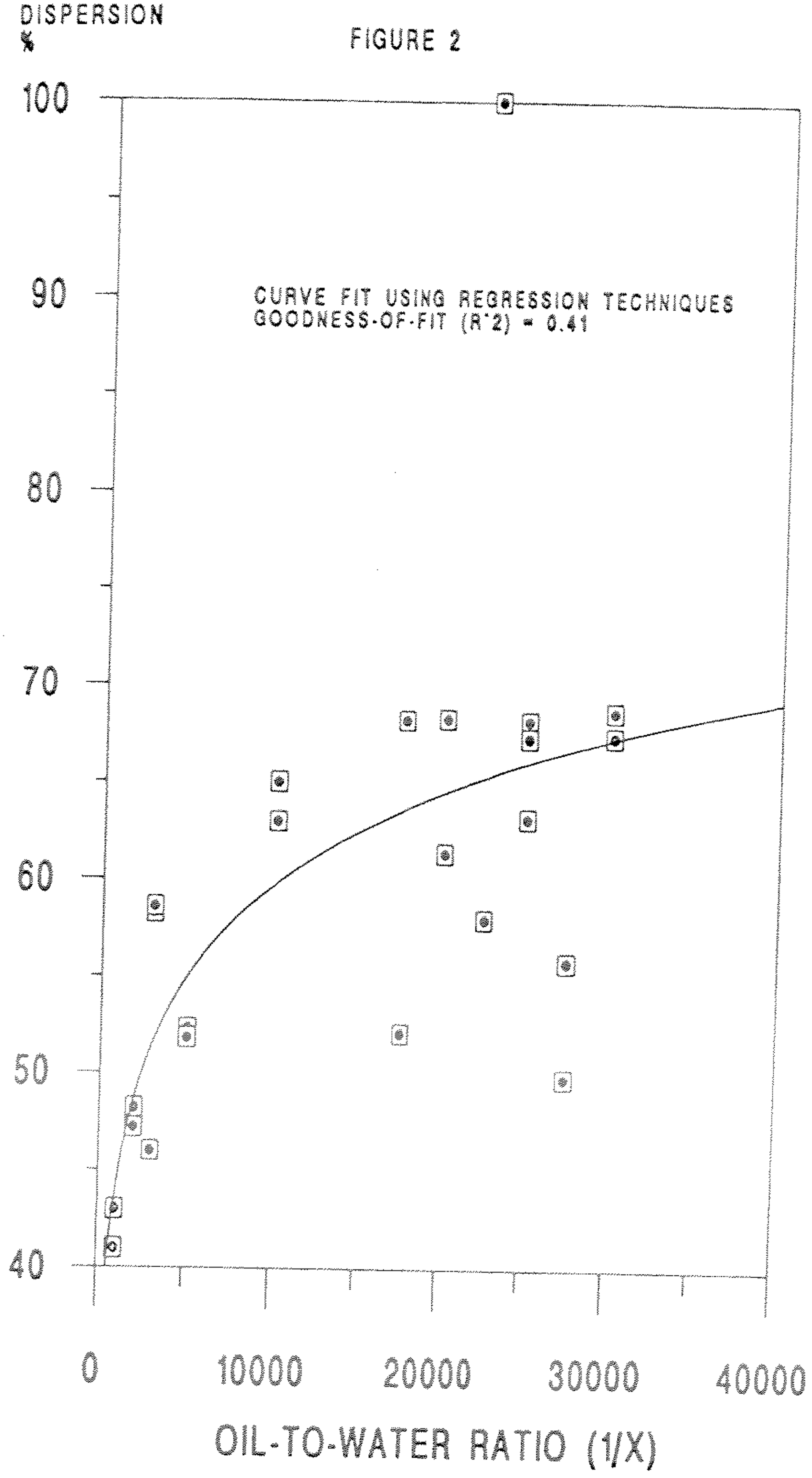
MEASUREMENT OF OIL-TO-WATER RATIO AND NATURAL DISPERSION IN THE LABOFINA

FIGURE 1



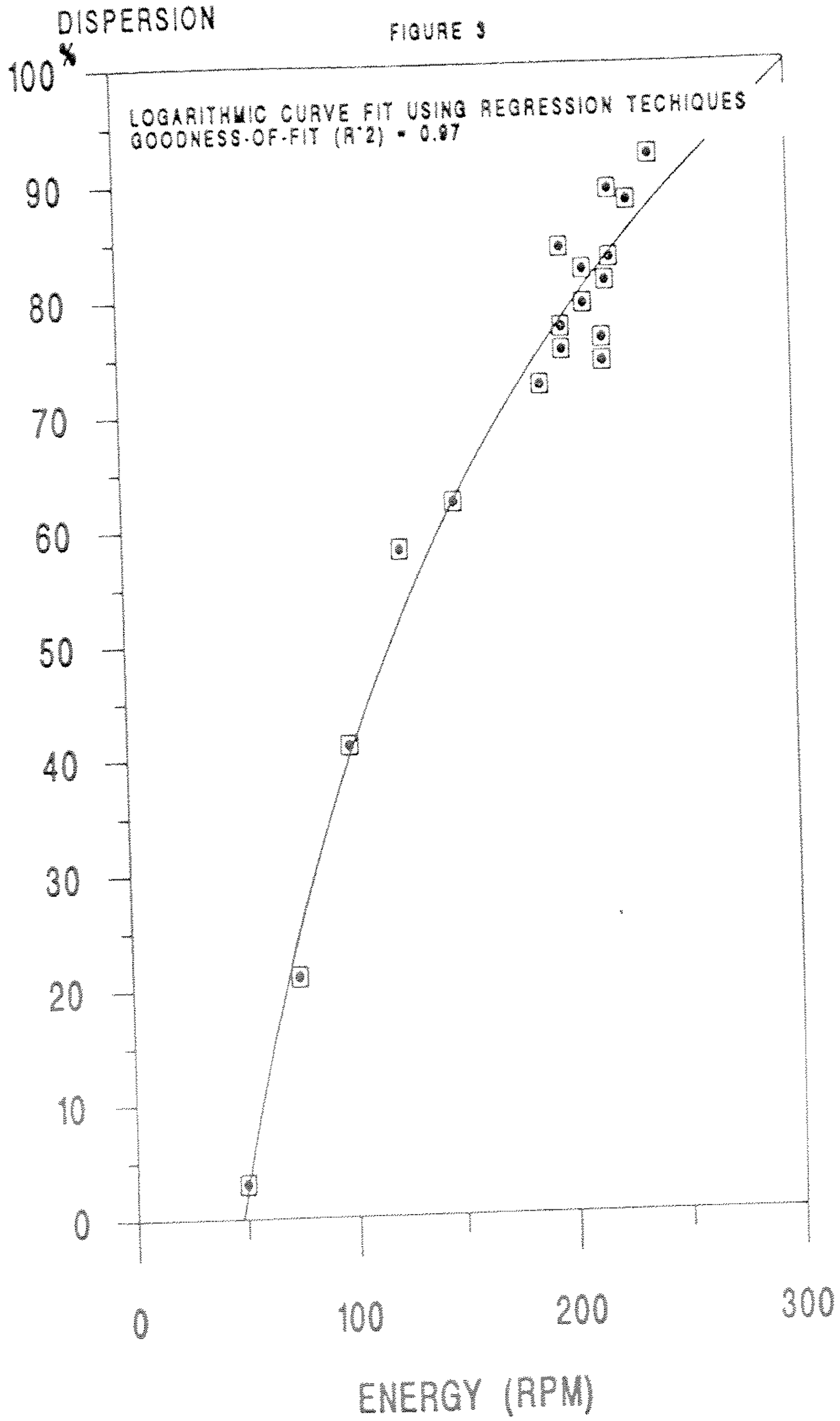
NATURAL DISPERSION AND OIL-TO-WATER RATIO IN THE BLENDER APPARATUS

FIGURE 2



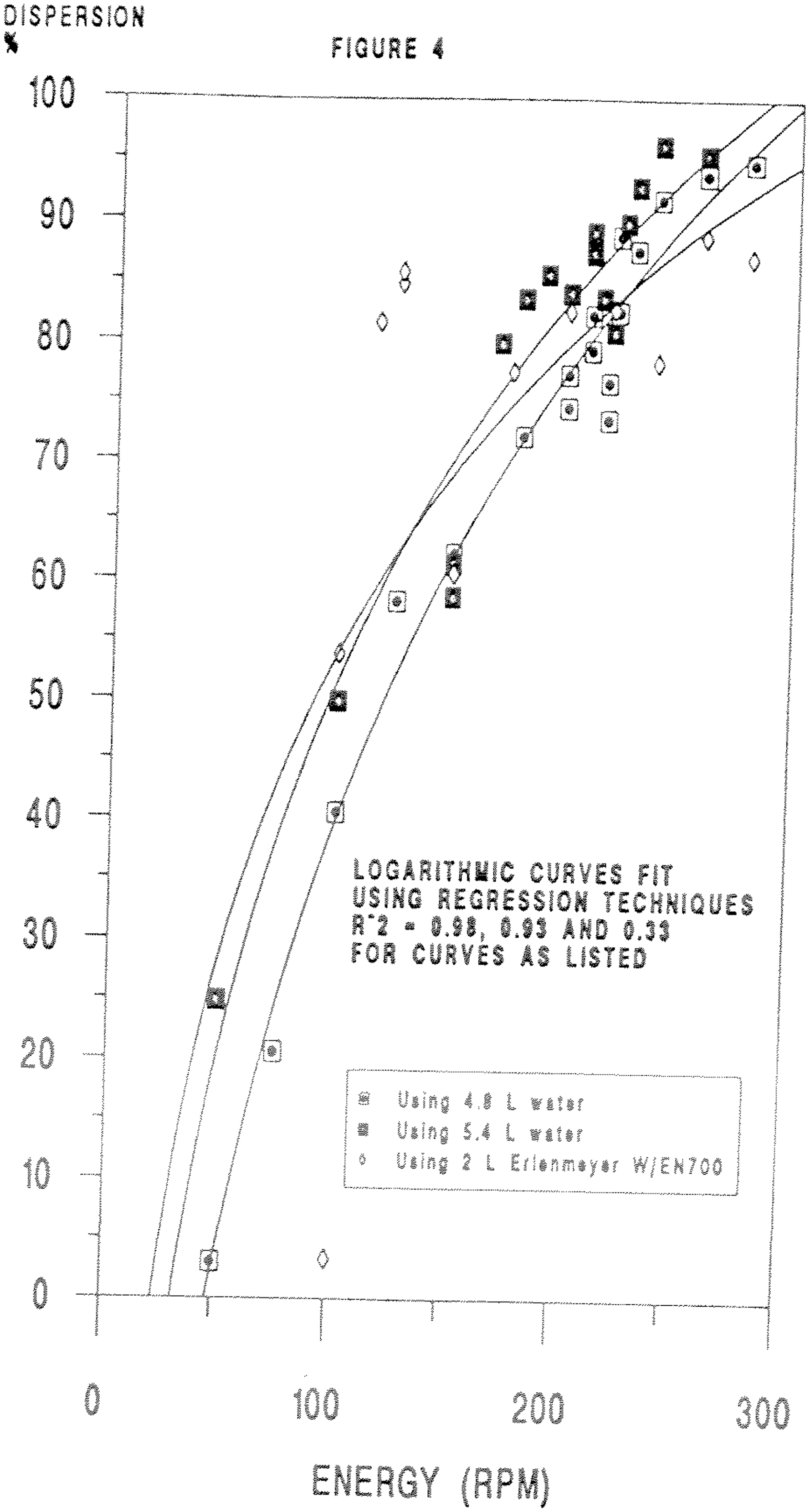
DISPERSION IN THE ROUND HIGH ENERGY APPARATUS

FIGURE 3



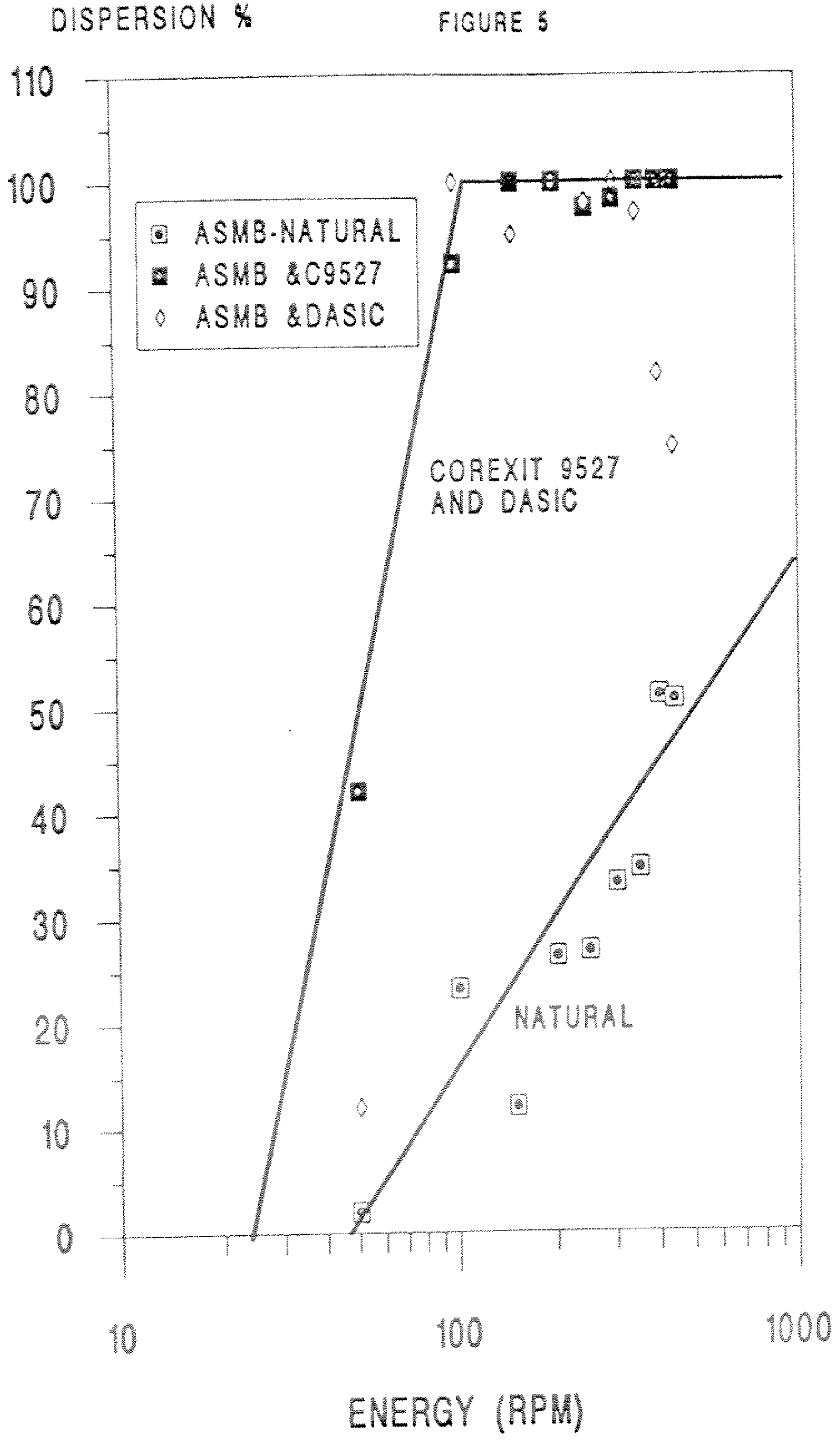
ENERGY RELATIONSHIP IN THE ROUND AND 2-L HIGH ENERGY APPARATUS

FIGURE 4



HIGH ENERGY DISPERSION OF ALBERTA SWEET MIXED BLEND

FIGURE 5



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 indispersable under normal conditions. Similar trends are seen in the data in Figure 6 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 7. 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 8. These results again show that dispersion rises rapidly in a linear fashion until complete dispersion is achieved.

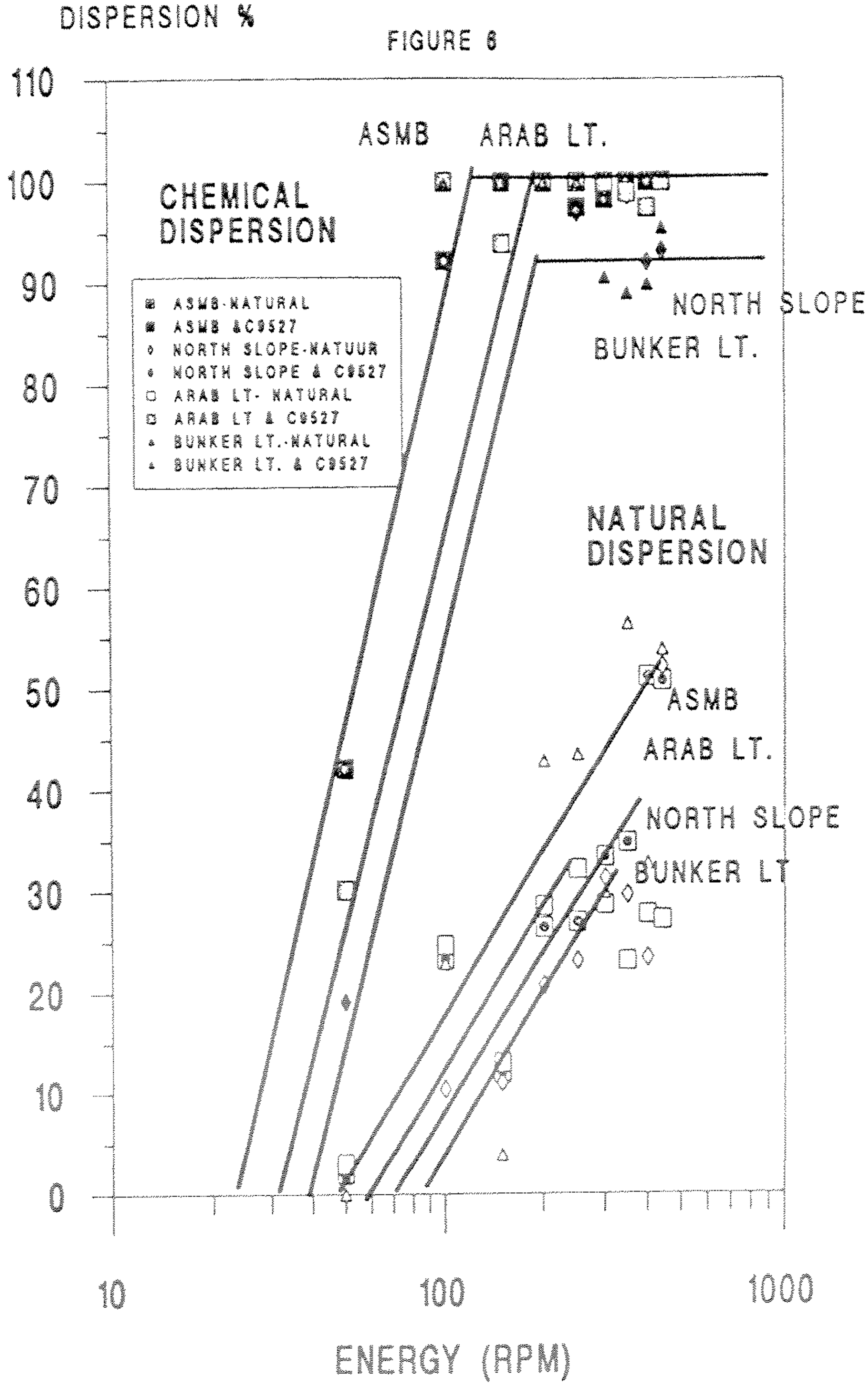
Curve fitting on the data from the square apparatus was done and is shown in Table 3. This shows that the best approach is the use of a combination of two linear curves. Similarly curve-fitting techniques were applied to the natural dispersion curves. These data as given in Table 4 and show that the best approach is a linear function.

SUMMARY AND CONCLUSIONS

The idealized relationships between energy and dispersion are shown in Figure 9, 10 and 11. Chemical dispersion increases with energy in a linear

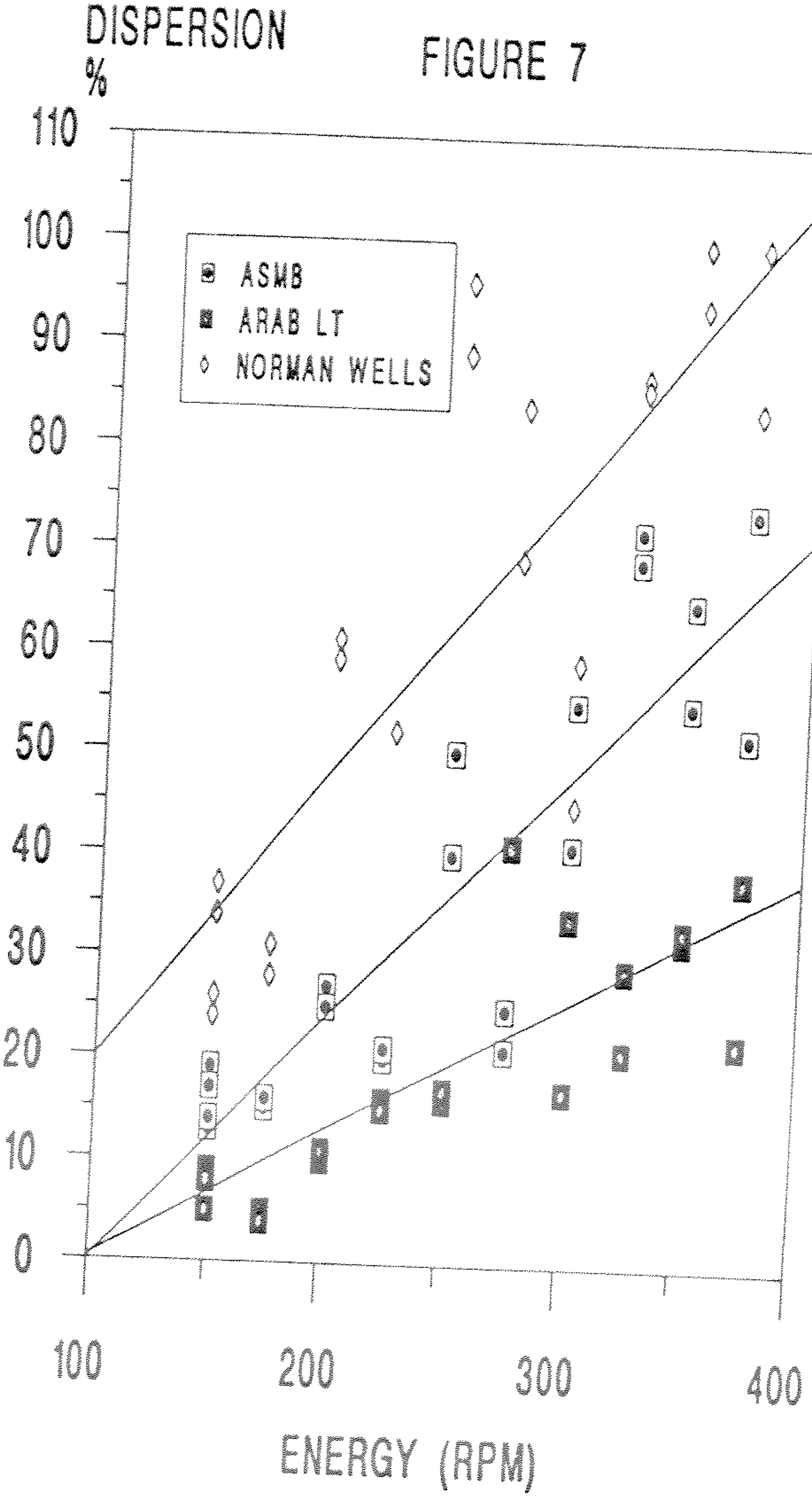
HIGH ENERGY DISPERSION OF FOUR OIL TYPES

FIGURE 6



CORRELATION OF ENERGY AND DISPERSION IN THE SWIRLING FLASK APPARATUS

FIGURE 7



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

FIGURE 8

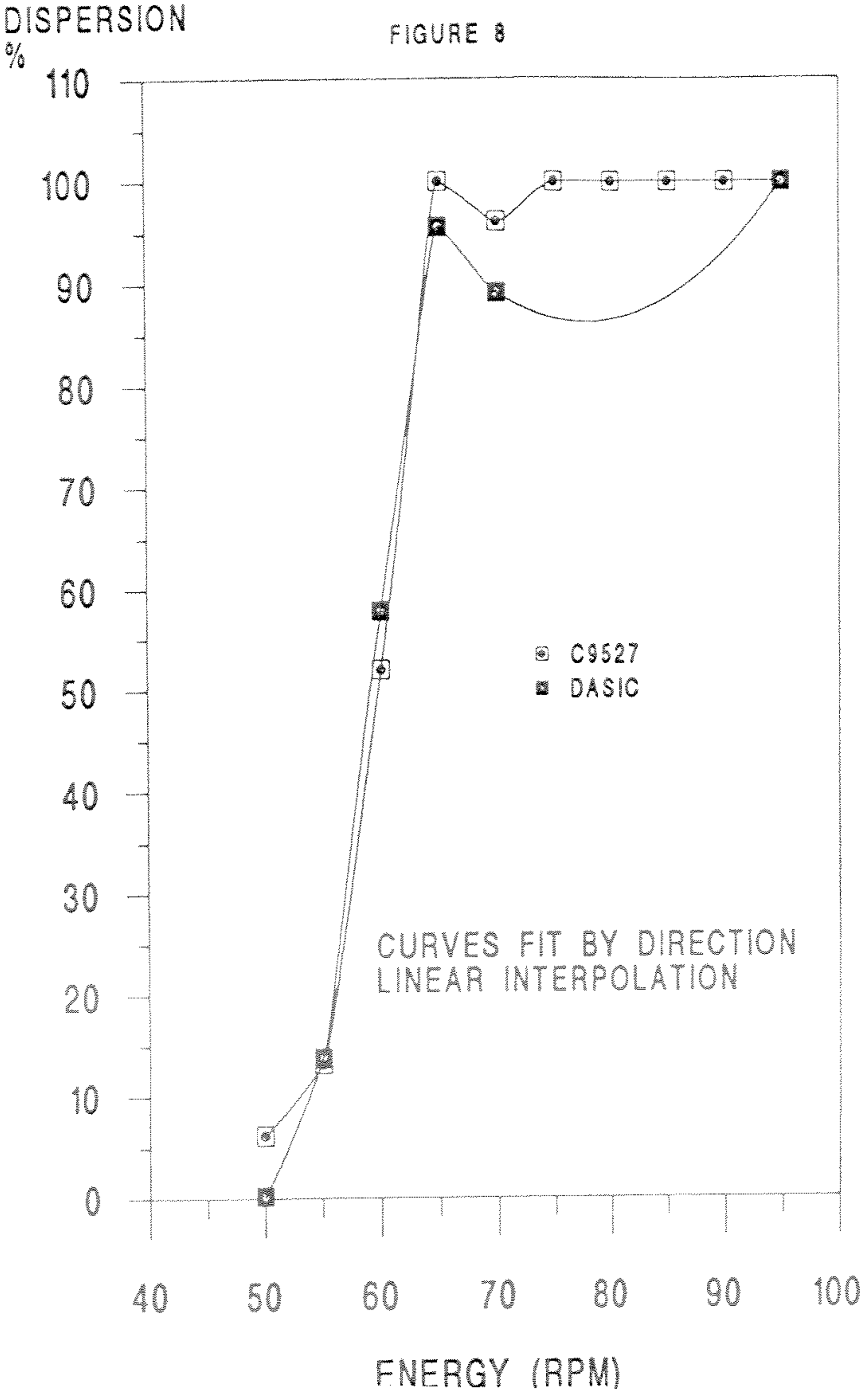


TABLE 2 CORRELATION MATRIX FOR THE HIGH ENERGY CURVE

CURVE TYPE	FORMULA	GOODNESS OF FIT (R*R) FOR OIL/DISPERSANT COMBINATION					
		ASMB C9527	ASMB DASIC	NORTH SLOPE C9527	ARAB LT. C9527	ARAB LT. DASIC	BUNKER C9527
EXPONENTIAL	Y = A + B EXP(X)	0.35	0.2	0.26	0.31	0.28	0.28
LOGARITHMIC	Y = A + B LOG(X)	0.64	0.32	0.47	0.56	0.44	0.49
3-ORDER POLY	Y = A + B X ....DXXX	0.91	0.82	0.84	0.84	0.84	0.84
4-ORDER POLY	Y = A + B X ....EXXXX	0.99	0.93	0.95	0.92	0.94	0.95
5-ORDER POLY	Y = A + B X ....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

		GOODNESS OF FIT = UNCORRECTED R^2
STEP - MULTI	A + BX/(1 + CXX) + D LOGX	*0.99*
LIN-LOG	Y = A + BX + C LOG(X)	*0.98*
INV-BINOMIAL	Y = AXX/1 + BX + CXXX	*0.94*
INV-LINEAR	Y = AX/1 + BX	*0.94*
LOG	Y = A + B LOG(X)	*0.94*
INV-LINEAR	Y = AX/B + CX	*0.94*
STEP - X/LOG	Y = A + BX/C LOG(X)	*0.88*
LINEAR, ALT	Y = A + B (C + X)	*0.88*
EXPON. MOD.	Y = A + B EXP(CX)	*0.88*
STEP - POLY	Y = AX/1 + BX + CXX	*0.88*
STEP - SQ/LOG	Y = A + B XX/C LOG(X)	*0.83*
STEP - LOG/SQ	Y = A + B(LOGX)/(CX + DXX	*0.78*

TABLE 3 CORRELATION MATRIX FOR NATURAL DISPERSION

CURVE TYPE	FORMULA	GOODNESS OF FIT (R^2) FOR OIL TYPE		
		ASMB	ARAB LIGHT	NORMAN WELLS
LINEAR	Y = A + BX	0.77	0.63	0.7
LOG	Y = A + B LOG(X)	0.73	0.65	0.73
EXPONENTIAL	Y = A + B EXP(X)	0.81	0.71	0.7

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 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 11. 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.[19] The EKOFISK BRAVO oil was observed to disperse naturally at sea states around Beaufort 5 or 6.[20] 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 mount of oil that a given volume of water can hold, and
4. increasing the dispersant droplet stability in the water column.

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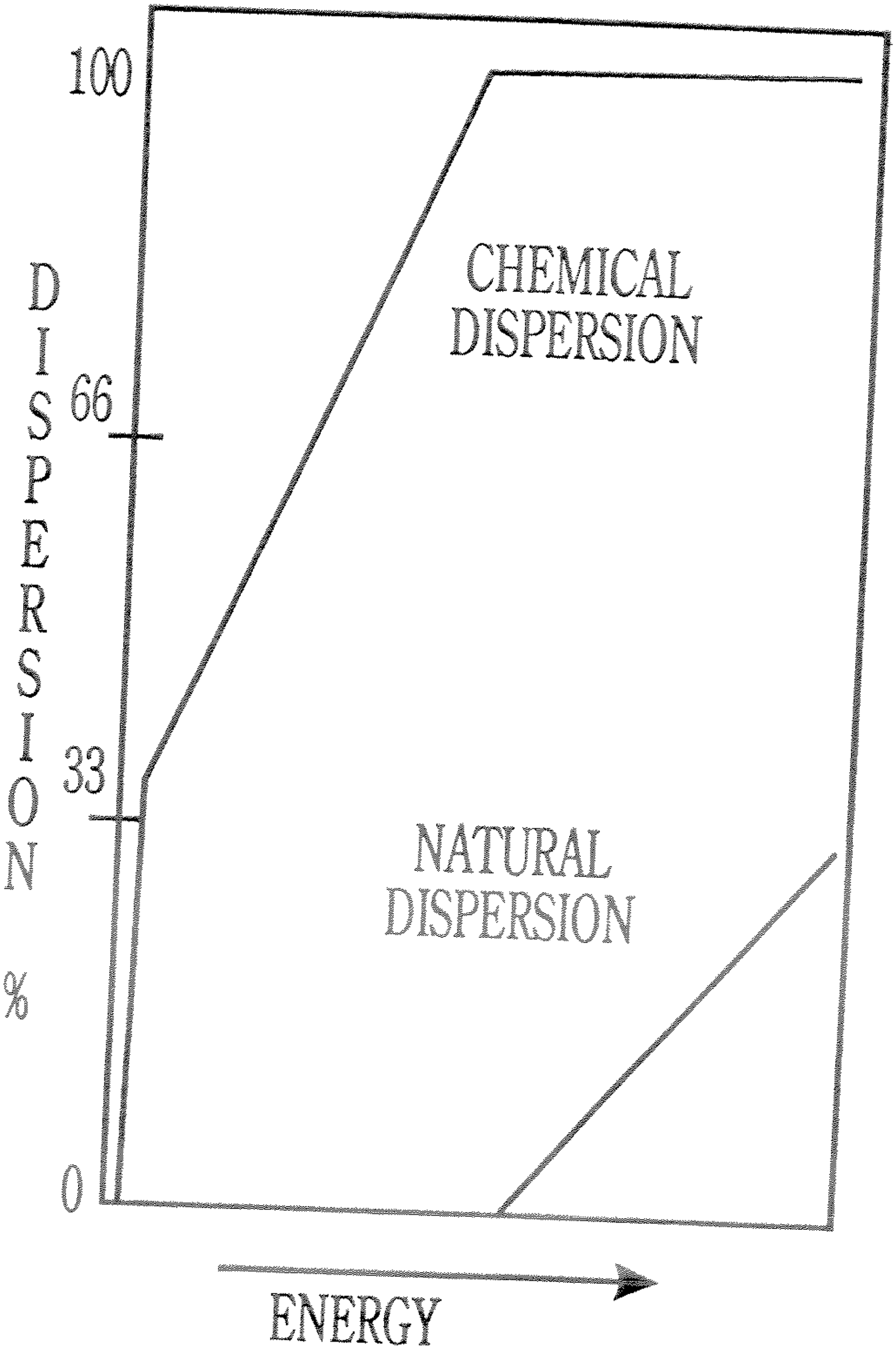
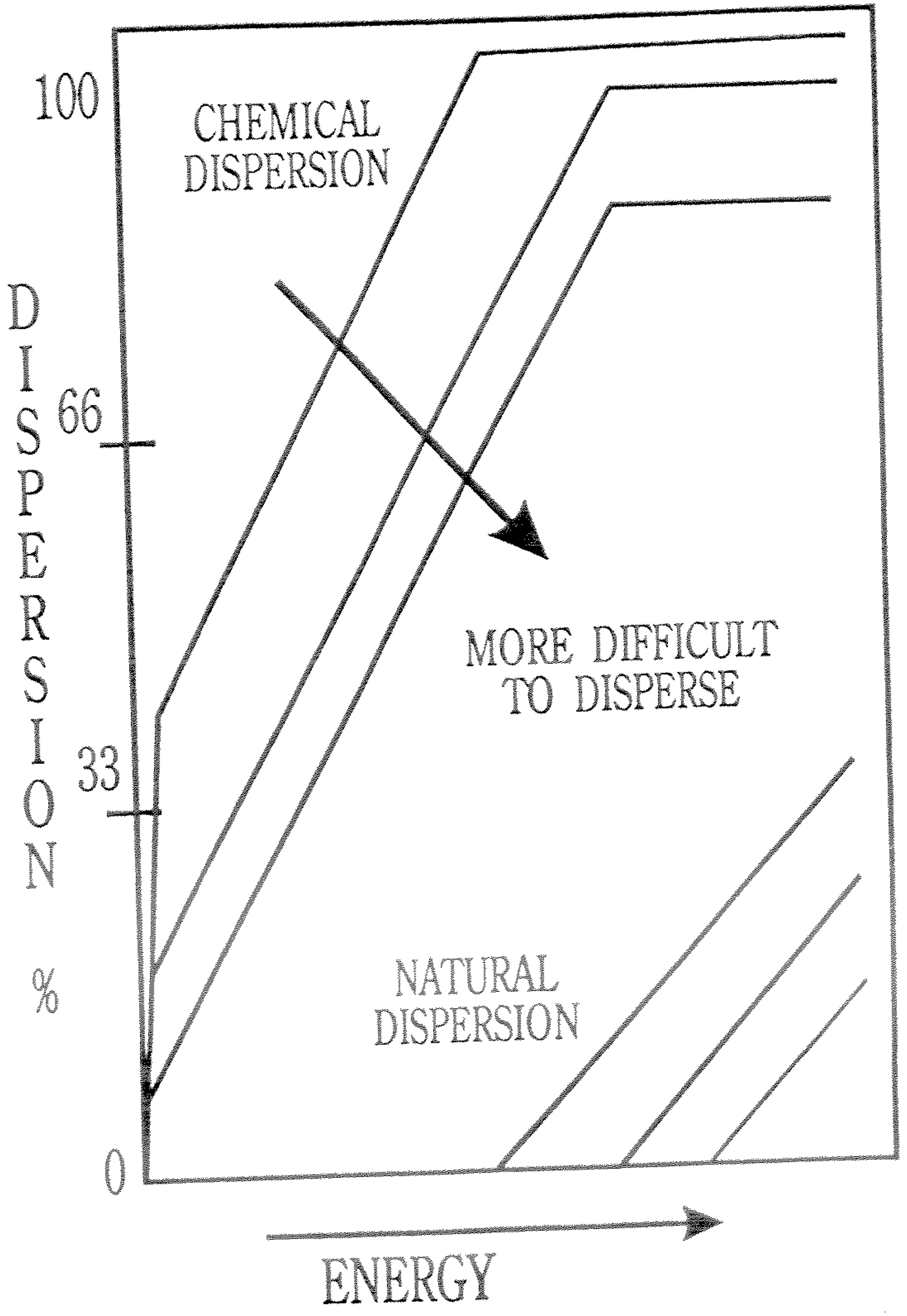
SCHEMATIC OF THE DISPERSION OF A TYPICAL LIGHT CRUDE OIL

FIGURE 9



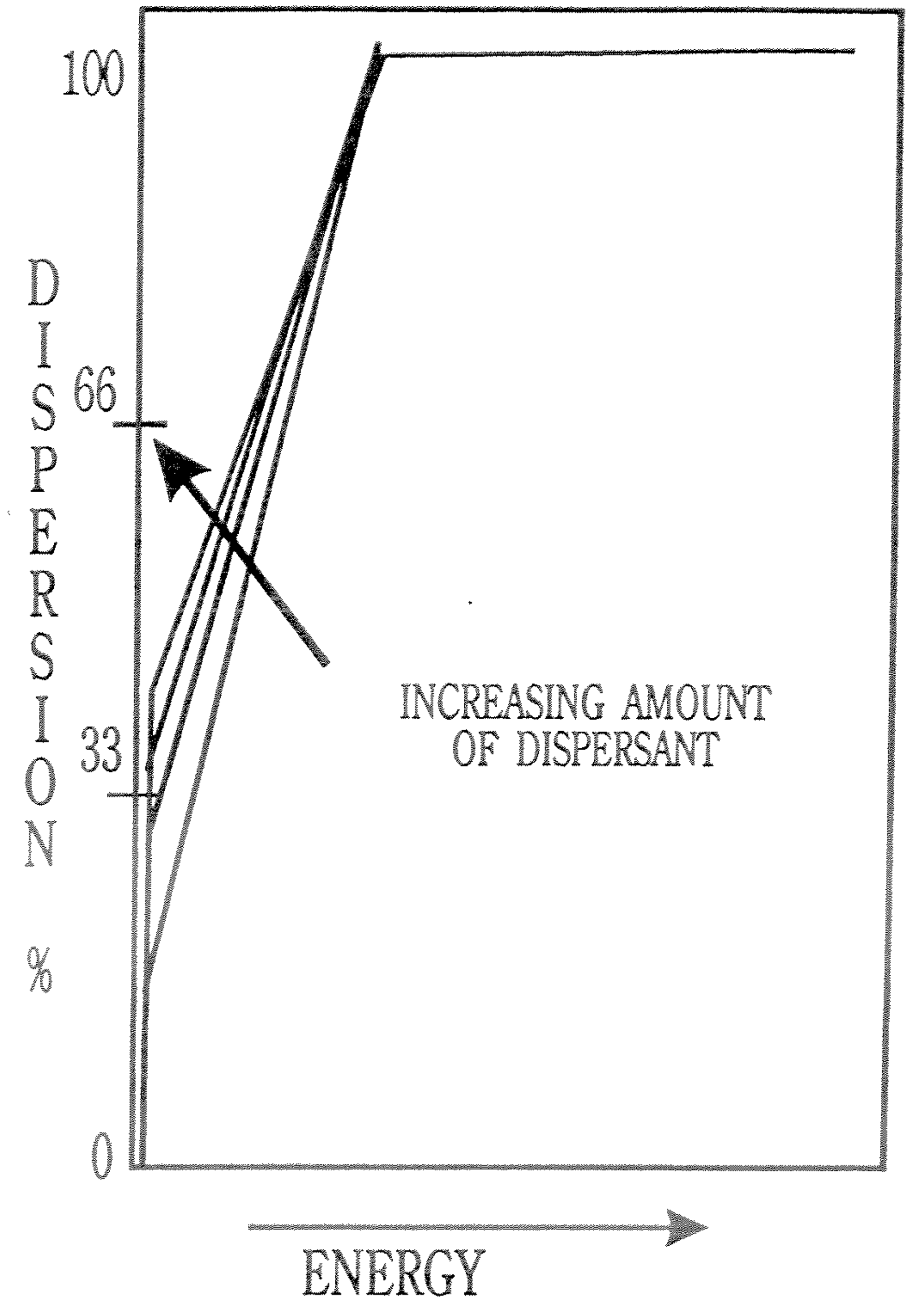
SCHEMATIC OF ENERGY RELATIONSHIP AND DISPERSION WITH DIFFERENT OILS

FIGURE 10



SCHEMATIC OF THE VARIATION OF DISPERSION WITH DISPERSANT AMOUNT

FIGURE 11



THE PHYSICAL-CHEMICAL PROPERTIES OF BITUMEN IN RELATION TO OIL SPILL RESPONSE

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ABSTRACT

Viscous bitumen from northeastern Alberta must be diluted with gas condensate before it can be transported by pipeline to export markets. If a spill of this material occurs, its properties will likely change rapidly as the light condensate evaporates. Laboratory measurements have been made of evaporation rates and the changes which occur in this mixture in viscosity, density, and flash point. The predictions of two fate-of-oil computer models which might be used by on-scene commanders, have been compared to the observed laboratory measurements. The results of the laboratory and computer studies will help spill responders to determine the strategies and equipment needed to combat a spill of this material.

INTRODUCTION

Bitumen or Heavy Oil is produced from the Athabasca Tar Sands of northeastern Alberta at several large extraction plants. While much of the produced bitumen is subsequently upgraded to a synthetic crude oil at on-site facilities, a substantial amount is transported 'as is' by pipeline throughout Canada and to export markets. At its Cold Lake extraction plant, Esso Resources produces about 15000 m^3 of bitumen per day. The bitumen is very viscous and must be transported either at elevated temperatures (as is done around the plant site) or mixed with a suitable miscible liquid to lower its viscosity. Before transport from Cold Lake, the bitumen is mixed with a gas condensate to form a product called Dilbit with properties somewhat like those of a medium gravity oil. Dilbit is moved to Edmonton through the Alberta Energy Company pipeline and from there to a number of export points (including the western U.S., Chicago, and Vancouver). About 950,000 m^3 of dilbit per year is transported from Edmonton to Vancouver through the Trans Mountain Pipeline system for export.

Dilbit is a unique material containing both the remaining heavy ends of reservoired oil which has been water washed and biodegraded and a large light end component of gas condensate which has been added to facilitate pipelining. The exact mix of condensate and bitumen varies slightly from time to time because a number of gas condensate sources are used in the blending. The only specification on the Dilbit is that the summer Dilbit density be less than 927 kg/m^3 at 15°C and that the winter viscosity be less than 250 cSt at temperatures