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STUDIES ON THE PHYSICAL AND CHEMICAL BEHAVIOUR OF OIL AND DISPERSANT MIXTURES

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ABSTRACT

Laboratory studies on dispersant effectiveness have been conducted to assess the effect of several variables and to determine the action mechanisms of dispersants. The variables examined were temperature, salinity, and dispersant quantity. Dispersant effectiveness was measured and correlated with the five oil bulk components, asphaltenes, aromatics, polar compounds, saturate compounds and waxes.

The effect of water temperature variation is logarithmically correlated to dispersant effectiveness. The effect of salinity on typical commercial dispersant formulations is that effectiveness is at a peak when salinity is about 40 ‰ (parts per thousand) and falls to nearly zero as salinity decreases to 0. Effectiveness also falls to 0 as salinity rises from 40 to 80 ‰. This behaviour is explained by the necessity for a certain level of ionic strength to stabilize the surfactant between the oil droplet and the water. Dispersant quantity is found to be an important factor. Dispersant-to-oil ratios greater than 1:40 to 1:60 result in very low dispersant effectiveness. Effectiveness is logarithmic with respect to dispersant-to-oil ratio.

Dispersion experiments were conducted to investigate the effect of oil composition. Dispersant effectiveness is positively and strongly correlated with the saturate concentration in the oil and is negatively correlated with aromatic, asphaltene and polar compound contents of the oil. Dispersant effectiveness is only weakly correlated with oil viscosity. Dispersant effectiveness is primarily limited by oil composition.

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INTRODUCTION

Dispersants continue to be a lively topic of discussion twenty years after the TORREY CANYON incident. There is still no undisputed documentation on large-scale use or experiments showing the effectiveness of dispersants or the lack thereof (Fingas, 1988; Fingas 1989d). The current focus on dispersants is now more on effectiveness and mechanisms of action than on the toxicity which was the primary concern twenty years ago.

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 hydrophillic-lipophilic balance. 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 may be best suited to removing oil from solid surfaces such as shorelines, roads and parking lots.

Current dispersant formulations consist of a mixture of surfactants having an HLB approaching 10.0. Experiments have shown that this value is critical to performance. A large part of dispersant effectiveness revolves around HLB and the question of how individual surfactants in the mixture act and interact.

PREVIOUS MECHANISM STUDIES

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 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 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 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 revealed that all were naturally dispersable. 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 (Fingas et. al., 1989a).

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 on-going. 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 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 may be incorrect in open systems such as 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 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 (Fingas, Kolokowski and Tennyson, 1990). 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 (Becher 1977). 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 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 had no 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 (Fingas et. al, 1989b.). 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. 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 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 dispersable. 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 dispersable.

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.

EFFECT OF TEMPERATURE, 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 (Fingas et. al, 1989b). 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.

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. An exponential curve provides the best fit to the data. There is approximately a two-fold rise in effectiveness with a three-fold rise in temperature.

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. Results of this experiment are shown in Figure 2. 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. 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 3. 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 4. 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.

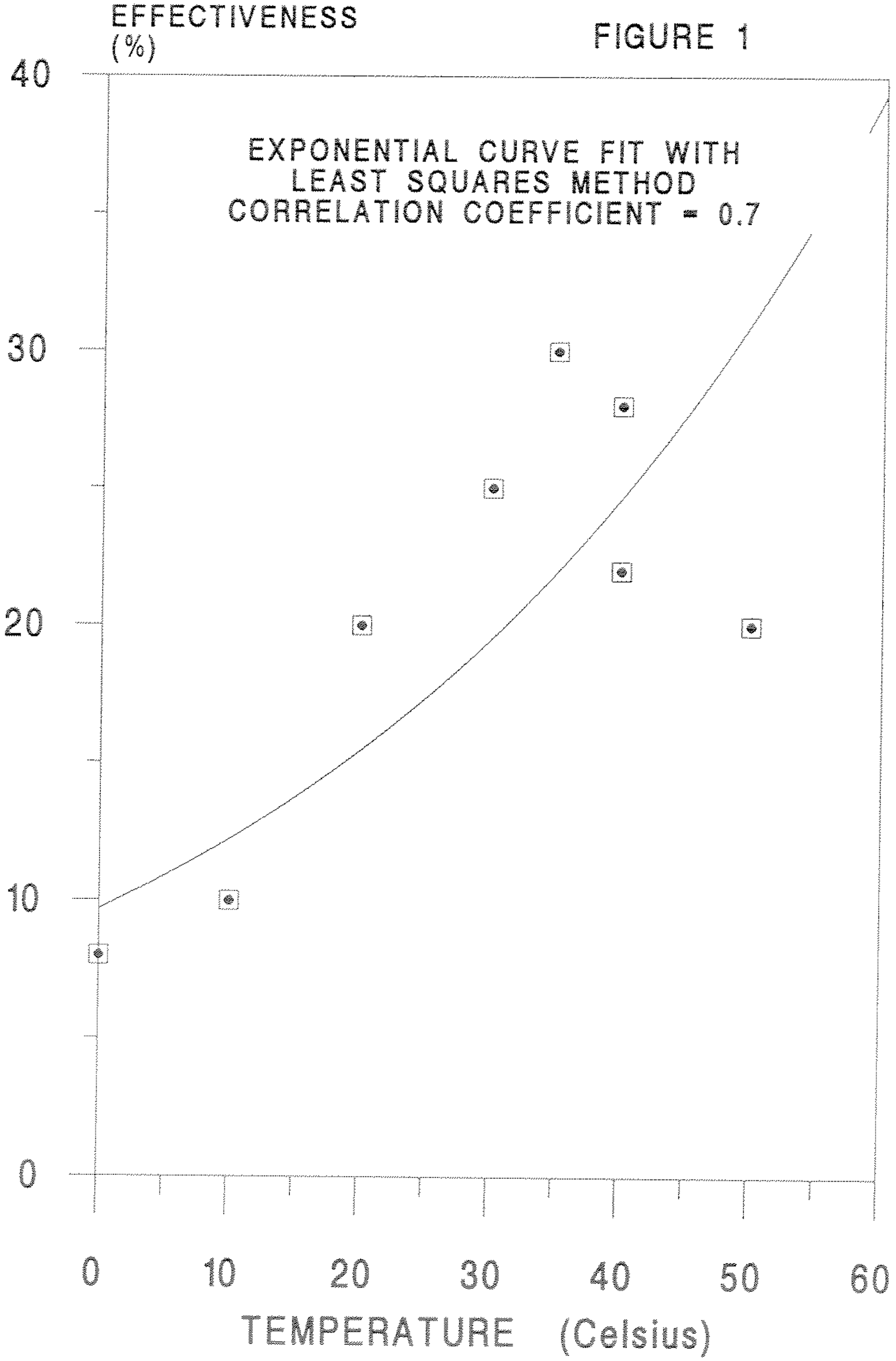
EFFECT OF OIL PROPERTIES ON DISPERSANT EFFECTIVENESS

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 (Lee et. al., 1981). 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 (Canevari, 1984).

Composition data were found for a number of oils for which dispersant effectiveness was measured (Bobra, 1989). 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 (Fingas

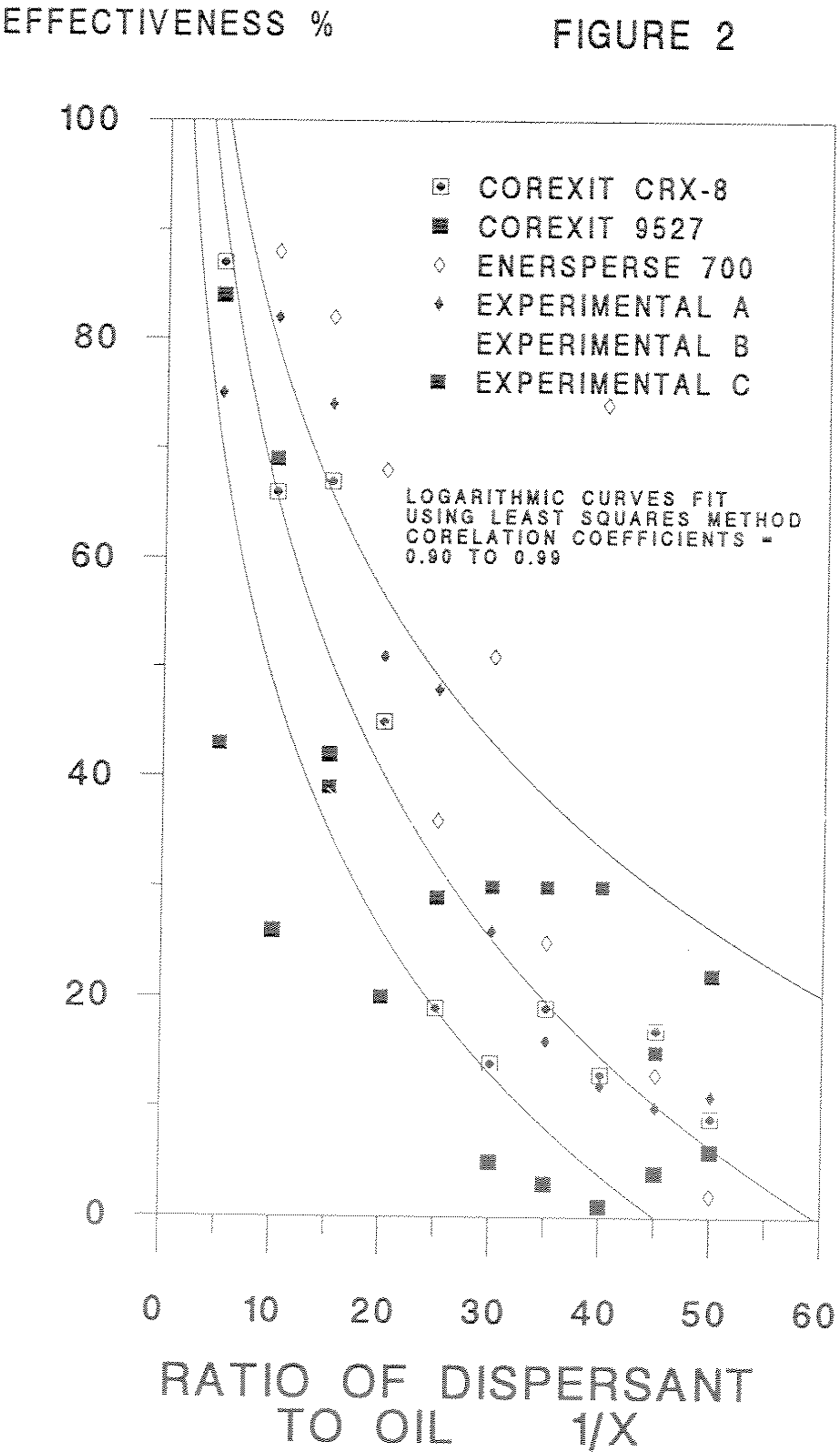
VARIATION OF EFFECTIVENESS WITH TEMPERATURE

FIGURE 1



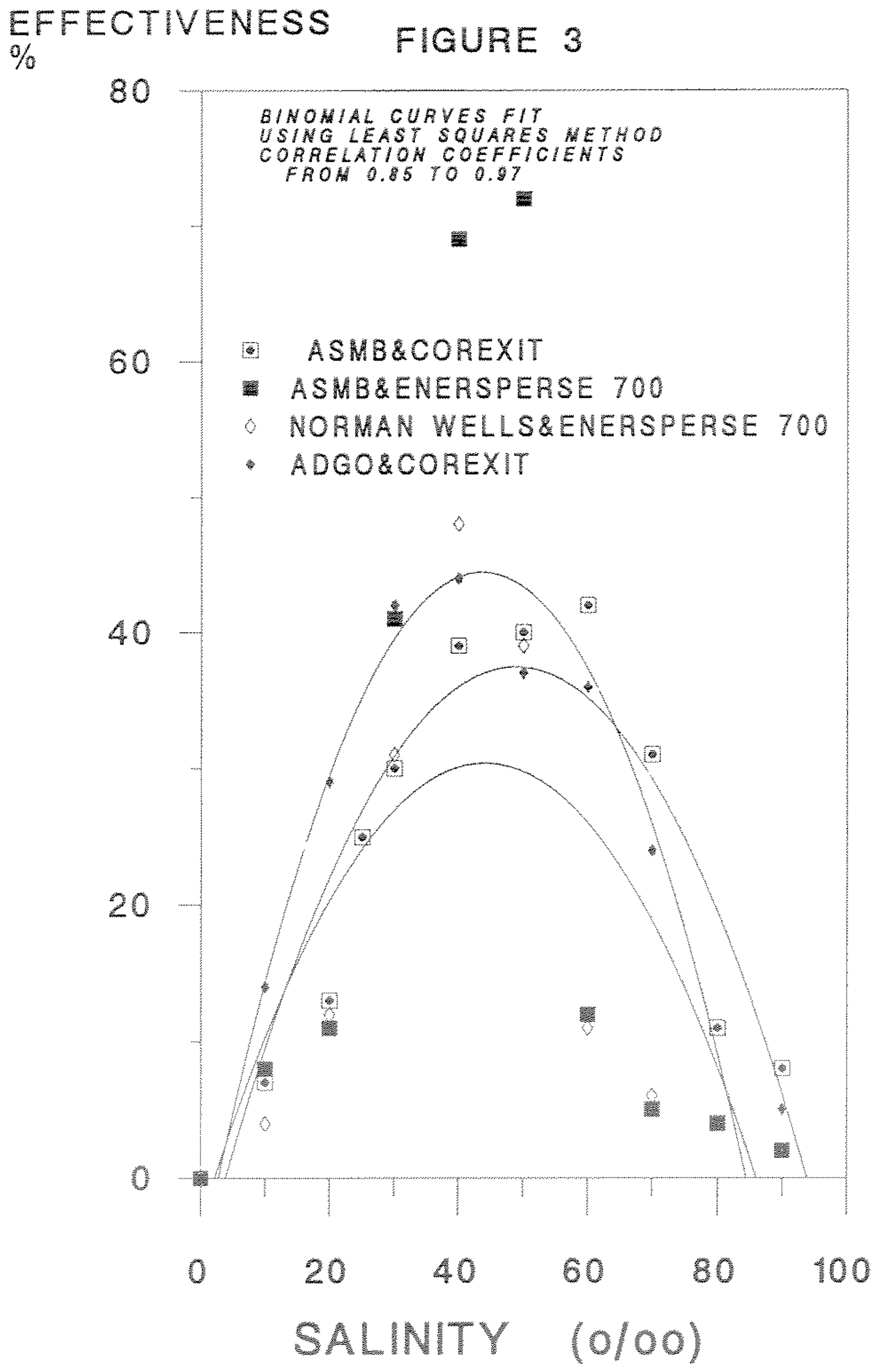
VARIATION OF EFFECTIVENESS WITH DISPERSANT QUANTITY

FIGURE 2



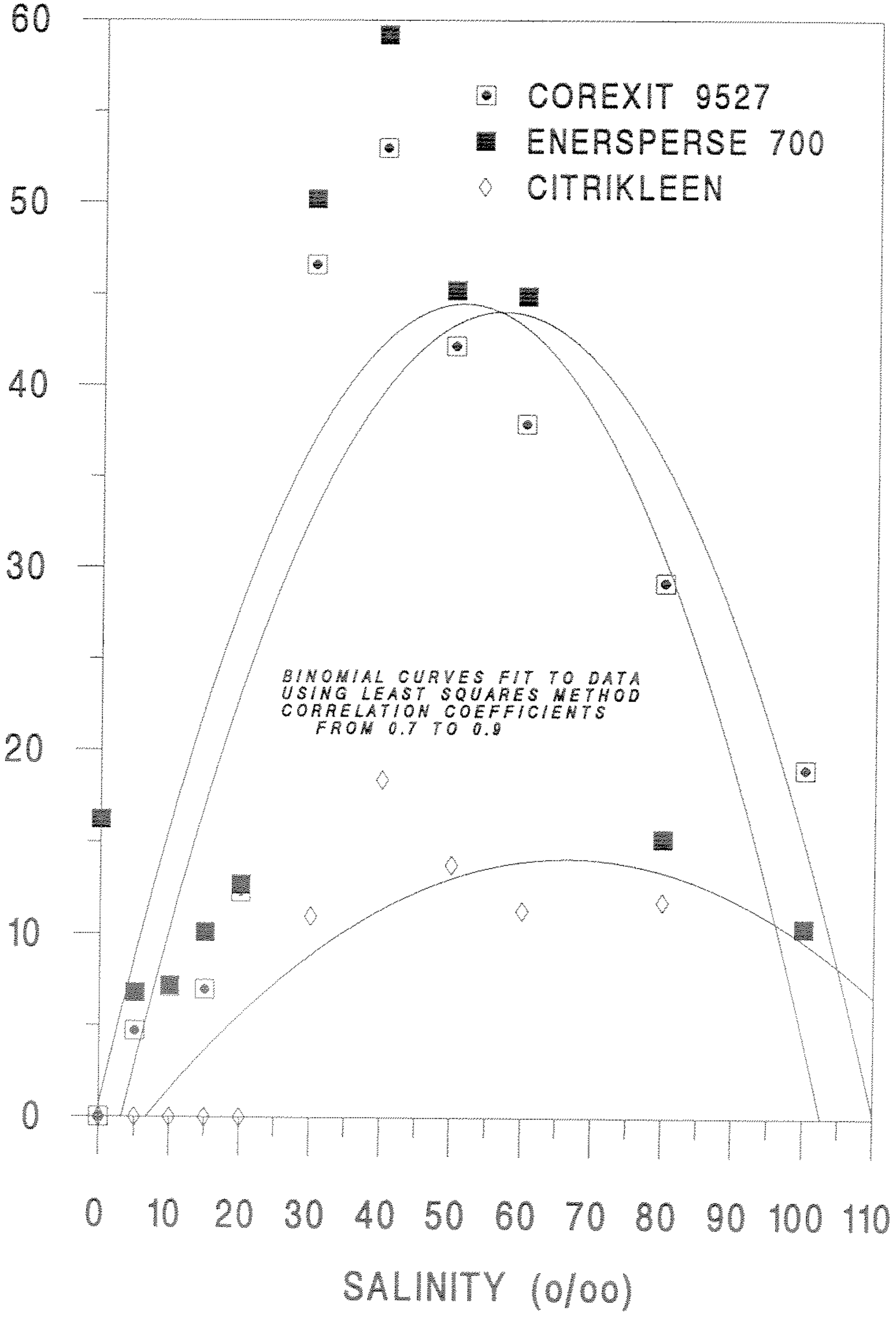
VARIATION OF EFFECTIVENESS WITH SALINITY

FIGURE 3



VARIATION OF EFFECTIVNESS WITH SALINITY

FIGURE 4



et. al., 1989c). These data are presented in Table 1. 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. The correlation coefficients between the oil properties and the dispersant effectiveness are shown in Table 2. 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. Dispersant effectiveness for the three dispersants used was averaged for Table 2. There is little differentiation found between data sets for the different 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 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 5 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 been seen by this figure and by Table 2, there is a strong correlation between dispersant effectiveness and saturate content. The greater the saturate content, the greater is the effectiveness. Table 2 also shows that effectiveness is strongly correlated with the other oil constituents except for wax content. Figure 6 shows the correlation of average dispersant effectiveness with aromatic content. Dispersant effectiveness goes down as oil aromatic content increases. Figure 7 illustrates the same effect with asphaltene content and Figure 8 the same with polar compound content. The correlation of effectiveness with wax content of the oil is not shown. As demonstrated by the correlation coefficient of 0.02, 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, as is illustrated by Figure 9 and the correlation coefficient of 0.04. 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 10. The correlation coefficient 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.

Table 2 shows 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.

TABLE 1

DISPERSANT EFFECTIVENESS AND OIL PROPERTIES

OIL	DISPERSANT EFFECTIVENESS			HYDROCARBON ANALYSES			ASPHALTENES	WAXES	VISCOSITY
	COREXIT	ENERSPERSE	DASIC	SATURATES	AROMATICS	POLARS			
	EFFECTIVENESS IN PERCENT			WEIGHT PERCENT OF TOTAL			WEIGHT %	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 LIGHT	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 J-34	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
CALIFORNIA API = 1	1	1	1	13.7	29.8	31.4	18.63	2.37	34000
CALIFORNIA API = 1	1	1	1	13.7	36.4	24.1	20.13	1.6	6400
COHASSET A-52	95			90	2		0.35	0.9	2
COLD LAKE HEAVY	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
NORMAN WELLS	36	51	26	85.1	11.1	1.6	1.15	1.25	6
PANUKE F-99	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
SOUTH 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
TRANSMOUNTAIN	20	28	27	81	13.6	1.9	3.23	1.39	12

TABLE 2

CORRELATION BETWEEN OIL PROPERTIES AND EFFECTIVENESS

	DISPERSANT EFFECTIVENESS	VISCOSITY	SATURATE CONTENT	AROMATIC CONTENT	POLAR CONTENT	ASPHALTENE CONTENT	WAX CONTENT
EFFECTIVENESS		-0.04	0.86	-0.66	-0.71	-0.68	-0.02
VISCOSITY	-0.04		-0.9	0.86	0.79	0.67	0.02
SATURATES	0.86	-0.9		-0.85 (lin)	-0.91 (lin)	-0.81 (lin)	-0.02
AROMATICS	-0.66	0.86	-0.85 (lin)		-0.71 (lin) -0.86	-0.57 (lin)	-0.01
POLARS	-0.71	0.79	-0.91 (lin)	-0.71 (lin) -0.86		-0.89 (lin)	-0.06
ASPHALTENES	-0.68	0.67	-0.81 (lin)	-0.57 (lin)	-0.89 (lin)		-0.01
WAXES	-0.02	0.02	-0.02 (lin)	-0.01 (lin)	-0.06	-0.01	

LEGEND: (lin) = LINEAR, A LINEAR EQUATION PROVIDED BEST FIT
ALL OTHERS ARE FIT USING AN EXPONENTIAL CURVE
- ALL VALUES ARE THE CORRELATION COEFFICIENT CALCULATED USING LEAST SQUARES METHODOLOGY

CORRELATION OF EFFECTIVENESS WITH SATURATE CONTENT

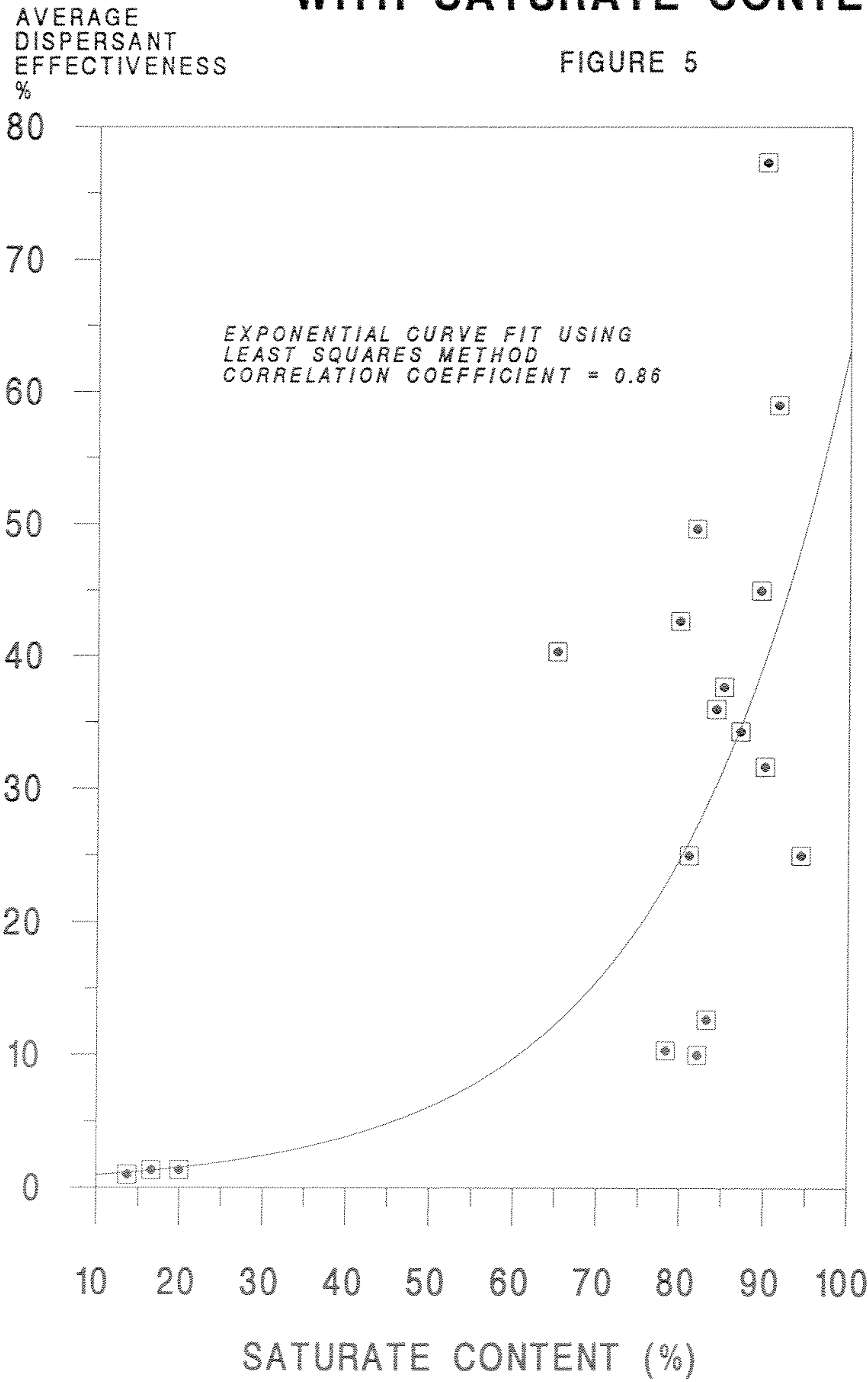
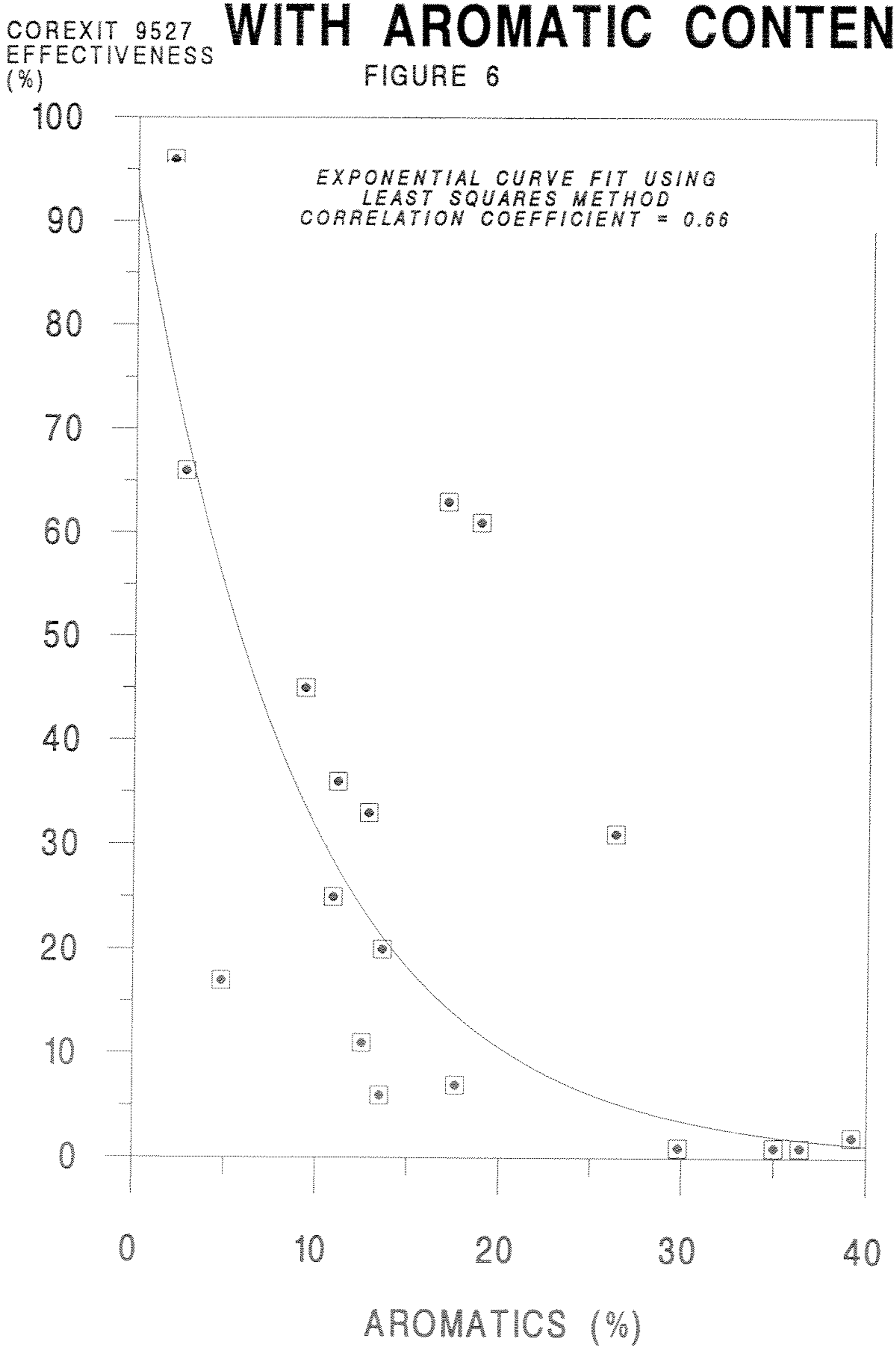


FIGURE 5

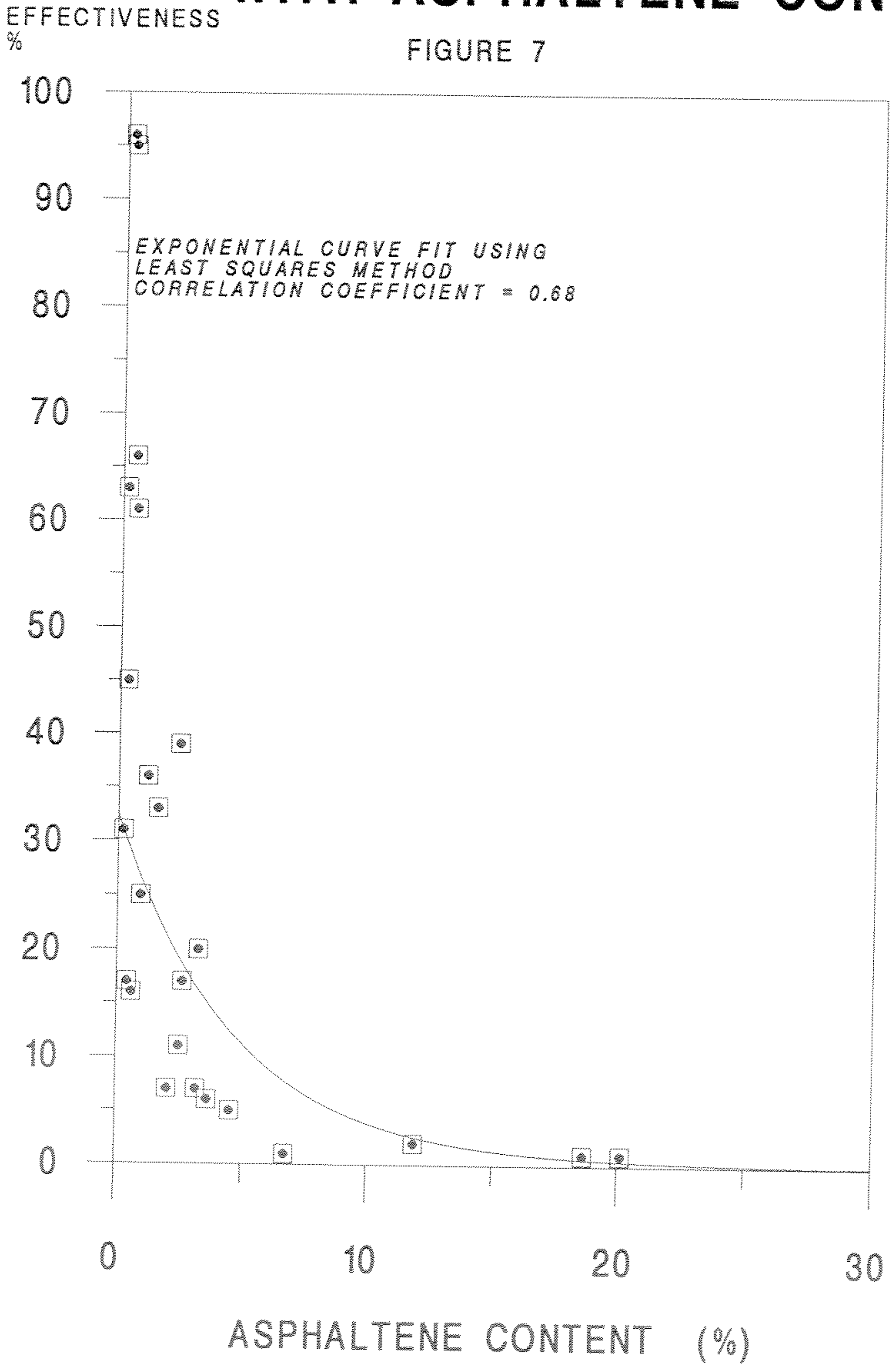
CORRELATION OF EFFECTIVENESS WITH AROMATIC CONTENT

FIGURE 6



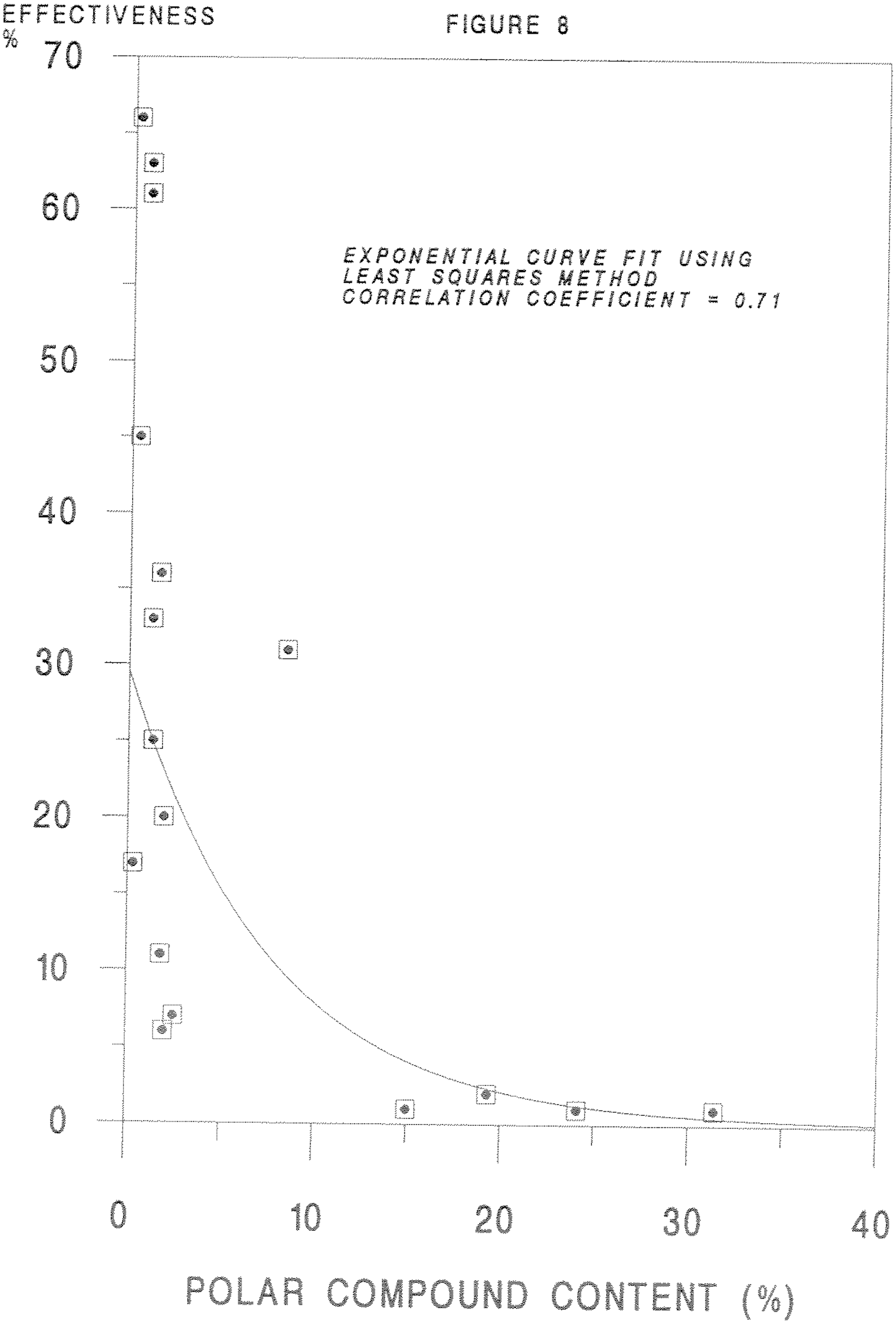
CORRELATION OF EFFECTIVENESS WITH ASPHALTENE CONTENT

FIGURE 7



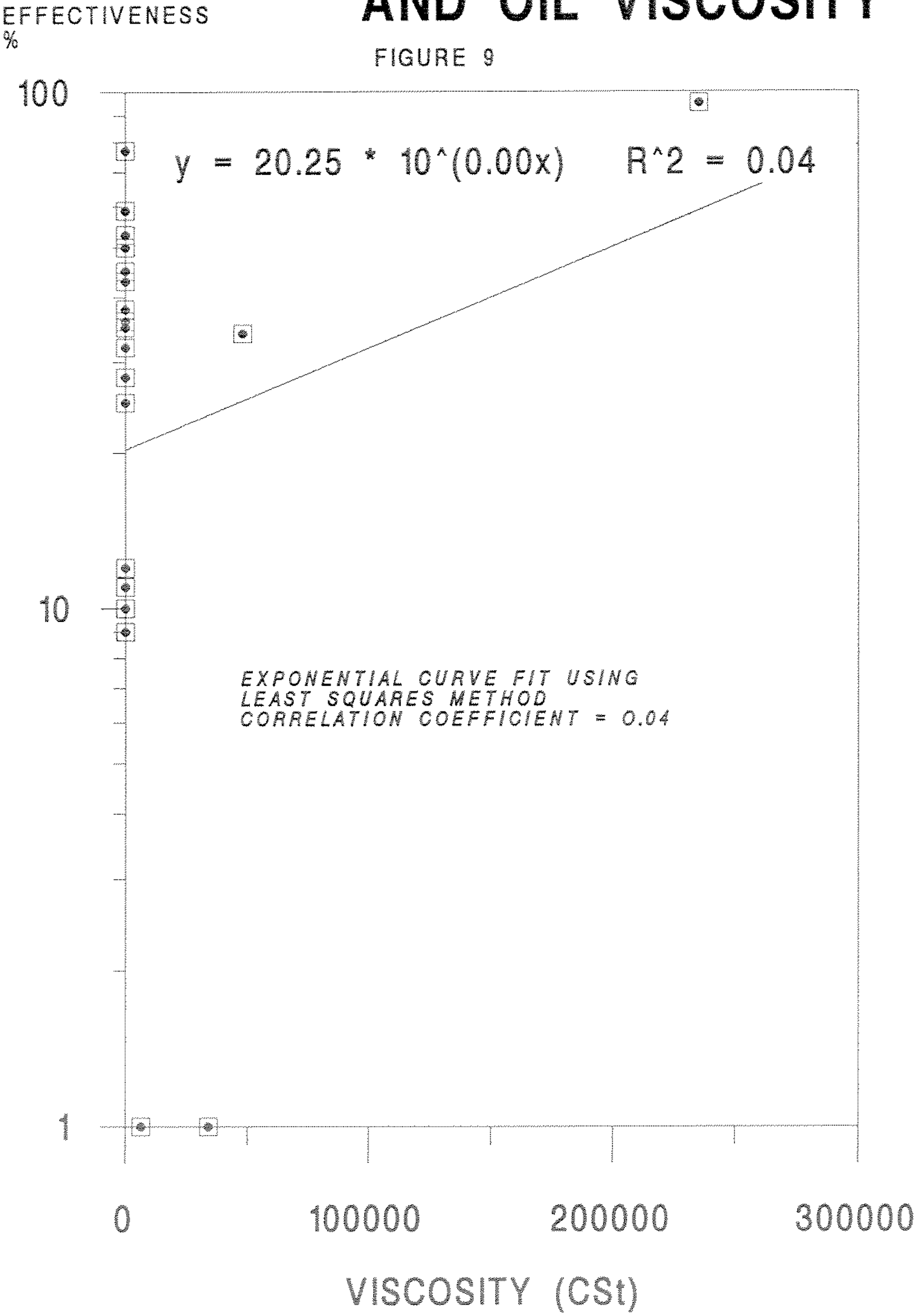
CORRELATION OF EFFECTIVENESS WITH POLAR COMPOUND CONTENT

FIGURE 8



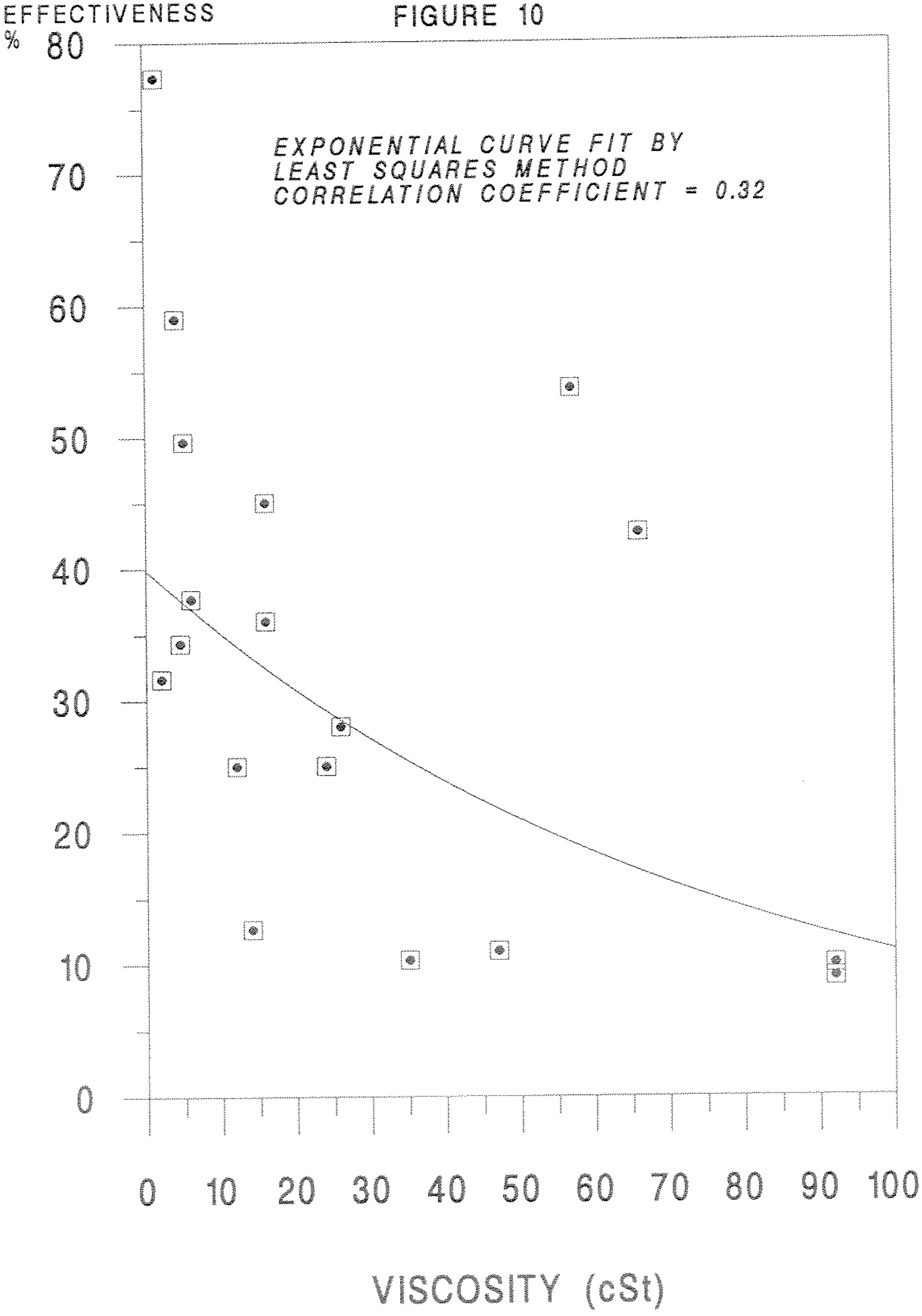
CORRELATION OF EFFECTIVENESS AND OIL VISCOSITY

FIGURE 9



CORRELATION OF EFFECTIVENESS AND VISCOSITY OF LIGHTER OILS

FIGURE 10



SUMMARY AND CONCLUSIONS

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

1. Dispersant effectiveness increases exponentially with temperature increase, a three-fold increase or decrease in temperature (taken in Celsius) will cause a two-fold change in dispersant effectiveness

2. 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,

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. 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.

5. 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.

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REFERENCES

Becher, Paul, 1977. Emulsions: Theory and Practice, Robert E. Krieger Publishing Company, Huntington, New York

Bobra, M.A., 1989, A Catalogue of Crude Oil and Oil Product Properties (1989 version), Environment Canada Manuscript Report EE-114, Ottawa, Ontario

Canevari, Gerard P., 1984. A Review of the Relationship Between the Characteristics of Spilled Oil and Dispersant Effectiveness, Oil Spill Chemical Dispersants: Research, Experience and Recommendations, STP 840, Tom E. Allen, Ed., American Society for Testing and Materials, philadelphia, pp. 87-93

Fingas, M., 1988, Dispersant Effectiveness at Sea: A Hypothesis to Explain Current Problems With Effectiveness, Proceedings of the Eleventh Annual AMOP Technical Seminar, Environment Canada, Ottawa, Ontario, p. 455-479

Fingas, Merv F., Debra L. Munn, Barton White, Robert G. Stoodley and Irene D. Crerar, 1989a. Laboratory Testing of Dispersant Effectiveness: The Importance of Oil-To-Water Ratio and Settling Time, Proceedings of the 1989 Oil Spill Conference, American Petroleum Institute, Washington, D.C., p. 365-373

Fingas, M.F., M. Di Fruscio, B. White and E. Tennyson, 1989b. Studies on the Mechanism of Dispersant Action: Weathering and Selection of Alkanes, Proceedings of The Twelfth Arctic and Marine Oil Spill Seminar, Environment Canada, Ottawa, Ontario, pp. 61-89

Fingas, M.F., V.M. Dufort, K.A. Hughes, M.A. Bobra and L.V. Duggan, 1989c, Laboratory Studies on Oil Spill Dispersants, Chemical Dispersants - Countermeasures For the 90's, M. Flaherty, Ed., ASTM 1084, American Society for Testing and Materials, Philadelphia, pp. 207-219, 1989.

Fingas, M.F., 1989d. Field Measurement of Effectiveness: Historical Review and Examination of Analytical Methods, Chemical Dispersants - Countermeasures For the 90's, M. Flaherty, Ed., ASTM 1084, American Society for Testing and Materials, Philadelphia, pp. 157-178

Fingas, Merv. F., Beata Kolokowski and E.J. Tennyson, 1990, Study of Oil Spill Dispersants - Effectiveness and Physical Studies, Proceedings of The Thirteenth Arctic and Marine Oil Spill Seminar, Environment Canada, Ottawa, Ontario, pp. 265-287

Lee, M.F., F. Martinelli, G. Lynch and P.R. Morris, 1981. The Use of Dispersants on Viscous Fuel Oils and Water-in-Crude-Oil Emulsions, Proceedings of the 1981 Oil Spill Conference, American Petroleum Institute, Washington, D.C., p. 31-35