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WATER-IN-OIL EMULSIFICATION: A PHYSICOCHEMICAL STUDY

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ABSTRACT

This paper summarizes the results of a study which examined the basic mechanism by which asphaltenes, resins, and waxes stabilize water-in-oil emulsions. Experiments were conducted on the emulsification behaviour of model oils which consisted of an alkane component, an aromatic component, and the emulsifying agents. Results from this study clearly demonstrate the importance that the physical state of an emulsifying agent has upon its ability to stabilize emulsions. It was found that to be effective emulsifiers, asphaltenes, resins and waxes must be in the form of finely divided, sub-micron particles. In addition, it was shown that the solvency strength of an oil, which is determined by its alkane and aromatic components, controls the solubility/precipitation behaviour of these high emulsifiers. The chemical composition of the oil determines not only the amount and size of precipitated particles, but also the composition and wetting properties of the particles. All these factors were shown to have an influence upon emulsification.

The application of a solubility model, using the Hildebrand-Scatchard equation, to predict the physicochemical conditions which favour water-in-oil emulsification, is discussed.

INTRODUCTION

It is well known that the emulsification of spilled oil into stable water-in-oil emulsions (chocolate mousse) has numerous detrimental effects upon clean-up operations. The increase in volume due to the incorporation of water means that the amount of polluted material that must be dealt with is multiplied several times. The viscous nature of mousse not only impedes the efficient operation of most mechanical recovery equipment, but it also results in a cohesive slick that resists dispersion, both natural and chemical. To a large extent, it is the rate at which

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spilled oil emulsifies that determines the effective window of opportunity for specific countermeasures.

Much has been learned from previous studies on petroleum emulsification (Bansbach, 1970; Berridge, Thew and Loriston-Clarke, 1968; Bridie, Wanders, Zegveld and Vander Heijde, 1980; Brown, Weiss and Goodman, 1990; Canevari, 1982; Desmaison, Piekarski and Desmarquest, 1984; Eley, Hey and Symonds, 1988; Eley, Hey, Symonds and Willison, 1976; Graham, 1988; Haegh and Ellingsen, 1977; Jacob and Mackay, 1977; Jones, Neustadter and Whittingham, 1978; Lamathe, 1982; Little, 1981; Mackay, 1987; Mackay and Zagorski, 1982; Mackay, McLean, Betancourt and Johnson, 1973; Payne and Phillips, 1985; Thingstad and Penerud, 1983; Thompson, Taylor and Graham, 1985; Walters and Fennell, 1976) but it still remains a phenomenon that is poorly understood. Although most crude oils can be emulsified, not all spills result in the formation of stable mousse. Whether an oil will form mousse or not, and if so, at what rate, depends upon an array of different factors including the properties of the oil and the prevailing environmental conditions. The formation of mousse is the result of a complex series of processes. A better understanding of the emulsification process is desirable in order to better predict the emulsification behaviour of oil spills, and thus utilize the most appropriate countermeasures available.

The aim of this work was to elucidate the role that physico-chemical factors play in determining an oil's susceptibility to emulsify. This was done by studying the emulsification behaviour of oils of known composition to examine the importance of oil chemistry in the emulsification process.

THEORY

It has long been recognized that indigenous petroleum emulsifying agents are concentrated in the higher boiling fractions (boiling point > 370°C) and particularly in the residuum (Lawrence and Killner, 1948). It is generally accepted that asphaltenes, resins and waxes play key roles in the emulsion process but specific mechanisms have not been clearly established (Bridie, Wanders, Zegveld and Vander Heijde, 1980; Canevari, 1982; Mackay, 1987). These compounds are believed to be the main constituents of the interfacial films which encapsulate the water droplets contained in mousse. These films have been shown to have high mechanical strength and thus act as effective physical barriers which prevent droplet coalescence (Blair, 1960; Canevari, 1982; Eley, Hey and Lee, 1987; Hasiba and Jessen, 1967; Jones, Neustadter and Whittingham, 1978). This in turn gives rise to the stable nature of mousse.

The main constituents of any oil can be grouped into four broad classes of compounds. These are alkanes (also called saturates or aliphatics), aromatics, resins; and asphaltenes. The lower molecular weight compounds in petroleum are generally alkanes and aromatics, while the resins, asphaltenes, and waxes (which are high molecular weight alkanes) account for the higher molecular weight compounds. In a complex mixture like petroleum, all these compounds interact in such a way that all components are maintained in the liquid oil phase. In other words, the lighter components of the oil act as solvents for the higher molecular weight compounds. As long as this solvency interaction is maintained in the oil and thermodynamic conditions remain constant, the oil will remain stable. Should this equilibrium state be changed, a point will be reached where the solvency strength of the oil is insufficient to maintain the heavy components in solution and as a result, they will precipitate out as solid particles. This is a frequent and problematic occurrence seen during petroleum production, transportation, and storage (Griffith and Siegmund, 1985; Kawanaka, Leontaritis, Park and Mansoori, 1989; Majeed, Bringedal and Overa, 1990; Mochida, Sakanishi and Fujitsu, 1986).

The precipitation of asphaltenes and waxes from oil has been modelled by several researchers (Griffith and Siegmund, 1985; Kawanaka, Leontaritis, Park and Mansoori, 1989; Majeed, Bringedal and Overa, 1990) using the basic solubility theory as described by the Hildebrand-Scatchard equation (Barton, 1983). In this case, oil is viewed as being comprised of a solute and a solvent. If one uses the solubility/precipitation behaviour of asphaltenes, the solute consists of the asphaltenes and the solvent consists of the remaining compounds in the oil. The solubility behaviour of asphaltenes in petroleum is:

$$RT \ \ln (A_a / X_a) = \frac{M_a \phi_s^2}{p_a} (\delta_a - \delta_s)^2$$

where:

A_a = activity coefficient of asphaltenes
X_a = mole fraction of asphaltenes
M_a = molecular weight of asphaltenes
ϕ_s = volume fraction of solvent
δ_a = Hildebrand solubility parameter of the asphaltenes

δ_s = Hildebrand solubility parameter of the solvent
p_a = density of asphaltenes
R = gas constant
T = temperature

Note to editor: Reads as "R, T, LN of {A subscript a divided by X subscript a} equals {M subscript a, phi subscript a squared, divided by rho subscript s} times {delta subscript a minus delta subscript s} squared".

With the assumption that asphaltenes are a homogeneous material and that $A_a = 1$, the above equation can be re-written in terms of the maximum amount of asphaltenes soluble in the oil, X_a.

$$\ln X_a = \frac{-M_a \phi_s^2 (\delta_a - \delta_s)^2}{p_a RT}$$

Note to editor: Reads as "LN of {X subscript a} equals negative {M subscript a, phi subscript s squared, divided by rho subscript a, R, T} times {delta subscript a minus delta subscript s} squared".

If the amount of asphaltenes present in the oil exceeds X_a, the excess asphaltenes will precipitate.

The role of solid particles in petroleum emulsification has been recognized for some time (Van der Waarden 1958), however the importance of this mechanism to mousse formation has not been completely appreciated. Examination of crude oil mousse using an electron microscope, clearly showed particles in the interfacial film surrounding water droplets (Eley, Hey, Symonds and Willison, 1976). Thompson et al. (Thompson, Taylor and Graham, 1985) showed that wax particles and associated solids exert considerable influence upon the emulsion stability of a waxy North Sea crude. They found that removing the indigenous particles from this oil inhibited the oil's tendency to form stable emulsions. Similarly, Eley et al. (Eley, Hey and Symonds, 1988) demonstrated that by varying the aromatic/aliphatic character of a synthetic oil containing asphaltenes, they could control the extent of emulsification.

For solids to act as emulsifying agents, the particles must possess certain properties. The particles must be very small relative to the droplet size of the emulsified phase. The particles must collect at the interface and they must be 'wetted' by both the oil and water phases. Figure 1 shows three ways that particles may distribute themselves between an oil-water interface. If the particle is preferentially wetted by the oil, the contact angle between the oil-water-solid boundary, Θ, is greater than 90° and a water-in-oil emulsion will form. If the particle is preferentially wetted by water, Θ is less than 90° and an oil-in-water emulsion will form. If the contact angle is much greater or lesser than 90°, the emulsion will be unstable. Stable emulsions form when the contact angle is near 90° (Becher, 1983; Canevari, 1982).

EXPERIMENTAL

Only a brief review of the methodology is given here, full details are given by Bobra (Bobra, 1990). Model oils were made up an alkane component, an aromatic component, and the potential emulsifying agent(s). Four different alkane components were tested: n-octane, n-tetradecane, a light paraffin oil, and a heavy paraffin oil (paraffin oils are refined, mixtures of alkanes). Aromatic components tested were p-xylene, phenyl octane, dimethyl naphthalene, and diphenyl methane. Asphaltenes, resins and waxes were used as emulsifying agents, either individually or in combinations. The asphaltenes and resins used were extracted from a California crude oil. The wax used was a commercial paraffin wax (melting point: 56-61°C).

Model oils were prepared by adding the emulsifying agent to the aromatic component. The mixture was vigorously shaken for one hour. The alkane component was then added and the mixture was again shaken for one hour. 30 mL of the oil was poured into a 500 mL Fleaker containing 300 mL of artificial seawater. The Fleaker was stoppered and allowed to stand for approximately 20 hours before being subjected to the emulsion formation and stability test (Bobra, 1989). This test involves rotating the Fleaker at 65 rpm for one hour and then allowing the mixture to remain static for one-half hour before measuring the size of the emulsion and the fraction of oil that emulsifies, F. The rotation/rest cycle is repeated three more times. An indication of an oil's tendency to emulsify is given by F_o, the fraction of oil that emulsifies when F is extrapolated to time zero. The stability of the emulsion is obtained by allowing the emulsion to stand for 24 hours and then measuring the fraction of oil that remains in the emulsion, F_{final}. The water content of stable emulsions was also measured. The following criteria set by Mackay and Zagorski (Mackay and Zagorski, 1982) classify emulsion behaviour:

F_o	Emulsion formation tendency
0 to 0.25	not likely
0.25 to 0.75	fairly likely
0.75 to 1	very likely

F_{final}	Emulsion stability
0 to 0.25	unstable
0.25 to 0.75	fairly stable
0.75 to 1	very stable

The yield point, which is a measure of the force that must be applied to a emulsion in order to induce liquid flow, was measured using a Haake RV20 Rotoviscometer equipped with a M5/SV1 sensor. The programmed shear rate was 0 to 100 (s^{-1}) in 10 minutes.

All experiments were conducted at 15°C.

RESULTS AND DISCUSSION

Asphaltenes as Emulsifying Agents

Figure 2 shows that the amount of asphaltenes precipitated out of the model oil is determined by the alkane and aromatic composition of the oil, which on the graph is expressed as percent alkane in the oil. The alkane component of this particular oil series is the heavy paraffin oil, the aromatic component is xylene, and the asphaltene concentration is 0.05 g/mL. When these oils are subjected to the emulsification test, differences in the tendency to form stable emulsions are clearly evident as seen in Figure 3. The emulsion formation tendency of the oil as a function of alkane content is presented in Figure 4. There is a strong tendency ($F_o = 1$) for this oil to emulsify when the alkane content is between 50 and 95%. As shown in Figure 5, these emulsions are very stable ($F_{Final} > 0.75$), and as shown in Figure 6, they have water contents between 50 and 90%. Yield point data are given in Figure 7. The results show that there is a maximum yield point value reached when the model oil contains 80% alkane/20% aromatic. Rheologically, this emulsion is the most stable emulsion formed for this series of model oil. It is at this point in the oil's composition that the asphaltene particles have the optimum size and contact angle with the interface to form emulsions. For the sake of comparison, two samples of mousse taken 18 days after the Exxon Valdez spill had yield points of 17 and 121 Pa under the same shear conditions.

The results illustrate several important points concerning the influence of the alkane/aromatic ratio upon an oil's emulsification behaviour. The amount of asphaltenes precipitated out of solution is determined by the alkane/aromatic ratio of the oil. Clearly, this is important in determining the emulsification of the oil. Results from experiments where different concentrations of asphaltenes were used, indicate that a minimum particulate concentration of about 0.03 g/mL must exist in the oil for stable emulsions to form. But it would also appear that the alkane/aromatic ratio controls other factors which are involved in emulsification. The size of the asphaltene particles is determined by the alkane/aromatic ratio and this is particularly true given the method by which these model oils were prepared. Asphaltenes were first dissolved in the appropriate quantity of xylene and then the paraffin oil was added, this causes the asphaltenes to precipitate out of solution. When the model oil is predominantly composed of alkane (i.e. 100% alkane), this precipitation mechanism does not occur, and the asphaltenes maintain their original dimensions which are aggregates of approximately one micron. These particles are too large to effectively stabilize water droplets.

Figure 8 shows that the addition of asphaltenes to the alkane/aromatic mixtures lowers the interfacial tension. However, an additional increase in the concentration of asphaltenes has no apparent effect on the interfacial tension. This illustrates that when particulates are the emulsifying agent, extreme lowering of interfacial tension is not required to form emulsions, as is the case with typical surfactants (Becher, 1983).

Effect of Changing Alkane and Aromatic Components

From the Hildebrand-Scatchard equation, it can be seen that the amount of asphaltenes soluble in oil, X_a, is controlled by the term $(\delta_a - \delta_s)^2$. As $(\delta_a - \delta_s)^2$ increases, the amount of asphaltenes soluble in oil decreases, and any excess asphaltenes precipitates. Therefore, the probability of producing a stable emulsion should correlate with the value of $(\delta_a - \delta_s)^2$. In Figure 9, F_{Final} values are plotted as a function of $(\delta_a - \delta_s)^2$ for eight model oils containing different alkane and aromatic components. It can be seen that stable emulsions only form when $(\delta_a - \delta_s)^2$ has a value of approximately 60 MPa or greater. Note that data on the graph does not include points where the model oils are 100% alkane. As previously mentioned, it is an artifact of the method used to prepare the oils that prevents these oils from forming emulsions.

Solubility parameters can either be measured experimentally or calculated using compositional data. For the model oils, the solvency strength is determined by the alkane and aromatic composition. For aromatic compounds, the value of the solubility parameter decreases as the molecular weight is increased along a homologous series. Therefore, asphaltenes will be less soluble in model oils as the solubility parameter of the aromatic component is decreased. Results from experiments where different aromatic solvents were used as the aromatic component for the model oil showed that as the solubility parameter of the aromatic solvent decreased, the oil would form stable emulsions over a larger range of alkane/aromatic ratios.

The effect of using different alkane solvents as the precipitation medium for asphaltenes has been studied by Long (Long, 1979), Speight and Moschopedis (Speight and Moschopedis, 1979). Their findings indicate that as the carbon number of the alkane solvent increases, the amount of asphaltenes which precipitate decreases, and that the composition of the precipitated material also changes. Higher alkane solvents were shown to yield asphaltenes which have a higher degree of aromaticity, a higher proportion of heteroatoms, a higher degree of polarity, and higher molecular weights. Results from this study indicate that the model oils have a stronger tendency to form stable emulsions as the molecular weight of the alkane component increases and if the component is a mixture of alkanes (i.e. the paraffin oils) rather than a single alkane solvent.

To date, no study has examined either the change in solvency or the precipitation of asphaltenes as a function of oil weathering. But undoubtedly the rapid loss of C_{10} and lighter hydrocarbons from oil within hours of a spill (McAuliffe, 1989) has a dramatic effect upon solvency and phase equilibrium. Results from this study indicate that the compositional changes which occur as a result of oil weathering, would strongly favour the precipitation of asphaltenes. It is speculated that spilled oil rapidly emulsifies into stable mousse once this precipitation is initiated. It is known that weathered oil has a greater tendency to form mousse than fresh oil, but this has largely been attributed to the physical changes which are induced by weathering. Indeed, weathering causes an increase in oil density and viscosity, and concentrates the indigenous emulsifiers in the remaining oil. All of these changes would enhance the formation of water-in-oil emulsions (Becher, 1983).

Resins as Emulsifying Agents

Figure 10 presents the emulsification behaviour for model oils where the emulsifying agents are: 1. asphaltenes; 2. resins; and 3. asphaltenes and resins together. The results show that resins alone can act as effective emulsifiers. The range of alkane/aromatic ratios over which stable emulsions are produced is smaller than for asphaltene-containing oils. When asphaltenes and resins are both present, the range over which stable emulsions are formed is larger than either resins or asphaltenes alone.

Waxes as Emulsifying Agents

Model oils containing only waxes as the emulsifying agent had no tendency to emulsify. Figure 11 shows the effect of adding 0.05 and 0.1 g/mL of wax to a model oil containing 0.01 g/mL of asphaltenes. The oil containing 0.01 g/mL of asphaltenes had no tendency to form stable emulsions but the addition of wax clearly increases the tendency of the oil to form stable emulsions at nearly all alkane/aromatic ratios. As the concentration of wax is increased, the oil has a greater tendency to produce stable emulsions.

Waxes are too hydrophobic to make sufficient contact with the interface to act as emulsifying agents by themselves. However, the waxes can interact with the asphaltenes in such a way that precipitated wax is able to stabilize the emulsion. It is estimated that when waxes constitute the majority of particles present in these oils, a minimum particulate concentration of around 0.06 g/mL must exist in the oil and that 0.01 g/mL of these particles must be asphaltenes.

CONCLUSIONS

The results from this study demonstrate the importance that the physical state of an emulsifying agent has upon its ability to stabilize emulsions. It was found that to be effective emulsifiers, asphaltenes, resins and waxes must be in the form of finely divided, sub-micron particles. The chemical composition of the oil determines not only the amount and size of these particles but also their composition and their wetting properties. All these factors were shown to have an influence upon the emulsification process.

Asphaltenes and resins, by themselves and in combination, were effective emulsifying agents. Model oils containing only wax as the emulsifying agent did not form stable emulsions. But the addition of a nominal amount of asphaltenes, an amount insufficient by itself to produce emulsions, to oils containing wax, lead to the formation of stable emulsions. This indicates that different emulsifying particulates can synergistically interact to stabilize emulsions.

The solubility/precipitation behaviour of asphaltenes in model oils follows the solubility theory as described by the Hildebrand-Scatchard equation. Therefore, it could potentially be adapted to model the precipitation behaviour of indigenous petroleum emulsifiers as spilled oil weathers, and thus be used to predict the physicochemical conditions in oil which favour mousse formation.

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CAPTIONS

FIGURE 1: Three ways solid particles may be distributed in an oil/water interface. The particle on the left is more wetted by the water than the oil thus being situated primarily in the aqueous phase, whereas the particle to the right exists primarily in the oil phase. The center situation illustrates a solid particles equally wetted by both the oil and water phase.

FIGURE 2: Percent of asphaltenes precipitated out of solution as a function of the alkane content of the oil.

FIGURE 3: Appearance of model oils after undergoing the emulsion test.

FIGURE 4: Emulsion formation tendency, F_o as a function of the alkane content of the oil. $F_o = 0$ means there is no tendency to emulsify, and $F_o = 1$ represents a strong tendency.

FIGURE 5: Emulsion stability, F_{Final} as a function of the alkane content of the oil. $F_{Final} = 0$ means emulsion completely broke after 24 hours. All oil remains emulsified if $F_{Final} = 1$.

FIGURE 6: Water content of stable emulsions formed versus % alkane in oil.

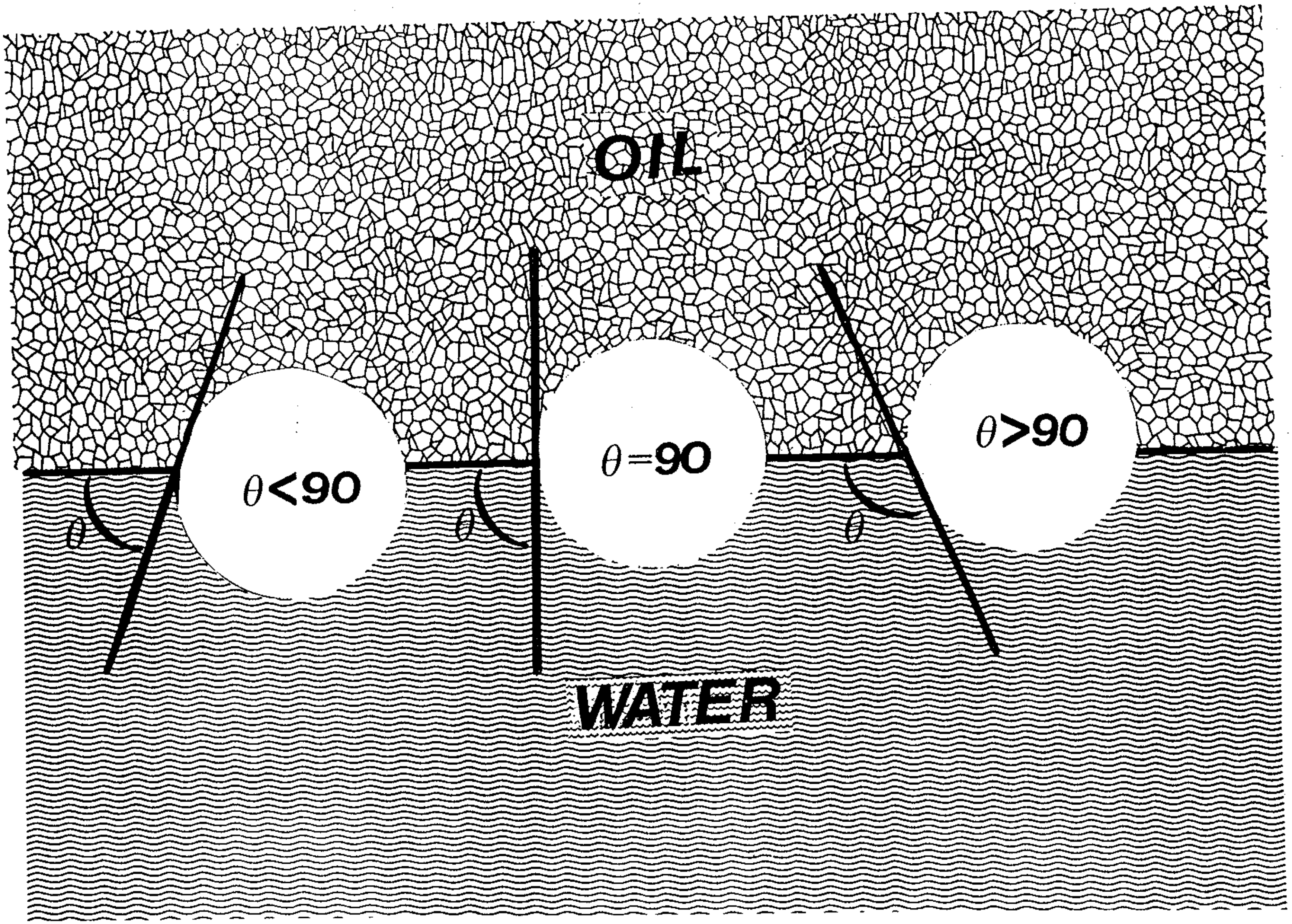
FIGURE 7: Yield point of stable emulsions versus % alkane in oil.

FIGURE 8: Effect of asphaltene concentration on oil/water interfacial tension.

FIGURE 9: F_{Final} as a function of $(\delta_a - \delta_s)^2$ for eight model oils containing different alkane and aromatic components.

FIGURE 10: Comparison of F_{Final} for oils containing resins and asphaltenes, individually and in combination.

FIGURE 11: Effect of adding wax to an asphaltene-containing model oil.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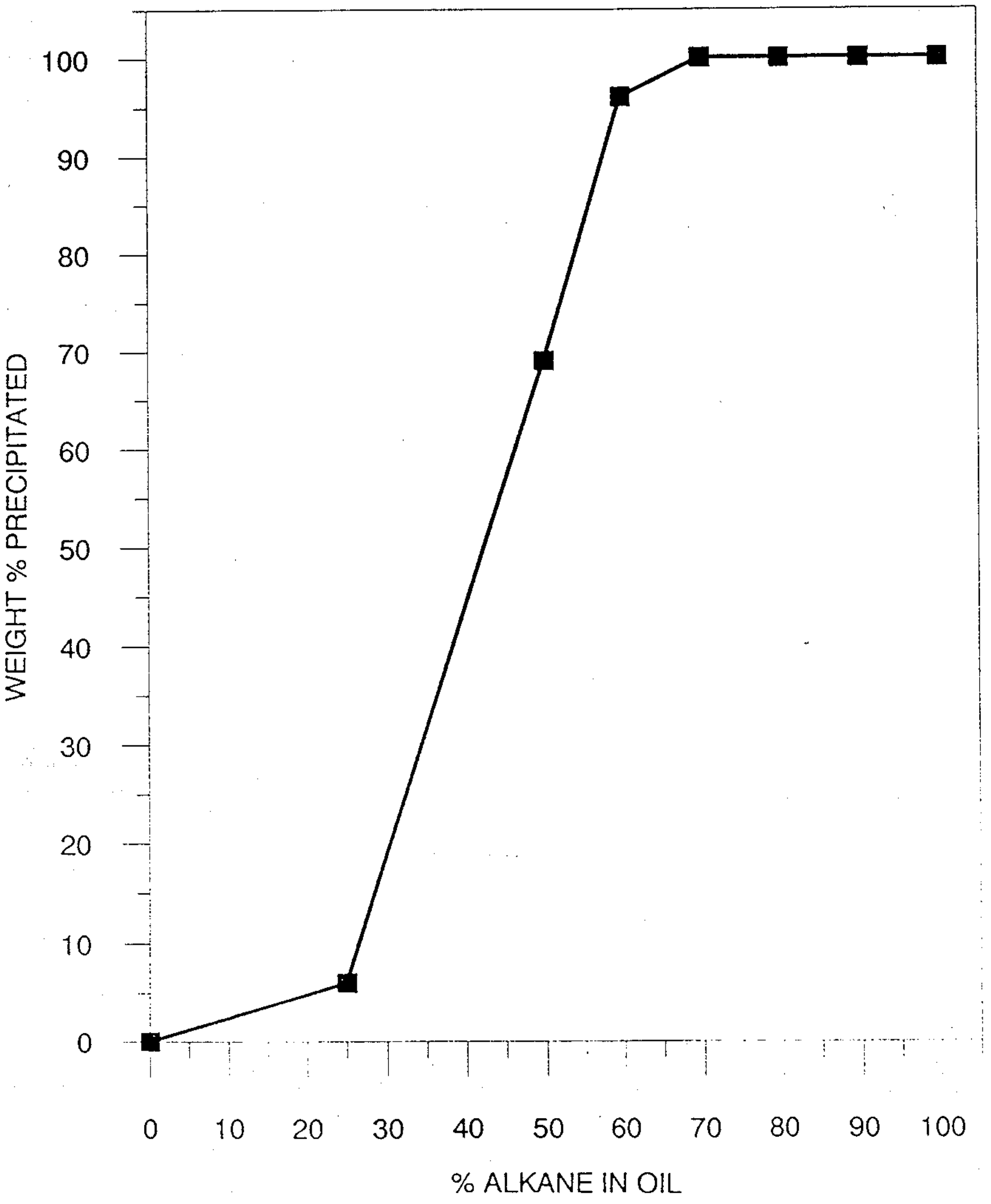
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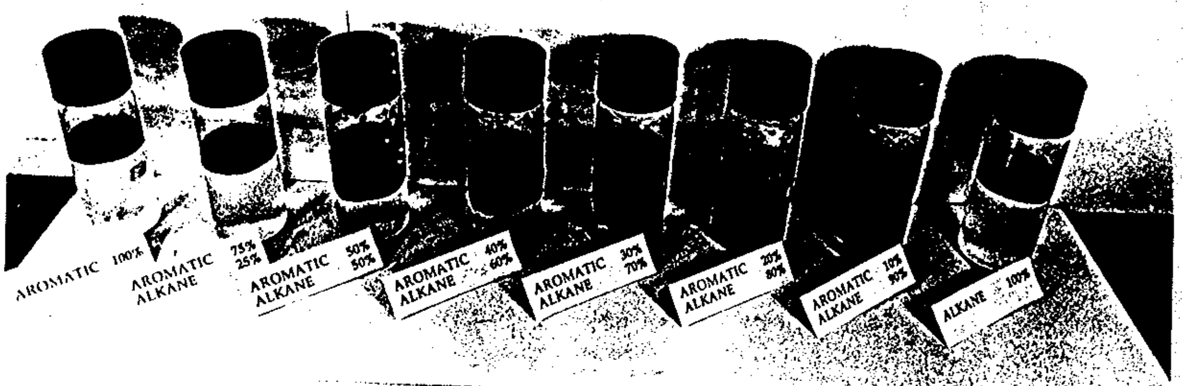
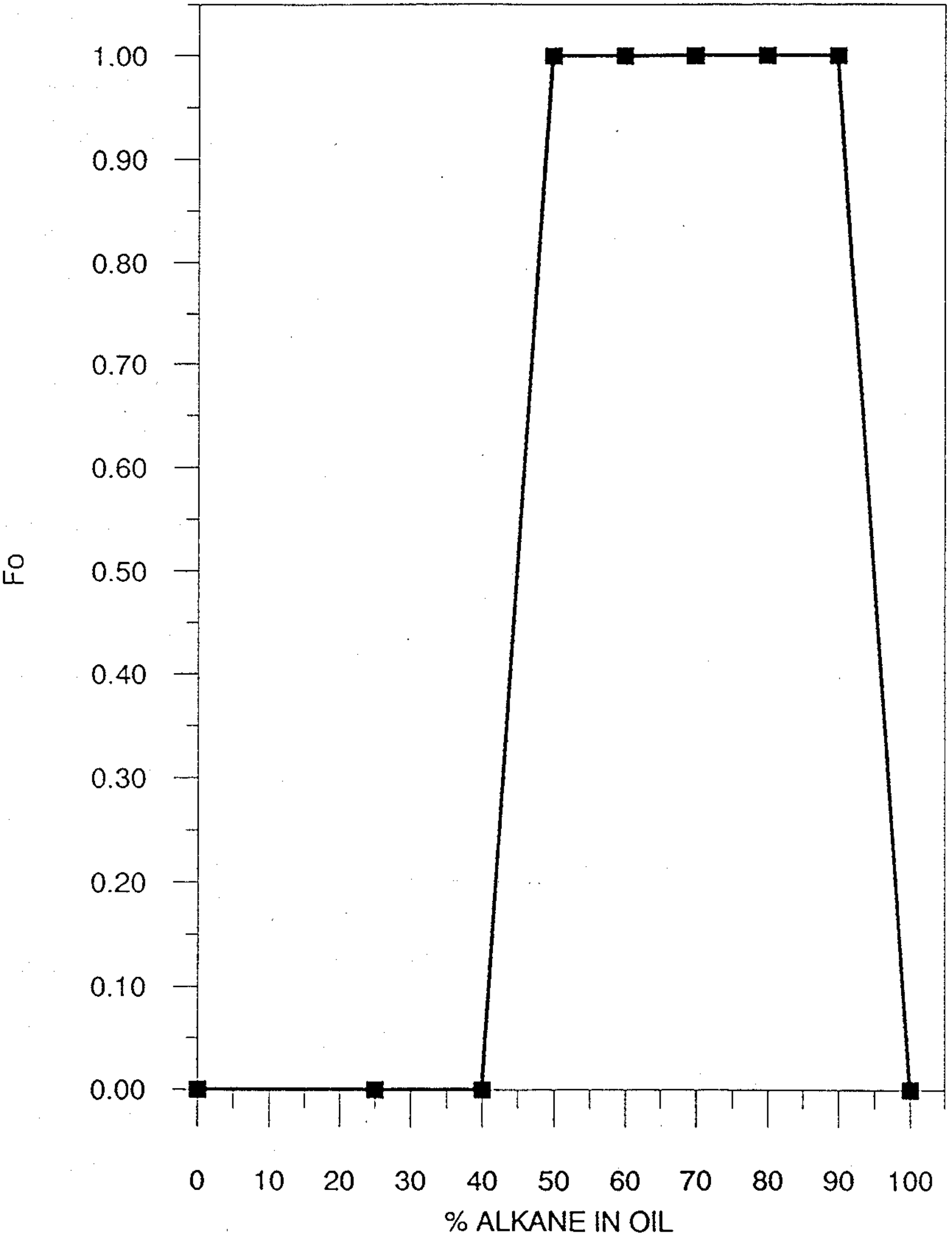
INCREASING ALKANE CONTENT ⟶



EACH OIL HAS AN ASPHALTENE CONCENTRATION OF 0.05 g/mL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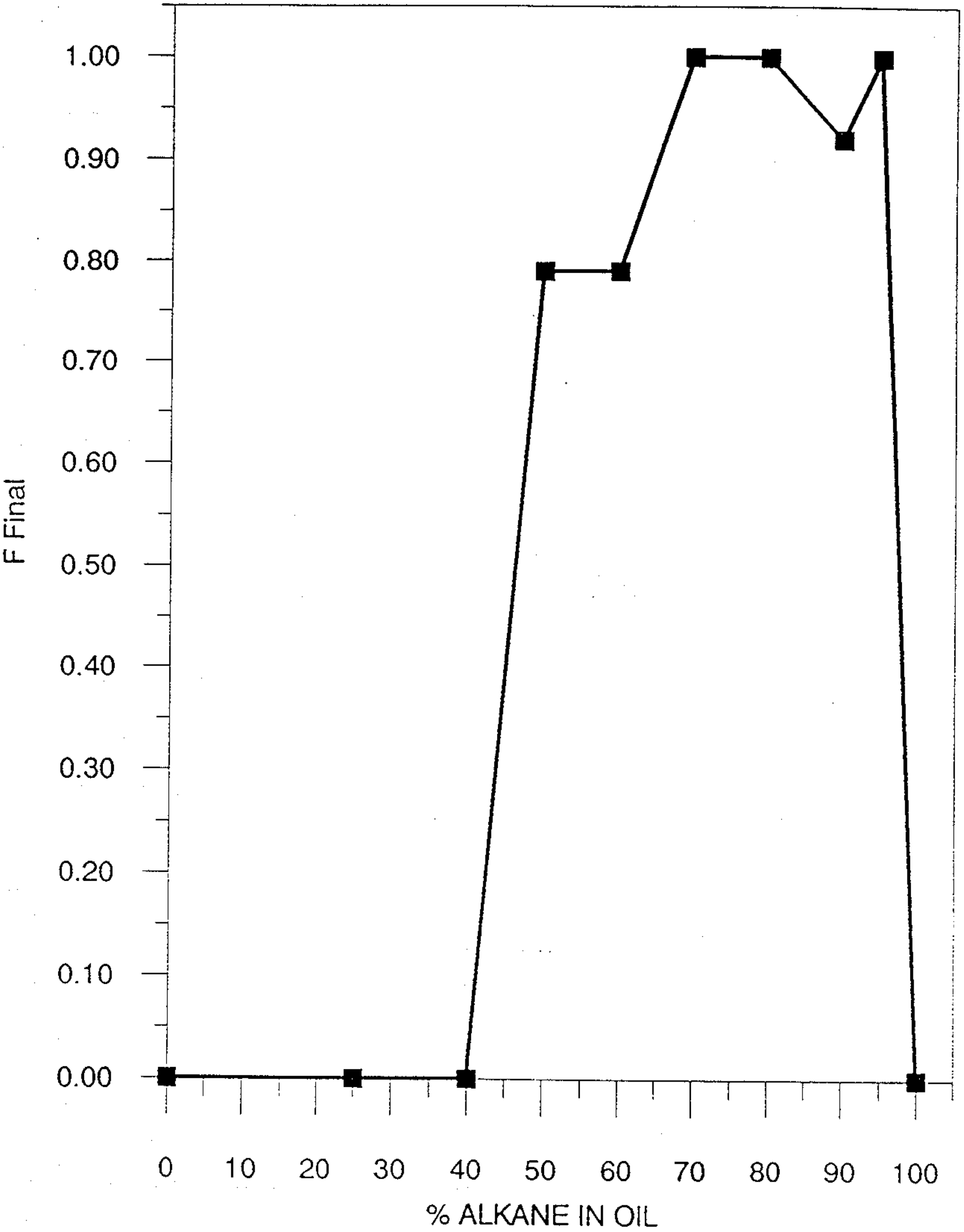
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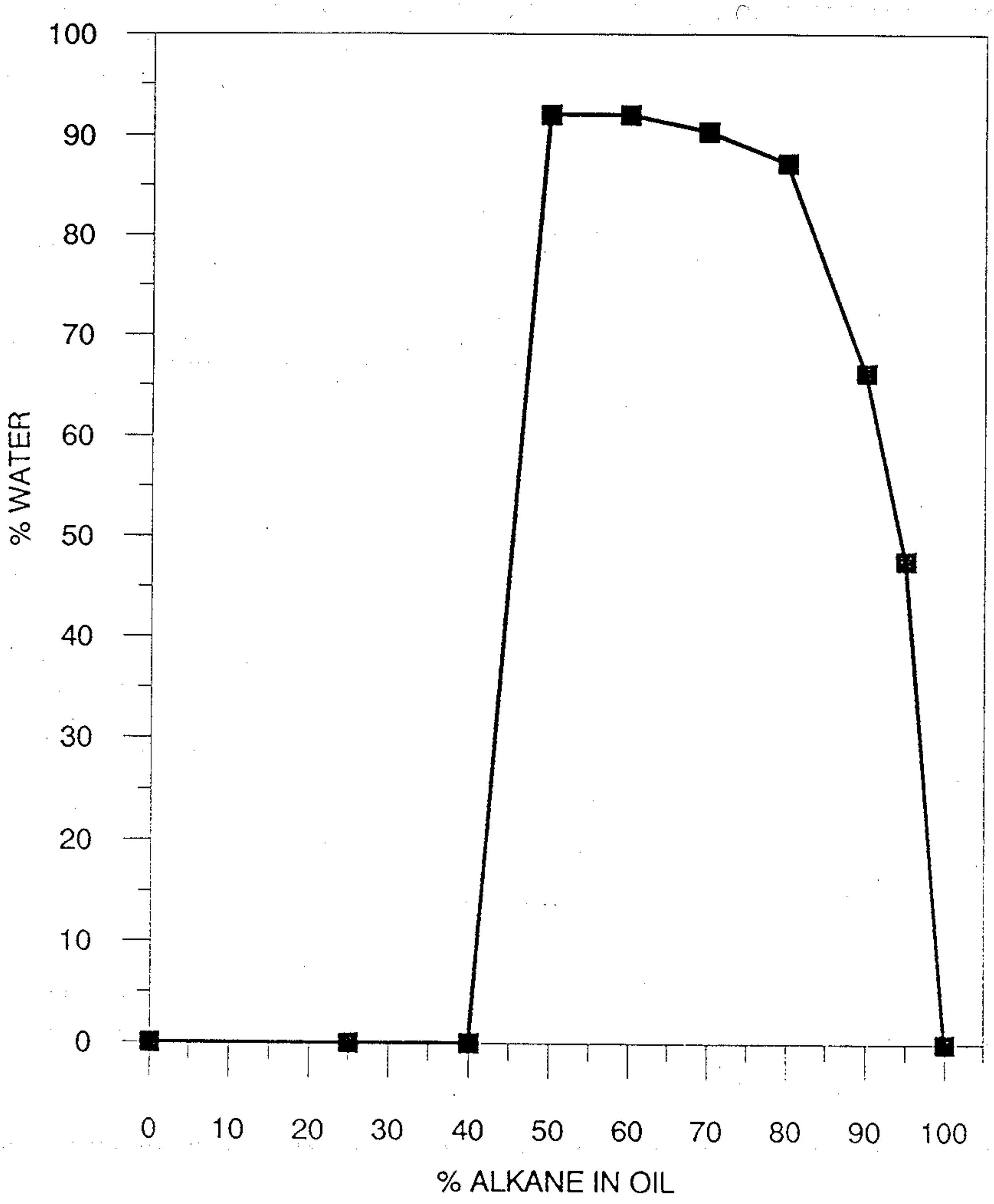
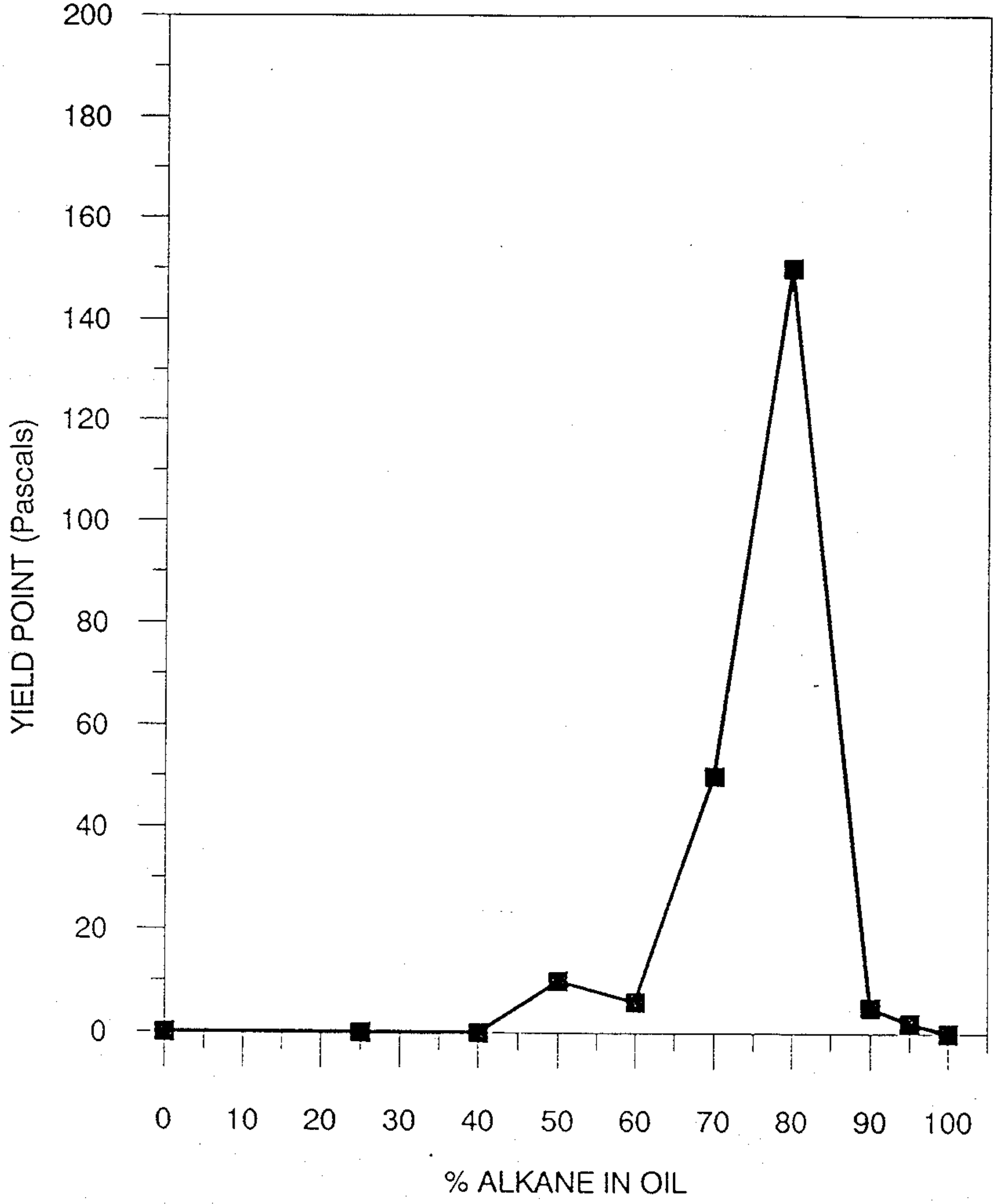
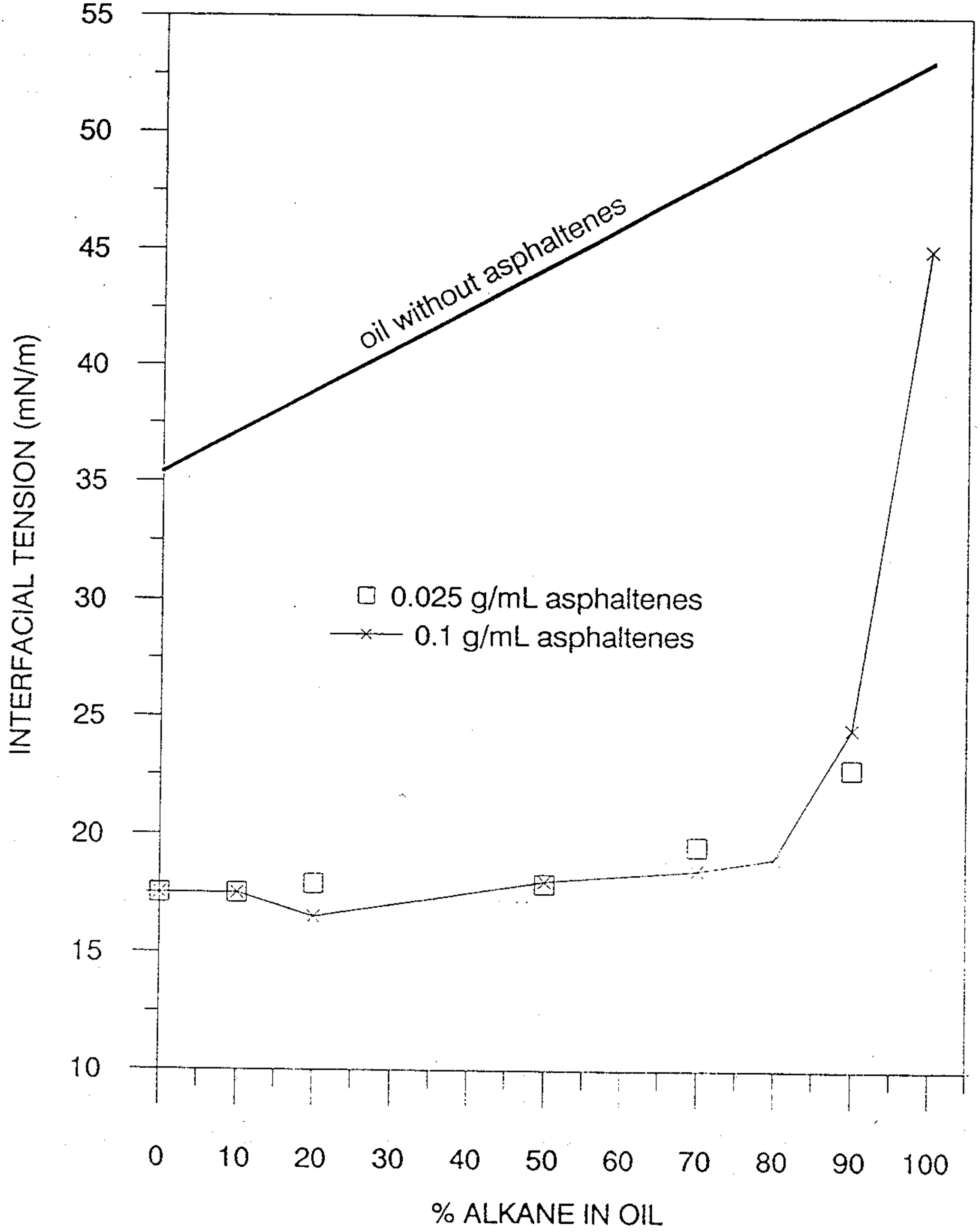
100
% ALKANE IN OIL

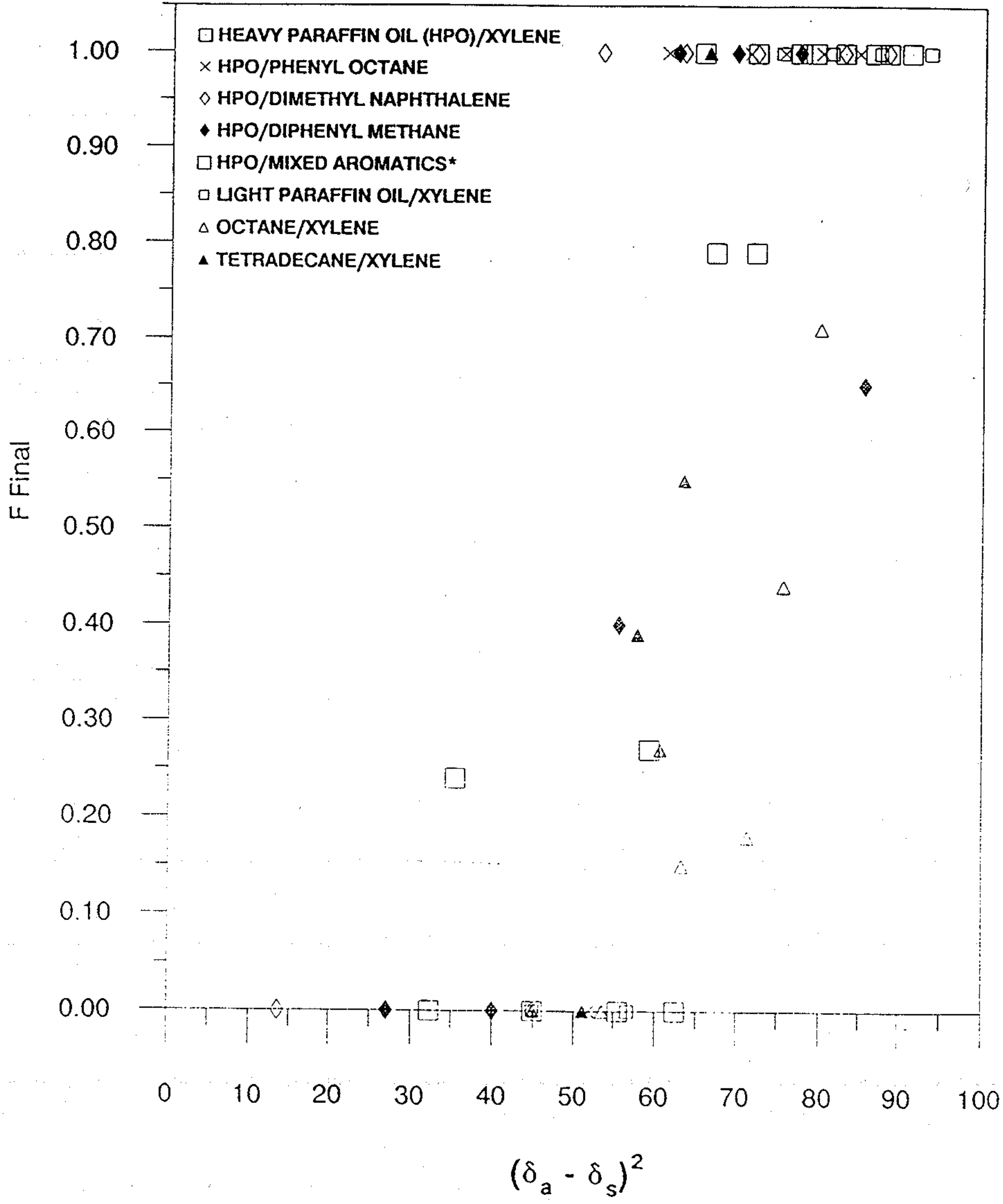

100
90
80
70
60
50
40
30
20
10
0
% WATER
0
10
20
30
40
50
60
70
80
90
100
% ALKANE IN OIL

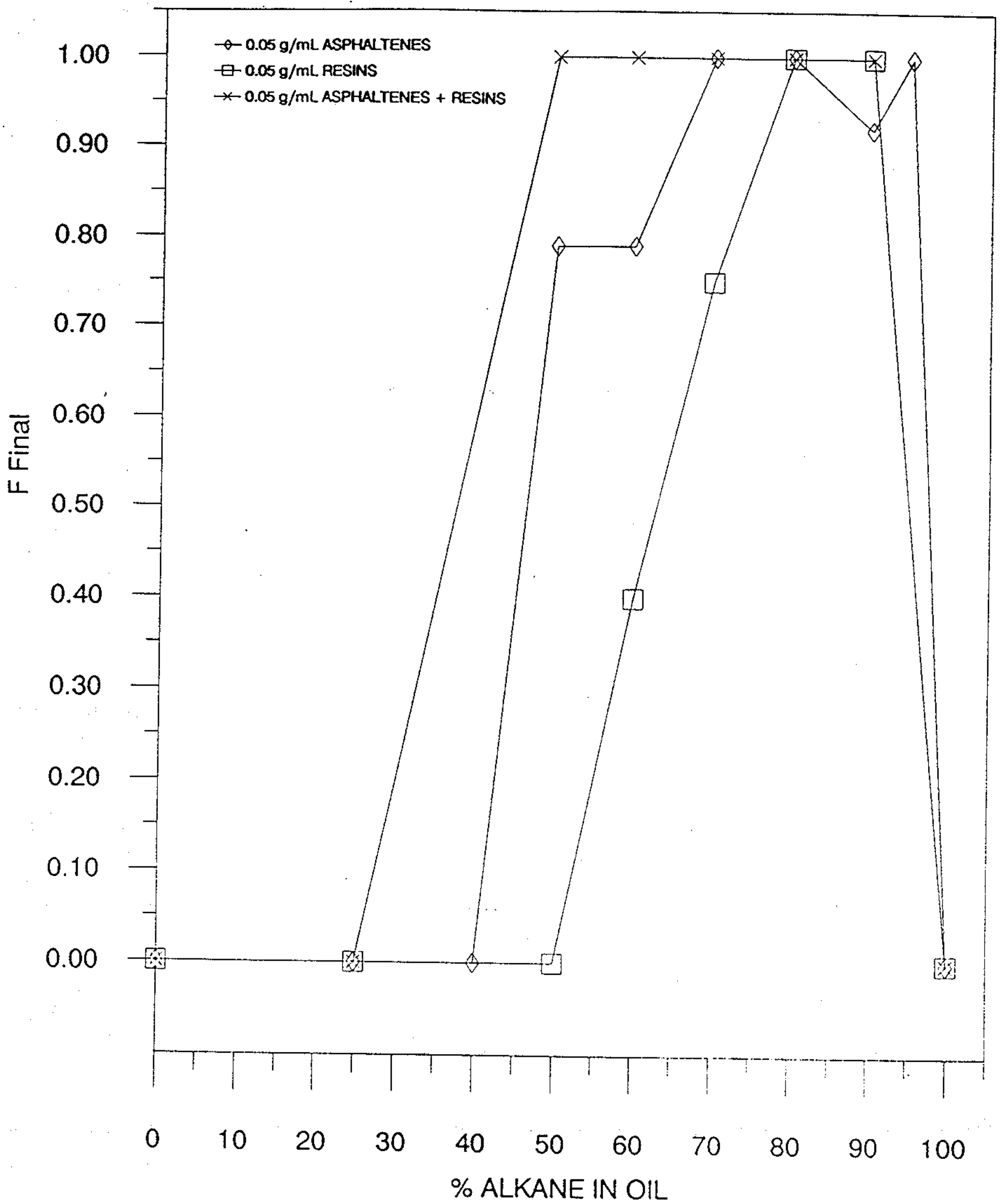


200
180
160
140
120
100
80
60
40
20
0
YIELD POINT (Pascals)
0
10
20
30
40
50
60
70
80
90
100
% ALKANE IN OIL

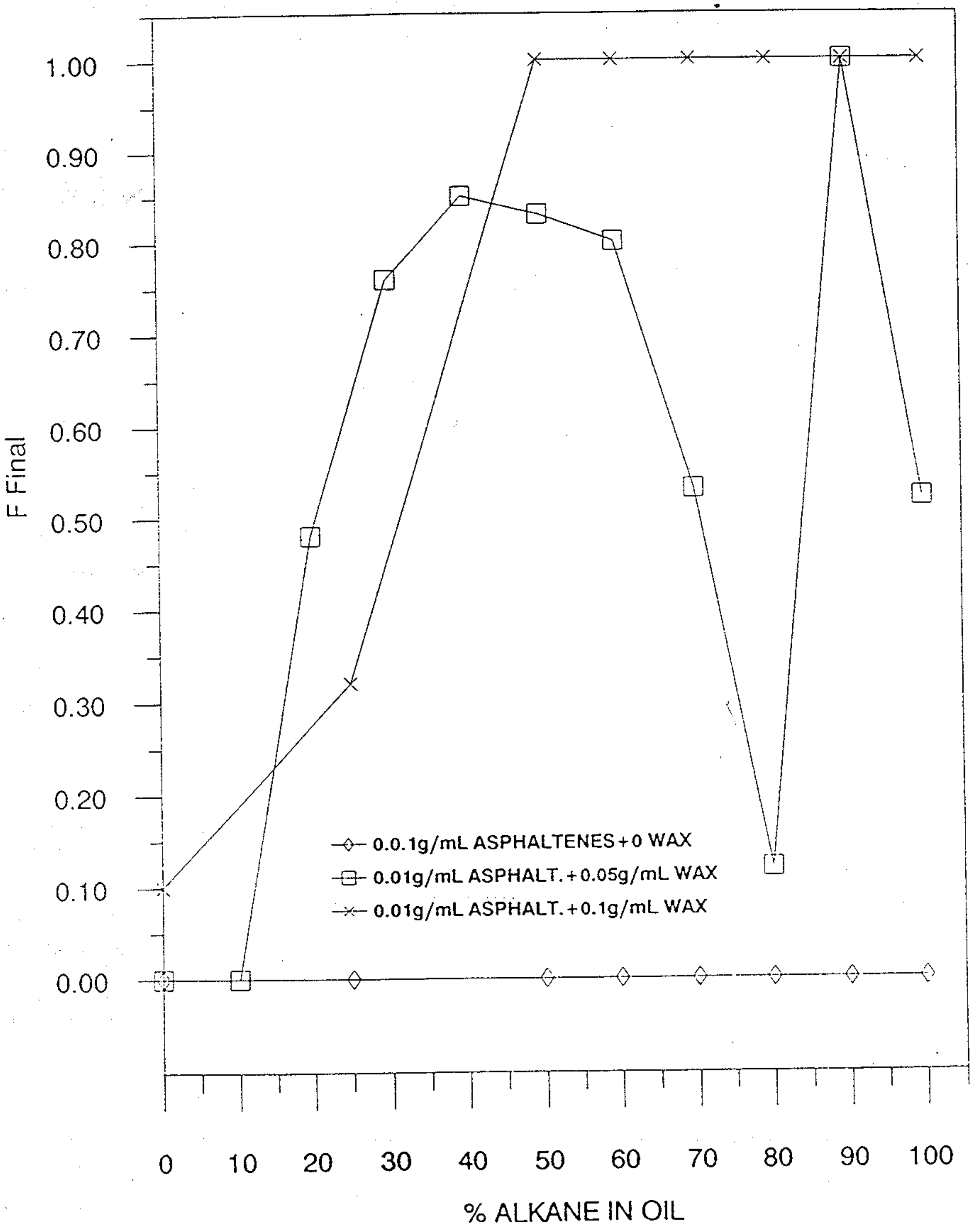


55
50
45
40
35
30
25
20
15
10
INTERFACIAL TENSION (mN/m)
oil without asphaltenes
□ 0.025 g/mL asphaltenes
—×— 0.1 g/mL asphaltenes
0
10
20
30
40
50
60
70
80
90
100
% ALKANE IN OIL


□ HEAVY PARAFFIN OIL (HPO)/XYLENE
× HPO/PHENYL OCTANE
◇ HPO/DIMETHYL NAPHTHALENE
◆ HPO/DIPHENYL METHANE
□ HPO/MIXED AROMATICS*
□ LIGHT PARAFFIN OIL/XYLENE
△ OCTANE/XYLENE
▲ TETRADECANE/XYLENE
F Final
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
10
20
30
40
50
60
70
80
90
100
$(\delta_a - \delta_s)^2$



◇ 0.05 g/mL ASPHALTENES
□ 0.05 g/mL RESINS
× 0.05 g/mL ASPHALTENES + RESINS
F Final
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
10
20
30
40
50
60
70
80
90
100
% ALKANE IN OIL


1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
F Final
0.0.1g/mL ASPHALTENES+0 WAX
0.01g/mL ASPHALT.+0.05g/mL WAX
0.01g/mL ASPHALT.+0.1g/mL WAX
0
10
20
30
40
50
60
70
80
90
100
% ALKANE IN OIL