Water-in-Oil Emulsions Formed at Sea, in Test Tanks, and in the Laboratory

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Abstract

This report summarizes studies to determine the stability of water-in-oil emulsions formed in the laboratory, in the OHMSETT test tank, and at sea.

These studies have confirmed that emulsions can be grouped into four states: stable, unstable, mesostable, and entrained water. These states are differentiated by physical measures as well as by differences in visual appearance. The viscosity of a stable emulsion at a shear rate of one reciprocal second is about three orders-of-magnitude greater than that of the starting oil. An unstable emulsion usually has a viscosity of no more than about 20 times greater than that of the starting oil. A stable emulsion has a significant elasticity, whereas an unstable emulsion does not. A mesostable emulsion has properties between stable and unstable, but breaks down within a few days of standing. The usual situation is that emulsions are either obviously stable, mesostable, or unstable. Entrained water, water suspended in oil by viscous forces alone, is also evident. Very few emulsions have questionable stability. Analytical techniques were developed to test these observations.

The type of emulsion produced is determined primarily by the properties of the starting oil. The most important of these properties are the asphaltene and resin content and the viscosity of the oil. The composition and property ranges of the starting oil that would be required to form each of the water-in-oil states are discussed in this report.

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1.   Introduction

Emulsification is the process whereby water-in-oil emulsions are formed. These emulsions are often called "chocolate mousse" or "mousse" by oil spill workers. When emulsions form, the properties and characteristics of oil spills change to a very large degree. For example, stable emulsions contain from 60 to 80% water, thus expanding the spilled material from 2 to 5 times the original volume. The density of the resulting emulsion can be as great as 1.03 g/mL compared to a starting density as low as 0.80 g/mL. Most significantly, the viscosity of the oil typically changes from a few hundred mPa.s to about 100,000 mPa.s, a typical increase of 1,000. A liquid product is thereby changed to a heavy, semi-solid material.

Many researchers feel that emulsification is the second most important behavioural characteristic of oil after evaporation. Emulsification has a significant effect on the behaviour of oil spills at sea. As a result of emulsification, evaporation of oil spills slows by orders-of-magnitude, spreading slows by similar rates, and the oil rides lower in the water column, showing different drag with respect to the wind. Emulsification also significantly affects other aspects of a spill, such as cleanup response. Spill countermeasures are quite different for emulsions as they are hard to recover mechanically, to treat, or to burn.

In terms of understanding emulsions and emulsification, the oil spill industry has not kept pace with the petroleum production industry and colloid science generally. Workers in the spill industry often revert to old papers published in oil spill literature, which are frequently incorrect and outdated. A basic understanding of the formation, stability, and processes of emulsions is now evident in literature in both the colloid science and oil spill fields, although some new papers still appear with references only to 15-year-old literature.

The availability of methodologies to study emulsions is very important. In the past ten years, both dielectric methods and rheological methods have been exploited to study formation mechanisms and stability of emulsions made from many different types of oils (Sjöblom et al., 1994; Fingas et al., 1998). Standard chemical techniques, including Nuclear Magnetic Resonance (NMR), chemical analysis techniques, microscopy, interfacial pressure, and interfacial tension, are also being applied to emulsions. These techniques have largely confirmed findings noted in the dielectric and rheological mechanisms.

2.   Background and Literature Survey

The mechanism and dynamics of emulsification were poorly understood until the 1990s. It was not recognized until recently that the basics of water-in-oil emulsification were understood in the surfactant industry, but not in the oil spill industry. In the late 60s, Berridge and coworkers (1968) were the first to describe emulsification in detail and measured several physical properties of emulsions. Berridge described the emulsions as forming because of the asphaltene and resin content of the oil. Workers in the 1970s concluded that emulsification occurred primarily due to increased turbulence or mixing energy (Haegh and Ellingson, 1977; Wang and Huang, 1979). The oil's composition was not felt to be a major factor. Some workers speculated that particulate matter in the oil may be a factor and others suggested it was viscosity. Evidence could be found for and against all these hypotheses.

Twardus (1980) studied emulsions and found that emulsion formation might be correlated with

oil composition. It was suggested that asphaltenes and metal porphyrins contributed to emulsion stability. Bridie and coworkers (1980) studied emulsions in the same year and proposed that the asphaltenes and waxes in the oil stabilized water-in-oil emulsions. The wax and asphaltene content of two test oils correlated with the formation of emulsions in a laboratory test. Mackay and coworkers hypothesized that emulsion stability was due to the formation of a film in oil that resisted water droplet coalescence (Mackay and Zagorski, 1981, 1982a, 1982b). The nature of these thin films was not described, but it was proposed that they were caused by the accumulation of certain types of compounds. Later work led to the conclusion that these compounds were asphaltenes and waxes. A standard procedure was devised for making emulsions and measuring stability. This work formed the basis of much of the emulsion formation theory in the oil spill literature over the past two decades.

In 1983, Thingstad and Pengerud conducted photooxidation experiments and found that photooxidized oil formed emulsions. Nesterova and coworkers (1983) studied emulsion formation and concluded that it was strongly correlated with both the asphaltene and tar content of the oil and the salinity of the water with which it was formed. Mackay and Nowak studied emulsions and found that stable emulsions had low conductivity and therefore a continuous phase of oil (Mackay and Nowak, 1984; Mackay, 1984). Stability was discussed and it was proposed that it was a function of oil composition, particularly waxes and asphaltenes. It was proposed that a water droplet could be stabilized by waxes, asphaltenes, or a combination of both. The viscosity of the resulting emulsions was correlated with water content.

Later work by the same group reported examination of Russian hypotheses that emulsions are stabilized by colloidal particles which gather at the oil-water interface and may combine to form a near-solid barrier that resists deformation and thus water-water coalescence (Stiver et al., 1983). It was speculated that these particles could be mineral, wax crystals, aggregates of tar and asphaltenes, or mixtures of these. It was felt that asphaltenes were the most important of these particles and that they controlled the formation of all particles. A formation equation relating the asphaltene, paraffin, aromatic, and silica gel (resin) content was proposed, but it was later shown to be a poor predictor of oil emulsion tendencies.

Desmaison and coworkers (1984) conducted studies on Arabian crudes and noted that emulsion formation was correlated with two factors, photooxidation exposure and the amount of asphaltenes in the oil. The photooxidation was found to occur on the aromatic fractions of the oil. Asphaltenes were found to become structured with time and this was associated with emulsion formation.

Miyahara (1985) reported that the stability of emulsions was primarily controlled by the composition of the oil, specifically that which resided in the hexane-insoluble fraction of the oil, but he did not define what this content was. Miyahara also reported that salt and freshwater emulsions were relatively similar in stability, although in one case the salt water emulsion appeared to be more stable.

Payne and Philips (1985) reviewed the subject in detail and reported on their own experiments of emulsification with Alaskan crudes in the presence and absence of ice. Their studies showed that emulsions can form in an ice field, thus indicating that there was sufficient energy in this

environment and that the process could occur at relatively low temperatures.

Because of the many differing theories in the literature, many oil spill workers were confused about the stability, source of stability, and properties of water-in-oil emulsions. Furthermore, until about 1995, neither advanced rheological techniques nor other techniques such as dielectric studies were applied to emulsions.

3.   Current Studies and Results
3.1 Field Studies
Much of the information on emulsions available in the oil spill industry has been obtained by practical studies in the laboratory or in the field. Jenkins and coworkers (1991) studied emulsions formed in the laboratory and concluded that the formation did not correlate with previously established codes of properties, nor with pour point, asphaltene, and wax contents of the fresh oils. Jenkins and coworkers suggest that, in the absence of any correlation, every oil should be characterized using a standardized procedure in the laboratory.

Other examples of empirical studies include a two-year study conducted on emulsions by Walker (1993) at Warren Spring Laboratory in Britain in which approximately 40 North Sea crude oils were prepared and characterized in the laboratory. Some of these oils were subsequently spilled at sea and some of their properties measured. Walker concluded that the laboratory procedures did not result in emulsions similar to those found at sea, but also noted that there was a marked lack of characterization techniques to study emulsions.

The same group participated in another field trial conducted in 1994 (Walker et al., 1995). The correlation between parallel experiments, physical properties, and emulsion characteristics was poor. It was concluded that delays in sampling and analysis were partially responsible for the poor results as well as the lack of standard measurement and characterization techniques. It was also noted that slight differences in release conditions resulted in major differences in slick behaviour. It was found that there must be a high level of energy in order for emulsions to form and the oil must be weathered to a degree before release. Stability could not be characterized, but appeared to be a continuum through the process.

3.2 General Reviews and Influences on Emulsions
In 1992, Schramm reviewed the basics of emulsions and provided the oil spill industry with the basis for much subsequent understanding of water-in-oil emulsions (Schramm, 1992). In 1993, Becher reviewed emulsion stability in mathematical terms (Becher, 1993).

3.3 Stability
Sjöblom and coworkers surveyed several oils from the Norwegian continental shelf. After the interfacially active fraction was removed from the oils, none would form water-in-oil emulsions (Sjöblom et al., 1990a, b, 1992a). Model emulsions could be made from the extracted interfacially active fractions. Stability was gauged by measuring the separation of water over time. Destabilization studies showed that the rigidity of the interfacial film or reaction with the film components are the principle methods of emulsion breakdown. Medium chain alcohols and amines destabilized emulsions the most.

In 1992, Friberg reviewed the stability of emulsions, noting that a primary measure of stability is the separation into two phases (Friberg, 1992). Friberg noted the focus on two factors, the rheology of the continuous phase and the barrier between the dispersed droplets. It was demonstrated that an increase in viscosity of the continuous phase of the emulsion is not a viable alternative to increasing the halflife of the emulsion. Friberg noted that the continuous phase must show a small yield value to demonstrate stability.

In 1994, Tambe and Sharma proposed a model for the stability of colloid-stabilized emulsions (Tambe and Sharma, 1994). They noted that colloidal particles stabilize emulsions both by providing steric hindrance to drop-drop coalescence and by modifying the rheological properties of the interfacial region. Tambe and Sharma noted that the effectiveness of colloidal particles in stabilizing emulsions depends in part on the ability of these particles to reside at a state of equilibrium at the oil-water interface and showed that the adsorption of particles at the oil-water interface also affects the rheological properties of the interfacial region. If the concentration of the particles is high, the colloid-laden interface will exhibit viscoelastic behaviour. Viscoelastic interfaces in turn, affect emulsion stability by retarding the rate of film drainage between coalescing emulsion droplets and by increasing the energy required to displace particles from the contact region between water droplets or, in other words, by increasing the magnitude of the steric hindrance.

3.4 Source of Stability
3.4.1 Asphaltenes
More than 30 years ago, it was found that asphaltenes were a major factor in emulsion stability (Berridge et al., 1968). Specific roles of emulsions have not been defined until recently. The Sjöblom group in Norway defined the interfacial properties of asphaltenes in several local offshore crudes (Nordli et al., 1991). Asphaltenes were separated from the oils using consecutive separations involving absorption to silica. Molecular weights ranged from 950 to 1,450 Daltons. Elemental analysis revealed that 99 mole % of the asphaltenes was carbon and hydrogen, while up to 1% was nitrogen, oxygen, and/or sulphur. The films form monomolecular layers at the air/water interface. Aromatic solvents such as benzylalcohol have a strong influence on the asphaltenes and will destabilize water-in-oil emulsions. Asphaltenes were shown to be the agent responsible for stabilizing the Norwegian crudes tested.

Workers in the same group separated resins and asphaltenes and studied the Fourier-transform infrared spectrum and the emulsions formed by each fraction (Mingyuan et al., 1992). The asphaltenes were separated using pentane precipitations and the resins by desorption from silica gel using mixtures of benzene and methanol. The fractions were tested in model systems for their emulsion-forming tendencies. Model emulsions were stabilized by both asphaltene and resin fractions, but the asphaltene fractions were much more stable.

Acevedo and coworkers (1993) studied the interfacial behaviour of a Cerro Negro crude by a planar rheology. Distilled water and salt water were used with a 30% and a 3.2% xylene-diluted crude. The elasticity and viscosity were obtained from creep compliance measurements. The high values of viscoelastic and elastic moduli were attributed to the flocculation of asphaltene:resin micelles at the interface. The high moduli were associated with the elastic interface. In the absence of resins, asphaltenes were not dispersed and did not form stable

interface layers and then, by implication, stable emulsions.

Mohammed and coworkers (1993a, b) studied surface pressure, as measured in a Langmuir film balance, of crude oils and solutions of asphaltenes and resins. They found that the pseudodilational modulus has high values for low resin-to-asphaltene ratios and low values for high resin-to-asphaltene ratios. They suggest that low resin-to-asphaltene ratios lead to more stable emulsion and vice-versa.

Chaala and coworkers (1994) studied the flocculation and the colloidal stability of crude fractions. Stability was defined as the differential in spectral absorption between the bottom and top of a test vessel. The effects of temperature and of additions of waxes and aromatics on stability were noted. Increasing both waxes and aromatics generally decreased stability. Temperature increased stability up to 60°C and then stability decreased. In another study, the resins and asphaltenes were extracted from four crude oils by various means (Schildberg et al., 1995). It was found that different extraction methods resulted in different characteristics as measured by FT-IR spectroscopy as well as different stabilities when the asphaltenes and resins were used as stabilizers in model systems. It was concluded that the interfacially active components in crude oil were interacting and were difficult to distinguish. Both the resins and asphaltenes appeared to be involved in interfacial processes.

Urdahl and Sjöblom (1995) studied stabilization and destabilization of water-in-crude oil emulsion. It was concluded that indigenous, interfacially active components in the crude oils are responsible for stabilization. These fractions would be the asphaltenes and resins. Model systems stabilized by extracted interfacially active components had stability properties similar to the crude oil emulsions. The same group studied the ageing of the interfacial components (Sjöblom et al., 1995a). Resins and asphaltenes were extracted from North Sea crudes and exposed to ageing under normal atmospheric and ultraviolet conditions. The FT-IR spectra shows that the carbonyl peak grew significantly as indicated by the C=C mode. Spectra also showed that condensation was occurring. The interfacial activity increased in all fractions as the ageing process proceeded. In the case of two crude oils, the ageing was accompanied by an increase in the water/oil emulsion stability.

McLean and Kilpatrick (1997a) studied asphaltene aggregation in model emulsions made from heptane and toluene. The resins and asphaltenes were extracted from four different crude oils - two from Saudia Arabia, Alaskan North Slope, and San Joaquin Valley crudes. The asphaltenes were extracted using heptane and the resins, using open-column silica columns. Asphaltenes dissolved in heptol consisting of only about 0.5% asphaltenes generated more stable emulsions than those generated by the originating crude oils. Although some emulsions could be generated using resins, they were much less stable than those generated by asphaltenes. The model emulsions showed that the aromaticity of the crude medium was a prime factor. This was adjusted by varying the heptane:toluene ratio. It was also found that the concentration of asphaltenes and the availability of solvating resins were important. The model emulsions were most stable when the crude medium was between 30 to 40% toluene and with low resin:asphaltene ratios.

McLean and Kilpatrick (1997b) put forward the thesis that asphaltenes were the most effective

in stabilizing emulsions when they are near the point of incipient precipitation. It was noted that there are specific resin-asphaltene interactions, as differing combinations yielded different results in the model emulsions. The resins and asphaltenes were characterized by elemental and neutron activation analyses. The most effective emulsion stabilizers of the resins and asphaltenes were the most polar and the most condensed. McLean and Kilpatrick concluded that the most significant factor in emulsion is the solubility state of asphaltenes.

In 1998, Mouraille and coworkers studied the stability of emulsions using separation/sedimentation tests and high voltage destabilization. It was found that the most important factor was the stabilization state of the asphaltenes. The wax content did not appear to affect the stability except that a high wax content displayed a high temperature dependence. Resins affected the solubilization of the asphaltenes and thus indirectly, the stability.

In the same year, McLean and coworkers (1998) reviewed emulsions and concluded that the asphaltene content is the single most important factor in the formation of emulsions. Even in the absence of any other synergistic compounds (i.e., resins, waxes and aromatics), asphaltenes were found to be capable of forming rigid, cross-linked, elastic films which are the primary agents in stabilizing water-in-crude oil emulsions. It was noted that the exact conformations in which asphaltenes organize at oil-water interfaces and the corresponding intermolecular interactions have not been elucidated. McLean and colleagues suggest that the intermolecular interactions must be either π-bonds between fused aromatic sheets, H-bonds mediated by carboxyl, pyrrolic, and sulfoxide functional groups, or electron donor-acceptor interactions mediated by porphyrin rings, heavy metals, or heteroatomic functional groups.

It is suggested that specific experimental designs to test these concepts are needed to understand the phenomenon on a molecular level. Such knowledge would aid in the design of chemical demulsifiers. The oleic medium plays a large role in the surface activity of asphaltenic aggregates and in the resulting emulsion stability. It is noted that the precise role of waxes and inorganic solids in either stabilizing or destabilizing emulsions is not known. Emulsions are stabilized primarily by rigid, elastic asphaltenic films.

Recently, Singh, McLean, and Kilpatrick (1999) studied the effect of the fused-ring solvents including naphthalene, phenanthrene, and phenanthridine in destabilizing emulsions. They note that the primary mechanism for emulsion formation is the stability of asphaltene films at the oil-water interface. They suggest that the mechanism is one in which planar, disk-like asphaltene molecules aggregate through lateral intermolecular forces to form aggregates. The aggregates form a viscoelastic network after absorption at the oil-water interface. The network is sometimes called a film or skin and the strength of this film correlates with emulsion stability. The strength of the film can be gauged by shear and elastic moduli. Singh and coworkers probed the film-bonding interactions by studying the destabilization by aromatic solvents. It was found that fused-ring solvents, in particular, were effective in destabilizing asphaltene-stabilized emulsions. It is suggested that both π-bonds between fused aromatic sheets and H-bonds play significant roles in the formation of the asphaltene films.

Sjöblom and coworkers (1999) used dielectric spectroscopy to study emulsions over a period of years. It is concluded that the asphaltenes, not the resins, are the stabilizing fraction in water-in-

oil emulsions. It was noted, however, that some resins must be present to give rise to stability. It is suggested that the greater mobility of the resins is needed to stabilize the emulsions until the asphaltenes, which migrate slowly, can align at the interface and stabilize the emulsions.

3.4.2 Resins

In 1996, Neuman and Paczynka-Lahme studied the stability of petroleum o/w emulsions and found that they are stabilized by 'thick films' which appeared to be largely composed of petroleum resins. These thick films demonstrate elasticity and thus increase stability. Temperature increases showed increasing structure formation of the films. Isolated petroleum resins showed structure formation as well.

Rønningsen and coworkers (1995) studied the ageing of crude oils and its effect on the stability of emulsions. The oil was exposed to air and light and it was found that the interfacial tension of the oil towards formation water decreased as a result of the ageing. This was caused by the formation of various oxidation products, mainly carbonyl compounds. In general, the emulsions became more stable. In some cases, however, the opposite was observed, namely, that although the interfacial tension was high, the emulsion stability was lower, presumably because new compounds with less beneficial film properties are formed. Presumably, the compounds that were formed could be loosely classified as resins.

3.4.3 Waxes

Johansen and coworkers (1998/89) studied water-in-crude oil emulsions from the Norwegian continental shelf. The crudes contained a varying amount of waxes (2 to 15%) and few asphaltenes (0 to 1.5% by weight). Emulsion stability was characterized by visual inspection as well as by ultracentrifugation at 650 to 30,000 g. Mean water droplet sizes of 10 to 100 μm were measured in the emulsions. It was found that higher mixing rates reduced the droplet size and a longer mixing time yielded a narrow distribution of droplet size. The emulsion stability correlated with the emulsion viscosity, the crude oil viscosity, and the wax content.

McMahon (1992) studied the effect of waxes on emulsion stability as monitored by the separation of water over time. The size of the wax crystals showed an effect in some emulsions but not in others. Interfacial viscosity indicated that the wax crystals form a barrier at the water/oil interface which retards the coalescence of colliding water droplets. Studies with octacosane, a model crude oil wax, show that a limited wax/asphaltene/resin interaction occurs. A wax layer, even with absorbed asphaltenes and resins, does not by itself stabilize an emulsion. McMahon concludes that the effect of wax on emulsion stability does not appear to be through action at the interface. Instead, the wax may act in the bulk oil phase by inhibiting film thinning between approaching droplets or by a scavenging demulsifier. It was found that the asphaltenes and resins affected stability via interfacial action and are primarily responsible for the emulsion formation.

Puskas and coworkers (1996) extracted paraffinic deposits from oil wells and pipelines. This hydrophobic paraffin derivative had a high molar mass and melting point and contained polar end groups (carbonyls). This paraffinic derivative stabilized water-in-oil emulsions at concentrations of 1 to 2%.

3.5   Methodologies for Studying Emulsions
3.5.1 Dielectric

Dielectric spectroscopy is one of the methods used to study emulsions. The permittivity of the emulsion can be used to characterize an emulsion and assign a stability (Sjöblom et al., 1994, 1997, 1999; Sjöblom and Førdedal, 1996; Førdedal et al., 1996a; Gestblom et al., 1994; Skodvin et al, 1994a, b; Skodvin and Sjöblom, 1996). The Sjöblom group has measured the dielectric spectra using the time domain spectroscopy (TDS) technique. A sample is placed at the end of a coaxial line to measure total reflection. Reflected pulses are observed in time windows of 20 ns, Fourier transformed in the frequency range from 50 MHz to 2 Ghz and the complex permittivity calculated. Water or air can be used as reference samples. The total complex permittivity at a frequency (ω) is given by:

$$\varepsilon^*(\omega) = \frac{\varepsilon_s - \varepsilon_\phi}{1 + i\omega\tau} \qquad (1)$$

Where: ϵ_s is the static permittivity,
ϵ_ϕ is the permittivity at high frequencies,
ω is the angular frequency, and
τ is the relaxation time.

The measuring system used by the Sjöblom group includes a digital sampling oscilloscope and a pulse generator. A computer is connected to the oscilloscope and controls the measurement timing as well as performing the calculations.

The data are used to indicate stability and the geometry of the droplets. Flocculation of the emulsion can be detected. In tests of flowing and static emulsions, it was shown that the flowing emulsions have lower static permittivities, which was interpreted as indicating flocculation in the static emulsions (Skodvin et al., 1994a).

Skodvin and Sjöblom (1996) used dielectric spectroscopy in conjunction with rheology to study a series of emulsions. A close connection was found between the viscosity and dielectric properties of the emulsions. The large effects of shear on both the static permittivity and the dielectric relaxation time for the emulsion was ascribed, at least in part, to the degree of flocculation in the emulsion system. At high shear rates, at which emulsions are expected to have a low degree of flocculation and high stability, the dielectric properties still varied from those expected from a theoretical model for spherical emulsion droplets.

Førdedal and coworkers used dielectric spectroscopy to study several real crude oil emulsions and model systems stabilized with either separated asphaltenes and resins from crude oil or by commercial surfactants (Førdedal et al., 1996b). Emulsions could be stabilized by the asphaltene fraction alone, but not by the resin fraction alone. A study of a combination of mixtures shows an important interaction between emulsifying components. Førdedal and coworkers used dielectric spectroscopy to study model emulsions stabilized by asphaltenes extracted from crude oils. Analysis showed that the choice of organic solvent and the amount of asphaltenes, as well as the interaction between these variables, were the most significant parameters for determining the stability of the emulsions.

Ese and coworkers (1997) found similar results on model emulsions stabilized with resins and asphaltenes extracted from North Sea oil. The dielectric spectroscopy results showed that the stability of model emulsions could be characterized. Stability was found to depend mainly on the amount of asphaltenes, the degree of aging of asphaltenes and resins, and the ratio between asphaltenes and resins.

3.5.2 Rheology

In 1983, Steinborn and Flock studied the rheology of crude oils and water-in-oil emulsions. Emulsions with high proportions of water exhibited pseudo-plastic behaviour and were only slightly time-dependent at higher shear rates. Omar and coworkers (1991) also measured the rheological characteristics of Saudi crude oil emulsions. Non-Newtonian emulsions exhibit pseudoplastic behaviour and followed a power-law model. Mohammed and coworkers (1993b) studied crude oil emulsions using a biconical bob rheometer suspended at the interface. More stable emulsions displayed a viscoelastic behaviour and a solid-like interface. Demulsifiers changed the solid-like interface into a liquid one.

Tadros (1994) summarized the fundamental principles of emulsion rheology. Emulsions stabilized by surfactant films (such as resins and asphaltenes) behave like hard sphere dispersions. These dispersions display viscoelastic behaviour. Water-in-oil emulsions show a transition from a predominantly viscous to a predominantly elastic response as the frequency of oscillation exceeds a critical value. Thus, a relaxation time can be determined for the system, which increases with the volume fraction of the discontinuous phase. At the critical value, the system shows a transition from predominantly viscous to predominantly elastic response. This reflects the increasing steric interaction with increases in volume of the discontinuous phase.

In 1996, Pal studied the effect of droplet size and found it had a dramatic influence on emulsion rheology (Pal, 1996). Fine emulsions have much higher viscosity and storage moduli than the corresponding coarse emulsions. The shear thinning effect is much stronger in the case of fine emulsions. Water-in-oil emulsions age much more rapidly than oil-in-water emulsions. More recently, Lee and coworkers (1997) and Aomari and coworkers (1998) examined model emulsions and found that a maximum shear strain existed which occurred around 100 s^{-1}.

3.5.3 Nuclear Magnetic Resonance (NMR)

Urdahl and coworkers (1992) studied crude oils and the silica-absorbed compounds (asphaltenes and resins) using ^{13}C NMR techniques. It was found that the asphaltenes and resins are enriched in condensed aromatics compared to the whole crude oils. There was strong indications of a long, straight-chain aliphatic compound containing a heteroatom substituent which is abundant in paraffinic oils. There was also reason to believe that this compound was active in the formation of stable water-in-crude oil emulsions. The range from 130 to 210 ppm in the ^{13}C NMR was of particular interest as this region represents quaternary aromatic and heteroatom-bonded carbons.

Balinov and coworkers (1994) studied the use of ^{13}C NMR to characterize emulsions using the NMR self-diffusion technique. The technique uses the phase differences in consecutive pulses to measure the diffusion length of the target molecules. As such, the technique indicates the relative particle size in an emulsion. The NMR technique was compared to optical microscopy and

showed good correlation over several experiments involving ageing and breaking of the emulsions.

LaTorraca and coworkers (1998) used proton NMR to study oils and emulsions. They found that the amount of hydrogen was inversely proportional to the viscosity. The amount of water could be determined in an emulsion because of the separation downfield of the proton on water and on hydrocarbons. The viscosity and water content of emulsions could be simultaneously determined.

3.5.4 Interfacial Properties

Sjöblom and coworkers (1992a) studied model emulsions stabilized by interfacially active fractions from crude oil. A good correlation was found between interfacial pressure of the fractions, as measured in a Langmuir trough, and the stability of emulsions as measured by the amount of water separated with time. Surface tension, as measured by the drop volume method, did not show a surfactant-like behaviour for the asphaltenes and resins.

Børve and coworkers (1992) studied the pressure-area isotherms and relaxation behaviour in a Langmuir trough. In one study, model polymers, styrene, and allyl alcohol (PSAA, molecular weight 150 g mol^{-1}) and mixtures of PSAA with 4-hexadecylaniline or eicosylamine, were used as comparative polymers to the natural surfactants in oils. The mixtures of PSAA with the amines reproduce the π-A isotherms and relation properties shown by the interfacially active fractions of crude oils. The main difference was found to be a lower maximum compressibility and a higher surface activity. The crude oil fractions are well modelled by a relatively low-molecular weight aromatic, weakly polar, water-insoluble hydrocarbon polymer to which has been added long-chain amines.

In a similar study, Ebeltoft and coworkers (1992) mixed surfactants (sodium dodecylsulphate, and cetyltrimethlyammonium bromide or cetylpyridinium chloride) with PSAA and studied the pressure-area isotherms. All the surfactants appeared to interact with the PSAA and in similar ways. It was concluded that PSAA monolayers are good models for emulsion-stabilizing monolayers in Norwegian crude oils. Monolayers of both PSA and crude oil interfacially active fractions responded similarly to the presence of ionic surfactants, indicating analogous dissolution mechanisms.

Hartland and Jeelani (1994) performed a theoretical study of the effect of interfacial tension gradients on emulsion stability. Dispersion stability and instability were explained in terms of a surface mobility which is proportional to the surface velocity. When the interfacial tension gradient is negative, the surface mobility is negative under some conditions, which greatly reduces the drainage so that the dispersion is stable. This is a normal situation as surfactant is present at the interface. Demulsifier molecules penetrate the interface within the film, thereby lowering the interfacial tension sufficiently and causing a positive interfacial tension gradient. Drainage is subsequently increased and the emulsion becomes unstable.

Ese and coworkers (1998) studied the film-forming properties of asphaltenes and resins using a Langmuir trough. Asphaltenes and resins were separated from different crude oils. It was found that the asphaltenes appear to pack closer at the water surface and form a more rigid surface than

the resins. The size of asphaltene aggregates appears to increase when the spreading solvent becomes more aliphatic and with increasing asphaltene bulk concentration. Resin films show high compressibility, which indicates a collapse of the monomolecular film. A comparison between asphaltenes and resins shows that resins are more polar and do not aggregate to the same extent as the asphaltenes. Resins also show a high degree of sensitivity to oxidation. When resins and asphaltenes are mixed, resins begin to dominate the film properties when resins exceed about 40 wt %.

3.5.5 Optical Methods

Miller and Böhm (1993) studied the coalescence of water-in-oil emulsions using a specially designed optical instrument dependent on light scattering of the emulsions. The instrument could be used in either a transmission or backscatter mode.

3.6   Physical Studies
3.6.1 Structure and Droplet Sizes

Eley and coworkers (1988) studied the size of water droplets in emulsions using optical microscopy and found that the droplet sizes followed a log-normal distribution. The number mean diameters of the droplets varied from about 1.4 to 5.6 µm. Paczynska-Lahme (1990) studied several mesophases in petroleum using optical microscopy. Petroleum resins showed highly organized laminar structures and water-in-oil emulsions were generally unstructured, but sometimes hexagonal.

Toulhoat and coworkers (1999) studied asphaltenes extracted from crude oils of various origins using atomic force microscopy. The asphaltenes were dried onto freshly cleaved mica and in some cases were present in discoids of approximately 2 nm × 30 nm. It was noted that these dimensions were similar to those measured using neutron scattering of asphaltenes in solvents. An increase in discoid size was observed with increasing sulphur content of the asphaltenes, but no correlation in size was observed with increasing asphaltene molecular weight. Absorption of asphaltenes from unfiltered solutions revealed fractal-like asphaltene clusters with lengths of a few micrometers, width 1 µm, and a thickness of 10 to 20 m.

Balinov and coworkers (1994) studied the use of ^{13}C NMR to characterize emulsions using the NMR self-diffusion technique and compared this to optical microscopy. The optical microscopy showed an average droplet size of about 4 µm with a volume mean of approximately 8 µm (estimated by the present author).

3.6.2 Dynamics and Thermodynamics

Eley and coworkers (1988) studied the formation of emulsions and found that the rate was first order with respect to stirring time. As the asphaltene content increased, the rate constant decreased.

4.   Laboratory Studies on Emulsion Stability and Separation of Stability Classes
4.1   Studies on Stability Classes

The most important characteristic of a water-in-oil emulsion is its 'stability'. The reason for this is that one must first characterize an emulsion as stable (or unstable) before one can characterize its properties. Properties change significantly for each type of emulsion. Until

recently, emulsion stability has not been defined (Fingas et al., 1995). Therefore, studies were difficult because the end points of analysis were not defined.

This section summarizes studies to measure the stability of water-in-oil emulsions and define characteristics of different stability classes. Four 'states' in which water can exist in oil will be described. These include: stable emulsions, mesostable emulsions, unstable emulsions (or simply water and oil), and entrained water. These four 'states' are differentiated by visual appearance as well as by rheological measures.

Studies in the past three years have shown that a class of very 'stable' emulsions exists, characterized by their persistence over several months. The viscosity of these stable emulsions actually increases over time. These emulsions have been monitored for as long as 3 years in the laboratory. 'Unstable' emulsions do not show this increase in viscosity and their viscosity is less than about 20 times greater than the starting oil. The viscosity increase for stable emulsions is at least three orders-of-magnitude more than the starting oil.

The present authors have studied emulsions for many years (Bobra et al., 1992; Fingas et al., 1993; 1995; 1996; 1997; 1998; 1999; 2000a, 2000b; 2001a; 2002b; Fingas and Fieldhouse, 1994). The last two of these references as well as Fingas et al., 1995 describe studies to define stability. The findings of these earlier studies are summarized here. Both on the basis of the literature and experimental evidence, it was concluded that certain emulsions can be classed as stable. Some (if not all or many) stable emulsions increase in apparent viscosity with time, i.e., their elasticity increases. It is suspected that the stability derives from the strong viscoelastic interface caused by asphaltenes, perhaps along with resins. Increasing viscosity may be caused by increasing alignment of asphaltenes at the oil-water interface.

Mesostable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) (Fingas et al., 1995). It is suspected that mesostable emulsions either lack sufficient asphaltenes to render them completely stable or still contain too many destabilizing materials, perhaps some aromatics and aliphatics. The viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Mesostable emulsions may degrade to form layers of oil and stable emulsions. Mesostable emulsions can be red or black and are probably the most commonly formed emulsions in the field.

Unstable emulsions are those that decompose (largely) to water and oil rapidly after mixing, generally within a few hours. Some water (usually less than about 10%) may be retained by the oil, especially if the oil is viscous.

The most important measurements to characterize emulsions are forced oscillation rheometry studies. The presence of significant elasticity clearly defines whether a stable emulsion has been formed. The viscosity by itself can be an indicator of the stability of the emulsion, although it is not necessarily conclusive, unless one is fully certain of the viscosity of the starting oil. Colour is an indicator, but may not be definitive. This laboratory's experience is that all stable emulsions were reddish. Some mesostable emulsions had a reddish colour and unstable emulsions were always the colour of the starting oil. Water content is not an indicator of stability and is error-prone because of 'excess' water that may be present. It should be noted, however, that stable

emulsions contain more than 70% water and unstable emulsions or entrained water-in-oil generally contain less than 50% water. Water content after a period of about one week is found to be more reliable than initial water content because separation will occur in emulsions that are less stable.

4.1.1 Summary of Laboratory Experiments

Detailed experimental procedures are given in the literature (Fingas et al., 1998). Water-in-oil emulsions were made in a rotary agitator and then the rheometric characteristics of these emulsions were studied over time. Eighty-two oils were used, taken from the storage facilities at the Emergencies Science Division. Properties of these oils are given in standard references (Jokuty et al., 1999).

Emulsions were made in an end-over-end rotary mixer (Associated Design). The apparatus was located in a temperature-controlled cold room at a constant 15°C. The mixing vessels were 2.2 L FLPE wide-mouthed bottles. The mixing vessels were approximately one-quarter full, with 600 mL of salt water (3.3% w/v NaCl) and 30 mL of the sample crude oil or petroleum product. The vessels were mounted into the rotary mixer and allowed to stand for 3 hours to thermally equilibrate. The vessels were then rotated for a period of 12 hours at a rate of 55 rpm. The vessels were approximately 20 cm in height, providing a radius of rotation of about 10 cm. The resulting emulsions were then collected into jars, covered, and stored in the same 15°C cold room. Analysis was performed on the day of collection and again one week later.

The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoStress RS Ver. 2.10 P software, 35-mm and 60-mm parallel plates with corresponding base plates, clean air supply at 40 p.s.i., and a circulating bath maintained at 15°C. Analysis was performed on a sample spread onto the base plate and raised to 2.00 mm from the measuring plate, with the excess removed using a Teflon spatula. This was left for 15 minutes to thermally equilibrate at 15°C. A stress sweep at a frequency of 1 reciprocal second was performed first to determine the linear viscoelastic range (stress-independent region) for frequency analysis. This also provides values for the complex modulus, the elasticity and viscosity moduli, the low shear dynamic viscosity, and the tan (δ) value. A frequency sweep was then performed at a stress value within the linear viscoelastic range, ranging from 0.04 to 40 Hz. This provides the data for analysis to determine the constants of the Ostwald-de-Waele equation for the emulsion. The apparent dynamic viscosity was determined on the plate-plate apparatus as well and corrected using the Weissenberg equation. A shear rate of 1 reciprocal second was employed for a period of one minute, without ramping.

A Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti Stand were used to measure water content. The reagent was Aquastar Comp 5 and the solvent, 1:1:2 Methanol:Chloroform:Toluene.

4.1.2 Laboratory Results and Discussion

The rheological data are given in Table 1. The second column of the table is the evaporation state of the oil in mass percent lost. The third column is the assessment of the stability of the emulsion based on both visual appearance and rheological properties. The power law constants, K and n, are given next. These are parameters from the Ostwald-de-Waele

equation which describes the Newtonian (or non-Newtonian) characteristics of the material. The viscosity of the emulsion is next and in column 7, the complex modulus which is the vector sum of the viscosity and elasticity. Column 8 lists the elasticity modulus and column 9, the viscosity modulus. In column 10, the isolated, low-shear viscosity is given. This is the viscosity of emulsion at very low shear rate. In column 9, the tan delta, the ratio of the viscosity to the elasticity component, is given. Finally, the water content of the emulsion is presented.

Observations were made on the appearance of the emulsions and used to classify the emulsions. All of the stable emulsions appeared to be stable and remained intact over 7 days in the laboratory. All of the mesostable emulsions broke into water, free oil, and emulsion within about 1 to 3 days. The emulsion portion of these broken down emulsions appears to be somewhat stable, although separate studies have not been performed on this portion because of the difficulty in separating them from the oil and water. All entrained water appeared to have larger suspended water droplets. The appearance of non-stable water in oil was just that - the oil appeared to be unchanged and a water layer was clearly visible.

Table 2 provides the data on the oil properties as well as a new parameter called 'stability' which is the complex modulus divided by the viscosity of the starting oil. It is noted from this table that this parameter correlates quite well with the assigned behaviour of the oils. High stability parameters imply stable emulsions and low ones imply unstable emulsions. Stability has nominally the units of mPa/mPa.s or s^{-1}, however, it can be converted to a unitless parameter by multiplying by s which is 1 in these cases.

The 'stability' parameter was used to study the correlations between the properties of the oil and the stability of the resulting emulsion. The correlations are summarized in Table 3 which shows the regression coefficient (r^2) correlations of stability with the properties of the starting oil. The regression coefficients were calculated using the program 3D TableCurve (Jandel Scientific, San Rafael, California). The regression coefficients are taken from the highest consistent value of the simple curves fit to a given set of data.

Table 3 shows that the correlations vary with each type of emulsion. For all the emulsions and oil-in-water situations, none of the parameters correlates well with stability, except for the final water content of the emulsion. This is because the less stable emulsions have little water content. It should also be noted that this is not a property of the starting oil. For stable emulsions, there is only a slight correlation with density and saturates. For mesostable emulsions, there is a relatively good correlation with density, viscosity, resins, saturates, and aromatics. This may indicate that these emulsions are temporarily stabilized by a combination of viscous forces and resin stabilization. Entrained water stability correlates best with density, aromatics, viscosity, and resin content, which indicates that these may be most dominated by viscous forces. Finally, in the case of unstable emulsions, no parameter correlates well. This appears to confirm the findings that none of the stabilization forces noted is operative.

It is important to recognize that there may be a strong interaction between parameters. To check for this, the TableCurve 3D program was used to correlate three parameters simultaneously. Results of this are shown in Table 4. Again, only the consistently highest regression coefficient (r^2) was taken. This table shows that there are several two-way interactions. For all water-in-oil

forms, there is no significant correlation between the parameters tested. For stable emulsions, there is a strong correlation between stability and viscosity and asphaltenes. This did not show on a two-way parameter correlation, presumably because of the interaction between parameters.

The best correlation for mesostable emulsions is that of stability with resins and viscosity, followed very closely by correlations of stability, viscosity with asphaltenes, aromatics, and density. The correlation of stability with viscosity and resins for water entrained in oil shows that the stability of entrained water correlates best with aromatics and density. Similarly, for unstable emulsions, 'stability' correlates highly with aromatics and density along with the viscosity.

In all four correlations, sharply defined regions of stability are noted. It is also noted on the basis of these correlations that different forces are evident. For stable emulsions, there appears to be a region where viscosity, asphaltenes, and resins interact to form a stable emulsion. This is similar in mesostable emulsions, except that the importance of asphaltenes and resins is reversed. There is a region defined for entrained water on the basis of aromatic content and density. Similarly, for unstable emulsions this is also defined by aromatics and density. This confirms previous findings that stable emulsions are the result of stabilization by asphaltenes and to a secondary extent by viscous retention. Resins are only partially responsible and, in fact, if the resin/asphaltene ratio rises, the result appears to be a mesostable emulsion. Mesostable emulsions are largely the result of resin and viscosity stabilization, with asphaltenes playing a secondary role. It is interesting to note that there is a viscosity 'window' for both stable and mesostable emulsions. Oils with very high viscosity do not seem to make either stable or mesostable emulsions.

It was noted that a stability index calculated by dividing the complex modulus of the emulsion (or remains) after one week, divided by the viscosity of the starting oil, correlates very well to the assignment of the stability class. The stability parameter was correlated with other parameters that might be used as indicators of stability and the results are shown in Table 5. It can be seen from this table that the correlation varies with the type of emulsion or water-in-oil state considered. For all types, there is only a moderate correlation with the water content. It should be noted that this would be expected since the correlation is with the 7-day old sample and all but stable emulsions have lost a significant amount of water.

There is also a moderate correlation of the Ostwald-de-Waele equation parameters, which indicates non-Newtonian behaviour in the case of both stable and mesostable emulsions and Newtonian behaviour in the case of the entrained water. The entrained water class shows a high correlation with the low-shear viscosity indicating that these are largely viscosity-stabilized. Given the high correlation of the 'stability' index with the assigned properties of the emulsion, there does not appear to be other rheological parameters that can discriminate to the same extent. This is largely a result of the fact that the other parameters are generally relevant to specific water-in-oil classes and none other than the stability covers all four classes.

Ternary diagrams of the aromatic, resin, and asphaltene components of the four classes of water-in-oil states discussed here are provided in Figures 1 to 4. These diagrams show that there are overlapping regions for composition of all four types. Unfortunately, a simple compositional analysis will not discriminate between those oils that form emulsions and those that do not. This

again indicates that there is a complex interaction between components and the viscosity (and perhaps density) of the oil.

The differences in the properties of the starting oil and those of the final states after one week are shown in Table 6. This indicates that the factor defined as emulsion stability is capable of discriminating among the various states of water-in-oil studied here. Although there are overlapping ranges, the differences are generally sufficient to act as a single-value discriminator. It is noted that there are different viscosity ranges for the different states. This shows that viscous forces are responsible for part of the stability, but that after viscosity of the starting oil rises to a given point (about 20,000 mPa.s), mesostable or stable emulsions are no longer produced. This may also explain two outstanding mysteries, that of why Bunker C generally does not form emulsions and why stable emulsions are not commonly seen in actual spills. Bunker C, especially after a short period of weathering, is too viscous to form either stable or mesostable emulsions. Furthermore, if the viscosity of formation is too great, the weathering of an emulsion could increase its viscosity past a certain point and destabilization may then occur.

Table 6 also shows that the deviation from Newtonian behaviour (as shown by the power law constants) is greatest for the stable emulsions, then for mesostable emulsions, with almost no deviation noted for the entrained and unstable cases. This is the result of a high elastic component to the viscosity, as evidenced by the elastic modulus and tan delta for the stable emulsions and slightly for the mesostable emulsions. As would be expected, the water content correlates very highly with the state after one week. This is accentuated by the fact that mesostable emulsions and entrained water-in-oil have separated to a significant degree after this time.

Table 7 shows the properties of the water-in-oil states studied here. As can be seen, the properties of the starting oil differ somewhat for oils that form the various states. The properties of oil that form stable and mesostable emulsions are similar. These are oils of medium viscosity that contain a significant amount of resins and asphaltenes. Mesostable emulsions may form from oils that have higher or lower viscosities than oils that might form stable emulsions. Stable emulsions are more likely to form from those oils containing more asphaltenes than resins. Entrained water is likely to form from more viscous oils with relatively high densities. Oils of very high or very low viscosities (and densities) are unlikely to uptake water in any form. These oils typically have no asphaltenes or resins (associated with low viscosity and density) or very high amounts of these.

Table 7 also shows that the differences between the four water-in-oil states are readily discernible by appearance and rheological properties. The reddish or brown colour on formation indicates either a stable or mesostable emulsion, although stable emulsions always have a more solid appearance. The increase in apparent viscosity (from the starting oil) on formation averages about 1,100 for a stable emulsion, 45 for a mesostable emulsion, 13 for entrained water-in-oil, and an unstable emulsion shows little or no increase. This difference increases after one week. The increase in apparent viscosity after one week averages about 1,500 for a stable emulsion, 30 for a mesostable emulsion, 3 for entrained water-in-oil, and an unstable emulsion shows little or no increase. It is noted that apparent viscosity does not decrease after one week for stable emulsions only.

There are several other features noted in the summary data presented in Table 7. The wax content shows that, while there may be some correlation to viscosity, the specific wax content is not associated with the formation of any state. It is noted that density is associated with the viscosity and somewhat with the state. It is also noted that the water content correlates somewhat with the state. The average water content of stable emulsions is 80% on the day of formation, of mesostable emulsions is 62%, of entrained water is 42%, and is 5% for unstable emulsions. One must be cautious in using this as a sole discriminator, however, because of overlapping ranges. As would be expected, the water content after one week correlates very highly with the state. As already noted, this is accentuated by the fact that mesostable emulsions and entrained water-in-oil have separated to a significant degree.

These data indicate that there are 'windows' of composition and viscosity which result in the formation of each of the types of water-in-oil states. The important factors in terms of oil composition are the asphaltene and resin contents. While asphaltenes are responsible for the formation of stable emulsions, a high asphaltene content can also result in a viscosity that is higher than the region in which stable emulsions form. The asphaltene/resin ratio is generally higher for stable emulsions. In a previous work by the present author, it was shown that the migration rate of asphaltenes in emulsions is very slow (Fingas et al., 1996). This indicates that in very viscous oils, asphaltenes may migrate too slowly to allow emulsions to stabilize.

4.1.3 Conclusions on Stability Studies
Four clearly defined states of water-in-oil have been shown to be characterized by a number of measurements as well as by their visual appearance, both on the day of formation and one week later. The differences between these states and the oils that form them are summarized in Table 8.

The results of this study indicate that both stable and mesostable emulsions form due to the combination of surface-active forces from resins and asphaltenes and from viscous forces. Each type of water-in-oil state exists in a range of compositions and viscosities. There is a small difference in composition between stable and mesostable emulsions. Stable emulsions have more asphaltenes and less resins and a narrow viscosity window. Instability results when the oil has a high viscosity (over about 50,000 mPa.s) or a very low viscosity (under about 6 mPa.s) and when the oil contains less than about 3% of resins and asphaltenes. Water entrainment, rather than emulsion formation, occurs when the viscosity is from about 2,000 to 50,000 mPa.s. Stable or mesostable emulsions may not form in highly viscous oils because the migration of asphaltenes (and resins) is too slow to allow droplets to stabilize.

The role of other components of the oil is still unclear at this time. Aromatics dissolve asphaltenes and there is a small correlation observed with the stabilities. Waxes appear to have no role in emulsion formation. Density of the starting oil is highly correlated with viscosity and thus shows a correlation with stability.

The state of the final water-in-oil emulsion can be correlated with the single parameter of the complex modulus divided by the starting oil viscosity. This stability parameter also correlates somewhat with the non-Newtonian behaviour of the resulting water-in-oil mixture, the elasticity of the emulsion, and the water content. These properties are more decisive in defining the state

one week after formation because all states have largely separated into oil and water except for stable emulsions. The water content retained one week after the formation process is a very clear discriminator of state.

4.2   Studies on Energy Threshold of Formation

The kinetics of emulsion formation and the energy levels associated with their formation are important aspects of emulsions that have not yet been studied extensively. Information in these areas is needed to understand and model the emulsification process. This section reports on initial experiments to examine the kinetics and the formation energy of emulsions. It is important to note that turbulent energy is thought to be the most important form of energy related to emulsion formation. Turbulent energy could not be measured in the experiment described here, so the total energy was used as an estimate of the energy available for emulsion formation.

4.2.1 Experimental Summary

Details of the experimental work are given in Fingas et al., 1999. Water-in-oil emulsions were made in a rotary agitator and the rheometric characteristics of these emulsions studied over time. Oils were taken from the storage facilities at the Emergencies Science Division. Properties of these oils are given in standard references (Jokuty et al., 1999). The energy threshold measurements were conducted by varying the rotational rate and hence the energy of the apparatus used to make the emulsions. The emulsions were analyzed using rheological measurements as described in this report and using standard visual observations.

Emulsions were made in an end-over-end rotary mixer as noted in Section 4.1.1. After temperature equilibration, the vessels were rotated for 12 hours at between 1 and 55 rpm. The resulting emulsions were then collected into jars, covered, and stored in a 15°C cold room. Analysis was performed on the day of collection a short time after formation.

Rheology and water content were measured in the same manner as noted in Section 4.1.1. Energy calculation was related to the total kinetic energy exerted on the oil/water in the device. The total kinetic energy in each bottle is given by:

$$KE = \frac{1}{2} MV^2 \tag{2}$$

where: KE is the energy in ergs,
M is the mass in grams, here approximately 620 g of water and oil, and
V is the velocity in cm/s which is $2\pi r$ - which is rpm/60 × 7.5 cm.

By this formula, kinetic energy is then 196 x rpm^2 ergs. Ergs were used in this study because they are a much more convenient unit than the SIU Joules at these low energy levels. This simple formulation was used to assign an energy level to each rotational velocity. Again, it is important to note that the energy estimated here is the total energy input to the system and not turbulent energy which is the prime factor in emulsion formation.

Work can be defined by looking at the force applied to the system by gravity.

Since $F = ma$ $\tag{3}$

where: F = force applied to the system in newtons,
m = mass which here is 0.62 kg, and
a = the acceleration of gravity which is 9.8 m/s^2.

Thus F = 6.08 newtons

$$Work = F \times D \qquad\qquad (4)$$

where: F= the force in newtons = 6.08
D = distance through which the force moves, which here is the average height
through which the water falls, which is 15/2 cm or 0.075m

Thus, work is 6.08 × 0.075 J per revolution of the apparatus or 0.456 J per revolution of the apparatus.

4.2.2 Results and Discussion

The rheological data associated with the energy threshold experiments are given in Table 9. The second column of Table 9 is the rotational rate of the formation vessel (mixing energy). The third column is the time from mixing until the measurement was taken. The fourth column is the complex modulus which is the vector sum of the viscosity and elasticity. The fifth column gives the water content of the emulsion. The sixth column shows stability of the emulsion which is the complex modulus divided by the starting oil viscosity. The seventh column is the calculated kinetic energy applied to the system in ergs and the eighth column gives the work applied to the emulsions in J.

Observations were made on the appearance of the emulsions and these were used to classify the emulsions. All the stable emulsions remained intact over 7 days in the laboratory. All the mesostable emulsions broke down into water, free oil, and emulsion within 3 days. The emulsion portion of these breakdown fractions appears to be somewhat stable, although separate studies have not been performed on this portion because of the difficulty in separating them from the oil and water. All entrained water mixtures appeared to have larger suspended water droplets initially. The appearance of non-stable water in oil was just that - the oil appeared to be unchanged and a water layer was clearly visible.

The appearance of the oil/water throughout the process is very important in terms of understanding the process. The observations reported for each series of experiments are given in Table 10. It has also been noted that there is a progression in the formation of the emulsions. At the onset of agitation, a coarse mixture is formed, which looks like a sponge or foam. If a stable emulsion is to be formed, this occurs quickly and did not appear to revert with the oils in this study. A mesostable emulsion forms after about 20 minutes of agitation at low energy. In some cases, the mesostable emulsion can change to a less stable, three-way, water-in-oil-in-water emulsion. Most often a mesostable emulsion would remain as mesostable. The coarse mixture often remains as such.

In summary, a coarse mixture is often formed at the beginning before any other type of water-in-oil state is observed. Stable emulsions usually appear very rapidly and the coarse mixture is

sometimes not observed, probably because it is only apparent for a very short time. Mesostable emulsions appear about 20 minutes later and may stay as mesostable emulsions, but under high energy, some oils may break back down into a coarse mixture. The coarse mixture may convert into a three-way, water-in-oil-in-water emulsion which is not stable for longer than about one day until mixing ceases. The three-way emulsions retain some of the characteristics of the emulsion from which they are formed, either a mesostable or coarse mixture. Three-way emulsions do not convert into other water-in-oil states and break down after mixing ceases.

The stability and energy of formation are plotted for the four types of emulsions in Figure 5. The stability in these figures is the complex modulus divided by the viscosity of the starting oil. In summary, it was found that the 'stability', as here defined, was the only single parameter that could be used to describe the emulsions mathematically. Furthermore, stability was found to correlate very highly with other indices related to the formation of emulsions.

Figure 5 shows that for Arabian Light oil, the onset of stability is rapid and stability increases somewhat after onset. Stability is generally taken as the point at which the stability is approximately 1,000 and this is achieved at a very low energy level corresponding to a rotational rate of about 5 rpm.

The uptake of water by one sample of Bunker C is shown in Figure 6. The Bunker C takes up water very rapidly between 200 to 300 ergs (1 to 1.3 rpm). After the rapid initial uptake, the stability of the water-oil mixtures remains the same and is typical of entrained water in oil. Figure 5 also shows the relationship of stability of Prudhoe Bay with increasing energy. Water uptake is again rapid as in Bunker C, but at a higher energy threshold and a mesostable emulsion is formed. The uptake of water for Sockeye is very rapid at first, between the energy levels of 300 to 1,500 ergs (1.3 to 2.8 rpm), and after this point stability increases slowly with increasing energy.

All four oils have several similar features: initial water uptake occurs very rapidly over a short energy range; the energy threshold for initial water uptake is very low, typically around 300 ergs, except for that of Prudhoe Bay which is about 250,000 ergs; there is no stability increase for the Bunker C in which the water is entrained and for the Prudhoe Bay which forms a mesostable emulsion; and there is a slow increase in stability with increasing energy for the oils, Sockeye and Arabian Light, which form stable emulsions.

4.2.3 Conclusions on Energy Threshold
The energy threshold at the onset of the two states known as stable and entrained water is very low, 300 to about 1,500 ergs, which corresponds to a rotational rate of about 1 to 3 rpm in the formation apparatus. Total energy applied to the system was used as an indicator value. Turbulent energy could not be measured.

This study also shows that for Bunker C, which forms an entrained water state, there is no increase in stability with increasing energy input after the initial formation point. The oil that forms a mesostable emulsion, Prudhoe Bay, shows a similar tendency in that after the energy onset, which occurs at a high level of about 25,000 ergs, there is no apparent increase in stability. Both oils that form stable emulsions, Arabian Light and Sockeye, show an increasing stability

with increasing energy, although the rate of increase is gradual with increasing energy.

4.3   Studies on Migration of Asphaltenes and Resins

A series of studies was conducted to indicate the rate of asphaltene and resin migration in emulsions. Basically, the technique was to measure the asphaltene and resin content of the starting oil, in the bulk emulsion, and at the oil-water interface in the emulsion.

4.3.1 Experimental Summary

Emulsions were formed using the specified crude oil according to selected standard emulsion formation procedures outlined in Sections 4.1.1 and 4.2.1. The emulsion was then placed in a large beaker and allowed to stand in a 10°C cold room for 1 week. The oil layer on top was removed using a syringe with a large-gauge needle. The oil was collected as close to the surface as possible, with care taken to avoid the emulsion below. This sample was called the "free oil".

If the emulsion was semi-solid, the beaker was tipped to concentrate the oil at one end. Oil remaining on top of the emulsion was collected later and discarded. The emulsion remaining after the free oil was removed constituted the emulsion layer. The emulsion was broken using freeze/thaw cycles from -36°C to room temperature. The thawed emulsion was then centrifuged at >2,500 rpm for 30 minutes to separate as much water as possible.

After several cycles, the water content was minimal. It has been shown that the method of analysis of the oil for asphaltenes, saturates, aromatics, and resins is able to tolerate a small quantity of water without significantly affecting the results. This method was therefore deemed acceptable for the given application.

The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The eluted maltenes were blown dry using compressed air. The maltene components of the oil were then determined according to the methods described in Jokuty et al., 1999. Only the non-volatile portions of the oil were analyzed.

For the long-term experiment, 1,000 mL of emulsion was then placed in a large beaker and allowed to stand in a 10°C cold room for 3 months. The layer of oil was removed using a syringe with a large-gauge needle. The oil was collected as close to the surface as possible, with care taken to avoid the emulsion below. If the emulsion was semi-solid, the beaker was tipped to concentrate the oil at one end. Oil remaining on top of the emulsion was collected after and discarded. It was found that an emulsion that has survived three months has elasticity, giving the emulsion some rigidity. The top 20% of the emulsion could therefore be collected using a spatula. The top layer of the emulsion was scooped up in small quantities covering the surface of the emulsion and placed in a graduated cylinder until 200 mL had been collected. The middle layer of emulsion between the top and bottom 20% was removed in the same manner as the top portion. It was not possible to collect a full 600 mL as coalesced water on the bottom distorted the proportion. An estimation was made to leave approximately 200 mL of emulsion, which was collected for extraction.

The extraction procedure was used on both of the emulsion layers from the experiment, as well

as on the oil layer. The sampling procedure collected approximately 10 mL of oil. The sample was homogenized by simple mixing/stirring and an estimated amount of emulsion sampled to yield 10 to 15 mL of oil. In the case of the oil layer, 10 mL of mixed oil was sampled for extraction using a 10-mL disposable plastic syringe. The sample was put into a 500-mL glass separatory funnel and 100 mL of dichloromethane (DCM) and 50 mL of salt water (3.3% NaCl) were added to the sample. The separatory funnel was shaken for one minute and allowed to settle until most of the water and DCM had separated. The DCM layer was drained off to the turbid layer between the water and DCM phases and collected into a 500-mL beaker. Care was taken to ensure that there were no water droplets in the DCM layer, as the dark colour makes it difficult to determine the presence of water. A 70/30 mixture of DCM and pentane, respectively, was added to the separatory funnel. This was again shaken for one minute and allowed to settle until most of the water and DCM phases had separated and the DCM layer was drained off into the 500-mL beaker. The rinsing of the sample with 50-mL aliquots of DCM/pentane was continued until the DCM layer was clear, usually between 4 and 6 rinse cycles, depending on the oil. When the DCM layer was clear and most of the DCM/pentane removed, 50 mL of benzene was added. The separatory funnel was shaken for one minute and allowed to settle. The water layer was then drained off, down to the turbid layer, into a separate beaker to be discarded. Two rinses of de-ionized water in the amount of 100 mL were performed, discarding the water from each rinse. The remaining benzene layer and the turbid layer containing water were both collected in the 500-mL beaker containing the rest of the effluent. The contents of the 500-mL collection beaker were evaporated down in a 100-mL boiling flask until the oil sample was obtained. The oil sample was then placed under a blow-down apparatus and blown with compressed air until the remaining solvent was driven off.

The asphaltene content of the oil sample was determined by asphaltene precipitation according to ASTM Standard Method D 2007. The maltenes were blown dry using compressed air. Weight difference was used in both instances to determine quantities. Only the non-volatile portions of the oil were analyzed.

Centrifuging was used to extract oil for analysis for some experiments. Salt water (2 mL of 3.3% NaCl) was poured into a 15-mL disposable centrifuge tube. Oil (10 mL) was injected over the water from a 10-mL disposable plastic syringe. A total of 6 tubes were filled in this manner. The centrifuge tubes were then placed into a centrifuge and spun at 3,300 rpm for 2.5 hours. The tubes were not moved from their places in the centrifuge as 2 mL of oil was removed from each tube by a syringe with a large-gauge needle, keeping the tip as close to the surface as possible. The oil was collected for later analysis.

Next, 6 mL of oil was removed from the centrifuge tube using the needle-tipped syringe, again without moving the tube from the top of the remaining oil. The oil was sucked up slowly to reduce turbulence in the oil remaining in the tube. When all 6 tubes were sampled, the water under the remaining 2 mL of oil was removed by needle-tipped syringe and discarded. Then the oil and small layer of water were rinsed with two 5-mL volumes of de-ionized water. At this point, the contents of two centrifuge tubes were combined in a 25-mL beaker by washing with dichloromethane. The oil sample was blown down with compressed air until all solvent was driven off.

One series of experiments consisted of placing oil and emulsion side by side to measure the migration of asphaltenes and resins without the influence of gravity. Emulsion (120 mL) was placed into a 125-mL, wide-mouthed bottle. Teflon tape was wound around the threads of the bottle and upper rim. The mouth of the bottle was covered with a 10 x10 cm square of 105-micron nylon mesh. A 60-mm ID Teflon collar was forcefully inserted over the mouth of the bottle, to make a firm seal between the mesh and the rim of the bottle, aided by Teflon tape. An aliquot of 120 mL of the crude oil was added into another 125-mL, wide-mouthed bottle and used to form the emulsion. Teflon tape was wound around the threads and rim of the bottle and covered with a 10 x10 cm square of 105-micron nylon mesh. The first bottle was placed over the second and inserted into the Teflon collar, using the necessary force to complete the union. The bottles in the collar were laid on their sides and clamped into place with a C-clamp. Neoprene spacers were used to protect the bottles from the contact pressure of the C-clamp. The bottles remained horizontal for one week in a 10°C cold room.

The extraction procedure was used on both the emulsion side of the experiment and the source oil side. The procedure varied, depending on the quantity of water expected to be contained in the emulsion. If 25 mL or less of oil was expected in the emulsion, the entire sample was extracted. If there was more oil present, then the sample was homogenized by simple mixing/stirring and an estimated amount of emulsion sampled to yield 10 to 15 mL of oil. In the case of the oil layer, 10 mL of mixed oil was sampled for extraction using a 10-mL disposable plastic syringe, using the liquid extraction procedure described above.

4.3.2 Results and Discussion

The results of all four series of experiments are shown in Table 11 and the summary results are provided in Table 12. The experiments entitled "one-week standing" were designed to determine if there was a separation of asphaltenes between the top oil layer and the lower emulsion layer. Table 11 shows that there is a concentration of both asphaltenes and resins in the emulsion layer. While one particular experiment shows low concentration (-.04%), this result is felt to be anomalous.

It is interesting to note that both the resins and asphaltenes are concentrated in the emulsion layer. In terms of relative percent, asphaltenes are concentrated an average of 18% and resins an average of 10%. When the emulsions were formed in the blender, perhaps leading to a more stable emulsion, asphaltenes are concentrated an average of 32% and resins an average of 1%. This appears to indicate that asphaltenes move downward to the emulsion layer, whereas a much lesser amount of resins migrate. Because the emulsion layer is underneath the oil layer in this case, at least part of this migration may be due to gravity separation of the heavier asphaltenes.

The second set of experiments involved the testing of an emulsion that had been standing for 3 months. Three layers were sampled, a free oil layer from the top, the top 20% (by height measurement) of the emulsion, and the lower 20% of the emulsion. As shown in Table 12, the oil layer is depleted 0.23% in asphaltene content in absolute terms or 6% in relative terms. The top 20% is enriched by 15% in asphaltenes (relative percent) and the bottom by 74%, which indicates a strong partitioning of asphaltenes to the lower part of the emulsion system. Again, part of this may be due to gravitational settling of the asphaltenes.

A third experiment measured the asphaltene content of a salt water-emulsion-oil system in a centrifuge tube. This experiment was designed to measure whether asphaltenes would migrate to the oil-water interface. Gravity might be a factor, because the centrifugal force should move the heavier asphaltenes to the bottom. In fact, the results as shown in Table 12, indicate that there is a greater concentration of asphaltenes at the oil-water interface (47% relative). This shows that the asphaltenes will move to the oil-water interface and will be influenced by gravity.

A fourth series of experiments was conducted to examine how asphaltenes would migrate in the absence of a strong gravity effect. Two vessels were placed side by side, one with oil and the other with emulsion, with only a mesh separating the two materials. Sampling after one week showed an increase of 38% (relative) in asphaltenes in the emulsion formed from Arabian light crude and an increase of 17% in the emulsion formed from Transmountain blend oil.

These experiments show that asphaltenes migrate to the oil-water interface from the oil, which explains why an emulsion that sits for a period of time may become more viscous and stable as time progresses. During this time, asphaltenes are still migrating to the oil-water interface, thus rendering the emulsion more stable. The experiments show that migration still occurs after one or more weeks of contact. Furthermore, these experiments provide evidence that asphaltenes are the primary hydrocarbon group responsible for emulsion stability. Further work is necessary to determine if the resins will act in the same manner.

4.3.3 Conclusions on Migration of Asphaltenes and Resins

Asphaltenes are the primary agents responsible for the formation and stability of water-in-oil emulsions. These large compounds are interfacially active and behave like surfactants. Like surfactants, they can stabilize droplets of oil and water within eachother, in this case water-in-oil. While the role of resins may also be important, the experimental results in this paper did not encompass resins to the same extent as asphaltenes.

Asphaltenes migrate to the oil-water interface from solution in oil. This process can continue over weeks. Experiments conducted as long as 3 months after emulsion formation indicate that the asphaltene migration may still continue. This migration may explain the observation that many emulsions increase in stability and viscoelasticity after sitting for periods of time. Furthermore, bonding may be occurring in the film, thus increasing the elasticity and strength of the emulsion.

Table 1   Rheological Data on the Emulsions Produced from the Oils

Oil	% evap.	Visual Stability	Day of Formation Power Law Constants K	n	Viscosity (mPa.s)	Complex Modulus (mPa)	Elasticity Modulus (mPa)	Viscosity Modulus (mPa)	Isolated Low-shear Viscosity (mPa.s)	tan delta (V/E)	Water Content (%wt/wt)	One Week After Formation Power Law Constants K	n	Viscosity (mPa.s)	Complex Modulus (mPa)	Elasticity Modulus (mPa)	Viscosity Modulus (mPa)
Arabian Light	0	Stable	4.544E+04	0.0673	2.3E+04	4.7E+05	4.7E+05	5.0E+04	8.0E+04	0.11	87.42	2.521E+04	0.0660	2.3E+04	4.8E+05	4.8E+05	4.0E+04
Arabian Light	12.04	Stable	8.221E+04	0.0450	4.6E+04	4.0E+05	4.0E+05	3.7E+04	6.0E+04	0.10	88.96	3.538E+04	0.0257	3.1E+04	2.0E+05	2.0E+05	2.7E+04
Arabian Light	24.20	Stable	8.560E+04	0.0785	4.8E+04	5.1E+05	5.0E+05	5.7E+04	8.6E+04	0.11	84.71	4.081E+04	0.1226	4.3E+04	3.6E+05	3.5E+05	7.3E+04
Arabian Medium	0	Stable	8.297E+04	0.0764	5.3E+04	5.5E+05	5.5E+05	5.2E+04	8.2E+04	0.09	84.30	6.029E+04	0.0944	5.5E+04	6.8E+05	7.7E+05	7.9E+04
Arabian Medium	13.15	Stable	1.879E+04	0.5689	2.2E+04	1.5E+05	1.1E+05	1.0E+05	1.6E+04	0.93	76.52	2.663E+04	0.452	2.8E+04	2.1E+05	1.8E+05	1.2E+05
Arabian Medium	20.77	Stable	9.727E+03	0.6308	2.2E+04	7.4E+04	2.4E+04	7.2E+04	1.7E+04	2.9	73.10	1.117E+04	0.6129	2.3E+04	1.0E+05	5.0E+04	9.2E+04
Arabian Medium	30.93	Stable	2.635E+04	0.6802	5.0E+04	1.9E+05	1.0E+05	1.7E+05	2.0E+04	1.7	67.92	5.757E+04	0.4117	5.4E+04	4.0E+05	3.2E+05	2.2E+05
Belridge Heavy	0	Entrained	2.452E+04	0.7025	4.5E+04	1.4E+05	7.8E+00	1.1E+05	2.0E+04	1.5	57.20	2.609E+04	0.6933	5.4E+04	1.6E+05	8.2E+04	1.2E+05
Belridge Heavy	2.74	Entrained	2.659E+04	0.6235	5.2E+04	2.0E+05	1.1E+05	1.6E+05	2.5E+04	1.7	59.55	2.779E+04	0.6374	6.2E+04	1.8E+05	1.0E+05	1.4E+05
Bunker C (Anchorage)	0	Entrained	1.924E+04	0.8035	2.8E+04	1.3E+05	1.6E+04	1.2E+05	1.8E+04	2.4	37.77	1.903E+04	0.8567	1.5E+05	1.4E+05	3.2E+04	1.3E+05
Bunker C (Anchorage)	8.41	No									5.62						
Bunker C (1987)	0	Entrained	2.359E+04	0.1204	1.1E+05	7.2E+05	1.4E+05	6.6E+05	8.8E+04	1.3	26.47	8.419E+04	0.8335	1.4E+05	5.5E+05	6.2E+05	5.8E+05
Carpenteria	0	No									8.74						
Carpenteria	10.31	Meso	1.771E+04	0.6292	2.3E+04	7.3E+04	4.7E+04	5.8E+04	8.0E+03	1.2	71.90	4.815E+03	0.9765	2.3E+04	3.6E+04	3.2E+03	3.6E+04
Carpenteria	14.87	Meso	8.424E+04	0.4340	3.4E+04	1.3E+05	8.2E+04	9.9E+04	7.8E+04	1.2	54.28	3.024E+03	0.8845	2.1E+04	2.9E+05	2.6E+05	1.5E+05
Cook Oil Point Seep Sample	0	*Same	1.929E+05	0.7772	2.8E+05	1.2E+05	5.3E+05	1.1E+05	7.7E+04	1.8	32.15	2.191E+05	0.7207	4.0E+05	1.5E+05	8.1E+05	1.4E+05
Cook Inlet - Granite Point	0	No									<1						
Cook Inlet - Granite Point	45.32	Meso	1.893E+01	0.1983	9.8E+02	3.4E+05	3.3E+05	1.1E+05	7.8E+04	0.38	83.95	1.725E+04	0.1407	8.5E+02	2.8E+05	2.8E+05	7.4E+04
Cook Inlet - Swanson River	0	Meso	9.919E+02	0.8680	2.4E+02	1.0E+04	6.9E+03	7.7E+03	7.2E+03	0.86	75.95	4.378E+02	0.3120	1.9E+02	2.7E+04	2.2E+04	1.7E+04
Cook Inlet - Swanson River	39.89	Stable	5.914E+04	0.1624	1.6E+04	2.9E+05	2.8E+05	8.8E+04	7.4E+04	0.30	81.46	1.393E+05	0.2708	1.8E+05	8.2E+05	7.4E+05	3.3E+05
Cook Inlet - Trading Bay	0	Meso									80.83						
Cook Inlet - Trading Bay	33.30	Meso	9.539E+04	0.1852	3.8E+04	4.5E+05	4.3E+05	1.4E+05	2.3E+04	0.34	76.22	1.361E+05	0.1867	4.3E+04	5.3E+05	4.9E+05	1.5E+05
Diesel (Anchorage)	0	No									<1						
Diesel (Anchorage)	37.44	No									<1						
Diesel (Michille Burn #3)	0	No									<1						
Diesel (Michille Burn #3)	6.21	No									<1						
Diesel (Michille Burn #3)	16.32	No									12.57						
Dos Cuadras	11.17	Meso	8.550E+02	1.0000	8.0E+02	3.3E+03	1.3E+03	3.3E+03	5.0E+02	2.5	77.80	5.253E+02	1.0000	5.3E+02	4.6E+03	1.6E+03	4.2E+03
Dos Cuadras	20.30	Meso	5.839E+03	0.5776	9.8E+03	3.3E+01	2.3E+04	2.7E+04	3.6E+03	1.6	68.55	2.145E+03	1.0000	1.9E+03	1.7E+01	3.0E+03	1.3E+07
Hondo	0	Stable	1.810E+05	0.1737	1.1E+05	8.2E+05	9.1E+05	2.2E+05	3.8E+01	0.24	84.90	1.669E+05	0.1625	1.7E+05	8.8E+05	8.3E+05	2.5E+05
Hondo	16.67	Stable	2.744E+05	0.2970	1.9E+05	1.3E+05	1.1E+05	5.3E+05	8.4E+04	0.45	86.20	1.597E+05	0.5758	2.8E+05	8.4E+05	8.2E+05	8.1E+05
Hondo	32.29	No									6.24						
Jet Fuel (Anchorage)	0	No									<1						
Jet Fuel (Anchorage)	52.72	No									<1						
North Slope (Kinnic Pipeline)	0	No									<1						
North Slope (Kinnic Pipeline)	30.54	Meso	5.575E+03	0.7398	6.8E+03	1.2E+05	1.0E+05	4.8E+04	7.0E+03	0.52	61.92	1.211E+03	0.9844	1.8E+03	1.1E+04	1.3E+03	1.1E+02
North Slope (Kinnic Pipeline)	0	No									1.00						
North Slope (Northern Pipeline)	31.14	Meso	3.757E+03	0.9195	2.8E+03	1.1E+05	9.6E+04	4.7E+04	7.4E+03	0.55	69.82	1.653E+03	0.8623	1.7E+03	9.8E+03	2.2E+03	9.6E+03
North Slope (Southern Pipeline)	0	No									<1						

Table 1 ctd   Rheological Data on the Emulsions Produced from the Oils

Oil	% evap.	Visual Stability	Day of Formation Power Law Constants K	n	Viscosity (mPa.s)	Complex Modulus (mPa)	Elasticity Modulus (mPa)	Viscosity Modulus (mPa)	Isolated Low-shear Viscosity (mPa.s)	tan delta (V/E)	Water Content (%wt/w)	One Week After Formation Power Law Constants K	n	Viscosity (mPa.s)	Complex Modulus (mPa)	Elasticity Modulus (mPa)	Viscosity Modulus (mPa)
North Slope (Southern Pipeline)	29.62	Meso	8.681E+04	0.7207	8.7E+03	1.9E+05	1.7E+05	8.1E+04	1.3E+04	0.48	63.47	2.598E+04	1.001	2.2E+03	2.0E+04	7.7E+03	1.8E+04
Ptas Point	0	No									<1						
Ptas Point	23.56	No									<1						
Point Arena	0	Entrained	2.231E+05	0.6272	3.9E+05	1.4E+06	7.6E+05	1.2E+06	7.9E+05	1.52	62.22	2.744E+05	0.6255	5.4E+05	3.3E+06	2.1E+06	2.5E+06
Point Arguello Comingled	0	Stable	1.788E+05	0.1822	1.8E+06	7.8E+05	7.2E+05	3.2E+05	5.0E+04	0.49	82.31	1.483E+05	0.2883	1.8E+06	1.1E+05	1.0E+06	4.1E+05
Point Arguello Comingled	9.05	Stable	1.838E+05	0.2776	1.5E+05	8.5E+05	7.9E+05	3.0E+05	4.7E+04	0.38	87.32	1.651E+05	0.3100	1.5E+05	6.2E+05	4.7E+05	4.3E+05
Point Arguello Comingled	15.19	Entrained	8.871E+04	0.7296	1.4E+05	6.1E+05	2.7E+05	5.5E+05	8.7E+04	2.0	90.15	9.211E+04	0.7623	1.6E+05	8.0E+05	3.5E+05	7.0E+05
Point Arguello Comingled	22.12	No									4.96						
Point Arguello Heavy	0	Stable	7.054E+04	0.4375	1.5E+05	4.9E+05	4.0E+05	2.8E+05	4.5E+04	0.71	72.95	8.767E+04	0.4322	1.8E+05	7.2E+05	5.8E+05	3.9E+05
Point Arguello Heavy	17.78	No									<1						
Point Arguello Light	0	Stable	9.299E+04	0.0879	6.7E+04	6.5E+05	6.4E+05	6.8E+04	7.0E+04	0.11	93.12	9.671E+04	0.0887	9.6E+04	6.3E+05	6.2E+05	1.4E+05
Point Arguello Light	10.19	Stable	4.891E+05	0.028	2.8E+05	3.3E+06	3.3E+06	1.7E+05	2.0E+04	0.05	88.52	4.187E+05	0.0372	2.5E+05	2.8E+06	2.8E+06	3.3E+05
Point Arguello Light	19.04	Stable	5.253E+05	0.0492	2.7E+05	3.4E+06	3.4E+06	2.8E+05	4.3E+04	0.08	85.50	5.054E+05	0.0539	3.1E+05	3.5E+06	3.6E+06	4.2E+05
Point Arguello Light	28.33	Stable	1.838E+05	0.1635	1.4E+05	9.8E+05	9.6E+05	2.5E+05	4.0E+04	0.26	79.80	1.920E+05	0.1723	1.6E+05	1.5E+06	1.4E+06	4.2E+05
Port Hueneme	0	Entrained	9.899E+03	0.7689	1.6E+01	6.1E+01	2.1E+01	6.1E+01	8.6E+03	2.6	37.97	7.953E+03	0.8633	2.8E+03	4.3E+01	1.8E+01	4.7E+01
Port Hueneme	3.14	Entrained	2.464E+04	0.6939	4.6E+04	1.7E+05	8.2E+04	1.5E+05	2.3E+04	1.7	45.33	1.918E+04	0.8713	2.7E+04	1.3E+05	2.1E+04	1.2E+05
Port Hueneme	6.37	Entrained	3.895E+04	0.6873	7.1E+04	2.7E+05	1.4E+05	2.3E+05	3.6E+04	1.7	43.37	3.438E+04	0.8070	5.4E+04	2.6E+05	6.4E+04	2.4E+05
Santa Clara	0	Meso	7.315E+03	0.9272	2.1E+04	1.8E+04	2.2E+03	1.8E+04	2.8E+03	6.5	80.83	2.125E+03	0.9800	2.6E+03	2.9E+04	1.7E+04	2.4E+04
Santa Clara	11.40	Meso	3.441E+04	0.1924	2.0E+04	7.0E+05	6.9E+05	1.0E+05	7.5E+04	0.15	50.43	1.087E+05	0.1688	1.5E+04	7.5E+05	2.0E+04	7.3E+02
Santa Clara	21.63	Meso	5.440E+04	0.6664	1.0E+05	3.6E+05	2.0E+05	2.9E+05	4.7E+04	1.4	38.89	5.784E+04	0.675*	9.2E+04	3.7E+05	2.0E+05	3.3E+05
Sockeye	0	Stable	1.275E+06	0.0462	6.9E+05	6.4E+06	6.3E+06	4.0E+05	6.2E+04	0.06	87.12	8.586E+05	0.0544	6.9E+05	4.3E+06	1.0E+06	3.1E+05
Sockeye	12.50	Stable	1.805E+06	0.1873	1.7E+06	9.3E+06	8.9E+06	2.4E+06	3.9E+04	0.27	80.05	1.608E+06	0.187*	2.2E+06	1.1E+06	4.3E+06	4.9E+06
Sockeye	22.10	Stable	2.383E+05	0.1980	2.6E+05	1.4E+06	1.3E+06	3.9E+05	9.8E+04	0.35	77.34	2.385E+05	0.1948	3.1E+05	1.5E+06	1.4E+06	5.0E+05
Sumatran Heavy	0	No									20.37						
Sumatran Heavy	5.26	No									2.95						
Sumatran Light	0	No									12.54						
Taching	0	No									3.53						
Takula	0	Stable	2.573E+05	0.1063	3.9E+04	1.1E+06	1.1E+06	1.6E+05	2.5E+04	0.14	86.40	1.629E+05	0.137*	1.2E+05	1.2E+06	1.2E+06	2.1E+05
Takula	8.31	Stable	1.399E+05	0.1655	1.1E+06	1.1E+06	1.0E+06	2.1E+05	3.0E+04	0.21	82.21	1.529E+05	0.1714	1.3E+05	1.2E+06	1.1E+06	2.3E+05
Takula	15.88	Stable	1.452E+05	0.1952	1.5E+05	1.1E+06	1.1E+06	2.5E+05	4.0E+04	0.23	75.56	1.877E+05	0.179*	1.7E+05	1.2E+06	1.2E+06	2.8E+05
Taps	0	No									15.87						
Taps	13.90	No									22.64						
Taps	28.62	No									8.02						
Taps	43.43	No									7.75						
Ucang	0	Entrained	1.321E+04	0.7288	3.2E+04	1.3E+05	5.6E+04	1.1E+05	1.8E+04	2.0	37.95						
Waxy Light Heavy Blend	0	No									4.11						
Waxy Light Heavy Blend	12.00	Entrained	4.028E+04	0.7738	6.0E+03	3.1E+04	1.0E+04	3.0E+04	4.6E+03	2.8	33.37	2.703E+03	0.9194	3.7E+03	1.5E+04	2.4E+03	1.5E+04
Waxy Light Heavy Blend	19.60	Meso	2.754E+04	0.6667	4.5E+04	1.9E+05	9.6E+04	1.6E+05	2.7E+04	1.7	34.85	1.894E+04	0.7088	3.7E+04	1.1E+05	5.3E+04	1.0E+05

NM = not measurable
* Starting sample is an emulsion itself

Table 2 Properties of Starting Oil Compared to Properties of Emulsion One Week after Formation

				Starting Oil Properties								Emulsion Rheological Properties - One Week After Formation					
Oil	% evap.	Visual Stability	Density	Viscosity	Saturates	Aromatics	Resins	Asphaltenes	Waxes	Emulsion Stability	Power Law Constants K	Power Law Constants n	Viscosity (mPa.s)	Complex Modulus (mPa)	Elasticity Modulus (mPa)	Viscosity Modulus (mPa)
Sockeye	0	Stable	0.9965	45	48	31	13	8	6	95555.56	8.596E+05	0.0544	6.9E+05	2.3E+06	1.0E-06	3.1E+05
Point Arguello Light	0	Stable	0.8738	22	57	27	9	6	6	37727.27	9.671E+04	0.0581	9.6E+04	8.3E+05	8.2E+05	1.4E+05
Point Arguello Light	10.18	Stable	0.8979	76	54	30	9	8	6	36842.11	4.167E+05	0.0372	2.5E+05	2.8E+06	2.8E+06	3.3E+05
Arabian Light	0	Stable	0.8658	12	51	39	6	3	5	32857.14	3.037E+04	0.0260	2.3E+04	2.0E+05	4.6E+05	4.0E+04
Arabian Medium	0	Stable	0.8723	20	54	32	7	6	6	23148.28	8.828E+04	0.0374	5.5E+04	6.8E+05	7.7E+05	7.8E+04
Point Arguello Light	19.01	Stable	0.9132	183	48	31	12	9	7	19125.68	5.057E+05	0.0539	3.1E+05	3.5E+06	3.5E+06	2.1E+05
Takula	0	Stable	0.8637	110	55	22	13	5	0	10909.09	1.808E+05	0.1371	1.2E+05	1.2E+06	1.2E+06	2.1E+05
Sockeye	12.50	Stable	0.9166	163	44	32	15	5	5	5740.47	1.806E+05	0.1871	2.2E+05	1.1E+06	4.3E+06	4.9E+05
Arabian Light	12.04	Stable	0.8921	53	49	31	8	5	5	6060.61	3.596E+04	0.0957	3.1E+04	2.0E+05	2.0E+05	2.7E+04
Cook Inlet Swanson River	39.68	Stable	0.9143	159	56	28	7	7	3	5592.11			8.9E+05		7.4E+05	3.3E+05
Arabian Light	24.76	Stable	0.9111	92	46	38	10	6	5	5829.79	4.091E+04	0.1726	4.3E+04	3.6E+05	3.3E+05	7.3E+04
Sockeye	22.16	Stable	0.9262	629	39	34	15	16	5	2388.54	2.386E+05	0.1945	3.1E+05	1.5E+06	1.4E+06	5.0E+05
Arabian Medium	13.15	Stable	0.9102	91	42	41	7	7	5	2307.69	2.863E+04	0.1521	2.8E+04	2.1E+05	1.8E+05	1.2E+05
Point Arguello Light	26.32	Stable	0.9238	671	45	32	12	11	8	2335.17	1.820E+05	0.1733	1.6E+05	1.5E+06	1.3E+06	1.2E+05
Point Arguello Comingled	0	Stable	0.9240	523	36	25	23	16	8	2063.79	1.493E+05	0.2883	1.8E+05	1.1E+06	1.0E+06	4.1E+05
Takula	8.37	Stable	0.9086	844	52	24	10	4	0	1421.80	1.520E+05	0.1744	1.3E+05	1.2E+06	1.7E-06	2.3E+05
Hondo	0	Stable	0.9356	735	33	31	24	12	4	1197.28	1.865E+05	0.1825	1.7E+05	8.8E+05	8.3E+05	2.5E+05
Arabian Medium	20.77	Stable	0.9263	275	40	46	8	7	5	363.64	1.117E+04	0.8129	2.3E+04	1.0E+05	5.0E+04	9.2E+04
Point Arguello Heavy	0	Stable	0.9447	3250	32	32	17	18	6	221.54	8.767E+04	0.4322	1.8E+05	7.2E+05	5.8E+05	3.9E+05
Arabian Medium	30.98	Stable	0.9495	2165	33	51	9	7	5	185.61	5.757E+04	0.4417	5.4E+04	2.0E+05	3.2E+05	2.2E+05
Point Arguello Comingled	9.05	Stable	0.9628	4988	31	33	19	17	7	124.36	1.051E+05	0.2100	1.5E+05	6.2E+05	4.7E+05	4.3E+05
Hondo	16.57	Stable	0.9677	8583	27	33	20	12	7	67.06	1.037E+05	0.5753	2.8E+05	8.1E+05	6.2E+05	6.1E+05
North Slope (Southern Pipeline)	29.82	No	0.9431	961	42	39	13	5	2	97.71	N/A	N/A	1.5E+05	1.9E+05	1.7E+05	7.4E+04
North Slope (Northern Pipeline)	31.14	No	0.9402	749	44	37	12	7	7	47.06	N/A	N/A	1.2E+03	1.1E+05	9.4E-04	4.7E+04
North Slope (Middle Pipeline)	30.54	No	0.9418	900	42	38	12	7	2	32.22	N/A	N/A	1.4E+03	1.1E+05	1.0E-05	4.8E+04
Santa Clara	0	No	0.9909	504	36	22	24	13	6	95.39	2.129E+03	0.9600	2.8E+03	2.8E+03	1.7E-04	2.4E+04
Bunker C (Anchorage)	9.17	No	1.006	380000	23	42	20	15	2	1				280000		
Carpentaria	0	No	0.9155	164	44	30	17	8	7	1				164		
Hondo	32.26	No	0.9831	149700	27	28	32	13	0	1				148700		
Jet Fuel (Anchorage)	0	No	0.81	2	61	18	0	0	0	1				2		
Jet Fuel (Anchorage)	52.72	No	0.8354	2	80	19	0	0	0	1				3		
North Slope (Middle Pipeline)	0	No	0.8761	16	52	35	9	5	1	1				16		
North Slope (Northern Pipeline)	0	No	0.8719	14	51	34	9	5	1	1				14		
North Slope (Southern Pipeline)	0	No	0.8766	18	54	32	8	6	0	1				18		
Pitas Point	0	No	0.8341	2	80	18	3	0	0	1				2		
Pitas Point	23.56	No	0.8637	2	62	35	6	0	0	1				2		
Point Arguello Comingled	22.12	No	0.9853	2260000	24	33	21	22	5	1				2280000		
Point Arguello Heavy	17.78	No	0.99.2	4953000	25	31	21	22	2	1				4953000		
Sumatran Heavy	0	No	0.9372	13300	16	30	13	8	5	1				13300		
Sumatran Heavy	5.26	No	0.9372	17000	45	32	16	6	2	1				17000		
Sumatran Light	0	No	1.05	414980	70	15	8	7	24	1				414820		

Table 2 ctd. Properties of Starting Oil Compared to Properties of Emulsion One Week after Formation

		Starting Oil Properties								Emulsion Rheological Properties - One Week After Formation						
Oil	% evap.	Visual Stability	Density	Viscosity	Saturates	Aromatics	Resins	Asphaltenes	Waxes	Emulsion Stability*	Power Law Constants K	Power Law Constants n	Viscosity (mPa.s)	Complex Modulus (mPa)	Elasticity Modulus (mPa)	Viscosity Modulus (mPa)
Tacting	0	No	0.87	5138000	74	12	9	4	23	1				5138000		
Waxy Light Heavy Blend	0	No	0.9371	184	39	35	21	5	2	1				184		
Cook Inlet - Granite Point	0	No	0.8794	4	77	22	5	1	6	1				4		
Diesel (Anchorage)	0	No	0.83	2	74	24	1	0	0	1				3		
Diesel (Anchorage)	37.11	No	0.8675	5	75	23	1	0	0	1				5		
Diesel (Mobile Burn #3)	0	No	0.8380	4	76	22	2	0	0	1				4		
Diesel (Mobile Burn #3)	8.27	No	0.8427	5	73	20	2	0	0	1				5		
Diesel (Mobile Burn #3)	16.32	No	0.8147	6	73	20	2	0	0	1				6		
Dos Cuadras	0	No	0.9	51	43	30	17	6	6	1				51		
Cook Inlet - Swanson River	0	Meso	0.842	6	65	25	6	5	5	4500	4.976E+02	0.4120	1.9E+03	2.7E+04	2.2E-04	1.7E+04
Cook Inlet - Trading Bay	33.30	Meso	0.9242	278	51	32	9	8	8	1606.47	1.361E+05	0.1861	4.3E+04	5.3E+05	4.9E-05	1.5E+05
Takula	15.88	Meso	0.8961	3148	60	25	11	4	8	361.19	1.877E+05	0.1791	1.7E+05	1.2E+06	1.2E-06	2.8E+05
Carpenteria	14.87	Meso	0.9482	3426	31	36	22	11	2	84.85	3.734E+03	0.8845	2.1E+04	2.9E+05	2.6E-05	1.5E+05
Cook Inlet - Granite Point	45.32	Meso	0.9028	4119	62	28	7	3		63.12	7.725E+04	0.1401	8.5E+03	2.8E+05	2.6E-05	7.4E+04
Carpenteria	10.31	Meso	0.9298	755	40	30	19	11	5	47.56	4.85E+03	0.8765	2.3E+04	3.6E+04	3.2E-03	3.6E+04
Santa Clara	11.40	Meso	0.9479	1859	32	28	27	13	4	40.34	1.087E+05	0.1688	1.5E+04	7.5E+04	2.0E-04	7.3E+04
Dos Cuadras	11.17	Meso	0.927	187	42	31	20	7	4	24.6	N/M	N/M	6.3E+02	4.6E+03	1.5E-03	4.2E+03
Dos Cuadras	20.36	Meso	0.9467	741	41	31	19	9	6	22.94	N/M	N/M	1.9E+03	1.7E+04	3.0E-03	1.3E+04
Santa Clara	2.63	Meso	0.9672	22760	28	32	23	17	5	16.26	5.784E+04	0.8751	9.2E+04	3.7E+05	2.0E-05	3.3E+05
Beldridge Heavy	0	Meso	0.9746	72610	23	39	30	3	1	12.59	2.638E+04	0.6938	5.4E+04	1.6E+05	8.2E-04	1.2E+05
Beldridge Heavy	2.74	Meso	0.977	77135	29	38	30	4	1	10.52	2.779E+04	0.0374	6.2E+04	1.8E+05	1.0E-05	1.4E+05
Waxy Light Heavy Blend	19.65	Meso	0.9749	77580	30	35	28	6	1	6.37	1.842E+04	0.7086	3.7E+04	1.1E+05	5.3E-04	1.0E+05
Cook Inlet - Trading Bay	0	Meso	0.8602	10	62	26	7	5		1				10		
Platform Irene	0	Entrained	0.9807	7600	26	28	22	22	2	431.21	2.737E+05	0.8255	5.4E+05	3.3E+06		
Point Arguello Commingled	15.16	Entrained	0.9608	41850	27	33	21	16		19.11	9.07E+04	0.7533	1.6E+05	6.0E+05	3.5E-05	7.0E+05
Port Hueneme	3.14	Entrained	0.9745	7835	23	41	21	11	3	16.5	1.078E+04	0.8713	2.7E+04	1.2E+05	2.1E-01	1.2E+05
Bunker C (Anchorage)	0	Entrained	0.9891	18706	25	47	17	11	2	16.08	1.905E+04	0.8567	1.5E+05	1.0E+05	3.2E-01	1.3E+05
Bunker C (1987)	0	Entrained	0.982	450030	21	55	15	7	12	14.13	3.030E+04	0.0336	1.0E+05	6.5E+05	6.2E-05	5.5E+05
Port Hueneme	6.37	Entrained	0.9787	20630	23	37	20	12	5	12.39	3.130E+04	0.0070	5.4E+04	2.6E+05	6.4E-01	2.1E+05
Port Hueneme	0	Entrained	0.9662	415	24	43	20	12	5	10.4	7.255E+03	0.9533	8.8E+03	2.3E+04	4.8E-03	4.1E+04
Waxy Light Heavy Blend	12.00	Entrained	0.9582	2002	32	38	24	6	1	7.49	2.763E+03	0.9194	2.7E+03	1.5E+04	2.4E-03	1.5E+04
Beta	0	Entrained	0.9739	33390	21	38	31	7	3	1				12590		
California API 11.0	0	Entrained	0.9882	34030				16	1	1				34000		
California API 15.0	0	Entrained	0.977	6400	19	35	23	22	1	1				6400		
Point Arguello Heavy	8.83	Entrained	0.9706	58930	26	35	18	20	2	1				58990		
Udang	0	Entrained	0.9701	10700	32	41	24	3	1	1				10700		

* emulsion stability is the complex viscosity of the emulsion divided by the starting oil viscosity

Table 3	Correlation of Stability with Oil Parameters				
	All Water in Oil	Stable Emulsions	Mesostable Emulsions	Entrained Water	Unstable
Oil	Regression Coefficient	Regression Coefficient	Regression Coefficient	Regression Coefficient	Regression Coefficient
Parameter	R^2	R^2	R^2	R^2	R^2
Density	0.05	0.23	0.73	0.99	0.14
Viscosity	0.05	0.4	0.84	0.36	0.16
Saturates	0.04	0.16	0.83	0.02	0.11
Aromatics	0	0.04	0.38	0.99	0.2
Resins	0.04	0.06	0.8	0.69	0.06
Asphaltenes	0.02	0.09	0.04	0.43	0.08
Waxes	0.05	0.09	0.09	0.25	0.04
Water in emulsion -- 0.49					

Table 4	Two-Way Correlation of Stability with Oil Parameters				
	All Water in Oil	Stable Emulsions	Mesostable Emulsions	Entrained Water	Unstable
Oil	Regression Coefficient	Regression Coefficient	Regression Coefficient	Regression Coefficient	Regression Coefficient
Parameters	R^2	R^2	R^2	R^2	R^2
Viscosity - Asphaltenes	0.19	0.83	0.85	0.54	0.45
Viscosity - Resins	0.19	0.66	0.87	0.08	0.29
Viscosity - Aromatics	0	0.4	0.85	0.99	0.98
Viscosity - Density	0.19	0.4	0.85	0.98	0.97
Viscosity - Asphaltenes & Resins	0.19	0.72	0.86		

Table 5	Correlation of Stability with Emulsion Parameters				
	All Water in Oil	Stable Emulsions	Meso-Stable Emulsions	Entrained Water	Unstable Water
Emulsion	Regression Coefficient	Regression Coefficient	Regression Coefficient	Regression Coefficient	Regression Coefficient
Parameter	R^2	R^2	R^2	R^2	R^2
k (Ostwald de Waele equation)	0.6	0.64	0.17	0.89	nr
n (Ostwald de Waele equation)	0.64	0.65	0.23	0.82	nr
Emulsion viscosity	0.66	0.61	0.06	0.94	few data
Complex modulus	0.21	0.5	0.16	0.96	0.01
Elasticity modulus	0.14	0.14	0.21	0.17	few data
Viscosity modulus	0.02	0.23	0.08	0.52	few data
Low-Shear Viscosity	0.05	0.17	0.09	0.95	few data
tan Delta (V/E)	0.64	0.56	0.11	0.42	few data
Water content	0.74	0.76	0.51	0.4	0.7

Table 6   Ranges of Properties for the Various Emulsion Stabilities

Emulsion Stability	Property Range	Starting Oil Properties Density g/mL	Viscosity mPa.s	Saturates %	Aromatics %	Resins %	Asphaltenes %	Waxes %	Emulsion Stability*	Power Law Constants K	n	Viscosity (mPa.s)	Complex Modulus (mPa)	Elasticity Modulus (mPa)	Viscosity Modulus (mPa)	Isolated low-shear viscosity (mPa.s)	tan delta (V/E)
Stable	high	0.8674	8580	65	54	29	19	8	95600	8.596E+05	0.8129	6.8E+05	4.3E+06	4.3E+06	6.1E+05	9.0E+04	1.8
	low	0.8637	14	27	22	6	3	4	66	1.117E+04	0.0372	2.3E+04	1.0E+05	5.0E+04	2.7E+04	1.1E+04	0.11
high difference from unstable		-0.0376	-5328000	-18	12	-3	-3	-16	95400	857475	-0.1671	887460	-538000	4130960	596000	78600	0.4
low difference from unstable		0.6527	12	4	10	6	3	4	87	11170	0.0372	23650	99998	50998	27000	11050	0.11
high difference from mesostable		-0.0096	-13200	0	15	-1	2	0	93700	671990	-0.1636	520960	3126000	3109960	280000	44000	-10.2
low difference from mesostable		0.6217	5	-1	-3	0	0	3	87	13732.4	-0.1029	224.70	99990	48496	22800	10300	-3.13
Meso	high	0.977	22760	65	39	30	17	8	1900	1.877E+05	0.9765	1.7E+05	1.2E+06	1.2E+06	3.3E+05	5.0E+04	12
	low	0.842	6	28	25	6	3	1	1	4.376E+02	0.1401	5.3E+02	10	1.6E+03	4.2E+03	7.0E+02	0.24
high difference from unstable		-0.028	-5120000	-18	-3	-2	-5	-16	1700	185575	-0.3835	167160	-3838040	1038060	256000	36000	10.8
low difference from unstable		2.031	4	5	13	6	3	1	0	437.0	0.1461	535	8	1600	4200	700	0.24
Entrained	high	0.8807	58390	32	55	31	22	12	430	2.744E+05	0.8633	5.4E+05	3.3E+06	6.2E+05	7.0E+05	4.0E+05	8.4
	low	0.9638	2002	19	29	15	3	1	1	2.763E+03	0.6255	3.7E+03	6400	2.4E+03	1.5E+04	2.4E+03	1.0
high difference from unstable		-0.0143	-5096000	-49	13	-1	0	-12	230	272275	-0.3167	537160	-4838040	450090	696000	359000	8
low difference from unstable		0.1578	2060	-4	17	15	3	1	0	2763	0.6255	3796	6398	2100	15000	2400	1
Unstable	high	1.005	5136000	81	42	32	22	24	196	2.125E+03	0.9800	2.6E+03	5136000	1.7E+05	7.4E+04	1.2E+04	1.1
	low	0.811	2	23	12	0	0	0	1	0.000E+00	0	0.0E+00	2	0.0E+00	0.0E+00	0.0E+00	0.00

Emulsion Rheological Properties - One Week After Formation

Table 7 — Summary of Properties for the Water-in-Oil States

			Stable		Meso		Entrained		Unstable	
Starting Oil										
	Property		high	low	high	low	high	low	high	low
	Density	g/mL	0.9674	0.8637	0.977	0.842	0.9907	0.9688	1.005	0.811
	Viscosity	(mPa.s)	9580	14	22800	6	59400	2002	5140000	2
	Saturates	%	65	27	65	28	32	19	81	23
	Aromatics	%	54	22	39	25	55	29	42	12
	Resins	%	29	6	30	6	31	15	32	0
	Asphaltenes	%	19	3	17	3	22	3	22	0
	Waxes	%	8	4	8	1	12	1	24	0
Asphaltene-Resin Ratio			1.12	0.4	0.89	0.1	1.11	0.13	1.17	0
Properties on Day of Formation										
	Appearance		brown solid		brown viscous liquid		black with large droplets		like oil	
Average Ratio of Viscosity Increase			1100		45		13		1	
	Range		15000	14	250	2	70	1	8	1
Average Water Content			80		62		42		5	
	Range		93	65	83	35	62	26	23	1
	Stability*		15000	20	400	1	50	1	60	1
Properties after One Week										
	Appearance		brown solid		broken, 2 or 3 phases		separated oil and water		like oil	
Average Ratio of Viscosity Increase			1500		30		2		1	
	Range		15000	20	150	1	3	1	2	1
Average Water Content			79		38		15		2	
	Range		94	64	61	2	35	12	24	0
	Stability*		95000	88	1900	1	434	1	198	1
Power Law Constants	K		8.596E+05	1.117E+04	1.877E+05	4.376E+02	2.744E+05	2.763E+03	2.125E+03	0.000E+00
	n		0.8129	0.0372	0.9765	0.1401	0.9633	0.6255	0.9800	0
Viscosity	(mPa.s)		6.9E+05	2.3E+04	1.7E+05	5.3E+02	5.4E+05	3.7E+03	2.6E+03	0.0E+00
Complex Modulus	(mPa)		4.3E+06	1.0E+05	1.2E+06	10	3.3E+06	6400	5138000	2
Elasticity Modulus	(mPa)		4.3E+06	5.0E+04	1.2E+06	1.6E+03	6.2E+05	2.4E+03	1.7E+05	0.0E+00
Modulus	(mPa)		6.1E+05	2.7E+04	3.3E+05	4.2E+03	7.0E+05	1.5E+04	7.4E+04	0.0E+00
Shear Viscosity	(mPa.s)		9.0E+04	1.1E+04	5.0E+04	7.0E+02	4.0E+05	2.4E+03	1.2E+04	0.0E+00
Delta	(V/E)		1.8	0.11	12	0.24	9.4	1.0	1.4	0.00
Water-Content	(%w/w)		93.79	64.23	61.43	1.89	34.94	12.21	24.48	0.00
			complex modulus/viscosity of starting oil							

Table 8 — Typical Properties of the Water-in-Oil States

		Stable	Meso	Entrained	Unstable
Day of Formation Appearance		brown solid	brown viscous liquid	black with large droplets	like oil
Water Content on First Day	%	80	62	42	5
Appearance after One Week		brown solid	broken, 2 or 3 phases	separated oil and water	like oil
Water Content after One Week	%	79	38	15	2
Stable Time	days	>30	<3	<0.5	not
Starting Oil					
Density	g/mL	0.85-0.97	0.84-0.98	0.97-0.99	0.8-1.03
Viscosity	(mPa.s)	15-10000	6-23000	2000-60000	$2 - 5.1 \times 10^6$
Saturates	%	25-65	25-65	19-32	23-80
Aromatics	%	20-55	25-40	30-55	5-12
Resins	%	5-30	6-30	15-30	0-32
Asphaltenes	%	3-20	3-17	3-22	0-32
Asphaltenes/Resins		0.74	0.47	0.62	0.45
Properties on Day of Formation					
Average Ratio of Viscosity Increase		1100	45	13	1
Properties after One Week					
Average Ratio of Viscosity Increase		1500	30	2	1

Oil	Mixing Energy rpm	Time (min)	Complex Modulus (mPa)	Water Content (% w/w)	Stability (s^{-1})	Energy (ergs)	Work (J)
Table 9			**Summary of Kinetic Results**				
Sockeye							
	10	10	9.3E+03	73.6	210	19600	2700
		20	2.5E+04	79.8	540	19600	5500
		30	1.4E+05	83.9	3160	19600	8200
		60	1.7E+05	89.3	3870	19600	16400
		120	2.7E+05	90.1	6070	19600	32800
		360	3.8E+05	89.8	8500	19600	98500
		1440	9.7E+05	88.2	21440	19600	394000
	30	10	1.3E+05	85.1	2790	176400	8200
		20	3.0E+05	85.7	6670	176400	16400
		30	4.2E+05	85.7	9220	176400	24600
		60	3.8E+05	86.1	8330	176400	49200
		120	4.5E+05	86.7	9890	176400	98500
		360	5.9E+05	87.8	13110	176400	295500
		1440	8.0E+05	87.9	17670	176400	1182000
	55	10	2.7E+05	82.2	6000	592900	15000
		20	6.6E+05	84.6	14670	592900	30100
		30	7.9E+05	85.3	17440	592900	45100
		60	1.2E+06	86.1	25780	592900	90300
		120	1.9E+06	85.6	41330	592900	180600
		360	2.9E+06	83.5	63330	592900	541700
		1440	4.7E+06	82.8	103330	592900	2166900
Point Arguello Light							
	10	10	1.3E+04	78.5	570	19600	2700
		20	3.7E+04	83.7	1680	19600	5500
		30	4.7E+04	86.6	2110	19600	8200
		60	1.3E+05	93.5	6110	19600	16400
		120	3.7E+05	92.1	16820	19600	32800
		360	5.2E+05	91.8	23640	19600	98500
		1440	7.9E+05	91.7	35680	19600	394000
	30	10	5.5E+04	82.9	2500	176400	8200
		20	2.3E+05	92.2	10230	176400	16400
		30	5.1E+05	92.0	23180	176400	24600
		60	8.6E+05	91.8	39090	176400	49200
		120	7.8E+05	92.0	35230	176400	98500
		360	6.6E+05	91.7	30000	176400	295500
		1440	8.2E+05	91.2	37050	176400	1182000
	55	10	5.3E+05	90.9	23860	592900	15000
		20	5.7E+05	91.0	25680	592900	30100
		30	5.8E+05	90.9	26360	592900	45100
		60	6.5E+05	91.3	29320	592900	90300
		120	6.4E+05	91.0	28860	592900	180600
		360	8.6E+05	90.5	39090	592900	541700
		1440	2.1E+06	89.8	97500	592900	2166900

Table 10 General Observations on Emulsion Formation Over Time at Three Rates of Mixing

Stable Emulsions
Sockeye

55 rpm — The oil rapidly emulsified and attained elastic properties in less than 5 minutes. By 30 minutes, it was characterized by a pasty quality, turning to a reddish brown by 60 minutes. At the 6-hour mark, it was a lighter brown and had segregated into smaller clumps. By 24 hours, the mass consisted of small (about 1 cm), semi-solid pellets.

30 rpm — The emulsion formed at the 10-minute observation time consisted of large water droplets surrounded by a web of emulsion, described here as "coarse" emulsion due to its wide range of particle size distribution - up to 3 mm diameter in size. This quickly changed by the 20-minute mark to demonstrate more elastic properties. The colour was lighter at 30 minutes and the emulsion remained primarily on the vessel walls. At 2 hours, there were small batches of emulsion in the water. The completion of the experiment after 24 hours revealed a mix of light reddish brown emulsion in the water and darker patches of emulsion on the walls.

10 rpm — A coarse emulsion, as described above, formed within 10 minutes. Elasticity was observed at 30 minutes. By 60 minutes, the emulsion was chocolate brown, moderately stable, and with some water resolution. The colour was lighter at 6 hours, and by the end of the 24-hour period, a ball of light brown, semi-solid emulsion had formed in the water, with dark smears of emulsion on the walls.

Point Arguello Light

55 rpm — The oil rapidly emulsified and attained elastic properties in less than 10 minutes, becoming pasty in quality. This appeared essentially the same for the first 2 hours, becoming lighter in colour at the 6-hour mark and at the end of the experiment. The changes in appearance were only small.

30 rpm — The emulsion formed at the 10-minute observation time was coarse, as described above. There was water resolved to yield foam over water. The emulsion improved until at 30 minutes it had a pasty quality. The colour became lighter by the 6-hour observation and ended essentially the same in appearance.

10 rpm — The coarse emulsion generated at the 10-minute observation point rapidly resolved to water. The droplet size visibly decreased by the 30-minute mark, but still resolved water. At 60 minutes, all water was trapped into the emulsion, with no excess water present in the vessel. By the end of the experiment, excess water had reappeared in small quantity - perhaps 100 of the original 600 mL - but the appearance of the emulsion had not changed except that it was lighter brown in colour.

Emulsions Difficult to Classify
Arabian Light

55 rpm — The initial observation at 10 minutes revealed a very fluid, coarse black emulsion. The colour lightened by the 20-minute point and the emulsion became more elastic at 30 minutes. The emulsion was distributed about the walls, with very little in the water. At 60 minutes, the reddish-brown colour

Table 10 (continued)

had appeared and remained essentially the same to the end. There was some water resolution from the emulsion at all sampling times, but the character of the remaining emulsion did not appear to change with the water loss.

The second experiment under the same conditions was essentially the same until the final observation and sampling, at which point the emulsion was darker and seemed more fluid, qualitatively indicating a stability reversal. The measurements indicated similar complex modulus to the first experiment, but the water content had decreased. It had been observed in the past that with Arabian Light, there can be dramatically different results between runs under the same test conditions over a 12-hour mixing time. It would appear that there was an as yet unidentified process that was causing these variances.

30 rpm   The first observation at 10 minutes revealed a coarse emulsion that quickly broke to rag. This was observed until the 2-hour point, when the coarse emulsion decayed to water and emulsion. By the end of the experiment, the emulsion was dark brown but water was still gradually resolved. The second experiment under the same conditions showed essentially the same results up to the 2-hour mark, at which point the emulsion seemed to reverse, completely breaking down by the end of the experiment. This appeared similar to, but more dramatic than, the run at 55 rpm.

10 rpm   The emulsion formed was essentially the same throughout the experiment, not changing from a coarse black emulsion that quickly resolved water, leaving rag over a layer of water.

Mesostable Emulsions
Green Canyon 7.7% (w/w) weathered

55 rpm   The emulsion formed was generally a coarse emulsion, smeared on the walls and decaying to water and emulsion. By 1 hour, there was a brownish colouration, but at the-2 hour observation point, the emulsion appeared "fatigued". The emulsion had lost its ability to retain the large droplets characteristic of the coarse emulsion initially formed. The emulsion was mostly at the water surface, with very little on the vessel walls. By 6 hours, it was obvious that the emulsified layer on the surface was coming from droplets in the water. The system was a water-in-oil-in-water (w/o/w) emulsion. The analysis supports these observations, as the peak in the complex modulus was reached at the 1 hour sampling time and drops thereafter. There was not a huge magnitude change in the complex modulus from the 10 minute to 60 minute to 2 hour fluctuation, but was lends support to the qualitative changes noted.

30 rpm   The coarse emulsion that formed up to the 60-minute mark had rapid resolution of water. At 60 minutes, there was a brownish colouration to the emulsion smeared on the walls. By 2 hours, the emulsion on the walls was becoming pasty. At 6 hours, there was a divergence by distribution, with the emulsion on the walls being a pasty smear, while the emulsion in the water can be characterized as a w/o/w emulsion. By the end of the experiment, all the emulsion resided in the water column as a w/o/w emulsion.

10 rpm   The initial observation at 10 minutes revealed a coarse mixture smeared on the vessel walls. This was consistent until the 1-hour observation, at which point the emulsion had a brown colouration and appeared thicker and more

Table 10 (continued)
elastic, which was maintained until the end. At all sampling times, the emulsion decayed to water and emulsion upon standing.

Sockeye Sweet 17.7% (w/w) weathered

55 rpm   The emulsion formed was smeared on the walls. This was generally a coarse mixture, decaying to water and rag. By 30 minutes, there was a brownish colouration, but at the 2-hour observation point, the emulsion appeared "fatigued". The emulsion had lost its ability to retain the large droplets characteristic of the coarse emulsion initially formed. The emulsion was mostly in the water, with very little on the vessel walls. By 6 hours, it

was obvious that the emulsified layer on the surface was coming from droplets in the water. The system was a water-in-oil-in-water (w/o/w) emulsion. The complex modulus did not change throughout this transition, indicating that the water-in-oil emulsion in the water was not undergoing further change.

30 rpm   The initial observation at 10 minutes revealed a coarse emulsion smeared on the vessel walls. After 60 minutes, the emulsion seemed to become more elastic, although there was decay of the emulsion to water and emulsion at all sampling times.

10 rpm   The emulsion formed was smeared on the walls and was generally a coarse mixture. By the 60-minute observation, it had become more elastic, appearing like a meringue. At the 2-hour mark, all water was entrapped in the emulsion. This remained the same to the end of the experiment. At all sampling times, there was water resolved from the emulsion.

Entrained Water
Bunker C

All rpm   A 60-mL sample was used for this oil as the sampling regime would quickly deplete the supply due to the low water content of the samples. In all cases, the visual character of the sample did not change from the beginning to the 6-hour observation point. At the end of the experiments, there was a slight change in the malleability of the sample, as it was easier to cleave than to spread like taffy.

Table 11   Experimental Results

Hydrocarbon Group Analysis Following One Week of Standing

	Maltenes	Asphaltenes			Saturates		Aromatics			Resins		
		Total	%		%		%	1	2	Total	%
Fresh Arabian Light Crude Oil												
Source Oil												
1	1.4259	0.0587	3.95	0.1769	46.59	0.1706	44.93	0.0278	0.0044	0.0322	8.48
2	1.3610	0.0530	3.75	0.2119	47.33	0.1994	44.54	0.0291	0.0073	0.0364	8.13
3	1.4326	0.0571	3.83	0.2209	47.34	0.2107	45.16	0.0284	0.0066	0.0350	7.50
Average			3.85		47.09		44.88				8.04
Std. Dev.			0.10		0.43		0.31				0.50
Arabian Light Oil Emulsion formed on the Rotary Agitator												
Free Oil Layer												
1	1.5345	0.0668	4.17	0.2241	47.11	0.2131	44.80	0.0289	0.0096	0.0385	8.09
2	1.5902	0.0635	3.84	0.2162	46.45	0.2104	45.21	0.0303	0.0085	0.0388	8.34
3	1.5530	0.0651	4.02	0.2178	47.20	0.2040	44.21	0.0295	0.0101	0.0396	8.58
Average			4.01		46.92		44.74				8.34
Std. Dev.			0.17		0.41		0.50				0.24
Free Oil Layer												
1	1.7085	0.0702	3.95	0.2277	46.95	0.2141	44.14	0.0344	0.0088	0.0432	8.91
2	1.7575	0.0732	4.00	0.2257	46.92	0.2144	44.57	0.0336	0.0073	0.0409	8.50
3	1.8284	0.0709	3.73	0.2245	46.79	0.2174	45.31	0.0299	0.0080	0.0379	7.90
4	1.5519	0.0645	3.99	0.2285	46.22	0.2261	45.73	0.0308	0.0090	0.0398	8.05
Average			3.92		46.72		44.94				8.34
Std. Dev.			0.12		0.34		0.71				0.46
Emulsion Layer												
1	1.1458	0.0453	3.80	0.2018	46.86	0.1874	43.52	0.0294	0.0120	0.0414	9.61
2	1.2642	0.0502	3.82	0.2320	48.78	0.1994	41.93	0.0329	0.0113	0.0442	9.29
3				0.2040	47.46	0.1879	43.72	0.0295	0.0084	0.0379	8.82
4				0.2198	48.04	0.2009	43.91	0.0296	0.0072	0.0368	8.04
Average			3.81		47.79		43.27				8.94
Std. Dev.			0.01		0.82		0.91				0.68
Emulsion												
1	1.6908	0.0917	5.14	0.2242	46.41	0.2169	44.90	0.0307	0.0113	0.0420	8.69
2	1.6979	0.0923	5.16	0.2207	45.70	0.2206	45.68	0.0316	0.0100	0.0416	8.61
3	0.9414	0.0514	5.18	0.2204	46.29	0.2118	44.49	0.0349	0.0090	0.0439	9.22
4				0.2209	45.91	0.2191	45.53	0.0312	0.0100	0.0412	8.56
Average			5.16		46.08		45.15				8.77
Std. Dev.			0.02		0.33		0.56				0.30
Arabian Light Oil Emulsion formed in the Blender				*Free Oil layer contaminated after sampling*							
Emulsion												
1	1.5282	0.0789	4.91	0.2273	47.37	0.2126	44.31	0.0323	0.0076	0.0399	8.32
2	1.0931	0.0610	5.29	0.2020	47.44	0.1870	43.92	0.0300	0.0068	0.0368	8.64
3				0.2197	47.67	0.2080	45.13	0.0253	0.0079	0.0332	7.20
4				0.2076	46.87	0.1979	44.68	0.0318	0.0056	0.0374	8.44
Average			5.10		47.34		44.51				8.15
Std. Dev.			0.27		0.34		0.52				0.65

Long-term Standing (3 months)

					Asphaltene content						
Free Oil Layer											
1	1.7294	0.0644	3.59		Average		Std. Dev.				
2	1.7857	0.0677	3.65		3.62		0.04				
Top 20% of Emulsion											
1	1.7116	0.0803	4.48		Average		Std. Dev.				
2	1.7604	0.08	4.34		4.41		0.10				
Bottom 20% of Emulsion											
1	1.8953	0.14	6.83		Average		Std. Dev.				
2	1.9559	0.14	6.60		6.71		0.16				

Centrifuging Fresh Oil Over Salt Water

Arabian Light Crude Oil											
Top 20% of Oil Layer											
1	1.9181	0.0915	4.55		Average		Std. Dev.				
2	1.9521	0.0934	4.57		4.56		0.01				
Bottom 20% of Oil Layer											
1	1.7630	0.1066	5.70		Average		Std. Dev.				
2	2.3609	0.1443	5.76		5.65		0.14				
3	2.2993	0.1335	5.49								

Table 12	Summary of Asphaltene and Resin Partitioning Studies					

Arabian Light Crude and Emulsion
Separation Following One-Week Standing

Location	Asphaltenes	Resins	Asphaltenes	Resins Now	Asphal Starting	Resins
Rotary shaker	% absolute change from starting oil					
Free oil layer	0.16	0.3	4.01	8.34	3.85	8.04
Free oil layer	0.07	0.3	3.92	8.34	3.85	8.04
Emulsion layer	-0.04	0.9	3.81	8.94	3.85	8.04
Emulsion layer	1.31	0.73	5.16	8.77	3.85	8.04
Blender formation						
Emulsion layer	1.25	0.11	5.1	8.15	3.85	8.04
Long-term standing (3 months)						
Free oil layer	-0.23		3.62		3.85	
Top 20% of emulsion	0.56		4.41		3.85	
Bottom 20% of emulsion	2.86		6.71		3.85	
Centrifuging oil over salt water						
Top 20% of oil layer	0.71		4.56		3.85	
Bottom 20% of oil layer	1.8		5.65		3.85	
Side-by-side experiment (1 week)						
Oil side	0.7		4.55		3.85	
Emulsion side	1.48		5.33		3.85	
Transmountain blend oil						
Oil side	0		4.55		4.55	
Emulsion side	0.85		5.4		4.55	

Separation Following One-Week Standing

Location	Asphaltenes	Resins
Rotary shaker	% relative change from starting oil	
Free oil layer	4.2	3.7
Free oil layer	1.8	3.7
Emulsion layer	-1	11.2
Emulsion layer	34	9.1
Blender formation		
Emulsion layer	32.5	1.4
Long-term standing (3 months)		
Free oil layer	-6	
Top 20% of emulsion	14.5	
Bottom 20% of emulsion	74.3	
Centrifuging oil over salt water		
Top 20% of oil layer	18.4	
Bottom 20% of oil layer	46.8	
Side-by-side experiment (1 week)		
Oil side	18.2	
Emulsion side	38.4	
Transmountain blend oil		
Oil side	0	
Emulsion side	18.7	
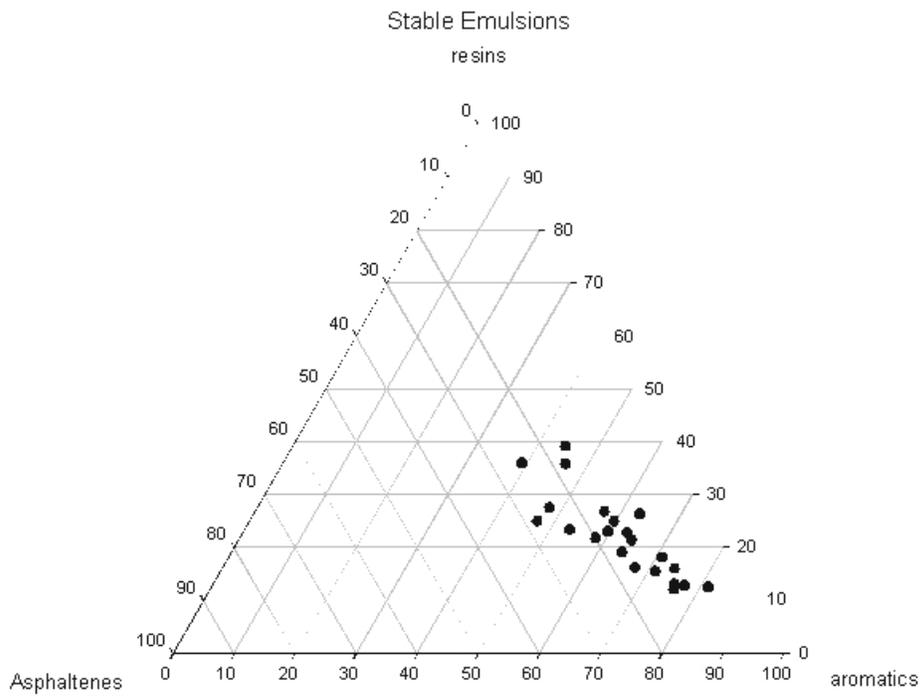
**Figure 1   Ternary Diagram of Group Contents
  - Stable Emulsions**
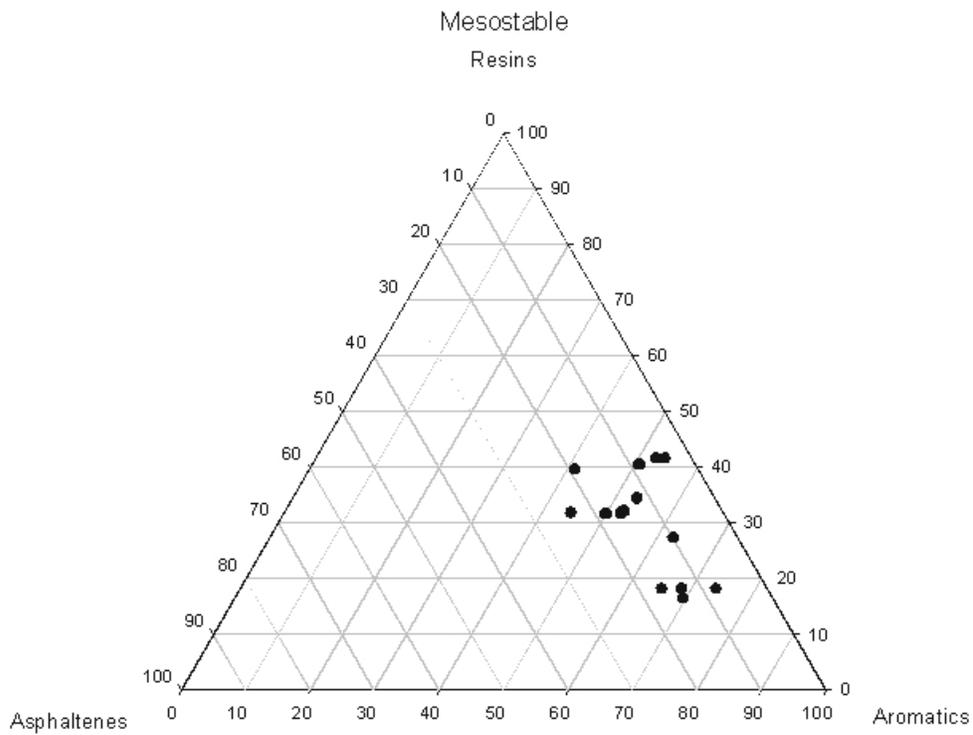
**Figure 2   Ternary Diagram of Group Contents
  - Mesostable Emulsions**
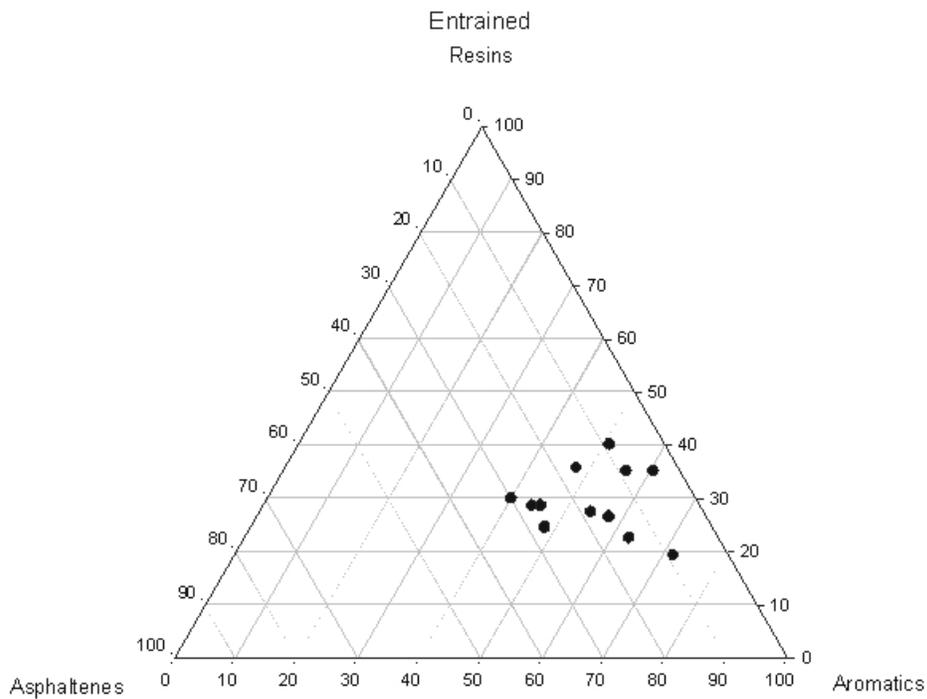
Figure 3   Ternary Diagram of Group Contents
- Entrained Water-in-Oil
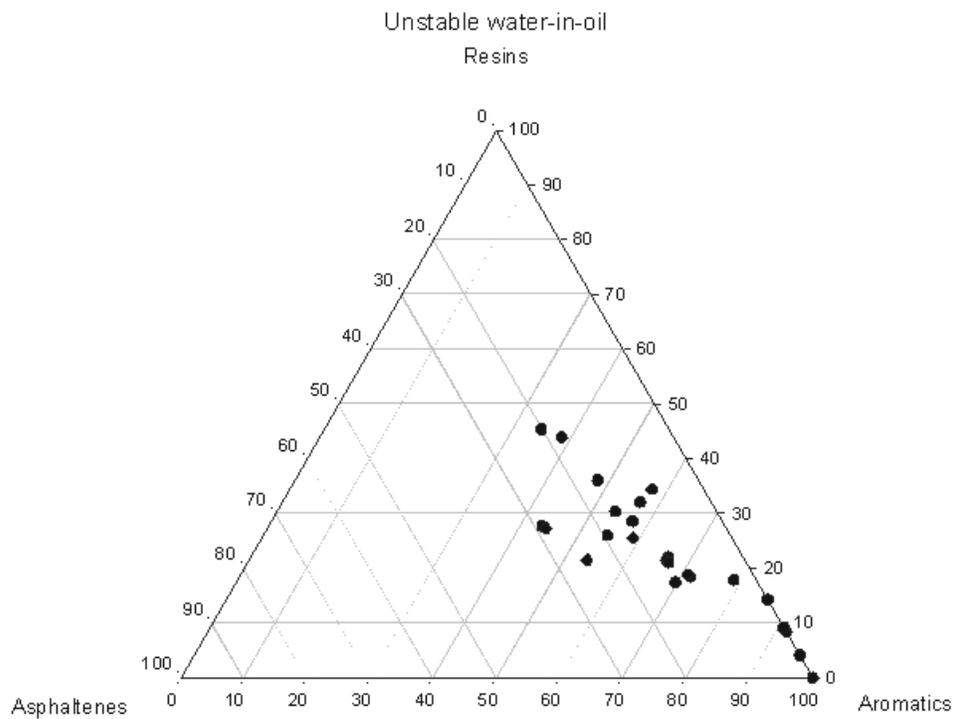
Figure 4   Ternary Diagram of Group Contents
- Unstable Emulsions
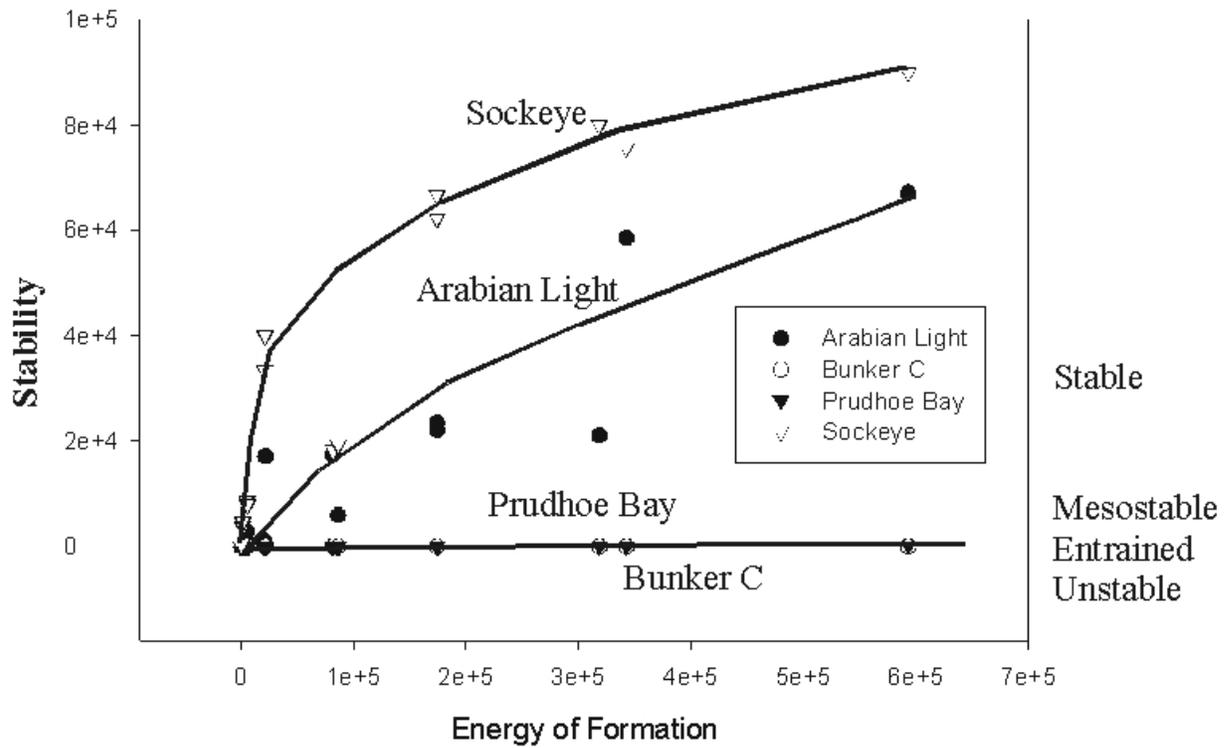
Figure 5   Relation of Stability and Energy of Formation for Emulsion for Four Oils
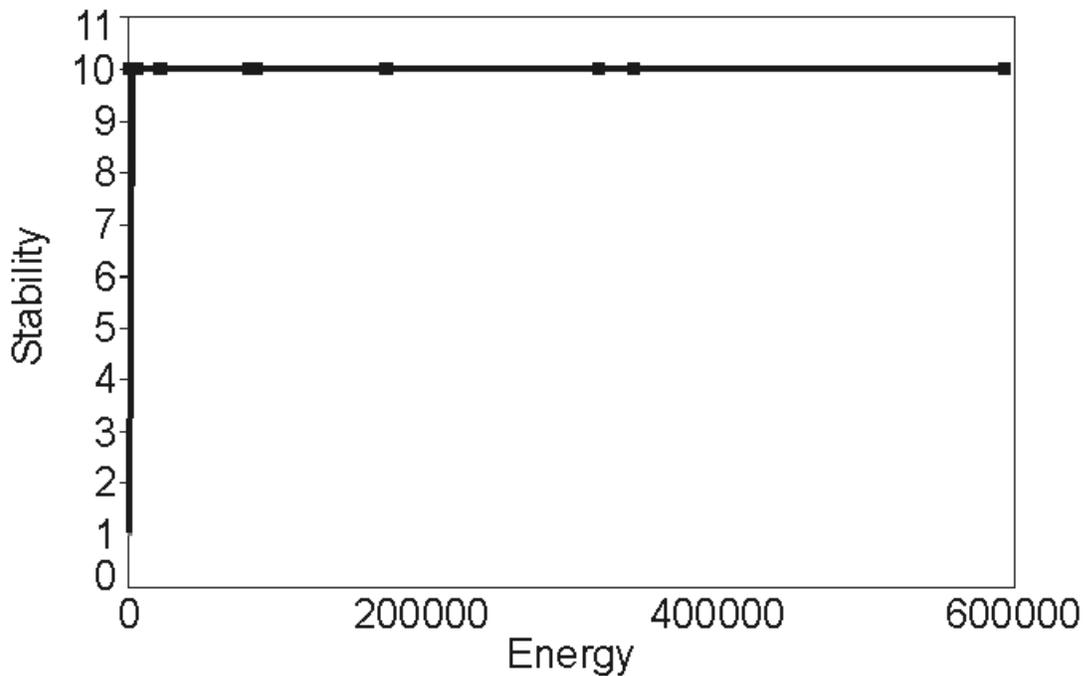
**Figure 6   Relation of Stability and Energy of Formation
for Water Inclusion of Bunker C - Water is Entrained**

5.   Study of Emulsion Formed at Sea - The *Erika*
One very important question was whether emulsions actually formed at sea would fit this concept of different water-in-oil states. An emulsion formed in the lab, the starting oil, and an emulsion formed at sea in the *Erika* spill were analyzed. The emulsion was stable. The water content was 57.2%, the complex modulus was 480,000 kPa, and the tan delta was 1. The asphaltene content was 7% and the resin content was 16%, yielding an asphaltene:resin ratio of 0.4. The data from this emulsion fit the parameters of a typical stable emulsion as described earlier (Fingas et al., 2000b). Thus, this emulsion formed at an actual spill fits the same parameters as emulsions formed in the laboratory.

6.   OHMSETT Tank Tests
6.1   Introduction
The relationship of the emulsions formed during the laboratory studies noted above to emulsions actually formed at sea is an important consideration. There are some concerns that laboratory studies may not be relevant to emulsions formed at actual spills. These concerns are based on the fact that there are major wall effects in laboratory vessels and the energy level may be undefined, as well as several other factors in the field that may not be accounted for in laboratory experiments.

A practical way to approach this study is to conduct parallel studies on real spills in the field and in the laboratory. The opportunities for studying the formation of emulsions at real spills, however, are very limited. Most oil spills do not result in the formation of stable emulsions that can be transported back to the laboratory. The water in oil from spills often changes significantly before it can be measured.

In order to study emulsions on a larger scale, the OHMSETT facility of the U.S. Minerals Management Service in New Jersey was used. It should be added, however, that using this facility does not preclude the problems of wall effects, energy, and possible other factors. The test slicks at OHMSETT must be contained and the energy levels are still unknown, as are the wave regime relationships to those of the open ocean.

6.2   First Round of OHMSETT Tests
The first round of OHMSETT tests consisted of two series of three tests each, one in July and the other in November, 2000. These tests were conducted at the OHMSETT facility to examine larger-scale water take-up and emulsion formation. These tests are described in this section.

6.2.1 Methodology
The tests were conducted in a manner similar to the laboratory tests described in Section 4.1.1, 4.2.1, and 4.3.1, although using the features of the OHMSETT tank. To compare the OHMSETT results to those of the laboratory, the same oils were run through the standard laboratory tests described in Section 4.1.1.

The OHMSETT facility has an above-ground concrete tank measuring 203 m long, 20 m wide, and 3.4 m deep. The tank is filled with 9.84 million L of brackish water from nearby Sandy Hook Bay. Salt is occasionally added to the tank to make the water more saline, although this is

diluted by rain water over time. The facility has a tow bridge capable of towing test equipment at speeds of up to 6.5 knots, which was used in these tests to anchor circular containment booms approximately 5 m in diameter. An auxiliary bridge provided an additional anchor point. A wave generator at one end of the tank can be set to 4 different stroke lengths and a relatively continuous variation in frequency of up to about 0.5 Hz.

The test oils were obtained by Mar through MMS regional contacts or contacts with refineries in the New Jersey area. Oils were poured from drums into smaller containers and enough oil was added to create the desired nominal slick thickness, calculated to be 20 L/mm. At the start of an experiment, the oil was placed in each of the four boom containment areas. A sample of the starting oil was taken and its properties measured. For the first series of tests conducted in July, samples were taken at intervals of approximately 1, 4, 7, 11, and 22 hours. (Some samples were taken at the 3- and 4-hour intervals.) For the second series of test, this sampling period was standardized to 1, 3, 6, 10, and 22 hours.

Rheology - The rheological properties of emulsions were measured using the Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoStress RS Ver. 2.10 P software, 35-mm parallel plate spindle with corresponding base plate, and a circulating bath maintained at 15.0°C. Analysis was performed on a sample spread onto the base plate and raised 2.00 mm from the measuring plate, with the excess removed using a Teflon spatula.

The sample was thermally equilibrated for only 5 minutes so that all 4 samples could be analyzed quickly, thus limiting decomposition of the emulsion. As a result, thermal equilibration was incomplete, with a corresponding impact on data values. This compromise is necessary, however, to avoid further decomposition of the emulsions over time. A stress sweep at a frequency of one reciprocal second was performed first to determine the linear viscoelastic range (stress-independent region).

The complex modulus is a measure of the overall resistance to flow under an applied stress, in units of force per unit area. This property is a matrix quantity combining the viscosity and elasticity of viscoelastic materials such as water-in-oil emulsions. Since crude oils generally do not possess significant elasticity, it has been found that dividing the complex modulus by the viscosity of the fresh oil is a useful indicator of stability of the emulsion, as a value greater than 1,000 generally indicates a stable emulsion.

Viscosity of oil - This was measured using an RV20 with RheoController, M5 measuring head, and NV cup and spindle with concentric cylinder geometry. The measurement protocol was a 5-minute ramp up to a shear rate of 100 L/s, holding for 5 minutes, then ramping back down to zero. The reported value for the oil is the average viscosity over the 5 minutes at 100 L/s.

Water content - This was measured using a Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti stand. The sample was dissolved in a 1:1:2 solution of methanol, chloroform, and toluene and titrated with the single component Karl-Fischer reagent Aquastar Comp 5. Water content is reported as percentage water by mass.

Water temperature was measured using an infrared emissivity instrument (Omega Corporation).

Data on waves was taken from the wave height meter installed at the OHMSETT facility. This instrument operates on acoustics and measures the height between the bridge and the water surface.

Water samples were taken for salinity and other analysis. It should be noted that for the second series of tests in at the end of November, the water was turbid and had a low surface tension as a result of dispersant tests conducted in the OHMSETT test tank about 2 weeks earlier.

6.2.2 Results

The results and test conditions of the first round of OHMSETT tests are summarized in Table 13. This shows that entrained water and mesostable states were produced in these tests. During the second series of tests, all states were categorized as unstable. This is probably a result of residual dispersant in the water from the dispersant tests two weeks earlier. The water content and complex modulus of the oils are given in Tables 14 and 15. The analysis was performed on the same oil in the laboratory and these results are listed in Table 16.

Observations were made on the appearance of the emulsions and used to classify the emulsions. All the stable emulsions appeared to be stable and remained intact over 7 days in the laboratory. All the mesostable emulsions broke down into water, free oil, and emulsion in about 1 to 3 days. All entrained water mixtures appeared to have larger suspended water droplets and broke down within hours to an oil and water layer, with retention of some water. The appearance of non-stable water in oil was just that - the oil appeared to be unchanged and a water layer was clearly visible. Observations were also made in another study on the formation of emulsions (Fingas *et al.*, 2000a). These show that the emulsions are formed fairly rapidly and that there is not a continuum of formation.

A comparison of the stability over time for the oils tested both in the OHMSETT facility and in the laboratory is given in Table 17. Stability is the complex modulus divided by the viscosity of the starting oil. While stability has units of s^{-1}, since the viscosity is measured at a shear rate of 1 s, it can be taken as unitless here. The stability of emulsions formed in OHMSETT and in the laboratory is summarized in Table 18. As can be seen from this table, the emulsions formed in the first series of OHMSETT tests are typically more stable than those formed in the laboratory. In the second series of tests, the emulsions were about equally stable, but generally the emulsions formed in the laboratory results are more stable.

Because of the high surfactant content of the water during the second series of tests, this inversion of stability is not surprising because even small amounts of surfactant will affect emulsion stability. The first series of tests show that the OHMSETT facility produces water-in-oil states very similar to those produced in the laboratory, indicating that the critical parameter of energy is similar in both types of tests. This is illustrated in Figures 7 to 10. These figures show the results summarized in Table 18. Table 18 summarizes the emulsions that were most stable in the two series of tests and clearly shows the OHMSETT ones were most stable in the first series and least stable in the second series.

Another important finding is that the water-in-oil states produced in both the lab and the OHMSETT tank are identical given that there are no surfactants in the tank. The hydrocarbon

group analysis results of the test oils are shown in Table 19. This shows that the asphaltene/resin ratio for Sockeye (0.74) is conducive to the formation of water-in-oil emulsions, although the product did not form a stable emulsion in any of the tests. One explanation is that asphaltene suspenders may have been added to the oil well at production time. Previous Sockeye oils formed stable emulsions (Fingas, *et al.*, 2000).

6.2.3 Summary of Findings

The first series of OHMSETT tests show that the conditions for emulsion formation are similar in the OHMSETT tank and in the laboratory tests. The prime variant is thought to be energy level. The conclusion is that the energy levels between the laboratory mixing experiments and the OHMSETT test tank are similar. During the second series of tests, surfactants left over from dispersant testing inhibited the formation of water-in-oil states. The confirmation of one emulsion formed at sea from the *Erika* spill provided some evidence that this is also similar to conditions at sea.

Four clearly defined states of water-in-oil have been characterized by a number of measurements and by their visual appearance, both on the day of formation and one week later (Fingas *et al.*, 2000). There exists a range of compositions and viscosities in which each type of water-in-oil state exist. The difference in composition between stable and mesostable emulsions is small. Stable emulsions have more asphaltenes and less resins and have a narrow viscosity window. Instability results when the oil has a high viscosity (over about 50,000 mPa.s) or a very low viscosity (under about 6 mPa.s) and when the resins and asphaltenes are less than about 3% each. Water entrainment occurs rather than emulsion formation when the viscosity is about 2,000 to 50,000 mPa.s. Stable or mesostable emulsions may not form in highly viscous oils because the migration of asphaltenes (and resins) is too slow to permit droplet stabilization.

The state of the final water-in-oil mixture can be correlated with the single parameter of the complex modulus divided by the viscosity of the starting oil (Fingas *et al.*, 2000). This stability parameter can be used to provide a clear indication of the final stability of a given emulsion and thus of its state.

6.3   Second Round of OHMSETT Tests

The second round of OHMSETT tests consisted of two series of tests, each conducted over two week periods. The first series of tests took place in July and August, 2001 and consisted of testing 9 oils and mixtures through a series of 12 experiments. The oils were sometimes tested over longer periods of time and one was tested for the full period of the experiment. During the second series of tests in November, 2002, 8 oils were used in 8 experiments. Two oils were tested for the entire period of the experiment. The rheological properties of the oils were measured and compared to the same oils undergoing emulsification in the laboratory. Some weathering studies were conducted in conjunction with the emulsification tests.

6.3.1 Methodology

The tests were conducted in a manner similar to the laboratory tests described in Section 4.1.1, 4.2.1, and 4.3.1, although using the features of the OHMSETT tank. The test oils were obtained by MAR through MMS regional contacts or contacts with refineries in the New Jersey

area. To compare the OHMSETT results to those of the laboratory, the same oils were run through the standard laboratory tests as described in Section 4.1.1. The tests and conditions are summarized in Table 1.

The rheological properties and viscosity of the oil were measured as described in Section 6.2.1.

Water content - This was measured using a Metrohm 701 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti stand. The sample was dissolved in a 1:1:2 solution of methanol, chloroform and toluene and titrated with the single component Karl-Fischer reagent Aquastar Comp 5. Water content is reported as percentage water by mass.

Water temperature was measured using an infrared emissivity instrument (Omega Corporation). Data on waves was taken from the wave height meter installed at the OHMSETT facility. This instrument operates on acoustics and measures the height between the bridge and the water surface.

Water samples were taken for salinity and other analysis.

Weathering - Samples of oils were placed in stainless steel basins and placed under the trailers to avoid direct sun exposure. At regular intervals, these were weighed and for some oils, samples were taken and the viscosity measured using the method described above.

6.4.2 Experiments in the Laboratory

Water-in-oil emulsions were made in a rotary agitator and then the rheometric characteristics of these emulsions were studied over time. Oil samples were taken from the oils poured at OHMSETT.

Emulsion Formation - Emulsions were made in an end-over-end rotary mixer (Associated Design), located in a temperature-controlled room at 15°Celsius. The mixing vessels were 2.2-L FLPE wide-mouthed bottles (Nalge). The mixing vessels were approximately one-quarter full, with 600 mL of salt water (3.3% w/v NaCl) and 30 mL of the sample crude oil or petroleum product. The vessels were mounted in the rotary mixer and allowed to stand for several hours (usually 4) to thermally equilibrate.

The vessels were placed in the rotary mixer so that the cap of each mixing vessel follows, rather than leads, the direction of rotation. The vessels were then rotated for 24 hours at the specified rate of rotation with stops at the indicated times for observation and sampling. The vessels were approximately 20 cm high, providing a radius of rotation of about 15 cm. At the conclusion of the mixing time, the emulsions were collected from the vessels to measure water content and the complex modulus.

Rheology - The following apparatuses were used for rheological analysis: Haake RS100 RheoStress rheometer, IBM-compatible PC with RheoWin software, 35-mm parallel plate with corresponding base plate, and a circulating bath maintained at 15.0ºC. Analysis was performed on a sample spread onto the base plate and raised to 2.00 mm from the measuring plate, with the excess removed using a Teflon spatula. This was left for 15 minutes to thermally equilibrate at

15°C. A stress sweep from 100 to 10,000 mPa at a frequency of one reciprocal second was performed to determine the linear viscoelastic range.

The complex modulus is a measure of the overall resistance of the material to flow under an applied stress, in units of force per unit area. This combines the elements of viscosity and elasticity for viscoelastic materials such as water-in-oil emulsions. Since crude oils generally do not possess significant elasticity, it has been found that dividing the complex modulus of the emulsion by the dynamic viscosity of the fresh oil is a useful indicator of the stability of the emulsion, as a value greater than 200 generally indicates a stable emulsion.

Water Content - A Metrohm 784 KF Titrino Karl-Fischer volumetric titrator and Metrohm 703 Ti Stand were used. The reagent was Aquastar Comp 5 and the solvent, 1:1:2 methanol:chloroform:toluene. Water content is reported as percentage.

6.4.3 Results

Results and test conditions of the second round of OHMSETT tests are summarized in Table 20. This shows that stable, entrained, and mesostable states were produced in both series of tests. The relative wave energy varied in the OHMSETT tank, despite identical settings, probably because of differences in wind direction and velocity. This does not appear to have affected the results as will be seen later.

The water content and complex modulus of the oils from the third and fourth tests are given in Tables 21 and 22. The 'stability' noted in these tables is the complex modulus (G*) divided by the viscosity of the starting oil. The stability was shown in earlier works to be a useful indicator of the state (Fingas *et al.* 1998). Stability is the complex modulus divided by starting oil viscosity. Stability has units of s^{-1}. A slight problem noted in the 2001 OHMSETT tests was that the stability of emulsions formed from heavy oils is lower than those from light oils and in some cases is not necessarily a positive indicator of water-in-oil state. It is still useful, however, and the development of an absolute indicator may be a worthwhile project in the future. For diagnostic purposes, it is useful to group the more viscous oils together and the less viscous oils together. Stability then becomes a better discriminator.

The analysis was performed on the same oil in the laboratory, as listed in Table 23. Table 24 provides a comparison of the stability over time for the oils tested both in the OHMSETT facility and in the laboratory. Stability, as given here, is the complex modulus divided by starting oil viscosity. OHM 3 and OHM 4 refer to the tests at OHMSETT, Series 3 and Series 4, respectively. This table shows that the stabilities with time compare very closely between the two OHMSETT series of tests. The stability of emulsions formed in the laboratory is usually a little higher, although the OHMSETT values later achieve comparable values. This indicates that the energy in the laboratory is slightly higher than that in the test tank. In the previous study, it was shown that the emulsions formed in the OHMSETT tests corresponded very closely to those formed in the laboratory at 30 to 50 rpm on the shaker (Fingas *et al.*, 2001).

The stability of the emulsions measured at the same points of time was compared for the three series of tests. This is shown in Table 25. The comparison is difficult because there are not many identical time points at which the measurements were made. The overall average is about 0.6.

This indicates that, overall, the ratio of energy in the OHMSETT tank during these tests and that lab was about 0.6. In Table 25, however, it can be seen that often the stability of the particular oil or mixture during the OHMSETT test is about the same as at a later point in time. This is better illustrated in graphs. Figures 11 to 14 show the results summarized in Table 24.

Figure 11 shows that the emulsions formed from the Sockeye and a mixture of Sockeye and Rock are about the same stability as those formed in the OHMSETT 3, 4, and laboratory trials. Similarly, Figure 12 shows that the same stabilities are achieved in the OHMSETT 3 trials as achieved in the laboratory for two batches of Mars oil. Figure 13 shows that similar stabilities for Fuel Oil #6 are reached in the OHMSETT 3 trials as in the laboratory. The Sockeye/Fuel Oil #6 mixture is more stable in the laboratory than at the OHMSETT 3 trials, however, a stable emulsion was achieved in either case. It was noted in these trials that the stability of emulsions formed from heavier oils is indicated better by the complex modulus than the 'stability' index used throughout this paper. This will be further investigated in the future.

Figure 14 shows that the mixtures of Arabian light and heavy crude oils were more stable in the laboratory than in the test tank. This may be due to the unique emulsions formed by these two oils. It was noted that both of these oils form a mesostable emulsion which is interwoven with threads of 'rag'. Rag is the standard industry terminology for the remnants of a broken emulsion. Preliminary investigations into the nature of rag in the Environment Canada laboratory shows that it has many of the characteristics of a stable emulsion. The Arabian light and Arabian medium crude oils form a mesostable emulsion interlaced with the rag material. This shows a higher stability than normal because of the presence of the rag. The mesostable emulsion, however, breaks down in about one day leaving the rag material.

Weathering data collected during both series of OHMSETT tests are shown in Table 26. These data compare well to other weathering studies conducted in the laboratory. The use of the viscosity data collected during the weathering studies is illustrated in Figure 15. This figure shows that using the viscosity values at the same time as the stability measure is taken results in a much better view of the emulsion state. In the case of Sockeye, the oil forms a mesostable emulsion, then breaks. The breaking is not shown well in the upper plot using only the starting viscosity. In fact, because the viscosity rises again with weathering, it may appear that the emulsion has re-formed as it appears

6.4.4 Conclusions

This second round of testing shows that the conditions for emulsion formation are similar in the OHMSETT tank and in the laboratory tests. The prime variant is thought to be energy level. The conclusion is that the energy levels between the laboratory mixing experiments and the OHMSETT test tank are similar. With the exception of the Arabian crude oils, nearly identical water-in-oil states with similar stability are produced in similar times. The energy levels used in the laboratory for this set of experiments were high and thus the levels in the OHMSETT tank appear lower. The stability of emulsions formed in the OHMSETT tank lagged behind the laboratory ones in time, although by about 24 hours, similar stabilities were achieved. This also indicates that, if there is an energy threshold, both the laboratory and OHMSETT conditions are above that energy threshold to produce emulsions.

Four clearly defined states of water-in-oil have been characterized by a number of measurements and by their visual appearance, both on the day of formation and within one week later (Fingas *et al.*, 2000). All four states were produced during these experiments. Identical states were produced in the OHMSETT and laboratory experiments. The energy levels in the laboratory tests and those in the OHMSETT tank are comparable. The test results indicate that the OHMSETT levels are similar to those conducted in the laboratory at between 50 and 70% of maximum energy.

The state of the final water-in-oil mixture can be correlated with the single parameter of the complex modulus divided by the starting oil viscosity (Fingas *et al.*, 2000). This stability parameter has been used to provide an indication of the final stability of a given emulsion and thus of its state. It was noted in these series of experiments that stability may not provide a definitive indication of the state for heavier oils. Mars and Fuel Oil #6 yielded stable emulsions at relatively low values of stability.

The Arabian light and Arabian medium crude oils used for this study produced mesostable emulsions interlaced with threads of rag which gave high stability values. The emulsions, however, broke in about a day, leaving recoverable rag.

	First Series - July			Second Series - November		
Table 13				**Summary of Tests and Conditions - First Round of OHMSETT Tests**		
	First Series - July			**Second Series - November**		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Start Date	18-Jul	19-Jul	20-Jul	28-Nov	29-Nov	30-Nov
Oil Boom 1	Sockeye	Sockeye	Sockeye	Fuel Oil #6	Arabian Light	Sockeye
Nominal thickness (mm)	1	2	4	2	2	2
Final Result	entrained	entrained	entrained	unstable	unstable	unstable
Oil Boom 2	Sockeye	Sockeye	Sockeye	Fuel Oil #6	Arabian Light	Sockeye
Nominal thickness (mm)	3	2	0.5	2	2	2
Final Result	entrained	entrained	entrained	unstable	unstable	unstable
Oil Boom 3	Fuel Oil #6	Fuel Oil #6	Fuel Oil #6	Arabian Medium	Mars	Fuel Oil #6
Nominal thickness (mm)	1	2	4	2	2	2
Final Result	entrained	meso	meso	unstable	unstable	unstable
Oil Boom 4	Fuel Oil #6	Fuel Oil #6	Fuel Oil #6	Arabian Light	Rock	Arabian Light
Nominal thickness (mm)	3	2	0.5	2	2	2
Final Result	entrained	meso	meso	unstable	unstable	unstable
Water Temperature (^{o}C)	27	27	27	3	3	3
Salinity (o/oo)	38	38	38	26	26	26
Water Condition	clear	clear	clear	turbid/low ST	turbid/low ST	turbid/low ST
Average Wave Height (cm)	25	27.6	28.1	18.3	19.4	11.8
Average Wave Deviation (cm)	9	7.9	6.7	10.2	10.8	4.1
Average Wave Period (sec)	2	1.9	1.92	1.8	1.8	1.4
Relative Wave Energy (cm^2/sec)	1.2	1.2	1	1.3	1.2	0.4

| Table 14 | Results from the First Series of OHMSETT Tests (First Round) | | | | | | | | | | | |

		Test 1				Test 2				Test 3			
		Boom 1		Boom 2		Boom 1		Boom 2		Boom 1		Boom 2	
		1 mm, side by side		3 mm, side by side		2 mm, front to back		2 mm, front to back		4 mm, side by side		0.5 mm, side by side	
Oil	Hours	G*	% water	G*	% water	G*	% water	G*	% water	G*	% water	G*	% water
Sockeye													
	1	9.8E+04	31.61	4.3E+04	24.28					3.7E+04	25.7	8.2E+04	27.22
	2						33.95		30.55				
	3									7.8E+04	37.1	2.7E+05	42.73
	4	1.7E+05	30.75	1.1E+05	29.52								
	7	2.8E+05	37.84	1.8E+05	34.75					1.8E+05	45.63	4.3E+05	47.95
	11	6.2E+05	44.45	2.7E+05	39.29					3.0E+05	51.87	5.2E+05	49.27
	22	1.2E+06	49.79	4.0E+05	46.66	8.3E+05	49.42	3.4E+05	54.06	1.0E+06	56.64	1.1E+06	50.71
Fuel Oil #6													
	1	5.0E+05	30.31		18.62					9.6E+05	31.5	5.0E+05	41.27
	2						43.46		55.76				
	3									4.8E+05	55.11	6.0E+05	50
	4	6.8E+05	59.47	5.8E+05	62.71								
	7	5.7E+05	60.79	6.3E+05	66.35					6.3E+05	50.06	7.0E+05	60.13
	11	6.5E+05	61.62		61.83					7.0E+05	57.27		58.23
	22	8.3E+05	65.07	8.8E+05	61.96	1.0E+06	68.65	8.0E+06	71.77	1.7E+06	64.63	8.7E+05	68.82
Beach													
End of test		9.4E+05	80.64							1.9E+06	79.9		
		9.1E+05	77.86							1.8E+06	78.13		

Starting Oil Viscosity		Barrel #1	Barrel #2	ave.		G* is complex modulus (mm^2)						
Sockeye @ 15 degrees		275.4	270.5	272.95								
Fuel Oil #6 @ 15 degrees		843.4	1033.0	938.2								

Table 15 **Results from the Second Series of OHMSETT Tests (First Round)**

Test	Hours	Boom 1		Boom 2		Boom 3		Boom 4	
		G*	% water	G*	% water	G*	% water	G*	% water
Test 1		Fuel Oil #6		Fuel Oil #6		Arabian Medium		Arabian Light	
	1	8.2E+03	7.77	3.2E+05	4.92		13.32	2.0E+03	59.51
	3	2.0E+04	7.59	2.6E+05	7.46		57.34	1.5E+03	73.78
	6	3.2E+04	10.32	9.4E+04	10.12	2.0E+03	58.57	1.0E+04	72.62
	10		10.61	1.5E+05	10.95	5.0E+03	54.21	2.4E+03	58.66
	22	1.6E+04	12.23	2.4E+05	23.78	1.2E+04	49.17	4.4E+03	41.85
Test 2		Arabian Light		Arabian Light		MARS		Rock (California)	
	1	2.4E+03	65.86		74.32			2.0E+04	6.15
	3	6.6E+03	70.73	9.3E+03	72.46		7.29	2.1E+04	10.66
	6	8.2E+03	65.45	6.1E+03	71.23	6.5E+03	64.37	2.6E+04	16.86
	10	4.0E+03	54.21	9.0E+03	53.62	8.0E+03	39.98	2.8E+04	16.01
	22	3.7E+03	47.15	3.6E+03	53.61	5.5E+03	52.42	4.3E+04	18.37
Test 3		Sockeye		Sockeye		Fuel Oil #6		Arabian Light	
	1	5.5E+03	12.94		7.13		7.51		31.91
	3	1.6E+04	26.67	1.3E+04	17.88	1.4E+04	9.84		30.56
	6	3.0E+04	31.12	2.0E+04	26.95	2.5E+05	18.75	2.0E+03	54.02
	10	5.0E+04	33.74	2.8E+04	27.95	2.4E+04	20.95	5.0E+03	61.56
	22	8.0E+04	36.67	6.1E+04	34.2	3.9E+04	30.91	1.2E+04	63.69

Oil	Starting Oil Viscosity (cP)	G* is complex modulus (mm^2)
Arabian Light	18	
Arabian Medium	24	
Fuel Oil #6	1129	
Mars	25	
Rock	3620	
Sockeye	275	

Table 16   Results from Emulsion Formation Experiments in Laboratory (First Round)

	G*	% water	G*	% water	G*	% water	G*	% water	
Time Oil			Arabian Light				Weathered		
(min) Rotation	10 RPM		30 RPM		55 RPM		55 RPM		
10	-	-	1.6E+04	78.3	8.2E+04	87.4	1.4E+04	82.5	
30	-	-	2.9E+04	82.5	1.1E+05	87.9	3.8E+04	80.4	
60	-	-	1.6E+04	81.9	7.3E+04	87.4	5.5E+04	81.1	
120	-	-	1.0E+04	76.1	7.0E+04	88.3	3.7E+04	82.6	
360	-	-	6.0E+03	68.2	8.2E+04	87.5	4.1E+04	82.6	
1440	-	-	-	61.5	7.2E+04	85.3	2.6E+04	81.0	
Stability	Unstable		Unstable		Meso		Meso		
Time Oil			Arabian Medium						
(min) Rotation	10 RPM		30 RPM		55 RPM				
10	-	-		57.3	-	-			
30	-	-		60.3	-	-			
60	-	-		52.2	-	-			
120	-	-		75.6	-	-			
360	-	-		49.3	-	-			
1440	-	-		68.5	7.6E+03	51.1			
Stability	Unstable		Unstable		Unstable				
Time Oil			Fuel Oil #6				Weathered		
(min) Rotation	10 RPM		30 RPM		55 RPM		55 RPM		
10	-	-	-	25.6	2.0E+04	26.4	-	26.9	
30	-	-	-	30.1	3.5E+04	41.6	3.4E+04	41.3	
60	-	-	1.7E+04	37.8	7.2E+04	58.3	8.0E+04	58.7	
120	-	-	2.0E+04	37.0	4.8E+05	61.4	2.2E+05	64.5	
360	-	-	2.1E+04	40.3	5.8E+05	68.9	6.3E+05	66.8	
1440	8.0E+04	-	2.6E+04	37.6	1.6E+06	76.7	1.8E+06	79.1	
Stability	Entrained		Entrained		Meso		Meso		
Time Oil			MARS				Weathered		
(min) Rotation	10 RPM		30 RPM		55 RPM		55 RPM		
Stability	Dispersed		Dispersed		Dispersed		Dispersed		
Time Oil			Rock				Weathered		
(min) Rotation	10 RPM		30 RPM		55 RPM		55 RPM		
10	-	-	2.4E+04	7.7	3.2E+04	23.5	3.8E+04	13.4	
30	-	-	-	-	4.9E+04	32.1	5.1E+04	25.2	
60	4.0E+04	33.3	3.9E+04	25.6	6.8E+04	43.2	6.5E+04	34.6	
120	5.5E+04	44.4	6.6E+04	42.3	1.1E+05	47.0	1.0E+05	49.1	
360	7.6E+04	51.5	9.8E+04	53.2	1.1E+05	51.3	1.5E+05	53.6	
1440	1.4E+05	66.0	1.1E+05	49.1	1.7E+05	58.4	1.5E+05	52.8	
Stability	Unstable		Unstable		Unstable		Unstable		
Time Oil			Sockeye				Weathered		
(min) Rotation	10 RPM		30 RPM		55 RPM		55 RPM		
10	9.5E+03	47.9	1.7E+04	44.7	1.6E+04		2.0E+04	43.9	
30	2.6E+04	64.1	3.1E+04	64.9	3.4E+04		3.8E+04	50.7	
60	3.7E+04	62.4	3.7E+04	60.3	5.1E+04		5.9E+04	57.4	
120	4.9E+04	68.9	5.4E+04	62.0	7.5E+04		9.2E+04	65.6	
360	6.1E+04	74.0	6.9E+04	63.1	8.9E+04		1.5E+05	74.0	
1440	3.0E+04	55.1	1.2E+05	64.8	1.5E+05	71.2	2.7E+05	73.3	
Stability	Entrained		Entrained		Entrained		Entrained		

Table 17 Comparision of Stability of Emulsions in OHMSETT Tests and in the Laboratory* (First Round)

Oil	Hours	OHMSETT Emulsions Original Oil Thickness 1mm	2mm	4mm	0.5	Second Round Average 2mm	Laboratory Emulsions Mixing Speed (rpm) 30	55	55W
Sockeye									
	0.17						1.0E+02	3.0E+02	5.0E+01
	0.5						1.0E+02	4.0E+02	1.0E+02
	1	4.0E+02	2.0E+02	1.0E+02	3.0E+02	4.0E+01	1.0E+02	3.0E+02	2.0E+02
	2						4.0E+01	3.0E+02	1.0E+02
	3			3.0E+02	1.0E+03	1.0E+02	2.0E+01	3.0E+02	1.0E+02
	4	6.0E+02	4.0E+02						
	6					1.0E+02			
	7	1.0E+03	7.0E+02	7.0E+02	1.6E+03				
	10					2.0E+02			
	11	2.3E+03	1.0E+03	1.1E+03	1.9E+03				
	22	4.4E+03	1.5E+03	3.7E+03	4.0E+03	3.0E+02			
	24							3.0E+02	1.0E+02
Fuel Oil #6									
	0.17							2.0E+01	
	0.5							3.0E+01	3.0E+01
	1	4.4E+02		8.5E+02	4.4E+02	1.5E+02		6.0E+01	7.0E+01
	2							4.2E+02	1.9E+02
	3			4.2E+02	5.3E+02	9.0E+01	1.0E+01	5.1E+02	5.6E+02
	4	6.0E+02	5.1E+02				2.0E+01		
	6					1.1E+02			
	7	5.0E+02	5.6E+02	5.6E+02	6.2E+02		2.0E+01		
	10					8.0E+01			
	11	5.7E+02		6.2E+02			2.5E+04		
	22	7.3E+02	7.8E+02	1.5E+03	7.7E+02	9.0E+01			
	24						8.8E+02	1.4E+03	1.6E+03
Arabian Light									
	0.17						9.0E+02	4.6E+03	8.0E+02
	0.5						1.6E+03	5.9E+03	2.1E+03
	1	1.0E+02	1.0E+02				9.0E+02	4.1E+03	3.1E+03
	2						6.0E+02	3.9E+03	2.1E+03
	3	4.0E+02	1.0E+02	5.0E+02			3.0E+02	4.6E+03	2.3E+03
	6	5.0E+02	6.0E+02	3.0E+02	1.0E+02				
	10	2.0E+02	1.0E+02	5.0E+02	3.0E+02				
	22	2.0E+02	2.0E+02	2.0E+02	7.0E+02				
	24							4.0E+03	1.4E+03
Arabian Medium									
	6		1.0E+02						
	10		2.0E+02						
	22		5.0E+02						
	24							3.0E+02	
Rock									
	0.17						1.0E+01		
	1		1.0E+01				1.0E+01		
	2						3.0E+01		
	3		1.0E+01				4.0E+01		
	7		1.0E+01						
	11		1.0E+01						
	22		2.0E+01						
	24						4.0E+01		
Mars									
	0.17					dispersed in lab			
	6		2.6E+02						
	10		3.2E+02						
	22		2.2E+02						

* Stability is the complex modulus divided by starting viscosity

Table 18		Summary of the Stabilities Achieved (First Round)					
Oil	Type Formed (most stable)	Most Stable	Stability	Second Stable	Stability	Comparison	Stability
Sockeye	entrained	OHMSETT I (1 mm)	4.40E+03	OHMSETT I (0.5 mm)	4.00E+03	Lab (55 rpm)	3.00E+02
Fuel Oil #6	meso	Lab (30 rpm)	8.80E+02	OHMSETT I (2 mm)	7.80E+02	OHMSETT II	9.00E+01
Arabian Light	meso	Lab (55 rpm)	4.00E+03	Lab weath (55 rpm)	1.30E+03	OHMSETT II	7.80E+02
Arabian Medium	unstable	OHMSETT II	5.00E+02			Lab (55 rpm)	3.00E+02
Rock	unstable	Lab (30 rpm)	4.00E+02			OHMSETT II	2.00E+02
Mars	unstable	OHMSETT II	2.20E+02			Lab	dispersed

Table 19		Hydrocarbon Group Analysis of Test Oils (First Round)			
		% Asphaltenes	% Resins	Asph/Res Ratio	
Arabian Light	Fresh	3.3	5.1	0.64	
Arabian Medium	Fresh	4.7	7.1	0.66	
Fuel Oil #6	Fresh	6.0	9.2	0.65	
MARS	Fresh	1.3	7.2	0.19	
Rock	Fresh	9.7	18.0	0.54	
Sockeye	Fresh	13.3	17.9	0.74	
Arabian Light	Weathered	3.4	5.3	0.64	
Fuel Oil #6	Weathered	5.9	9.0	0.65	
MARS	Weathered	1.3	7.2	0.19	
Rock	Weathered	10.2	18.8	0.54	
Sockeye	Weathered	16.3	21.9	0.74	
ERIKA	Fresh	8.9	15.1	0.59	

Table 20   Summary of Tests and Conditions - Second Round of OHMSETT Tests

	First Series - July-August				Second Series - October		
	Test 1	**Test 2**	**Test 3**	**Test 4**	**Test 1**	**Test 2**	**Test 3**
Start Date	July 24	July 25	July 30	01-Aug	Oct 2	Oct 3	Oct 5-11
Oil Boom 1	**Sockeye**	Same Oil	Same Oil	Same Oil	**Sockeye/Rock**	Same Oil	Same Oil
Final Result	in formation	stable	stable	stable	stable	stable	stable
Oil Boom 2	**Sockeye**	**Arabian Medium**	**Mix-Rock/Sock**	**Mix-FO#6/Sockeye**	**Sockeye**	Same Oil	Same Oil
Final Result	mesostable	mesostable	entrained	stable	stable	stable	stable
Oil Boom 3	**Fuel Oil #6**	**Rock**	**Mars**	**Bunker C**	**Mars**	**Rock**	**FO#6/Sock**
Final Result	stable	entrained	stable	entrained	stable	entrained	stable
Oil Boom 4	**Fuel Oil #6**	**Arabian Light**	**Mix-Rock/Sock**	Same Oil	**Arabian Medium**	**Arabian Light**	**Mars**
Final Result	stable	meso-stable	entrained	entrained	meso-stable	meso-stable	stable
Water Temperature (°C)	27.2	28	28	25	14	17	11 to 17
Salinity (o/oo)	28	28	28	28	23	23	23
Water Condition	clear	clear	clear	clear	clear	clear	clear
Average Wave Height (cm)	25.1	25.3	24	22.5	15.2	23.6	16.1
Average Wave Deviation (cm)	6	7.8	8.7	8.4	9.4	8.5	9.6
Average Wave Period (sec)	1.7	1.5	1.9	1.9	2	1.9	2
Relative Wave Energy (cm²/sec)	1	0.9	0.8	0.7	0.5	0.8	0.6

Table 21 — Results from the Third OHMSETT Test (Second Round)

Test	Hours	Sockeye time	Boom1 Stability	Boom1 G*	Boom1 % water	Boom2 Stability	Boom2 G*	Boom2 % water	Boom3 Stability	Boom3 G*	Boom3 % water	Boom4 Stability	Boom4 G*	Boom4 % water	
Test 1			Sockeye			Sockeye			Fuel Oil #6			Fuel Oil #6			
1			100	4.0E+04	25.62	100	4.1E+04	24.82	400	4.7E+05	68.52	400	4.8E+05	72.74	
3			600	1.5E+05	44.63	300	9.3E+04	37.04	500	5.8E+05	62.68	500	5.4E+05	61.62	
6.5			1000	2.7E+05	48.66	600	1.7E+05	48.71	400	4.4E+05	64.69	400	4.4E+05	62.99	
10.5			1400	3.9E+05		1200	3.2E+05	47.11	600	6.4E+05	67.63	600	6.5E+05	74.45	
23			2200	6.1E+05	54.91	2100	5.7E+05	54.78	500	5.6E+05	63.15	500	5.8E+05	73.31	
Test 2		Sockeye time	Same Oil			Arabian Medium			Rock			Arabian Light			
1	27					600	1.5E+04	54.75	0	3.5E+04	9.92	300	5.2E+03	48.77	
3	30					1600	3.8E+04	73.56	0	5.2E+04	17.84	300	6.2E+03	82.30	
6	33					1500	3.7E+04	70.21	0	5.0E+04	22.69	600	1.0E+04	71.44	
10	37		1000	2.9E+05	55.84	2700	6.5E+04	73.11	0	1.1E+05	24.50	500	9.5E+03	76.20	
23	50		900	2.6E+05	70.35	3000	7.1E+04	78.27	0	1.5E+05	48.66	2700	4.8E+04	82.05	
Test 3			Same Oil			Mix - Rock/Sock			Mars			Mix - Rock/Sock			
1	98		900	2.4E+05	73.19	100	2.6E+05	12.64	1100	5.6E+04	26.47	100	2.6E+05	9.19	
3	100					100	2.4E+05	27.97	2200	1.2E+05	65.29	100	2.7E+05	22.07	
6	103					100	2.7E+05	42.82	3000	1.6E+05	59.76	200	3.5E+05	28.06	
10	107		900	2.5E+05	72.88	200	3.2E+05	36.19	4200	2.2E+05	66.66	200	3.8E+05	39.21	
23.5	121		900	2.5E+05	75.04	200	4.0E+05	49.86	5100	2.6E+05		200	4.5E+05	53.14	
30	127		1200	3.3E+05	69.09	300	5.2E+05	47.88	5300	2.8E+05	59.03	300	5.7E+05		
47	144		1300	3.7E+05	77.22	300	6.1E+05	61.38	5600	2.9E+05	73.20	400	7.3E+05	58.05	
Test 4			Same Oil			Mix - Fuel #6/Sock			Bunker C			Same oil			Rock/Sock
1.5	145					0	3.0E+04	14.08	0	1.1E+05	17.80				48
3.5	147					100	1.1E+05	50.34	0	1.3E+05	25.29				50
6.5	150					200	2.5E+05	60.31	0	1.7E+05	32.71				53
9.5	153		1700	4.8E+05	78.91	700	7.9E+05	61.10	0	2.1E+05	40.37	400	7.3E+05	58.15	56
23	167		1900	5.3E+05	82.11	900	1.1E+06	66.24	0	3.0E+05	53.79	400	8.1E+05	59.30	69.5
30	174		2400	6.5E+05	81.79	1300	1.5E+06	71.87	0	3.7E+05	55.74	500	8.9E+05	55.95	76.5
47	191		4800	1.3E+06	80.20				100	5.2E+05	56.99	600	1.2E+06	62.17	93.5
48	192		2700	7.5E+05	80.12				100	5.4E+05	53.37	600	1.1E+06	64.38	94.5

G* is complex modulus (mPa)

Oil	Starting Oil Viscosity (mPa.s)
Arabian Light	18
Arabian Medium	24
Fuel Oil #6	1129
Mars	52
Rock	3620
Sockeye	275
Rock/Sockeye	1948
Sock/#6	725
Bunker C	8.7E+03
Sockeye/Mars	145
Fuel Oil #6/Mars	260
Fuel Oil#6/Sock	1137

Table 22 — Results from the Fourth OHMSETT Test (Second Round)

Test / Hours	Rock/Sock time	Stability	Boom 1 G*	Boom 1 % water	Stability	Boom 2 G*	Boom 2 % water	Stability	Boom 3 G*	Boom 3 % water	Stability	Boom 4 G*	Boom 4 % water
Test 1			**Mix - Rock/Sock**			**Sockeye**			**Mars**			**Arabian Medium**	
1		0	4.88E+03	30.58	0	1.14E+04	16.2	100	3.40E+03	37.62	100	1.55E+03	56.1
3		0	1.10E+04	20.44	100	3.44E+04	16.62	100	3.79E+03	25.50	100	2.35E+03	62.67
7		0	4.31E+04	46.94	300	1.09E+05	48.38	100	6.18E+03	17.65	200	3.88E+03	39.80
10.5		0	7.75E+04	62.50	500	1.53E+05	52.31	600	2.86E+04	58.57	500	1.21E+04	58.98
25		200	2.90E+05	73.58	1400	4.58E+05	60.44	2000	1.02E+05	73.60	3300	7.96E+04	76.38
Test 2	Rock/Sock time		**Same Oil**			**Same Oil**			**Rock**			**Arabian Light**	
1	27							0	2.64E+04	11.10	100	1.92E+03	61.63
3	29							0	4.10E+04	13.04	300	3.82E+03	80.87
7	33							0	6.55E+04	29.56	200	3.19E+03	69.06
11	37	100	2.76E+05	73.72	1800	5.81E+05	59.19	0	8.82E+04	37.78	200	2.90E+03	52.66
22	48	200	4.50E+05	73.98	2400	7.63E+05	61.05	100	2.19E+05	51.07	8100	1.13E+05	81.94
28.5	55	200	4.64E+05	75.67	2800	9.10E+05	63.89	100	3.06E+05	57.04			
48	74	300	6.38E+05	74.04	3100	9.80E+05	63.80	100	3.88E+05	61.24			
Test 3			**Same Oil**			**Same Oil**			**Mix - Fuel #6/Sock**			**Mars**	
68	142	300	5.06E+05	68.97	8100	2.58E+06	61.49	0	5.40E+04	39.81	600	2.88E+04	27.55
71	145							100	1.40E+05	53.95	1200	6.10E+04	51.91
74	148							200	2.50E+05	65.13	2100	1.10E+05	69.26
77	151	300	6.10E+05	71.54	7600	2.44E+06	68.37	100	1.14E+05	67.67	2200	1.14E+05	77.89
93	167	400	6.55E+05	72.24	8000	2.55E+06	64.57	100	1.47E+05	70.65	2400	1.27E+05	74.61
99.5	174	300	6.50E+05	73.00	8000	2.55E+06	58.24	200	2.14E+05	71.53	4000	2.10E+05	75.28
117	191	300	6.39E+05	74.56	7700	2.45E+06	61.22	300	3.09E+05	73.43	5200	2.72E+05	72.96
123.5	198	400	6.84E+05	70.16	8600	2.75E+06	57.41	500	5.50E+05	72.46	5900	3.05E+05	73.92
141	215	400	7.42E+05	72.04	10900	3.48E+06	63.81	600	6.80E+05	74.76	6200	3.21E+05	77.14
148	222	400	8.10E+05	71.26	9400	3.00E+06	65.12	900	9.90E+05	77.28	6700	3.50E+05	77.84

G^* is complex modulus (mPa)

Oil	Starting Oil Viscosity (mPa·s)
Arabian Light	14
Arabian Medium	24
Fuel Oil #6	1129
Mars	52
Rock	3400
Sockeye	320
Rock/Sockeye	1860
Sock/#6	725
Bunker C	8700
Sockeye/Mars	145
Fuel Oil #6/Mars	260
Fuel Oil#6/Sock	1137

Table 23   The Properties of Emulsions formed in the Laboratory (Second Round)

Oil

Time (min)	Arabian Light				Arabian Medium				Fuel Oil #6				MARS				Rock	
	Stability	G*	tan (delta)	H$_2$O (%)	Stability	G*	tan (delta)	H$_2$O (%)	Stability	G*	tan (delta)	H$_2$O (%)	Stability	G*	tan (delta)	H$_2$O (%)	Stability	G*
10	9300	1.3E+05	0.31	44.3	2300	5.4E+04	0.68	83.5	300	3.8E+05	0.34	15.4	600	3.3E+04	1.13	39.7	0	4.2E+04
30	14600	2.0E+05	0.21	44.6	4700	1.1E+05	0.26	82.5	100	7.4E+04	1.70	20.5	1800	1.0E+05	0.42	78.7	0	7.4E+04
60	14100	2.0E+05	0.25	44.9	6200	1.5E+05	0.27	82.5	100	1.1E+05	1.42	28.2	2200	1.1E+05	0.50	81.1	0	1.3E+05
120	12900	1.8E+05	0.27	45.6	7900	1.9E+05	0.26	84.0	600	6.9E+05	0.37	32.6	2400	1.2E+05	0.52	82.1	100	2.2E+05
360	15400	2.2E+05	0.35	44.6	11100	2.7E+05	0.19	82.6	1200	1.4E+06	0.26	38.4	5000	2.6E+05	0.52	81.8	100	2.9E+05
1440	15100	2.1E+05	0.35	45.4	20400	4.8E+05	0.16	84.5	2500	2.9E+06	0.24	40.7	4300	2.7E+05	0.81	83.4	100	4.8E+05
Stability	Meso-stable				Meso-stable				Stable				Stable				entrained	

Mixture

Time (min)	Fuel Oil #6 & MARS				Fuel Oil #6 & Sockeye				Sockeye & MARS				Sockeye & Rock			
	Stability	G*	tan (delta)	H$_2$O (%)	Stability	G*	tan (delta)	H$_2$O (%)	Stability	G*	tan (delta)	H$_2$O (%)	Stability	G*	tan (delta)	H$_2$O (%)
10	200	4.1E+04	1.27	65.6	100	3.1E+04	2.33	53.0	600	8.8E+04	0.59	81.5	0	2.4E+04	3.90	33.8
30	300	8.0E+04	0.90	70.6	200	6.4E+04	1.61	62.3	1200	1.7E+05	0.37	82.2	0	4.6E+04	2.81	60.0
60	1000	2.6E+05	0.61	73.4	400	1.1E+05	1.21	67.6	1500	2.1E+05	0.33	82.2	0	8.6E+04	1.66	59.3
120	800	2.1E+05	0.68	76.1	700	2.0E+05	0.91	74.8	1500	2.2E+05	0.40	82.4	100	1.6E+05	1.04	68.6
360	1400	3.6E+05	0.54	77.1	1300	3.7E+05	0.68	76.4	1700	2.5E+05	0.60	81.6	100	2.7E+05	1.05	72.1
1440	4700	1.2E+06	0.28	81.8	3900	1.1E+06	0.60	78.2	2200	3.2E+05	1.01	82.8	200	4.3E+05	1.32	75.5
Stability	Stable				Stable				Stable				entrained			

Oil	Starting Oil Viscosity (mPa.s)
Arabian Light	14
Arabian Medium	24
Fuel Oil #6	1129
Mars	52
Rock	3400
Sockeye	325
Rock/Sockeye	1860
Sock#6	725
Bunker C	8700
Sockeye/Mars	145
Fuel Oil #6/Mars	260
Fuel Oil#6:Sock	290

Table 24 Comparison of Emulsion Stability Between the Laboratory and Two Series of OHMSETT Tests (Second Round)

Time (hours)	Rock/Sock			Sockeye			Fuel Oil #6		Mars		Rock			Fuel #6/Sock		Mars			Arabian Medium			Arabian Light	
	OHM 3	OHM 4	Lab	OHM 3	OHM 4	Lab	OHM 3	Lab	OHM 3	Lab	OHM 3	OHM 4	Lab	OHM 3	Lab	OHM 3	OHM 4	Lab	OHM 3	OHM 4	Lab	OHM 3	OHM 4
0.17								300		600	0	0	0		100			600			2300		
0.5								100		1900	0	0	0		200			1900			4700		
1	100	0	0	100	0	100	100	100	1100	2200	0	0		400	400	1100	100	2200	600	100	6200	300	100
3	100	0	0	300	100	300	600	600	2200	2400	0	0		500	700	2200	100	2400	1600	100	7900	300	300
6	100	0	100	600	300	400	1000		3000		0	0		400		3000	100		1500	200		600	400
10.5	200	0	100	1200	500	700	1400	1200	4200	5000	0	0	100	600	1300	4200	600	5000	2700	500		500	500
22																							
24	200	200	200	2100	1400	1000	2200	2500	5100	4300	0	100	100	500	3900	5100		4300	3000	3300		2700	8100
25	200																2000						
28.5																							
30	300	100				1500																	
37	300				1800		1000		5300			100	100			5300							
44																							
47	300	300			2400				5600			100	100			5600							
50							900																

Table 25	Comparison of 'Work' Levels - Second Round of OHMSETT Tests				
Oil/Mixture	**Phase**	**Ratio***			
Rock/Sock	OHM 3	1.2			
	OHM 4	0.9			
Sockeye	OHM 3	0.825			
	OHM 4	0.5			
Fuel Oil #6	OHM 3	1.025			
Mars	OHM 3	0.85			
Rock	OHM 3	0.1			
	OHM 4	1			
Fuel #6/Sock	OHM 3	0.575			
Mars	OHM 3	0.73			
	OHM 4	0.23			
Arabian Medium	OHM 3	0.15			
	OHM 4	0.15			
Arabian Light	OHM 3	0			
	OHM 4	0			
	Overall Average	0.57			
	Average of OHM 3	0.61			
	Average of OHM 4	0.53			
* Ratio is the ratio of Laboratory Energy					
to that in the OHMSETT tank as measured					
by the ratio of the stability of the water-in-oil state					

Table 26 Weathering Study Results - Second Round of OHMSETT Tests

Sockeye crude oil

Cumulative time (min)	Weight loss (%)
0	0.0
118	6.4
250	9.0
444	11.1
647	12.4
1398	14.1
2062	16.4
2909	17.2
3268	17.4
4442	18.0
8728	18.9
9032	18.9
9251	18.9
10006	19.0
10448	19.1
11553	19.2
11929	19.2
12132	19.2

Fuel Oil #6

Cumulative time (min)	Weight loss (%)
0	0.0
115	0.8
247	1.4
442	1.8
645	2.1
1394	2.4

Rock crude oil

Cumulative time (min)	Weight loss (%)
0	0.0
99	1.7
224	2.4
400	2.9
560	3.2
1409	3.8
1669	3.9
2901	4.6

Mars crude oil

Cumulative time (min)	Weight loss (%)
0	0.0
4006	15.4
4312	17.0
4534	17.5
5288	17.7
5731	19.7
6834	20.2

Bunker C fuel oil

Cumulative time (min)	Weight loss (%)
0	0.0
112	0.4
370	0.6
572	0.7
527	0.8
1788	1.5
2976	1.8

Sockeye - Mars Crude Oils Mix

Cumulative time (min)	Weight loss (%)	Viscosity of Weathered oil (cP) @ 15 C
0	0.0	145
80	3.6	185
331	5.8	250
506	6.6	
1300	8.2	340
1537	9.5	
1961	10.8	
2833	11.6	745
3147	12.2	
4168	12.9	1810
8558	14.2	
9155	14.3	
10083.00	14.4	

Sockeye Crude Oil

Cumulative time (min)	Weight loss (%)	Viscosity of Weathered oil (cP) @ 15 C
0	0.0	320
143	3.0	380
333	5.4	710
508	6.4	
1302	8.0	1620
1477	8.9	
2021	9.7	
2861	10.5	6800
3147	10.8	
4151	11.2	14000
8551	11.6	
9151	11.6	
9986	11.7	

Arabian Light Crude Oil

Cumulative time (min)	Weight loss (%)	Viscosity of Weathered oil (cP) @ 15 C
0	0	14
129	7.6	22
312	10.0	
442	11.3	23
1156	11.8	41
1615	14.1	
2610	14.8	59
7030	16.6	
7620	16.9	
8585	17.7	

Mars Crude Oil

Cumulative time (min)	Weight loss (%)	Viscosity of Weathered oil (cP) @ 15 C
0	0.0	52
145	9.7	160
345	11.8	175
503	12.4	
1309	13.2	340
1537	14.3	
1957	15.1	
2864	15.5	430
3143	16.0	
4159	16.2	1400

Rock Crude Oil

Cumulative time (min)	Weight loss (%)	Viscosity of Weathered oil (cP) @ 15 C
0	0.0	3400
126	0.2	3750
313	0.3	
440	0.4	3300
1174	0.5	3700
1560	0.7	
2619	0.9	3700
7034	1.4	
7636	1.5	
8599	1.6	

Fuel Oil #6 - Mars Crude Oils Mix

Cumulative time (min)	Weight loss (%)	Viscosity of Weathered oil (cP) @ 15 C
0	0	
3953	5.0	260
4450	5.4	
4654	5.5	
5515	5.7	
6945	6.1	
7325	6.3	
8315	6.4	
8625	6.6	

Figure 7 The Stabilities of Arabian Light Water-in-Oil States during the Second OHMSETT and Laboratory Tests
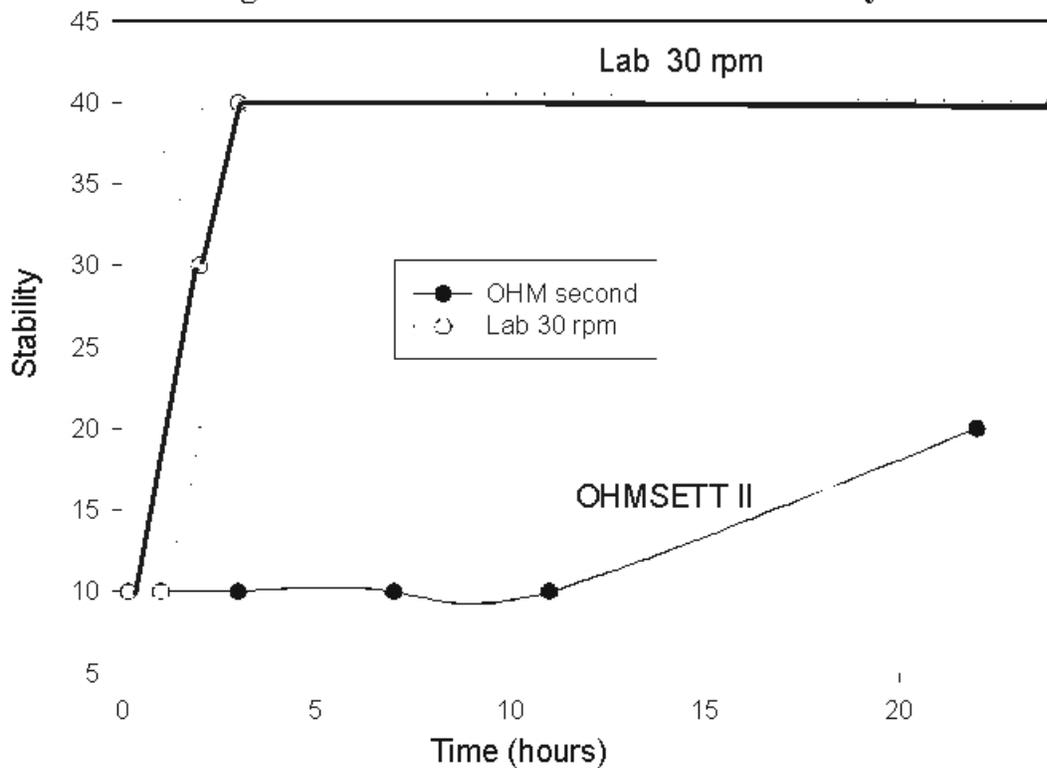
Figure 8 The Stabilities of Rock Water-in-Oil States during the Second OHMSETT and Laboratory Tests
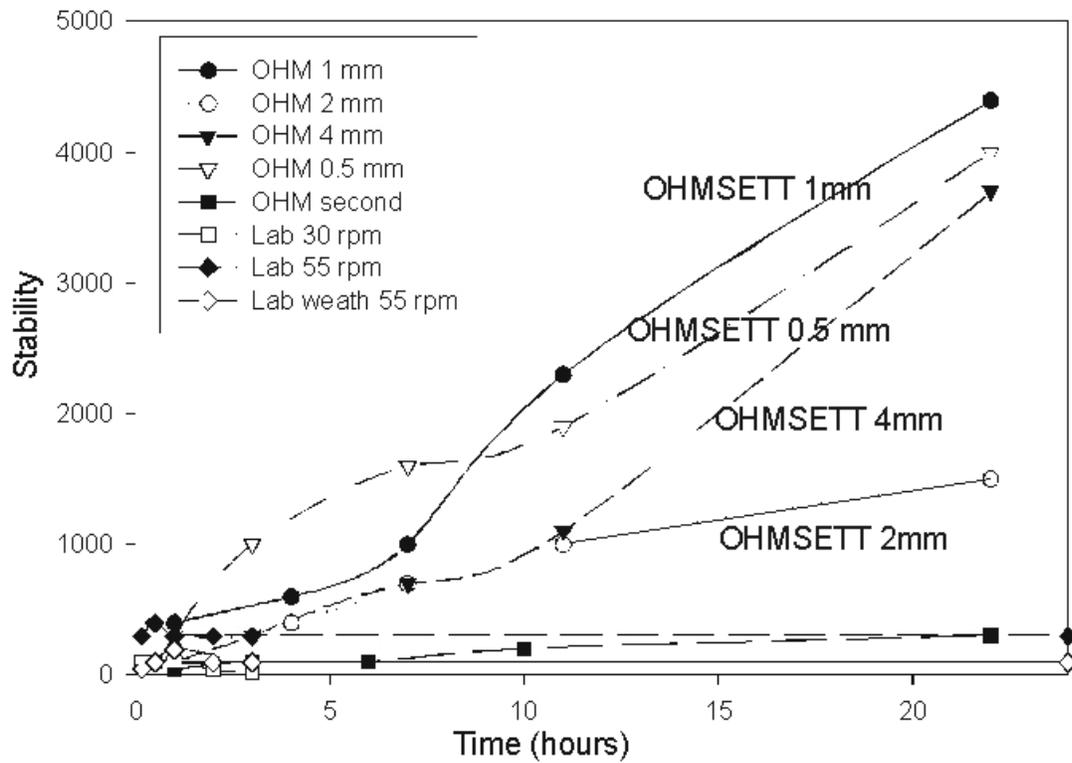
Figure 9   The Stabilities of Sockeye Water-in-Oil States during the First OHMSETT Test
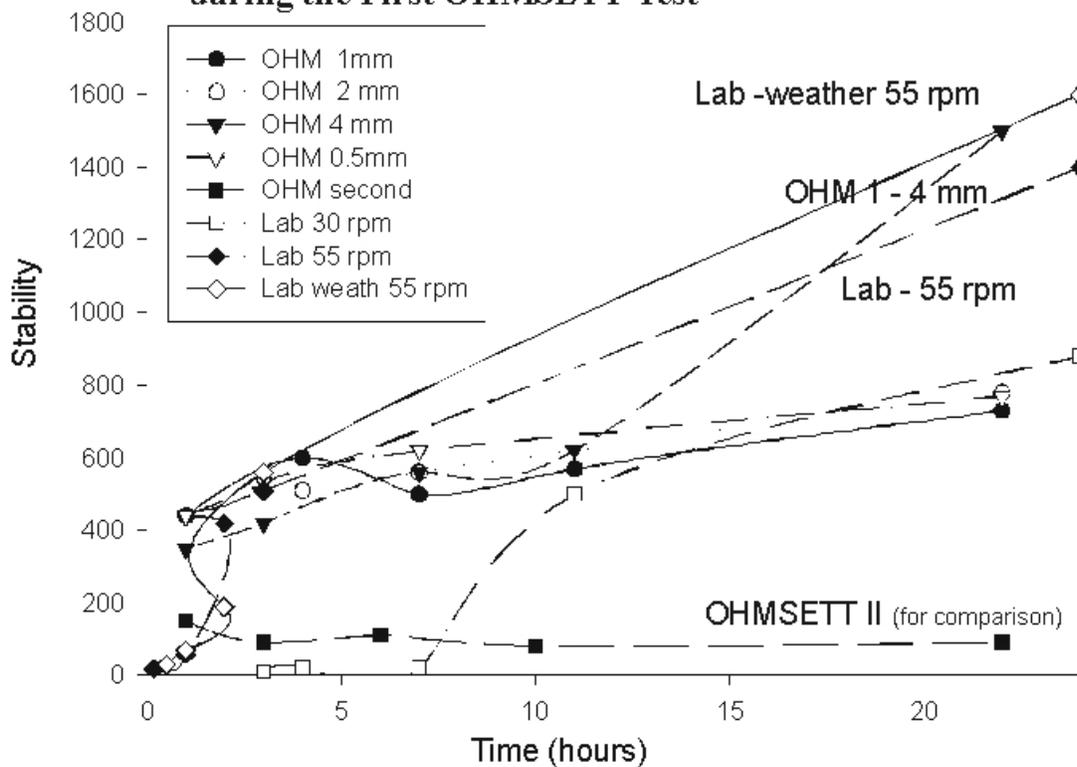
Figure 10   The Stabilities of Fuel Oil Water-in-Oil States during the First OHMSETT Test
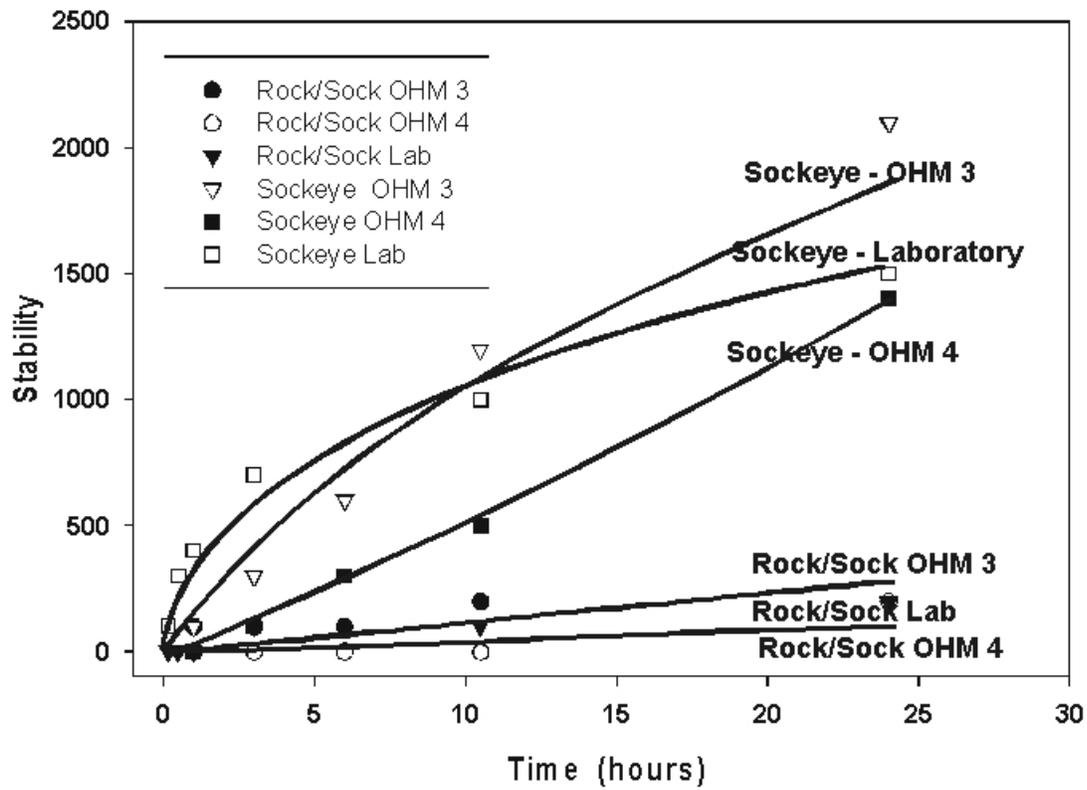
Figure 11   Stability of Sockeye and Rock/Sockeye Mixture
in Various Trials
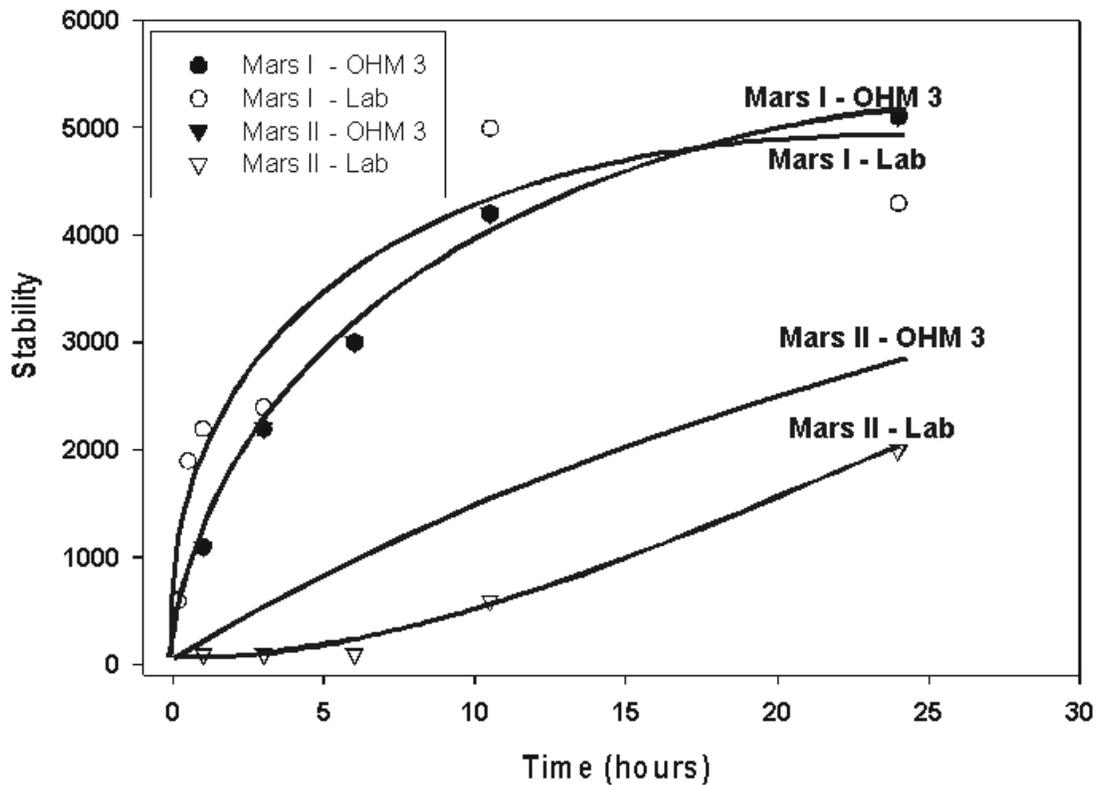
Figure 12   Stability of Two Batches of Mars
in Various Trials
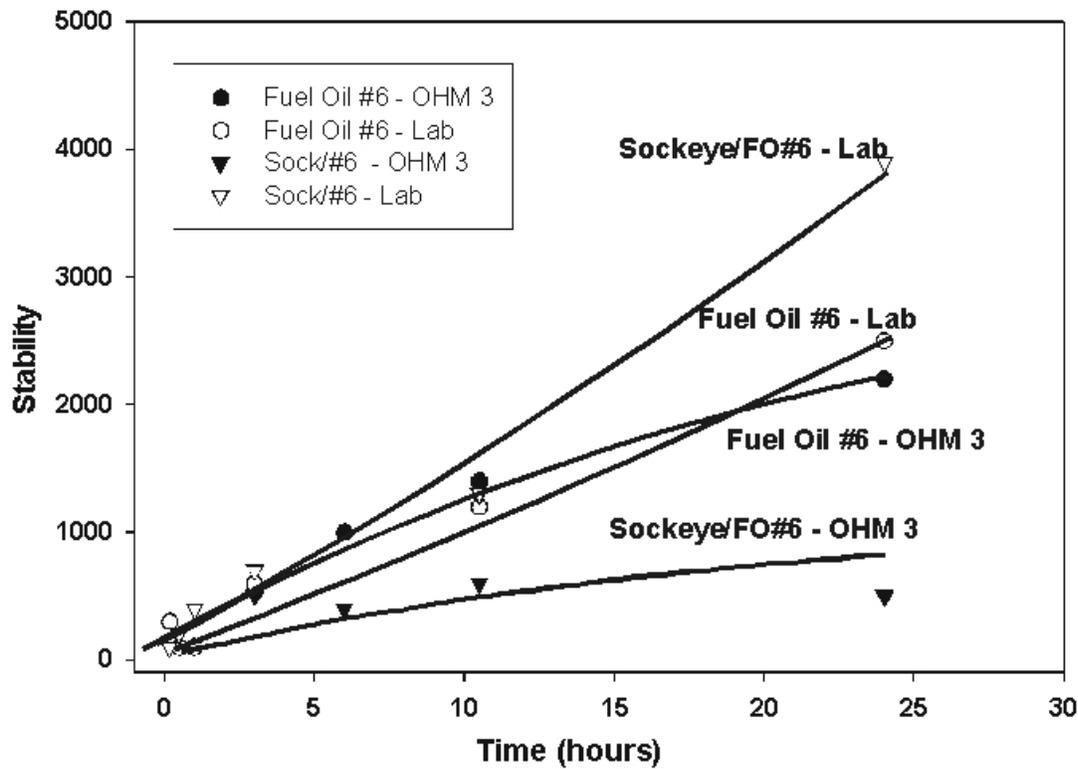
Figure 13   Stability of Fuel Oil #6 and Sockeye/ Fuel Oil #6 Mixtures in Various Trials
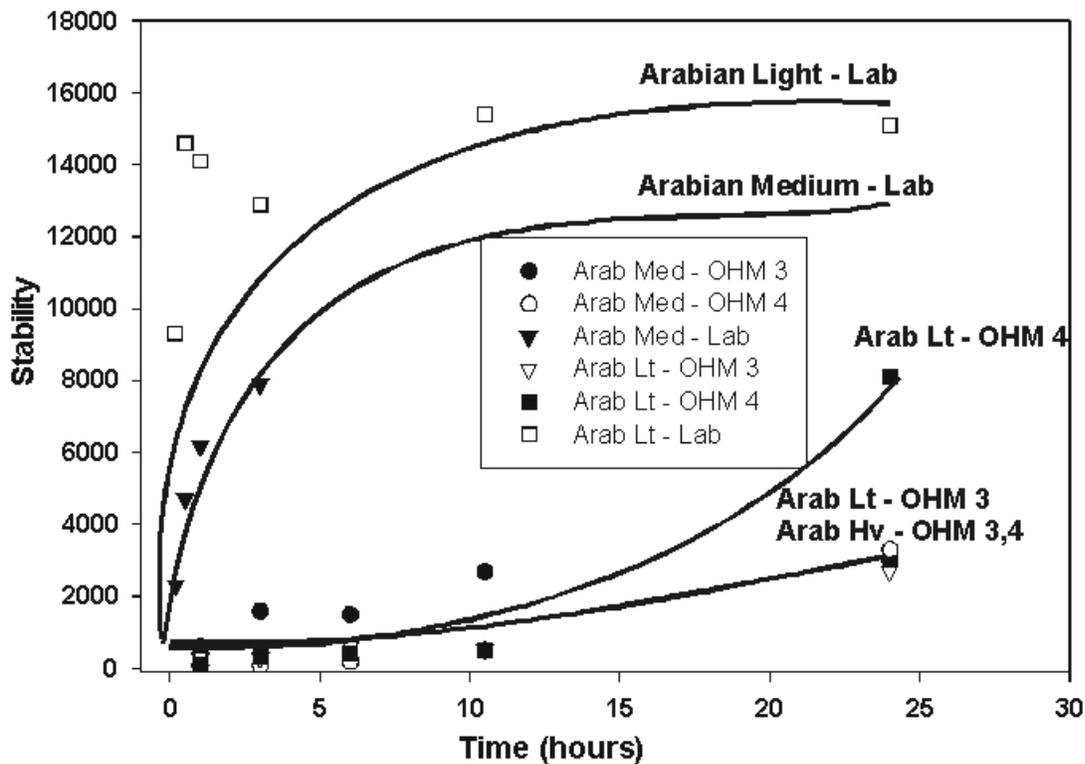
Figure 14   Stability of Arabian Light and Heavy Crudes in Various Trials

7. Recommendations for Future Research

The following phenomena were noted which require further investigation.

1. Emulsification of heavy oil requires separate investigation. The current results are somewhat unclear on the state to which heavy oil can be emulsified.

2. The role of 'rag' in the breakup of emulsions requires investigation. Furthermore, the composition and fate of rag should be investigated.

3. A better indicator of 'stability' than the one defined here by the complex modulus divided by starting oil viscosity is needed. One suggestion may be that only the elastic component be used.

4. Further work is needed on defining exact energies and work for the formation of emulsions.

8. Summary and Conclusions

Four clearly defined states of water-in-oil have been shown to exist. These are established by their stability over time, their appearance, and by rheological measurements. The states are stable water-in-oil emulsions, mesostable water-in-oil emulsions, entrained water, and unstable water-in-oil emulsions.

Stable emulsions are brown solid materials with an average water content of about 80% on the first day of formation and about the same one week later. Stable emulsions remain stable for at least 4 weeks under laboratory conditions. The properties of the starting oil required to form a stable emulsion are: density 0.85 to 0.97 g/mL; viscosity 15 to 10,000 mPa.s; resin content 5 to 30%; asphaltene content 3 to 20%; asphaltene-to-resin ratio 0.74; and average increase in viscosity 1,100 at day of formation and 1,500 one week later.

Mesostable water-in-oil emulsions are brown or black viscous liquids with an average water content of 62% on the first day of formation and about 38% one week later. Mesostable emulsions remain so less than 3 days under laboratory conditions. The properties of the starting oil required to form a mesostable emulsion are: density 0.84 to 0.98 g/mL; viscosity 6 to 23,000 mPa.s; resin content 6 to 30%; asphaltene content 3 to 17%; asphaltene-to-resin ratio 0.47; and average increase in viscosity 45 at day of formation and 3 one week later.

The greatest difference between the starting oils for stable and mesostable emulsions is the asphaltene-to-resin ratio (stable - 0.74; mesostable - 0.47) and the ratio of viscosity increase (stable 1,100, first day and 1,500 in one week; mesostable 45, first day and 30 in one week).

Entrained water-in-oil states are black liquids with an average water content of 42% on the first day of formation and about 15% one week later. Entrained water-in-oil states remain so less than 1 day under laboratory conditions. The average properties of the starting oil required to form entrained water are: density 0.97 to 0.99 g/mL; viscosity 2,000 to 60,000 mPa.s; resin content 15 to 30%; asphaltene content 3 to 22%; asphaltene-to-resin ratio 0.62; and average increase in viscosity 45 at day of formation and 30 one week later.

The greatest differences between the starting oils for entrained water-in-oil compared to stable

and mesostable emulsions are the narrow density range (entrained = 0.97 to 99; stable = 0.85 to 0.99; mesostable = about the same as stable) and the ratio of viscosity increase (entrained = 13, first day and 2 in one week; stable 1,100, first day and 1,500 in one week; mesostable 45, first day and 30 in one week). Furthermore, the viscosity of the starting oil is 2,000 to 60,000 mPa.s compared to 15 to 10,000 mPa.s for stable emulsions and 6 to 23,000 mPa.s for mesostable emulsions.

Unstable water-in-oil emulsions are characterized by the fact that the oil does not hold significant amounts of water and, when it does, the water remains for only a short time. There is a much broader range of properties of the starting oil than for the other three water-in-oil states. For example, viscosities are very low or very high. Included in this group are light fuels such as diesel fuel and very heavy, viscous oil products.

The stability of emulsions is due to the formation of asphaltene and resin films at the oil and water interface. Asphaltenes form strong, elastic films which are largely responsible for the stability of emulsions. While there is clear evidence of interaction between resins and asphaltenes in forming emulsions, asphaltenes can form emulsions without resins. The most stable emulsions are formed when the asphaltene-to-resin ratio is about 0.75. The migration experiments show that asphaltenes migrate to the interface very slowly and that this process can continue for longer than one month. This leads to the possibility that the resins migrate very quickly and temporarily stabilize water droplets before stronger asphaltene films form and displace the weaker resin films.

It has been found that asphaltene films are a highly viscoelastic barrier to coalescence of water droplets. The films may be strengthened by H- or π-bonding between individual asphaltene molecules. Oil viscosity alone may be a partial barrier to re-coalescence of water droplets. This mechanism is proposed as the primary stabilizer for entrained water and partially for mesostable emulsions. This may also explain why waxes are seen as important in certain circumstances. They may increase viscosity enough to allow entrained water states to form. Waxes are not a factor in the formation of either stable or mesostable emulsions.

Weathering of oil is a factor in determining the stability of emulsions in a number of ways. First, the elimination of saturates and smaller aromatic compounds leads to the formation of emulsions. Second, viscosity increases as oil weathers, inhibiting the re-coalescence of water droplets. Finally, oxidation and photooxidation create more polar compounds, some of which may be regarded as resins.

The energy required to form emulsions is quite low in most cases. Further study is required on a wide variety of emulsions to determine if there is a relationship to oil properties or to emulsion types.

The properties and stability of emulsions can be measured by rheological studies and dielectric spectroscopy. Rheological studies include forced oscillation experiments. The formation of stable emulsions is marked by a sharp increase in the elastic modulus. Water content is not a good indicator of emulsion characteristics other than that low water contents (<50%) indicate that an emulsion has not been formed and that the product is entrained water-in-oil. Interfacial

measurements are useful for measuring the film strength of asphaltene and resin components.

The state of the final water-in-oil mixture can be correlated with the single parameter of the complex modulus divided by the viscosity of the starting oil (Fingas *et al.*, 2000). This stability parameter has been used to provide an indication of the final stability of a given emulsion and thus an indication of its state. It was noted in these series of experiments that stability may not provide a definitive indication of the state for heavier oils. Mars and Fuel Oil #6 yielded stable emulsions at relatively low values of stability. Other parameters should be further investigated.

Many mesostable emulsions degrade into 'rag' which is the standard industrial term for the remnants of an emulsion. While it appears that rag may be large asphaltene-resin aggregates with trapped emulsion, further work is needed in this area.

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