A Review of the Emulsification Tendencies and Long-term Petroleum Trends of Alaska North Slope (ANS) Oils and the “White Paper on Emulsification of ANS Crude Oil Spilled in Valdez”

Prepared for

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Abstract

This paper reviews three topics: the potential for formation and the stability of water-in-oil states (emulsions) of Alaska North Slope (ANS) oils, the change in the lightness or heaviness of these oils, and the report prepared by S.L. Ross Environmental Research Ltd. on these first two topics.

A review of the emulsification of Alaskan North Slope oils shows that these oils do not typically form entrained water-in-oil or stable emulsions. After weathering, however, many of these oils will form meso-stable emulsions, which are not as stable and have a lifetime of less than 3 days.

The following are the prime indicators of emulsion formation.

1. The major indicator is the stability of the emulsions as measured by the stability index. The overall tendency of the stability analysis of ANS meso-stable emulsions is that there is a slight decrease in the stability over time.
2. The asphaltene/resin ratio, another strong indicator, is decreasing over time, indicating a slight decrease in emulsion stability or formation tendency.
3. The asphaltene content is slowly rising over the years, but this is offset by a greater increase in the resin content, which decreases the asphaltene/resin ratio.
4. The resin content is increasing over the years, lowering the asphaltene/resin ratio and creating a meso-stable emulsion.
5. The viscosity of the oil is decreasing. This may decrease the emulsification potential, especially that of the entrained water-in-oil state.
6. The prediction of emulsification using the latest model shows a lower prediction factor (related to stability).
7. The measured stability of meso-stable emulsions shows a slight decrease over the years.

Overall, it is concluded that both the potential for formation of meso-stable emulsions and the stability of these emulsions will decrease if the current trend in petroleum properties continues.

The comparison and analysis of the oil analytical and properties data show apparent trends in the nature of the ANS oils. Most indicators show that the mix that constitutes ANS oil is becoming lighter, probably due to the mix of crude oils added to the start of the pipelines. It is important to note that the sampling points, sampling times, and other conditions of the feed and pipeline operations were not always recorded. The important indicators of distillation data, chemical composition, viscosity, and density show a general increase in the lightness of ANS oils. The amount of volatile organic compounds (VOCs) in the oil is rising. Despite indicators that the oil is becoming lighter, the resins are rising somewhat. This indicates that the oil may become lighter but more resiny.

The comparison of the data shows several considerations about the analytical data and conclusions presented in the report on ANS oils prepared by S.L. Ross Environmental Research Ltd. Several crucial parameters to consider when making decisions about oil behaviour and emulsification are missing from the report, including standard distillation data, standard emulsification procedures, and SARA and VOC analyses. Several data points varied considerably from the data in the literature including flash point, density, pour point, oil-air interfacial tensions, distillation data, and viscosity measurements. The emulsification data was quite different and could not be related to the data in the literature. None of the important concepts or references about emulsification was included in the report. Despite this, the report does indicate that the oil is becoming lighter and may thus be less prone to emulsification.

Summary and Issues

Overall

The emulsification tendency of Alaska North Slope (ANS) oils is considered, both in the past and the future, as well as the long-term changes in the properties of the oil. In addition, the report on the emulsification of ANS oils prepared by S.L. Ross Environmental Research Ltd. is reviewed.

Specific Issues

The following is a summary of the specific issues and technical concerns related to these topics.

1. In terms of the long-term emulsification trend of Alaska North Slope crude oil, will it be more or less prone to form emulsions in the future? Will these emulsions or water-in-oil be more or less stable?

2. In relation to the properties of ANS crudes, are they becoming lighter or heavier?

3. Are the conclusion implied by the report on ANS crude oil prepared by S.L. Ross Environmental Research Ltd. correct? Are the methods and analytical results in this report in line with industry standards? Is the emulsification data in this report valid?

Conclusions

The following are the overall conclusions of this study.

1. Emulsification

Overall, it is concluded that both the potential for formation and the stability of meso-stable emulsions will decrease if the current trend in petroleum properties continues. This is based on the following indicators.

A. The strongest indicator is the stability of the emulsions as measured by the stability index of complex modulus of the formed product, divided by the viscosity of the starting oil. The overall tendency of the stability analysis of the ANS meso-stable emulsions is that there is a slight decrease in the stability over time, although there is no extensive data on this.

B. The asphaltene/resin ratio is decreasing over time, indicating that there is a slight decrease in emulsion stability or formation tendency over the years.

C. The asphaltene content is slowly rising over the years, but this is offset by the greater increase in the resin content, which is decreasing the asphaltene/resin ratio.

D. The resin content is increasing over the years. This will lower the asphaltene/resin ratio and create a meso-stable emulsion.

E. The viscosity of the oil is decreasing. This may decrease the emulsification potential, especially that of the entrained water-in-oil state.

F. The prediction of emulsification using the latest model shows a lower prediction factor (related to stability). This model incorporates a variety of factors including density and viscosity, as well as saturate, asphaltene, and resin content.

G. The measured stability of meso-stable emulsions shows a slight decrease over the years.

2. Long-term Trends

Most indicators show that the mix that constitutes ANS oil is becoming lighter, probably due to the mix of crude oils added to the start of the pipelines. It is important to note that the sampling points, sampling times, and other conditions of the pipeline and feed operations were not always recorded. These trends are indicated by the following.

A. The important indicators of distillation data, viscosity, and density confirm the conclusions.

B. The amount of VOCs in the oil is rising.

C. Despite the indicators that the oil is becoming lighter, the resins are rising somewhat. This indicates that the oil may become a lighter, but more resiny oil.

3. The S.L. Ross Report

The comparison of the data shows the following about the analytical data presented in the report prepared by S.L. Ross Environmental Research Ltd.

A. Several parameters that are crucial to making decisions on oil behaviour and emulsification are missing from the report, including standard distillation data, standard emulsification procedures, and SARA and VOC analyses.

B. The flash point measured was high.

C. The density at 15ºC was low.

D. The pour point was high.

E. The viscosity measurements were either higher or lower than the results in the literature.

F. The oil-air interfacial tensions were high.

G. The distillation curves were different.

H. The emulsification data was quite different and could not be related to the data in the literature. None of the important concepts or references about emulsification was included in the report.

Despite this, the report does indicate that the oil is becoming lighter and may thus be less prone to emulsification.

List of Acronyms

ANS	Alaska North Slope - This usually refers to the crude oil mixture at the end of the pipeline.
DLVO	Derjaguin Landau Verway Overbeek - This refers to a theory on surfactant stabilization, with each letter referring to the author of the original theory.
EPA	U.S. Environmental Protection Agency
FT-IR	Fourier transform-infrared
GC	Gas chromatograph - This is a chemical analytical technique.
IFT	Interfacial tension
NMR	Nuclear magnetic resonance
PAH	Polynuclear aromatic hydrocarbons
PWSRCAC	Prince William Sound Regional Citizens' Advisory Council
RSD	Relative standard deviation
SARA	Saturates, aromatics, resins, and asphaltenes
VOCs	Volatile organic compounds

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1. Introduction

1.1 Background

The objective of this paper is to comment on the report entitled, “White Paper on Emulsification of ANS Crude Oil Spilled in Valdez” by S.L. Ross Environmental Research Limited, published in November, 2004. In addition, the two topics in the report, namely the emulsification of ANS oil and the long-term trends in the oil, will be examined separately.

1.2 Oil Properties and Alyeska Crude

It is important to recognize the nature of a crude oil that stems from the inputs into the pipeline and the changing blends that occur over time. A crude oil sample drawn at one point in time from a pipeline may be completely different than a sample drawn at a later time.

The Alaska crude is an example of this principle. The Trans-Alaska Pipeline begins at pump station number one (International Petroleum Encyclopedia, 2004). At this point, it is a mixture of crude oils in varying proportions from several fields. These fields include the major fields of Prudhoe Bay and Kuparuk and several minor fields including Tarn, Alpine, Fiord, Kabulkic, Milne Point, Point Mcintyre, West Beach, Point Thompson, Endicott, and Sandpiper. The characteristics of these fields vary and thus, as they are blended into pump station number 1 at the head of the Alyeska pipeline, the starting crude varies as well. Oil is withdrawn from the pipeline for the refinery at Fairbanks where residual oils are re-injected into the pipeline. The sequence of this changes the composition of the oil when it arrives in Valdez.

1.3 A Summary of Oil Composition and Behaviour

Crude oils are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, non-volatile compounds (Fingas, 2000). This mixture of compounds varies according to the geological formation of the area in which the oil is found and strongly influences the properties of the oil. Petroleum products such as gasoline or diesel fuel are mixtures of fewer compounds and thus their properties are more specific and less variable. Hydrocarbon compounds are composed of hydrogen and carbon, which are therefore the main elements in oils. Oils also contain varying amounts of sulphur, nitrogen, oxygen, and sometimes mineral salts, as well as trace metals such as nickel, vanadium, and chromium.

In general, the hydrocarbons found in oils are characterized by their structure. The hydrocarbon structures found in oil are the saturates, olefins, aromatics, and polar compounds. The saturate group of components in oils consists primarily of alkanes, which are compounds of hydrogen and carbon with the maximum number of hydrogen atoms around each carbon. Thus, the term 'saturate' is used because the carbons are ‘saturated’ with hydrogen. Larger saturate compounds are often referred to as ‘waxes’. The aromatic compounds include at least one benzene ring of six carbons. Three double carbon-to-carbon bonds float around the ring and add stability. Because of this stability, benzene rings are very persistent and can have toxic effects on the environment.

The most common smaller and more volatile compounds found in oil are often referred to as BTEX, or benzene, toluene, ethyl-benzene, and xylenes. Polyaromatic hydrocarbons or PAHs are compounds consisting of at least two benzene rings.

Polar compounds are those that have a significant molecular charge as a result of bonding with compounds such as sulphur, nitrogen, or oxygen. The 'polarity' or charge that the molecule carries results in behaviour that is different than that of unpolarized compounds, under some circumstances. In the petroleum industry, the smallest polar compounds are called 'resins', which are largely responsible for oil adhesion. The larger polar compounds are called 'asphaltenes' because they often make up the largest percentage of the asphalt commonly used for road construction. Asphaltenes often have very large molecules and, if in abundance in an oil, they have a significant effect on oil behaviour.

1.3.1 Oil Properties

The properties of oil discussed here are viscosity, density, specific gravity, solubility, flash point, pour point, distillation fractions, interfacial tension, and vapour pressure.

Viscosity is the resistance to flow in a liquid (Fingas, 2000). The lower the viscosity, the more readily the liquid flows. For example, water has a low viscosity and flows readily, whereas honey, with a high viscosity, flows poorly. The viscosity of the oil is largely determined by the amount of lighter and heavier fractions that it contains. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower the viscosity.

As with other physical properties, viscosity is affected by temperature, with a lower temperature giving a higher viscosity. For most oils, the viscosity varies as the logarithm of the temperature, which is a very significant variation. Oils that flow readily at high temperatures can become a slow-moving, viscous mass at low temperatures. In terms of oil spill cleanup, viscosity can affect the oil's behaviour. Viscous oils do not spread rapidly, do not penetrate soil as readily, and affect the ability of pumps and skimmers to handle the oil.

Density is the mass (weight) of a given volume of oil and is typically expressed in grams per cubic centimetre (g/cm^3). It is the property used by the petroleum industry to define light or heavy crude oils. Density is also important as it indicates whether a particular oil will float or sink in water. As the density of water is 1.0 g/cm^3 at 15ºC and the density of most oils ranges from 0.7 to 0.99 g/cm^3, most oils will float on water. As the density of seawater is 1.03 g/cm^3, even heavier oils will usually float on it. As the light fractions evaporate with time, the density of oil increases.

Occasionally, when the density of an oil becomes greater than the density of freshwater or seawater, the oil will sink. Sinking is rare, however, and happens only with a few oils, usually residual oils such as Bunker C. Significant amounts of oil have sunk in only about 25 incidents out of thousands.

Another measure of density is specific gravity, which is an oil's relative density compared to that of water at 15°C. It is the same value as density at the same temperature. Another gravity scale is that of the American Petroleum Institute (API). The API gravity is based on the density of pure water which has an arbitrarily assigned API gravity value of 10º (10 degrees). Oils with progressively lower specific gravities have higher API gravities.

The following is the formula for calculating API gravity: API gravity = [141.5 ÷ (density at 15.5°C)] - 131.5. Oils with high densities have low API gravities and vice versa. In the United States, the price of a specific oil may be based on its API gravity as well as other properties of the oil.

Solubility in water is the measure of how much of an oil will dissolve in the water column on a molecular basis. Solubility is important in that the soluble fractions of the oil are sometimes toxic to aquatic life, especially at higher concentrations. As the amount of oil lost to solubility is always small, this is not as great a loss mechanism as evaporation. In fact, the solubility of oil in water is so low (generally less than 100 parts per million) that it would be the equivalent of approximately one grain of sugar dissolving in a cup of water.

The flash point of an oil is the temperature at which the liquid gives off sufficient vapours to ignite upon exposure to an open flame. A liquid is considered to be flammable if its flash point is less than 60°C. There is a broad range of flash points for oils and petroleum products, many of which are considered flammable, especially when fresh. Gasoline, which is flammable under all ambient conditions, poses a serious hazard when spilled. Many fresh crude oils have an abundance of volatile components and may be flammable for as long as one day until the more volatile components have evaporated. On the other hand, Bunker C and heavy crude oils are not generally flammable when spilled.

The pour point of an oil is the temperature at which it takes longer than a specified time to pour from a standard measuring vessel. As oils are made up of hundreds of compounds, some of which may still be liquid at the pour point, the pour point is not the temperature at which the oil will no longer pour. The pour point represents a consistent temperature at which an oil will pour very slowly and therefore has limited use as an indicator of the state of the oil. In fact, pour point has been used too much in the past to predict how oils will behave in the environment. For example, waxy oils can have very low pour points, but may continue to spread slowly at that temperature and can evaporate to a significant degree. Because pour point is not the solidification point of oil, it is not the best predictor of how oil will behave or even more specifically, how it will move in the environment. Pour point is often used incorrectly as a parameter of oil behaviour.

Distillation fractions of an oil represent the fraction of an oil (generally measured by volume) that is boiled off at a given temperature. This data is obtained on most crude oils so that oil companies can adjust parameters in their refineries to handle the oil. This data also provides environmentalists with useful insights into the chemical composition of oils. For example, while 70% of gasoline will boil off at 100ºC, only about 5% of a crude oil will boil off at that temperature and an even smaller amount of a typical Bunker C. The distillation fractions correlate strongly to the composition of the oil as well as to other physical properties of the oil.

The oil/water interfacial tension, sometimes called surface tension, is the force of attraction or repulsion between the surface molecules of oil and water. Together with viscosity, surface tension is an indication of how rapidly and to what extent an oil will spread on water. The lower the interfacial tension with water, the greater the extent of spreading. In actual practice, the interfacial tension must be considered along with the viscosity because it has been found that interfacial tension alone does not account for spreading behaviour.

The vapour pressure of an oil is a measure of how the oil partitions between the liquid and gas phases, or how much vapour is in the space above a given amount of liquid oil at a fixed temperature. Because oils are a mixture of many compounds, the vapour pressure changes as the oil weathers. Vapour pressure is difficult to measure and is not frequently used to assess oil spills.

While there is a high correlation between the various properties of an oil, these correlations should be used cautiously as oils vary so much in composition (Jokuty et al., 1995). For example, the density of many oils can be predicted based on their viscosity. For other oils, however, this could result in errors. For example, waxy oils have much higher viscosities than would be implied from their densities. There are several mathematical equations for predicting one property of an oil from another property, but these must be used carefully as there are many exceptions.

The measurement of oil properties is an important consideration. While there are many standards for measuring fuel, e.g., ASTM, many of these standards are not applicable to crude oils and especially not to heavier crudes and residual oils. Similarly, many of the apparatuses for measurement are only appropriate for lighter fuels. The best examples of inappropriate measurements are the use of Brookfield viscometers for measuring heavier crudes (McDonagh et al., 1995). These can result in errors of over 3 orders-of-magnitude (Durrell et al., 1994). An extensive report on measurement techniques and standards is available in Wang et al. (2004).

1.3.2 Behaviour of Oil

Oil spilled on water undergoes a series of changes in physical and chemical properties which in combination are termed 'weathering' (Fingas, 2000). Weathering processes occur at very different rates, but begin immediately after oil is spilled into the environment. Weathering rates are not consistent throughout the duration of an oil spill and are usually highest immediately after the spill.

Both weathering processes and the rates at which they occur depend more on the type of oil than on environmental conditions. Most weathering processes are highly temperature-dependent, however, and will often slow to insignificant rates as temperatures approach zero degrees. The processes included in weathering are evaporation, emulsification, natural dispersion, dissolution, photooxidation, sedimentation, adhesion to materials, interaction with mineral fines, biodegradation, and the formation of tar balls. These processes are listed in order of importance in terms of their affect on the percentage of total mass balance, i.e., the greatest loss from the slick in terms of percentage and what is known about the process.

Evaporation is usually the most important weathering process. It has the greatest effect on the amount of oil remaining on water or land after a spill. Over a period of several days, a light fuel such as gasoline evaporates completely at temperatures above freezing, whereas only a small percentage of a heavier Bunker C oil evaporates. The rate at which an oil evaporates depends primarily on the oil's composition. The more volatile components an oil or fuel contains, the greater the extent and rate of its evaporation. Many components of heavier oils will not evaporate at all, even over long periods of time and at high temperatures.

Oil and petroleum products evaporate in a slightly different manner than water and the process is much less dependent on wind speed and surface area. Oil evaporation can be considerably slowed down, however, by the formation of a 'crust' or 'skin' on top of the oil. This happens primarily on land where the oil layer does not mix with water. The skin or crust is formed when the smaller compounds in the oil are removed, leaving the larger compounds, such as waxes and resins, at the surface. These then seal off the remainder of the oil and prevent evaporation. Stranded oil from old spills has been re-examined over many years and it has been found that, when this crust has formed, there is no significant evaporation in the oil underneath. When this crust has not formed, the same oil could be weathered to the hardness of wood.

The rate of evaporation is very rapid immediately after a spill and then slows considerably. About 80% of evaporation occurs in the first few days after a spill. The evaporation of most oils follows a logarithmic curve with time. Some oils such as diesel fuel, however, evaporate as the square root of time, at least for the first few days. This means that the evaporation rate slows very rapidly in both cases. The properties of an oil can change significantly with the extent of evaporation. If about 40% (by weight) of an oil evaporates, its viscosity could increase by as much as a thousand-fold. Its density could rise by as much as 10%

and its flash point by as much as 400%. The extent of evaporation can be the most important factor in determining properties of an oil at a given time after the spill and in changing the behaviour of the oil.

Emulsification is the process by which one liquid is dispersed into another one in the form of small droplets. Water droplets can remain in an oil layer in a stable form and the resulting material is completely different. These water-in-oil emulsions are sometimes called 'mousse' or 'chocolate mousse' as they resemble this dessert. In fact, both the tastier version of chocolate mousse and butter are common examples of water-in-oil emulsions.

The mechanism of emulsion formation is not yet fully understood, but it probably starts with sea energy forcing the entry of small water droplets, about 10 to 25 µm (or 0.010 to 0.025 mm) in size, into the oil. If the oil is only slightly viscous, these small droplets will not leave the oil quickly. On the other hand, if the oil is too viscous, droplets will not enter the oil to any significant extent. Once in the oil, the droplets slowly gravitate to the bottom of the oil layer. Any asphaltenes and resins in the oil will interact with the water droplets to stabilize them. Depending on the quantity of asphaltenes and resins, as well as aromatic compounds that stabilize asphaltenes and resins in solution, an emulsion may be formed. The conditions required for emulsions of any stability to form may only be reached after a period of evaporation. Evaporation lowers the amount of low-molecular weight aromatics in the oil and increases the viscosity to the critical value.

Water can be present in oil in four ways. First, some oils contain about 1% water as soluble water. This water does not significantly change the physical or chemical properties of the oil. The second way is called 'entrainment', whereby water droplets are simply held in the oil by its viscosity to form an unstable emulsion. These are formed when water droplets are incorporated into oil by the sea's wave action and there are not enough asphaltenes and resins in the oil or if there is a high amount of aromatics in the oil which stabilizes the asphaltenes and resins, preventing them from acting on the water droplets. Unstable emulsions break down into water and oil within minutes or a few hours, at most, once the sea energy diminishes. The properties and appearance of the unstable emulsion are almost the same as those of the starting oil, although the water droplets may be large enough to be seen with the naked eye.

Semi- or meso-stable emulsions represent the third way water can be present in oil. These are formed when the small droplets of water are stabilized to a certain extent by a combination of the viscosity of the oil and the interfacial action of asphaltenes and resins. For this to happen, the asphaltene or resin content of the oil must be at least 3% by weight. The viscosity of meso-stable emulsions is 20 to 80 times higher than that of the starting oil. These emulsions generally break down into oil and water or sometimes into water, oil, and stable emulsion within a few days. Semi- or meso-stable emulsions are viscous liquids that are reddish-brown or black in colour.

The fourth way that water exists in oil is in the form of stable emulsions. These form in a way similar to meso-stable emulsions except that the oil must contain at least 8% asphaltenes. The viscosity of stable emulsions is 500 to 800 times higher than that of the starting oil and the emulsion will remain stable for weeks and even months after formation. Stable emulsions are reddish-brown in colour and appear to be nearly solid. Because of their high viscosity and near solidity, these emulsions do not spread and tend to remain in lumps or mats on the sea or shore.

The formation of emulsions is an important event in an oil spill. First, and most importantly, it substantially increases the actual volume of the spill. Emulsions of all types contain about 70% water and thus when emulsions are formed the volume of the oil spill more than triples. Even more significantly, the viscosity of the oil increases by as much as 1000 times, depending on the type of emulsion formed. For example, a highly viscous oil such as a motor oil can triple in volume and become almost solid through the process of emulsification.

These increases in volume and viscosity make cleanup operations more difficult. Emulsified oil is difficult or impossible to disperse, to recover with skimmers, or to burn. Emulsions can be broken down with special chemicals in order to recover the oil with skimmers or to burn it. It is thought that emulsions break down into oil and water by further weathering, oxidation, and freeze-thaw action. Meso- or semi-stable emulsions are relatively easy to break down, whereas stable emulsions may take months or years to break down naturally.

Emulsion formation also changes the fate of the oil. It has been noted that when oil forms stable or meso-stable emulsions, evaporation slows considerably. Biodegradation also appears to slow down. The dissolution of soluble components from oil may also cease once emulsification has occurred.

The process of emulsion formation is discussed in detail in Section 2 of this report.

Natural dispersion occurs when fine droplets of oil are transferred into the water column by wave action or turbulence. Small oil droplets (less than 20 µm or 0.020 mm) are relatively stable in water and will remain so for long periods of time. Large droplets tend to rise and larger droplets (more than 100 µm) will not stay in the water column for more than a few seconds. Depending on oil conditions and the amount of sea energy available, natural dispersion can be insignificant or it can remove the bulk of the oil. In 1993, the oil from a stricken ship, the *Braer*, dispersed almost entirely as a result of high seas off Scotland at the time of the spill and the dispersible nature of the oil cargo.

Natural dispersion is dependent on both the oil properties and the amount of sea energy. Heavy oils such as Bunker C or a heavy crude will not disperse naturally to any significant extent, whereas light crudes and diesel fuel can disperse significantly if the saturate content is high and the asphaltene and resin contents are low. In addition, significant wave action is needed to disperse oil. In 30 years of monitoring spills on the oceans, those spills at which oil has dispersed naturally have all occurred in very energetic seas.

The long-term fate of dispersed oil is not known, although it probably degrades to some extent as it consists primarily of saturate components. Some of the dispersed oil may also rise and form another surface slick or it may become associated with sediment and be precipitated to the bottom.

Through the process of dissolution, some of the most soluble components of the oil are lost to the water under the slick. These include some of the lower molecular weight aromatics and some of the polar compounds, broadly categorized as resins. As only a small amount actually enters the water column, usually much less than a fraction of a percent of the oil, dissolution does not measurably change the mass balance of the oil. The significance of dissolution is that the soluble aromatic compounds are particularly toxic to fish and other aquatic life. If a spill of oil containing a large amount of soluble aromatic components occurs in shallow water and creates a high localized concentration of compounds, then significant numbers of aquatic organisms can be killed.

Gasoline, diesel fuel, and light crude oils are the most likely to cause aquatic toxicity. A highly weathered oil is unlikely to dissolve into the water. On open water, the concentrations of hydrocarbons in the water column are unlikely to kill aquatic organisms.

Dissolution occurs immediately after the spill occurs and the rate of dissolution decreases rapidly after the spill as soluble substances are quickly depleted. Some of the soluble compounds also evaporate rapidly.

Photooxidation can change the composition of an oil. It occurs when the sun's action on an oil slick causes oxygen and carbons to combine and form new products that may be resins. The resins may be somewhat soluble and dissolve into the water or they may cause water-in-oil emulsions to form. It is not well understood how photooxidation specifically affects oils, although certain oils are susceptible to the process, while others are not. For most oils, photooxidation is not an important process in terms of changing their fate or mass balance after a spill.

Sedimentation is the process by which oil is deposited on the bottom of the sea or other water body. While the process itself is not well understood, certain facts about it are. Most sedimentation noted in the past has occurred when oil droplets reached a higher density than water after interacting with mineral matter in the water column. This interaction sometimes occurs on the shoreline or very close to the shore. Once oil is on the bottom, it is usually covered by other sediment and degrades very slowly. In a few well studied spills, a significant amount (about 10%) of the oil was sedimented on the sea floor. Such amounts can be very harmful to biota that inevitably come in contact with the oil on the sea bottom. Because of the difficulty of studying this, data are limited.

Oil is very adhesive, especially when it is moderately weathered, and binds to shoreline materials or other mineral material with which it comes in contact. A significant amount of oil can be left in the environment after a spill in the form of residual amounts adhering to shorelines and man-made structures such as piers and artificial shorelines. As this oil usually contains a high percentage of aromatics and asphaltenes with high molecular weight, it does not degrade significantly and can remain in the environment for decades.

Oil slicks and oil on shorelines sometimes interact with mineral fines suspended in the water column and the oil is thereby transferred to the water column. Particles of mineral with oil attached may be heavier than water and sink to the bottom as sediment or the oil may detach and refloat. Oil-fines interaction does not generally play a significant role in the fate of most oil spills in their early stages, but can have an impact on the rejuvenation of an oiled shoreline over the long term.

A large number of microorganisms are capable of degrading petroleum hydrocarbons. Many species of bacteria, fungi, and yeasts metabolize petroleum hydrocarbons as a food energy source. Bacteria and other degrading organisms are most abundant on land in areas where there have been petroleum seeps, although these microorganisms are found everywhere in the environment. As each species can utilize only a few related compounds at most, however, broad-spectrum degradation does not occur. Hydrocarbons metabolized by microorganisms are generally converted to an oxidized compound, which may be further degraded, may be soluble, or may accumulate in the remaining oil. The aquatic toxicity of the biodegradation products is sometimes greater than that of the parent compounds.

The rate of biodegradation depends primarily on the nature of the hydrocarbons and then on the temperature. Generally, rates of degradation tend to increase as the temperature rises. Some groupings of bacteria, however, function better at lower temperatures and others function better at higher temperatures. Indigenous bacteria and other microorganisms are often the best adapted and most effective at degrading oil as they are acclimatized to the temperatures and other conditions of the area. Adding 'super-bugs' to the oil does not necessarily improve the degradation rate.

The rate of biodegradation is greatest on saturates, particularly those containing approximately 12 to 20 carbons (Haus et al., 2004). Aromatics and asphaltenes, which have a high molecular weight, biodegrade very slowly, if at all. This explains the durability of roof shingles containing tar and roads made of asphalt, as both tar and asphalt consist primarily of aromatics and asphaltenes. On the other hand, diesel fuel is a highly degradable product as it is largely composed of degradable saturates. Light crudes are also degradable to a degree. While gasoline contains degradable components, it also contains some compounds that are toxic to some microorganisms. These compounds generally evaporate more rapidly, but in many cases, most of the gasoline will evaporate before it can degrade. Heavy crudes contain little material that is readily degradable and Bunker C contains almost none.

The rate of biodegradation is also highly dependent on the availability of oxygen. On land, oils such as diesel can degrade rapidly at the surface, but very slowly if at all only a few centimetres below the surface, depending on oxygen availability. In water, oxygen levels can be so low that degradation is limited. It is estimated that it would take all the dissolved oxygen in approximately 400,000 L of sea water to completely degrade 1 L of oil. The rate of degradation also depends on the availability of nutrients such as nitrogen and phosphorus, which are most likely to be available on shorelines or on land. Finally, the rate of biodegradation also depends on the availability of the oil to the bacteria or microorganism. Oil degrades significantly at the oil-water interface at sea and, on land, mostly at the interface between soil and the oil.

Biodegradation can be a very slow process for some oils. It may take weeks for 50% of a diesel fuel to biodegrade under optimal conditions and years for 10% of a crude oil to biodegrade under less optimal conditions. For this reason, biodegradation is not considered an important weathering process in the short term.

Tar balls are agglomerations of thick oil less than about 10 cm in diameter. Larger accumulations of the same material ranging from about 10 cm to 1 m in diameter are called tar mats. Tar mats are pancake-shaped, rather than round. Their formation is still not completely understood, but it is known that they are formed from the residuals of heavy crudes and Bunker C. After these oils weather at sea and slicks are broken up, the residuals remain in tar balls or tar mats. The reformation of droplets into tar balls and tar mats has also been observed, with the binding force being simply adhesion.

The formation of tar balls is the ultimate fate of many oils. These tar balls are then deposited on shorelines around the world. The oil may come from spills, but it is also residual oil from natural oil seeps or from deliberate operational releases such as from ships. Tar balls are regularly recovered by machine or by hand from recreational beaches.

2. Emulsion Formation

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 20-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.

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 were the first to describe emulsification in detail and measured several physical properties of emulsions (Berridge et al., 1968). 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 in emulsion formation. 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 (Thingstad and Pengerud, 1983). Nesterova and coworkers 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 (Nesterova et al., 1983). 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 that 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 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 (Desmaison et al., 1984). 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 Phillips (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.

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. In the early 90s, Jenkins and coworkers studied emulsions formed in the laboratory and concluded that the formation did not correlate with previously established codes of properties, or with pour point, asphaltene, and wax contents of the fresh oils (Jenkins et al., 1991). They 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 analyses 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 for emulsions to form and that the oil must be weathered to a degree before release. Stability could not be characterized, but appeared to be a continuum through the process.

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 also 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. In turn, viscoelastic interfaces 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 and, in other words, by increasing the magnitude of the steric hindrance.

2.1 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 strongly influence 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 studied the interfacial behaviour of a Cerro Negro crude by a planar rheology (Acevedo et al., 1993). 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 studied surface pressure, as measured in a Langmuir film balance, of crude oils and solutions of asphaltenes and resins (Mohammed et al., 1993a, 1993b). They found that the pseudo-dilational 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 emulsions and vice-versa.

Chaala and coworkers studied the flocculation and the colloidal stability of crude fractions (Chaala et al., 1994). Stability was defined as the differential in spectral absorption between the bottom and top of a test vessel. The effects of temperature and additions of waxes and aromatics on stability were noted. Increasing both waxes and aromatics generally decreased stability. Temperature increased stability up to 60ºC 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., 1995). Resins and asphaltenes were extracted from North Sea crudes and exposed to ageing under normal atmospheric and ultraviolet conditions. The FT-IR spectra show 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 from 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 solubility state of asphaltenes is the most significant factor in emulsion formation.

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 reviewed emulsions and concluded that the asphaltene content is the single most important factor in the formation of emulsions (McLean et al., (1998). 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 an important 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 and coworkers studied the effect of the fused-ring solvents including naphthalene, phenanthrene, and phenanthridine in destabilizing emulsions (Singh et al., 1999). 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 (Singh et al., 1999). 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.

2.2 Resins

Neuman and Paczynska-Lahme (1996) 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 studied the ageing of crude oils and its effect on the stability of emulsions (Rønningsen et al., 1995). 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.

2.3 Waxes

Johansen and coworkers studied water-in-crude oil emulsions from the Norwegian continental shelf (Johansen et al., 1988/89). 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 that 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 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) (Puskas et al., 1996). This paraffinic derivative stabilized water-in-oil emulsions at concentrations of 1 to 2%.

3. Methodologies for Studying Emulsions

3.1 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:

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

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., 1996a,b). 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 found similar results on model emulsions stabilized with resins and asphaltenes extracted from North Sea oil (Ese et al., 1997). 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.

3.2 Rheology

In 1983, Steinborn and Flock studied the rheology of crude oils and water-in-oil emulsions (Steinborn and Flock, 1983). Emulsions with high proportions of water exhibited pseudo-plastic behaviour and were only slightly time-dependent at higher shear rates. Omar and coworkers also measured the rheological characteristics of Saudi crude oil emulsions (Omar et al., 1991). Non-Newtonian emulsions exhibit pseudo-plastic behaviour and followed a power-law model. Mohammed and coworkers studied crude oil emulsions using a biconical bob rheometer suspended at the interface (Mohammed et al., 1993b). 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 and Aomari and coworkers examined model emulsions and found that a maximum shear strain existed that occurred around 100 s^{-1} (Lee et al., 1997; Aomari et al., 1998).

3.3 Nuclear Magnetic Resonance (NMR)

Urdahl and coworkers studied crude oils and the silica-absorbed compounds (asphaltenes and resins) using ^{13}C Nuclear Magnetic Resonance (NMR) techniques (Urdahl et al., 1992). 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 studied the use of ^{13}C NMR to characterize emulsions using the NMR self-diffusion technique (Balinov et al., 1994). 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 used proton NMR to study oils and emulsions (LaTorraca, 1998). 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.

3.4 Interfacial Studies

Sjöblom and coworkers studied model emulsions stabilized by interfacially active fractions from crude oil (Sjöblom et al., 1992a). 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 studied the pressure-area isotherms and relaxation behaviour in a Langmuir trough (Børve et al., 1992). 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 long-chain amines have been added.

In a similar study, Ebeltoft and coworkers mixed surfactants (sodium dodecylsulphate, and cetyltrimethlyammonium bromide or cetylpyridinium chloride) with PSAA and studied the pressure-area isotherms (Ebeltoft et al., 1992). 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 that 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 studied the film-forming properties of asphaltenes and resins using a Langmuir trough (Ese et al., 1998). 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 Physical Studies - Structure and Droplet Sizes

Eley and coworkers studied the size of water droplets in emulsions using optical microscopy and found that the droplet sizes followed a log-normal distribution (Eley et al., 1988). 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 studied asphaltenes extracted from crude oils of various origins using atomic-force microscopy (Toulhoat et al., 1994). 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 a few micrometers long, 1 µm wide, and 10 to 20 m thick.

Balinov and coworkers studied the use of ^{13}C NMR to characterize emulsions using the NMR self-diffusion technique and compared this to optical microscopy (Balinov et al., 1994). 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).

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

3.6 Recent 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). Studies were therefore 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, meso-stable 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.

Fingas and coworkers 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.

Meso-stable emulsions are emulsions that have properties between stable and unstable emulsions (really oil/water mixtures) (Fingas et al., 1995). It is suspected that meso-stable 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. Meso-stable emulsions may degrade to form layers of oil and stable emulsions. Meso-stable 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 absolutely 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 meso-stable 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. Emulsion Formation Modelling

The early emulsion formation theories were translated into modelling equations at that time. Unfortunately, the processes described above were not apparent until about 10 years ago and have not yet been translated into modelling equations. Furthermore, the presence of different water-in-oil states dictates that one simple equation is not adequate to predict formation. Information on the kinetics of formation at sea and other modelling data was less abundant in the past than it is now. It is now known that emulsion formation is a result of surfactant-like behaviour of the polar asphaltene and resin compounds. These are similar compounds and both behave like surfactants when they are not in solution, but asphaltenes form much more stable emulsions. Emulsions begin to form when the above chemical conditions are met and when there is sufficient sea energy.

In the past, the rate of emulsion formation was assumed to be first-order with time. This can be approximated with a logarithmic (or exponential) curve. Although not consistent with the knowledge of how emulsions formed, this assumption has been used extensively in oil spill models. Most models that incorporate the phenomenon use the estimation technique developed by Mackay and coworkers (Mackay and Zagorski, 1982a,b; Mackay et al., 1980a,b, 1982) or a variation of this.

Mackay suggested an equation to model water uptake:

$$\Delta W = K_{\mathrm{a}}(U + 1)^2\,(1 - K_b W)\Delta t, \qquad (2)$$

where: ΔW is the water uptake rate,
W is the fractional water content,
K_{a} is an empirical constant,
U is the wind speed,
K_{b} is a constant with the value of approximately 1.33, and
t is time.

Because eqn (1) predicts that most oils will form emulsions rapidly given a high wind speed, most users have adjusted the equation by changing constants or the form slightly.

Mackay and Zagorski (1982a,b) proposed two relationships to predict the formation of emulsions on the sea. They proposed that the stability could be predicted as follows:

$$S = x_a \gamma_a \exp[K_{ao}(1 - x_a - x_w)^2 + K_{aw} x_w^2]\, \exp^{[-0.04(T-293)]}, \qquad (3)$$

where: S is the stability index in relative units, high numbers indicate stability,
x_{a} is the fraction of asphaltenes,
γ_{a} is the activity of asphaltenes,
K_{ao} is a constant which here is 3.3,
x_{w} is the fraction of waxes,
K_{aw} is a constant which is 200 at 293 K, and
T is the temperature in kelvin.

Water uptake was given as:

$$\begin{aligned}\Delta W_{\mathrm{T}} &= \Delta W_{\mathrm{L}} + \Delta W_{\mathrm{s}} \\ &= \Delta T[k_{\mathrm{f}} - k_{\mathrm{l}} W_{\mathrm{l}}], \qquad (4)\end{aligned}$$

where: ΔW_{T} is the total change in water content,
ΔW_{L} is the change in water content for large droplets,
ΔW_{s} is the change in water content for small droplets,
ΔT is time, k_{f} is the rate constant for formation, typically 1 h^{-1}, k_{l} is the rate constant for large droplet formation and is about 3 h^{-1}, and
W_{l} is the fraction of large droplets which is typically 3 to 4.

Kirstein and Redding (1988) used a variation of the Mackay equation to predict emulsification:

$$(1 - k_2 W)\exp\frac{-2.5W}{1 - k_1 W} = \exp(-k_5 k_3 t), \qquad (5)$$

where: k_2 is a coalescing constant which is the inverse of the maximum weight fraction water in the mixture,

W is the weight fraction water in the mixture,

k_1 is the Mooney constant which is 0.62 to 0.65,

k_5 is the increase in mousse formation by weathering,

k_3 is the lumped water incorporation rate constant and is a function of wind speed in knots, and

t is the time in days.

The change in viscosity due to mousse formation was given by:

$$\mu = \mu_0 \exp \frac{-2.5W}{1-k_1 W}, \qquad (6)$$

where: μ is the resulting viscosity,

μ_0 is the viscosity of the starting oil, and

the remainder are identical to the above.

Reed (1989) used the Mackay equations in a series of models. The constants were adjusted to correspond to field observations:

$$\frac{dF_{wc}}{dt} = 2\times10^{-5}(W+1)^2\left(1-\frac{F_{wc}}{C_3}\right), \qquad (7)$$

where: dF_{wc} /dt is the rate of water incorporation,

W is the wind speed in m/s,

F_{wc} is the fraction of water in oil, and

C_3 is the rate constant equal to 0.7 for crude oils and heavy fuel oils.

The viscosity of the emulsion was predicted using the following variant of the Mooney equation:

$$\frac{\mu}{\mu_0} = \exp\frac{2.5F_{wc}}{1-0.65F_{wc}}, \qquad (8)$$

where: μ is the viscosity of the mixture,

μ_0 is the viscosity of the starting oil, and

F_{wc} is the fraction of water in oil.

The effect of evaporation on viscosity is modelled as:

$$\mu = \mu_0 \exp (C_4 F_{\text{evap}}), \qquad (9)$$

where: μ is the viscosity of the mixture,

μ_0 is the viscosity of the starting oil,

C_4 is a constant which is 1 for light fuels and 10 for heavy fuels, and

F_{evap} is the fraction evaporated from the slick.

All of the above work has a basis in the Mackay equations, which were developed before extensive work on emulsion physics took place. The present author suggests that both the tendency and the formation of emulsions could be predicted with a greater degree of accuracy using empirical data as described below.

4.1 Fingas 2001 Model

In 2001, Fingas proposed that a characteristic table be used to predict the formation of water-in oil emulsions (Fingas et al., 2001a, b). A table of threshold properties relevant to predicting the formation of emulsions is used. Starting at the bottom of this table, it is presumed that unstable emulsions are the most common state, which they are. The properties of the oil are then compared, up to the final state or stable emulsions. The properties of the starting oil change as it weathers and most models already incorporate formulae to estimate density and viscosity as the oil weathers. Since resins and emulsions do not evaporate, it can be presumed that they increase proportionately to the loss by weathering. For example, if an oil containing 5% resins and 5% asphaltenes weathers to 50%, the resin content is now 10% and the asphaltene content is 10% as well.

4.2 Fingas 2004 Model

In 2004, Fingas proposed a continuous model to predict any of the four emulsion states (Fingas and Fieldhouse, 2004a,b,c). The formation data were used to develop mathematical correlation equations. The value for each parameter was correlated in a series of models using DataFit (Oakdale Engineering), which calculates linear models. A two-step process was necessary as DataFit is not able to calculate the specific mathematical function with more than 2 variables due to the large number of possibilities. Thus, the function, e.g., linear, square, log, were calculated using a two-way regression (TableCurve) and these functions were in turn used to develop a predictor model for emulsification.

The steps to produce the model are summarized here. First the parameters available were correlated one at a time. Regression coefficients were optimized by adjusting the class criteria from a starting value of 1 to 4 to a logarithm of this value. This was performed on a trial-and-error basis to yield the highest regression coefficient. The resulting criteria are: - 0.22 is unstable, 0.69 is entrained, 1.1 is meso-stable, and 1.38 is stable. Several of these parameters can have a zero value which causes calculation problems. If this is the case, the 0 is adjusted to either delete these values or to adjust it to the typical high value for the parameter. This is called the ‘first transform’. A second transformation is performed to adjust the data to a singular increasing or decreasing function. Most parameters have an optimal value with respect to class, that is the values have a peak function with respect to stability or class.

This is illustrated in Figure 1 and Figure 2. The resin content without any adjustment is plotted against the stability in Figure 1. As can be seen in this figure, the values of stability peak at about 5% resins. After this correction is made to the values, the regression coefficient increases. The modified distribution is shown in Figure 2. The arithmetic converts values in front of the peak to values behind the peak, thus yielding a singular declining or increasing function. The optimal value of this manipulation is found by trial and error, beginning with the estimated peak from the first correlation such as can be seen in Figure 1. The arithmetic to perform this manipulation is: if the initial value is less than the peak value, then the adjusted value is the peak value less the initial value, and if the initial value is more than the peak value, the adjusted value is the initial value less the peak value. The peak values are shown as the ‘second transform’ value.

The values of the second correction were then correlated using the package Data Fit. Several models were developed. It had been noted in earlier work that heavy oils were somewhat different in emulsion formation than were light oils (Fingas and Fieldhouse, 2003). For this reason, trial models were created separately for light and heavy oils. These were actually poorer than the other combined models and so ultimately were not used. The best model was one that included only five parameters: density, viscosity, saturates, resins, and asphaltenes. It was found that the regression coefficients of class with aromatic content, asphaltene/resin ratio, and waxes were too low to include in the model. It should be noted that there are some problems with the fundamental process of categorizing water-in-oil states at the onset. Some crude oils are enhanced when emulsion preventors, also called asphaltene suspenders, are added directly at the well-head because they are very emulsion-prone. Some emulsion-prone oils may therefore not form emulsions during the laboratory or field tests because of these emulsion-preventing materials. Although attempts are made to obtain oils that do not contain these emulsion-preventing materials, it is impossible to know this fact in every case.

The oils and resulting water-in-oil states used for this correlation were studied to yield the average water content and increase in the viscosity from the starting oil to the water-in-oil class. This will be used to predict the water content and the viscosity, given the known class of water-in-oil mixture formed.

The kinetics of emulsion formation have been studied and data are available to compute the time to formation. A kinetics study has shown the times to formation for stable emulsions are particularly rapid and that of entrainment is also rapid - both in a matter of minutes (Fingas et al., 2000b). This study yields data in terms of relative formation time and energy (rpm) of the mixing apparatus. This particular data set is thought to be especially accurate. A study in a large test-tank has yielded data on the formation time of the various water-in-oil states (Fingas et al., 2002b). The data of the relative formation times and the wave height are available. The average data over 25 runs was used to make the calculations. The formation time is taken as that time at which 75% of the maximum stability measured occurs. The conditions under which these tests took place and the measurements taken are described in the literature (Fingas et al., 2002b). The wave height for each experiment was measured and used to indicate relative sea energy, taken for a fully developed sea. The laboratory data was converted from relative rotational energy to wave height by equating formation times and then using this multiplier to calculate the equivalent wave height. Formulae were fitted to each of the three categories and the common formula among all three relevant classes, was found to be $1/x^{1.5}$. Application of the equations will then provide a user with a time to formation of a particular water-in-oil state, given the wave height.

The first step in using the model is to obtain or estimate the oil properties as they are at the weathering condition of concern. The properties needed are the density, viscosity, and saturate, resin and asphaltene contents. These values require transformation as noted below.

Density - If the density is less than 0.96, then the density parameter is 0.96 less the density and if it is greater than 0.96, it becomes the density less 0.96. The value used in the equation is then the exponential of this transformed value. (10)

Viscosity - Take the natural logarithm (ln) of the viscosity. If the natural log of the viscosity is less than 7.7, then the viscosity parameter is 7.7 less the viscosity natural log and if it is greater than 7.7, it becomes the natural log of viscosity less 7.7. The value used in the equation is this transformed value. (11)

Saturate Content - If the saturate content (in percent) is less than 39, then the saturate content parameter is 39 less the saturate content and if it is greater than 39, it becomes the saturate content less 39. The value used in the equation is this transformed value. (12)

Resin Content - If the value of the resins is zero, then set this value to 20. If the resin content is less than 2.4, then the resin content parameter is 2.4 less the resin content and if it is greater than 2.4, it becomes the resin content less 2.4. The value used in the equation is the natural logarithm of this transformed value. (13)

Asphaltene Content - If the value of the asphaltene content is zero, then set the value to 30. If the asphaltene content is less than 15.4, then the asphaltene content parameter is 15.4 less the asphaltene content and, if it is greater than 15.4, it becomes the asphaltene content less 15.4. The value used in the equation is then the exponential of this transformed value.
(14)

The class of the resulting emulsion is then calculated as follows:

$$\text{Class} = -1.36 + 2.62*\text{Dt} - 0.18*\text{Vt} - 0.01*\text{St} + 0.02*\text{Rt} - 2.25\ 10^{-7}*\text{At} \qquad (15)$$

where: Class is the numerical index of classification,
Dt is the transformed density as calculated in equation (10),
Vt is the transformed viscosity as calculated in equation (11),
St is the transformed saturate content as calculated in equation (12),
Rt is the transformed resin content as calculated in equation (13), and
At is the transformed saturate content as calculated in equation (14).

The second step in calculating the emulsion formation and its properties is to apply the numeric class value as yielded from equation (15). This is simply accomplished by using Table1a.

The third step is to predict the properties of the resulting water-in-oil emulsion. Table 1b gives the average water content and increase in viscosity of the various types of emulsions.

The fourth step is to predict the time to formation after the oil is weathered to the stated percentage. This calculation can be made using the equations given in Table 1c:

$$\text{Time to formation (min)} = a + b/\text{Wh}^{1.5} \qquad (16)$$

where: a is a constant and is 27.1 for a stable emulsion formation, 47 for meso-stable, and 30.8 for an entrained water-in-oil class,
b is a constant and is 7,520 for a stable emulsion formation, 49,100 for meso-stable, and 18,300 for an entrained water-in-oil class, and
Wh is the wave height in cm.

4.3 Fingas 2005 Model

The 2004 model was totally revised in 2005 to provide a model of greater accuracy (Fingas and Fieldhouse, 2005). The development methodology was similar to that above. The mathematical procedures still required transformations of the data for the reasons stated above.

These transformations of input values are summarized below.

Density - If the density is less than 0.97, then the density parameter is 0.97, less the density and, if it is greater than 0.97, it becomes the density, less 0.97. The value used in the equation is this transformed value. (17)

Viscosity - Take the natural logarithm (ln) of the viscosity. If the natural log of the viscosity is less than 8.7, then the viscosity parameter is 8.7 less the viscosity natural log, and if it is greater than 8.7, it becomes the natural log of viscosity less 8.7. The value used in the equation is this transformed value. (18)

Resin Content - If the value of the resins is zero, then set this value to 20. If the resin content is less than 5.4, then the resin content parameter is 5.4, less the resin content and if it is greater than 5.4, it becomes the resin content, less 5.4. The value used in the equation is this transformed value. (19)

Asphaltene Content - If the value of the asphaltene content is zero, then set the value to 30. If the asphaltene content is less than 12, then the asphaltene content parameter is 12 less the asphaltene content and, if it is greater than 12, it becomes the asphaltene content less 12. The value used in the equation is this transformed value. (20)

The class of the resulting emulsion is then calculated as follows:

$$\text{Class} = 0.738 - 0.197*Dt - 0.0126*Vt - 0.0007*Rt - 0.00358*At \quad (21)$$

where: Class is the numerical index of classification,
Dt is the transformed density as calculated in equation (17),
Vt is the transformed viscosity as calculated in equation (18),
Rt is the transformed resin content as calculated in equation (19), and
At is the transformed asphaltene content as calculated in equation (20).

The second step in calculating the emulsion formation and its properties is to apply the numeric class value as yielded from equation (21). This is simply accomplished by using Table 2.

The third step is to predict the properties of the resulting water-in-oil emulsion. The average water contents and increase in viscosity are given in Table 2.

The fourth step is to predict the time to formation after the oil is weathered to the stated percentage. This calculation can be made using the equations in Table 2:

$$\text{Time to formation (min)} = a + b/Wh^{1.5} \quad (22)$$

where: a is a constant and is 27.1 for a stable emulsion formation, 47 for meso-stable, and 30.8 for an entrained water-in-oil class,
b is a constant and is 7,520 for a stable emulsion formation, 49,100 for meso-stable, and 18,300 for an entrained water-in-oil class, and
Wh is the wave height in cm.

5. Review of the "White Paper on Emulsification of ANS Oil" by S.L. Ross

This section will focus on summarizing the report by S.L. Ross, emphasizing those areas where there are issues of fact or procedure. As much of the report contains introductory or summary material, this will not be dealt with here. When there are differences from the general knowledge on oil properties as already noted, this will be highlighted by references to the specific section in this review. The report will be referred to as the SLR report. Direct quotes from the report are shown in italics.

Page 3 - Evaporation - the report states: *It is known that evaporation of an oil slick is controlled or affected by:*

1) the temperature of the oil and the air;
2) the surface area of the oil in contact with air ;
3) the thickness of the oil;
4) wind speed; and
5) the concentration and vapor pressure of the individual components of the oil.

This is old boundary-layer regulation evaporation theory and does not reflect the new findings on oil evaporation such as described in Fingas (2004). Nor is there mention of the newer, more accurate findings noted in this paper or its references. The report goes on to list only 1978, 1983, and 1984 references for evaporation behaviour. In fact, Fingas (2004) noted that, of the factors listed, only the temperature and the basic oil properties are factors and inclusion of the other factors, derived from water evaporation equations, lead to great inaccuracies in prediction.

Page 4 - Emulsification- The report does not cite any of the most important references on emulsification (over 50 references) noted in Section 2 of this review. Furthermore, it cites only references from 1990, 1991, and 1993 that are not part of the main stream of emulsification theory. It does not include references that are key to modern understanding of emulsification such as those by Førdedal, Sjöblom, McLean, Kilpatrick, Fingas, Masliyah, and others in the peer-reviewed literature.

The report states: *The mechanisms and rates of the emulsification of oils spilled at sea are still poorly understood. Through some mechanism, the mixing energy associated with waves causes small water droplets to become entrapped in the oil layer. Several theories have been advanced about the main chemical mechanisms involved in the process (Bobra 1990, 1991, Walker et al., 1993). Most experts believe that precipitates of asphaltenes and resins in the oil act as surface-active agents to stabilize the smaller water droplets in the forming emulsion. These natural surfactants form a "skin" around the smaller water droplets, preventing them from coalescing to form larger droplets. Without such stabilizing agents the small water droplets in the oil layer would tend to combine into larger droplets that would sink through and leave the oil slick. An increase in the number of water droplets retained in the slick increases its viscosity, which in turn decreases the rate at which water droplets settle out, thus emulsification tends to occur rapidly once the appropriate conditions for forming a stable emulsion are reached. In any case, emulsification inhibits natural dispersion because the process greatly increases slick viscosity. Spills of some crude oils (generally those with higher concentrations of asphaltenes and resins) will start to form an emulsion within a few minutes of environmental exposure, and will form a highly viscous and stable emulsion within hours. This has been recorded many times during actual and experimental spills. On the other hand, some crude oils must lose some of their lighter components through evaporation before the concentrations of their asphaltenes and resins are raised to the levels required to stabilize emulsions. Most refined petroleum products* *do not easily emulsify at all.*

This section is not entirely inaccurate but misses any relevant reference to the formation of emulsions as noted in Section 2 of this review and other very extensive literature on this topic. Most of the discoveries have been after the references noted by the SLR report. The remainder of the paragraph is relatively correct, but lacks the detail to render it useful to the prediction or understanding of emulsification. The SLR report misses the absolutely critical factor that there are four water-in-oil states, only two of which are emulsions.

Page 5 - Emulsification prediction - The report states: *Oil spill emulsification is one of the most difficult processes to model or predict on a spill-specific basis. Except perhaps for a few oils that have been tested extensively, such as ANS, it is virtually impossible to quantitatively predict when a particular crude oil will start to emulsify once spilled in a particular environment, and, once the emulsification process begins, to predict how long it will take for the spilled oil to form a "stable", highly viscous emulsion. Nonetheless, modellers of spill behavior have to deal with the problem of spill emulsification because it is such an important process. The usual tactic is to take advantage of a laboratory test, called the Mackay-Zagorski Test (Mackay and Zagorski, 1982) that was developed to measure (1) an oil's tendency to form an emulsion and (2) the stability of the emulsion once formed. The test provides some indication of an oil's emulsion forming characteristics, but does not predict rates of spill emulsification in the field.*

This section misses the very important set of references by Fingas and Fieldhouse (2001, 2004a,b,c, and 2005) on reviews of existing emulsification models and development of new models. Furthermore, very early after it was written, it was shown that there were severe problems with the Mackay-Zagorski emulsification test and it was subsequently abandoned (Bobra et al., 1990). It must also be stated that this method has little to do with modelling, but was only a proposed method to examine emulsion stability and has no predictive power.

Page 5 - Modelling - The report states: *The major spill processes discussed above that determine the behavior of oil spilled on water are interrelated and must be considered together to arrive at an accurate estimate of an oil's likely behavior. That is the purpose of oil spill behavior models, of which there are several available internationally. Most are similar in many ways because they use similar mathematical algorithms in the structure of the models. For this work we have used the model developed by S. L. Ross Environmental Research Ltd., which is particularly useful in this study because it is able to deal with high pour-point oils.*

It should be noted that the S.L. Ross model is relatively unknown and unproven and is not documented at all in the peer-reviewed literature, while several other models are. The most common models are the suite of models by Applied Science Associates (ASI) such as Oilmap, Simap, etc. As will be shown later in this review, the S.L. Ross paper does not contain any algorithms more recent than about 1985. The algorithms in the report are at least 20 years old and many have been shown to be outdated and inaccurate.

The next item that stands out is the 'high-pour point oils'. As noted in Section 1.3.1 on oil properties in this review, pour point is a very poor descriptor of oils and should not be used today.

Page 6 - Oil sample - The report states: *One gallon of ANS crude oil was obtained from the Valdez Terminal in the spring of 2004 and shipped to the SL Ross laboratory in Ottawa.*

It should be noted that the entire emulsification results in the S.L. Ross report are based on one sample. As noted in Section 1.3.1 of this review, the oil properties of any field system are constantly changing and thus one sample may not be representative and can in no way be used to predict a trend.

Page 6 - The report notes: *A wind tunnel was used to determine the evaporative characteristics of the ANS crude oil, and to prepare weathered samples for physical property analysis. Three 900-mL samples of oil were withdrawn from the shipping container. One of these was reserved, while the remaining two were poured into shallow metal trays and placed in a wind tunnel operating at a wind speed of approximately 3 m/s, and an air temperature of approximately 15˚C. The initial thickness of oil in the trays was 2 cm. One sample was removed from the tunnel after two days, and the second after two weeks. Depending on the conditions at a spill site, this duration is typically equivalent to a few hours and a few days at sea.*

The wind tunnel method is not an accurate method of weathering oil for the purposes of studying evaporation (Fingas, 1994). Furthermore, the relationship of this type of weathering to a 'few hours or a few days' has never been established.

Page 7 - Table 1 - Analytical methods - It is stated that evaporation is performed by ASTM D86. This is not the method used in this study and the wind tunnel does not conform to any standard.

The viscosity was purportedly measured by a Brookfield viscometer which is out of range for these measurements and is not shear-stress controlled (Wang et al., 2004).

The CSC DuNuoy ring tensiometer is a low-grade instrument and will yield poor repeatability (Wang et al., 2004).

The pour point tests and the standard it refers to are highly questionable.

The rotating flask apparatus noted (Mackay and Zagorski, 1982a,b) was never accepted and was never a standard. As already stated, several references noted difficulties with this test very soon after it was written.

Page 8 - Oil gelling - The SLR report states: *It is this increase in pour point, and eventual gelling of the oil at freezing temperatures, that accounts for the higher stability, water content, and viscosity of the moderately stable emulsions created with the evaporated samples at 0˚C as opposed to the unstable emulsions created at 15˚C. At freezing temperatures, the oil, as it weathers, will gel when it reaches about 20% evaporated, trapping the low amounts of water it has incorporated to this point. No further emulsification will occur once the oil has gelled, and the encapsulated water drops will be trapped until the oil is heated above its pour point.*

Oil does not gel, rather its viscosity increases with decreasing temperature. This statement is entirely spurious and is not backed by references. It is true that at lower temperatures, emulsions may be more prone to form, for different reasons. The correct process of emulsification is described in Section 2 of this review.

Page 8 - Additions of demulsifier and gelling - The report states: *In the original scope of this study, it was expected that a stable emulsion would indeed form. As such it was proposed to investigate the potential beneficial effects of adding demulsifying chemical. Because the oil did not form a stable emulsion, this was examined only briefly, in two tests at 0˚C and 15˚C. The addition of demulsifier had no effect on the gelled "emulsion" at 0˚C. It did resolve the light emulsion created at 15˚C; however, its use on such low water content, low viscosity mixtures would not be justified.*

There was no reason to expect that a stable emulsion would form, as literature on the topic indicated that meso-stable emulsions form (Fingas et al., 2001b). Part of the problem with this work is that the water-in-oil states created here are not characterized. The result of the experiment was probably entrained water in oil, in which case de-emulsifier has no effect. Again, there is no such thing as ‘gelled oil’ or ‘gelled emulsion’.

Page 9 - Table 3 - Spill-related properties - Evaporation was carried out as volume %. This is an incorrect procedure as it results in inaccuracies due to adhesion of oil to vessel surfaces and the change in density with weathering. The latter results in a change of volume that is difficult to relate to weight % weathering (Wang et al., 2004). Dynamic viscosity is given. This method is only for fuels (Wang et al., 2004) and cannot be extended to denser crude oils. The distillation is also given as ‘modified ASTM’, which is not ASTM as ASTM specifies very clearly that only the vapour temperature yields an accurate measurement (Wang et al., 2004). The weathering model given is a Mackay model including three constants. Such a model does not yield accurate data as will be shown later.

Page 10 - Formation of emulsions - The SLR report states: *What was somewhat surprising, and of particular interest to this study, was the fact that the oil was unlikely to form a stable emulsion, even at 0˚C when weathered up to 39% by volume. Previous analyses of ANS crude (SL Ross, 1994 and 1997, Jokuty et al., 1999) indicated that once approximately 20% of the light ends of ANS crude had evaporated, a stable emulsion would form. Potential reasons for this difference are discussed below.*

The Jokuty et al. report did not indicate the formation of emulsions to the stable state but rather to the meso-stable state and, for lighter weathering, to the unstable state. The literature never reported on a stable emulsion forming from ANS.

Page 10 - Changes in ANS crude oil properties over time - The SLR report states: *The fact that the 2004-vintage ANS crude does not form a stable emulsion is likely due to continuing changes in the characteristics of the “sales” oil as a result of an ever-changing blend of crude oil feeds on the North Slope. ANS crude oil has been subjected to similar spill-related property analysis over the last 20 years, and the results indicate a steady decline in both oil density and oil viscosity. Figure 3 shows a graph of the density and Figure 4 shows the oil's viscosity; both are for fresh, unweathered ANS crude at 15˚C, and data is shown from 1983 to the present sample. Both density and viscosity have been decreasing significantly with the passage of time; presumably as more high API gravity crudes are added to the mixture at Pump Station 1. Figure 5 is a similar graph showing the change in pour point over time for ANS crude. This graph indicates a significant decrease over time of the pour point up until the late 1990s, with an equally significant increase in more recent years.*

These conclusions are drawn from unspecified sources, e.g., the sources of the density, viscosity, and pour point data in Figure 3, 4, and 5 of the SLR report are not specified. Figure 5 of the SLR report shows the pour point. The above quote from the text indicates that the pour point is decreasing, however, this is not shown distinctly in Figure 5. Rather, Figure 5 shows why pour point is not a good value. As pour point can vary as much as 20 degrees with operator and test conditions, Figure 5 is anomalous.

Page 11 - Model inputs - The slick is presumed to be 100 mm in thickness due to containment. This appears to be quite thick and would in reality certainly escape under the boom.

Page 12 - ADIOS Model - The SLR report states: *Although many oil property prediction features of the ADIOS 2.0 model are similar to those in the SL Ross model (note that ADIOS 2.0 does not predict pour point), two differences are worthy of note. First, the ADIOS 2.0 model uses a pseudo-component approach to estimating evaporation rates (the oil is divided into ten components representing different boiling ranges and the evaporation rate of each is estimated), whereas the SL Ross model uses the analytical method (more simply, the crude is treated as one* *component with evaporation rates based on the slope and intercept of a modified ASTM distillation curve - Stiver and Mackay, 1984).*

The ADIOS model does not predict pour point for good reason. First, it is not a very useful number and second it is unreliable. There is also good reason for using the pseudo-component approach as is done in the ADIOS model as it yields more realistic results than the 'analytical' approach used in the S.L. Ross report. As will be seen later, neither model is as accurate as the empirical approach (Fingas, 2004).

Page 13 - Prediction on free-spreading oil - The SLR report states: *The free-spreading 155,000 bbl release is predicted to lose approximately 26% to evaporation in 72 hours, and emulsify to nearly 90% water content with a viscosity in excess of 100,000 mPas. This difference from the predicted behaviour of the contained slick is due to the difference in evaporation rate: the uncontained slick thins rapidly as it spreads and thus is predicted to evaporate much more quickly than the contained slick. The uncontained slick evaporates more than 18%, and is predicted to emulsify; the contained slick never reaches 18% evaporated in the 72 hour modeling period.*

The result that free-spreading oil achieves a weathering amount of 26% by volume whereas a contained slick only weathers to 14% by volume is only an artefact of the prediction scheme used. As is explained in the literature, the use of a boundary-layer regulated model derived from water evaporation inputs the wind and slick area (Fingas, 2004). However, extensive testing and measurement on actual spills shows that this is not the case and that slicks weather largely as a function of time and temperature (Fingas, 2004). While it is true that very thick slicks weather somewhat more slowly, this is a function of internal mass transfer of volatiles rather than a water-like evaporative behaviour (Berger and Mackay, 1994). Thus, the scenario differences between uncontained and contained slicks would not be much different except for the fact that, for emulsification to occur, wave energy would be required. This is unlikely to be sufficient in a boomed area.

Page 13 - Discussion - The SLR report states: *Both models predict that, in winter conditions, the contained slick of ANS crude would not evaporate to a great enough extent in 72 hours to begin emulsifying. The SL Ross model indicates that the contained oil, even in winter at freezing temperatures, would not evaporate enough to cause the pour point of the crude to exceed ambient temperatures, and commence gelling.*

As already noted, this is an artefact of the evaporation model used and not a true physical outcome.

Page 13 - Discussion - The SLR report states: *After the Exxon Valdez spill Allen (1991) observed that the slick was not significantly emulsified (20 to 30% water, based on the visual appearance of the slick and its ignition behavior during an in situ burning test) approximately 40 hours after the incident. Winds in this time period were in the 10-knot and less range with temperatures in the mid-30s°F. Within the next 24 hours, a storm passed through the area with winds up to 70 knots that resulted in significant emulsification of the oil (USCG, 1993). Samples of emulsion on the water collected two to three weeks after the spill had water contents in the 45 to 70% range and viscosities at 38°C (100°F) in the 450 to 2700 mPas (cP) range (Payne et al., 1991).*

Several issues are confused in this statement. As noted in Section 2 of this review, there are four water-in-oil states: unstable, entrained water in oil, meso-stable, and stable emulsions. Only the latter two are emulsions. Most oils uptake water to some degree. Those that do not retain very much water or form emulsions are ‘unstable’. Those that retain about 30% water do so by viscous entrainment. This is not emulsification. Those oils that emulsify can form an emulsion that breaks down rapidly, form meso-stable emulsions within 3 days, and those emulsions that last for longer than about 30 days can be called stable (Fingas et al., 2002a). What Allen (1991) observed was entrained water or unstable water-in-oil. Note that no measurement was carried out, only visual observation. Later sampling of the oil purportedly contained 45 to 70% water. These states would have been either entrained water or meso-stable emulsions. Unfortunately, no time resolution tests or rheometric tests were carried out to confirm these states, although the existing data would indicate that both entrained water (for the 45% water and 450 cP material) and meso-stable emulsions (for the 70% water and 2700 cP material) would be possible. Both results would be consistent with laboratory findings (Fingas et al., 2002a).

Page 14 and on - Pumping – There are no comments on this section as the pumping calculations are more or less correct and deviations do not change the calculations that significantly.

Page 16 and 17 references - The references used here are remarkably old and few. See the references for this review in Section 9.

Page 20 - Figure 5 and 6 - A change in pour point of fresh ANS and predicted evaporation from scenario 5 - Figure 5 illustrates why pour point should not be used as a predictor or any parameter for oil behaviour. Its value increases or decreases regardless of the overall trend and merely reflects the high variances in the measurement (plus or minus 10 to 20 degrees). The evaporation curve in Figure 6 predicts a loss of about 15% (by volume, inappropriately) compared to an empirical result of 22% by weight (Fingas, 2004). This is typical of the older, inaccurate evaporation prediction methods.

Page 21 - Figures 7 and 8 - Predicted slick thickness - It is predicted that the slick thickness goes from 100 mm (set initially) down to 80 mm. This is based only on evaporation and changes in volume. As noted above, this is not an appropriate calculation. Furthermore, setting the thickness to that great a value, based on containment, is unlikely since such a high thickness could not be successfully contained (Fingas, 2000).The predicted emulsification is 0 and, based only on water content, which is again inappropriate. The no-emulsification result is correct as there would be little energy to initiate emulsification.

Page 22 - Figures 9 and 10 - Predicted pour point and viscosity - These are based on a smooth increase function based on weathering. These are probably not accurate as will be shown in the analysis of the data in Section 6 of this review.

Page 23 - Figures 11 and 12 - Predicted evaporation and slick thickness for scenario 5 - It should be noted that all scenarios in this appendix are named as scenario 5. One presumes that the second one is the summer scenario. The predicted evaporation is about 18.5% by volume, compared to an empirical result of 30% by weight (Fingas, 2004). This is typical of the older, inaccurate evaporation prediction methods in that they typically under-predict the evaporation of crude oils and vastly over-predict the evaporation of diesel fuel. It is predicted that the slick thickness goes from 100 mm (set initially) down to about 80 mm. This is based only on evaporation and changes in volume, which is not an appropriate calculation. Furthermore, setting the thickness to that great a value, based on containment, is unlikely since such a high thickness could not be successfully contained (Fingas, 2000).

Page 24 and 25 - Figures 13, 14, and 15 - These cover the water content of the slick and predict pour point and viscosity. The same comments as noted above apply.

Appendix A - Description of the SL Ross model - It might be noted that the model is based on very old literature. An extensive body of new literature has superceded this older literature for most algorithms.

Appendix B - ANS 2004 Crude Analysis Page 2-1 Evaporation - It has been noted that the method referred to as ASTM D86-90 is actually not that method. The wind tunnel is not referred to in any peer-reviewed literature as such. A detailed up-to-date review of evaporation is given in the literature (Fingas, 2004).

Viscosity - Use of Brookfield viscometry - The ASTM standard referred to (ASTM D86-90) is actually for fuels and light oils. A cross-laboratory study of viscosity measurement is given in the literature (McDonagh, 1995). A detailed presentation of standard oil analytical methods is given in Wang et al. (2004).

Pour point - The method given here is different than that given in the front of the SLR report.

Emulsion formation tendency - It has been shown that the Mackay-Zagorski emulsification test had severe problems and it was subsequently abandoned soon after it was first written (Bobra et al., 1990). Furthermore, this method is not good for modelling. It was only a proposed method to examine emulsion stability and has no predictive power.

Section 2.1.1 Evaporation - Figure 2.1 shows an evaporation curve that is not a smooth curve. An empirical curve is shown later in the report that is a different shape than this one. Furthermore, the percent evaporated is much lower than the actual measured values.

Appendix A (second one - presumably an appendix to the oil property test measurement methods). A.1 Evaporation - As noted earlier, this includes modified data from Stiver and Mackay, 1984 and the main work of Mackay and Matsugu, 1973. These are older works of one theory progression and there are many differing theories on oil evaporation (Fingas, 1995). In the literature at this time, it is generally accepted that the behaviour of oil evaporation is not like that of water and that these older works used in the SLR report are not valid (Fingas 1997, 1998).

Appendix A.5 - Pour point - The SLR report states: *The pour point is the lowest temperature (to the nearest multiple of 3°C) at which an oil will still flow. Below this temperature, the oil develops an internal yield stress and, in essence, solidifies. The pour point of an oil increases with weathering. Pour point affects the following processes:*

- *spreading - oils at temperatures below their pour points will not spread;*
- *viscosity - an oil's viscosity increases dramatically at temperatures below its pour point;*
- *dispersion - an oil below its pour point is more difficult to disperse; and,*
- *recovery, transfer and storage - an oil below its pour point will resist flowing towards skimmers or down inclined surfaces in skimmers, and presents storage and transfer problems.*

Pour point is not the lowest temperature at which an oil will flow. As defined by the ASTM standard, pour point is the temperature at which the flow falls below a certain rate. As this involves some judgement, pour point is measured with poor repeatability. As it is a defined rate, there is lack of continuity in the values and pour point cannot be used to provide correlations. The points noted above are also in need of modification. Oil below its pour point will still spread, sometimes rapidly. The viscosity of the oil does not increase dramatically below the pour point and countermeasures are just a matter of continuity, i.e., there is no drastic change at temperatures above and below the pour point.

Appendix A.7 - Emulsion Formation - The report states: *A water-in-oil emulsion (colloquially named "chocolate mousse") is a stable emulsion of small droplets of water* *incorporated in oil. Oil spills on a water surface may form stable water-in-oil emulsions, which can have very different characteristics than the parent crude oil.*

The tendency of an oil to form water-in-oil emulsions (or "mousse") and the stability of the emulsion formed are measured by two indices: the Emulsification Tendency Index and the Emulsion Stability Index. The Emulsion Formation-Tendency Index can have a value of low, indicating that the oil will not form an emulsion, or high, indicating that the oil will form an emulsion. The Emulsion Stability Index can be low, which indicates the emulsion is unstable and will break quickly once it is removed from the mixing environment, moderate, which means the emulsion will break within a few hours, and high, which means the oil forms a very stable emulsion that is unlikely to break even after standing for 24 hours.

Both the Tendency Index and Stability Index generally increase with increased degree of evaporation. Colder temperatures generally increase both the Tendency Index and Stability Index (i.e., promote emulsification). Emulsion formation results in large increases in the spill's volume, enormous viscosity increases (which can reduce dispersant effectiveness), and increased water content.

The test procedure for emulsion tendency and stability follows the method now called the Mackay and Zagorski Test (Mackay, 1982a, Mackay, 1984). Three hundred millilitres of artificial seawater and 30 mL of oil are placed in a 500 mL Fleaker (oil to water ratio of 1:10), and the Fleaker is sealed. The Fleaker is rotated for one hour at a rotation speed of 65 rpm and then allowed to settle for 30 minutes. The fraction of oil that forms an emulsion, f, is determined by measuring the height of the emulsion and the height of the unemulsified oil. Three additional mixing/settling cycles are performed with measurements of f taken at each rotation interval. The tendency of an oil to form an emulsion is given by $f_{initial}$ *which is obtained by plotting f versus time, and by extrapolating f to time zero.*

The following criteria are used to classify the tendency of a crude oil to form a stable emulsion:

Range of $f_{initial}$	*Emulsion Formation Tendency*
0.0 to 0.25	*Not likely*
0.25 to 0.75	*Fairly likely*
0.75 to 1.0	*Very likely*

The stability of a water-in-oil emulsion is obtained by allowing the emulsion to settle for an additional 24 hours, and then measuring the fraction of oil in the emulsion (f_{final}) *visually. The stability of the water-in-oil emulsion is classified as follows:*

Range of f_{final}	*Emulsion Stability*
0.0 to 0.25	*Unstable*
0.25 to 0.75	*Fairly stable*
0.75 to 1.0	*Very stable*

The calculated water content of stable water-in-oil emulsions is also provided.

As already noted, these old, unaccepted procedures should be replaced with a modern understanding of emulsification. The Mackay-Zagorski procedure noted here was never accepted and was rapidly replaced by more modern procedures. The current state of the art in emulsion understanding and measurement is summarized in Section 2 of this review.

The basis of emulsification is summarized here. Emulsification is the process by which one liquid is dispersed into another one in the form of small droplets. Water droplets can remain in an oil layer in a stable form and the resulting material is completely different. These water-in-oil emulsions are sometimes called ‘mousse’ or ‘chocolate mousse’ as they resemble this dessert.

The mechanism of emulsion formation starts with sea energy forcing small water droplets, about 10 to 25 um (or 0.010 to 0.025 mm) in size, to enter the oil. If the oil is only slightly viscous, these small droplets will not leave the oil quickly. On the other hand, if the oil is too viscous, droplets will not enter the oil to any significant extent. Once in the oil, the droplets slowly gravitate to the bottom of the oil layer. Any asphaltenes and resins in the oil will interact with the water droplets to stabilize them. Depending on the quantity of asphaltenes and resins, as well as aromatic compounds that stabilize asphaltenes and resins in solution, an emulsion may be formed. The conditions required for emulsions of any stability to form are reached only after a period of evaporation. Evaporation lowers the amount of low-molecular weight aromatics in the oil and increases the oil’s viscosity to the critical value.

Water can be present in oil in four ways. First, some oils contain about 1% water as soluble water. This water does not significantly change the physical or chemical properties of the oil. The second way is called “entrainment”, whereby water droplets are simply held in the oil by its viscosity to form an unstable emulsion. These are formed when water droplets are incorporated into oil by the sea’s wave action and there are not enough asphaltenes and resins in the oil or if there is a high amount of aromatics in the oil that stabilizes the asphaltenes and resins, preventing them from acting on the water droplets. When the sea energy diminishes, unstable emulsions break down into water and oil within minutes or a few hours, at most. The unstable emulsion has almost the same properties and appearance as the starting oil, although the water droplets may be large enough to be seen with the naked eye.

Meso-stable emulsions represent the third way water can be present in oil. These are formed when the small droplets of water are stabilized to a certain extent by a combination of the viscosity of the oil and the interfacial action of asphaltenes and resins. For this to happen, the asphaltene or resin content of the oil must be about 3% by weight or greater. The viscosity of meso-stable emulsions is 50 to 150 times higher than that of the starting oil. These emulsions generally break down into oil and water or sometimes into water, oil, and stable emulsion within a few days. Meso-stable emulsions are viscous liquids that are reddish-brown or black in colour.

The fourth way that water exists in oil is in the form of stable emulsions. These form in a way similar to meso-stable emulsions except that the oil must contain at least 8% asphaltenes. The viscosity of stable emulsions is 1,000 to 1,500 times higher than that of the starting oil and the emulsion will remain stable for weeks and even months after formation. Stable emulsions are reddish-brown in colour and appear to be nearly solid. Because of their high viscosity and near solidity, these emulsions do not spread and tend to remain in lumps or mats on the sea or shore.

Each of these four ‘states’ is readily distinguished by lifetime and is quite different by this discriminator. In addition, rheological studies can be carried out to immediately distinguish types.

6. Analysis of Alaskan North Slope Oils from Literature and Data Comparison

The Environment Canada database contains a number of high quality data on the Alaskan North Slope Oils (ETC, 2005). These data will be useful for comparing the data in the SLR report and establishing the properties of the Alaskan oils, the emulsification behaviour, and the change in properties/behaviour over time. These data are shown in Table 3, which includes the data from the SLR report in the bottom rows.

In this section, the various data will be compared with emphasis on two critical factors - the change in properties over time that would indicate whether the oil is becoming lighter or heavier and the changes in emulsification properties. The differences between the SLR data and the ETC on-line data will then be summarized. Each parameter in the ETC database will be examined from two points of view: the year of the sample and the weathering percentage (by weight) of the sample.

The various figures providing comparison are summarized in Table 4. The first column lists the parameter of interest. The second lists the relevant figure in which the data is illustrated. The third column summarizes whether the parameter under discussion is indicative of the trend of the oil becoming heavier or lighter over the years and the next column indicates whether any changes in this parameter would show that emulsification is more or less likely. The fifth column indicates the significance of the data to the two questions of the heaviness trend and the emulsification trend. The sixth column provides a rating of the accuracy of the data. The seventh column assesses the accuracy of old data on the topic, and finally the eighth column assesses the accuracy of the data in the SLR report. This is repeated for the weathered oils. As the weathering percentage is different in most samples, it is difficult to directly compare properties over time.

Figure 3 shows the percentage of sulphur in the samples over the years, which is decreasing with time. This indicates the oil mixture is getting lighter, perhaps by the addition of lighter oils in the Trans-Alaska pipeline. Figure 4 shows that the sulphur content increases as the weathering percent increases. This is not highly significant in terms of the two major questions here, as it is expected that the sulphur content would increase with weathering percentage.

Figure 5 shows the change in flash point over the years. The data from the SLR report is shown in this figure and subsequent figures by the arrow. The flash point decreased over the past years indicating that there is a lighter oil in the pipeline than in previous years. Figure 6 shows the change in flash point with weathering percentage. As would be expected, the flash point rises with increasing weathering. The values from the subject point appear to be slightly lower than the other data.

Figure 7 shows the density (at 0°C) in the samples over the years. The density is decreasing with time, which indicates that the oil mixture is getting lighter, perhaps by the addition of lighter oils in the North Slope mix. The decrease in density over the years indicates that emulsification would also be slightly less likely. Figure 8 shows that the density (at 0°C) increases as the weathering percentage increases.

Figure 9 shows the change in density by both weathering and year. The density itself is shown by the size of the circle in the figure. The data from the SLR report is shown in this figure and subsequent figures by the arrow. Figure 10 shows the change in density (at 15°C) by year. The values show a similar trend to that of the density at 0°C. This shows a constantly decreasing value with time. Figure 11 shows the density change (at 15°C) with weathering percent. As expected this shows the density increasing with weathering. Figure 12 shows the change in density by both weathering and year. The density itself is shown by the size of the circle in the figure. There does not appear to be a 3-way correlation in the data.

Figure 13 shows the pour point of the samples over the years, which is decreasing with time. This indicates that the oil mixture is getting lighter, perhaps due to the addition of lighter oils in the Trans-Alaska pipeline. The high scatter of pour point shows the difficulty in pour point measurements. Figure 14 shows that the pour point increases as the weathering percentage increases. This is not highly significant in terms of the two major questions here, as it is expected that the pour point would increase with weathering percentage.

Figure 15 shows the change in viscosity at 0ºC over the years. The data from the SLR report is shown in this figure and subsequent figures by the arrow. The flash point increased over the past years indicating that there is a lighter oil in the pipeline than in previous years. Figure 16 shows the change in viscosity with weathering percentage. As would be expected, the viscosity rises with increasing weathering. The values from the subject point appear to be slightly higher than the other data. Figure 17 shows the viscosity at 15ºC of the samples over the years. The density is decreasing with time, indicating that the oil mixture is getting lighter, perhaps due to the addition of lighter oils in the North Slope mix. The density decrease over the years indicates that emulsification would also be slightly less likely. Figure 18 shows that the viscosity (at 15ºC) increases as the weathering percentage increases.

Figure 19 shows the change in saturate content by year, which appears to go down over the years. Contrary to the other trends, this would indicate that the oil is getting heavier and may be more prone to emulsification. This depends, however, on the types of saturates present as they may be of different chain lengths, which have different effects. Figure 20 shows the change in saturate content by weathering percentage. Figure 21 shows the aromatic content by year. Although this shows that the aromatic content is decreasing somewhat with time, there is significant scatter. Figure 22 shows the change in aromatic content with weathering and reveals that there is no particular drastic tendency.

Figure 23 shows the resin content of the samples over the years, which increases with time. This indicates that the oil mixture is becoming more prone to forming emulsions (meso-stable) over the years. Figure 24 shows that the resin content increases as the weathering percentage increases. Figure 25 shows that the asphaltene content is changing over the years, indicating that the oil may be more emulsion-prone. It should be noted that the rise in asphaltene content is not as great as that of the resin content. Figure 26 shows the change in asphaltene content with weathering percentage. As would be expected, the asphaltene content rises with increasing weathering. The SLR report did not provide measurements of SARA content.

Figure 27 shows the wax content of the samples over the years, which is decreasing with time. This indicates the oil mixture is getting lighter, perhaps due to the addition of lighter oils in the North Slope mix. The wax content decrease over the years is not any indication of emulsification behaviour. Figure 28 shows that the wax content increases as the weathering percentage increases, although the change is very slight. Figure 29 shows that there is little change in adhesion over the years. Figure 30 shows that there doesn’t appear to be a significant change in adhesion with weathering. Figure 31 shows the VOC content decreasing somewhat over the years, although there is significant scatter. Figure 32 shows the decrease in VOC content with weathering.

Figure 33 shows the decreasing interfacial tension of the samples with air over the years (at 0ºC), which indicates that the oil mixture is becoming lighter with time. Figure 34 shows that the interfacial tension with air increases as the weathering percentage increases. Figure 35 shows the interfacial tension of the samples with air decreasing over the years (at 15ºC), indicating that the oil mixture is becoming lighter over the years. Figure 36 shows the change in interfacial tension with air with weathering percentage. The SLR report provides interfacial values that are high.

Figure 37 shows interfacial tension of the samples with seawater over the years (at 0ºC). The interfacial tension is decreasing with time, indicating that the oil mixture is becoming lighter over the years. Figure 38 shows the change in interfacial tension with air with weathering percentage at 0ºC. Figure 39 shows interfacial tension of the samples with seawater over the years (at 15ºC). The interfacial tension is decreasing with time, which indicates that the oil mixture is becoming lighter over the years. Figure 40 shows the change in interfacial tension with seawater (at 15ºC) with weathering percentage. Figure 41 shows the interfacial tension of the samples with freshwater over the years (at 0ºC). The interfacial tension is decreasing with time. This indicates that the oil mixture is becoming lighter over the years. Figure 42 shows the change in interfacial tension of the samples with freshwater (at 0ºC) with weathering percentage.

Figure 43 shows that the interfacial tension of the samples with freshwater (at 15ºC) is decreasing with time, indicating that the oil mixture is becoming lighter over the years. Figure 44 shows that the interfacial tension with freshwater (at 15ºC) increases as the weathering percent increases. Figure 45 shows the chemical dispersibility with Corexit 9500 of the samples with air over the years. It should be noted that, although the trend appears upwards, the methods of analysis have changed and the trend may now be stable, not upward. Figure 46 shows the change in chemical dispersibility with weathering percentage. The downwards trend is expected.

Figure 47 shows that the distillation curves of the samples with seawater are decreasing with time, strongly indicating that the oil mixture is becoming lighter over the years. Figure 48 shows the change in distillation curves with weathering percentage. Figure 49 shows that the distillation curves (by percent distilled) of the samples are decreasing over the years, which is a strong indication that the oil mixture is becoming lighter with time. The non-standard distillation curve from the SLR report is indicated by the arrow. Figure 50 shows the change in distillation curves with weathering percentage.

Figure 51 shows water-in-oil and emulsion stability of the fresh ANS samples over the years. The fresh ANS largely does not form emulsions. Figure 52 shows water-in-oil and emulsion stability of the samples with weathering. The data from the SLR report are shown in the undefined region as this data was not obtained by standard procedure. Figure 53 shows the predicted water-in-oil and emulsion stability of the fresh ANS samples using the second Fingas model. This model predicts that fresh ANS would always form unstable water-in-oil states. This was also observed in tests. Figure 54 shows the predicted water-in-oil and emulsion stability of the weathered samples with weathering using the second Fingas model. This model predicts that fresh ANS would always form meso-stable emulsions. This was also observed in tests.

Figure 55 shows the water content of the various water-in-oil states as measured in laboratory experiments. As can be seen, the meso-stable emulsions have a higher water content, which is known from the extensive studies. The values from the SLR report are noted by an arrow. The low water content indicates that the data in the SLR report probably relate to the unstable state. Figure 57 shows a comparison of the stability of the meso-stable emulsions. The size of circle indicates the degree of weathering of the samples. Figure 57 shows that there is relatively little change in the stability of meso-stable emulsions with weathering over the years. Figure 58 shows the stability of the meso-stable emulsions with weathering percentage. There does not appear to be an increase in stability with increasing weathering percentage.

Figure 59 shows the asphaltene/resin ratio of ANS oil with the years. The asphaltene/resin ratio appears to be dropping over time which would indicate lesser emulsion stability over time. Figure 60 shows the asphaltene/resin ratio versus the weathering percentage. It appears that the asphaltene/resin ratio is not changing significantly with weathering percentage.

The comparison and analysis of the data show the following about the trend of the ANS oil.

1. Most indicators reveal that the mix that constitutes ANS oil is becoming lighter, probably because of the mix of crudes added to the start of the pipelines.
2. The crucial indicator of distillation data confirms this, as do the important indicators of viscosity and density.
3. Caution must be exercised on the use of the published data as this was never intended to show a long-term trend. Furthermore, the specific sample points, times, and pipeline conditions were not documented.
4. Despite the indicators that the oil is becoming lighter, the resins are rising somewhat. This indicates that the oil may become a lighter, but more resiny oil.

The comparison of the data shows the following about the analytical data presented in the S.L. Ross report.

1. Several crucial parameters required to make decisions on oil behaviour and emulsification are missing from the SLR report, including standard distillation data, standard emulsification procedures, and SARA analysis.
2. The flash point measured was high.
3. The density at 15ºC was low.
4. The pour point was high.
5. The viscosity measurements were either higher or lower than those in the literature.
6. The oil-air interfacial tensions were high.
7. The distillation curves were different.
8 The emulsification data was quite different and could not be related to the literature data.

7. Most Probable Emulsification Behaviour of Alaskan Oils

The historic tendency of ANS crudes is that the fresh ones will not form any type of emulsion and will result in an unstable water-in-oil state. After some amount of weathering, these oils will then sometimes form meso-stable emulsions. The question then becomes what the tendency for the future might be. The many data sets of parameters relating to the emulsion formation of ANS oils are summarized in Table 4.

The following is a summary of the tendencies of the water-in-oil states for ANS oils.

1. The most indicative tendency is the stability of the emulsions as measured by the stability index of complex modulus of the formed product, divided by the viscosity of the starting oil. The stability of the meso-stable emulsions was calculated and is illustrated in a number of figures. Figure 56 shows the emulsion stability by year and ignores the effect of weathering. On the basis of the one oil with a high stability, it is noted that there is a slight decrease in emulsion stability over the years. The same graph is shown in Figure 57, however, the weathering percentage of the emulsions is shown by the size of the circle. This graph appears to indicate

about the same trend as shown in Figure 56, except that the weathering does not appear to affect emulsion stability. Figure 58 shows the stability in relation to the weathering percentage. It appears that there is little correlation between the stability and the weathering percentage. The overall tendency of the stability analysis is that there is a slight decrease in the stability of the meso-stable emulsions over time. It should be noted, however, that this is based on one more stable emulsion from about 1995.

2. The asphaltene/resin ratio is a strong indication of the emulsification tendency of an oil. As noted in Section 2 of this review, asphaltene-stabilized emulsions are more stable. Figure 59 shows the variation of the asphaltene/resin ratio over the years that fresh ANS samples were taken. This shows a slight downward trend in the ratio, which would indicate that there is a slight decrease in emulsion stability or formation tendency over the years. Figure 60 shows the expected slight increase in asphaltene ratio with weathering percentage.

3. The asphaltene amount is also an indicator of emulsification tendency. Figure 25 shows that the asphaltene content is slowly rising over the years, although this is obviously offset by the greater increase in the resin content, which decreases the asphaltene/resin ratio.

4. The change in resin content over the years is shown in Figure 23. The resin content appears to be rising significantly, which has the effect of lowering the asphaltene/resin ratio as noted in point 2 and creating a meso-stable emulsion as noted in the discussion in Section 2 of this review.

5. The viscosity of the oil is decreasing as shown in Figures 15 and 17. To a certain extent, the effect of this may be to decrease the emulsification potential, especially of the entrained water-in-oil state.

6. The prediction of emulsification using the latest model shows a lower prediction factor (related to stability). As shown in Figures 53 and 54, a low tendency or stability value appears to be the trend over the years. This model incorporates a variety of factors including density and viscosity, as well as saturate, asphaltene, and resin content.

7. The measured stability of meso-stable emulsions shows a slight decrease as shown in Figure 56. This is an indicator of the trend.

Overall, the seven indicators show that there is a general decline in the tendency for emulsions to form and in the stability of those emulsions.

8. Conclusions

A review of the emulsification of Alaskan North Slope oils shows that these oils do not typically form entrained water in oil or stable emulsions. After weathering, however, many of these oils will form meso-stable emulsions. These are less stable emulsions with a lifetime of less than 3 days.

The examination of the prime indicators of emulsion formation included the following.

1. The major indicator is the stability of the emulsions as measured by the stability index of complex modulus of the formed product, divided by the viscosity of the starting oil. The overall tendency of the stability analysis of the ANS meso-stable emulsions is that there is a slight decrease in the stability over time. It should be noted, however, that this is based on limited data.

2. The asphaltene/resin ratio is another strong indicator of the emulsification tendency of an oil. Asphaltene-stabilized emulsions are more stable. The asphaltene/resin ratio is decreasing over time, indicating that there is a slight decrease in emulsion stability or formation tendency

over the years.

3. The amount of asphaltene in an oil is also an indicator of emulsification tendency. The asphaltene content is slowly rising over the years, although this is obviously offset by the greater increase in the resin content, which decreases the asphaltene/resin ratio.

4. The resin content is increasing over the years, which will lower the asphaltene/resin ratio and cause the formation of a meso-stable emulsion.

5. The viscosity of the oil is decreasing. This may decrease the emulsification potential, especially that of the entrained water-in-oil state.

6. The prediction of emulsification using the latest model shows a lower prediction factor (related to stability). This model incorporates a variety of factors including density and viscosity, and saturate, asphaltene, and resin content. This model shows a slight decrease in tendency to form emulsions and their stability.

7. The measured stability of meso-stable emulsions shows a slight decrease over the years.

Overall, it is concluded that both the potential for formation of meso-stable emulsions and their stability will decrease if the current trend in petroleum properties continues.

The comparison and analysis of the oil analytical and properties data show the following apparent trends in the nature of the ANS oil.

1. Most indicators show that the mix that constitutes ANS oil is becoming lighter, probably due to the mix of crudes added to the start of the pipelines. It is important to stress here that the sampling points, sampling times, and other conditions of the pipeline and feed operations were not always recorded.

2. The important indicators of distillation data, chemical composition, viscosity, and density show a general increase in the lightness of ANS oils.

3. The amount of volatile organic compounds (VOCs) in the oil is rising.

4. Despite the indicators that the oil is becoming lighter, the resins are rising somewhat. This indicates that the oil may become a lighter, but more resiny oil.

The comparison of the data shows the following about the analytical data presented in the S.L. Ross report.

1. Several crucial parameters to consider when making decisions about oil behaviour and emulsification are missing from the report, including standard distillation data, standard emulsification procedures, and SARA and VOC analyses.
2. The flash point measured was high.
3. The density at 15°C was low.
4. The pour point was high.
5. The viscosity measurements were either higher or lower than the results in the literature.
6. The oil-air interfacial tensions were high.
7. The distillation curves were different.
8. The emulsification data was quite different and could not be related to the data in the literature. None of the important concepts or references about emulsification was included in the report.

Despite this, in one place the report does indicate that the oil is becoming lighter and may thus be less prone to emulsification. This judgement was, however, based on inappropriate emulsification data.

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Table 1 Values for Fingas 2004 Emulsion Model

a Summary of Final Categorizations

Category	Class Number	
Unstable	<.56	
Entrained	<.9	>.56
Meso-stable	<1.09	<.9
Stable	>1.09	

b Properties of the Water-in-oil Classes

	Number of Samples	Average Water Content %	Std. Dev. %	Average Viscosity Increase Ratio	Std. Dev. %
Unstable	80	6.4	4.1	1.7	1.6
Entrained	34	44	17	6.5	8.0
Meso-stable	37	65	17	55	98
Stable	55	76	9	1200	330
	total 206				

c Wave Height Prediction

Input data (time to formation - minutes)

	Wave Height	Stable	Meso	Entrained
Test Tank Average	15	110	865	720
	24	150	300	140
	25	140	247	60
Laboratory Data	48	30	153	20
Conversions	77	20	60	10
	81	10	35	8

Resulting Equations

Predictor **equation** $y=a+b/x^{1.5}$

x is wave height in cm

y = time to formation in minutes

	a	b	R^2
Stable	27.1	7,520	0.51
Meso	47	49,100	0.95
Entrained	30.8	18,300	0.94

Table 2 Values for Fingas 2005 Emulsion Model

a Summary of Final Categorizations

Category	Class Number	
Unstable	<0.615	
Meso-stable	>0.615	<0.6.6
Stable	>6.6	
Entrained	>.64	<.72

but density >0.96 or viscosity >10,000

b Properties of the Water-in-oil Classes

	Number of Samples	Average Water Content %	Std. Dev. %	Average Viscosity Increase Ratio	Std. Dev. %
Unstable	103	6.0	4.0	1.5	10.0
Entrained	32	44	17	4.0	11.0
Meso-stable	51	67	14	45	52
Stable	51 total 237	74	9	1500	500

c Wave Height Prediction

Input data (time to formation - minutes)

	Wave Height	Stable	Meso	Entrained
Test Tank Average	15	110	865	720
	24	150	300	140
	25	140	247	60
Laboratory Data	48	30	153	20
Conversions	77	20	60	10
	81	10	35	8

Resulting Equations

Predictor **equation** $y=a+b/x^{1.5}$

x is wave height in cm

y = time to formation in minutes

	a	b	R^2
Stable	27.1	7,520	0.51
Meso	47	49,100	0.95
Entrained	30.8	18,300	0.94

Table 3 Properties of the Alaskan North Slope Oils

from ETC, 2005, and SLR Report

Oil	Year	Evap. Loss	API Gravity	Sulphur	Water Content	Flash Point	Density (g/mL)				Pour Point	Viscosity (mPa.s)			
		(%)		(%w/w)	(%w/w)	(deg C)	0C	5C	15C	30C		0C	5C	15C	30C
Prudhoe Bay (Mackay)	1982	0	24.8				0.9150	0.9110	0.9050		0	577	196	68	
Alaska North Slope	1989	0	26.8	1.15			0.9037		0.8936		-8			23	
Alaska North Slope	1989	9		1.19			0.9203		0.9086					66	
Alaska North Slope	1989	16		1.30			0.9342		0.9225					184	
Endicott	1989	0	23.0	1.34			0.9258		0.9149		-2	501		84	
Endicott	1989	8		1.34			0.9436		0.9318		8	1583		321	
Endicott	1989	13		1.40			0.9520		0.9401		14	2609		682	
Alaska North Slope (SOCSEX)	1994	0	25				0.8922		0.8814			42	32	21	
Alaska North Slope (SOCSEX)	1994	15					0.9087		0.8976						
Alaska North Slope (SOCSEX)	1994	22													
Prudhoe Bay	1995	0	28.5	0.96	0.3	-17	0.8948		0.8837		-15	46		22	
Prudhoe Bay	1995	9		1.01	<0.1	45	0.9163		0.9048		-9	141		55	
Prudhoe Bay	1995	18		1.13	<0.1	87	0.9319		0.9204		8	608		148	
Prudhoe Bay	1995	27		1.24	<0.1	> 95	0.9470		0.9352		12	4447		623	
Alaska North Slope (Middle Pipeline)	1996	0	29.9	1.16	0.2	-23	0.8869		0.8761		-54	34		16	
Alaska North Slope (Middle Pipeline)	1996	30.54		1.43	<0.1	> 95	0.9538		0.9418		14	5655		900	
Alaska North Slope (Northern Pipeline)	1996	0	30.6	1.14	0.1	-19	0.8828		0.8719		-55	29		14	
Alaska North Slope (Northern Pipeline)	1996	31.14		1.39	<0.1	> 90	0.9516		0.9402		8	4406		748	
Alaska North Slope (Southern Pipeline)	1996	0	29.8	1.13	0.2	-21	0.8875		0.8766		-30	36		18	
Alaska North Slope (Southern Pipeline)	1996	29.62		1.46	<0.1	> 95	0.9547		0.9431		14	6406		961	
Alaska North Slope	2002	0	30.9	1.11	<0.1	< -8	0.8777		0.8663		-32	23.2		11.5	
Alaska North Slope	2002	10.0		1.20	<0.1	19	0.9054		0.8940		-20	76.7		31.8	
Alaska North Slope	2002	22.5		1.38	<0.1	75	0.9303		0.9189		-9	614		152	
Alaska North Slope	2002	30.5		1.50	<0.1	115	0.9457		0.9340		-6	4230		625	
Prudhoe Bay USEPA Reference Oil	2004	0	26.7					0.9026	0.8947	0.8842			78.7	38.9	21.7
Prudhoe Bay USEPA Reference Oil	2004	6.3						0.9190	0.9112	0.9006			300.8	102.8	41.7
Prudhoe Bay USEPA Reference Oil	2004	13.1						0.9313	0.9235	0.9131			3302	318.4	93.4
Prudhoe Bay USEPA Reference Oil	2004	19.7						0.9413	0.9336	0.9233			10520	864.7	203.1
Alaska North Slope SLR 2004	*2004*	*0*				*-10*	*0.877*		*0.864*		*-12*	*25.4*		*11.3*	
Alaska North Slope SLR 2004	*2004*	*29.5*				*62*	*0.933*		*0.922*		*6*	*2619*		*198.8*	
Alaska North Slope SLR 2004	*2004*	*36.5*				*103*	*0.945*		*0.935*		*12*	*7768*		*617*	
Alaska North Slope SLR 2004 old distil	*2004*														

Table 3 Properties of the Alaskan North Slope Oils

from ETC, 2005, and SLR Report

Oil	Year	Evap. Loss	Hydrocarbon Groups					Adhesion	Volatile Organic Compounds (ppm)						
		(%)	Saturate	Aromatic	Resin	Asphaltene	Wax	(g/m^2)	Benzene	Toluene	E-Benzene	Xylenes	C3-benzenes	BTEX-total	VOC-total
Prudhoe Bay (Mackay)	1982	0	87	10	2	2	4		990	3790	910	4230	4700	9920	14620
Alaska North Slope	1989	0				2	7								
Alaska North Slope	1989	9				3									
Alaska North Slope	1989	16				5									
Endicott	1989	0				4	8		1390	4090	820	4660	4330	10960	15290
Endicott	1989	8				4									
Endicott	1989	13				4									
Alaska North Slope (SOCSEX)	1994	0	53	37	6	4		22	2080	4670	1620	7060	6650	15430	22080
Alaska North Slope (SOCSEX)	1994	15	52	38	7	3		19	320	2670	1490	7060	8780	11540	20320
Alaska North Slope (SOCSEX)	1994	22	47	40	9	5		32	130	90	520	2910	5860	3650	9510
Prudhoe Bay	1995	0	53	34	10	4	4	28	1836	6665	2672	9536	12121	20710	32831
Prudhoe Bay	1995	9	51	35	10	3	5	30	229	2941	1817	7056	10691	12043	22735
Prudhoe Bay	1995	18	52	32	12	4	5	24	0	16	166	1047	5414	1228	6642
Prudhoe Bay	1995	27	43	38	15	5	5	29	0	3	1	4	8	9	17
Alaska North Slope (Middle Pipeline)	1996	0	52	35	9	5		28	3698	9040	1689	8197	8038	22624	30662
Alaska North Slope (Middle Pipeline)	1996	30.54	42	38	12	7		33	38	9	1	3	4	52	56
Alaska North Slope (Northern Pipeline)	1996	0	51	34	9	5		26	2140	6197	1363	6544	7074	16243	23318
Alaska North Slope (Northern Pipeline)	1996	31.14	44	37	12	7		23	38	8	2	4	7	52	59
Alaska North Slope (Southern Pipeline)	1996	0	54	32	8	6		28	3524	8666	1566	8700	7315	22455	29770
Alaska North Slope (Southern Pipeline)	1996	29.62	42	39	13	7		30	37	7	1	4	3	50	53
Alaska North Slope	2002	0	75.0	15.0	6.1	4.0	2.6	20	2866	5928	1319	6187	5620	16300	21920
Alaska North Slope	2002	10.0	72.1	16.0	7.4	4.4	2.9	35							
Alaska North Slope	2002	22.5	69.2	16.5	8.9	5.4	3.3	38							
Alaska North Slope	2002	30.5	64.8	18.5	10.3	6.4	3.6	40	BDL	BDL	BDL	BDL	30	BDL	30
Prudhoe Bay USEPA Reference Oil	2004	0	60.8	28.3	7.7	3.2			2190	6200	1550	6460	6390	16400	23400
Prudhoe Bay USEPA Reference Oil	2004	6.3	60.4	27.7	8.2	3.8			600	3890	1210	5670	6220	11360	18300
Prudhoe Bay USEPA Reference Oil	2004	13.1	58.5	27.0	10.1	4.4			10	50	180	1190	3550	5000	5570
Prudhoe Bay USEPA Reference Oil	2004	19.7	53.9	25.2	15.7	5.2			0	0	0	0	0.8	0	0.8
Alaska North Slope SLR 2004	*2004*	*0*													
Alaska North Slope SLR 2004	*2004*	*29.5*													
Alaska North Slope SLR 2004	*2004*	*36.5*													
Alaska North Slope SLR 2004 old distil	*2004*														

Table 3 Properties of the Alaskan North Slope Oils

from ETC, 2005, and SLR Report

Oil	**Year**	**Evap. Loss**	**Interfacial Tension (mN/m)**												**Chemical Dispersibility (volume %**			
		(%)	**Air/Oil**				**Oil/Salt Water**				**Oil/Fresh Water**				**C9500**	**C9527**	**Dasic LTS**	**EN-700**
			0C	5C	15C	30C	0C	5C	15C	30C	0C	5C	15C	30C				
Prudhoe Bay (Mackay)	1982	0	30.4		28.3		15.0		9.7		17.6		16.9		10			
Alaska North Slope	1989	0			28.1		23.8		27.4		26.1		29.4		10		15	
Alaska North Slope	1989	9	29.6		29.1		27.6		26.6		28.7		27.7			10	10	10
Alaska North Slope	1989	16	31.1		29.7		24.2		24.9		25.7		25.1			5	0	5
Endicott	1989	0	29.9		29.1		26.1		25.8		26.2		25.4		10	10	5	10
Endicott	1989	8	30.8		27.7		29.0		26.0		28.7		24.4			5	0	5
Endicott	1989	13			30.9				23.0				25.5			5	0	0
Alaska North Slope (SOCSEX)	1994	0																
Alaska North Slope (SOCSEX)	1994	15																
Alaska North Slope (SOCSEX)	1994	22																
Prudhoe Bay	1995	0	28.6		27.6		13.5		3.9		17.6		4.2		18			
Prudhoe Bay	1995	9	29.9		29.5		16.9		11.5		19.5		15.5					
Prudhoe Bay	1995	18	31.3		30.2		22.4		14.2		24.2		16.5		0			
Prudhoe Bay	1995	27			30.9				15.5				16.5		0			
Alaska North Slope (Middle Pipeline)	1996	0	27.6		27.0		19.8		19.9		23.8		21.9		46			
Alaska North Slope (Middle Pipeline)	1996	30.54			31.5				14.7				19.3		5			
Alaska North Slope (Northern Pipeline)	1996	0	27.6		26.8		22.3		20.6		23.7		22.5		33			
Alaska North Slope (Northern Pipeline)	1996	31.14			31.4				21.5				22.4		6			
Alaska North Slope (Southern Pipeline)	1996	0	27.7		27.0		24.4		21.7		24.6		23.4		45			
Alaska North Slope (Southern Pipeline)	1996	29.62			31.4				17.7				20.2		6			
Alaska North Slope	2002	0	27.3		26.4		22.5		20.2		26.7		23.6		47			
Alaska North Slope	2002	10.0	29.8		28.4		25.3		23.1		28.1		25.5		45			
Alaska North Slope	2002	22.5	31.2		30.4		26.8		24.2		30.8		27.7		34			
Alaska North Slope	2002	30.5	33.1		31.8		30.1		25.6		33.2		30.2		15			
Prudhoe Bay USEPA Reference Oil	2004	0		29.2	28.7	27.5		28.6	31.3	27.3		29.2	28.1	25.1				
Prudhoe Bay USEPA Reference Oil	2004	6.3		30.2	29.8	27.5		19.0	25.2	24.9		17.5	23.8	26.4				
Prudhoe Bay USEPA Reference Oil	2004	13.1			30.8	28.9			24.5	22.3			22.4	22.8				
Prudhoe Bay USEPA Reference Oil	2004	19.7				29.8				19.6				19.8				
Alaska North Slope SLR 2004	*2004*	*0*			*31.2*				*18.2*									
Alaska North Slope SLR 2004	*2004*	*29.5*			*33.3*				*21.7*									
Alaska North Slope SLR 2004	*2004*	*36.5*			*34.2*				*24.2*									
Alaska North Slope SLR 2004 old distil	*2004*																	

Table 3 Properties of the Alaskan North Slope Oils

from ETC, 2005, and SLR Report

Oil	**Year**	**Evap. Loss**	**Boiling Point Distribution (weight %) - cumulative values, Temperature in degrees Celsius**																		
		(%)	**40**	**60**	**80**	**100**	**120**	**140**	**160**	**180**	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**	**600**	**650**	**700**
Prudhoe Bay (Mackay)	1982	0	1	1	2	4	6	9	11	14	16	24	33	43	52	62	69	76	82	87	90
Alaska North Slope	1989	0																			
Alaska North Slope	1989	9																			
Alaska North Slope	1989	16																			
Endicott	1989	0	1	1	3	5	7	7	8	9	11	17	24	33	43	54	63	71	78	83	87
Endicott	1989	8																			
Endicott	1989	13																			
Alaska North Slope (SOCSEX)	1994	0	2	2	5	8	10	13	15	18	21	28	37	46	55	64	71	78	83	87	91
Alaska North Slope (SOCSEX)	1994	15				1	3	6	9	13	16	25	35	46	56	66	74	80	86	90	94
Alaska North Slope (SOCSEX)	1994	22						1	3	5	8	17	27	38	49	59	68	76	82	88	92
Prudhoe Bay	1995	0	1	1	3	6	9	12	15	19	22	32	42	53	62	72	79	86	91	96	99
Prudhoe Bay	1995	9				1	2	5	8	11	15	25	36	48	58	69	77	84	90	95	99
Prudhoe Bay	1995	18							1	3	6	17	29	42	54	65	75	82	89	94	98
Prudhoe Bay	1995	27										7	19	34	47	60	71	80	87	93	98
Alaska North Slope (Middle Pipeline)	1996	0	3	4	7	10	13	16	19	22	25	33	42	51	60	69	76	82	88	92	95
Alaska North Slope (Middle Pipeline)	1996	30.54										5	16	30	43	55	65	74	81	87	92
Alaska North Slope (Northern Pipeline)	1996	0	4	5	8	11	14	17	20	23	26	34	43	53	62	70	77	83	88	92	96
Alaska North Slope (Northern Pipeline)	1996	31.14										6	17	31	43	55	66	74	81	87	92
Alaska North Slope (Southern Pipeline)	1996	0	3	4	7	9	12	15	18	20	23	31	39	49	58	67	75	81	86	90	94
Alaska North Slope (Southern Pipeline)	1996	29.62										5	16	30	43	56	67	76	83	90	95
Alaska North Slope	2002	0	2.5	3.9	6.5	10.0	13.4	16.6	19.8	22.6	25.2	32.6	40.7	49.5	57.7	66.0	72.8	79.0	84.1	88.4	
Alaska North Slope	2002	10.0	0.1	0.5	1.4	3.6	6.6	9.8	13.1	16.3	19.2	27.4	36.4	46.1	55.3	64.5	72.1	79.0	84.7	89.5	
Alaska North Slope	2002	22.5					0.1	0.6	2.0	4.4	7.3	16.6	27.0	38.2	48.7	59.3	68.2	76.0	82.6	88.0	
Alaska North Slope	2002	30.5									0.5	7.5	18.7	31.1	42.8	54.5	64.2	72.8	79.9	85.8	
Prudhoe Bay USEPA Reference Oil	2004	0																			
Prudhoe Bay USEPA Reference Oil	2004	6.3																			
Prudhoe Bay USEPA Reference Oil	2004	13.1																			
Prudhoe Bay USEPA Reference Oil	2004	19.7																			
Alaska North Slope SLR 2004	*2004*	*0*																			
Alaska North Slope SLR 2004	*2004*	*29.5*																			
Alaska North Slope SLR 2004	*2004*	*36.5*																			
Alaska North Slope SLR 2004 old distil	*2004*																				

Table 3 Properties of the Alaskan North Slope Oils

from ETC, 2005, and SLR Report

Oil	**Year**	**Evap. Loss**	**Distillation by %**													
		(%)	**IBP**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**	**70**
Prudhoe Bay (Mackay)	1982	0		108	152	193	226	255	283	308	333	360	387	414	441	
Alaska North Slope	1989	0	42	98	127	147	172	216	238	247	258	265	272	282		
Alaska North Slope	1989	9														
Alaska North Slope	1989	16														
Endicott	1989	0														
Endicott	1989	8														
Endicott	1989	13														
Alaska North Slope (SOCSEX)	1994	0		82	118	158	197	232	262	290	316	344	372			
Alaska North Slope (SOCSEX)	1994	15		134	165	196	222	249	273	299	320	345	369			
Alaska North Slope (SOCSEX)	1994	22		179	214	240	265	289	312	334	357	381	405			
Prudhoe Bay	1995	0		99	129	158	188	217	243	267	291	314	337	362	388	440
Prudhoe Bay	1995	9		141	173	202	227	250	271	294	315	337	360	383	407	458
Prudhoe Bay	1995	18		194	220	242	263	284	302	321	342	362	383	405	426	475
Prudhoe Bay	1995	27		242	264	284	301	317	335	354	372	391	410	429	450	497
Alaska North Slope (Middle Pipeline)	1996	0														
Alaska North Slope (Middle Pipeline)	1996	30.54														
Alaska North Slope (Northern Pipeline)	1996	0														
Alaska North Slope (Northern Pipeline)	1996	31.14														
Alaska North Slope (Southern Pipeline)	1996	0		74	105	140	177	216	246	275	303	329	356	382	410	469
Alaska North Slope (Southern Pipeline)	1996	29.62		251	273	294	312	330	349	368	386	405	424	443	465	513
Alaska North Slope	2002	0														
Alaska North Slope	2002	10.0														
Alaska North Slope	2002	22.5														
Alaska North Slope	2002	30.5														
Prudhoe Bay USEPA Reference Oil	2004	0														
Prudhoe Bay USEPA Reference Oil	2004	6.3														
Prudhoe Bay USEPA Reference Oil	2004	13.1														
Prudhoe Bay USEPA Reference Oil	2004	19.7														
Alaska North Slope SLR 2004	*2004*	*0*	*46*	*99*	*129*	*151*	*168*	*207*	*246*		*307*		*359*			
Alaska North Slope SLR 2004	*2004*	*29.5*														*moder.*
Alaska North Slope SLR 2004	*2004*	*36.5*														*moder.*
Alaska North Slope SLR 2004 old distil	*2004*		*102*	*147*	*178*	*205*	*238*	*279*	*313*		*376*		*423*			

Table 3 Properties of the Alaskan North Slope Oils

from ETC, 2005, and SLR Report

Oil	**Year**	**Evap. Loss**	**Emulsion Formation**												
		(%)	**Visual**	**Day of Formation**						**One week after formation**					
			Stability	G*	G'	G"	tan□	□*	H_2O content	G*	G'	G"	tan□	□*	H_2O content
				(Pa)	(Pa)	(Pa)	(G'/G")	(Pa.s)	(w/w%)	(Pa)	(Pa)	(Pa)	(G'/G")	(Pa.s)	(w/w%)
Prudhoe Bay (Mackay)	1982	0													
Alaska North Slope	1989	0													
Alaska North Slope	1989	9													
Alaska North Slope	1989	16													
Endicott	1989	0													
Endicott	1989	8													
Endicott	1989	13													
Alaska North Slope (SOCSEX)	1994	0													
Alaska North Slope (SOCSEX)	1994	15													
Alaska North Slope (SOCSEX)	1994	22													
Prudhoe Bay	1995	0	Meso	6.8	6.8	0.7	0.1		43.06	4.4	3.7	1.2	0.3		39.37
Prudhoe Bay	1995	9	Meso	640	640	60	0.11		85.07	340	340	6	0.02		85.13
Prudhoe Bay	1995	18	Unstable												
Prudhoe Bay	1995	27	Unstable	230	220	60	0.3		20.37						18.76
Alaska North Slope (Middle Pipeline)	1996	0	Unstable												
Alaska North Slope (Middle Pipeline)	1996	30.54	Meso	120	100	48	0.52		61.92	11	1.3	11	8.4		21.76
Alaska North Slope (Northern Pipeline)	1996	0	Unstable												
Alaska North Slope (Northern Pipeline)	1996	31.14	Meso	110	96	47	0.50		69.82	9.8	2.2	9.6	4.2		15.00
Alaska North Slope (Southern Pipeline)	1996	0	Unstable												
Alaska North Slope (Southern Pipeline)	1996	29.62	Meso	190	170	81	0.46		53.47	20	7.7	18	2.2		21.14
Alaska North Slope	2002	0	Unstable												
Alaska North Slope	2002	10.0	Unstable												
Alaska North Slope	2002	22.5	Unstable												
Alaska North Slope	2002	30.5	Meso	41.6	22.6	35	1.55	6.63	72.68						
Prudhoe Bay USEPA Reference Oil	2004	0	Meso	25.6	19.6	16.6	0.85	4.08	82.58	3.24	0	3.24	328000	0.515	53.06
Prudhoe Bay USEPA Reference Oil	2004	6.3	Meso	11.9	4.25	11.1	2.715	1.9	79.18	7.045	0	7.045	789000	1.125	62.63
Prudhoe Bay USEPA Reference Oil	2004	13.1	Meso	49.35	24.8	42.6	1.725	7.86	82.83	21.65	9.48	19.45	2.075	3.445	72.13
Prudhoe Bay USEPA Reference Oil	2004	19.7	Meso	103.5	45.55	93.25	2.045	16.5	73.63	80.95	45.5	66.95	1.475	12.9	76.86
Alaska North Slope SLR 2004	*2004*	*0*	*not likely*												*0*
Alaska North Slope SLR 2004	*2004*	*29.5*	*oderately likely*	*0.357*	*calculated here*										*9*
Alaska North Slope SLR 2004	*2004*	*36.5*	*oderately likely*	*1.829*	*calculated here*										*17*
Alaska North Slope SLR 2004 old distil	*2004*														

Table 4	**Assessment of Property Data Relevance**													
	Fresh Oil							**Weathered Oil**						
Parameter	**Figure Number**	**Indication of Oil tendency**	**Indication of Emulsification**	**Data Significance**	**Data Reliability**	**Old Data Reliable ?**	**SLR report**	**Figure Number**	**Indication of Oil tendency**	**Indication of Emulsification**	**Data Significance**	**Data Reliability**	**Old data Reliable ?**	**SLR Report**
Sulphur	3	lighter	no	low	medium	ok	nm	4	same	low	low	medium	ok	nm
Flash Point	5	same	no	low	medium	ok	high	6	same	no	low	medium	ok	high
Density at 0°C	7, 9	lighter	no	high	high	ok	ok	8	same	no	high	high	ok	high
Density at 15°C	10,11	lighter	no	high	high	ok	low	12	same	no	high	high	ok	low
Pour Point	13	lighter	no	low	low	no	high	14	lighter	no	low	low	no	high
Viscosity at 0°C	15	lighter	slight decrease	high	medium	no	low	16	lighter	slight decrease	high	medium	no	high
Viscosity at 15°C	17	lighter	slight decrease	high	medium	no	low	18	same	no	high	medium	no	ok
Saturate Content	19	heavier	increase	medium	medium	no	nm	20	same	slight increase	medium	medium	no	nm
Aromatic Content	21	same	no	medium	medium	no	nm	22	same	no	medium	medium	no	nm
Resin Content	23	heavier	increase	medium	medium	no	nm	24	heavier	slight increase	medium	medium	no	nm
Asphaltene Content	25	heavier	increase	medium	medium	no	nm	26	heavier	slight increase	medium	medium	no	nm
Wax Content	27	lighter	no	low	low	no	nm	28	same	no	low	low	no	nm
Adhesion	29	same	no	low	medium	no	nm	30	same	no	low	medium	no	nm
VOCs	31	lighter	no	high	high	no	nm	32	lighter ?	no	medium	high	no	nm
Interfacial Tension - Air 0°C	33	same	no	low	low	no	nm	34	same	no	low	low	no	nm
Interfacial Tension - Air 15°C	35	same	no	low	low	no	high	36	same	no	low	low	no	high
Interfacial Tension - seawater 0°C	37	same	no	low	low	no	nm	38	same	no	low	low	no	nm
Interfacial Tension - seawater 15°C	39	same	no	low	low	no	ok	40	same	no	low	low	no	ok
Interfacial Tension - freshwater 0°C	41	same	no	low	low	no	nm	42	same	no	low	low	no	nm
Interfacial Tension - freshwater 15°C	43	same	no	low	low	no	nm	44	same	no	low	low	no	nm
Dispersability	45	questionable	questionable	low	low	no	nm	46	questionable	questionable	low	low	no	nm
Distillation - by T	47	lighter	no	high	high	no	nm	48	indeterminable	no	medium	medium	no	nm
Distillation - by %	49	lighter	no	medium	medium	no	high	50	indeterminable	no	medium	medium	no	nm
Emulsification	51	indeterminable	same	high	medium	no	low	52	indeterminable	same	high	medium	no	low
Emulsification model	53	indeterminable	slight decrease	medium	medium	no	nm	54	indeterminable	slight decrease	medium	medium	no	nm
Emulsion water content	55	indeterminable	slight decrease	medium	medium	no	very low	55	indeterminable	slight decrease	medium	medium	no	very low
Emulsion Stability	56	indeterminable	slight decrease	high	high	ok	nm	57	indeterminable	same	high	high	ok	nm
Emulsion Stability								58	indeterminable	same	high	high	ok	nm
Asphaltene/Resin ratio	59	indeterminable	slight decrease	high	high	ok	nm	60	indeterminable	same	high	high	ok	nm

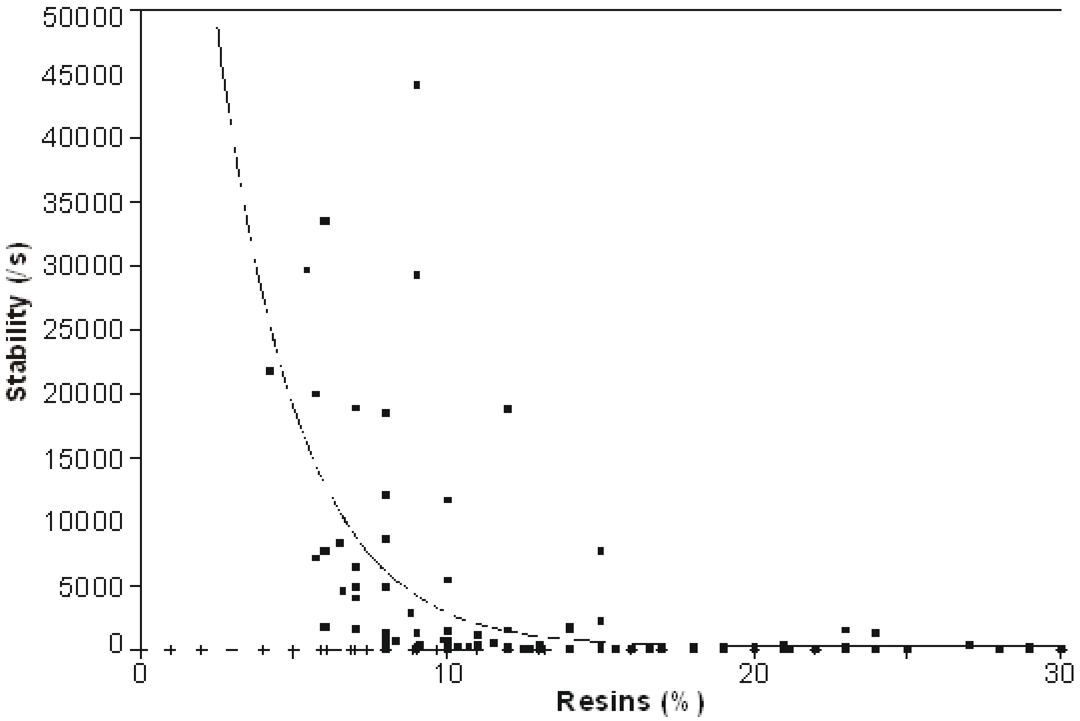

Figure 1 Correlation of Resins with Stability Before Correction

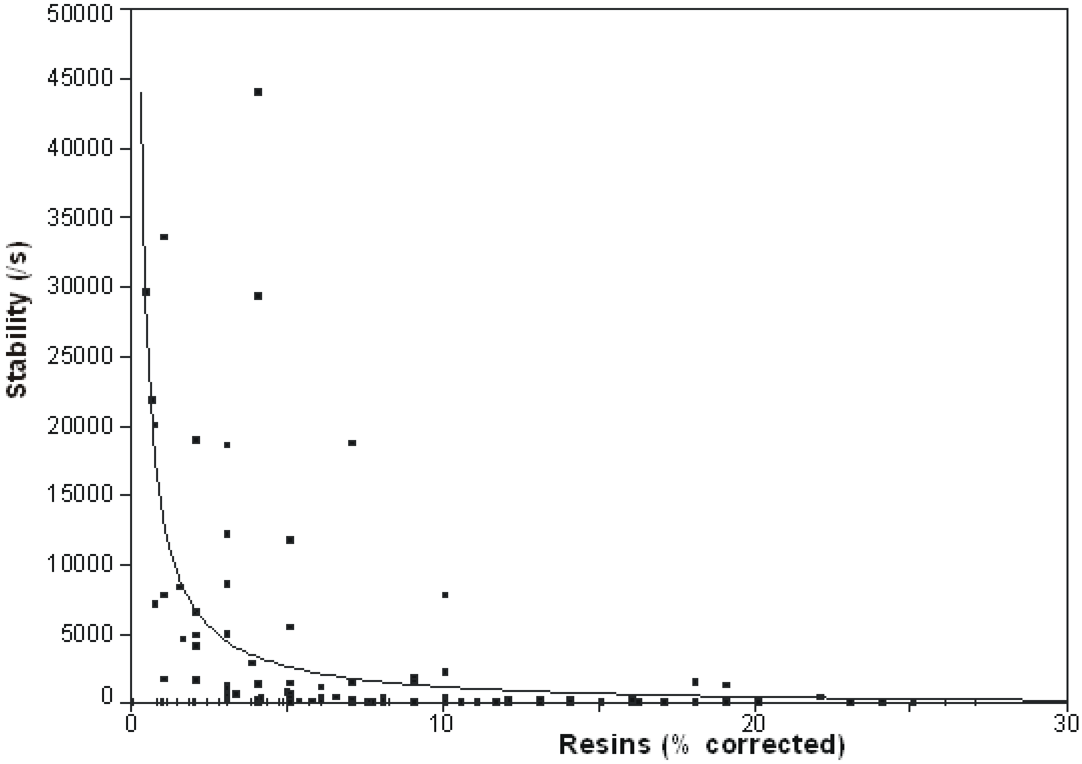

Figure 2 Correlation of Resins with Stability After Correction of 4.9

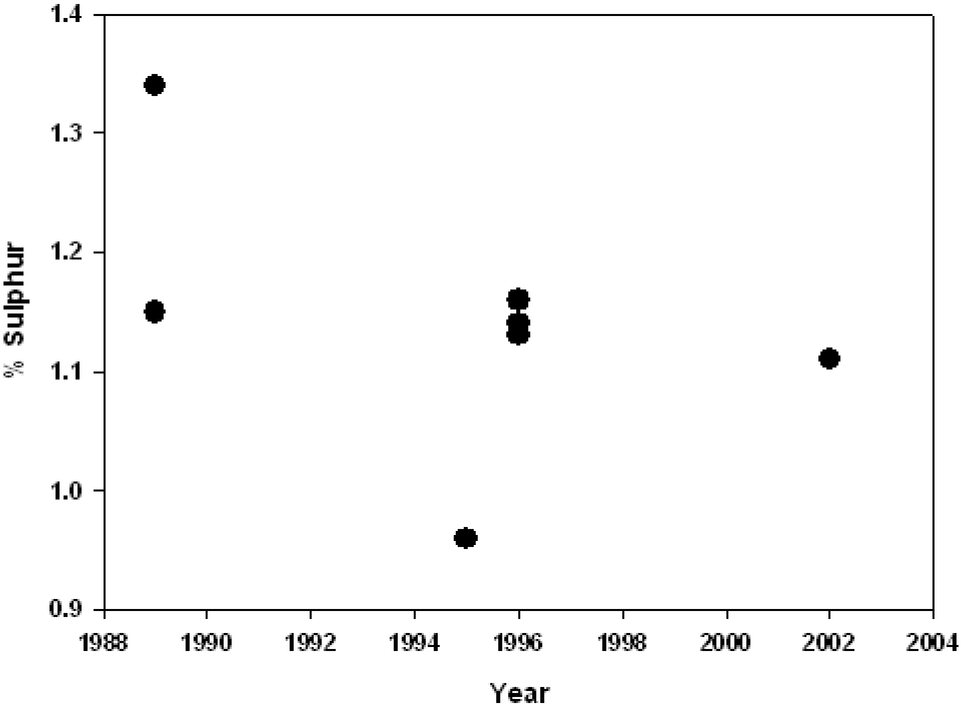

Figure 3 Sulphur Content of Fresh Alaska North Slope Oils by Year

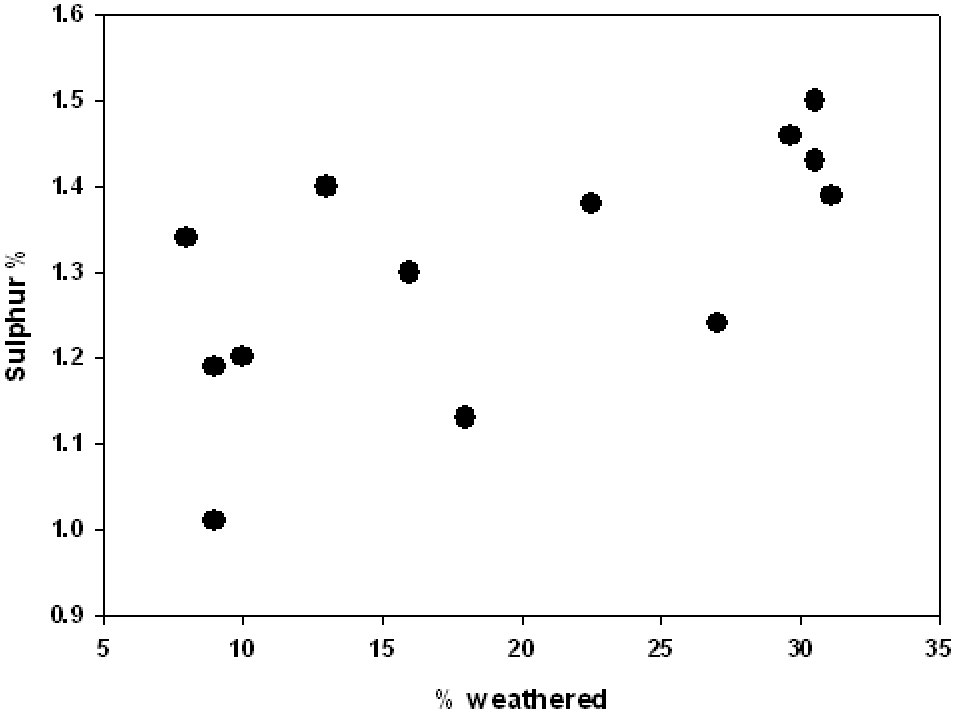

Figure 4 Sulphur Content of Weathered Alaska North Slope Oils by Weathering Percentage

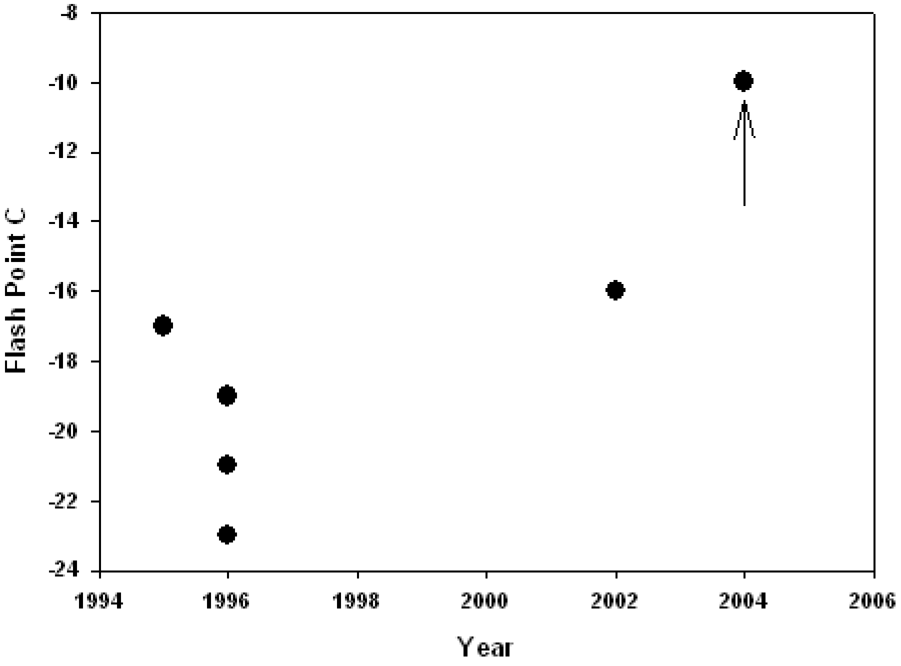

Figure 5 **Flash Point of Fresh Alaska North Slope Oils by Year** (Arrow indicates data from SLR Report.)

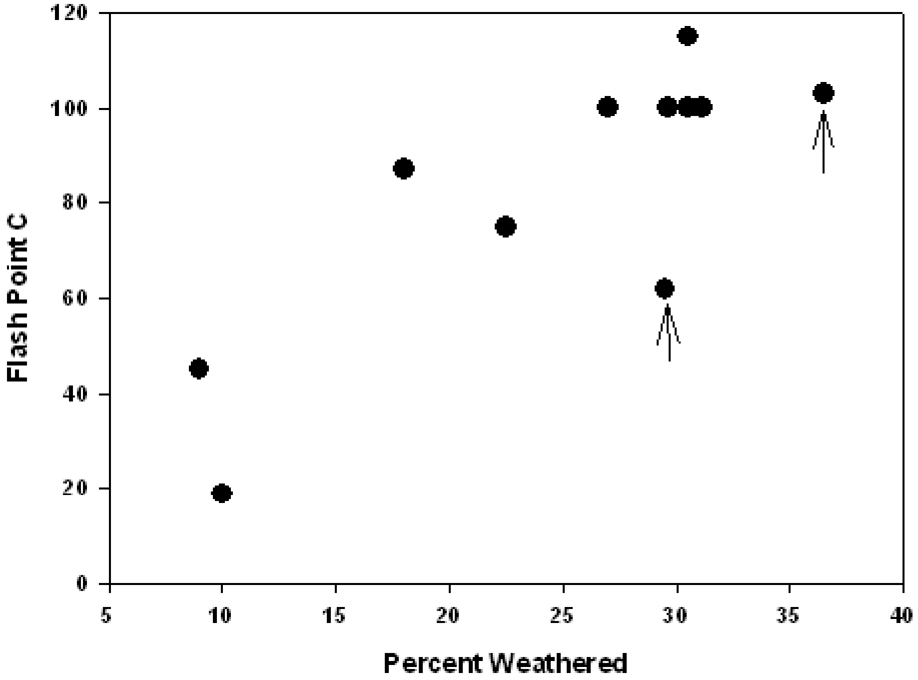

Figure 6 **Flash Point of Weathered Alaska North Slope Oils by Weathering Percentage**

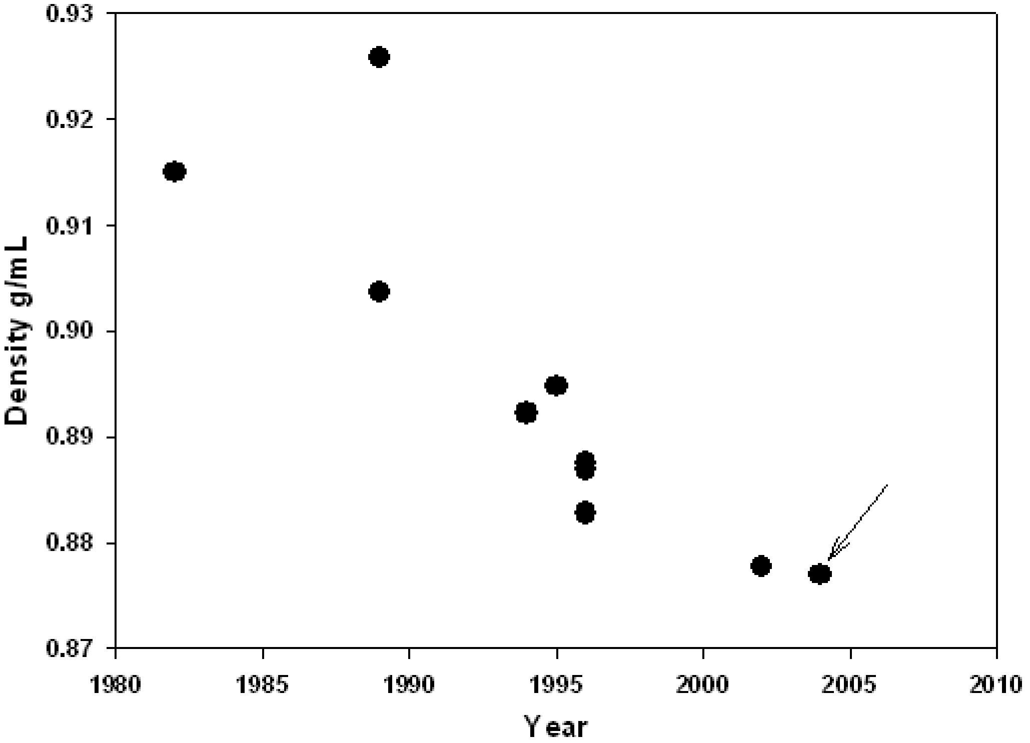

Figure 7 Density (at 0ºC) of Fresh Alaska North Slope Oils by Year (Arrow indicates data from the SLR Report.)

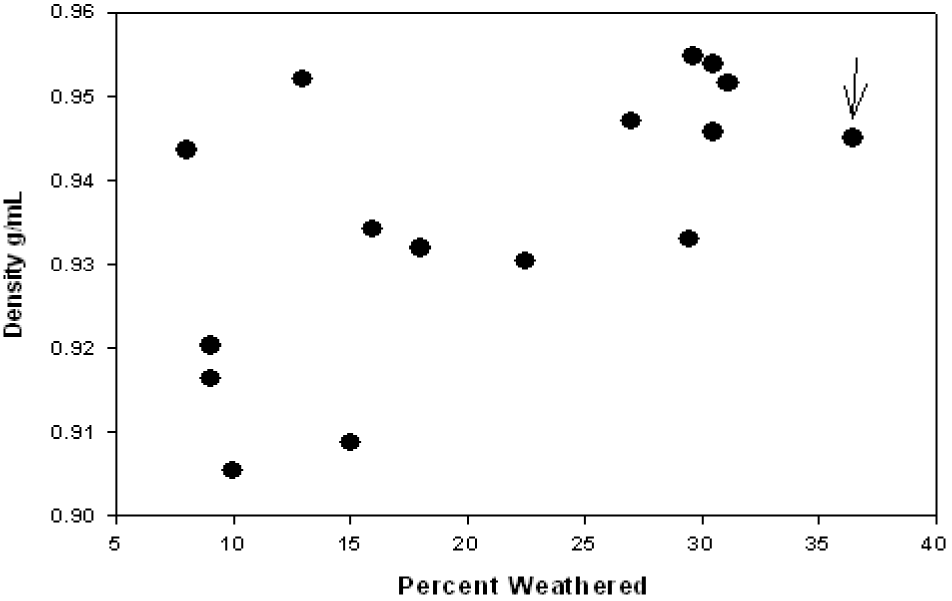

Figure 8 Density (at 0ºC) of Alaska North Slope Oils by Weathering Percentage

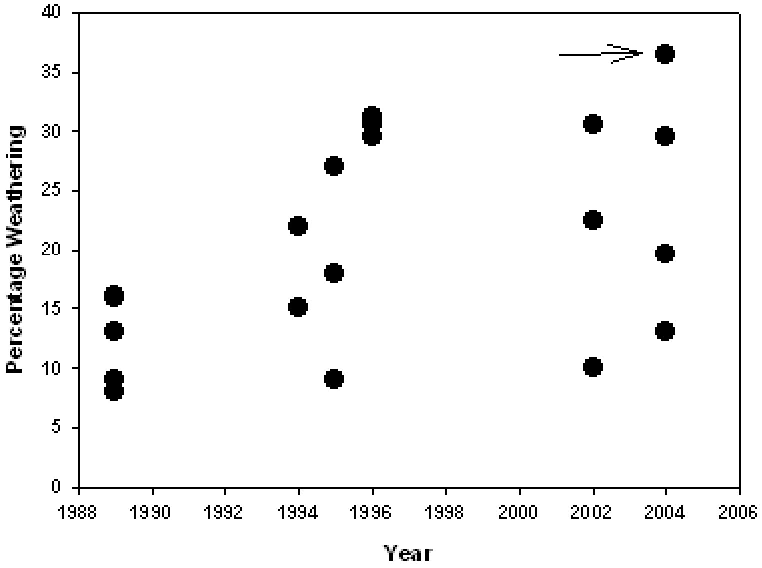

Figure 9 Density of Fresh Alaska North Slope Oils by Year and Weathering Percentage (Density is indicated by size of circle.)

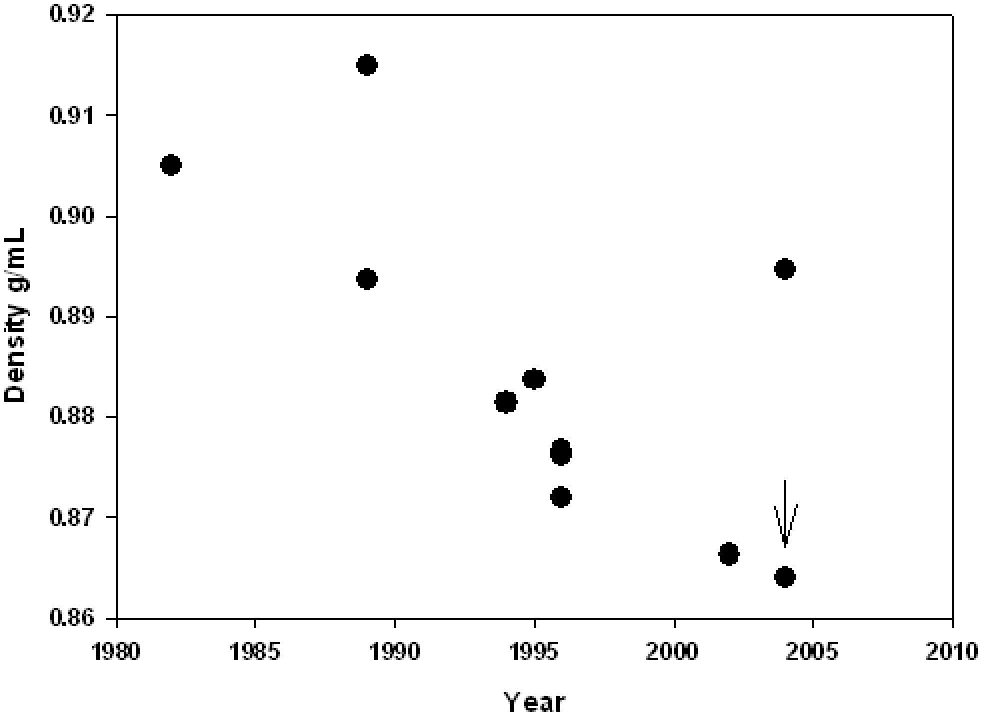

Figure 10 Density (at 15ºC) of Fresh Alaska North Slope Oils by Year

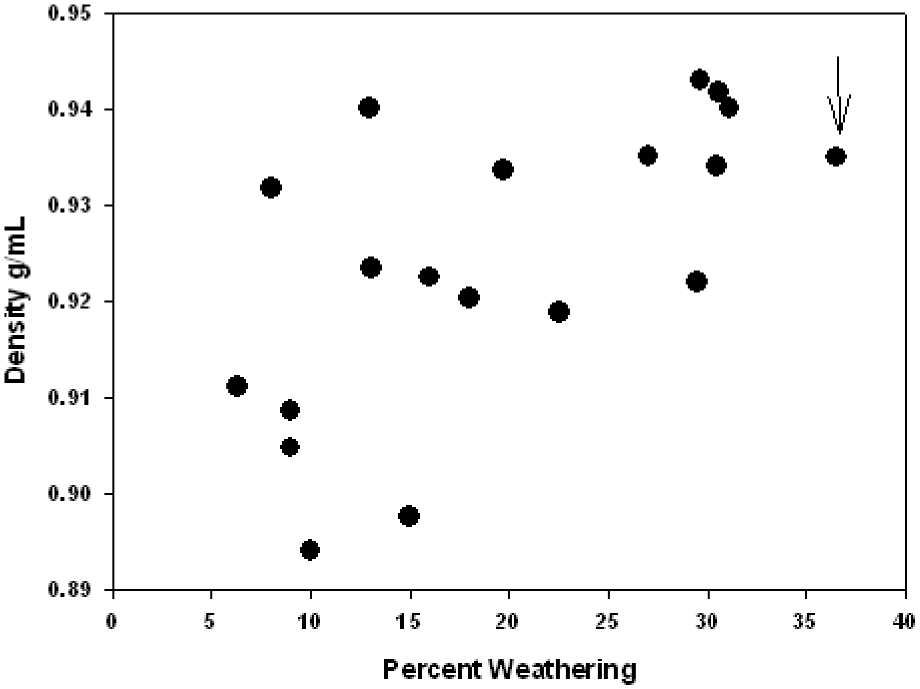

Figure 11 Density (at 15ºC) of Weathered Alaska North Slope Oils by Weathering Percentage

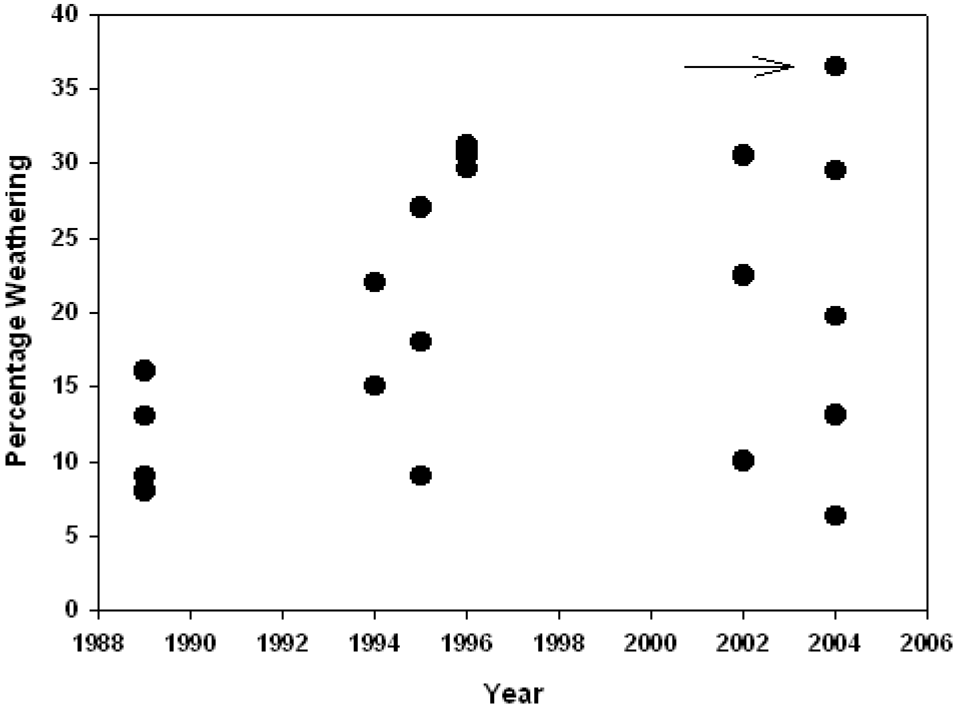

Figure 12 Density (at 15ºC) of Fresh Alaska North Slope Oils by Year and Weathering Percentage (Density indicated by size of circle.)

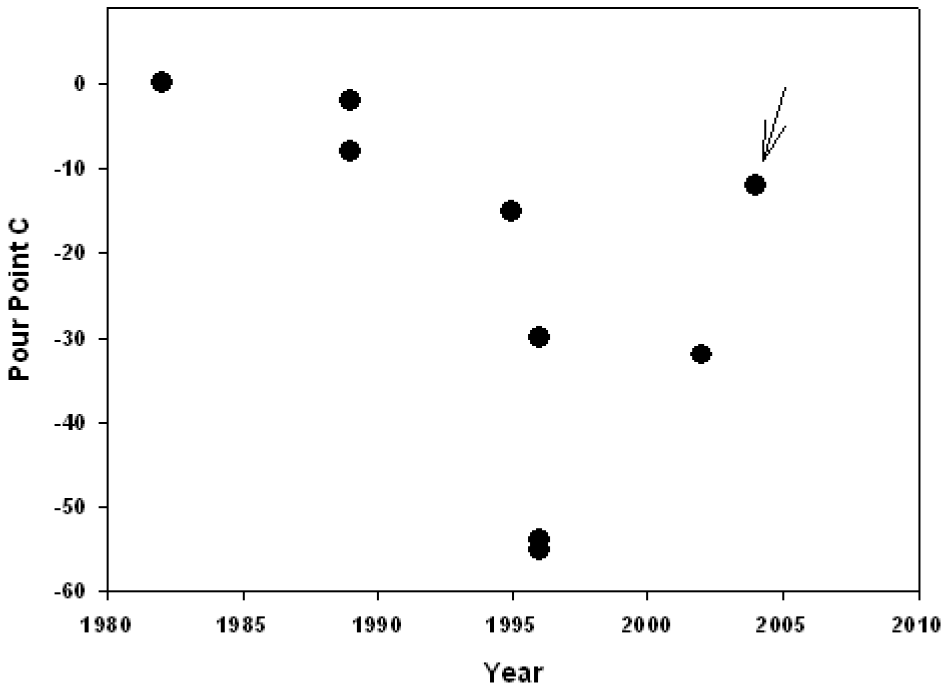

Figure 13 Pour Point of Fresh Alaska North Slope Oils by Year

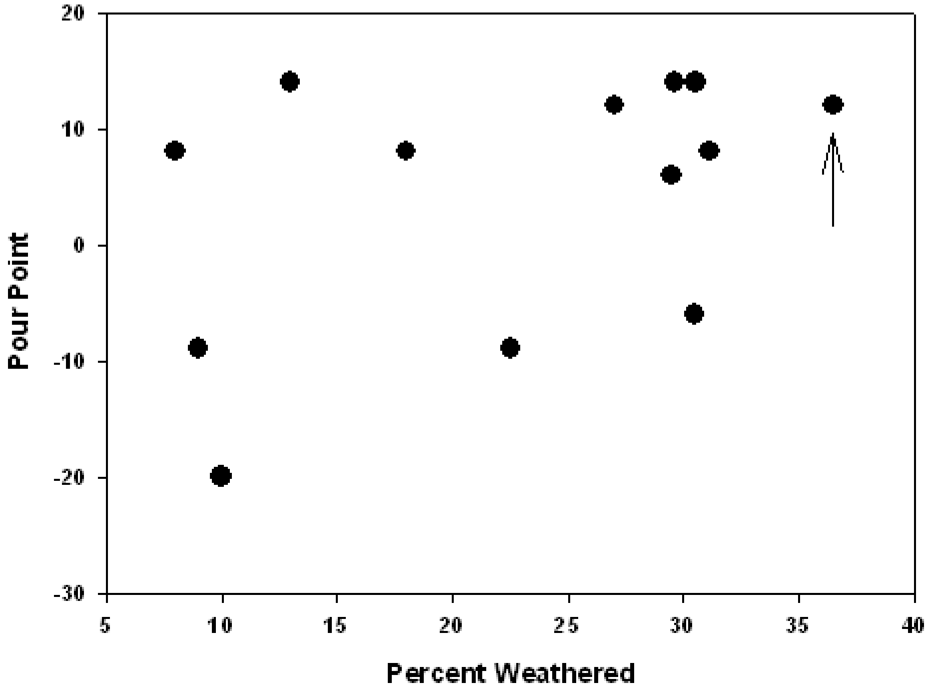

Figure 14 Pour Point of Weathered Alaska North Slope Oils by Weathering Percentage

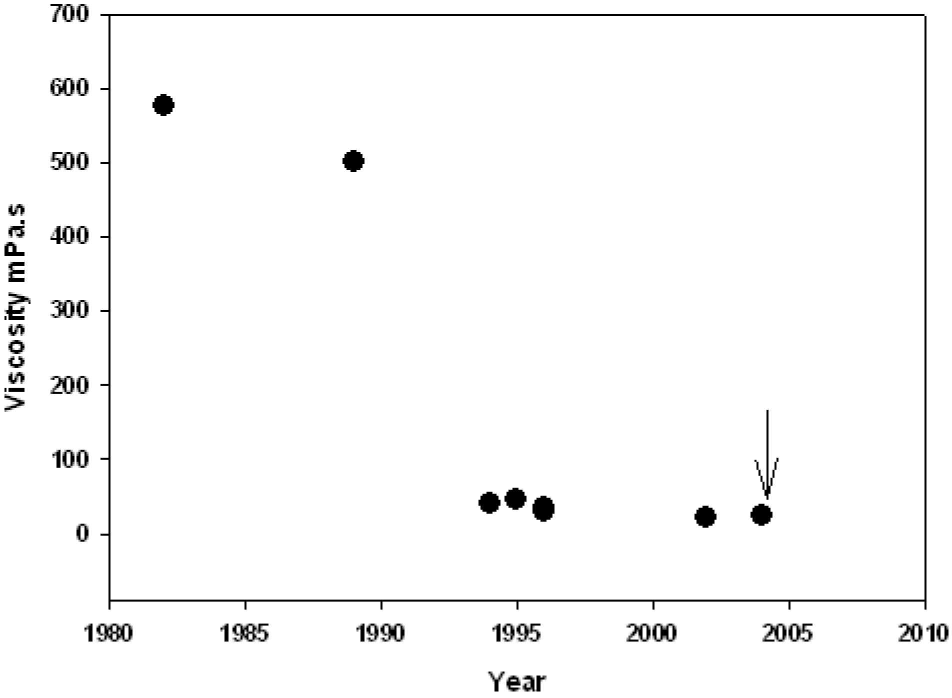

Figure 15 Viscosity (at 0ºC) of Fresh Alaska North Slope Oils by Year

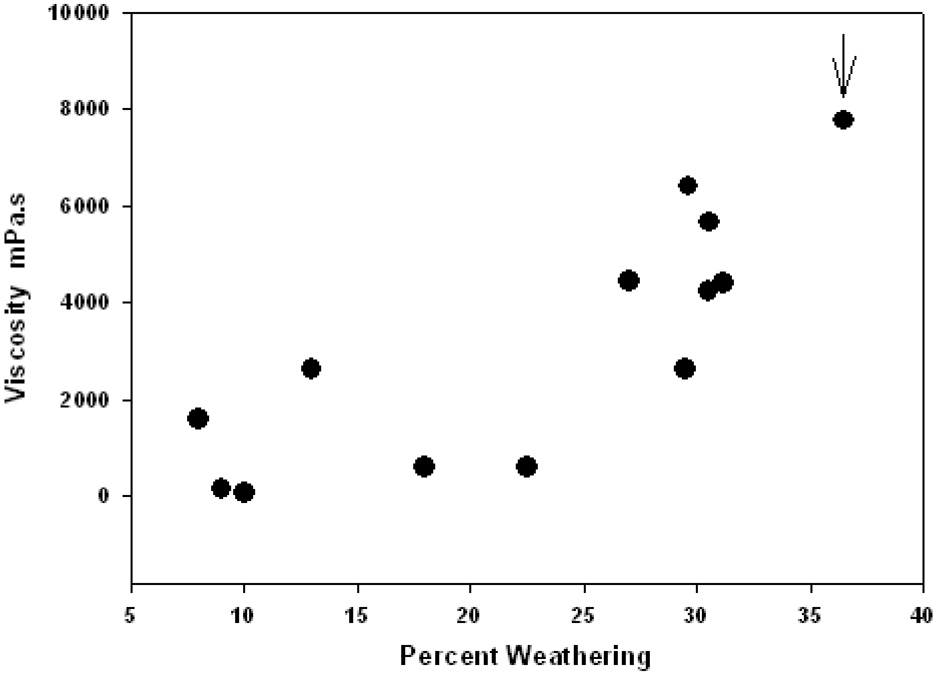

Figure 16 Viscosity (at 0ºC) of Weathered Alaska North Slope Oils by Weathering Percentage

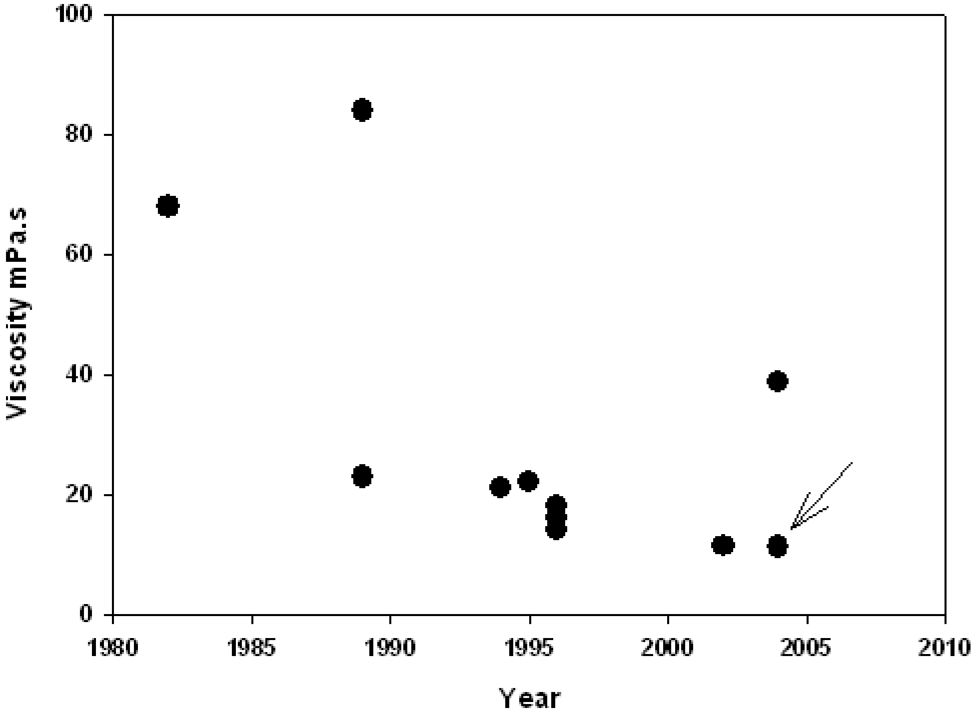

Figure 17 Viscosity (at 15ºC) of Fresh Alaska North Slope Oils by Year

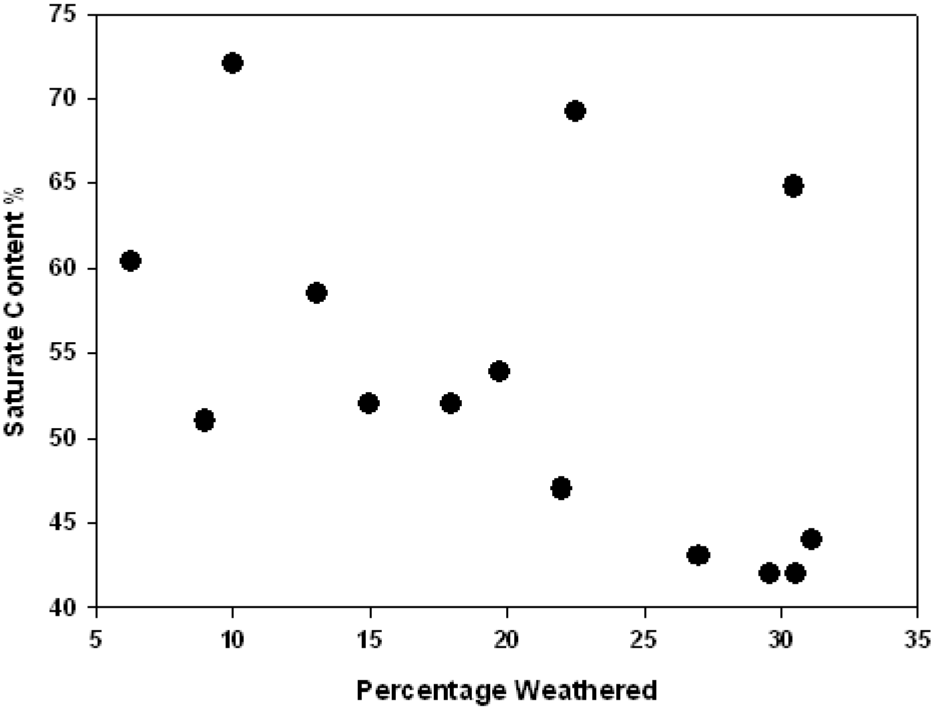

Figure 18 Viscosity (at 15ºC) of Weathered Alaska North Slope Oils by Weathering Percentage

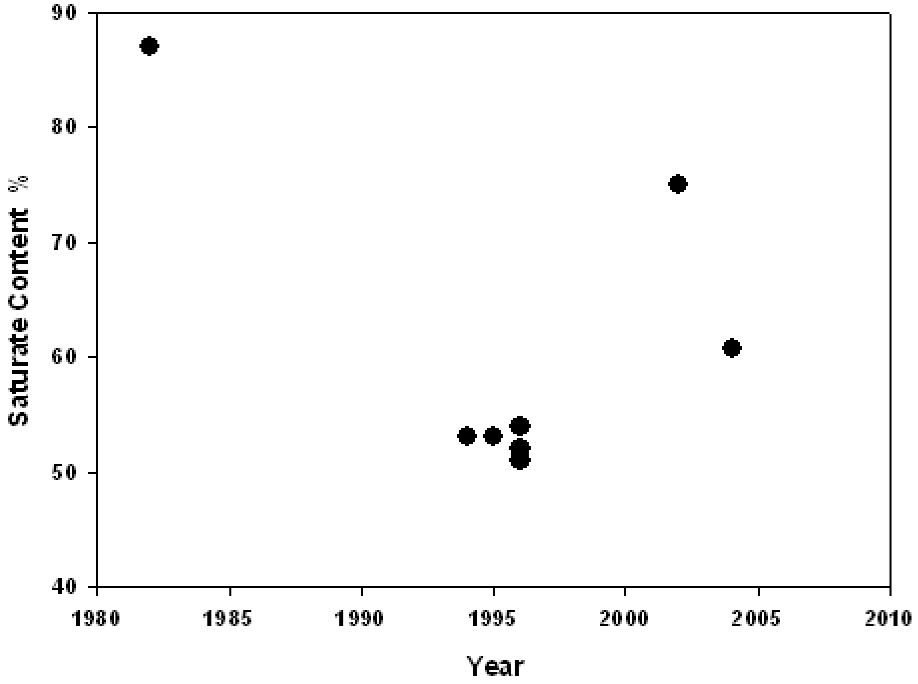

Figure 19 Saturate Content of Fresh Alaska North Slope Oils by Year

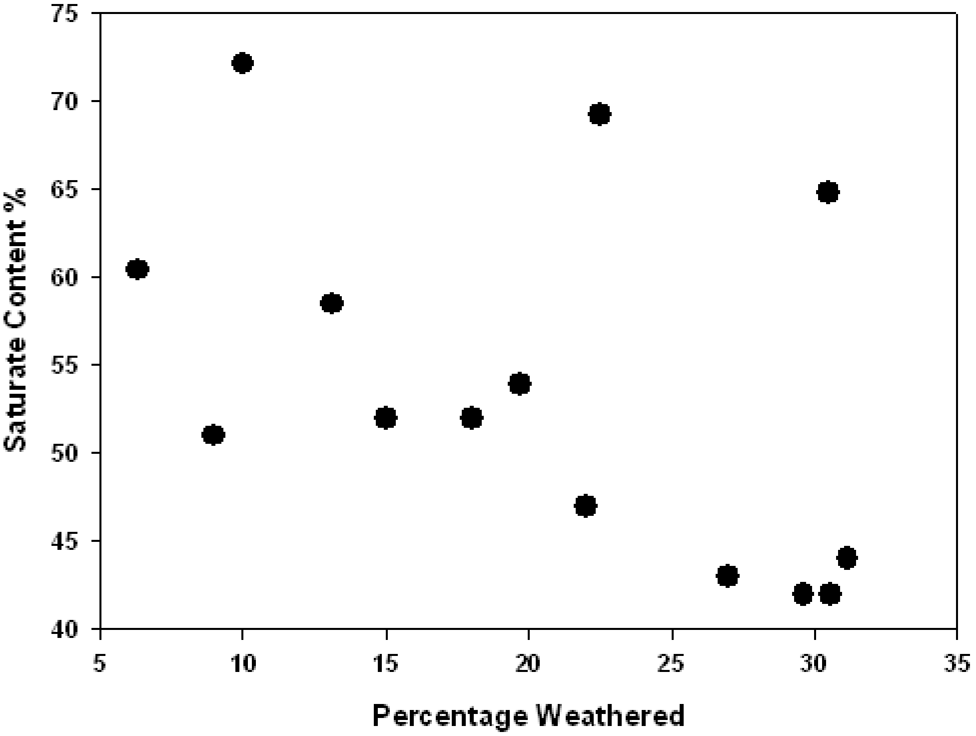

Figure 20 Saturate Content of Weathered Alaska North Slope Oils by Weathering Percentage

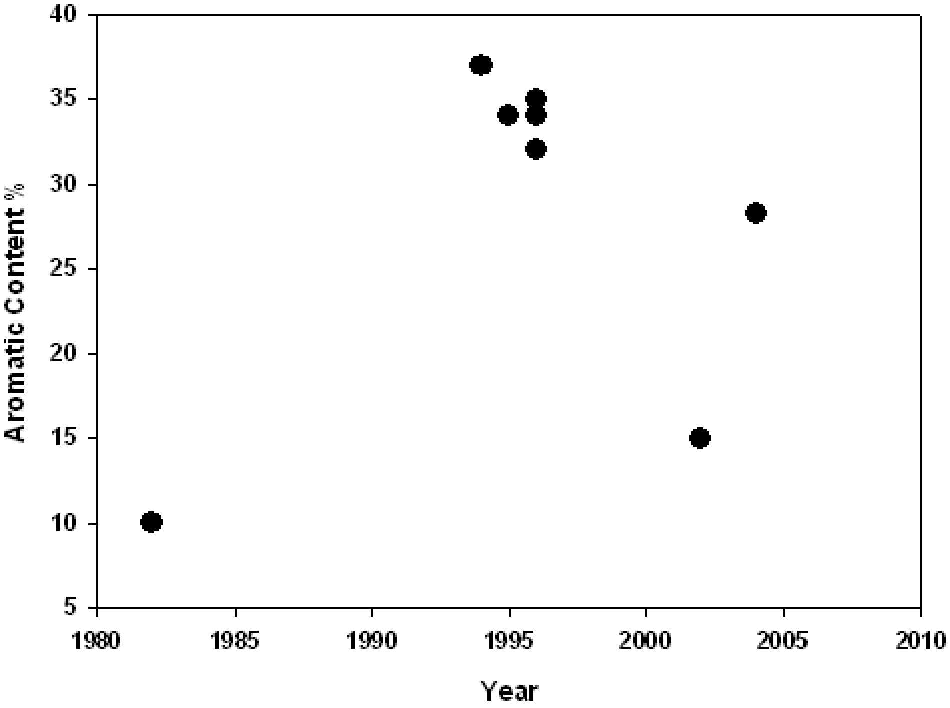

Figure 21 Aromatic Content of Fresh Alaska North Slope Oils by Year

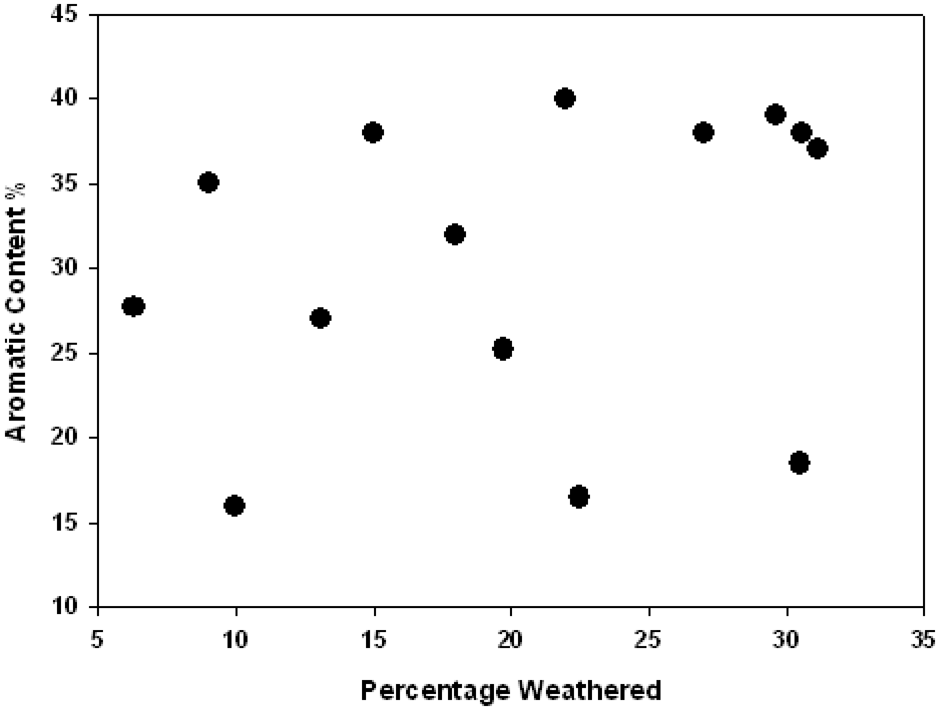

Figure 22 Aromatic Content of Weathered Alaska North Slope Oils by Weathering Percentage

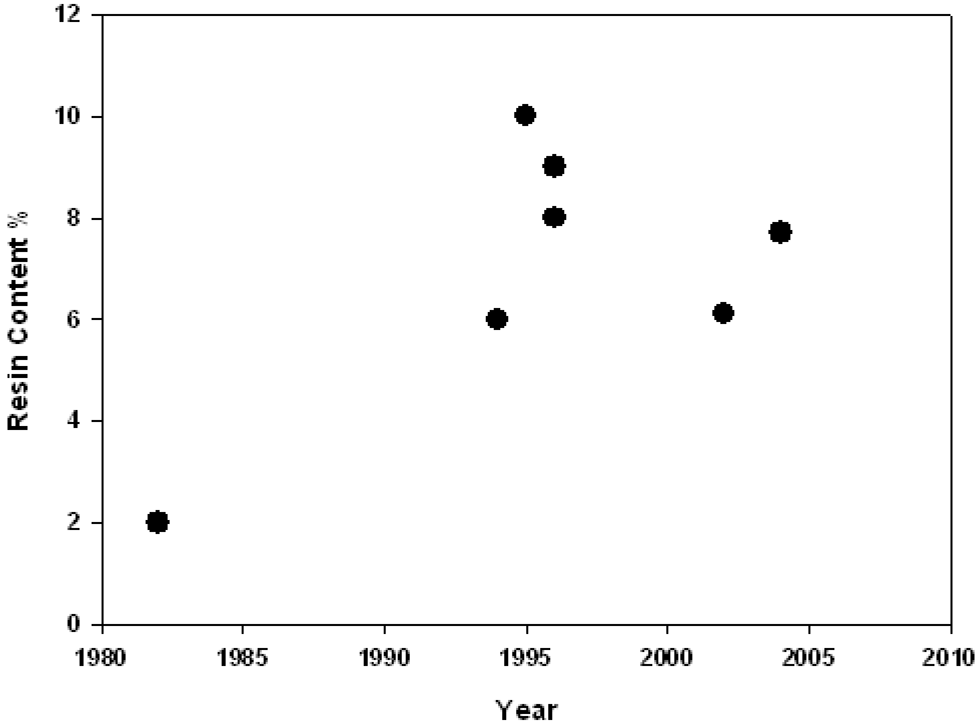

Figure 23 **Resin Content of Fresh Alaska North Slope Oils by Year**

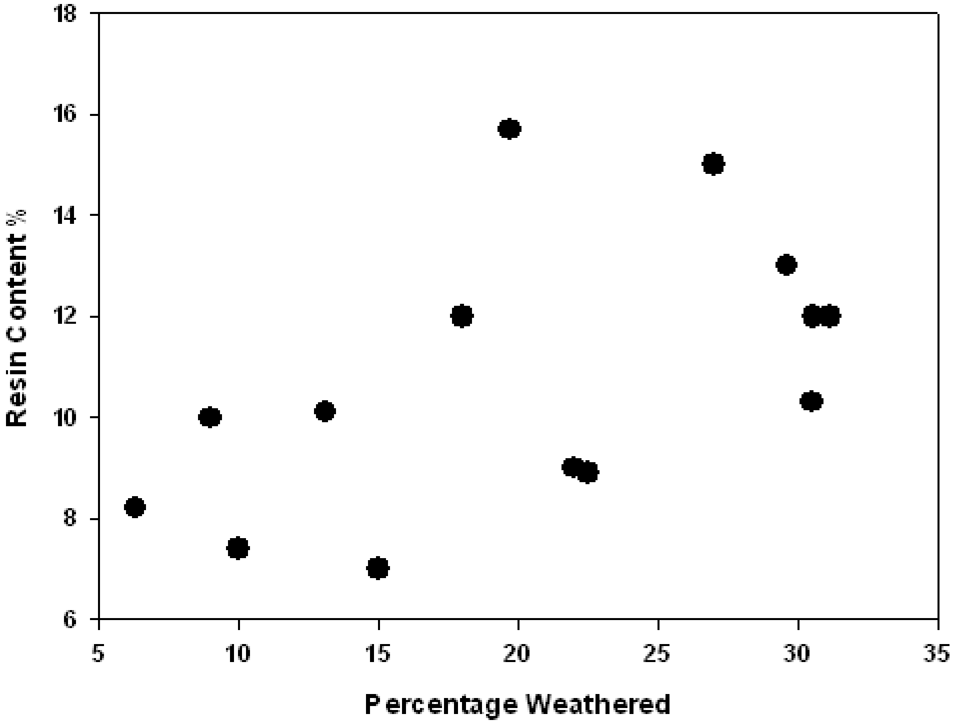

Figure 24 **Resin Content of Weathered Alaska North Slope Oils by Weathering Percentage**

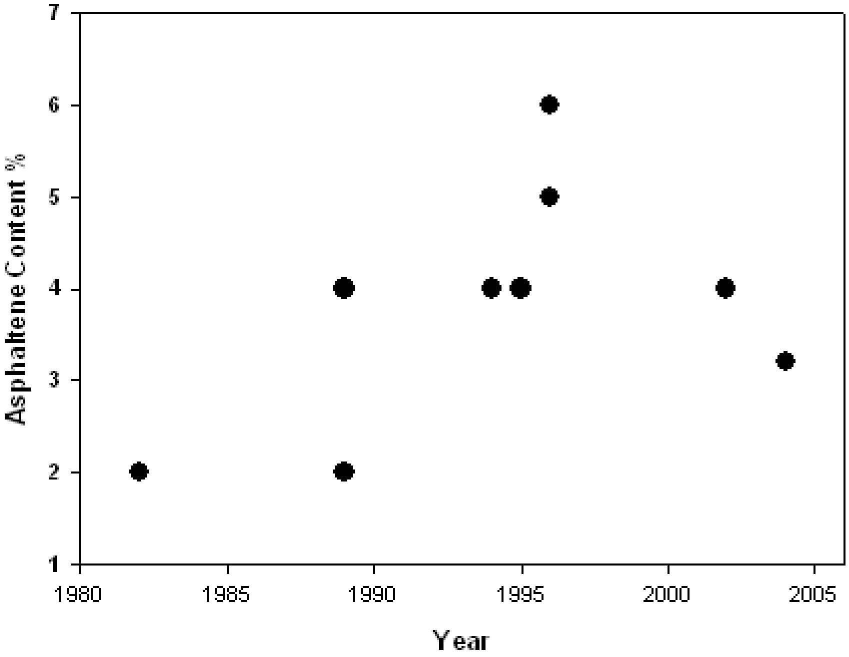

Figure 25 Asphaltene Content of Fresh Alaska North Slope Oils by Year

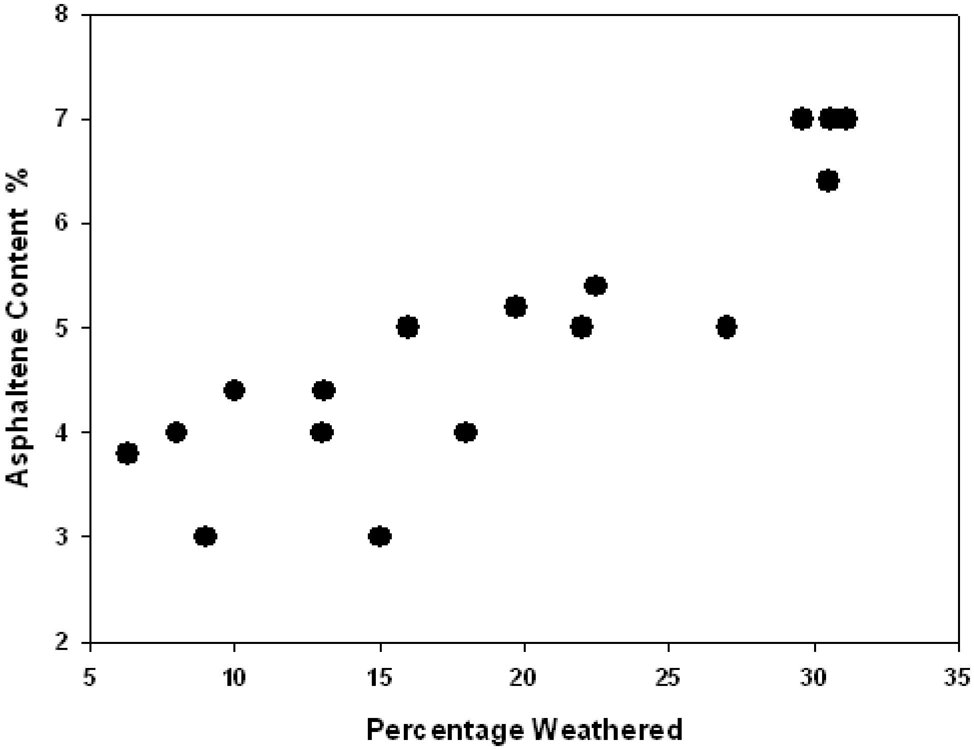

Figure 26 Asphaltene Content of Weathered Alaska North Slope Oils by Weathering Percentage

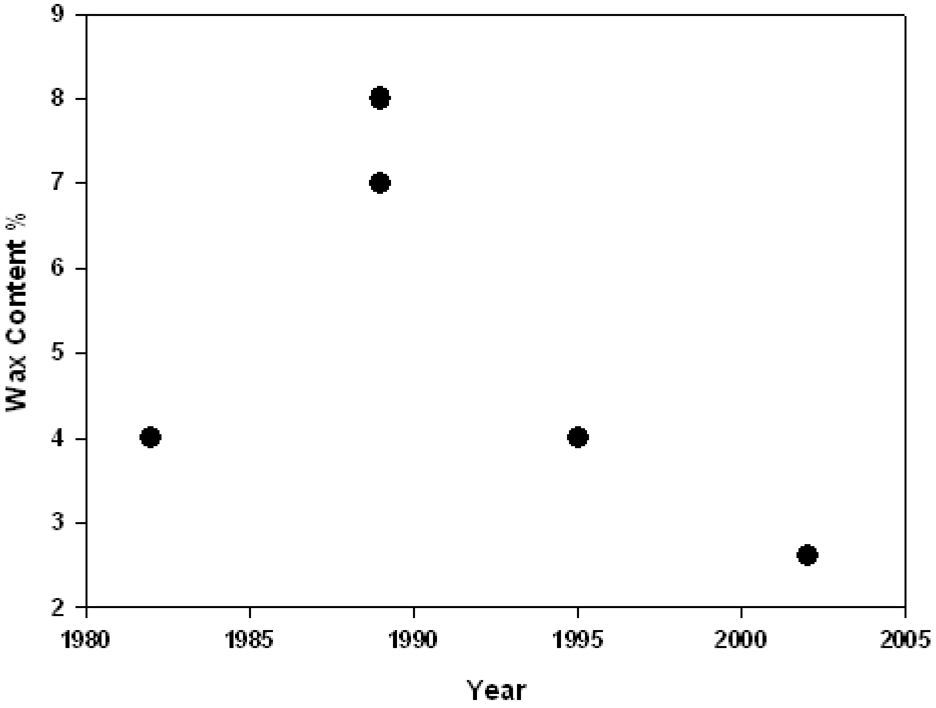

Figure 27 Wax Content of Fresh Alaska North Slope Oils by Year

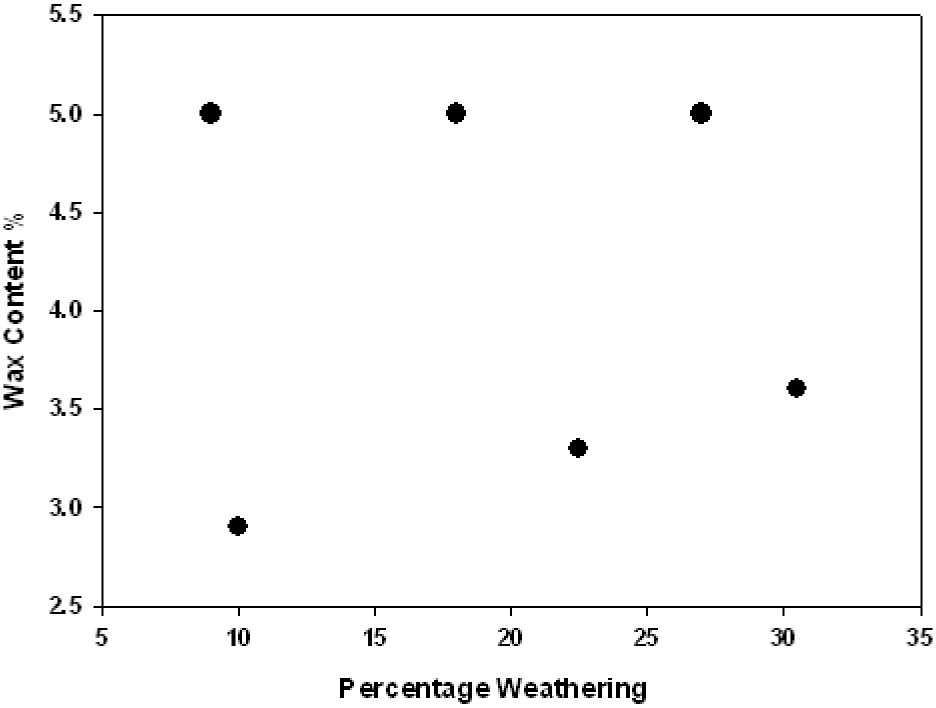

Figure 28 Wax Content of Weathered Alaska North Slope Oils by Weathering Percentage

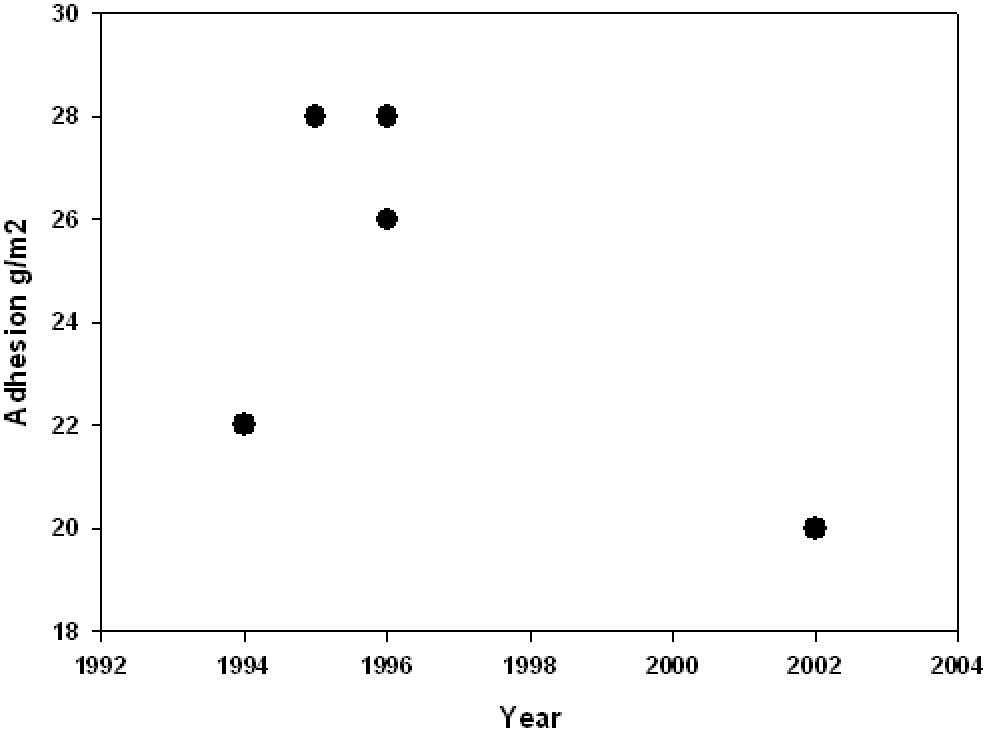

Figure 29 Adhesion of Fresh Alaska North Slope Oils by Year

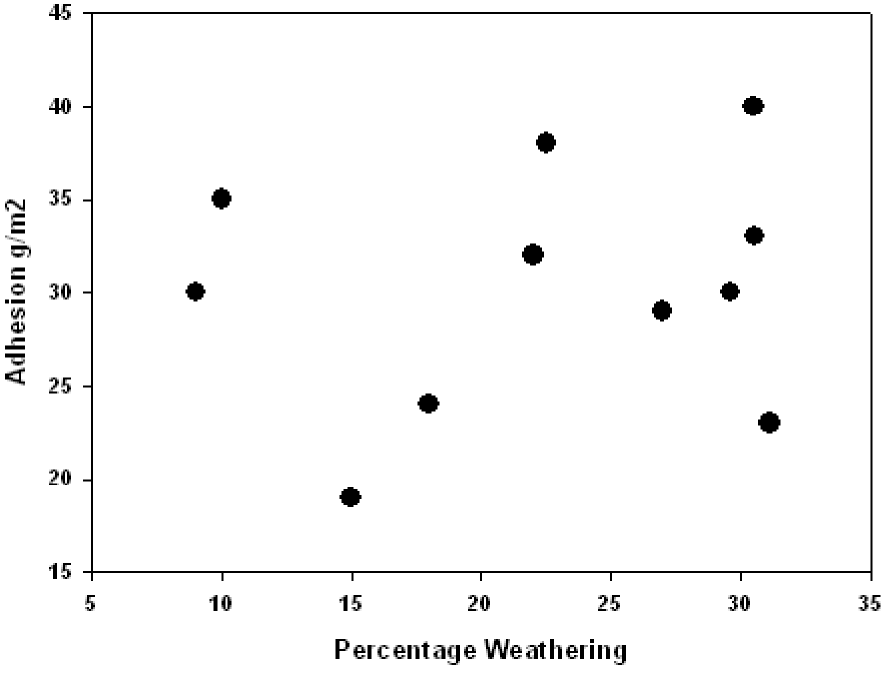

Figure 30 Adhesion of Weathered Alaska North Slope Oils by Weathering Percentage

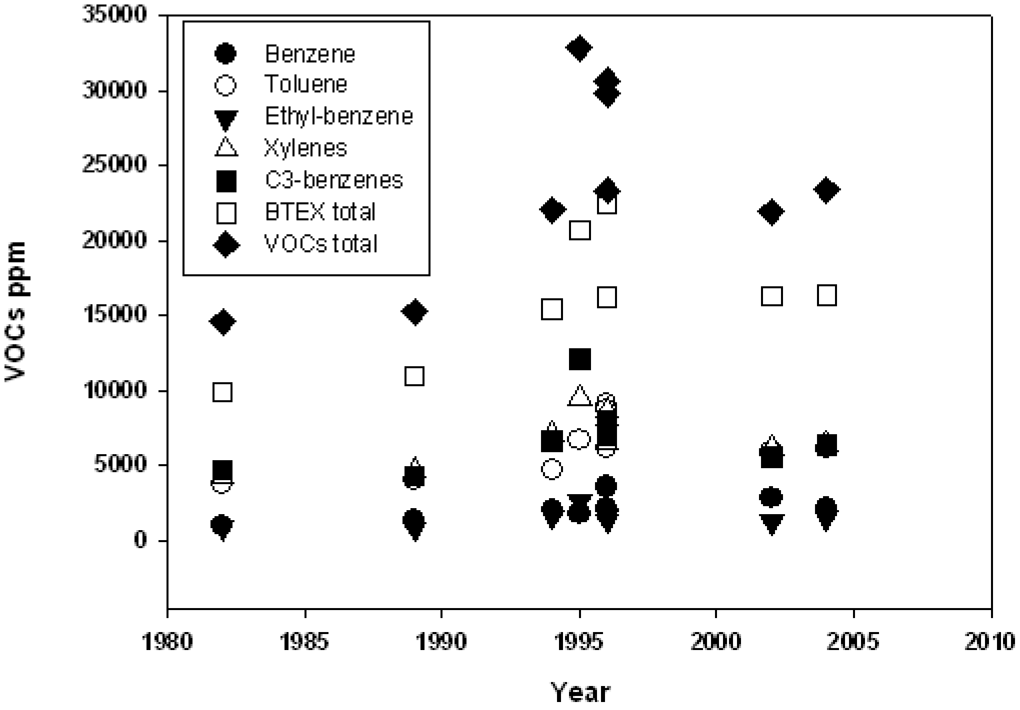

Figure 31 VOC Content of Fresh Alaska North Slope Oils by Year

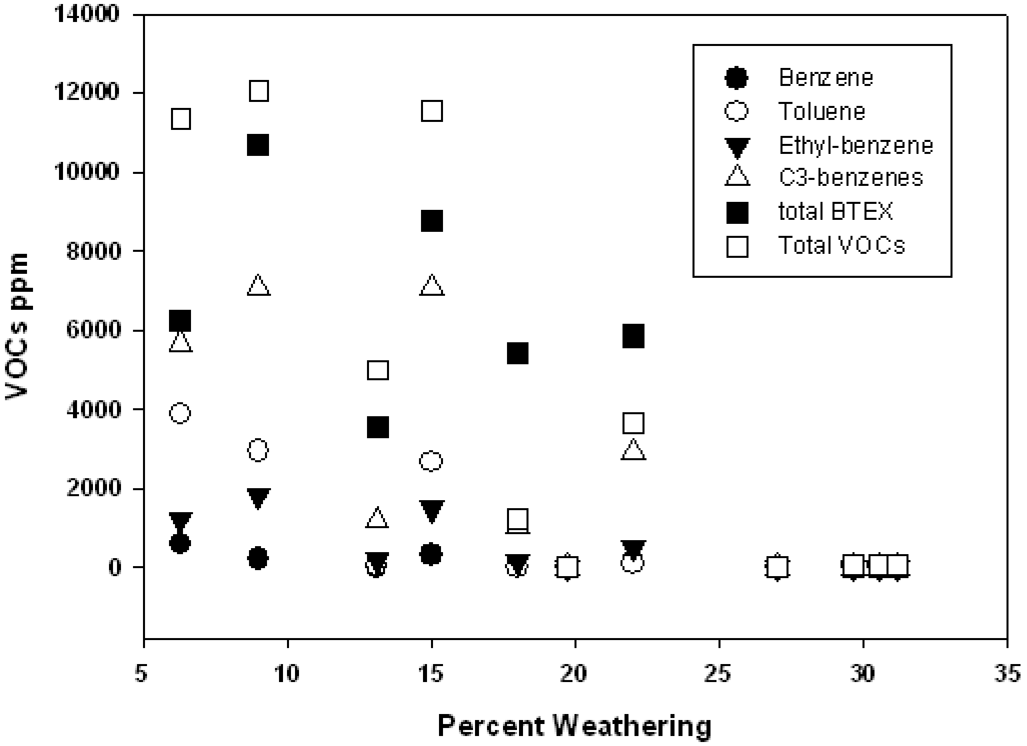

Figure 32 VOC Content of Weathered Alaska North Slope Oils by Weathering Percentage

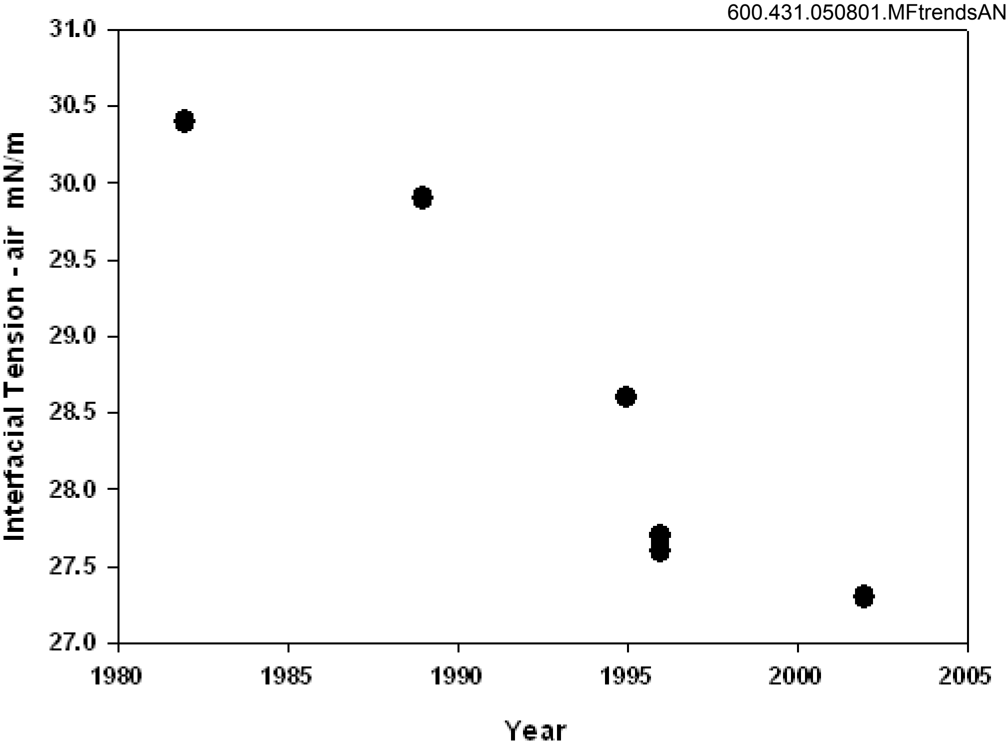

Figure 33 Interfacial Tension of Fresh Alaska North Slope Oils with Air (at 0ºC) by Year

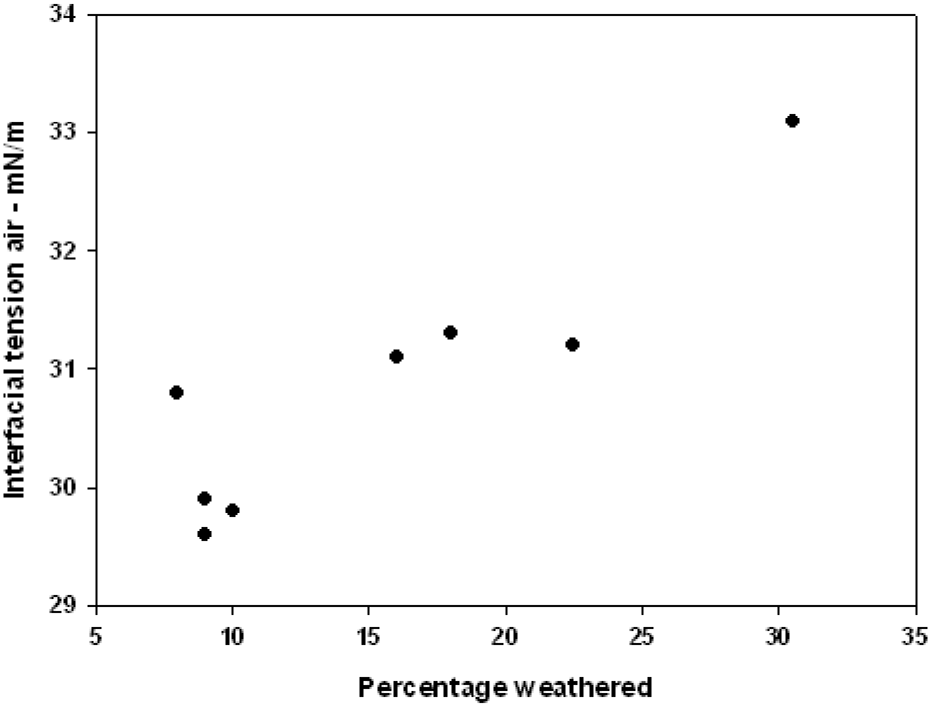

Figure 34 Interfacial Tension of Weathered Alaska North Slope Oils with Air (at 0ºC) by Weathering Percentage

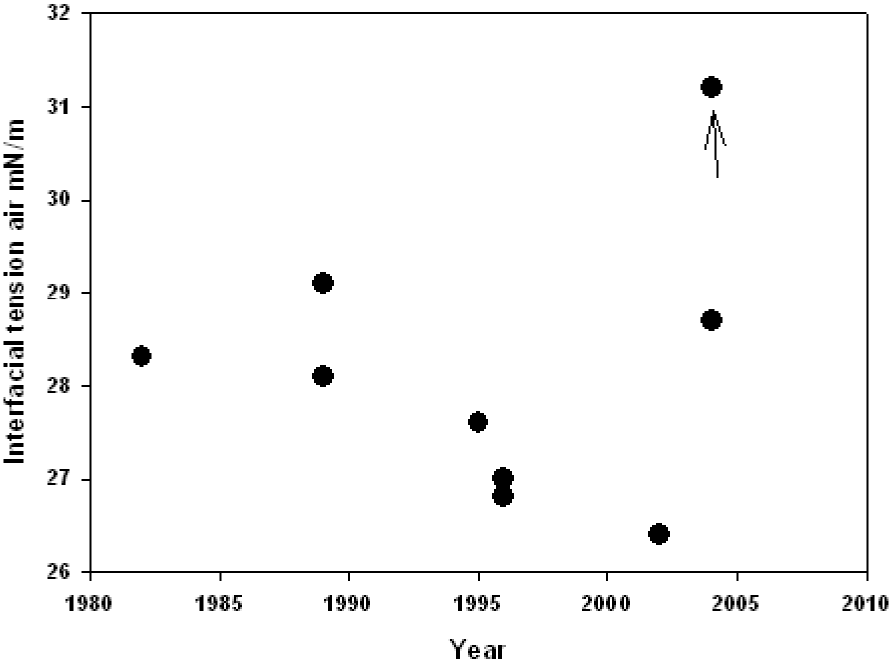

Figure 35 **Interfacial Tension of Fresh Alaska North Slope Oils with Air (at 15ºC) by Year**

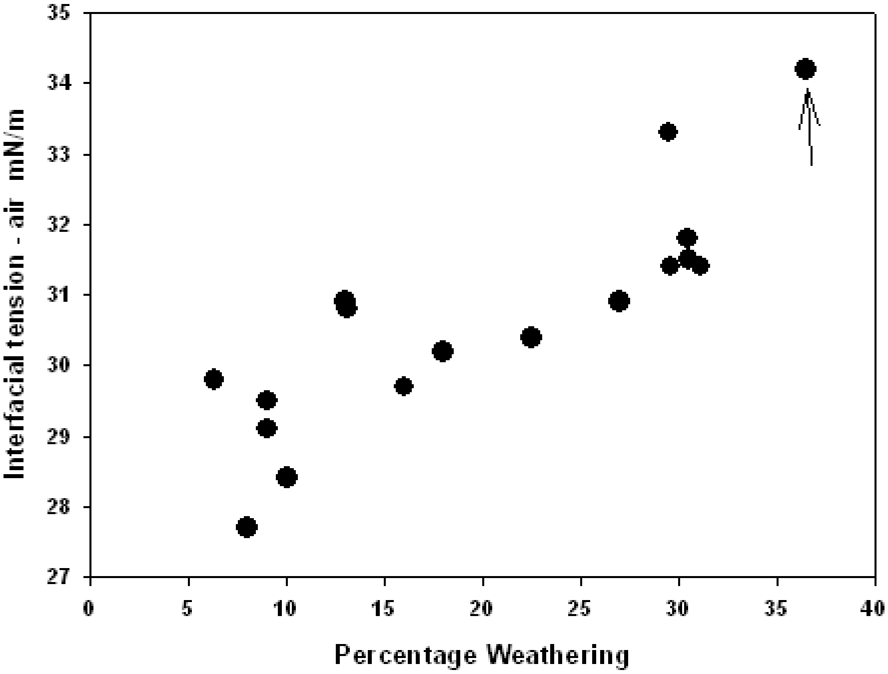

Figure 36 **Interfacial Tension of Weathered Alaska North Slope Oils with Air (at 15ºC) by Weathering Percentage**

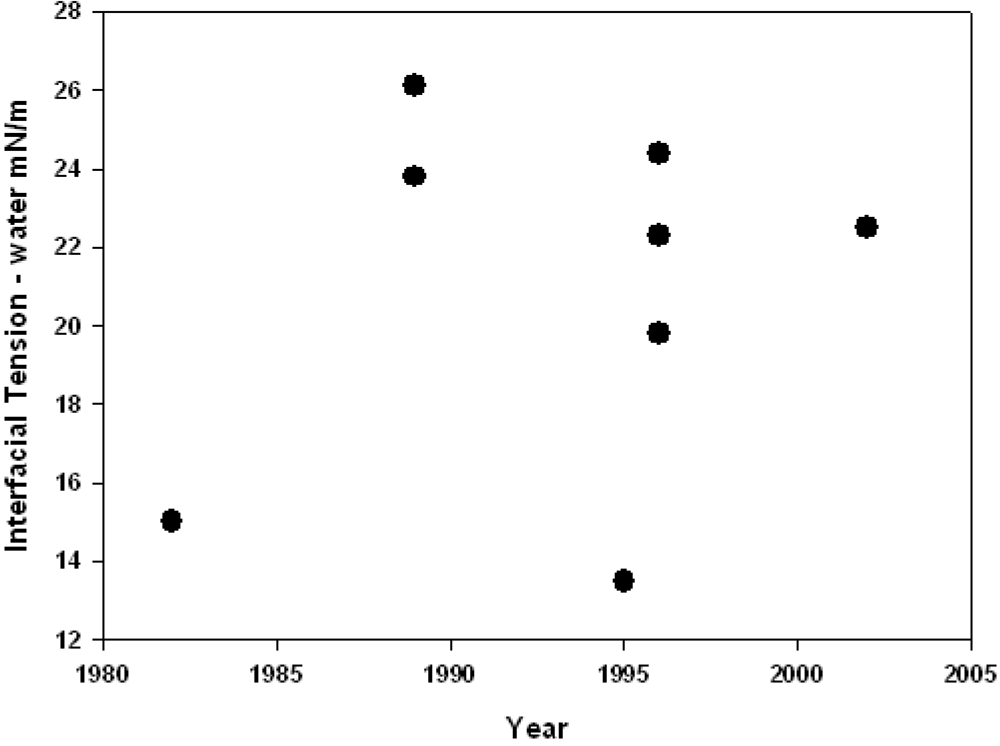

Figure 37 Interfacial Tension of Fresh Alaska North Slope Oils with Seawater (at 0ºC) by Year

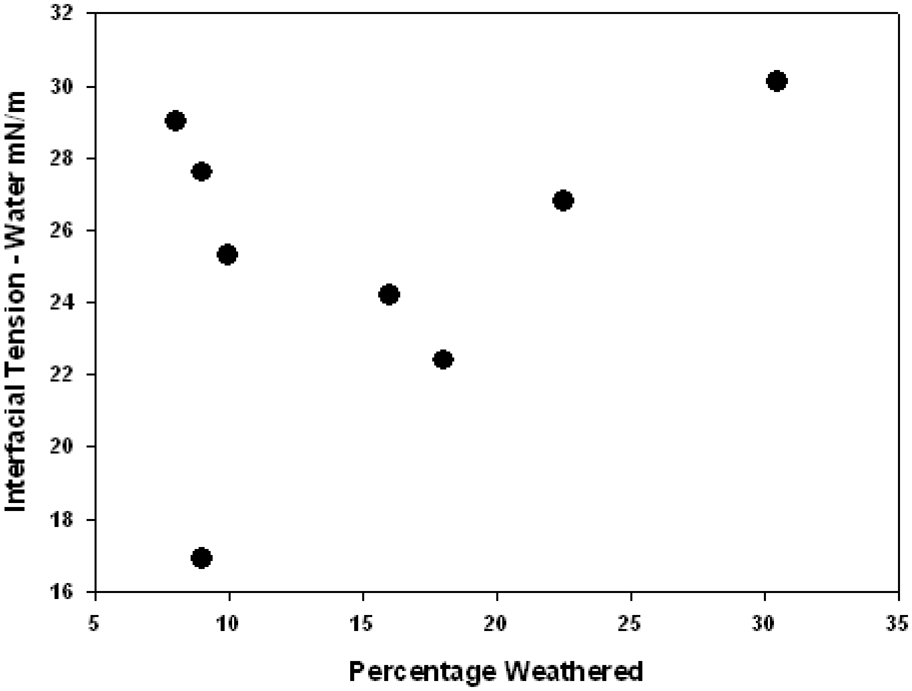

Figure 38 Interfacial Tension of Weathered Alaska North Slope Oils with Seawater (at 0ºC) by Weathering Percentage

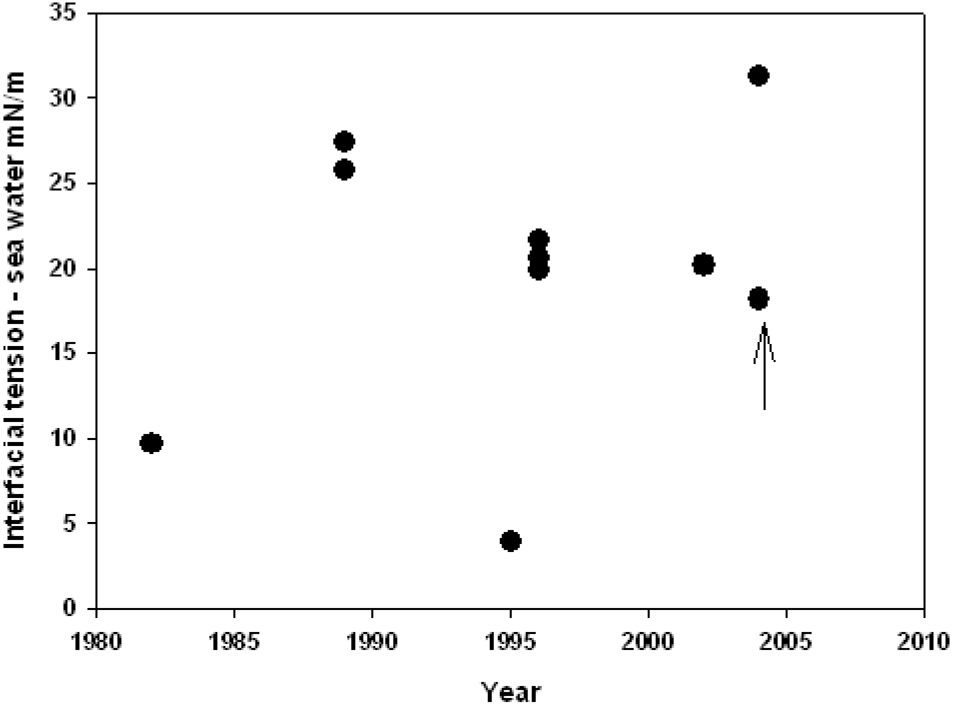

Figure 39 Interfacial Tension of Fresh Alaska North Slope Oils with Seawater (at 15ºC) by Year

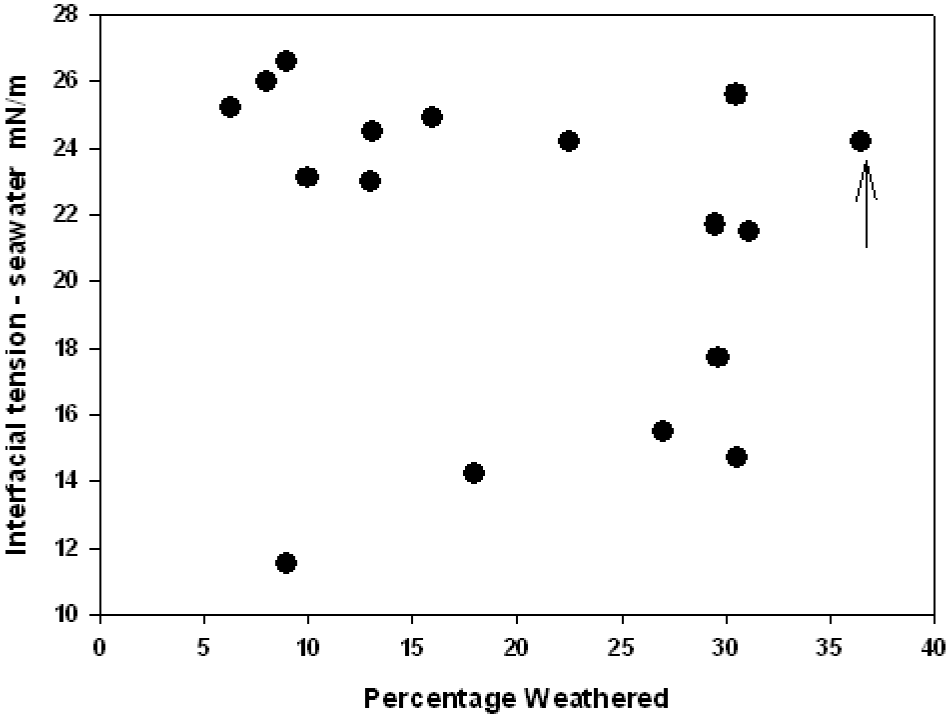

Figure 40 Interfacial Tension of Weathered Alaska North Slope Oils with Seawater (at 15ºC) by Weathering Percentage

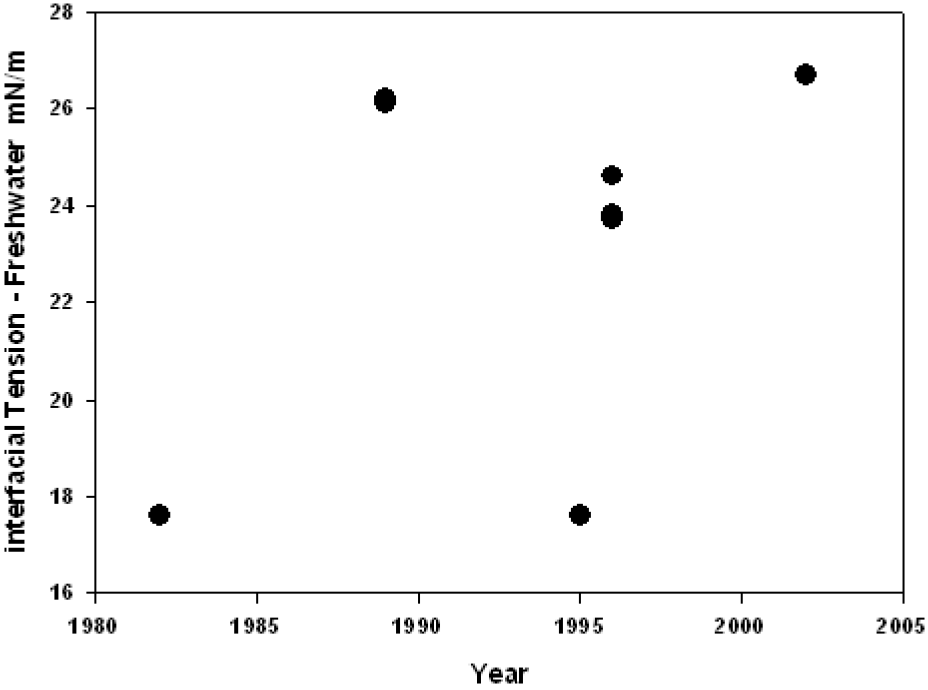

Figure 41 Interfacial Tension of Fresh Alaska North Slope Oils with Freshwater (at 0ºC) by Year

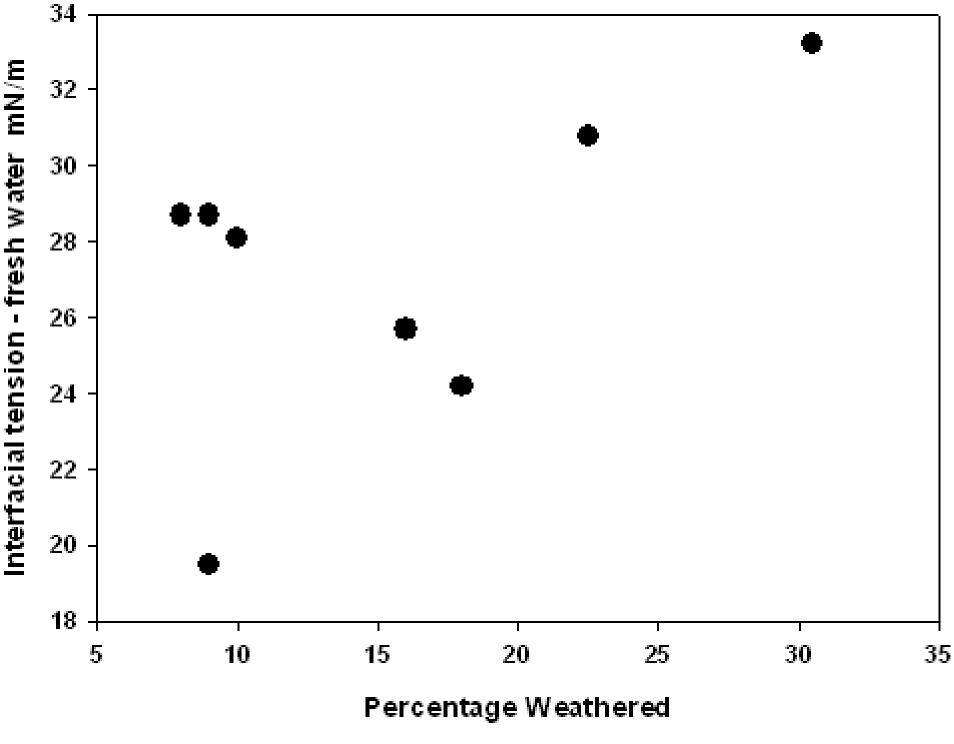

Figure 42 Interfacial Tension of Weathered Alaska North Slope Oils with Freshwater (at 0ºC) by Weathering Percentage

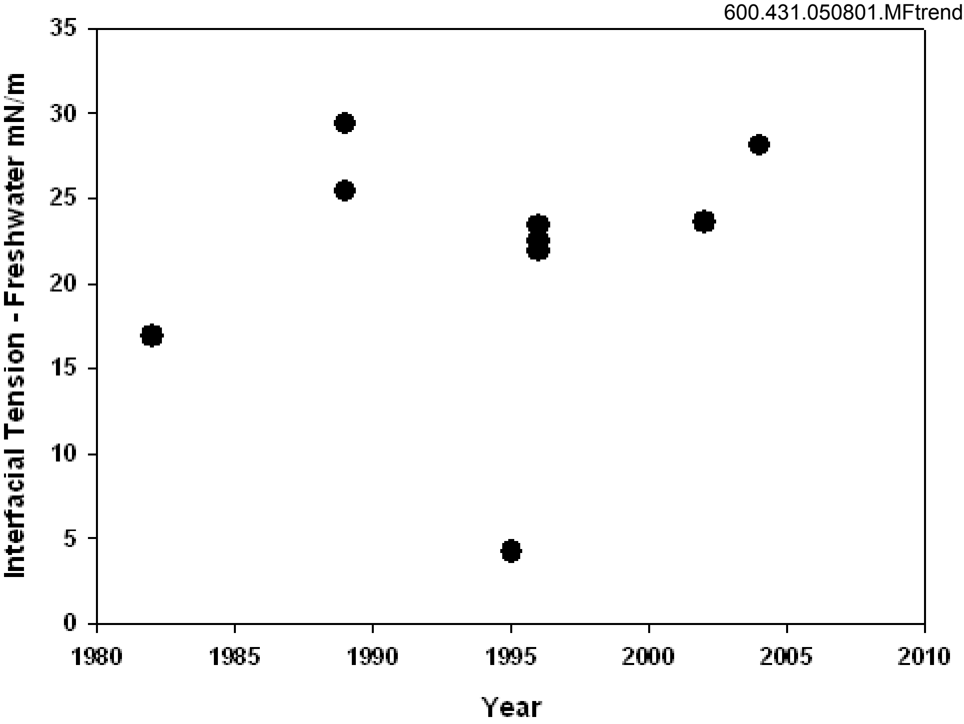

Figure 43 Interfacial Tension of Fresh Alaska North Slope Oils with Freshwater (at 15ºC) by Year

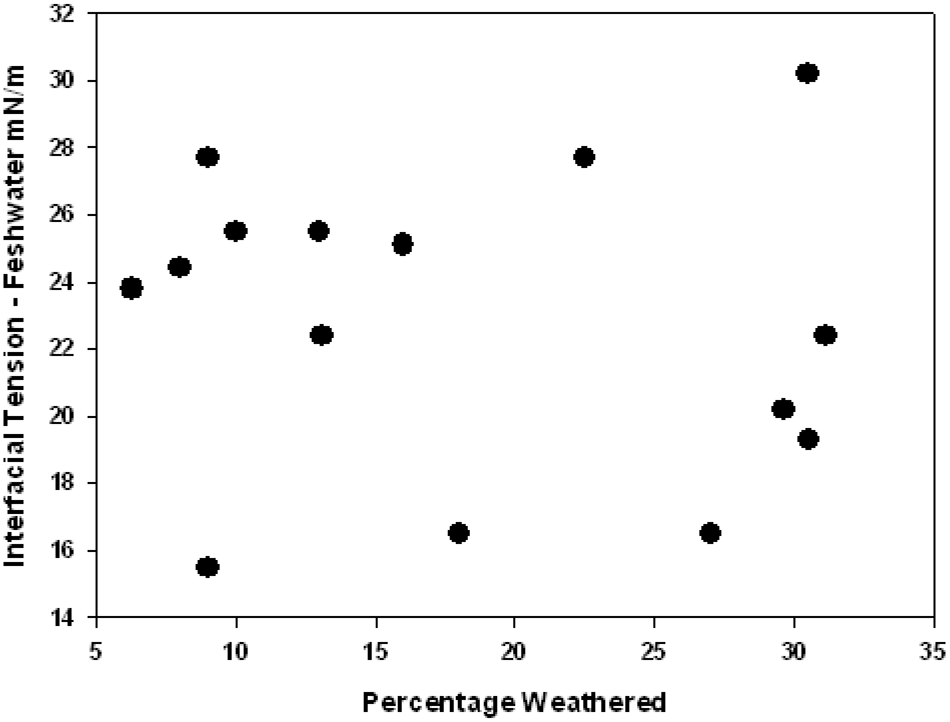

Figure 44 Interfacial Tension of Weathered Alaska North Slope Oils with Freshwater (at 15ºC) by Weathering Percentage

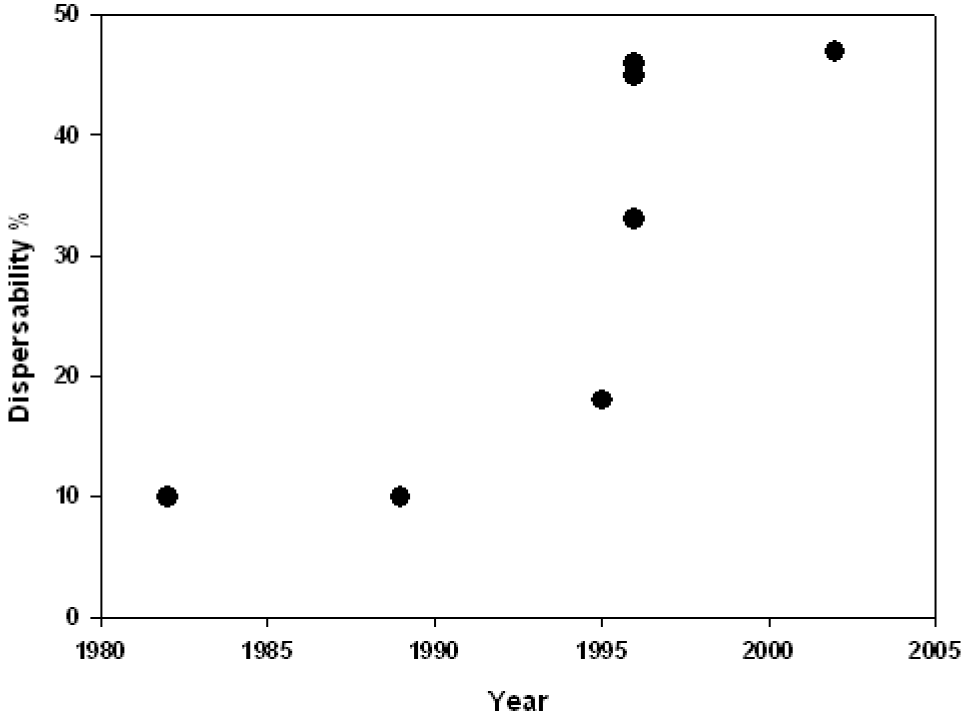

Figure 45 Corexit 9500 Dispersibility of Fresh Alaska North Slope Oils by Year (It should be noted that the method changed in 1995.)

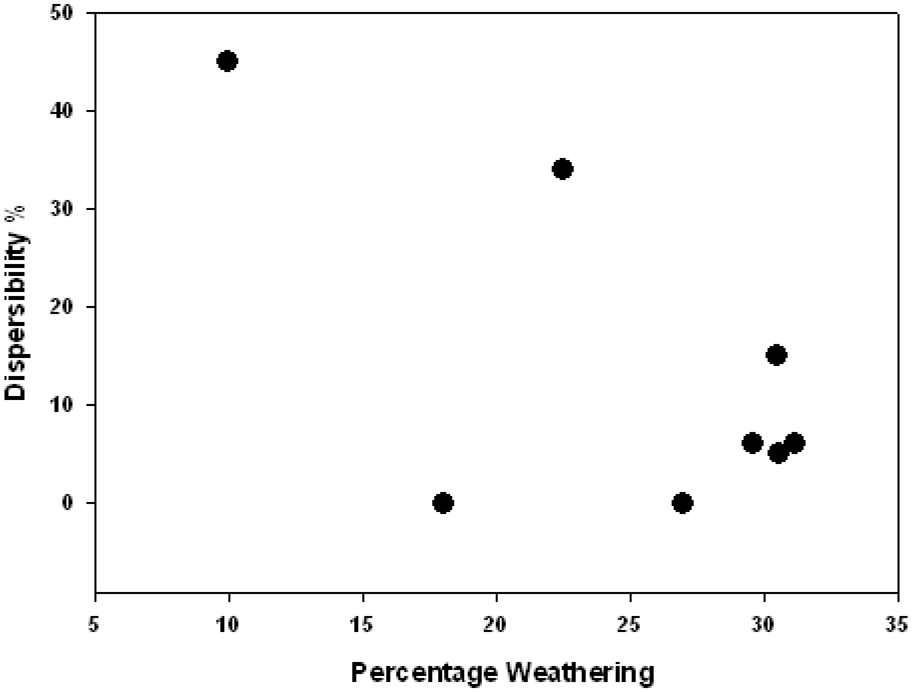

Figure 46 Dispersibility of Weathered Alaska North Slope Oils by Weathering Percentage

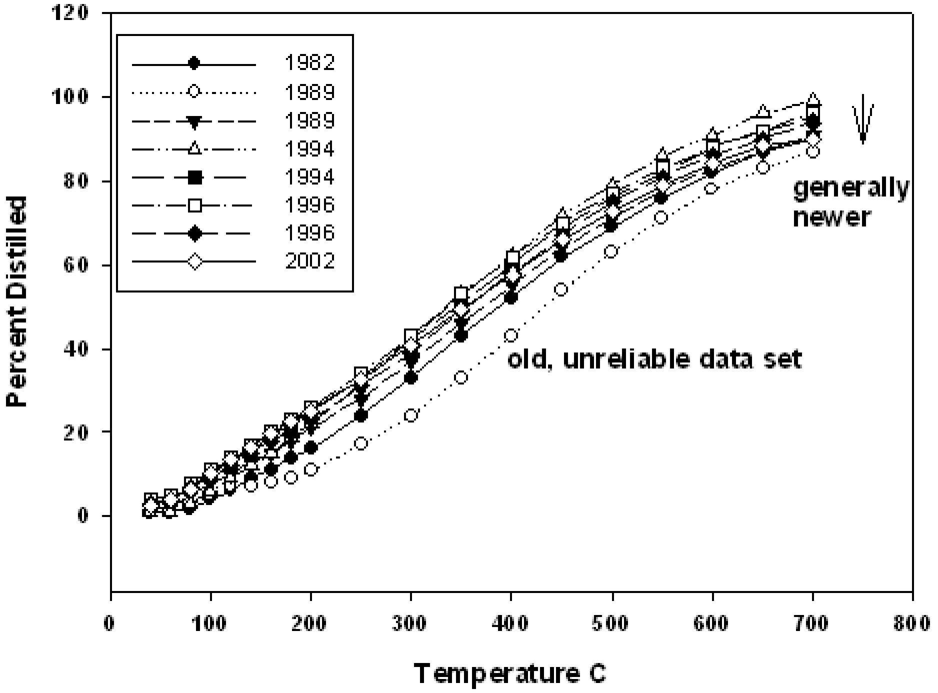

Figure 47 Distillation Curves of Alaska North Slope Oils by Year

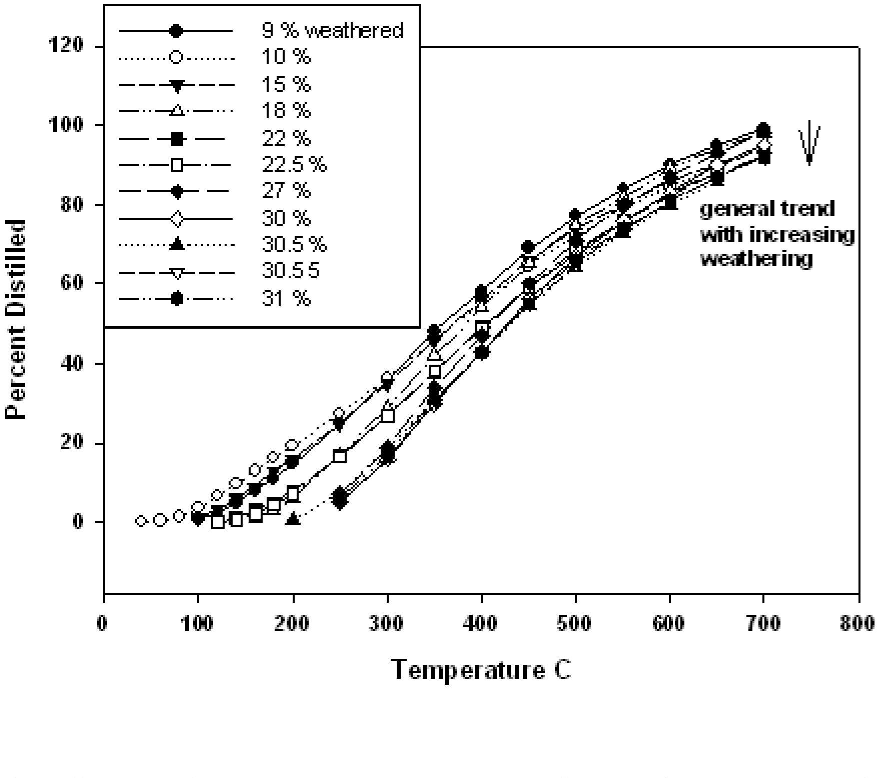

Figure 48 Distillation Curves of Weathered Alaska North Slope Oils by Weathering Percentage

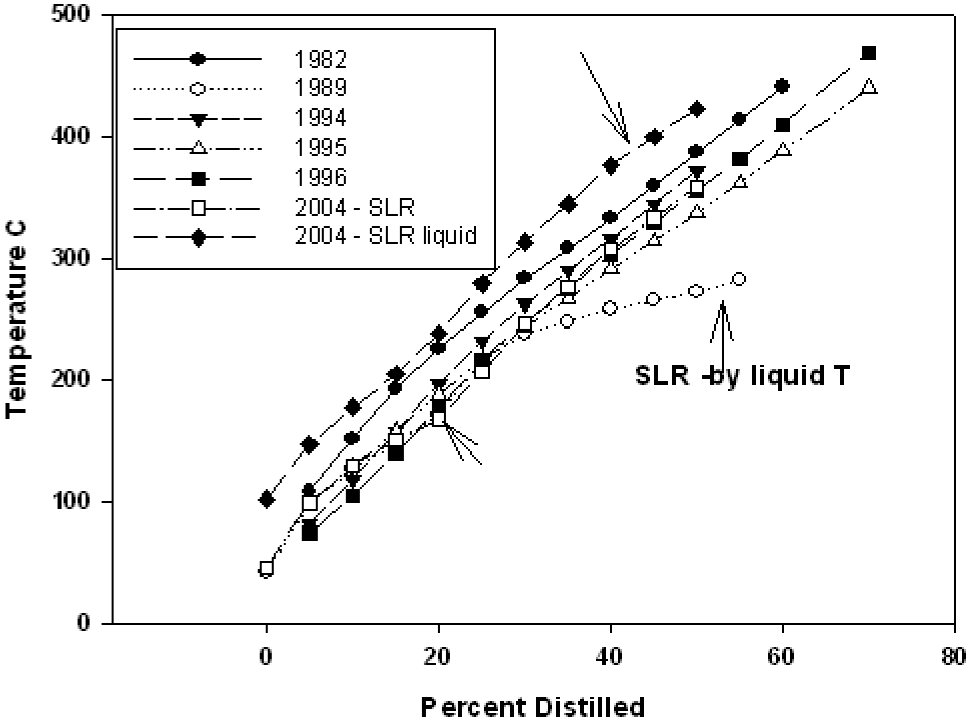

Figure 49 Distillation Curves of Alaska North Slope Oils by Year by Percent Distilled

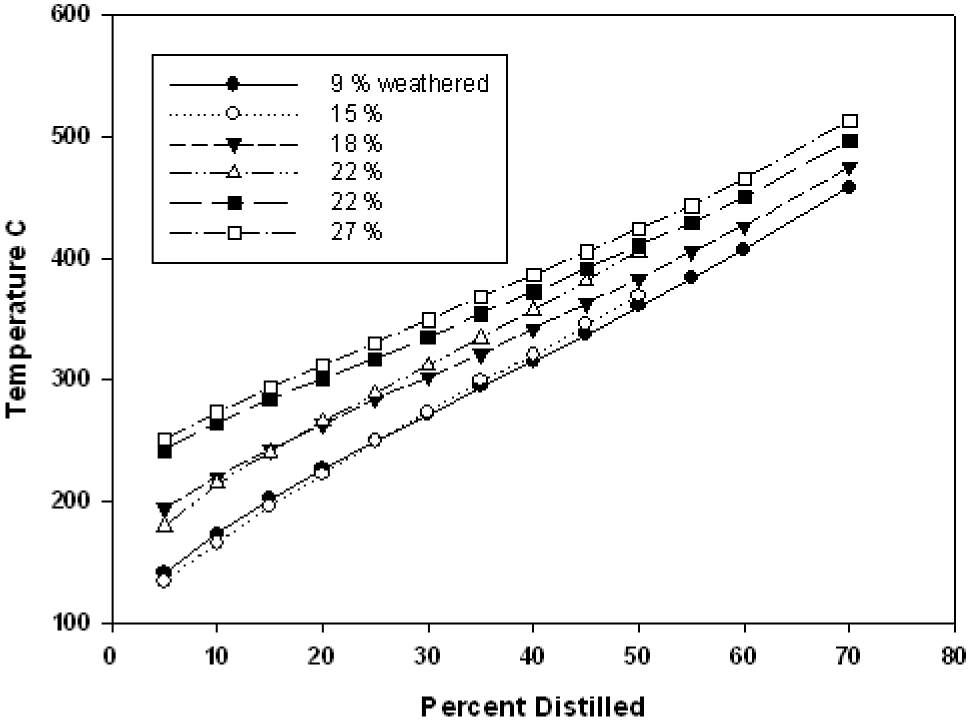

Figure 50 Percent Distillation of Weathered Alaska North Slope Oils by Weathering Percentage

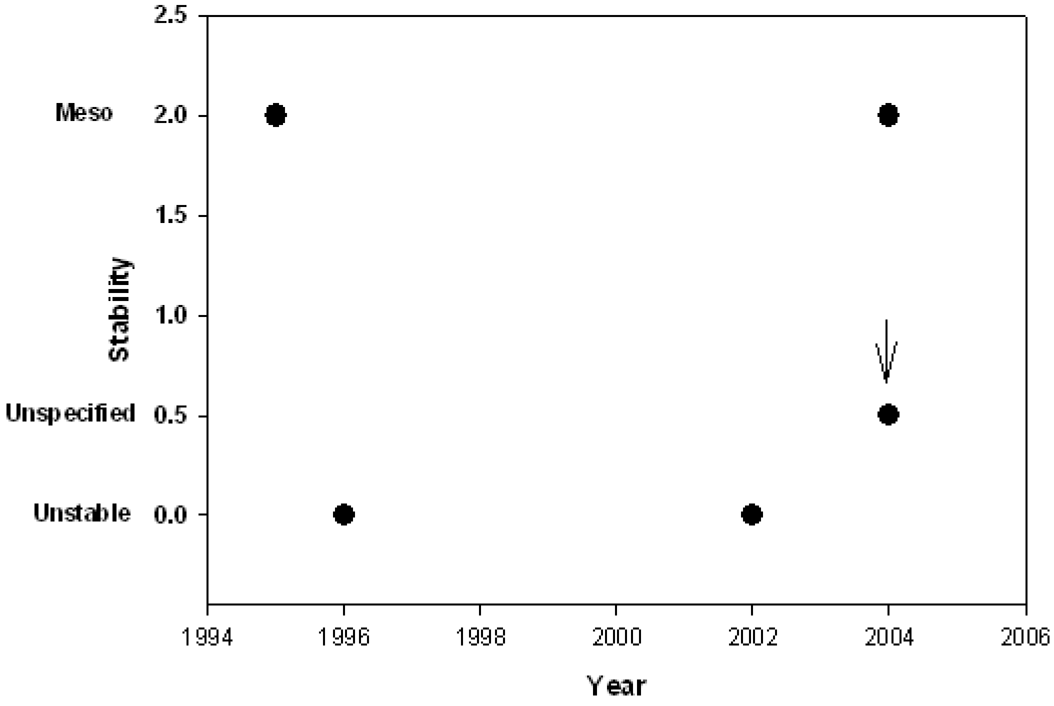

Figure 51 Stability of Emulsions of Fresh Alaska North Slope Oils by Year

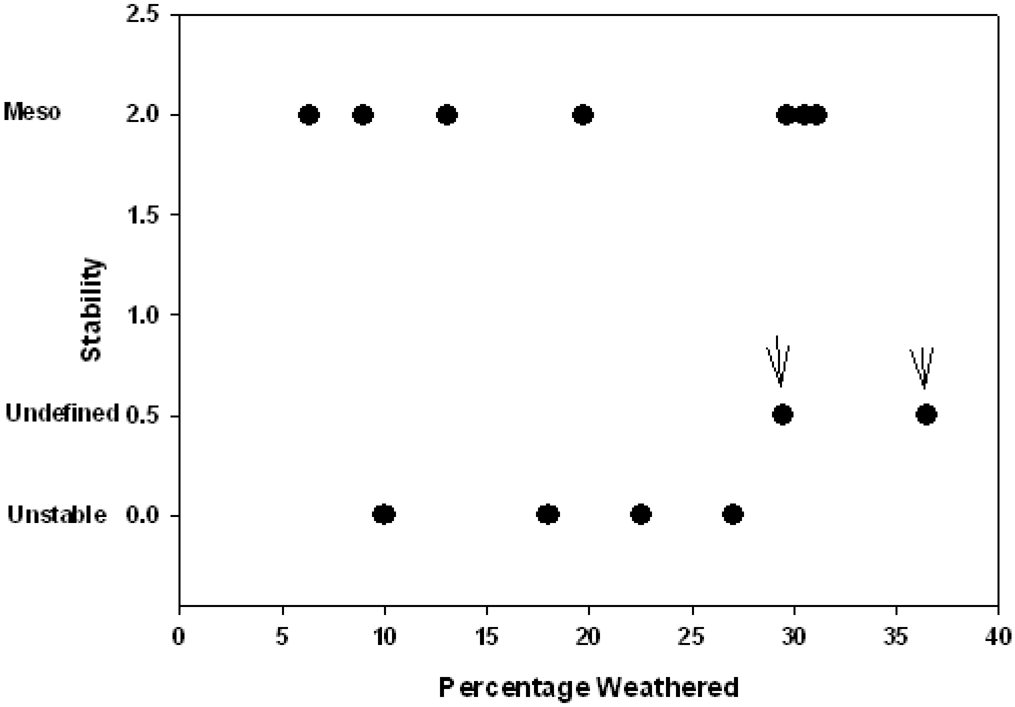

Figure 52 Stability of Emulsions of Weathered Alaska North Slope Oils by Weathering Percentage

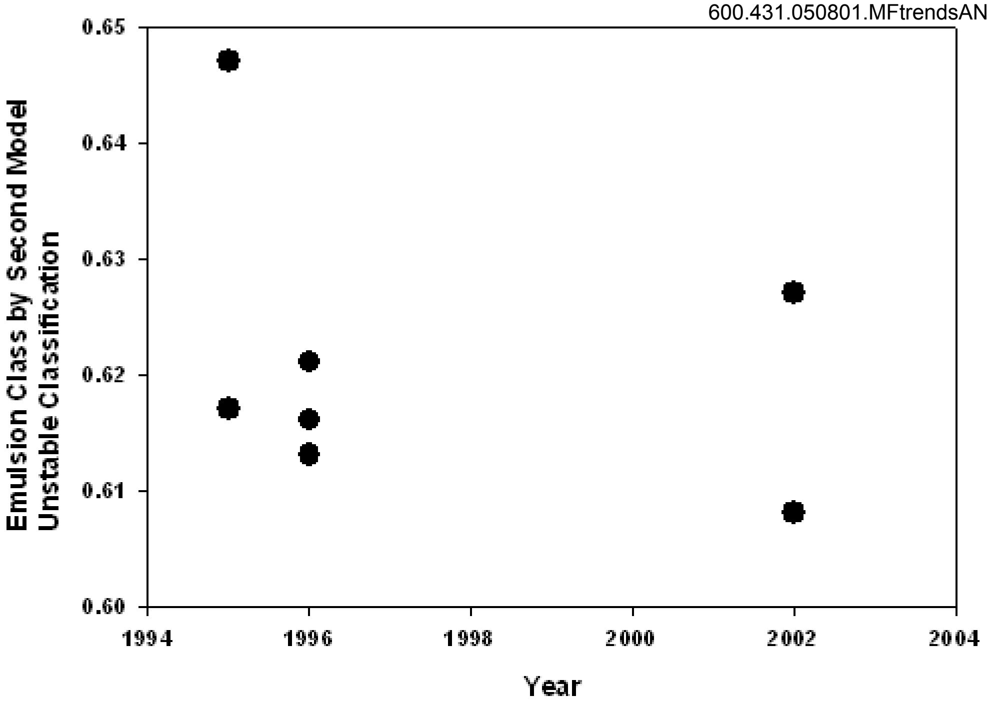

Figure 53 Emulsion Class by the Second Fingas Model for Fresh Alaska North Slope Oils (This predicts unstable water-in-oil states over the years.)

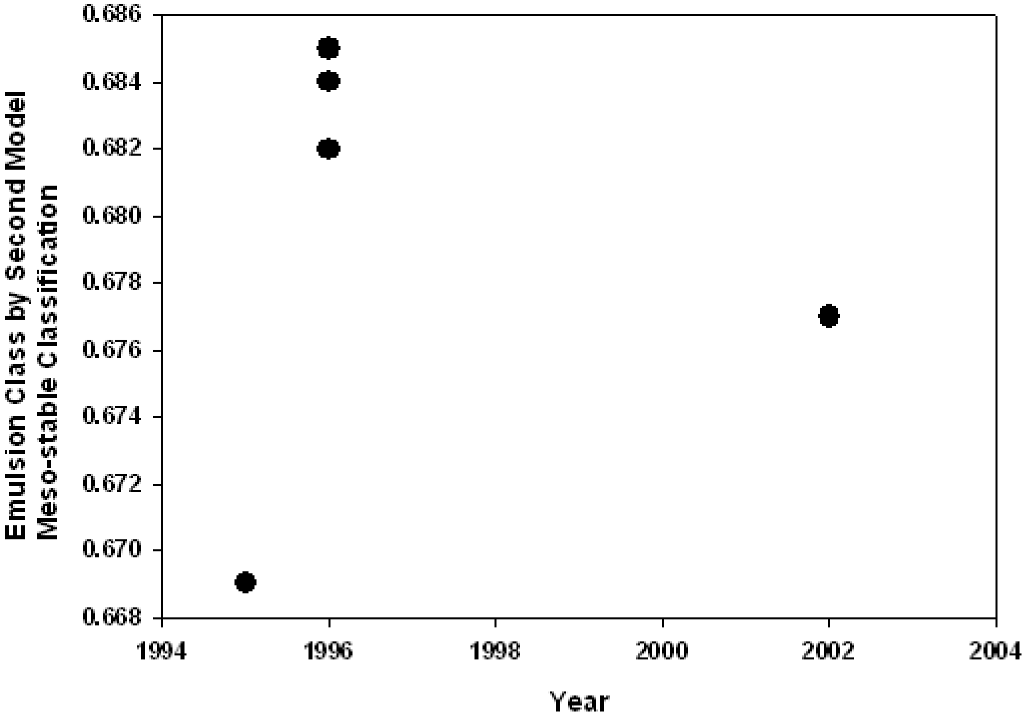

Figure 54 Emulsion Class by the Second Fingas Model for Weathered Alaska North Slope Oils (This predicts meso-stable emulsions over the years.)

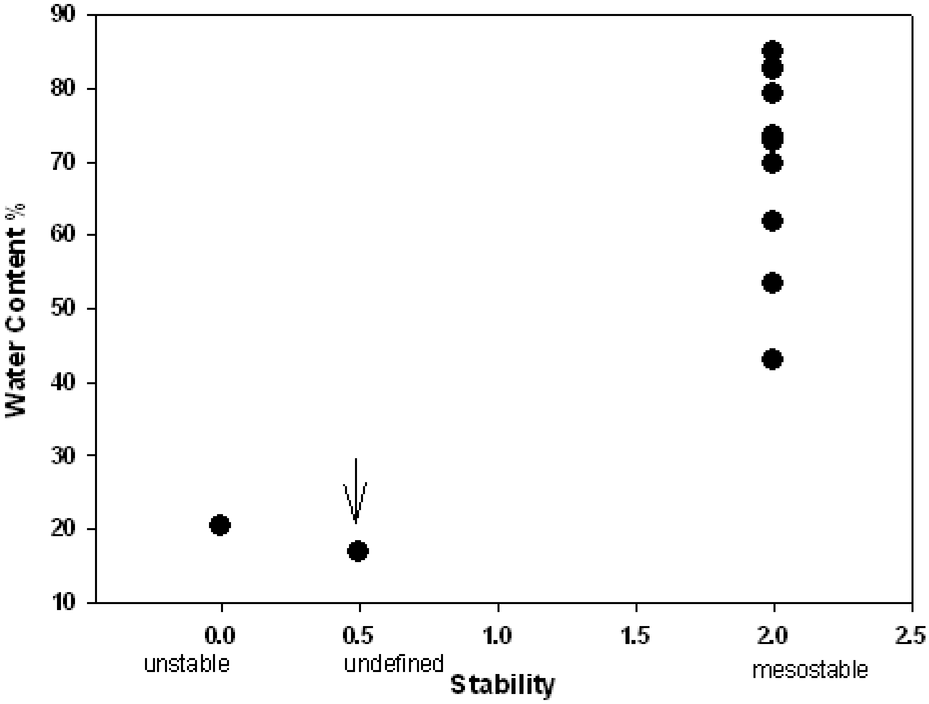

Figure 55 Water Content of the Water-in-oil States by Stability

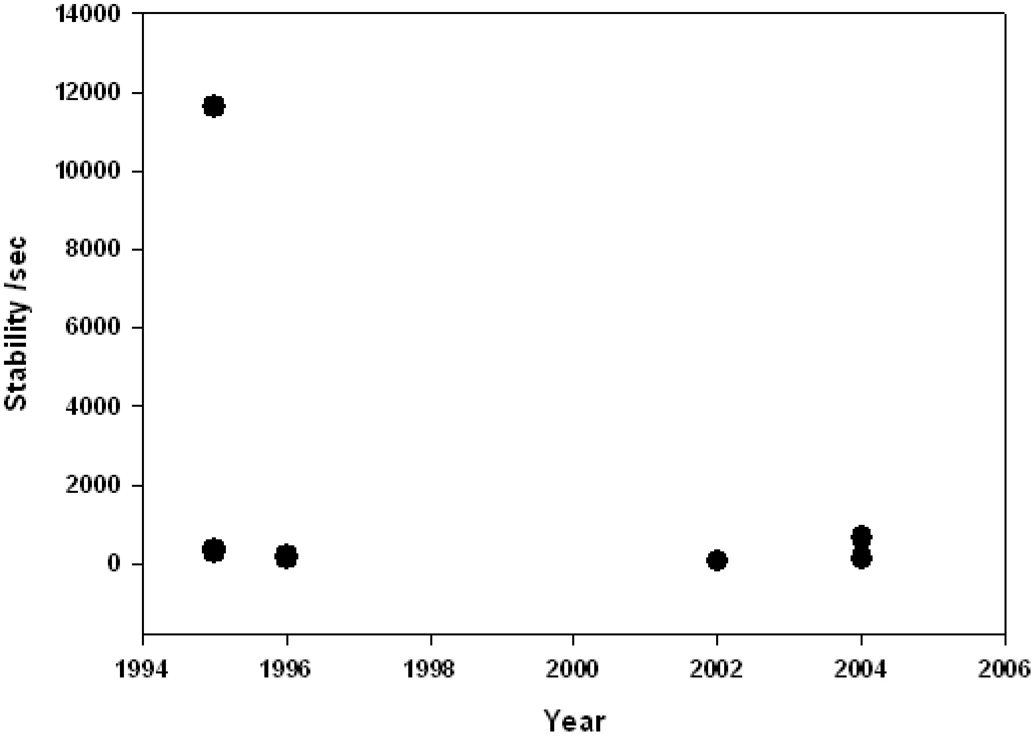

Figure 56 Stability of the Meso-Stable Emulsions by Year (Weathering percentage is not accounted for.)

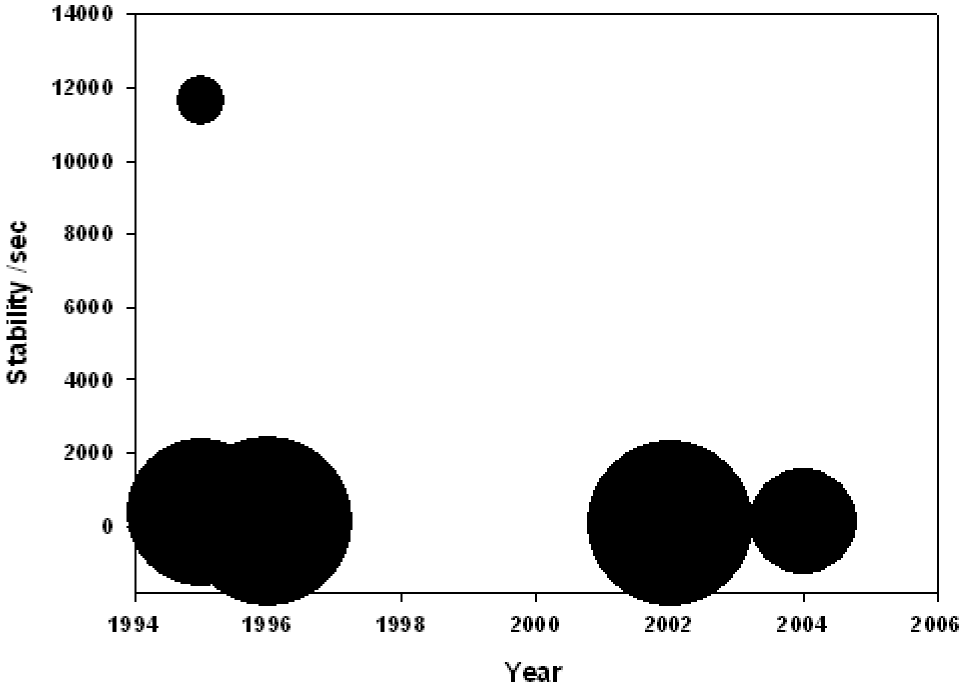

Figure 57 Stability of the Meso-Stable Emulsions by Year (Weathering percentage is indicated by the size of the circle.)

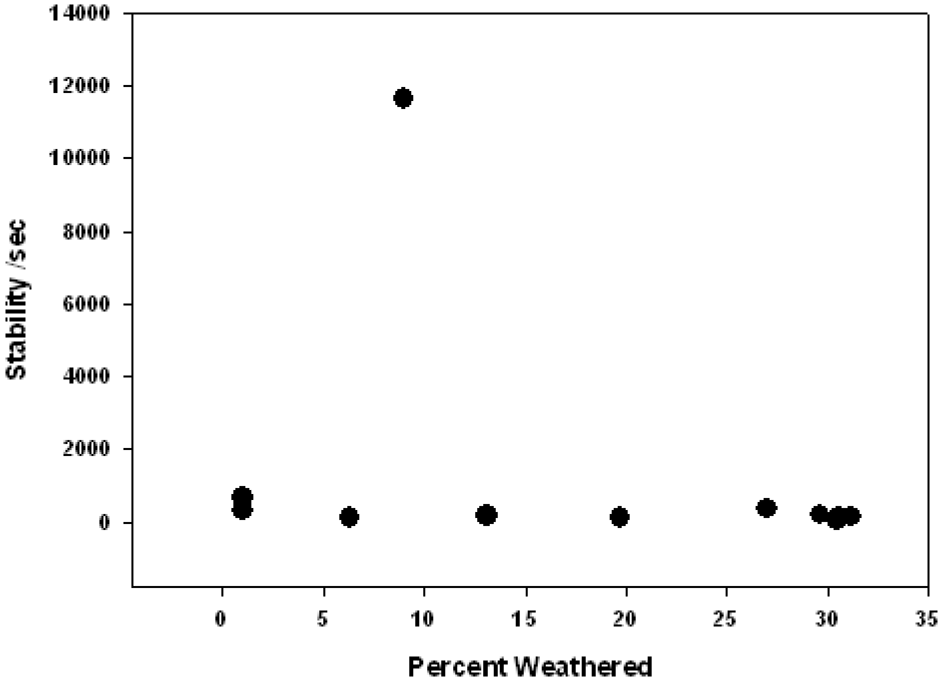

Figure 58 Stability of the Meso-Stable Emulsions by Weathering Percentage

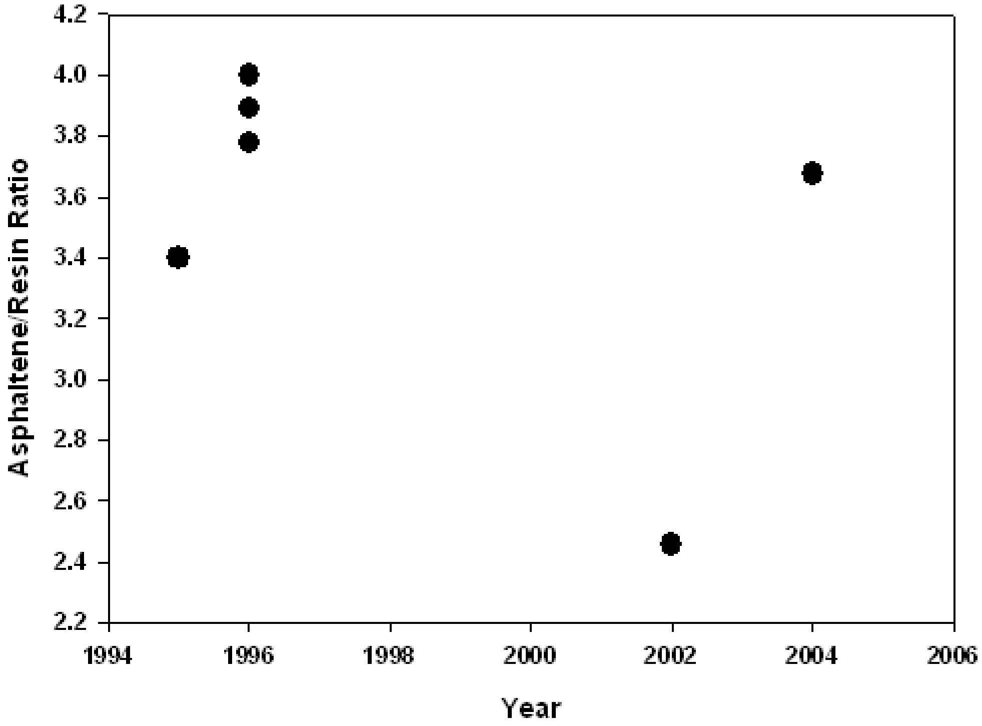

Figure 59 Asphaltene/Resin Ratio of Fresh Alaska North Slope Oils by Year

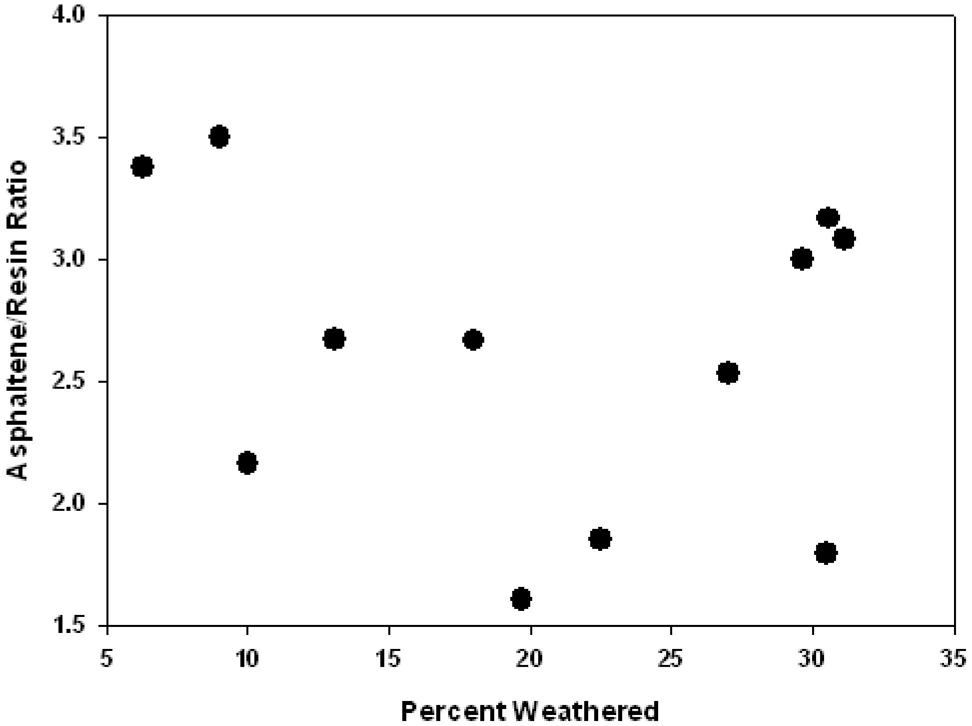

Figure 60 Asphaltene/Resin Ratio of Weathered Alaska North Slope Oils by Weathering Percentage