Development of a Method to Produce Large Quantities of Realistic Water-In-Oil Emulsions for Use in Evaluating Oil Spill Response Equipment and Methods

For

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Minerals Management Service

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Executive Summary

This report summarizes the efforts undertaken to develop a method for the generation of large quantities of realistic water-in-oil emulsions for use in testing oil spill response equipment such as skimmers and booms and response methods such as chemical dispersants and *in-situ* burning.

The characteristics of water-in-oil emulsions that form at sea were investigated to provide a basis for which “manufactured” emulsions could be compared. Very little data on the properties of emulsions formed at sea are available. Photos of water-in oil emulsions from the 1995 NOFO sea trial provide the best evidence of the visual characteristics of one realistic emulsion. These pictures are found in the main body of the report in Figure 2[1].

A number of methods for the creation of water-in-oil emulsions were then tested in the laboratory at small scales. These methods include using various pump types (gear, double-diaphragm, progressing cavity), bladed mixers (paint stirrer, cement mixer) and cascading water systems. The method that showed the most promise in the creation of emulsions with similar characteristics to those formed at sea was a bladed mixer or paint stirrer seen in Figure 6 in the main body of the report. This method proved to be both the most convenient and most flexible method for creating emulsions.

Four long-term emulsion formation tests were completed on the National Oil Spill Response Test Facility (Ohmsett) tank with uncontained slicks of IFO 120 fuel oil and Endicott crude oil subjected to breaking wave conditions. These emulsion formation tests provided samples of emulsions formed under conditions similar to those that would be present in an offshore situation. Comparisons of the properties of the emulsions generated on the Ohmsett test tank to those made with the paint stirrer in the small-scale tests are provided in Figure 22, for the IFO120 results, and Figure 25, for the Endicott crude. These graphs provide evidence that emulsions formed in a batch process using a paint stirrer have similar physical properties to those created in a breaking wave environment.

Large-scale “off-tank” emulsion formation tests were completed at the Ohmsett facility using a large bladed mixer with a shape similar to the small-scale paint stirrer. A comparison of the properties of emulsions formed in the large-scale batch processes with the on-tank emulsion properties can be seen in Figure 29, for the IFO 120 fuel oil, and Figure 30, for the Endicott crude. The batch process and on-tank emulsion properties were very similar for the IFO 120 fuel oil. The emulsion property differences evident in Figure 30, for Endicott crude oil, can be attributed to lower parent oil viscosities in the emulsions formed in the batch process. Photographs of emulsions with similar physical properties (viscosity and water content) formed on-tank and in the batch process are provided in Appendix D. The emulsions formed using these two methods have a similar appearance to the emulsion photos taken during the 1995 NOFO experiments (see Figure 2). This suggests that the Ohmsett tank and batch-generated emulsions are a reasonable substitute for emulsions formed in an at-sea environment.

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[1] Hyperlinks to many Figures present in the report are provided throughout the text of this document, including the Executive Summary, to assist the reader in navigating the document when it is accessed digitally.

Based on the results of the larger scale batch emulsion formation tests and the full-scale on-tank tests completed at Ohmsett, the following procedure is recommended for the “off-tank” formation of drum-sized quantities of realistic emulsions.

- Place 120 litres of salt water and 40 litres of oil into a 55 gallon drum. This water-to-oil ratio will generate a maximum 75% water content emulsion (the maximum water content achieved in the Ohmsett on-tank tests).

- Mix the oil and water with the bladed mixer operated at 350 to 400 rpm with the mixer submerged just below the oil surface only until the oil and water forms an obvious water-in-oil emulsion. Formation of the emulsion should occur within 15 to 30 minutes. Do not continue mixing at high rpm after the emulsion forms as this has been shown to form emulsion with excessive viscosities when compared to emulsions formed in a breaking wave environment.

- Micro-photographs of the emulsions can be taken for comparison to photos of emulsions formed on the Ohmsett tank to confirm that the emulsions have a similar structure to those created by breaking waves. Photos of emulsions formed with low viscosity crude oils should be compared to photos from the Endicott tests (Run #3) and photos of emulsions formed from high viscosity oils should be compared to photos from the IFO 120 tests (Runs #1, #2 and #4).

It is recommended that:

1. Additional long-term emulsion formation tests be completed on the Ohmsett tank to gather water-in-oil emulsion properties and characteristics for a variety of crude oils, and;

2. The batch process for creating realistic emulsions “off-tank” be further refined. Specifically, additional tests could be completed to determine if increasing the number of bladed mixers used in the mixing process will enable realistic emulsions to be formed, in a reasonable time frame, when oil to water ratios of 1:10 are used. Small-scale tests suggest that emulsions made under these “excess water” conditions may be somewhat more consistent with emulsions formed on the Ohmsett tank than those generated when smaller water quantities are used in the process.

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1. Introduction

This report summarizes the efforts undertaken to develop a method for the generation of large quantities of realistic water-in-oil emulsions for use in testing oil spill response equipment such as skimmers and booms and response methods such as chemical dispersants and *in-situ* burning.

The characteristics of water-in-oil emulsions that form at sea were investigated to provide a basis for which “manufactured” emulsions could be compared. This is provided in Section 2 of the report.

A number of methods for the creation of water-in-oil emulsions were then tested in the laboratory at small scales. These methods include using various pump types (gear, double-diaphragm, progressing cavity), bladed mixers (paint stirrer, cement mixer) and cascading water systems. The results of these investigations are provided in Section 3. The method that showed the most promise in the creation of emulsions with similar characteristics to those formed at sea (as described in Section 2) was then tested at a larger scale at the Ohmsett facility in Leonardo, New Jersey in conjunction with on-tank emulsion formation tests.

A series of long-term emulsion formation tests were completed on the Ohmsett tank with uncontained oil slicks subjected to breaking wave conditions. These emulsion formation tests were intended to provide samples of emulsions formed under conditions considered similar to those that would be present in an offshore situation. The results of these on-tank emulsion creation tests are provided in Section 4.

Section 5 provides the results of the large-scale “off-tank” emulsion formation tests using the most promising technique identified in the lab-scale work described in Section 3. A comparison of the emulsions formed in the lab- and large-scale batch processes with the on-tank emulsions is also presented in Section 5. The “off-tank” procedure that produced the most realistic emulsions is identified and test procedures are outlined to assist in the production of realistic emulsions for future test programs at Ohmsett.

This report contains a large number of graphs and photographs. Hyperlinks to these graphics have been provided throughout the text to improve the readability of the report for those reviewing it electronically.

2. Characterization of Emulsions Formed At-Sea

Observations made at numerous oil spill incidents show that water-in-oil (w/o) emulsions are produced by many crude oils when spilled at sea. Emulsification is characterized by progressive changes in the physical properties of the spilled oil leading to large increases in volume and viscosity. The emulsification process at sea involves the incorporation of water droplets by wave action and the precipitation of asphaltenes from the oil to the oil/water interface to mechanically stabilize these droplets within the body of the oil. At some oil spill incidents only ‘weak’, unstable emulsions that rapidly broke down at sea were formed, while at other incidents different crude oils produced ‘stronger’, more stable emulsions that persisted on the sea surface for a very long time or until the emulsified oil drifted ashore. The asphaltene content of the crude oil has been identified as the main cause of these differences; high asphaltene content crude oils tend to form ‘strong’, stable emulsions, while low asphaltene content crude oils form ‘weaker’, less stable emulsions. Asphaltenes are present in many crude oils in colloidal suspension; they are of extremely high molecular weight and are not in true solution. Precipitation of asphaltenes from the body of the crude oil appears to be driven in the short-term by the changes in oil composition caused by evaporation of the more volatile oil components and, in the longer-term, by photo-oxidation.

Numerous projects have been conducted over the last 35 years to study different aspects of the w/o emulsification process, such as the rate of emulsification under different conditions and the physical properties of the water-in-oil (w/o) emulsions formed. Many of these studies have involved laboratory, or small-scale, methods to produce small quantities of w/o emulsions for subsequent testing. It is generally not feasible to carry out evaporation of the oil and w/o emulsification simultaneously and the two processes are normally separated with evaporation being simulated by distillation, evaporation in pans, or sparging with compressed air and emulsification subsequently carried out in some form of low-shear mixing of water into the oil. The separation of the two weathering processes and the use of different forms of water and oil mixing is not ‘realistic’- i.e. is not the same as occurs at sea - and may introduce a degree of artificiality into the w/o emulsions produced that would be apparent in differences in the physical properties of emulsions produced at sea and by the laboratory methods. Similarly, w/o emulsions or emulsified oils are often required in larger quantities for testing of oil spill response equipment or techniques such as booms, skimmers, in-situ burning or the use of dispersants. In order to produce sufficient quantities of w/o emulsion in a reasonable time, the evaporation of volatile oil components can be simulated by air sparging and w/o emulsification at sea can be simulated by mixing water into the oil residue left after evaporation. The mixing conditions will influence the droplet size distribution of the water within the oil and hence other properties such as the viscosity, or rheology (flow behaviour), of the emulsions produced.

This task of the project was undertaken to gather data on the physical properties (viscosity, water content, water drop size distribution, stability) of w/o emulsions formed at sea at oil spill incidents, at experimental oil spills and in other methods that have been used to produce w/o emulsions of spilled oil.

2.1 The Formation And Stabilization Of Water-In-Oil Emulsions At Sea

2.1.1 Water-in-Oil Emulsion Formation

The precise process that causes water to become incorporated within spilled oil is not known with absolute certainty, but is known to be related to the presence of breaking waves. The most likely explanation is that freshly spilled crude oil of low viscosity on the sea surface is broken up into oil droplets with a wide variety of sizes as breaking waves pass through the oil slick. The majority of the volume of oil will be in the in the form of larger oil droplets that are only temporarily submerged and these will rapidly resurface due to their buoyancy and rejoin the underside of the slick. As these large oil droplets coalesce with the slick, the small amount of water that is entrained within the mass of resurfacing oil droplets will become trapped within the oil. As the oil droplets coalesce with the slick to form the continuous phase, the trapped, ‘interstitial’ water becomes small water droplets in the oil. Larger water droplets within the body of the oil will tend to sink the short distance through the oil layer fairly rapidly and rejoin the water mass because of the greater density of seawater than oil. Smaller water droplets will be slower to sink through the oil because of their small size and the resistance created by the higher viscosity of the oil. Nevertheless, they will slowly settle through the oil.

2.1.2 Water-in-Oil Emulsion Stabilization

The w/o emulsion that is being formed can be stabilized by asphaltenes from the body of the oil, provided that these asphaltenes are present in sufficient amount and that they are precipitated to the oil / water interface around the entrained water droplets (Eley et al., 1988 a and b, McLean et al., 1998, Kilpatrick and Spiecker, 2000 and Spiecker at al., 2003). Asphaltenes are present in different amounts in all crude oils. They normally exist in a colloidal suspension within the oil and this colloidal suspension is maintained by resins and other oil components. As the more volatile components of the oil evaporate, the asphaltenes become more concentrated in the oil residue that remains. The colloidal suspension can become destabilized by the change in relative composition of the oil and the asphaltenes will be precipitated. Asphaltenes possess a slightly surfactant character and they will orientate and congregate at the oil / water interface around the water droplets. Precipitated asphaltenes then form an elastic layer around the entrained water droplets and this layer resists coalescence of the water droplets. This stabilization mechanism will prevent the smaller water droplets from leaving the oil. Larger water droplets will slowly settle out of the oil, but this process will slow as the oil viscosity increases due to the evaporation of more volatile components from the oil and the emulsion viscosity increases due the incorporation of a greater proportion of water as small water droplets.

Mechanically weak w/o emulsions can be stabilized by the precipitation of wax crystals in association with some asphaltenes. However, the precipitated asphaltene and wax layer around the water droplets is much less elastic and is more easily disrupted.

2.1.3 The Rate Of Water-in-Oil Emulsification

The initial rate of w/o emulsification is essentially the product of two opposing mechanisms:

(i) water droplets being initially incorporated into the oil, and;
(ii) water droplets settling out due to the higher density of seawater.

The rate of initial water droplet incorporation will depend on the process that incorporates the water droplets, i.e. the frequency of breaking waves, or sea state, which is directly related to prevailing wind speed. It has been found that w/o emulsification proceeds only very slowly, if at all, at low wind speeds when breaking waves do not occur. There appears to be a threshold value of wind speed of approximately 8 knots (4 m/s) that is required for w/o emulsification of spilled oil (Walker, 1993 and Walker et al., 1995). The initial stage of emulsification will occur more rapidly in rougher seas. Since the wave action in much rougher seas will also start to break up the layers of w/o emulsion that have been formed, and this will lead to slick fragmentation and eventual dispersion of at least some of the oil and w/o emulsion, there must be a sea-state and wind speed where the rate of water-in-oil emulsification is at a maximum and then declines, but this limit will also be a function of oil viscosity, emulsion viscosity and emulsion stability.

The initial rate of emulsification will also depend on the oil viscosity, being most rapid for low viscosity oils. The high viscosity of some oils such as residual fuel oils, will resist the shearing forces of the waves to break the oil slick into oil droplets. It may also make it more difficult for the water to become incorporated into the oil because the high viscosity may make the oil slower to coalesce. However, once the water droplets have been entrained in the body of the oil they will be slower to settle out due to the higher viscosity of the oil.

Stabilization of the water droplets by precipitated asphaltenes from the oil will prevent the smaller water droplets from settling out and slow the settling-out of larger water droplets. The increase in oil viscosity due to evaporation of the more volatile oil components will also slow down the rate at which the water droplets settle out. The evaporative loss of the more volatile oil components is instrumental in destabilizing the asphaltenes from colloidal suspension within the oil because it raises their concentration in the remaining oil residue and disturbs the oil component balance that was maintaining the asphaltenes in suspension. If there are insufficient asphaltenes within the oil to precipitate and stabilize the oil / water interfacial area created as water droplets are incorporated, the emulsion formed will be less stable. The prevailing wave action will still cause water droplets to be incorporated into the oil, but they will not be stabilized within the oil and all but the smallest will settle out. The rate of water-in-oil emulsification will be slower than in the case of more robustly stabilised emulsions because the rate of emulsion breakdown due to the loss of water droplets is faster.

If the emulsion is being effectively stabilized by precipitated asphaltenes, the water content of the emulsion will tend towards 70% volume water, or more. Water droplets that are all precisely the same size would cause a maximum water content of 74% volume (theoretical maximum based on packing of spheres), but since the water droplet size distributions in the early stages of emulsification are quite broad, the water content of the emulsion formed can be higher, perhaps up to 85% water volume, as the smaller water droplets pack in between the larger water droplets. As the water droplets within the oil become, on average, smaller by the loss of larger water droplets to the water, the maximum water content tends to between 60 and 75% volume (Audunson et al.1984, Walker et al.1995, Lewis and Daling1995, Lewis et al.1998). The dense packing of the water droplets, plus the high viscosity of the w/o emulsion, will then prevent incorporation of more water.

2.2 Properties Of Water-in-Oil Emulsions Formed By Spilled Oils

Weathered spilled oils undergo changes in physical properties, including:

- A gradual increase in oil viscosity due to the loss by evaporation of the more volatile oil components;
- A gradual increase in the water content of the w/o emulsion up to a stable value, perhaps after passing through a higher, maximum water content value;
- A gradual decrease in average water droplet size and a ‘tighter’ droplet size distribution;

These processes combine to produce the most obvious indicator of w/o emulsification; an increase in viscosity of the w/o emulsion that is formed. The changes are progressive with time, inter-related with each other and are shown in Figure 1 (not to scale).

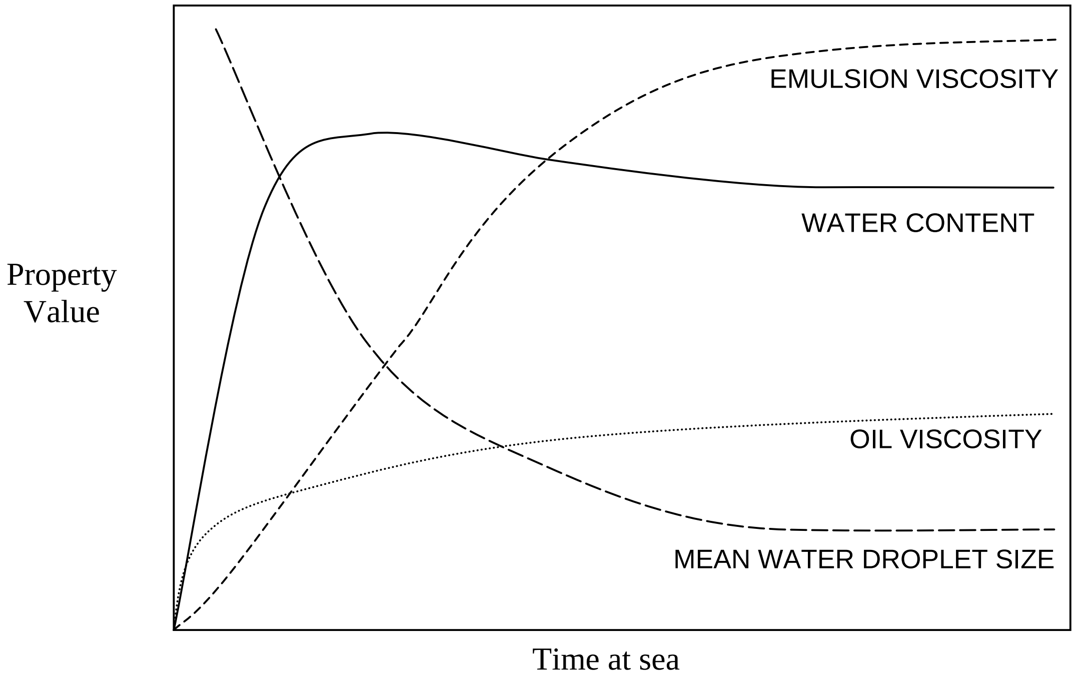


Figure 1. Changes in physical properties of weathered spilled oils

The increase in viscosity of the oil due to the evaporation of the more volatile oil components proceeds whether or not emulsification occurs. It is a background effect to the changes in physical properties caused by w/o emulsification, but affects the viscosity of the w/o emulsion that is being formed.

2.2.1 Increase In Water Content

The water content of w/o emulsions can be readily and accurately measured by several methods. Determination of the water content of w/o emulsions at various stages of development has been routinely used in laboratory studies and at experiments at sea.

2.2.2 Increase In Water-in-Oil Emulsion Viscosity

Determining the increase in w/o emulsion viscosity caused by the incorporation of water droplets is not simple.

The incorporation of small water droplets into the oil causes a significant increase in emulsion viscosity, particularly when the water content exceeds 30% volume, because of the mechanical interaction between the droplets impedes the flow of the w/o emulsion. This interaction causes a very marked increase in viscosity as the water content rises through 50% volume and up to 70% volume or more. The effect is greatest for the small water droplets because they are not easily deformed at low to medium shear rates. Larger water droplets can be more easily deformed and internal circulation within the droplet can contribute to a lower bulk viscosity.

Many different theoretical explanations have been used to calculate the viscosity of a w/o emulsion (η_r) as a function of the continuous phase (oil) viscosity and the disperse phase volume fraction (θ). Mooney (1951) proposed an exponential relationship for mono-disperse suspensions of solid spheres,

$$\ln \eta_r = \frac{2.5\theta}{1 - a\theta}$$

where geometrical arguments give $1.35 < a < 1.91$. For dispersions of smaller water droplets dispersed in oil, the viscosity ratio (viscosity of emulsion / viscosity of the oil phase, η_e / η_o) can be expressed:

$$\eta_e / \eta_o = A\theta^n + B$$

where θ is the water volume fraction, n is 2 or 2.5 and A and B are constants that depend on droplet size (Layrisse and Chirinos, 1987). Mackay et al., (1980) derived constants to fit the Mooney equation with data from emulsions produced by laboratory methods. This fitting is, of course, only valid for the emulsions produced by these laboratory methods and subsequent studies have shown that the constants that Mackay derived do not fit with the w/o emulsion formation for all crude oils. These discrepancies stimulated the development of specific oil weathering studies for crude oils using simulated weathering techniques, such as those carried out by SINTEF and others.

Since the viscosity of the oil phase increases as the more volatile components are lost by evaporation (and this degree of evaporative loss and the consequent viscosity increase varies with crude oil), the effect of water content on w/o emulsion viscosity should be related to the viscosity of the oil residue that remains at any stage of w/o emulsification, and not to that of the original oil. The viscosity of the oil residue that remains after evaporation cannot be reliably predicted from basic fresh crude oil assay data (although the degree of evaporative loss can be). If the oil is weathered in a controlled manner in the laboratory and the weathered oil properties are measured, a reliable model for the prediction of the viscosity of the crude oil after a specific degree of evaporation can be developed. Simulating the evaporative loss of crude oils by distillation or other methods is now a routine technique.

A major complication in determining the viscosity of w/o emulsions formed at sea and by laboratory methods is that they exhibit non-Newtonian flow behaviour, often behaving as pseudo-plastic liquids with a definite yield point and thixotropic flow behaviour (Fingas, 2001). In broad terms, this means that a single viscosity value cannot describe the flow behaviour of the w/o emulsion. This has been known for many years, but the cost and complexity of controlled-stress rheometers that are needed to measure the required parameters has limited their use for many researchers in this area.

Attempts have been made to standardize the shear rate ramping and shear rate used to determine viscosity of w/o emulsions by simple rotating cylinder viscometers (Hokstad et al, 1993). Although this does not avoid the complications of non-Newtonian flow behaviour of the w/o emulsions, it does make results from different studies broadly comparable.

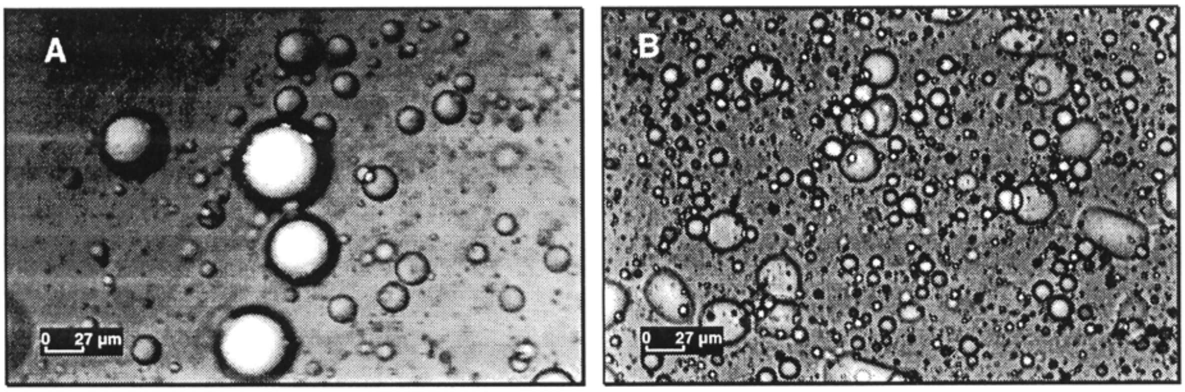
2.2.3 Water Droplet Size Distribution

The average or mean size of the water droplets in the water-in-oil emulsions formed from spilled oil at sea must decrease with time as the w/o emulsion takes up more water and the water droplets become stabilized within the oil. This decrease in average water droplet size as the oil emulsifies may be due to a gradual ‘sorting’ process as the larger water droplets settle out through the oil and rejoin the sea, but may also be caused by the larger individual droplets within the emulsion being reduced in size by the flexing, stretching and compression of the emulsified oil layer by the action of waves.

Measuring the average or mean water droplet size, or a more complete droplet size distribution, of w/o emulsions formed from spilled oils at sea (or in laboratory simulations of the formation) is difficult. Stable w/o emulsions are often high-viscosity, black or brown liquids or semi-solids with a high optical density. Manipulation of samples of w/o emulsion by dilution to allow the use of techniques such as the Coulter Counter or PDPA, which are frequently used to measure droplet size distributions of other materials, would cause changes to the original water droplet size distribution.

Bobra (1990 and 1991) includes a water droplet size distribution derived from a photograph taken through a microscope. It seems that this is a number size distribution, rather than a volume size distribution. This bi-modal size distribution of 5 µm and 20 µm diameter is that referred to in Fingas et al., 1993, but it should be noted that these were measurements made on emulsions prepared in the laboratory. Similarly, the oft-quoted Eley et al., 1988 paper giving a mean number distribution droplet size of 2 µm diameter was based on an emulsion produced in the laboratory.

The only recently published-photographs of water droplets in w/o emulsion formed at sea are from SINTEF (Strøm-Kristiansen et al., 1995)



1 hour at sea

11 hours 35 min. at sea

Figure 2 Microscope pictures of Troll crude oil from 1995 NOFO sea-trial

The w/o emulsions formed during the NOFO sea trials had the properties shown in Table 1.

Table 1. Properties of Emulsions Formed At Sea During 1995 NOFO Sea Trials

	1 hour at sea	11 hr. 35 min. at sea
Evaporative loss (% wt.)	7.4	17.7
Oil viscosity cP (@ 20 s^{-1} @15ºC)	64	193
Water content (% vol.)	66	78
Emulsion viscosity cP (@ 100 s^{-1} @15ºC)	405 ± 92	3280 ± 127

The water droplet size distribution within a w/o emulsion appears to decrease to the point where there are insufficient precipitated asphaltenes from the oil to stabilize the increase in water / oil interfacial area created by forming smaller water droplets. Mackay (1987) calculated the interfacial areas that could be stabilised by precipitated asphaltenes and came to the conclusion that water droplets of 3 to 4 μm diameter could be stabilised by approximately 3.7% asphaltene content in the oil, noting that the most stable emulsions tend to have particles (water droplets) in the 1 to 5 μm range. Larger water droplets, for example 10 μm diameter, would require less stabilising material (asphaltenes) in the oil and would be less stable in the w/o emulsion because of their greater negative buoyancy.

2.2.4 Water-in-Oil Emulsion Stability

A property of w/o emulsions that has been addressed by several workers is emulsion stability. The term is commonly used to describe the tendency of an w/o emulsion to separate into its constituent oil and water phases on standing, although other forms of emulsion stability are sometimes considered, such as stability to heating or stability to the effects of emulsion breakers.

Water-in-oil emulsions formed by spilled oil at sea exhibit a range of emulsion stability. Some emulsions remain in a strongly emulsified form with little or no water separation over prolonged periods in static conditions, while other emulsions revert to their component phases of oil and water over a relatively short time.

Several authors have defined emulsion stability into a series of classes. The most recent are those from Fingas, 2001b, described in Tables 2 and 3.

Table 2. Emulsion Stability Class Property and Composition Ranges (Fingas, 2001b)

		Stable	Meso	Entrained	Unstable
Density	g/mL	0.85-0.97	0.84-0.98	0.97-0.99	0.8-1.03
Viscosity	(mPa.s)	15 -10000	6 -23000	2000-60000	2 - 5.1 X 10^6
Saturates	%	25-65	25-65	19-32	23-80
Aromatics	%	20-55	25-40	30-55	5-12
Resins	%	5-30	6-30	15-30	0-32
Asphaltenes	%	3-20	3-17	3-22	0-32
Asphaltenes/Resins		0.74	0.47	0.62	0.45

Table 3. Emulsion Stability Class Characteristics

	Stable	Meso	Entrained	Unstable
Day of Formation Appearance	brown solid	brown viscous liquid	Black with large droplets	like oil
Water Content on first day %	80	62	42	5
Appearance after one week	brown solid	broken, 2 or 3 phases	Separated oil and water	like oil
Water Content after week %	79	38	15	2
Stable time days	>30	<3	<0.5	not
Properties on day of formation Average Ratio of Viscosity Increase*	1100	45	13	1
Properties after one Week Average Ratio of Viscosity Increase*	1500	30	2	1
Properties after one Year Average Ratio of Viscosity Increase*	1400	15	1	1

** the viscosity increase is the emulsion viscosity divided by that of the original oil viscosity, not the viscosity of the oil phase in the emulsion which may be considerably higher than that of the original oil because of the loss by evaporation of the more volatile components. The viscosities of the emulsions are those determined at a nominal* $1s^{-1}$.

Although more complex than earlier versions of stability, these most recent classifications share much in common with earlier work

Most have concluded that emulsion stability is related to the stabilisation mechanism and therefore to the asphaltene content of the original oil, but there is not a direct correlation because it is the propensity of the asphaltenes to precipitate from colloidal solution under the influence of other changes in oil composition, such as evaporation of the more volatile components or photo-oxidation during weathering, that determines emulsion stability.

2.2.5 The Relationship Between Water Content, Droplet Size Distribution, Viscosity And Stability Of Water-in-Oil Emulsions

When defining the similarities or differences between the physical properties of a w/o emulsion formed at sea or by a particular artificial preparation method, it is clear that more than one parameter is required. Two parameters of the w/o emulsion; water content and viscosity, produce a more adequate description of the physical properties of the w/o emulsions, but still do not provide a complete characterization of the emulsion. The water droplet size distribution in the emulsion is also an important factor.

Emulsion water content and emulsion viscosity can be the same for two different emulsions, but their behaviour (stability, effect of demulsifiers etc.) may still be different.

The easiest parameter to accurately measure is the water content, but two w/o emulsions, both with a water content of 70% volume, may have very different viscosities because they might be composed of oil phases with widely different oil viscosities. Knowing the original crude oil viscosity is insufficient to further define the relationship between water content and w/o emulsion viscosity; it is the viscosity of the oil residue in the emulsion that is needed. Since most crude oils exhibit substantial evaporative loss of the more volatile components and a consequent increase in viscosity, the degree of evaporative loss from the oil and oil viscosity increase that is likely to have taken place in the relevant period of emulsification needs to be known. If the oil residue viscosity is known, the viscosity ratio (η_e / η_o) can be broadly related to w/o emulsion viscosity, but this relationship is dependant on the water droplet size distribution that cannot be measured easily or accurately. However, a similarity in viscosity ratio and water content can be considered reasonable if the water droplet size distributions appear similar when examined under the microscope.

Stable, high water content w/o emulsions exhibit non-Newtonian flow behaviour and the viscosity (determined at any particular shear rate) is an inadequate parameter to define the w/o emulsion, but full rheological data on w/o emulsions formed at sea are non-existent.

2.3 Data On Water-In-Oil Emulsions Oils Formed At Sea After Oil Spill Incidents And Experimental Spills At Sea

The data on w/o emulsions formed at oil spill incidents tends to be sparse because major oil spills are rare events and the emphasis is usually on response rather than on technical assessment in the early stages of the spill. Emulsified oils (w/o emulsions) are often reported to be at sea and on the shore after large oil spills, but the precise time that the oil has been at sea after release is often not known with certainty because large amounts of oil may be released over a prolonged period in distinct episodes. Contamination of the w/o emulsions with sand and shoreline debris, plus the effects of emulsion breakdown in the sun, make the results of any analysis suspect. Scientific investigations are rarely carried out on minor spills.

WSL (Warren Spring Laboratory) conducted a series of sea trials using different types of crude oils from the mid-1970s until the late 1990s. A summary of these tests is shown in Table 4.

Table 4. Warren Spring Laboratory Sea Trials

Sea Trial date	Oil used	Reference
July 1975	Ekofisk crude oil	Cormack, 1983
June 1976	Ekofisk crude oil	Cormack, 1983
January 1976	Ekofisk crude oil	Cormack, 1983
May 1977	Beatrice crude oil	Cormack, 1983
May 1978	Beatrice crude oil	Cormack, 1983
July 1987	Forties crude oil	
August 1988	Flotta crude oil	
May 1992	Forties crude oil	Walker, 1993
June 1992	Marine Fuel Oil / Gas Oil	Walker, 1993
August 1994	Forties crude oil	
September 1997	Forties crude oil	Lewis et al., 1998
September 1997	Alaska North Slope crude oil	Lewis et al., 1998
September 1997	IFO-180	Lewis et al., 1998

Several sea trials were also conducted in the Norwegian sector of the North Sea over a similar period. These sea trials are summarized in Table 5.

Table 5. Norwegian North Sea Trials

Sea Trial date	Oil used	Reference
1978	Ekofisk crude oil	
July 1982	Statfjord crude oil	Audunson et al., 1984
1984	Statfjord crude oil	
1985	Statfjord crude oil	
July 1989	Sture Blend (Oseberg) crude oil	
August 1991	Statfjord / DUC crude oil blend	
August 1991	Statfjord / DUC crude oil blend	
1992	Sture Blend (Oseberg) crude oil	
June 1994	Sture Blend (Oseberg) crude oil	Lewis et al., 1995 a and b
1995	Troll crude oil	Daling et al., 1997

Although there have been 22 sea-trials in the North Sea involving crude oils, 4 used Ekofisk, Forties, Sture Blend (Oseberg) crude oils and 5 used Statfjord or Statfjord / DUC blend crude oils.

The 'hard' aphaltene[1] contents of the oils are: Statfjord – 0.04% wt., Ekofisk - 0.08% wt., Troll - 0.2% wt., Forties - 0.24% wt. and Sture Blend - 0.73%.

The results from the sea trials, plus in the case of Ekofisk and Forties crude oils the results from large oil spill incidents (*Ekofisk Bravo* blow-out and the *Sea Empress*), show that:

- Ekofisk and Statfjord crude oils, having a very low asphaltene content, rapidly form low viscosity (1000 cP at $10s^{-1}$ at 11ºC, 80% water content, 8 hours after release), weak, possibly wax-stabilised w/o emulsions that break down rapidly in moderate sea conditions. (Cormack, 1983), (Audunson et al., 1984)
- Troll crude oil rapidly formed more viscous (6,000 cP at $10s^{-1}$ at 13ºC, 75% water content, 24 hours after release) (Strøm-Kristiansen, 1995)
- Forties crude oil more slowly forms somewhat more stable, slightly higher viscosity (13,000 cP at 11ºC at $10s^{-1}$, 70% water content, 40 hours after release) more stable w/o emulsions. (Walker, 1993 and Walker et al., 1995).
- Sture Blend crude oil rapidly formed a high water content (80% vol), but unstable w/emulsion and it took 30 hours for the viscosity to rise to 10,000 cP (at $10s^{-1}$ at 10ºC) (Lewis et al., 1995)

There are other oil weathering effects, besides that of asphaltene content, such as those of evaporative loss and prevailing sea state, but the overall effect of crude oil asphaltene content is clear; stronger, more stable and higher viscosity w/o emulsions are produced at sea by oils with higher asphaltene contents.

The w/o emulsions form more slowly with higher asphaltene content oils, perhaps because the asphaltene stabilisation is hindering the initial incorporation of water. Also, the weak and possibly temporary stabilisation of w/o emulsions afforded by wax precipitation does occur rapidly, but the w/o emulsions can never be truly stable in the absence of precipitated asphaltenes.

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[1] 'Hard asphaltenes' are generally measured by heptane insolubles of the 370ºC+ residue. 'Soft' asphaltenes are measured as pentane insolubles or by Iatroscan (TLC/FID) SARA – Saturates, Aromatics, Resins, Asphaltenes).

2.4 Data On W/O Emulsions Formed In Large- And Small-Scale Tank Tests

Large quantities of emulsified oils have been prepared by a variety of methods for various purposes.

Environment Canada used Ohmsett to produce emulsions (Fieldhouse, 2003) and compared the properties of these emulsions with those of emulsions produced in the laboratory using the end-over-end rotary mixer. The properties of emulsions made from the same oils by both methods were similar.

Gear pumps to mix water and oil to produce emulsified oils have been used by several workers:

- Buist et al., 2002 and 2003
- Buist et al., 1994
- Buist et al., 1997
- Gåseidnes, 1993
- Guenette et al., 1995
- Jensen et al., 1995

DNV have recently developed a "Procedure for Preparation of Water-in-Oil Emulsion for Testing of Oil Spill Response Equipment", (Johannessen, 2003).

Some of the properties of emulsions formed by these methods are detailed in the individual reports. However, these properties have not been compared with emulsions formed at sea with the same oils or with oils weathered to a similar degree.

2.5 Data On Water-in-Oil Emulsions Oils Formed In Laboratory Test Methods

Several different methods have been used to prepare small batches of emulsified oil for use in tests.

The rotating flask method (Mackay and Zagorski, 1982) has been used by some workers to produce small quantities of emulsion while the end-over-end rotary mixer has been used at Environment Canada (Fingas, 1996, 1998, 2000, 2001, 2002). Both methods were said to produce emulsions with similar properties to those formed at sea. Food mixers or food blenders have also been used (Fingas, 1996). The frequently used Zagorski and Mackay rotating bottle method of emulsification appears to form w/o emulsions at approximately 6 times the rate at which they are formed at sea in a 20 knot (10 m/s) wind.

A comparison of the properties of emulsions produced in the laboratory by using a high-shear (Silverson) mixer and those produced at sea showed that the emulsions prepared in the laboratory had a higher viscosity than those produced at sea with a similar water content (Walker, 1993). This appears to indicate that the high-shear mixing produced water droplets that were much smaller than those incorporated into the oil at sea.

2.6 Summary

The data on physical properties of w/o emulsions formed at sea after oil spills is sparse because major oil spills are rare events. Large oil spill events have often been followed by short periods of research activity that focused on the oil spill that had occurred in an attempt to explain the consequences of the processes, including w/o emulsification, that were observed. Sea trials using the appropriate crude oils were conducted at various periods before and after the *Ekofisk*, *Braer*, *Sea Empress* and *Exxon Valdez* oil spills.

Sea trials have also been undertaken with some crude oils that have not been spilled in large quantities. Sea trials in the UK and in Norwegian waters have been used to 'validate' computer modelling of oil weathering and the results from the work at sea has been incorporated into the algorithms of the models.

There have been several tank tests and numerous smaller-scale laboratory investigations of different aspects of w/o emulsion formation and properties.

The available data shows generally consistent results:

1. Most crude oils will eventually form a w/o emulsion with a 60% to 75% volume water content when spilled at sea.

    1a. The water droplets that are initially incorporated into the oil have a wide size distribution, but the mean size rapidly decreases and the size distribution becomes 'tighter' as the w/o emulsion develops. The number average size of a "fully developed" w/o emulsion at sea (w/o emulsions formed after several days at sea with only gradually changing properties) has been variously estimated as approximately 2μm diameter, 5 μm diameter or bimodal at 5 and 20 μm diameter for stable emulsions and much larger for unstable emulsions. Most of these estimates have been based on w/o emulsions made by laboratory methods. There will be an effect of differences in w/o emulsion stability caused by oil type – more stable w/o emulsions with smaller water droplets will be formed with oils that have high asphaltene content (see 3a).

    1b. Limited data from sea-trials on the rate of w/o emulsification has been compared with the results of computer-modelled oil weathering derived from small-scale, step-wise laboratory studies by several organisations. There appears to be generally good agreement between modelling and the rate of w/o emulsification observed at sea for at least the first few days (most sea trials have been conducted over a period of 2 or 3 days).

2. Mixing energy is important for w/o emulsification:

    2a. There is a threshold sea-state, equivalent to a wind speed of approximately 8 knots, for w/o emulsification to proceed at a significant rate. The rate of w/o emulsification is then proportional to wind speed up to a limiting maximum of around 30 knots, when slick break-up becomes the dominant process.

    2b. Mixing energy variations in small-scale methods shows that higher intensity (higher shear) mixing produces smaller mean water droplet size and more prolonged mixing at a particular shear rate produces a tighter size distribution. Similar effects may be inferred to occur at sea, where the w/o emulsion viscosity continues to rise after the water content and degree of evaporation from the parent oil has stabilised, but there is only limited actual data to support this, albeit reasonable, inference.

2c. The use of relatively low-shear mixing, such as that achieved by progressive cavity pumps, for the preparation of larger batches of w/o emulsions is justified to prevent localised formation of very small water droplets. W/o emulsions produced by excessive shearing (mixing with gear pumps or Silverson mixers) have very small water drops and high viscosities (at relatively low water contents) that are not typical of emulsions produced at sea.

3. Crude oil composition has a great influence on the physical properties of the w/o emulsion formed by spilled oil in several ways:

3a. Crude oils with a high level of volatile components and that leave a high viscosity oil residue after evaporation form higher viscosity w/o emulsions than crude oils that leave a less viscous residue after evaporation.

3b. W/o emulsions are stabilised by asphaltenes precipitated from the oil that form an elastic coating around the water droplets. The asphaltenes are precipitated from the oil by changes in the oil composition that accompany oil weathering. Crude oil with high asphaltene contents (either greater than 0.5 % wt.'hard asphaltenes', generally measured by heptane insolubles of the 370ºC+ residue, or greater than 3 % wt. 'soft' asphaltenes, as measured as pentane insolubles or by Iatroscan (TLC/FID) SARA – Saturates, Aromatics, Resins, Asphaltenes) produce higher viscosity, more stable w/o emulsions than crude oils with a lower asphaltene content. The greater amount of precipitated asphaltenes can stabilise a greater area of water / oil interface and can therefore stabilise a greater number of smaller water droplets for a particular water content.

3c. Simulated weathering studies in the laboratory separate the simulated evaporation of oil from the formation of w/o emulsions. This is obviously not an accurate simulation of the two processes occurring simultaneously at sea. Asphaltenes precipitated from the body of the oil will be available to stabilise the w/o emulsion as it is formed at sea, but are retained in the oil in the step-wise procedure. However, correlation with the data available on the limited range of crude oils that have been used at sea-trials appears to indicate that the most commonly used step-wise laboratory procedure produces w/o emulsions with very similar properties to those produced at sea. This correlation is limited to the weathering period of time when sea-trial data is available, normally 2 or 3 days.

4. The water content, water droplet size distribution, viscosity and stability of w/o emulsions are interrelated:

    4a. The viscosity of a w/o emulsion will never be an adequate description of the more complex non-Newtonian flow behaviour exhibited by all w/o emulsions with a water content above approximately 30% vol. water. More thorough rheological measurements need to be made to properly describe the flow behaviour of w/o emulsions. However, a simple viscosity can be an adequate comparator to assess the differences in physical properties of w/o emulsions of the same oils prepared under similar conditions, provided that the viscosity is determined at the same shear rate and that the w/o emulsions are subjected to a microscopic examination to ensure that the water droplet distributions are similar.

3. Small-Scale Emulsion Formation Tests

3.1 Apparatus

Five main mixing methods were tested for their potential for the generation of realistic emulsions in batch processes. Photos of the five methods are provided in Figures 3 through 7. The methods include using a gear pump (GP), a progressing cavity pump (PC), a double-diaphram pump (DD), a paint stirrer (PS), and a cement mixer (CM).

Figure 3. Gear Pump (GP)

Figure 4. Progressing Cavity Pump (PC)

Figure 5. Double Diaphragm Pump (DD)

Figure 6. Paint Stirrer (PS) ... operated a two different speeds (300 and 700 rpm)

Figure 7. Cement Mixer (CM) ... operated at two speeds (20 and 30 rpm)

Several cascading water-fall concepts were tested in small-scale preliminary configurations but all failed to provide controllable flow of heavy oil through the system and interaction of the falling water and surface oil slicks. The concept was abandoned as it was considered impractical to implement. An example of a setup tested is shown in Figure 8.

Figure 8. Cascading Water

3.2 Test Methods

3.2.1 General Procedures

Two different types of tests were completed using the five emulsion formation methods. In the first series of tests between 250 and 500 ml of oil was mixed in the presence of excess water (10x's more water than oil). Water contents, viscosities and water drop size photos were taken after various mixing intervals. The oil-water mixing was completed in the presence of more water than was needed to form the final oil-in-water emulsion to better simulate what might happen in the field or on a large wave tank such as the Ohmsett tank. These tests have been labelled as "emulsions formed with excess water".

In the second series of tests only enough water to achieve a 60% water-in-oil emulsion was slowly added (over a period of 2 to 3 minutes) to 500 ml of the oil and mixed for 15 minutes. This was followed by the slow addition of enough additional water to make a 70% water-in-oil emulsion and 15 more minutes of mixing. This sequence was repeated for 75% and, in some cases, 80% water contents. The water was added over a period of about 2 to3 minutes so it could be quickly incorporated into the oil (usually) without excess water significantly reducing the rate of water uptake into the oil. After each 15-minute mixing period emulsion samples were taken for water content and viscosity measurements and water drop size photos. These tests have been labelled in the report as "emulsions formed with slow addition of water".

3.2.2 Analytical Methods

WATER CONTENT

The water contents of the emulsions were determined as follows. Approximately 30 milliliters of each emulsion were placed in a narrow diameter, straight-sided, vial. Five or six drops of demulsifier (Alcopol) were added to the emulsion and the vial was vigorously shaken to mix the contents. The mixture was left to settle for a number of hours and the height of the oil and water was recorded. The water content was then calculated by dividing the water height by the total liquid height.

VISCOSITY

Emulsion viscosities were determined using a Brookfield DV III+ Viscometer. All emulsion viscosities were recorded at 20 ˚C and the viscosities reported are for a shear rate of 10 s^{-1}.

EMULSION PHOTOGRAPHS

Emulsions were photographed through a microscope using a Nikon Coolpix 4300 digital camera (4 mega pixel) mounted on a Scopetronix microscope adapter. Photographs were taken at both 100 and 440 times magnification. The 100x photographs proved to be the most useful for this study and are the ones used in the report. An eyepiece reticle was in place during all of the photographs. A stage micrometer (1mm with 100 divisions: each division 10 microns) was photographed (Figure B25) at both magnifications to establish the relationship between the eyepiece reticle divisions and the linear scale on the drop size photos. Each division on the scale present on the photos represents 16.7 microns.

The microscope slides for the emulsions of the two test oils were prepared differently due to the characteristics of the emulsions that formed. For the IFO 120 samples a small dab of emulsion was placed on a glass microscope slide, a second glass slide was carefully placed on top and the emulsion was then photographed. The IFO 120 emulsions were "strong" enough such that the water drops in the emulsion did not coalesce with the placement of the cover slide. If required, a slight pressure was applied to the cover slide to achieve a thin layer of emulsion to permit adequate light transfer to enable details of the emulsion to be photographed. The Endicott emulsions were not as "strong" and the addition of the cover slide significantly altered the characteristics of the emulsion. For the Endicott emulsions a small dab was placed on the slide and then carefully "swiped" across the slide into a thin layer using the edge of another glass slide. This was then photographed.

3.3 Small Scale Test Results: Excess Water Present

IFO 120 TESTS

Figures 9 through 11 summarize the water content and emulsion viscosity measurements taken during the IFO 120 fuel oil small-scale tests. Figure 9 shows that emulsions with similar water contents had viscosities that varied by up to an order of magnitude, depending on the method used to form the emulsions. The likely reason for the variation in emulsion viscosity is the size distribution of the water drops in the different emulsions. Photographs of the emulsions provided in Appendix B give evidence of variations in the water drop size distributions in the emulsions formed by the various mixing methods. For readers accessing this report electronically, hyperlinks to the photos in Appendix B are provided in Table 6 and via the mixing device's name throughout the text. Right click on a link to jump to photos of the emulsions for that specific mixing method. The size of the water drops in these photos can be estimated using the scale that is superimposed on each image. Each of the smallest divisions in the scale (see Figure B25) on the photos is approximately 16.7 microns.

Table 6. Hyperlinks to Emulsion Water Drop Size Photos

Hyperlinks to Emulsion Drop Size Photos	Figure Name
Gear Pump	Figure B2
Double Diaphragm	Figure B3
Progressing Cavity	Figure B1
Paint Stirrer (750 rpm)	Figure B5
Paint Stirrer (300 rpm)	Figure B4
Cement Mixer (19 rpm)	Figure B6
Cement Mixer (30 rpm)	Figure B7

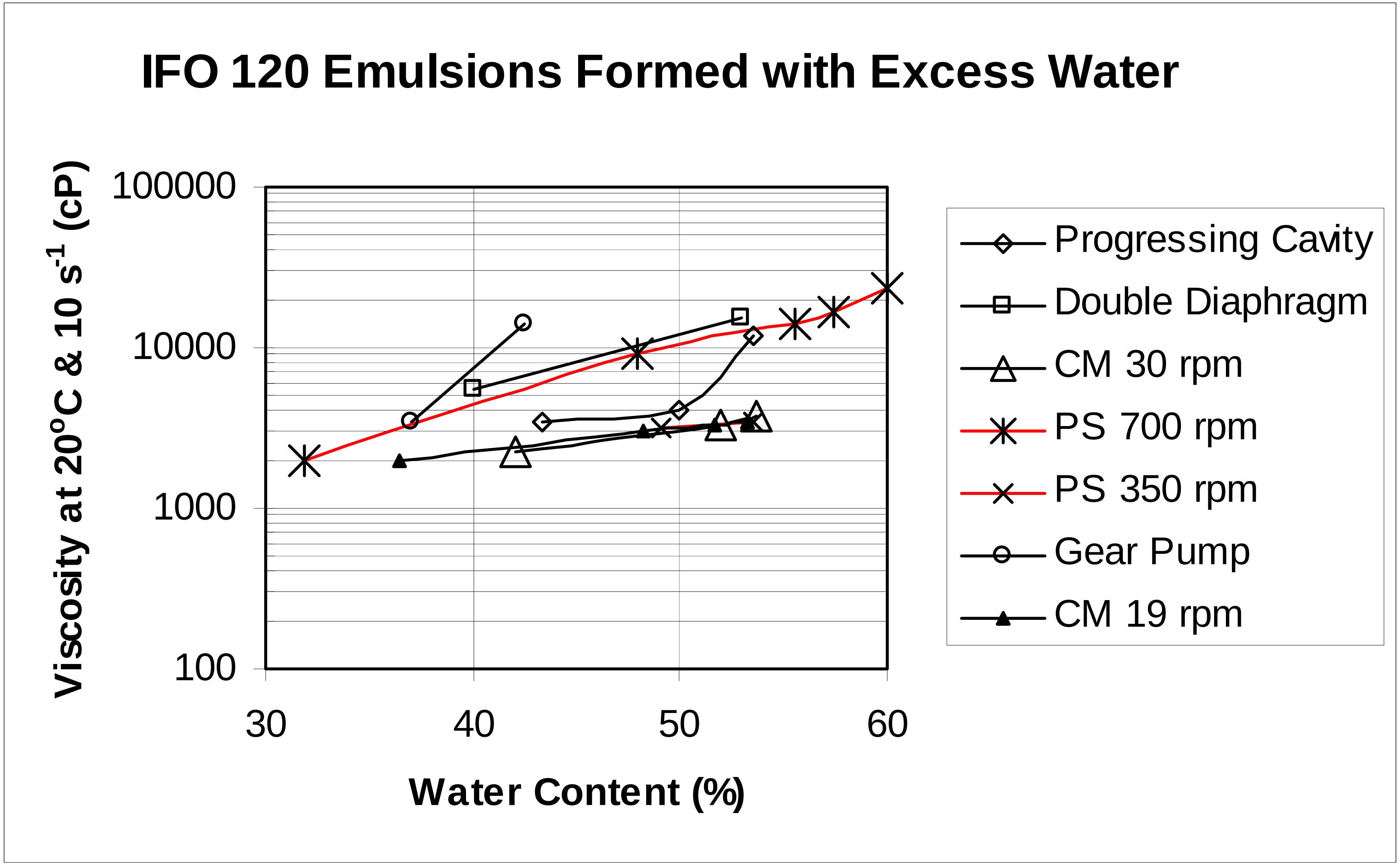


Figure 9. Viscosity vs Water Content for IFO 120 Emulsions Formed with Excess Water Present

The gear pump, double diaphragm and high-speed paint stirrer generated the highest viscosity emulsions at similar water contents. This is not surprising since these methods all impart significant mixing energy to the system and are capable of forming small water drops in the emulsion. The cement mixer generated the lowest viscosity emulsions regardless of the speed of the mixing drum. The IFO 120 fuel oil formed small balls of oil that moved with the bulk water during the cement mixer's drum rotation. The cement mixer's blades in the "excess water" mixing tests did not shear the balls of oil and small water drops were slow to form in these emulsions. The progressing cavity pump generated emulsions with viscosities in the mid-range of the methods tested. The paint stirrer operated at low speed (300 rpm) generated emulsions with low viscosities and relatively large water drop sizes.

The rate of water uptake in the IFO 120 emulsions for each of the mixing methods is shown in Figure 10. The paint stirrer was the quickest in incorporating water into the oil and the cement mixer was the slowest. The rapid incorporation of water by the paint stirrer is likely due to the fact that the mixing blades were placed at the oil-water interface and less water was mixed with oil at any given time when compared to the other mixing methods. As a result, less of the mixing energy applied was lost in mixing water and more was used effectively mixing oil in the presence of a smaller water fraction.

The change in emulsion viscosity with mixing time for the IFO 120 fuel oil, for each of the mixing methods, is shown in Figure 11. The cement mixer and the paint stirrer operated at low speed generated emulsions with the lowest viscosities and were the slowest devices in developing emulsions of IFO 120 fuel oil. The high-speed paint stirrer generated the most viscous emulsions and was quicker in developing the emulsions than all of the other devices. The gear, double diaphragm and progressing cavity pumps were somewhat slower than the high speed paint stirrer in developing emulsions of the IFO 120 oil but did eventually generate high viscosity emulsions.

The paint stirrer device demonstrated the most flexibility of all of the devices in forming emulsions of the IFO 120 oil. By adjusting the rpm of the mixer the paint stirrer was able to generate emulsions with properties that bracketed those generated by all of the other mixing methods.

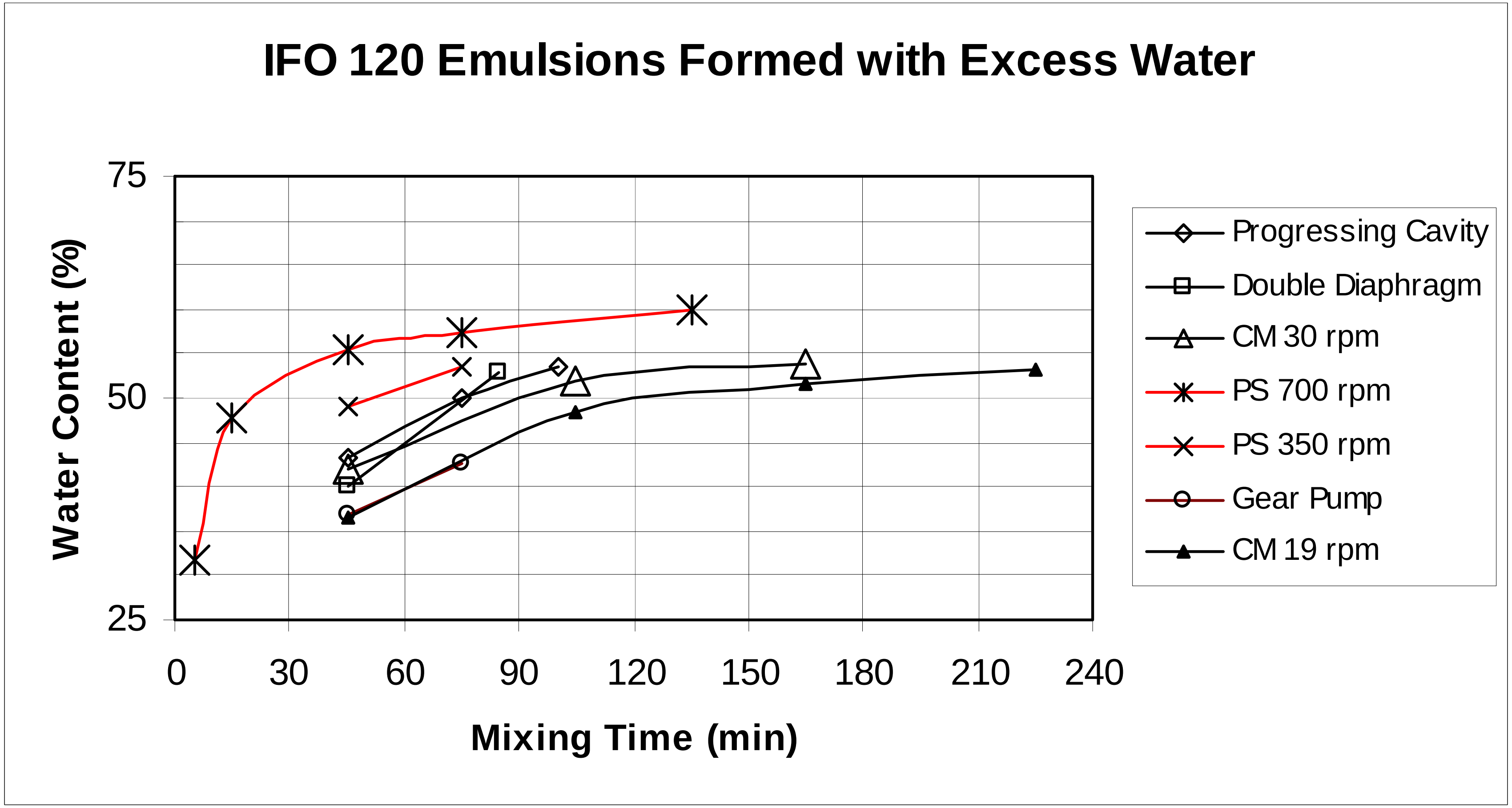


Figure 10. Water Content vs Time for IFO 120 Emulsions Formed with Excess Water Present

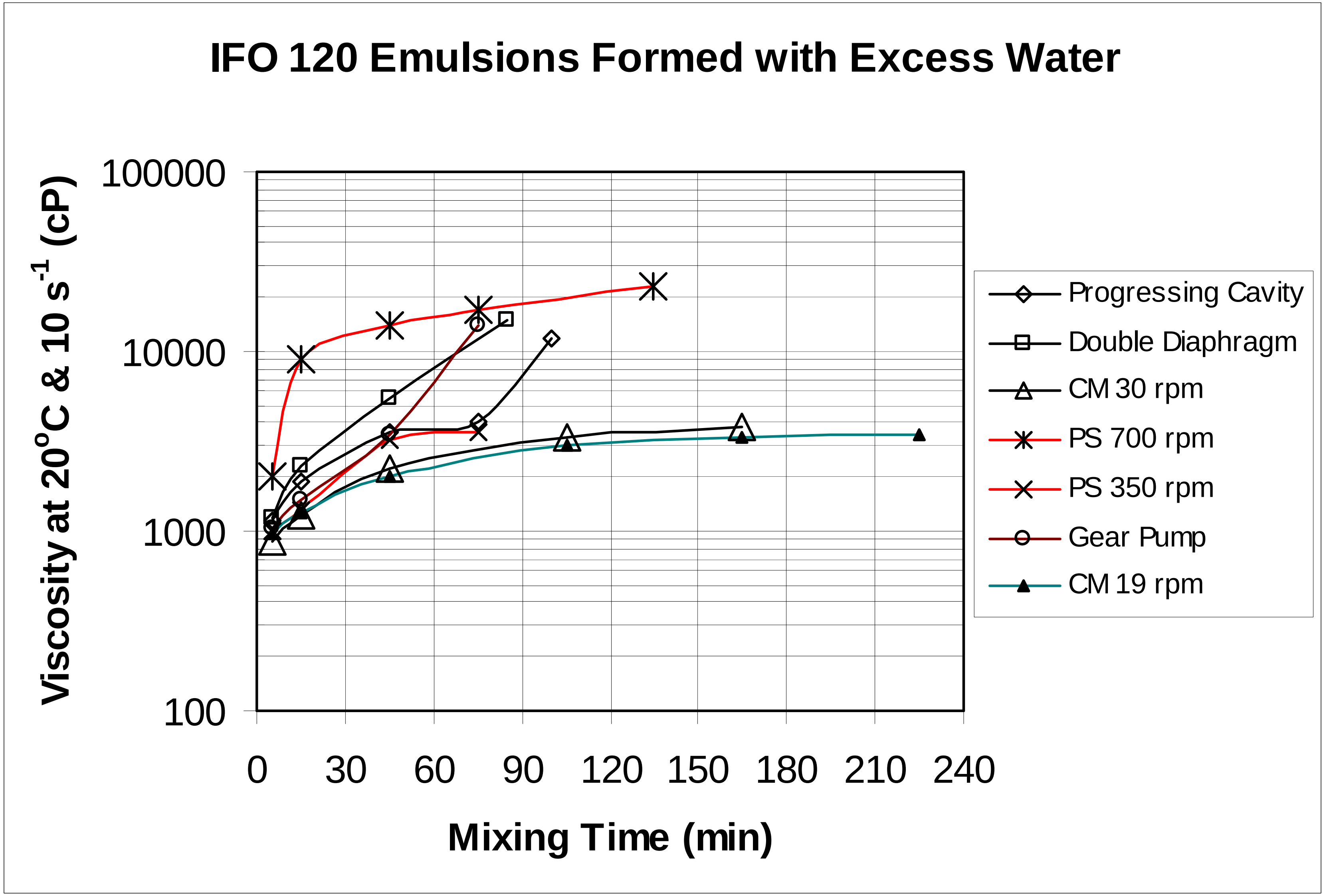


Figure 11. Viscosity vs Time for IFO 120 Emulsions Formed with Excess Water Present

ENDICOTT CRUDE OIL TESTS

Figures 12 through 14 summarize the water content and emulsion viscosity measurements taken during the Endicott crude oil small-scale emulsion formation tests completed with excess water. In general the Endicott crude oil (sampled in 2002) was slower to form emulsions when mixed in the presence of excess water and the emulsions were much less viscous than the IFO 120 oils, as would be expected with its lower parent oil viscosity. The Endicott emulsions generated by the various mixing methods again had different viscosities with similar water contents as seen in Figure 12. As with the IFO 120 oil, emulsions the likely reason for the variation in emulsion viscosity is the size distribution of the water drops in the different emulsions. Photographs of the emulsions provided in Appendix B give evidence of variations in the water drop size distributions in the emulsions formed by the various mixing methods. Hyperlinks to the photos in Appendix B are provided in Table 7 and via the mixing device's name throughout the text. The size of the water drops in these photos can be estimated using the scale that is superimposed on each image. Each of the smallest divisions in the scale on the photos is approximately 16.7 microns. The water drops in the Endicott emulsions were generally much larger than those in the IFO 120 emulsions and it was much more difficult to photograph these emulsions as the water drops were much more easy to disturb when the slides were prepared for the microscope.

Table 7. Hyperlinks to Emulsion Water Drop Size Photos

Hyperlinks to Emulsion Drop Size Photos	Figure Name
Gear Pump	Figure B9
Double Diaphragm	Figure B10
Progressing Cavity	Figure B8
Paint Stirrer (700 rpm)	Figure B11
Cement Mixer (30 rpm)	Figure B12

The progressing cavity, double diaphragm and high-speed paint stirrer generated the highest viscosity emulsions at similar water contents. This is not surprising since these methods all impart significant mixing energy to the system and are capable of forming small water drops in the emulsion. The cement mixer again generated the lowest viscosity emulsions. The gear pump was very slow to generate emulsions of the light Endicott crude oil when large quantities of water were present.

The rate of water uptake in the Endicott emulsions for each of the mixing methods is shown in Figure 13. The paint stirrer again was the quickest in incorporating water into the oil and the gear pump and cement mixer were the slowest.

The change in emulsion viscosity with mixing time for the fresh Endicott crude oil, for each of the mixing methods, is shown in Figure 14. The cement mixer and the gear pump generated emulsions with the lowest viscosities and were the slowest devices in developing emulsions of Endicott. The double diaphragm pump generated the most viscous emulsions and developed the emulsions the fastest of all methods tested. The water drops in the emulsions formed by the double diaphragm pump are smaller than those generated by all of the other devices. Even though the DD pump was slower to incorporate water into the emulsion than the paint stirrer the water drops that were incorporated were smaller thus resulting in a higher viscosity. The progressing cavity pump and the high-speed paint stirrer generated emulsions of the Endicott crude at a similar rate.

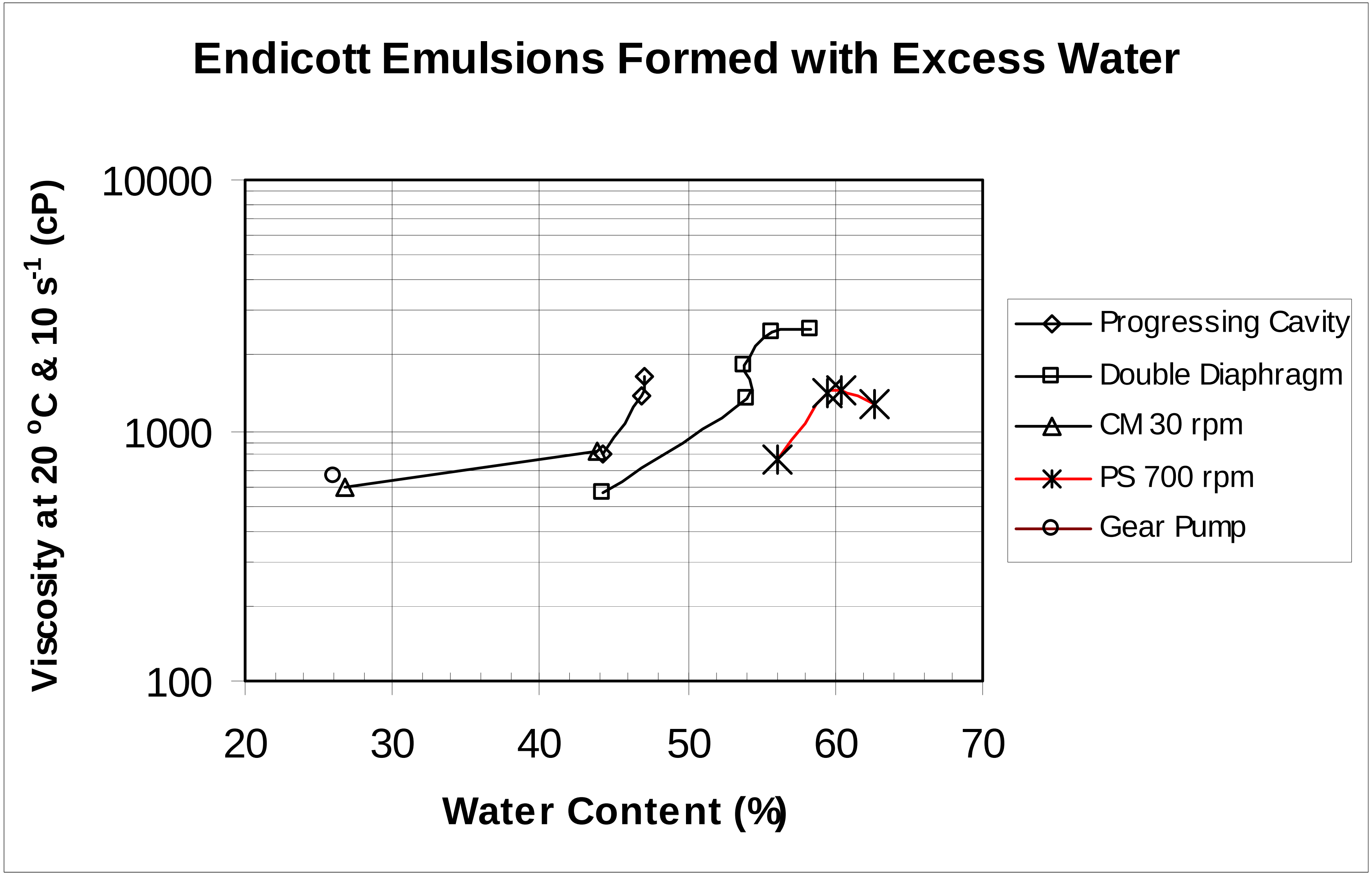


Figure 12. Viscosity vs Water Content for Endicott Crude Oil Emulsions Formed with Excess Water Present

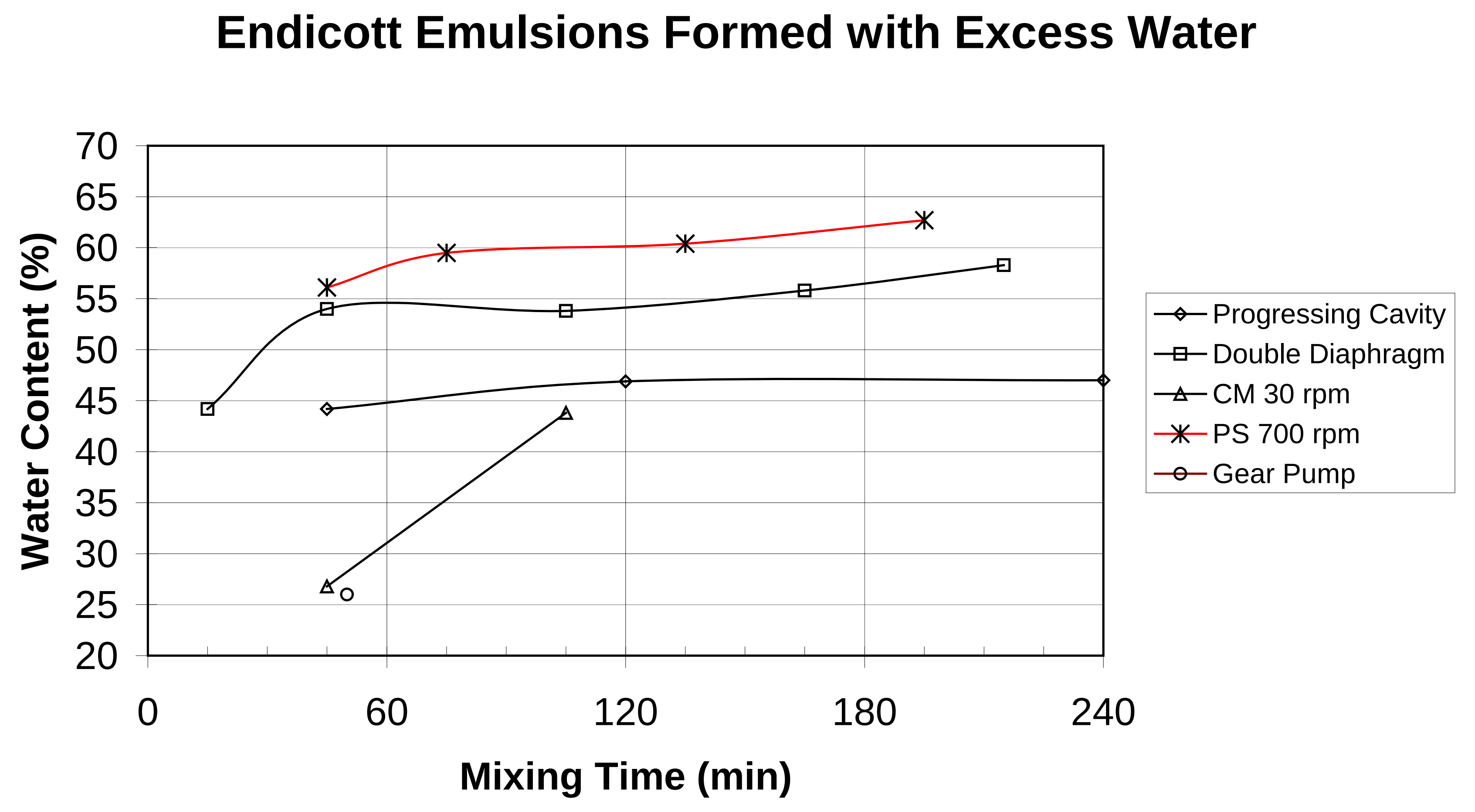


Figure 13. Water Content vs Time for Endicott Crude Oil Emulsions Formed with Excess Water Present

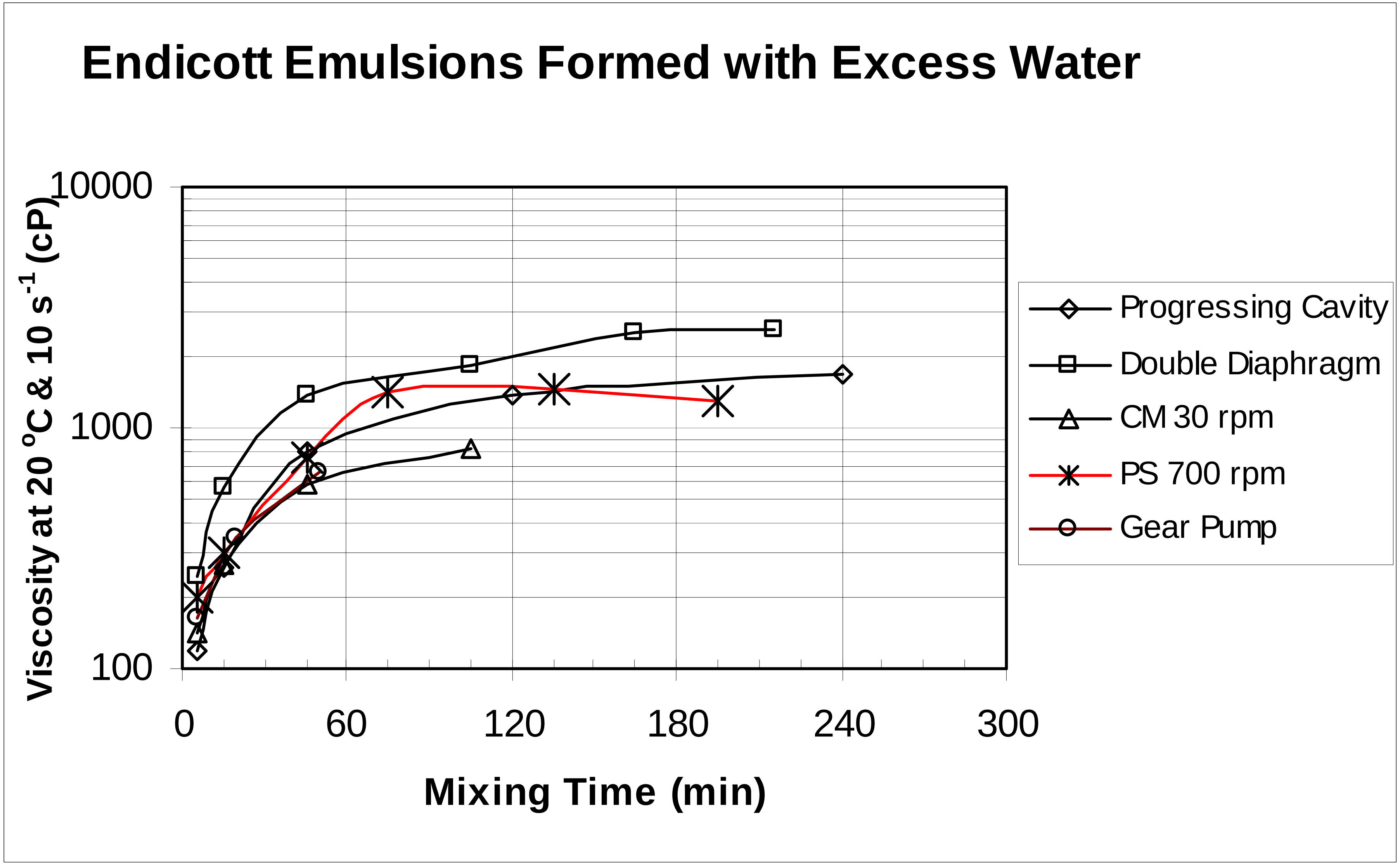


Figure 14. Viscosity vs Time for Endicott Crude Oil Emulsions Formed with Excess Water Present

3.4 Small Scale Test Results: Slow Water Addition

IFO 120 TESTS

Figures 15 through 17 summarize the water content and emulsion viscosity measurements taken during the small-scale emulsion formation tests completed with the slow addition of water to IFO 120 fuel oil during the mixing process. Figure 15 shows the variation in emulsion viscosity as a function of water content in emulsions created using the different mixing methods. The difference in viscosities for emulsions with similar water contents is likely due to the water drop size distributions in the emulsions. Photographs of the emulsions provided in Appendix B give evidence of variations in the water drop size distributions in the emulsions formed by the various mixing methods. Hyperlinks to the emulsion photos in Appendix B are provided in Table 8 and via the mixing device's name throughout the text. The size of the water drops in these photos can be estimated using the scale that is superimposed on each image. Each of the smallest divisions in the scale on the photos is approximately 16.7 microns.

Table 8. Hyperlinks to Emulsion Water Drop Size Photos

Hyperlinks to Emulsion Drop Size Photos	Table Name
Gear Pump	Figure B15
Double Diaphragm	Figure B14
Progressing Cavity	Figure B13
Paint Stirrer (700 rpm)	Figure B16
Paint Stirrer (300 rpm)	Figure B17
Cement Mixer (30 rpm)	Figure B18

The gear pump and high-speed paint stirrer generated the highest viscosity emulsions with similar water contents in this test series. Both the double diaphragm and progressing cavity pumps were unable to produce emulsions greater than about 30,000 cP due to pump limitations. The cement mixer and low speed paint stirrer generated the lowest viscosity oils at similar water contents.

The rate of water uptake in the IFO 120 emulsions for each of the mixing methods is shown in Figure 16. The paint stirrer (both speeds) was the slowest in incorporating water into the emulsions in these tests in contrast to the previous series where it was the fastest. In this series of tests relatively small quantities of water was slowly added to the mixing process so the energy imparted by the pumps or mixing systems was more focused on driving small water drops into the oil rather than moving large quantities of water (as in the excess water tests). The gear and double diaphragm pumps incorporated water into the emulsions at the highest rates (up to the point where both were no longer able to pump the emulsion due to their high viscosities). The rate of water uptake generated by the progressing cavity pump and cement mixer methods fell between the other extremes.

The change in emulsion viscosity with mixing time for the IFO 120 fuel oil, for each of the mixing methods, is shown in Figure 17. The cement mixer and the paint stirrer operated at low speed generated emulsions with the lowest viscosities and were the slowest devices in developing emulsions of IFO 120 fuel oil. The gear and double diaphragm pumps created high viscosity emulsions quickly but were only able to pump the emulsions up to viscosities of 50,000 and 30,000 cP, respectively. The high-speed paint stirrer generated the most viscous emulsions but was somewhat slower in developing the emulsions when compared to the gear and double diaphragm pumps. The progressing cavity pump created viscous emulsions (20,000 to 30,000 cP) quickly but was unable to generate higher viscosity emulsions over time due to the pumps inability to move the viscous fluid.

The paint stirrer device again was the most flexible of the devices tested in forming emulsions of the IFO 120 oil. By adjusting the speed of the mixer the paint stirrer was able to generate emulsions with properties that bracketed those generated by the other mixing methods. In some cases the paint stirrer was slower to form the emulsions but by extending the mixing time more viscous emulsions could be created. The water drop size distributions in the emulsions formed by the paint stirrer were also generally of a wider distribution. The emulsions formed using the gear and double diaphragm pumps tended to have more uniform and smaller water drop sizes.

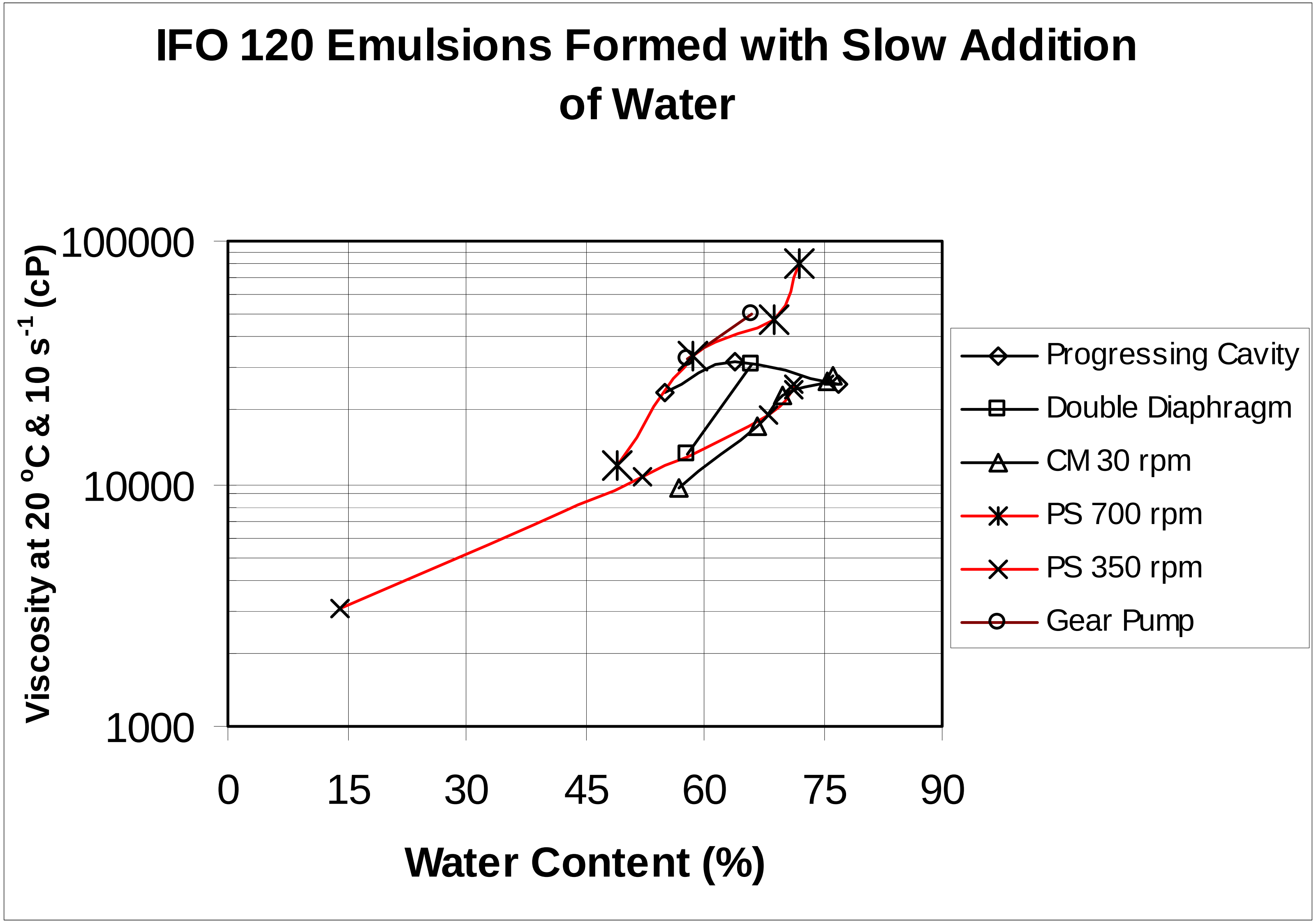


Figure 15. Viscosity vs Water Content for IFO 120 Oil Emulsions Formed with Slow Addition of Water

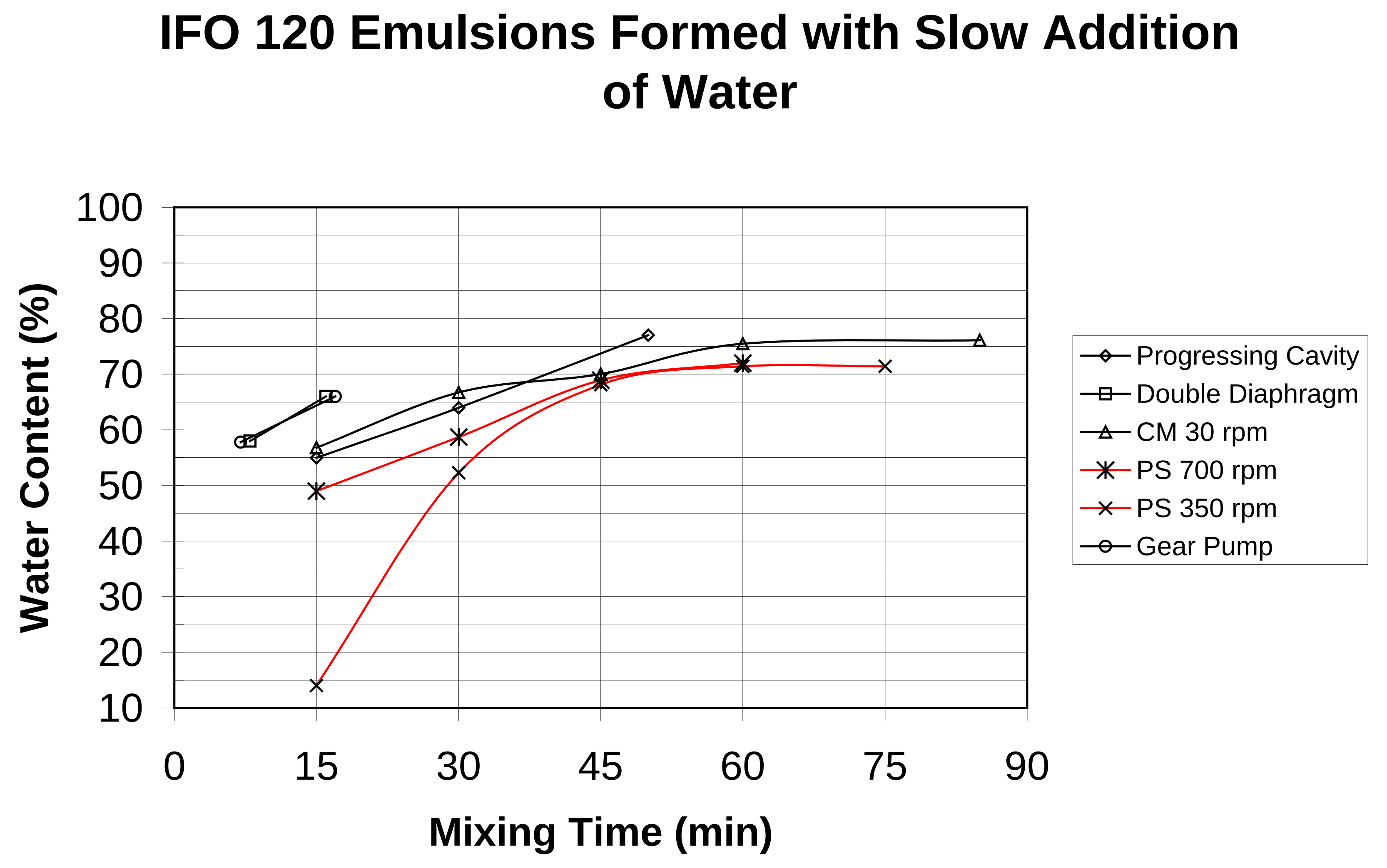


Figure 16. Water Content vs Time for IFO 120 Oil Emulsions Formed with Slow Addition of Water

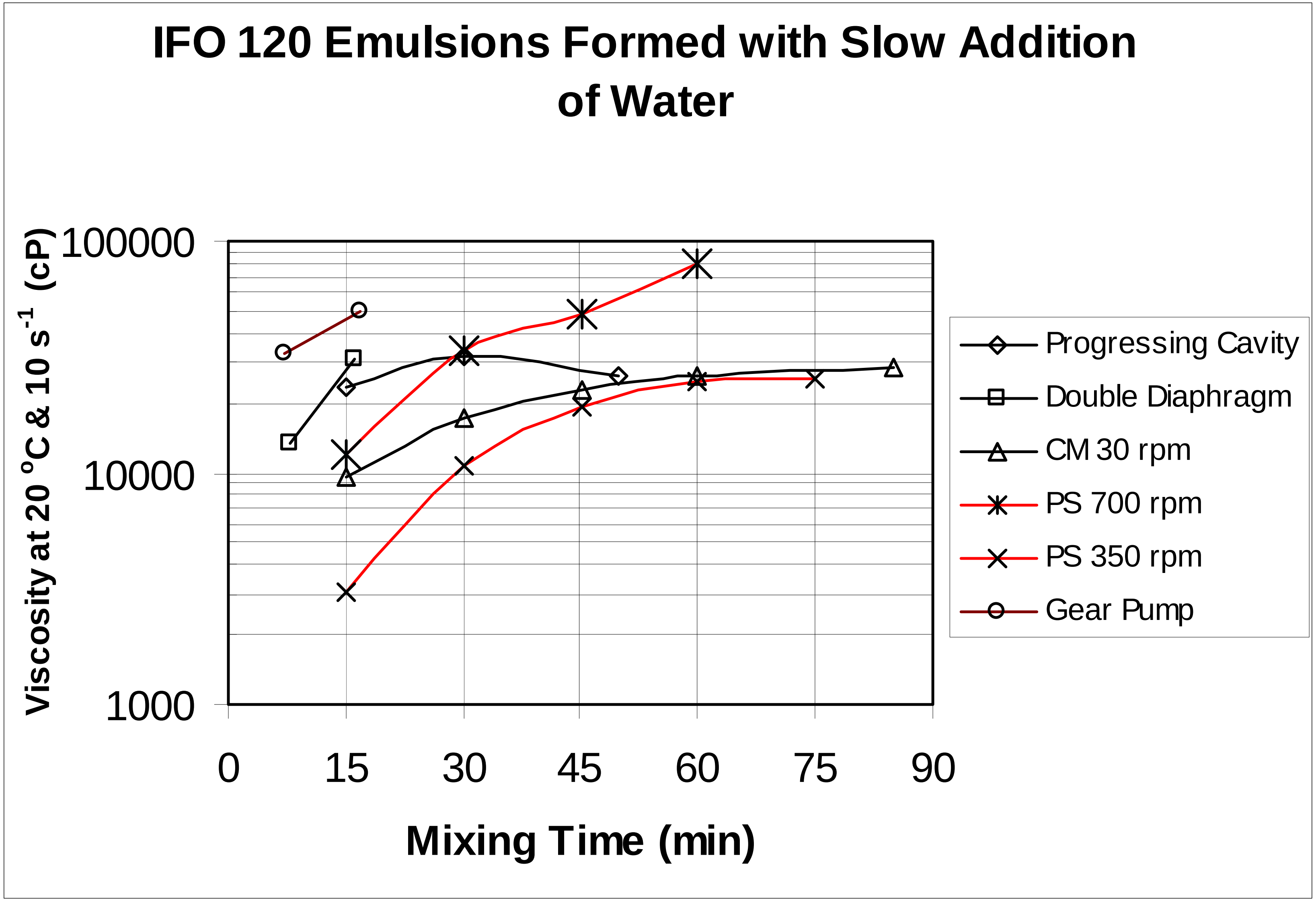


Figure 17. Viscosity vs Time for IFO 120 Oil Emulsions Formed with Slow Addition of Water

ENDICOTT CRUDE OIL TESTS

Figures 18 through 20 summarize the water content and emulsion viscosity measurements taken during the small-scale emulsion formation tests completed with the slow addition of water to Endicott crude oil during the mixing process. Figure 18 shows the variation in emulsion viscosity as a function of water content in emulsions created using the different mixing methods. Photographs of the emulsions provided in Appendix B. Hyperlinks to the emulsion photos in Appendix B are provided in Table 9 and via the mixing device's name throughout the text. The size of the water drops in these photos can be estimated using the scale that is superimposed on each image. Each of the smallest divisions in the scale on the photos is approximately 16.7 microns. The water drops in the Endicott emulsions were generally much larger than those in the IFO 120 emulsions and it was much more difficult to photograph these emulsions as the water drops were much more easily disturbed when the slides were prepared for the microscope.

Table 9. Hyperlinks to Emulsion Water Drop Size Photos

Hyperlinks to Emulsion Drop Size Photos	Figure Name
Gear Pump	Figure B21
Double Diaphragm	Figure B20
Progressing Cavity	Figure B19
Paint Stirrer (700 rpm)	Figure B22
Cement Mixer (30 rpm)	Figure B23
Cement Mixer (30 rpm) Weathered Oil	Figure B24

With the exception of the cement mixer the various mixing devices generated emulsions with similar viscosity/water content characteristics. The cement mixer emulsions for the fresh Endicott crude were significantly less viscous than the others as seen in Figure 18. The higher emulsion viscosities generated by the cement mixer in the weathered Endicott test were primarily due to the higher viscosity of the parent oil used in that test.

The rate of water uptake in the emulsions for each of the mixing methods is shown in Figure 19. With the exception of the gear pump all of the mixing methods resulted in a similar increase in water uptake over time. The gear pump more quickly built a 60% water content emulsion than the other devices but the water content did not increase with more mixing as was the case with the other systems.

The change in emulsion viscosity with mixing time for each of the mixing methods, is shown in Figure 20. In all cases the maximum viscosities of these emulsions was reached relatively early in the mixing process and the viscosity did not increase significantly even with the uptake of additional water over time.

The Endicott crude oil and water emulsions formed using the "slow addition of water" method were generally not as stable as those created with excess water. The emulsions formed with the gear and progressing cavity pumps were the only ones in this series of tests that remained stable overnight, all of the other emulsions broke with 24 hours or less.

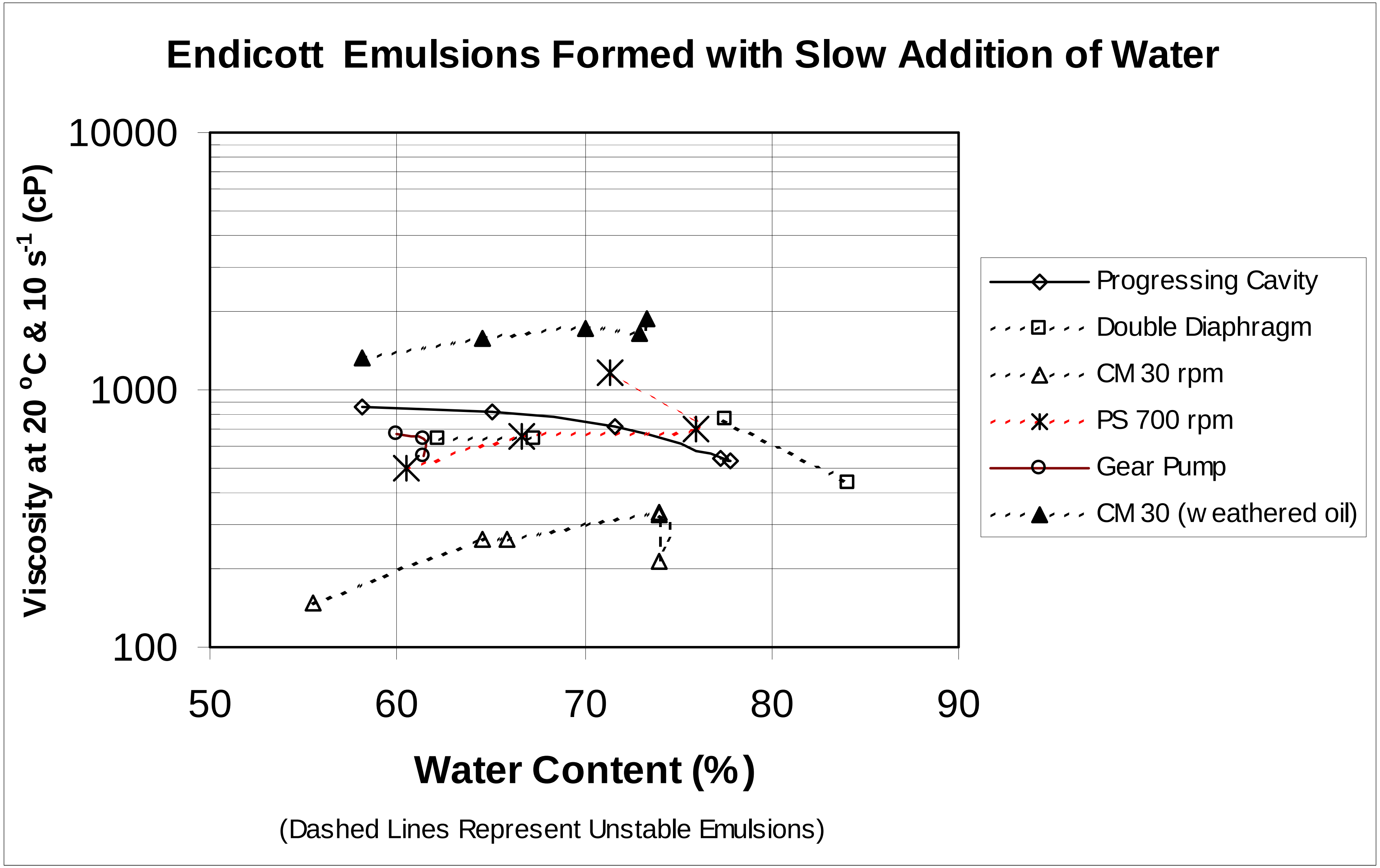


Figure 18. Viscosity vs Water Content for Endicott Crude Oil Emulsions Formed with Slow of Water

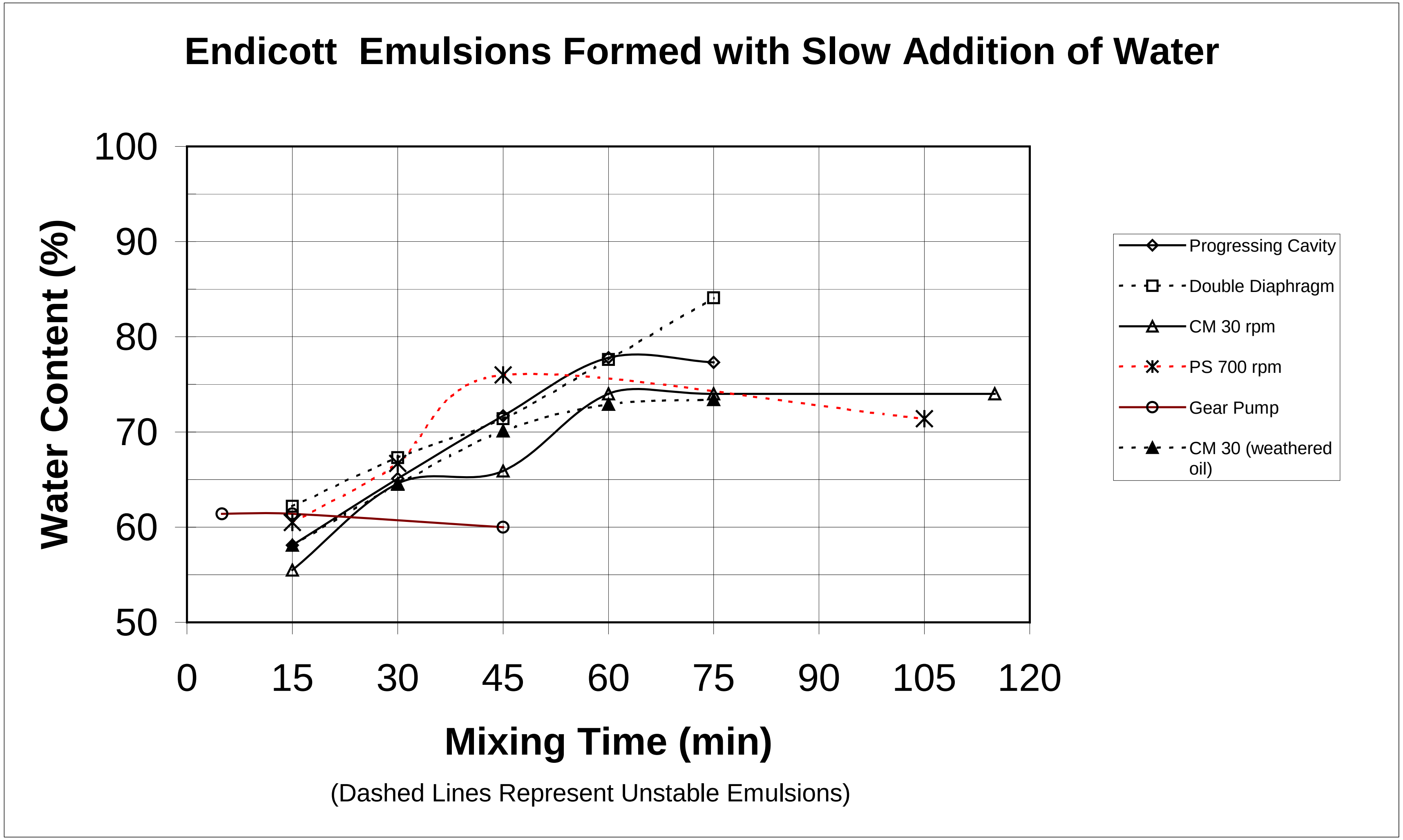


Figure 19. Water Content vs Time for Endicott Emulsions Formed with Slow Addition of Water

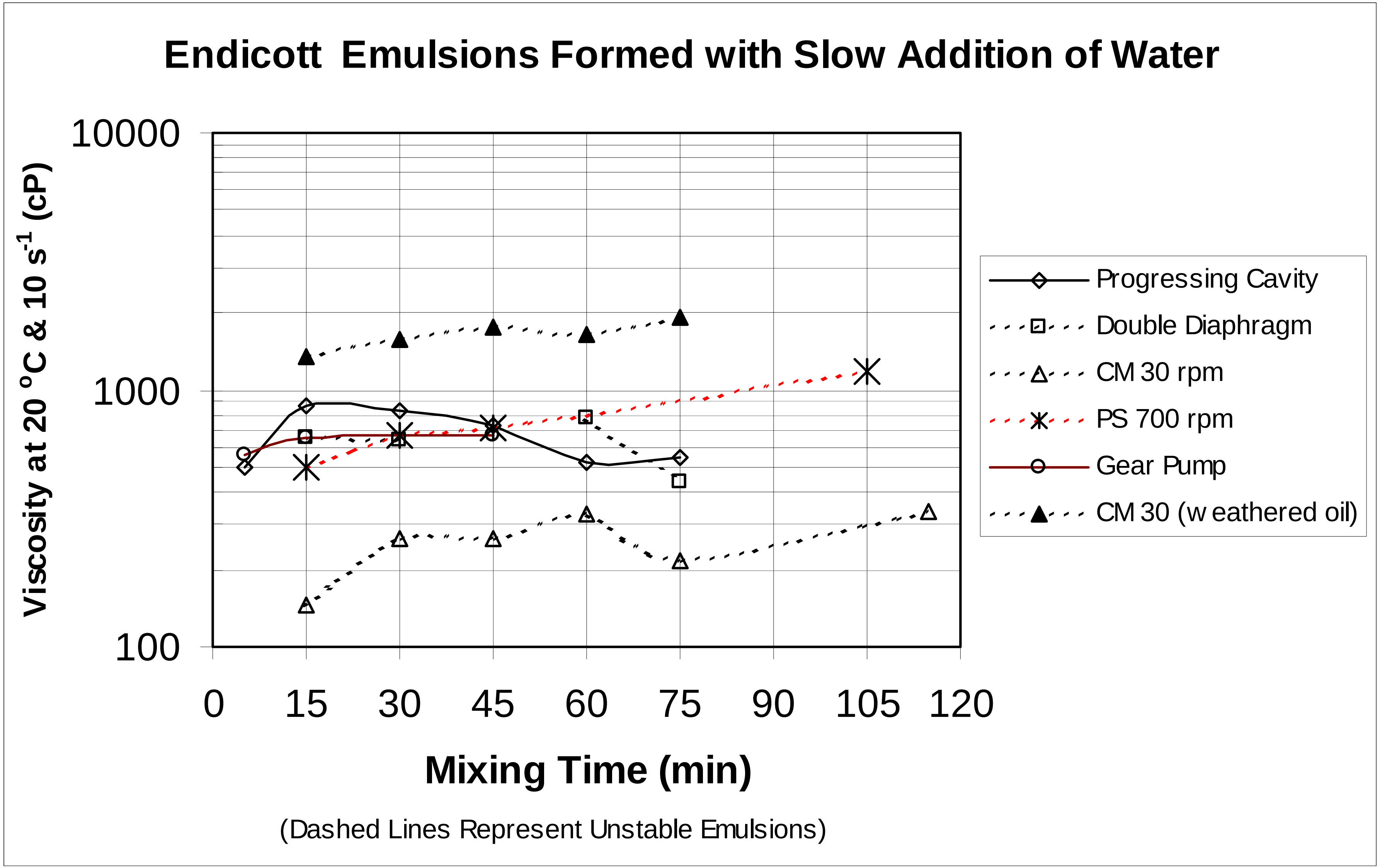


Figure 20. Viscosity vs Time for Endicott Emulsions Formed with Slow Addition of Water

4. Large-Scale On-Tank Emulsion Formation Tests at Ohmsett

Very little quantitative data exists on water-in-oil emulsions formed at sea. A series of long-term tests were completed on the Ohmsett test tank to simulate emulsion formation under conditions similar to those that spilled oil might be subjected to at sea. Emulsion samples were taken periodically and analysed for viscosity and water content and were photographed to record the water drop size characteristics of the emulsions. The data collected in these tests provides a basis for evaluating whether or not off-tank emulsion formation techniques can produce "realistic" water-in-oil emulsions.

4.1 Test Methods

4.1.1 General Procedures

In each long-term test between 30 and 60 litres of oil was spilled onto the tank surface. The surface water temperature during these tests was approximately 3 ˚C. The wave paddle was operated using a 3-inch stroke and a frequency ranging from 35 to 45 cycles per minute to generate cresting wave conditions over the tank surface. The oil was allowed to float freely on the tank surface and was mixed repeatedly by the breaking waves during the duration of the test. When the oil traversed to the north of the tank the waves were stopped and the oil was herded by fire-monitor or dragged by the auxiliary bridge boom back to the south end of the tank where it was released and the waves restarted for additional mixing action by the breaking waves. The time it took the oil to travel to the north end of the tank was highly dependent on the prevailing winds at the time. When the wind direction was from the south the oil travelled down the tank quickly and the oil was mixed for only 10 to 12 minutes before the waves were stopped and the oil moved back down the tank. When the wind blew from the north mixing times in excess of 30 minutes were possible prior to the oil reaching the north end of the tank.

Emulsion samples were taken periodically throughout each test and analysed for water content and emulsion viscosity. The viscosities throughout the report were measured at 20 ˚C and a shear rate of 10 s^{-1}. The viscosities of the emulsions when on the tank would have been considerably higher due to the low water temperature (about 3 ˚C). Comparisons of the emulsion viscosities when measured at 20 ˚C and 3 ˚C are presented in Appendix A for IFO 120 fuel oil and Endicott crude oil. Microscopic photos of the emulsions were also taken to record the characteristics of the water drops in each emulsion.

4.1.2 Analytical Methods

WATER CONTENT

The water contents of the emulsion samples taken in the large tank tests were determined using the procedures specified in ASTM D1796. The method involves splitting a well-shaken, 100-ml emulsion sample into two aliquots. Each aliquot is poured into a graduated centrifuge tube containing 50 ml of toluene filling the tube to the 100-ml mark. The tube is vigorously shaken, warmed and then placed in the centrifuge and spun for 10 minutes. The volume of water in the tubes is read directly from the graduations. For some samples, a small amount of demulsifier was added to the sample to aid in resolving the emulsion.

VISCOSITY

The viscosities of the emulsions sampled in these large tank tests were measured at 20 ˚C and a shear rate of 10 s^{-1} using a Haake VT550 rheometer.

EMULSION PHOTOGRAPHS

The emulsions were photographed as described in section 3.2.2 with one exception. A different microscope was used for the photos of these emulsions. As a result, the linear scale on these photos is slightly different from the other photographs. Each division of the scale in these photos represents 10.25 microns as shown in Figure C12.

4.2 IFO 120 Tests

Three different long-term tests were completed on the Ohmsett tank using IFO 120 Fuel Oil. In the first test 30 litres of IFO 120 were placed inside a 4.8 m diameter containment boom that was allowed to float freely on the tank. Shortly after the breaking waves started to form it was obvious that the oil would not remain inside the containment boom during the test. The boom was removed from the tank after its first pass down the tank and the oil was released to float freely on the tank for the remainder of the test. The oil in this test was subjected to breaking waves for a total of 4 hours and 24 minutes of mixing. The oil in the second and third IFO 120 tests were subjected to breaking waves for 2 hours and 45 minutes and 14 hours and 40 minutes, respectively. The third IFO 120 test (Run #4 on the Ohmsett tank) was completed over a 3-day span (January 3rd, 4th and 5th). Thirty litres of oil were used in the second IFO 120 test and 45 litres were used in the third IFO 120 test.

The viscosities of the emulsions sampled in the three tests are plotted in Figure 20. The emulsion viscosities for the first two tests were quite similar. The viscosity built to about 7000 cP over the 4 plus hours of mixing in these two tests. In the third IFO 120 test (Ohmsett Run #4) the emulsion viscosity increased somewhat more quickly and reached about 10,000 cP after 4 hours of mixing. This may have been due to the fact that the oil was better positioned in the middle of the tank during this tests series and subjected to more intense mixing as a result. The emulsion viscosity did not increase past approximately 15,000 cP after about 8 hours of mixing.

Emulsion water contents versus time are plotted in Figure 21 for the IFO 120 emulsions formed on the Ohmsett tank. The water uptake was fairly consistent in tests 1 and 4 where 60 to 65% water contents were achieved in about 4 hours. The maximum water contents achieved in the emulsions in Test 2 were only about 50%.

The viscosity versus water content of Figure 22 eliminates the rate of emulsion formation component of the three on-tank tests. When the emulsion viscosities at specific water contents are compared for the IFO 120 tests the trends are quite similar, especially for runs 2 and 4. The viscosities measured in Run #1 were somewhat lower than the other two runs at the lower water contents.

Example photos of emulsions from the three large-scale emulsion formation tests on the Ohmsett tank are provided in Appendix B. Links to these photos are provided in Table 10. The scale in the emulsion photos taken during the Ohmsett test program is different from that in the small-scale test photos. Each division of the eyepiece scale seen in the emulsion photos taken at Ohmsett represents approximately 10 microns. This was determined by photographing a 1 mm / 100 division stage micrometer (10 microns / division) with the eyepiece reticle in the eyepiece. An example of this photo is seen in Figure C12. Example emulsion photos taken at similar times from the three emulsion formation runs (Run #1, #2 and #4) are provided side-by-side in Appendix C for comparison. The emulsion photos for the three different runs show very similar water drop size characteristics when the water contents and viscosities of the emulsion samples are similar. For those accessing this report electronically, details in the emulsion photos can be made clearer using the zoom feature of the software being used to read the document.

Table 10. Hyperlinks to Photos of IFO 120 Emulsions Generated on the Ohmsett Tank

Hyperlinks to Emulsion Drop Size Photos	Figure Name
Early emulsions (24 to 33 minutes into runs)	Figure C1
Emulsions after 60+ minutes	Figure C2
Emulsions after 90 to 120 minutes	Figure C3
Emulsions at approximately 7000 cP	Figure C4
Run 4 Emulsions Late in Run (6 to 14 hours)	Figure C5

The small-scale test results for the paint stirrer, reported in Section 3.2.1, have also been plotted on Figures 20, 21 and 22 for comparison. The paint stirrer created similar emulsions to those formed on the Ohmsett tank when operated at 350 rpm. The rate of water uptake and increase in viscosity with time was slightly higher for the paint stirrer than that measured in the Ohmsett tests. The emulsion viscosity vs water content curves are very similar for the small-scale paint stirrer and Ohmsett generated emulsions. Based on these comparisons it would appear that the paint stirrer is able to create emulsions similar to those formed on the Ohmsett tank under realistic breaking wave conditions.

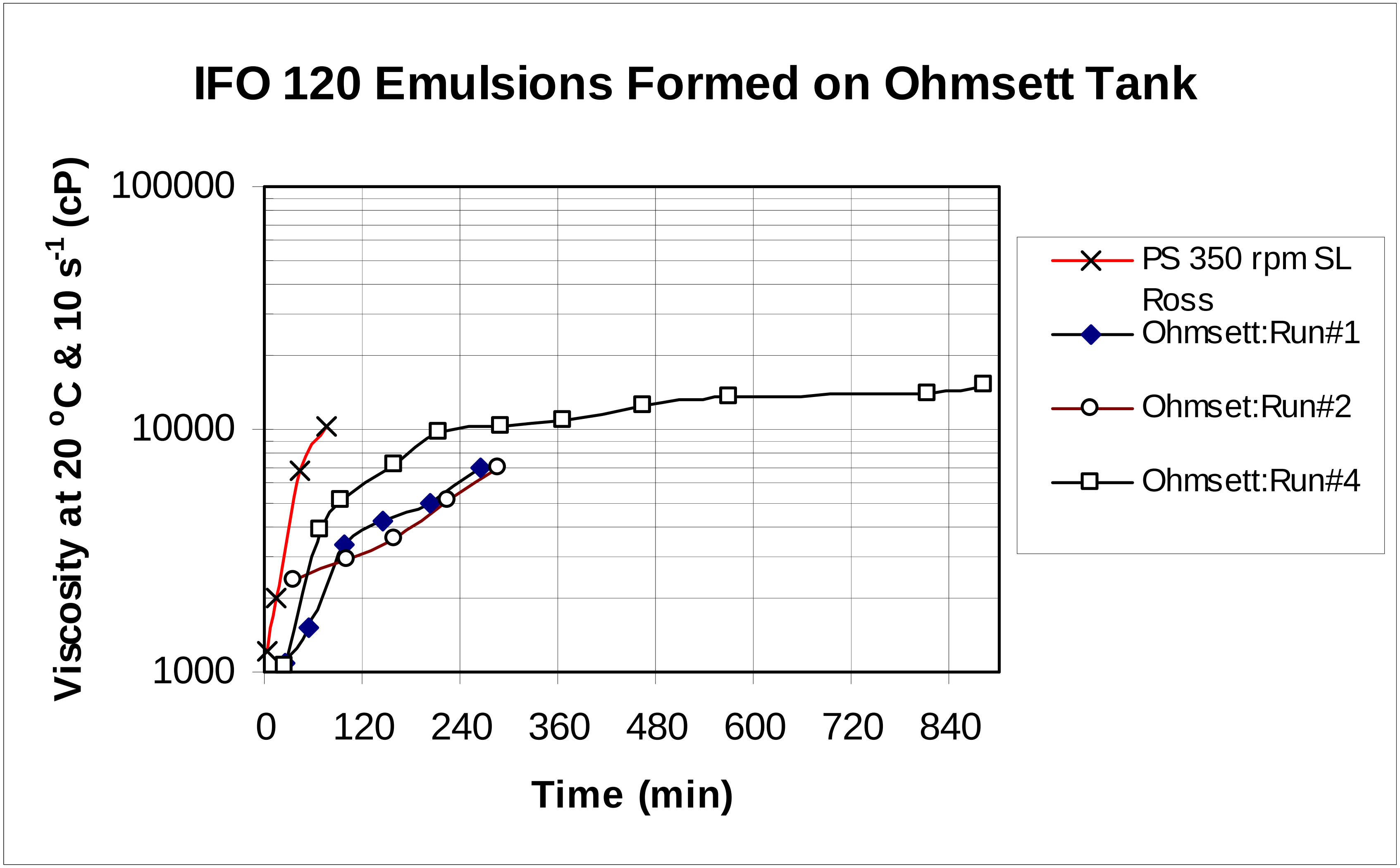


Figure 20. Ohmsett Test Tank Emulsion Viscosities for IFO 120 Fuel Oil

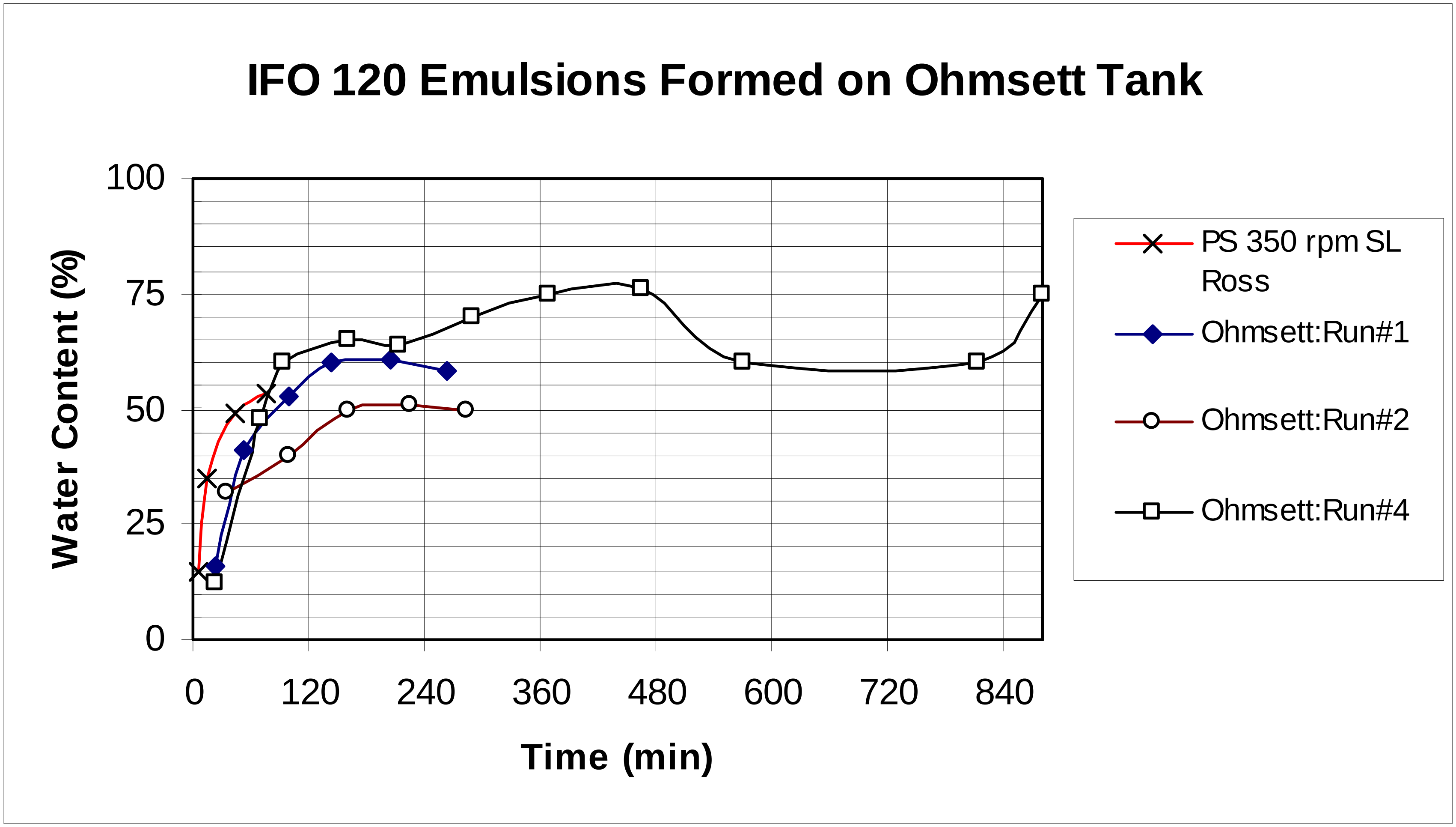


Figure 21. Ohmsett Test Tank Emulsion Water Contents for IFO 120 Fuel Oil

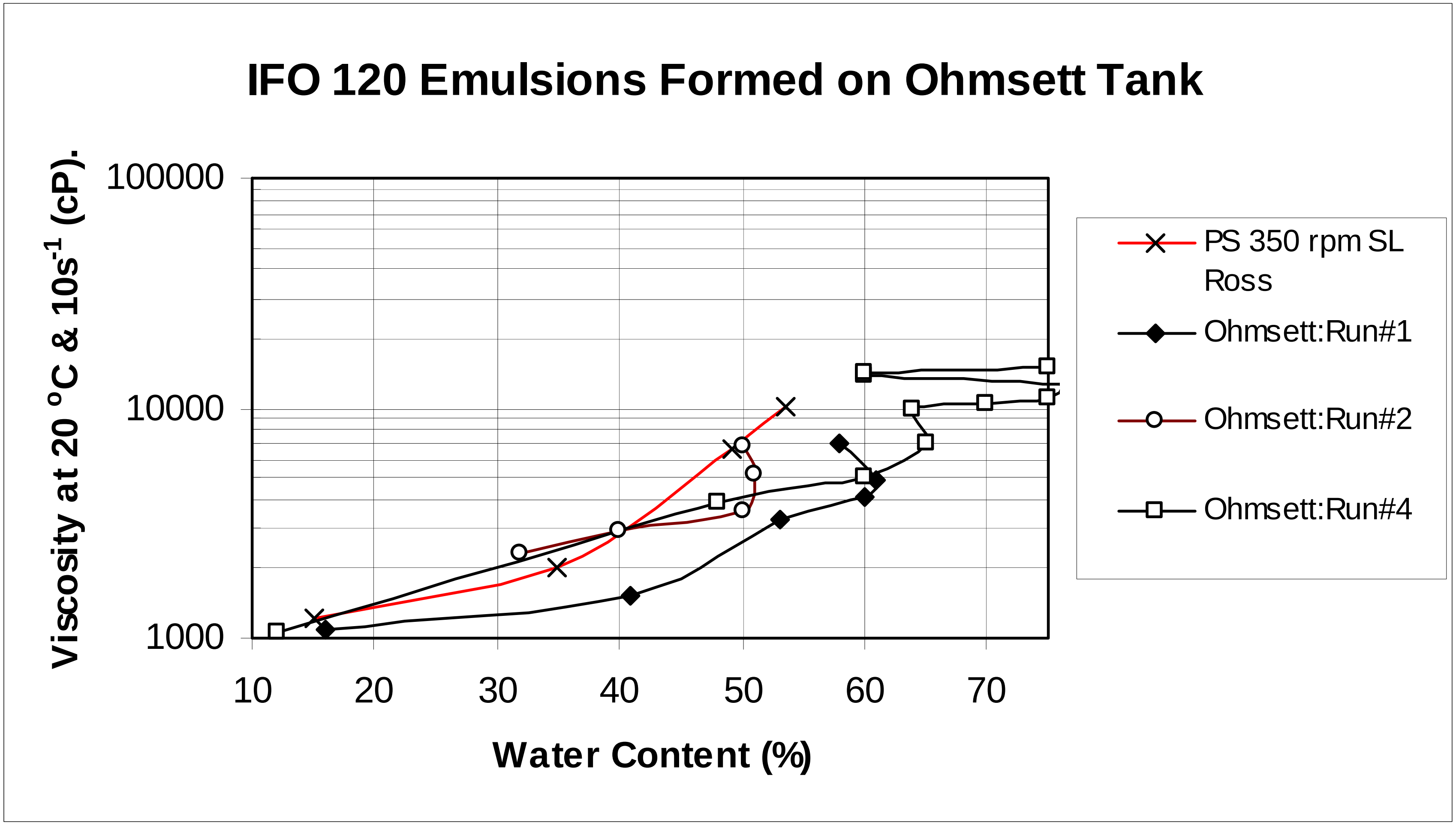


Figure 22. Ohmsett Test Tank Emulsion Viscosity versus Water Content for IFO 120 Fuel Oil

4.3 Endicott Crude Oil Test

One long-term emulsion formation test was completed on the Ohmsett tank using Endicott crude oil. A total of 65 litres was placed on the tank surface and was allowed to float freely on the tank. The oil in this test was subjected to breaking waves for a total of 5.5 hours of mixing over a 2-day period (December 15th and 16th).

The viscosities of the emulsions sampled in the test are plotted in Figure 23. The viscosity peaked at 4500 cP after about 4 hours of mixing.

Emulsion water contents versus time for the Endicott emulsion formed on the Ohmsett tank are plotted in Figure 24. The water content peaked at about 60 to 65% after 3 hours of mixing.

A viscosity versus water content plot for the Endicott emulsions formed on the Ohmsett tank is provided in Figure 25. The emulsion that formed increased in viscosity as the water content increased up to about 60%.

Example photos of emulsions from the large-scale Endicott crude oil emulsion formation tests on the Ohmsett tank are provided in Appendix C. These photos provide a visual record of the characteristics of the water-in-oil emulsions formed over the duration of the mixing period. Links to these photos are provided in Table 11. Details in these emulsion photos can be made clearer using the zoom feature of the software by readers accessing this report electronically.

Table 11. Hyperlinks to Photos of Endicott Emulsions Generated on the Ohmsett Tank

Hyperlinks to Emulsion Drop Size Photos	Figure Name
Emulsion after 20 minutes of mixing	Figure C6
Emulsions after 50 minutes	Figure C7
Emulsions after 100 minutes	Figure C8
Emulsions after 170 minutes	Figure C9
Emulsions after 230 minutes	Figure C10
Emulsions after 330 minutes	Figure C11

The small-scale test results for the paint stirrer, reported in Section 3.2.2, have also been plotted on Figures 23 through 25 for comparison. The paint stirrer created very similar emulsions to those formed on the Ohmsett tank when operated at 700 rpm, as seen in Figure 25. The rate of water uptake and increase in viscosity with time was slightly higher in the small scale paint stirrer tests than that measured in the Ohmsett tests but the emulsion viscosity vs water content curve is very similar in the two cases. Based on these comparisons it would appear that the paint stirrer is able to create emulsions similar to those formed on the Ohmsett tank under realistic breaking wave conditions.

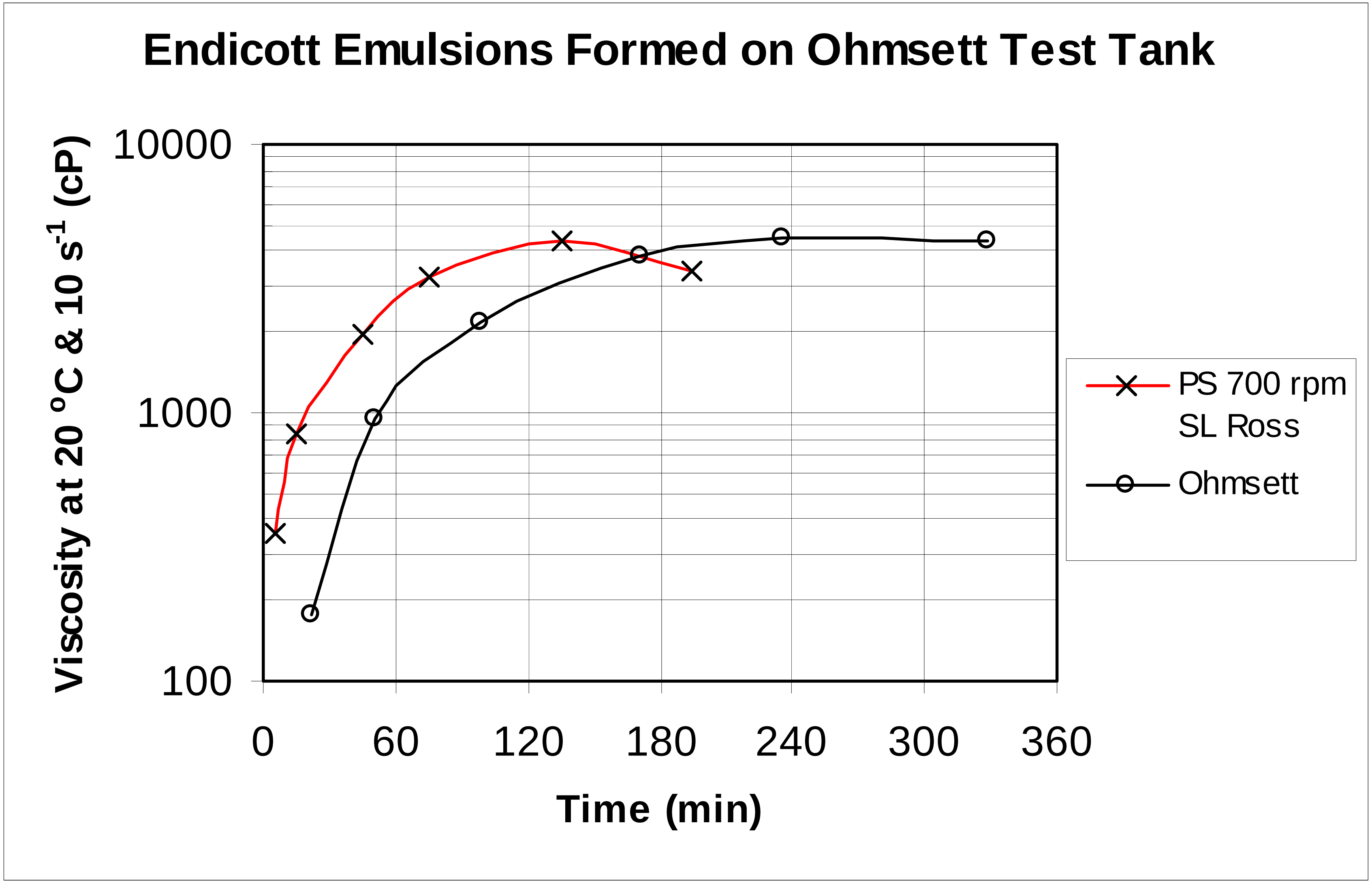


Figure 23. Ohmsett Test Tank Emulsion Viscosities for Endicott Crude Oil Test

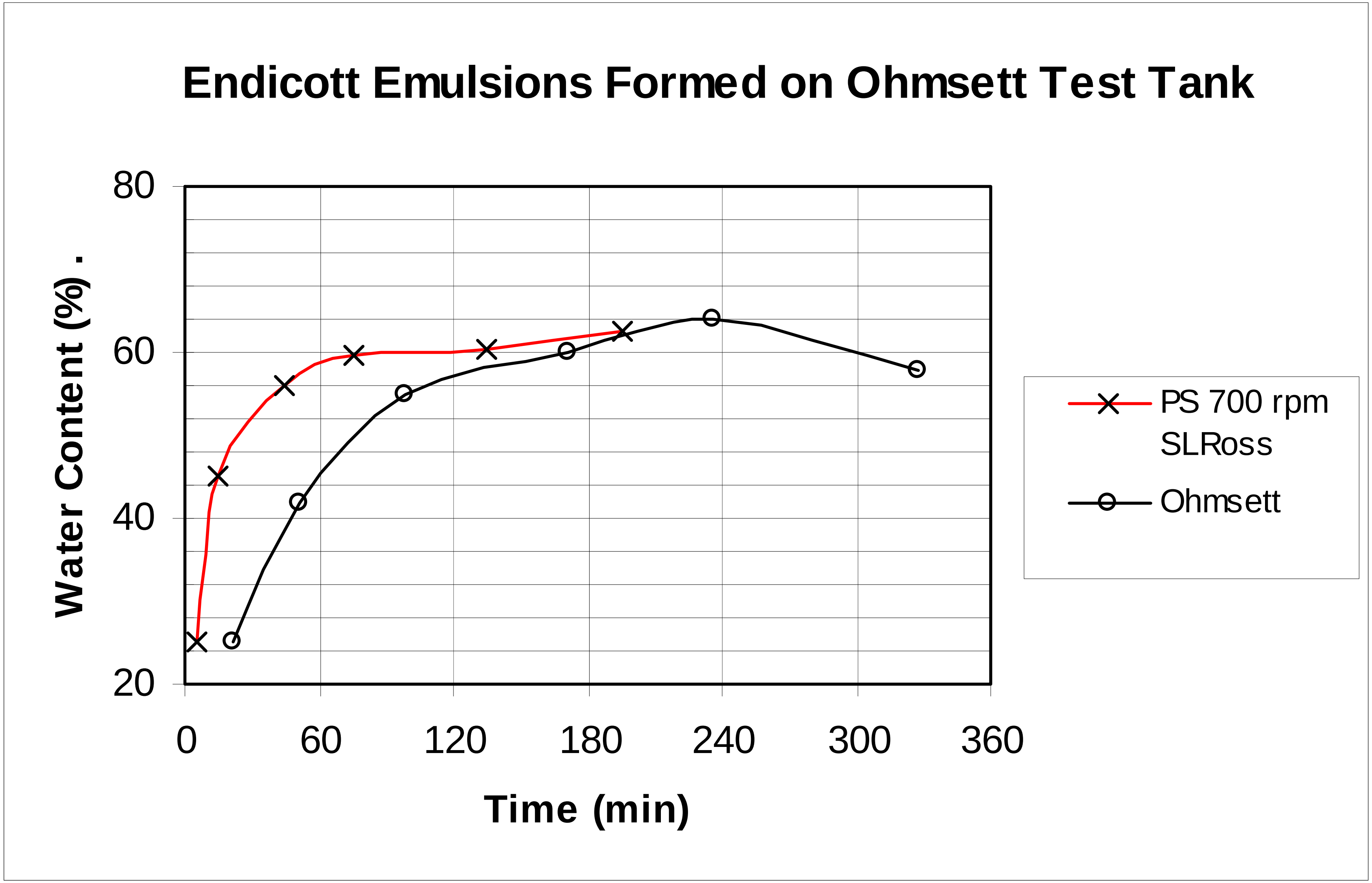


Figure 24. Ohmsett Test Tank Emulsion Water Contents for Endicott Crude Oil Test

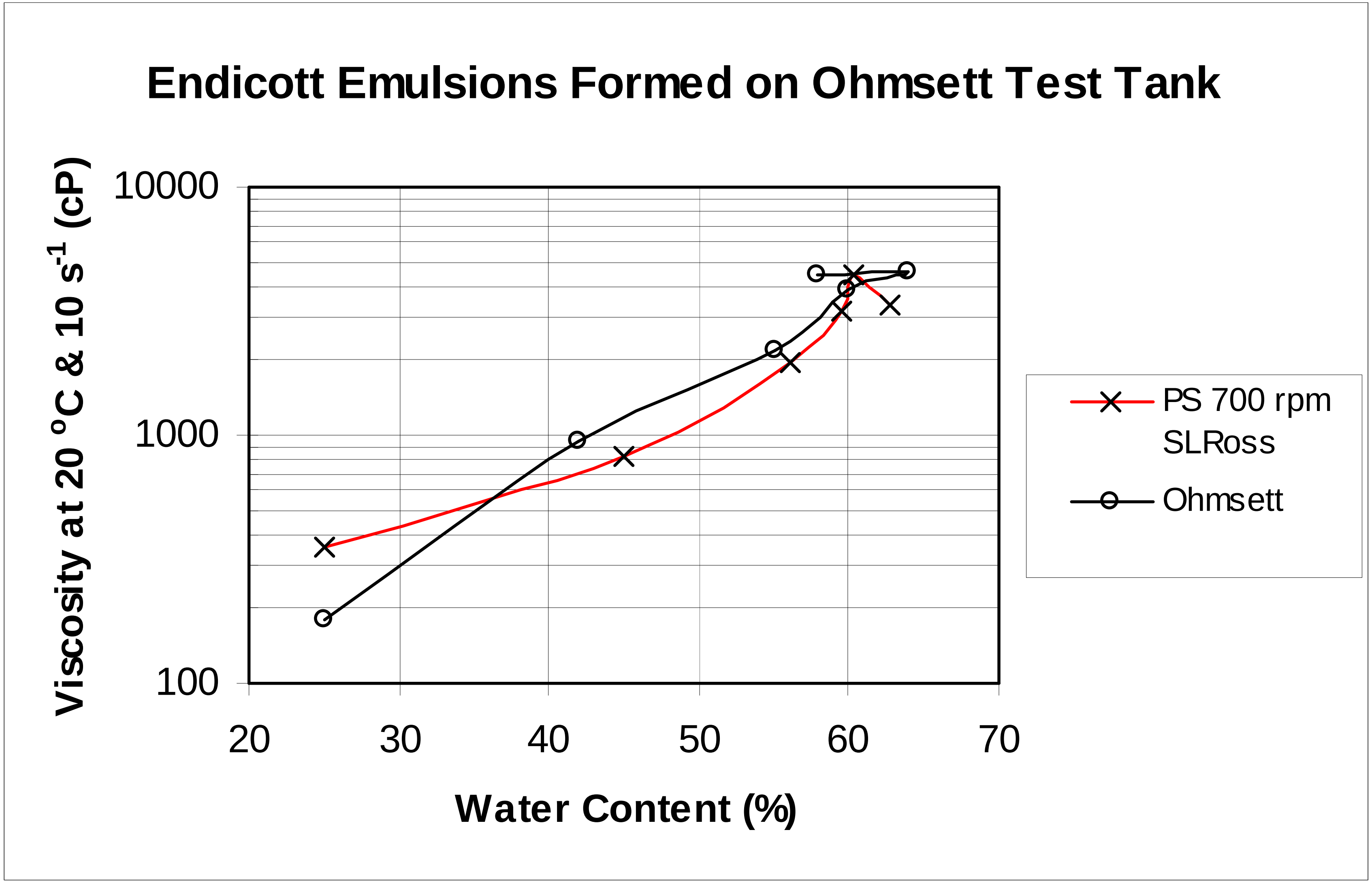


Figure 25. Ohmsett Test Tank Emulsion Viscosity versus Water Content for Endicott Crude Oil

5. Off-Tank Batch Emulsion Formation Tests at Ohmsett

A series of batch emulsion formation tests were completed at Ohmsett to determine if “drum-sized” quantities of water-in-oil emulsions could be generated with properties similar to the emulsions formed on the Ohmsett tank. A bladed mixer, with a design similar to the paint stirrer used in the small-scale emulsion formation tests described in Section 3, was used in this task. Figure 26 shows the mixing head used in the testing. These tests were completed in a standard open-top drum fitted with a plastic drum liner. A total of 11 tests were completed using IFO 120 fuel oil and two using Endicott crude oil. Fuel oil was used for most of these tests as emulsions made with the IFO 120 are more predictable than those made with the Endicott crude oil and a larger quantity of the IFO 120 fuel oil was available for testing. The water used in the tests was taken from the Ohmsett tank. Water temperatures during the tests ranged from 3˚C to 8˚C. The analytical methods used in this test series were identical to those described in Section 4.1.2.


Figure 26. Large Bladed Mixer

The bladed mixer shown in Figure 26 was chosen as the mixing method for these tests based on the results of the earlier small-scale testing described in Section 3 and the comparison of the small-scale paint stirrer results with the emulsions made on the Ohmsett tank (see Figure 22 and Figure 25).

The mixing blade tip speed of the larger mixer was initially set to the same value as was used in the small-scale mixing tests to achieve the similar mixing characteristics. Because the stirring paddle used in these larger batch-mixing tests has a larger diameter than the small-scale paint stirrer a lower rotational speed was necessary to match the blade tip speed of the smaller mixer. The first large-batch emulsion test used the large mixer operated at 130 rpm in 150 litres of salt water taken from the Ohmsett tank and 15 litres of oil. The oil-water ratio and mixing paddle tip speed matched that used in the small-scale emulsion tests in this first batch test completed at Ohmsett. Unfortunately the development of the emulsion in this test was much slower than that achieved in both the small-scale work and on the Ohmsett tank. This is evident from the plot of emulsion viscosities versus time in Figure 27. The rate of emulsion formation was too slow using these test conditions for the method to be practical.

A comparison of the mixer, and mixing container, geometries have been made in an attempt to explain the difference between these results and the small-scale paint stirrer results. The comparisons are summarized in Table 12.

Table 12. Scale Comparison of Mixing Devices

	Small-Scale Paint Stirrer	Large Bladed Mixer
Mixer Height (cm)	9	20
Oil Height (cm)	0.72	5.85
Height Ratio	12.5	3.42
Container Diameter (cm)	22.5	58.5
Mixer Diameter (cm)	6	14
Diameter Ratio	3.75	4.08
Blade Tip Speed (cm/s)	94 (@ 300rpm)	105 (@ 130 rpm)

The ratios of container and mixer diameters were very similar in the two cases (3.75 versus 4.08). This would suggest that the dynamics for drawing surface oil and water into the mixers would be similar in the two cases. The rotational speed of the mixer in test BST1 was set such that blade tip speeds was the same as that used in the small-scale tests. The main difference in the mixing device “scale” comparison between test BST1 and the small-scale paint stirrer tests is in the ratio of mixer height to oil (and water) depth. The small-scale paint stirrer blade’s height relative to the oil depth is greater than that of the large bladed mixer by a factor of about 3.6. The shorter length of the blades on the large mixer (relative to total fluid depth) means that there is less blade length per unit fluid depth to shear the oil and water mixture and is possibly the main reason for the slow emulsion development in this test configuration. Unfortunately, standard mixing blades of this size are available only in the height to diameter ratio similar to that used in the testing. Future testing could consider using multiple mixing heads to achieve the same degree of mixing as was achieved in the small-scale tests.

Modifications to the mixing process were investigated in a series of additional tests to speed up the emulsification process while still creating emulsions with properties similar to those generated on the Ohmsett tank. The changes studied involved increasing the mixing blade rpm and reducing the water-to-oil ratio in the test to increase the energy being applied to form the emulsion. A total of 10 additional tests were completed using IFO 120 fuel oil in an attempt to find an acceptable technique to generate large quantities of realistic emulsions. A brief description of each of these tests is provided in Table 13.

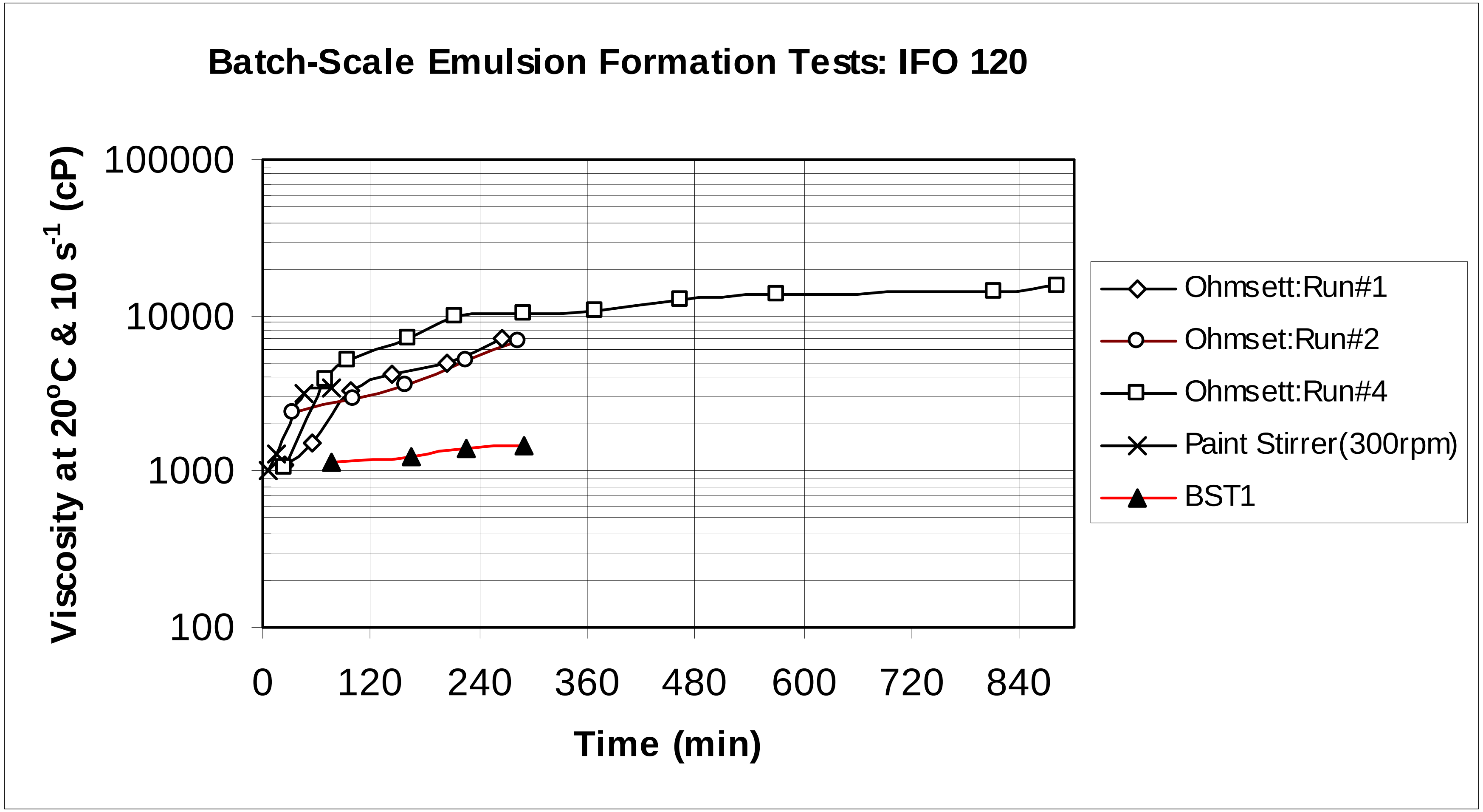


Figure 27. Initial Batch-Scale Emulsion Test Result

Table 13. Batch-Scale Test Condition Summary

Test ID	Oil Volume (L)	Initial Water Volume (L)	Final Water Volume (L)	# of Water Additions or Subtractions	Minimum Blade RPM	Maximum Blade RPM
IFO 120 Fuel Oil Tests						
BST1	15	150	150	1	130	200
	Mixed @130 rpm for 45 min. Mixer speed increased to 200 rpm.					
BST2	15	25	25	1	200	300
	Mixed at 200 rpm for 75 min. with little emulsification. Increased speed to 300rpm and emulsion formed within 15 min.					
BST3	15	25	25	1	130	300
	Mixed @ 300 rpm until brown emulsion formed (20 min.) then lowered rpm to 130 to “develop” emulsion further.					
BST4	15	150	150	1	320	320
	Emulsion built slowly over first 30 min. Emulsion appeared to be stable after 65 min. Unfortunately emulsion samples were not analysed for this run.					
BST5	15	150	150	1	330	330
	Mixer was placed deeper in the drum (top of mixer collar was submerged). Emulsion was slower to form than in test BST4 that was completed under similar conditions.					
BST6	15	150	150	1	330	330
	Mixer not placed as deep as in BST5. Top of blades just submerged. Emulsion formation was as slow as BST5 based on photos taken. No emulsion samples were taken in this test.					
BST7	15	25	25	1	150	325
	Mixed @325 rpm for 30 min. then @150 rpm for one hour to assess effect of additional low speed mixing on emulsion characteristics.					
BST8	15	50	50	1	150	340
	Mixed @340 rpm until brown emulsion first formed (45 min.) then mixed @ 150 rpm for another 30 min.					
BST9	15	100	50	2	150	350
	Mixed for 30 min. @350rpm and achieved very little emulsification. Removed 25 litres of water and mixed @320 rpm for 30 min. with little emulsification. Removed another 25 litres of water and mixed @320 rpm for 45 min. and brown emulsion finally formed. Mixed for another 30 min. @150 rpm.					
BST10	35	120	120	3	410	250
(large oil quantity)	Very little emulsification after 90 min. of mixing @350 rpm. Removed 30 L of water and mixed @320 rpm for 1 hour with minimal emulsification. Increased mixing speed to 410 rpm and stiff emulsion formed within 15 min. 30 L of water was added back into the drum and mixed @410 rpm for 15 min. Another 30 L of water was added to the drum and the mixer was lowered. Mixed for 30 min. @250 rpm then 20 min. @ 360 rpm. Motor overheated due to load from viscous emulsion.					
BST11	25	60	120	3	400	400
(large oil quantity)	Stiff emulsion formed after 70 min. of mixing @ 400rpm. Added 30 L of water mixed for another 15 min. and added another 30 L of water and mixed for an additional 20 min. @350 rpm.					
Endicott Crude Oil Tests						
BST12	15	25	25	1	150	400
	Full emulsion formed after 65 min. of mixing @400 rpm. Speed reduced to 200 rpm and mixing continued for 55 min.					
BST13	32	45	75	2	415	250
	Stiff emulsion formed after 148 min. of mixing @ 415rpm. Added 30 L of water and mixed @250 rpm for 30 min. after lowering the mixer to					

The oil-to-water ratios for tests BST1, BST4, BST5 and BST6 were similar (about 1 part oil to 10 parts of water). This high ratio results in the mixing of a significant amount of water with a small amount of oil and slows the emulsion formation process. However, the presence of a large amount of water in the mix better mimics the process that would occur at sea. Figure 28 shows the viscosity versus water content relationships for the emulsions of runs BST1 and BST5 compared against the results from Run #4 on the Ohmsett tank (the longest data set available for the IFO 120 emulsions generated on the Ohmsett tank). Viscosity data were not collected for runs BST4 and BST6. As discussed earlier, the low-speed mixing used in BST1 did not generate a strong emulsion over a reasonable time period. The characteristics of the emulsions formed did however match the emulsions formed in the very early stages of the on-tank emulsion formation tests. The emulsion viscosity-water content characteristics from tests BST5 also matched the emulsions formed on the tank quite well but again the time required to form the emulsion was prohibitive. One possible option to increase the emulsion formation rate could be to operate two or more of the bladed mixers at the same time in the high oil-to-water ratio environment.

A comparison of water drop sizes in the emulsions from the Ohmsett “on-tank” test (Run #4) and the batch runs (BST1 and BST5) are provided in Appendix D. Figure D1shows photos for the early emulsions with about 12% water content and Figure D2 shows photos for emulsions with about 60% water content. The photos from the on-tank and batch tests are very similar for the early emulsions. The photos from 60% water content emulsions have a similar but not identical appearance.

In an attempt to speed up the batch production of emulsion using the bladed mixer, a number of tests were completed with smaller amounts of water. Tests BST2, BST3 and BST7 all used 15 liters of oil and 25 litres of water (oil-to-water ratio (OWR) of 1: 1.7)). In all three of these tests emulsions formed relatively quickly depending on the speed of the mixer. Tests BST9 and BST10 were started with large quantities of water present but when emulsions were slow to form water was removed from the bottom of the drum in stages until rapid emulsification occurred. In these cases emulsification began once the oil-to-water ratio reached 1:3.3 for test BST9 and 1.2.6 for BST10. Test BST8 was completed with a 1:3.3 OWR and a 340-rpm mixer speed and the emulsion formed within 15 minutes. In all of these tests where emulsions formed within a reasonable time using the bladed mixer the OWR was 1:3.3 or greater. The only problem with starting with a small amount of water in these tests is the possibility that the emulsions formed might not match those formed on the tank at Ohmsett. A comparison of the viscosity-water content relationships for the batch scale tests and the Ohmsett generated emulsions from Run #4 is shown in Figure 29.

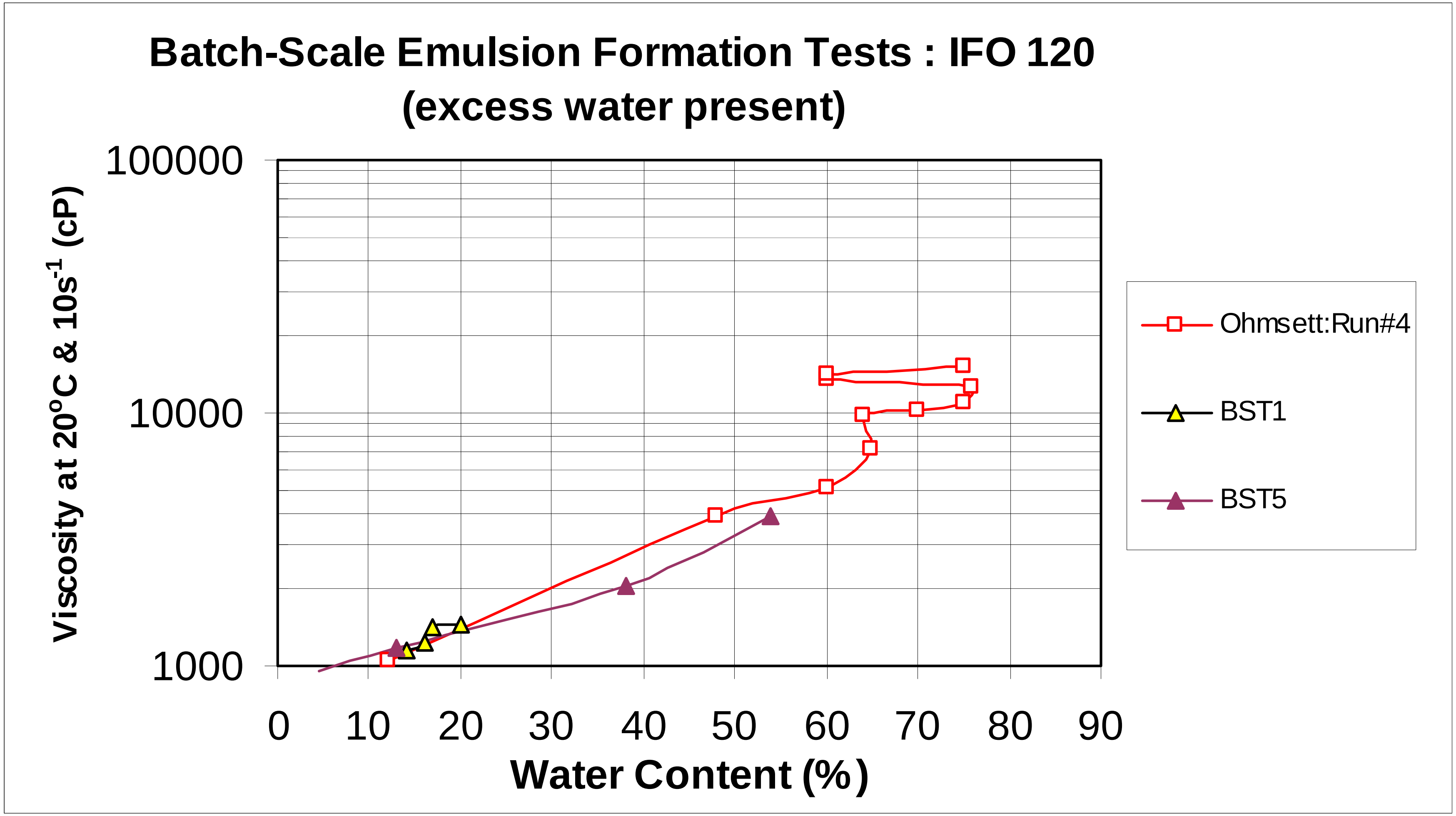


Figure 28. Batch Scale Test Emulsion Characteristics: IFO 120 Fuel Oil with Excess Water

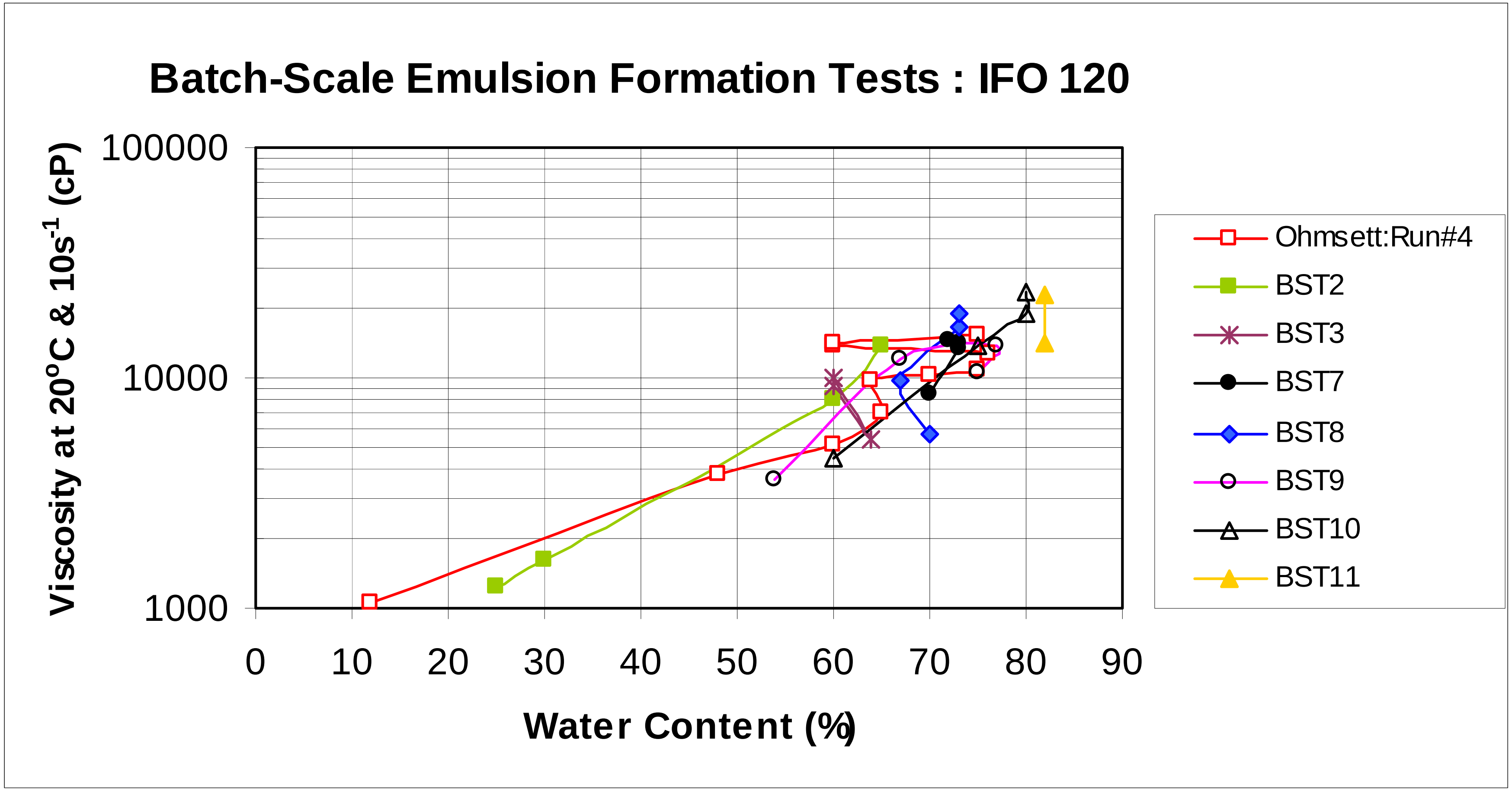


Figure 29.Batch Scale Test Emulsion Characteristics: IFO 120 Fuel Oil

Emulsion properties were measured only after the emulsions had significant water uptake for most of the batch scale tests whose results are shown in Figure 28. As a result, most of the data shown falls in the upper portion of the Ohmsett data from Run #4. While the data exhibit some scatter, the emulsions formed in the batch scale tests have viscosity-water content characteristics similar to the emulsions formed on the Ohmsett tank. Figures D3 through D7 show photos of emulsions from the batch tests and Ohmsett Run # 4 with similar water contents and viscosities. For most cases the water droplets in the emulsions formed on-tank and formed using the bladed mixer have similar appearances. Hyperlinks to these photos are provided in Table 14.

Table 14. Hyperlinks to Photos: Ohmsett Tank and Batch Generated IFO 120 Emulsions

Emulsion Descriptions	Hyperlinks
Run#4 & BST9 (approx. 50% water content)	Figure D3
Run #4 BST2, BST10 (60% wc)	Figure D4
Run #4, BST7, BST8 (70% wc)	Figure D5
Run #4, BST7, BST8, BST9, BST10 (75% wc)	Figure D6a, D6b
BST10 & BST11 (80% wc)	Figure D7

As the emulsion water contents and viscosities increase the difference in the appearance of the photos becomes less apparent. The photos of Figures D5, D6 and D7 are very similar even though the emulsion viscosities in these photos range from about 9000 to 23,000 cP. More sophisticated slide preparation techniques would possibly improve the ability to see differences in these emulsions.

Two batch scale tests were completed using Endicott crude oil. A comparison of the viscosity-water content characteristics of the emulsions formed in these tests with those generated on the Ohmsett tank is provided in Figure 30.

The emulsion viscosities generated in the batch process followed a similar trend to those formed on the Ohmsett tank but they were consistently lower in magnitude. This difference is likely due to a lower parent oil viscosity for the oil in the Ohmsett “on-tank” tests. Unlike the IFO 120 fuel oil the Endicott crude is made up of a significant amount of light ends and the oil evaporated quickly when spilled on the Ohmsett tank. Unfortunately parent oil viscosities were not measured for the emulsions sampled in this project so a direct comparison of parent oil viscosities cannot be made and can only be inferred based on the available density data. Table 15 shows the increase in density of the Endicott crude oil during the tank test. The Endicott crude oil used in the batch emulsion tests was artificially weathered using an air bubbler system prior to the tests. The oil used in the batch tests started with a density of approximately 0.90 g/cm^3. The higher densities recorded for the oils from the tank tests (particularly the 22 minute exposure sample) indicate that the viscosities of the parent oil in the on-tank emulsions would be higher than the viscosities of the parent oil in the batch tests. If the oil used in the batch tests had been artificially evaporated to a higher degree then the curves in Figure 30 would likely match more closely.

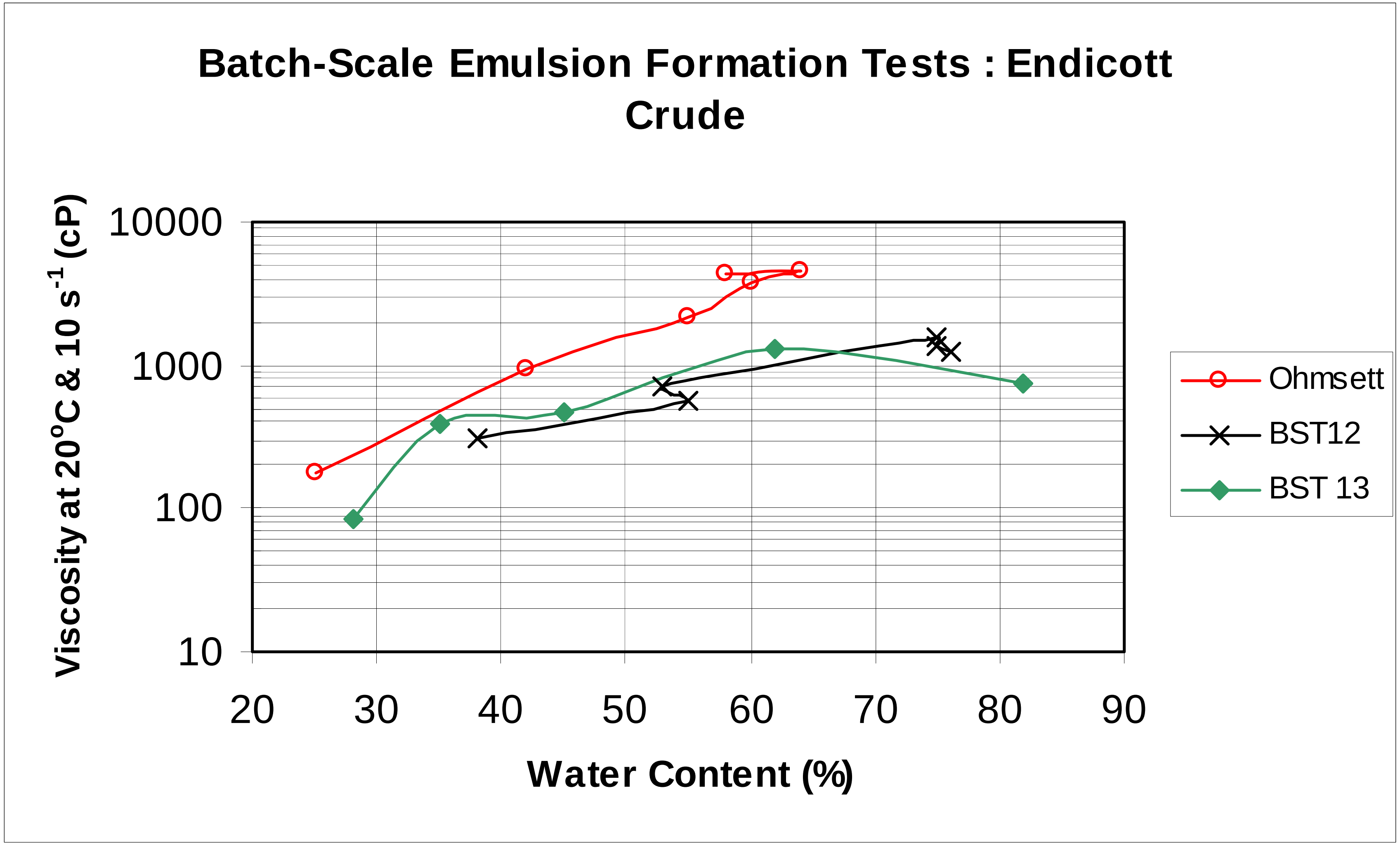


Figure 30. Endicott Crude Oil Emulsion Characteristics

Table 15. Endicott Crude Oil Properties From Ohmsett Tank Emulsification

Exposure Time (min)	Parent Oil Density (g/cm^3)
Fresh oil	0.897
22	0.920
171	0.942
328	0.972
Artificially Weathered Endicott	0.913

Photographs of the emulsions formed on the Ohmsett tank and in the batch mixes are provided in Appendix D in Figures D 8 through D11. Hyperlinks to these photos are provided in Table 16.

Table 16. Hyperlinks to Photos: Ohmsett Tank and Batch Generated Endicott Emulsions

Emulsion Descriptions	Hyperlinks
Run#3 & BST13 (approx. 25% water content)	Figure D8
Run #3 BST13 (45% wc)	Figure D9
Run #3, BST12 (55% wc)	Figure D10
Run #3, BST13 (60%)	Figure D11

The photos of the batch-mixed emulsions have a “cleaner” more transparent look than the emulsion photos of the on-tank emulsions. This may be because the on-tank oil is ore heavily weathered than the oil used in the batch mixes. The water drop sizes in the emulsions are similar but the batch mixed emulsions appear to have more intermediate sized water drops when compared to the Ohmsett tank formed emulsions.

6. Conclusions

A spiral paint stirrer was identified as the most appropriate mixing device to create emulsions with properties similar to those expected from oils spilled at sea.

Full-scale emulsion formation tests were completed on the Ohmsett tank using IFO 120 fuel oil and Endicott crude oil. The viscosities and water contents of these emulsions increased rapidly during the initial mixing and then stabilized indicating that the emulsions formed had reached a state that could be expected to exist at least during the first few days of exposure of oil at sea. The emulsions formed in the tests provide a realistic benchmark for emulsions of these oils created at sea.

Based on the results of the larger scale batch emulsion formation tests and the full-scale on-tank tests completed at Ohmsett, the following procedure is recommended for the “off-tank” formation of drum-sized quantities of realistic emulsions.

- Place 120 litres of salt water and 40 litres of oil into a 55 gallon drum. This water-to-oil ratio will generate a maximum 75% water content emulsion (the maximum water content achieved in the Ohmsett on-tank tests).
- Mix the oil and water with the bladed mixer operated at 350 to 400 rpm with the mixer submerged just below the oil surface only until the oil and water forms an obvious water-in-oil emulsion. Formation of the emulsion should occur within 15 to 30 minutes. Do not continue mixing at high rpm after the emulsion forms as this has

been shown to form emulsion with excessive viscosities when compared to emulsions formed in a breaking wave environment.

- Photographs of the emulsions can be taken for comparison to photos of emulsions formed on the Ohmsett tank to confirm that the emulsions have a similar structure to those created by breaking waves. Photos of emulsions formed with low viscosity crude oils should be compared to photos from the Endicott tests (Run #3) and photos of emulsions formed from high viscosity oils should be compared to photos from the IFO 120 tests.

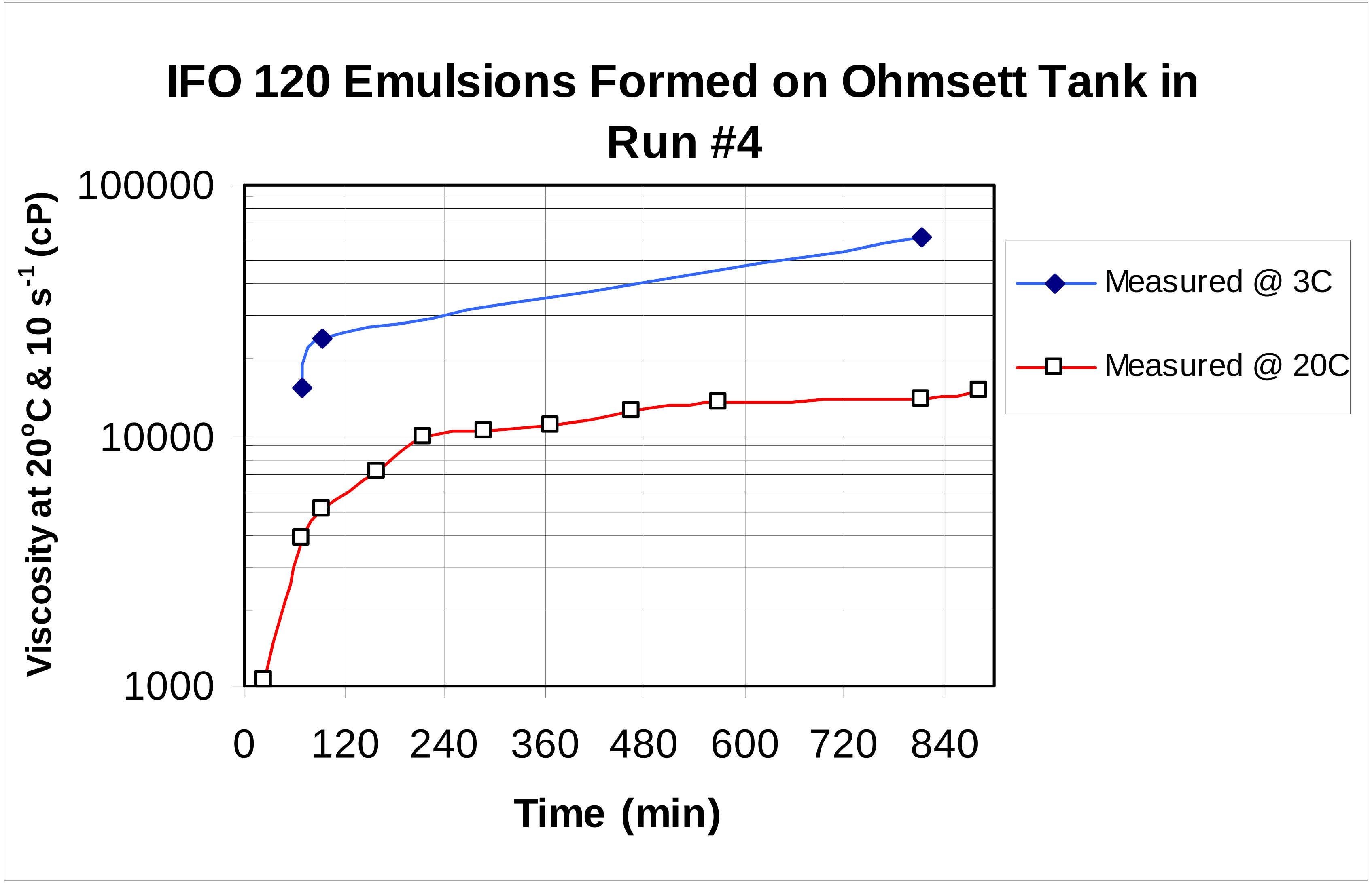
7. Recommendations

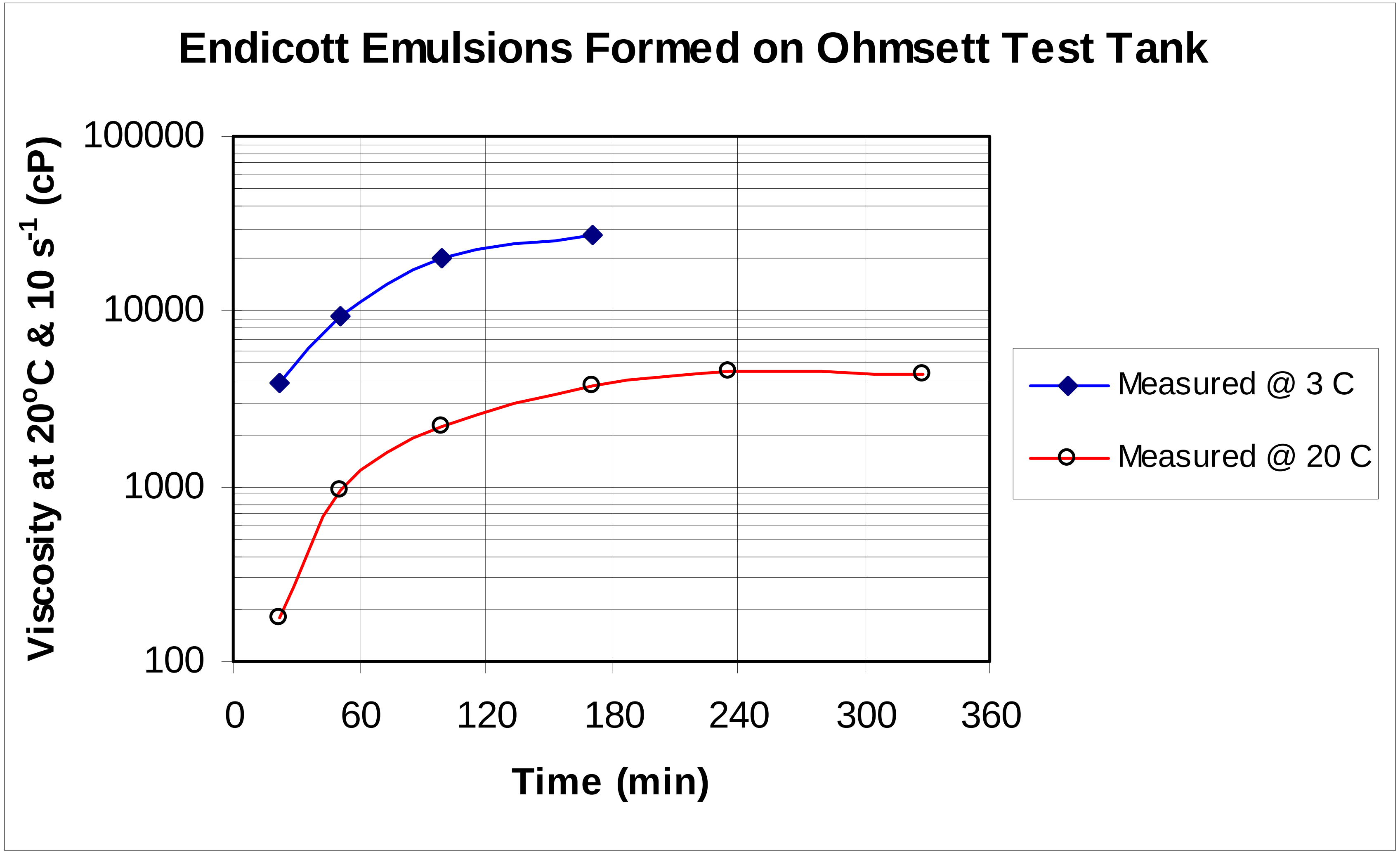
The following additional work is recommended to further advance the understanding of water-in-oil emulsions that are formed under conditions similar to when oil is spilled at sea.

1. Complete additional long-term emulsion formation tests on the Ohmsett tank to gather water-in-oil emulsion properties and characteristics for a variety of crude oils.

2. Refine the batch process for creating realistic emulsions “off-tank”. Specifically, determine if increasing the number of bladed mixers used in the mixing process will enable realistic emulsions to be formed, in a reasonable time frame, when oil to water ratios of 1:10 are used. Small-scale tests suggest that emulsions made under these “excess water” conditions may be more consistent than those generated when smaller water quantities are used.

8. Appendix A. Emulsion Viscosities at Ohmsett Tank Temperatures and at 20 ˚C

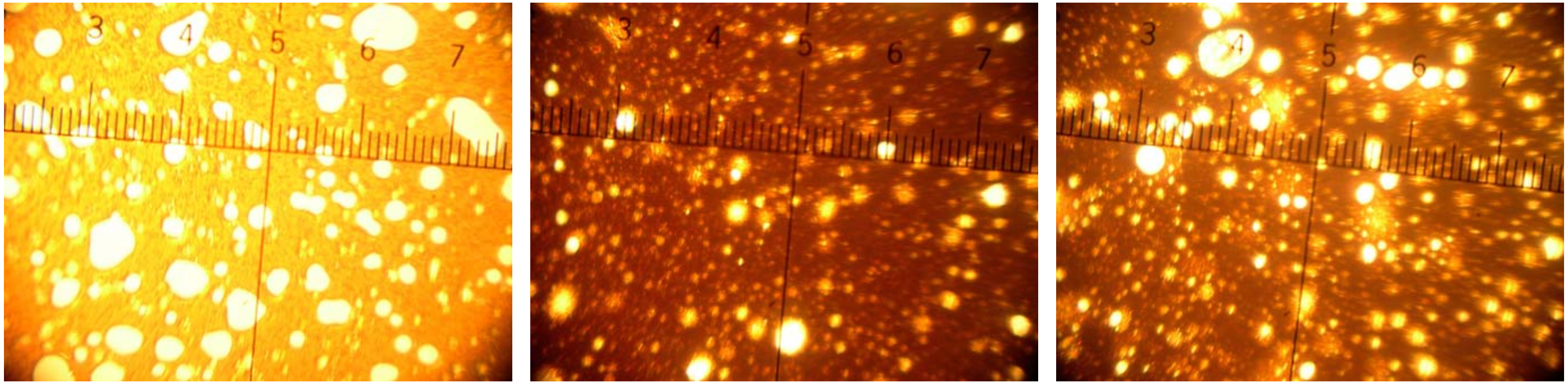



Endicott Emulsions Formed on Ohmsett Test Tank
Viscosity at 20°C & 10 s-1 (cP)
100000
10000
1000
100
0
60
120
180
240
300
360
Time (min)
Measured @ 3 C
Measured @ 20 C

9. Appendix B. Emulsion Photos from Small Scale Tests

9.1 IFO 120 Fuel Oil with Excess Water Present

Figure B1. Progressing Cavity Pump: IFO 120 Emulsions made with excess water present

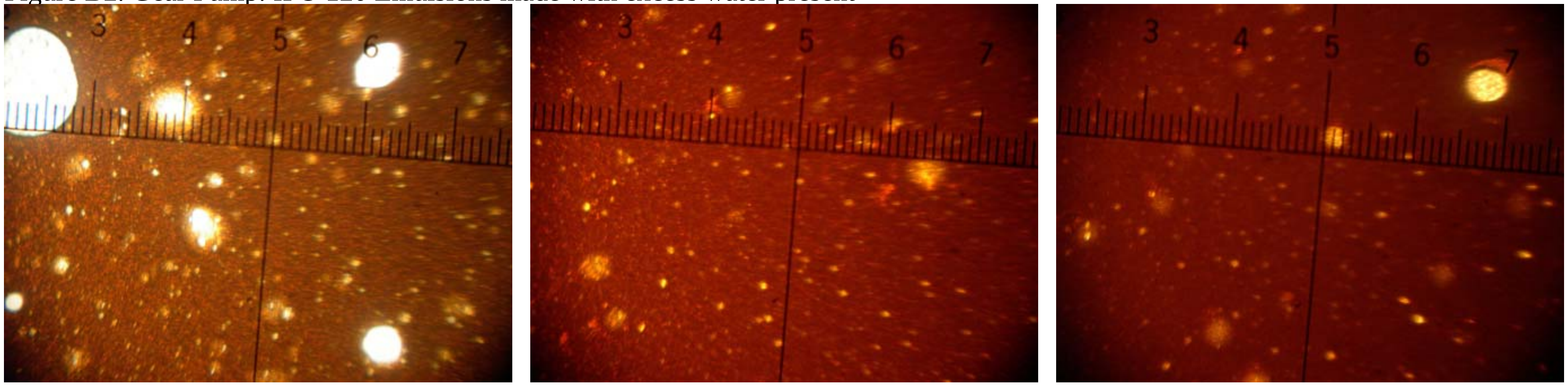


15 minutes
1900 cP

45 minutes
3500 cP
43% wc

105 minutes
4100 cP
50% wc

Figure B2. Gear Pump: IFO 120 Emulsions made with excess water present

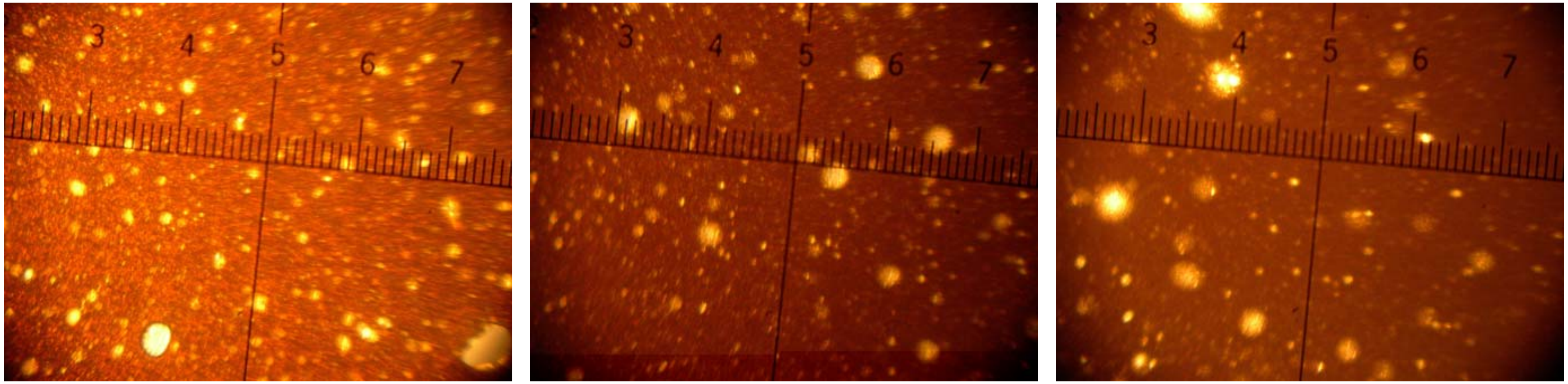


15 minutes
1500 cP

45 minutes
3400 cP
37% wc

75 minutes
14000 cP
42% wc

Figure B3. Double Diaphragm: IFO 120 Emulsions made with excess water present

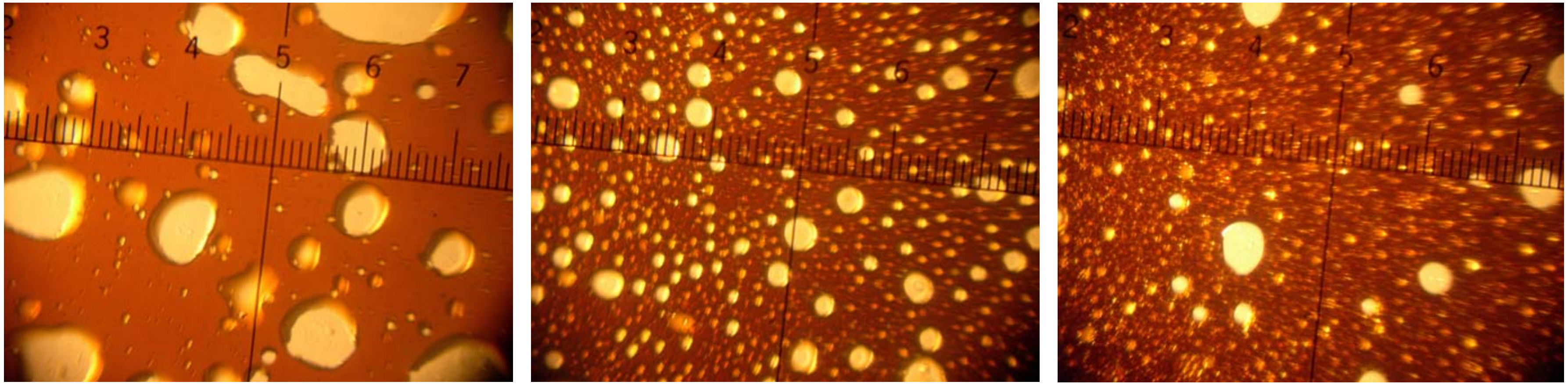


15 minutes
2300 cP

45 minutes
5500 cP
40% wc

85 minutes
15000 cP
53% wc

Figure B4. Paint Stirrer (300 rpm): IFO 120 Emulsions made with excess water present

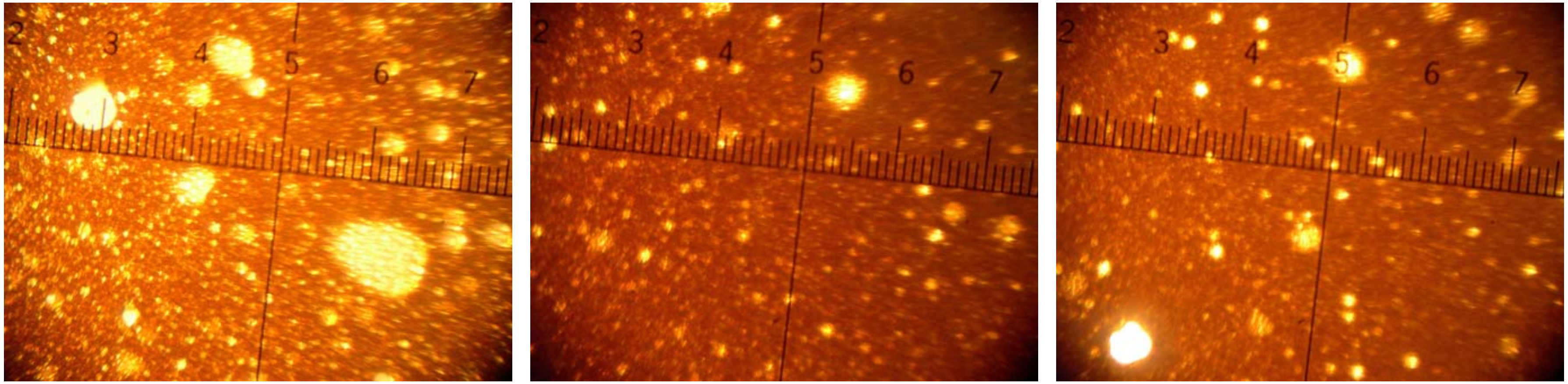


15 minutes
1300 cP

45 minutes
3200 cP
49% wc

75 minutes
3500 cP
53.5% wc

Figure B5. Paint Stirrer (750 rpm): IFO 120 Emulsions made with excess water present

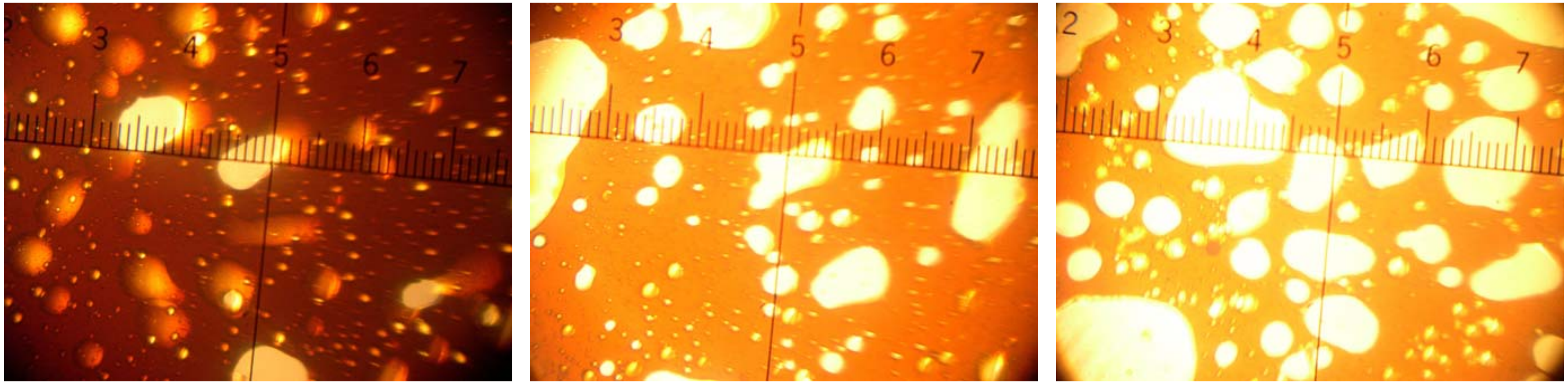


15 minutes
9000 cP
48% wc

45 minutes
14000 cP
56% wc

75 minutes
17000 cP
57% wc

Figure B6. Cement Mixer (19 rpm): IFO 120 Emulsions made with excess water present

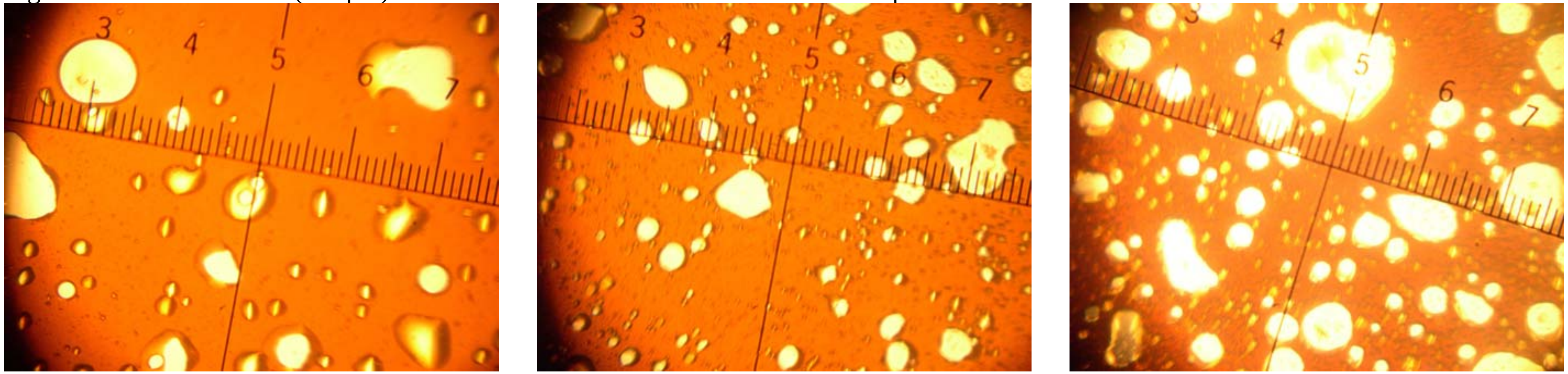


15 minutes
1200 cP

45 minutes
2000 cP
36% wc

75 minutes
3000 cP
48% wc

Figure B7. Cement Mixer (30 rpm): IFO 120 Emulsions made with excess water present



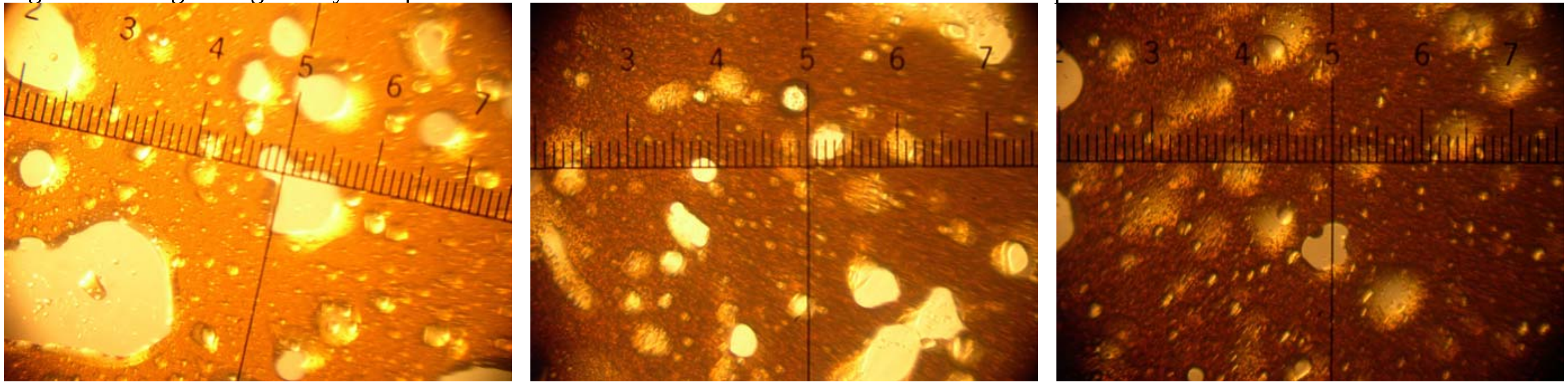
15 minutes
1240 cP

45 minutes
2260 cP
42% wc

75 minutes
3300 cP
52% wc

9.2 Endicott Crude Oil with Excess Water Present

Figure B8. Progressing Cavity Pump: Endicott Crude Oil Emulsions made with excess water present

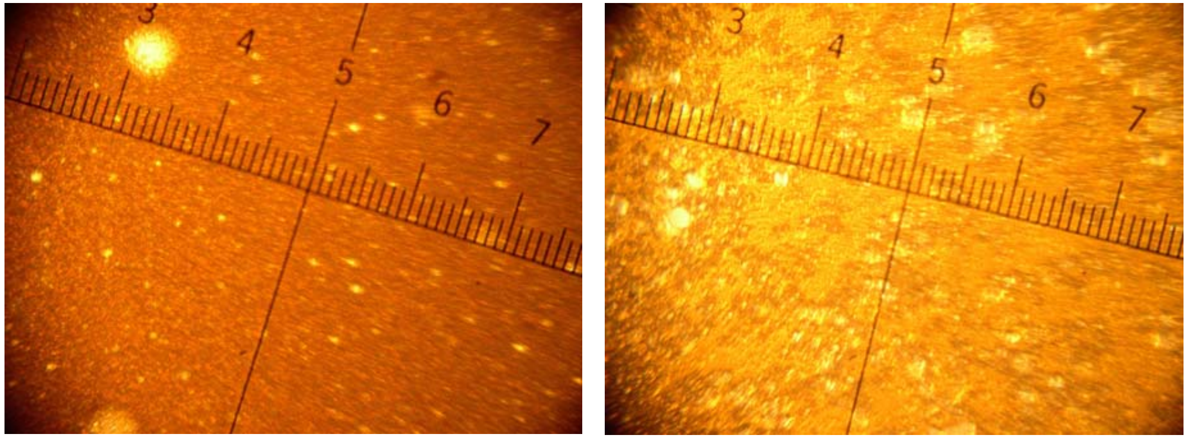


15 minutes
265 cP

45 minutes
800 cP
44% wc

120 minutes
1380 cP
47% wc

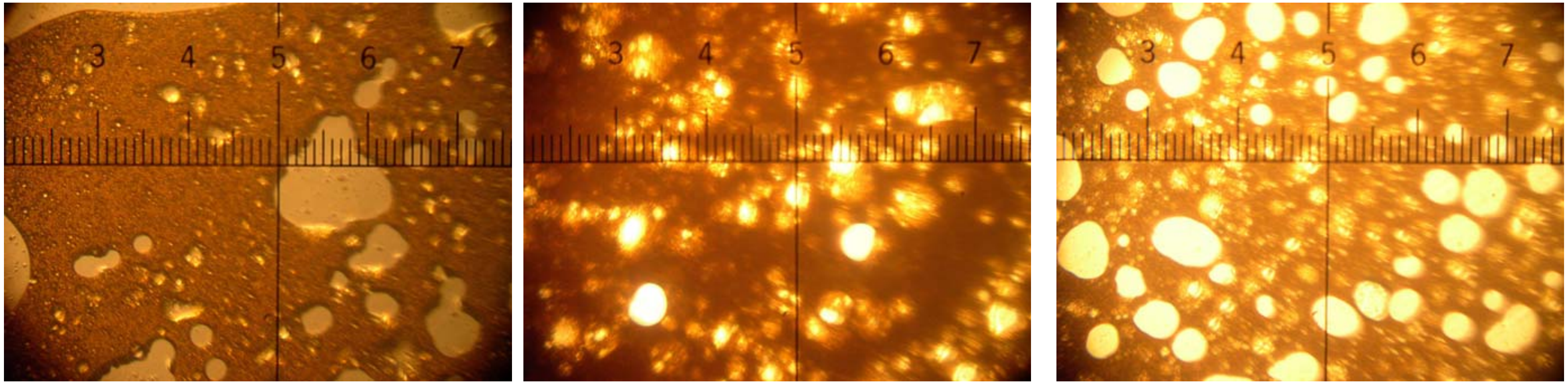
Figure B9. Gear Pump: Endicott Crude Oil Emulsions made with excess water present



20 minutes
350 cP

50 minutes
660 cP
26% wc

Figure B10. Double Diaphragm: Endicott Crude Oil Emulsions made with excess water present

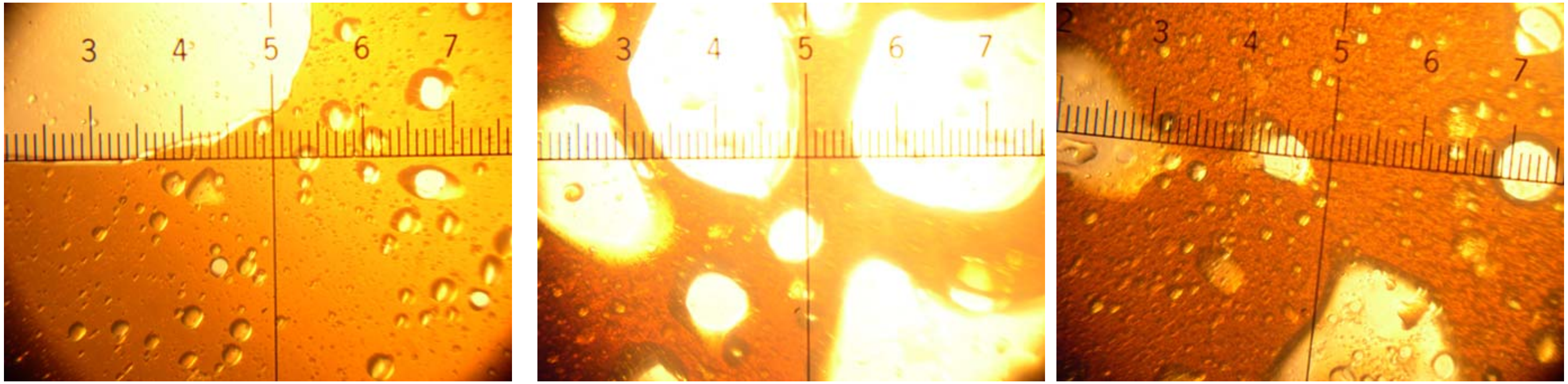


15 minutes
560 cP
44% wc

45 minutes
1350 cP
54% wc

105 minutes
1840 cP
54% wc

Figure B11. Paint Stirrer (700 rpm): Endicott Crude Oil Emulsions made with excess water present

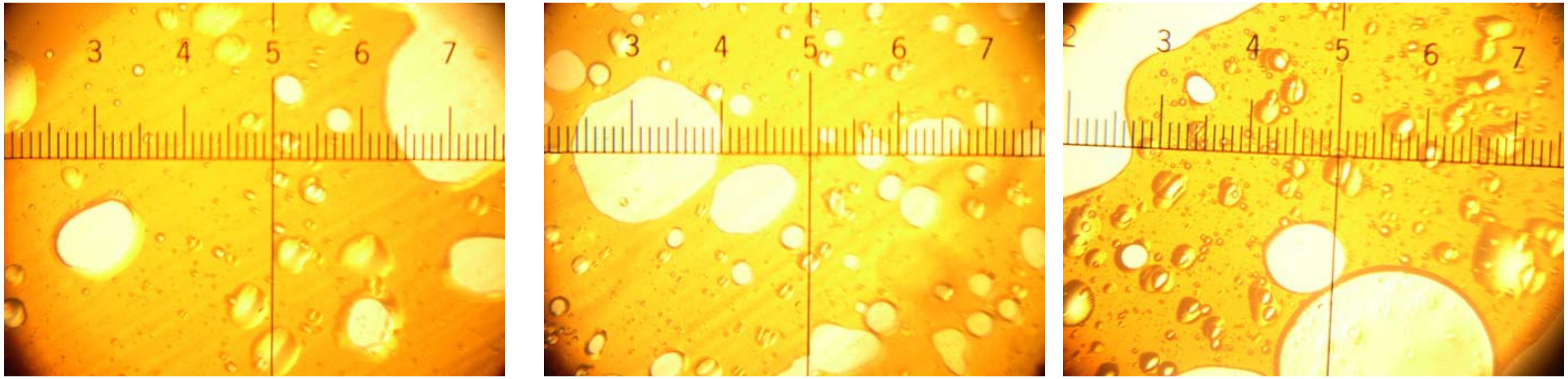


15 minutes
300 cP

45 minutes
760 cP
56% wc

75 minutes
1760 cP
60% wc

Figure B12. Cement Mixer (30 rpm): Endicott Crude Oil Emulsions made with excess water present



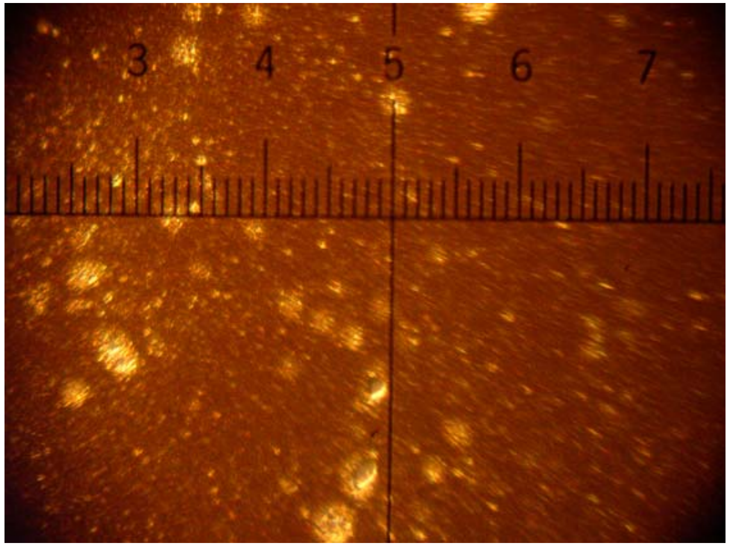
15 minutes
270 cP

45 minutes
590 cP
27% wc

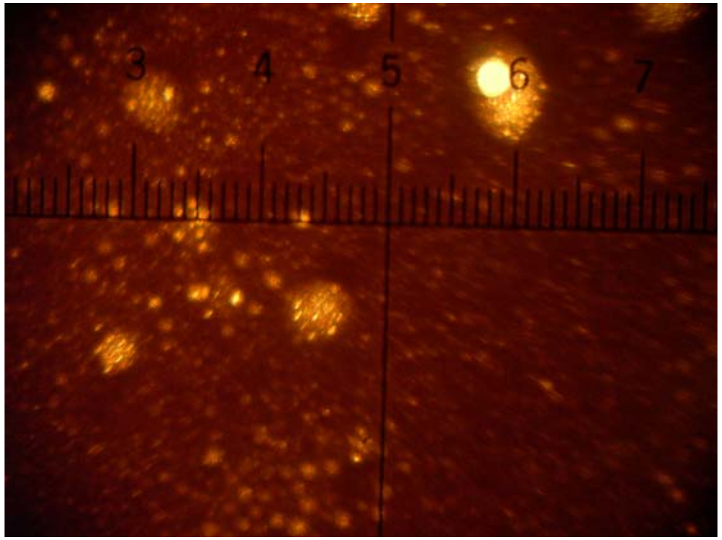
75 minutes
830 cP
44% wc

9.3 *IFO 120 Fuel Oil with Slow Water Addition*

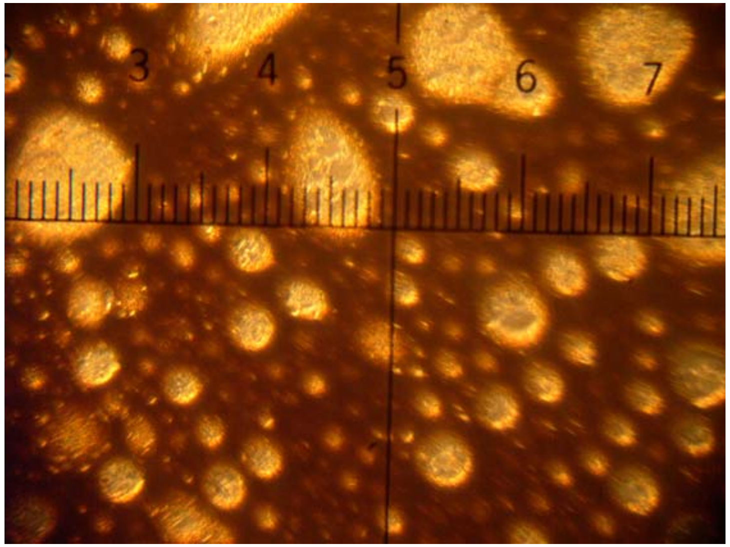
Figure B13. Progressing Cavity Pump: IFO 120 Fuel Oil Emulsions: Slow Addition of Water



15 min 23694 cP 55% wc (60)

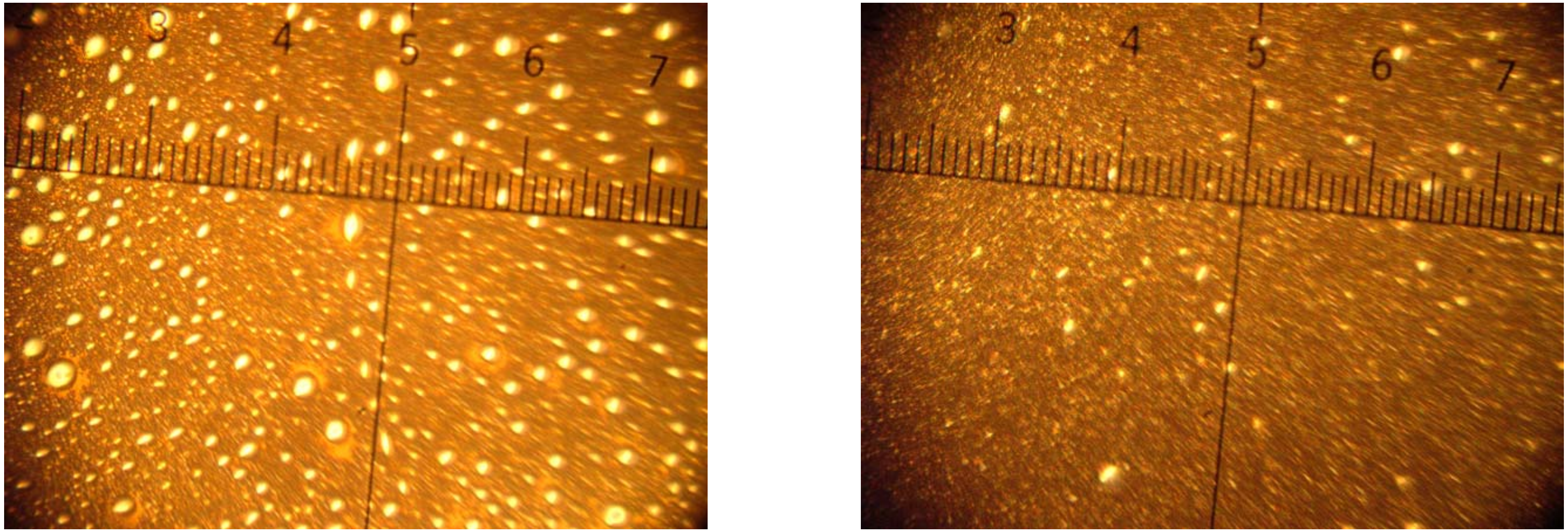


30 min 31949 cP 64% wc (70)



50 min 25996 cP 77% wc (80)

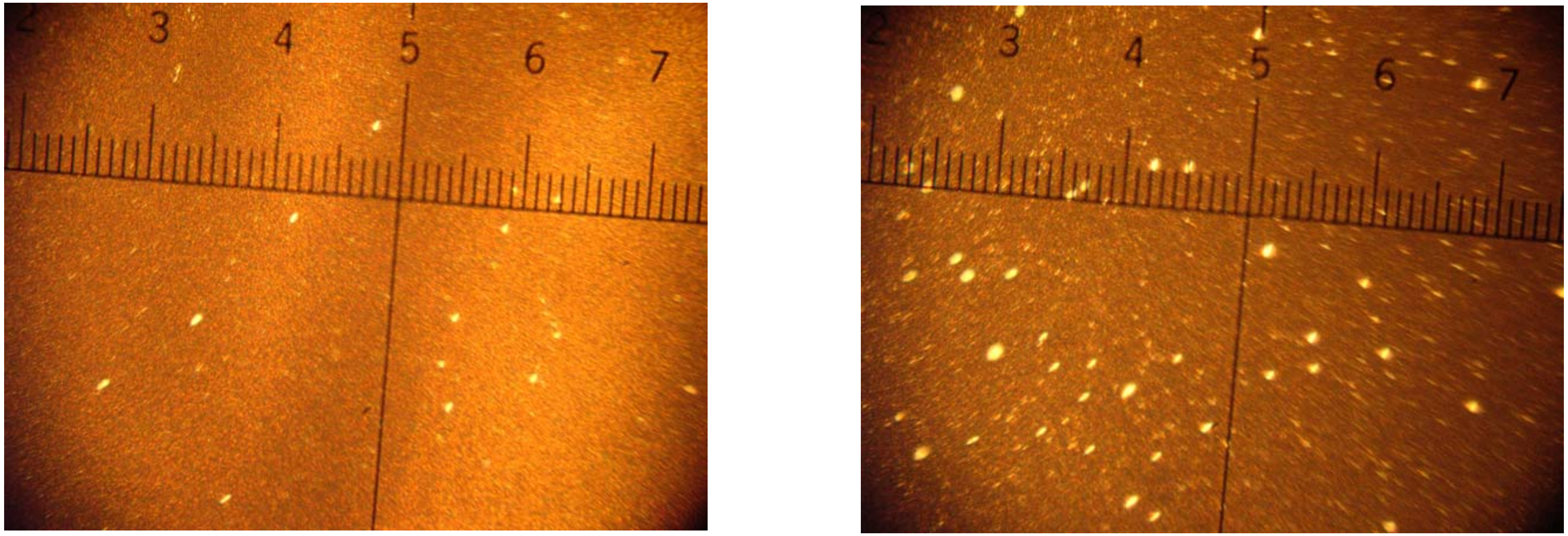
Figure B14. Double Diaphragm Pump: IFO 120 Fuel Oil Emulsions: Slow Addition of Water



8 min 13375 cP 58 %wc (60)

16 min 30,758 cP 66% wc (70)

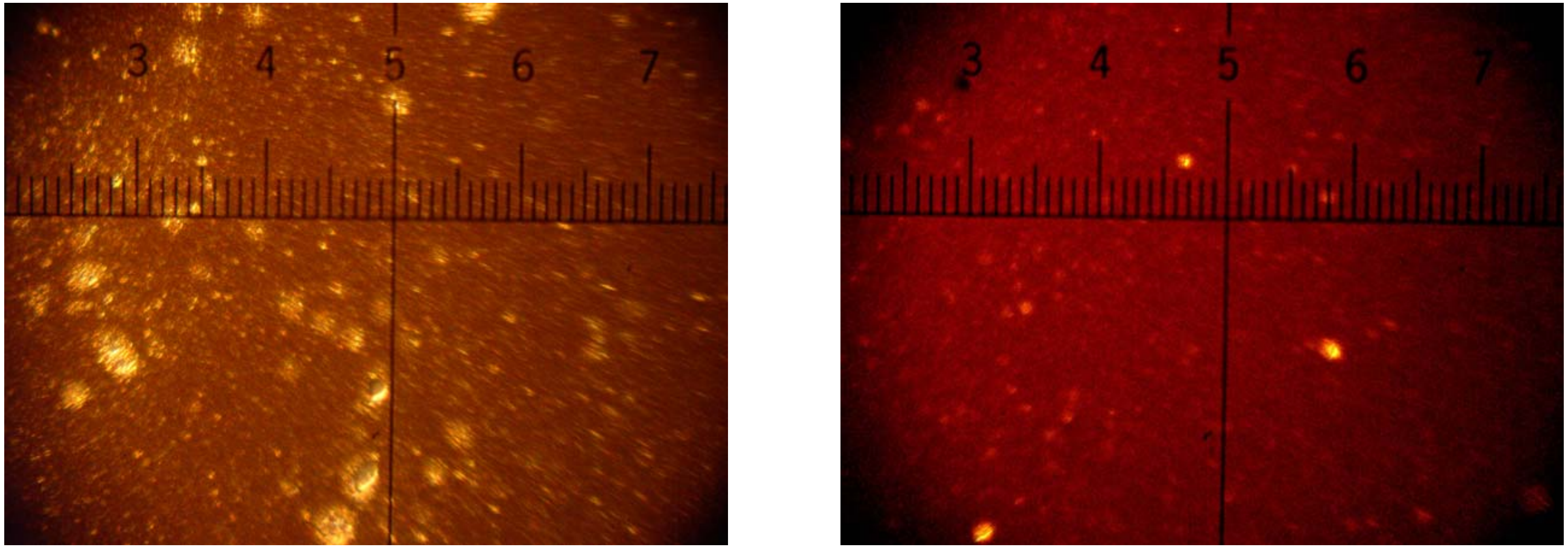
Figure B15. Gear Pump: IFO 120 Fuel Oil Emulsions: Slow Addition of Water



7 min 32,862 cP 57.8% wc (60)

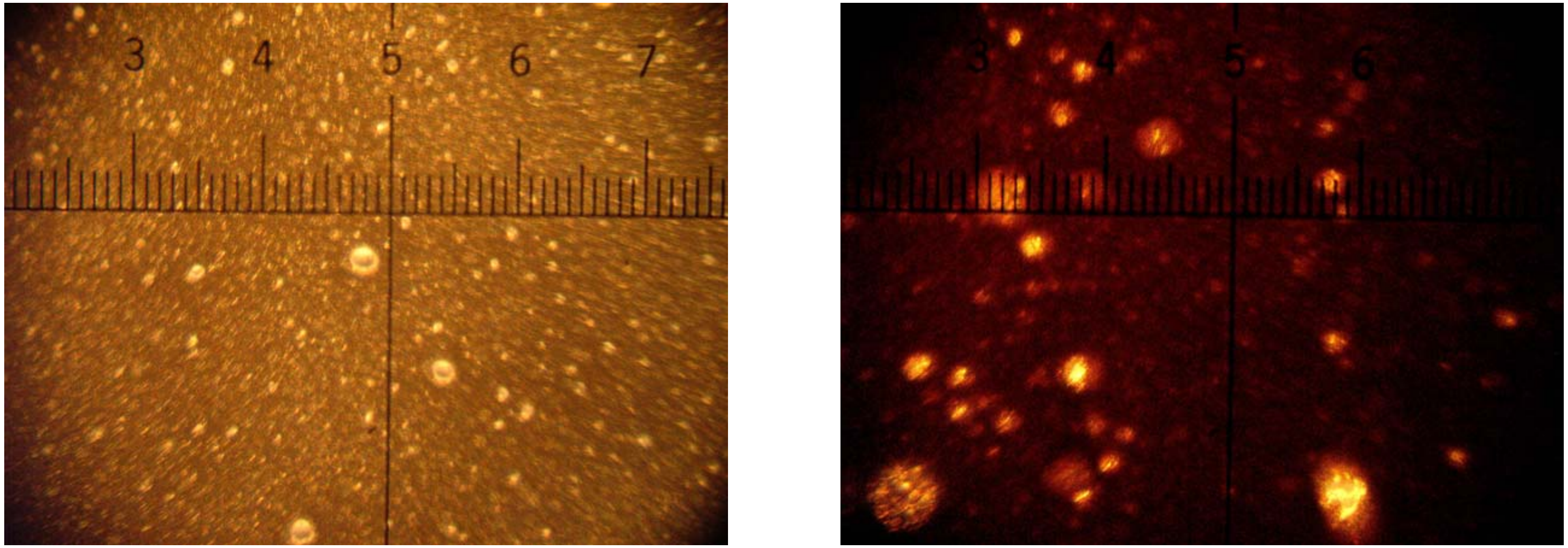
17 min 50,000 cP 66% wc (70)

Figure B16. Paint Stirrer (700 rpm): IFO 120 Fuel Oil Emulsions: Slow Addition of Water



15 min 11906 cP 49% wc (60)

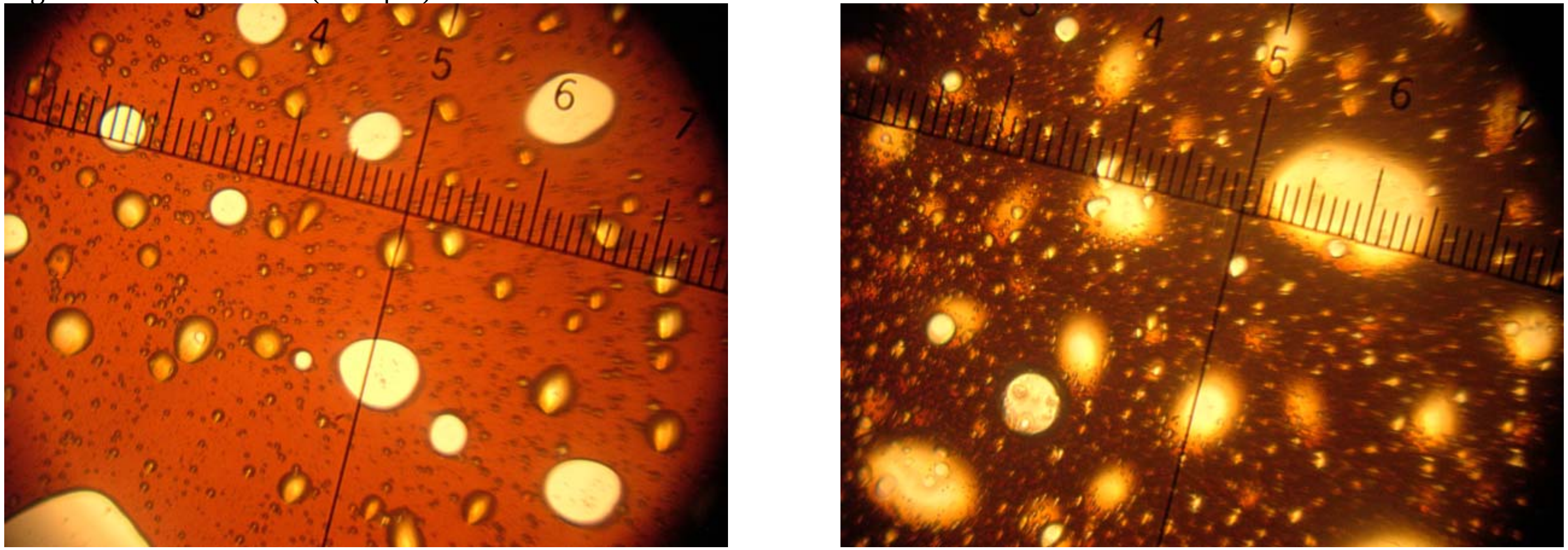
30 min 33259 cP 58.7% wc (70)



45 min 48000 cP 68.9% wc (75)

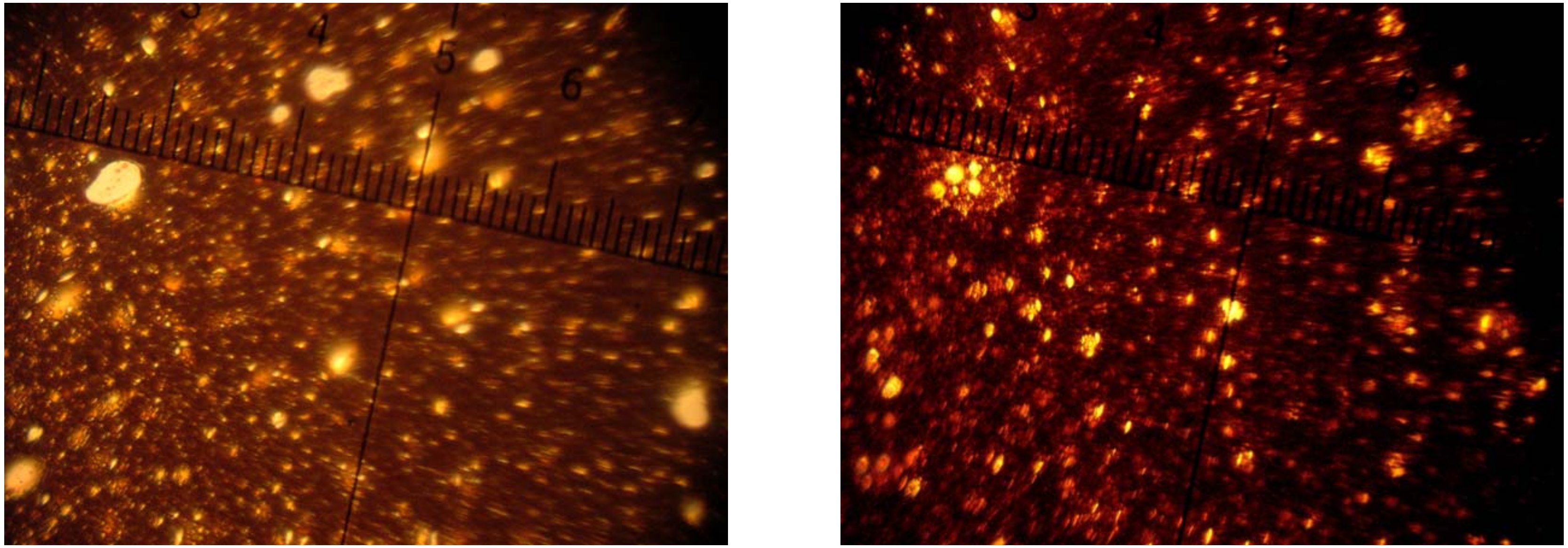
60 min 80000 cP 72% wc (80)

Figure B17. Paint Stirrer (300 rpm): IFO 120 Fuel Oil Emulsions: Slow Addition of Water



15 min 3096 cP 14% wc (60)

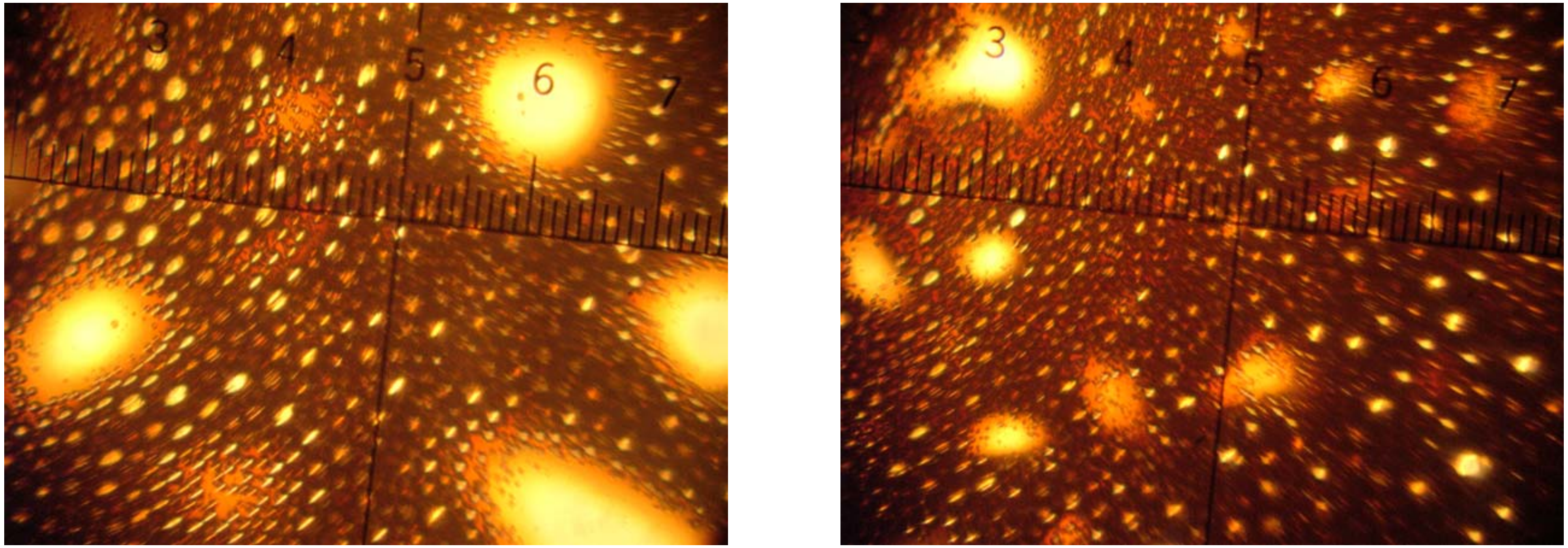
30 min 10795 cP 52.3% wc (60)



45 min 19447 cP 68.1% wc (70)

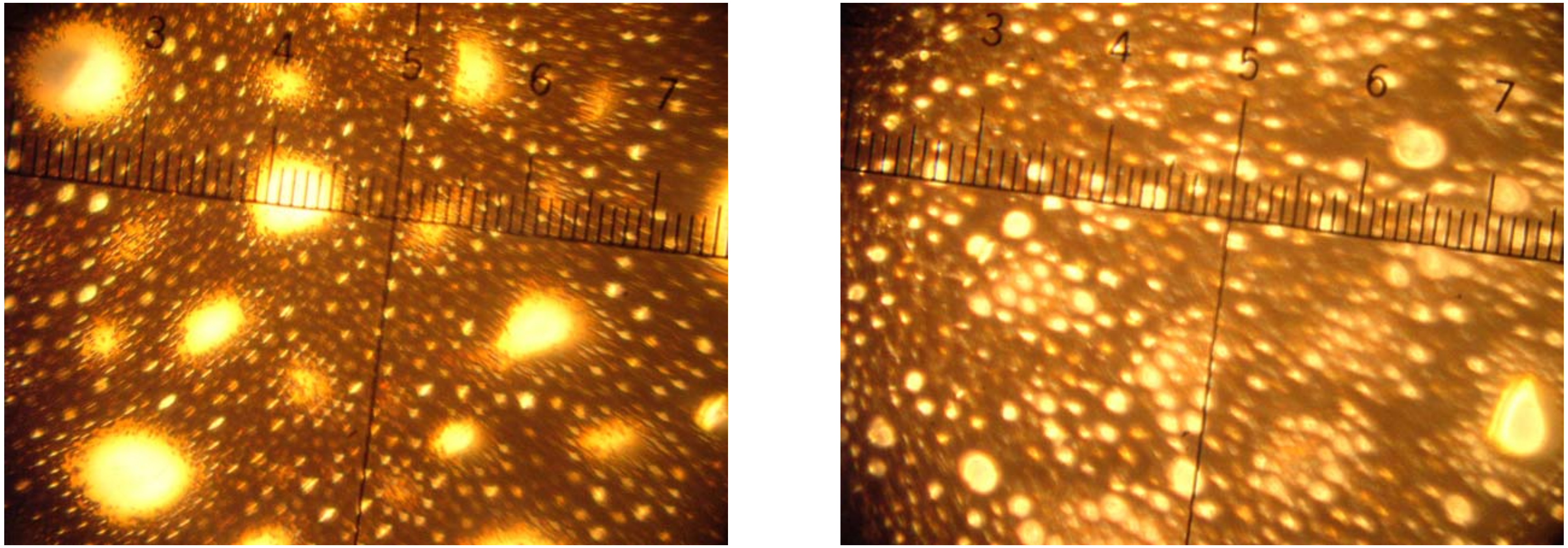
60 min 25487 cP 71.4% wc (75)

Figure B18. Cement Mixer at 30 rpm: IFO 120 Fuel Oil Emulsions: Slow Addition of Water



15 min 9684 cP 56.8% wc (60)

30 min 17225 cP 66.7% wc (70)

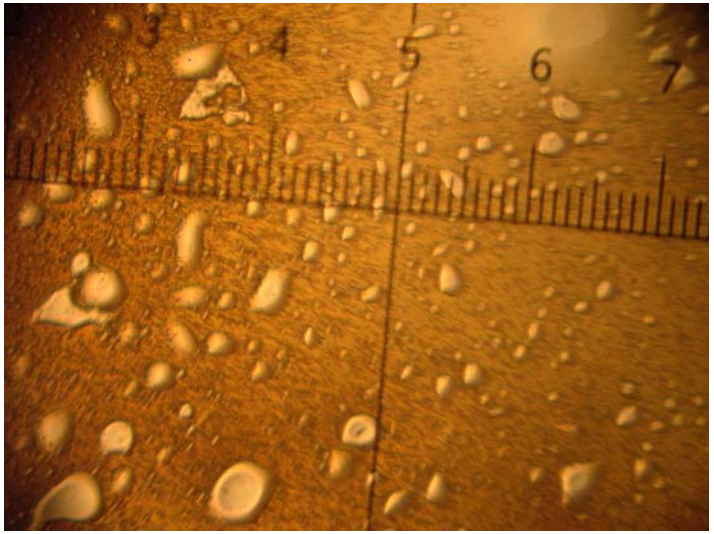


45 min 22928 cP 70% wc (75)

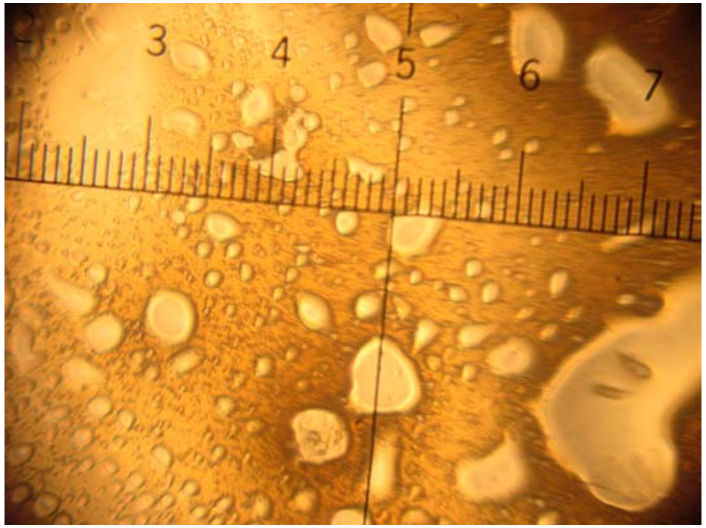
60 min 26434 cP 75.5% wc (80)

9.4 *Endicott Crude Oil with Slow Water Addition*

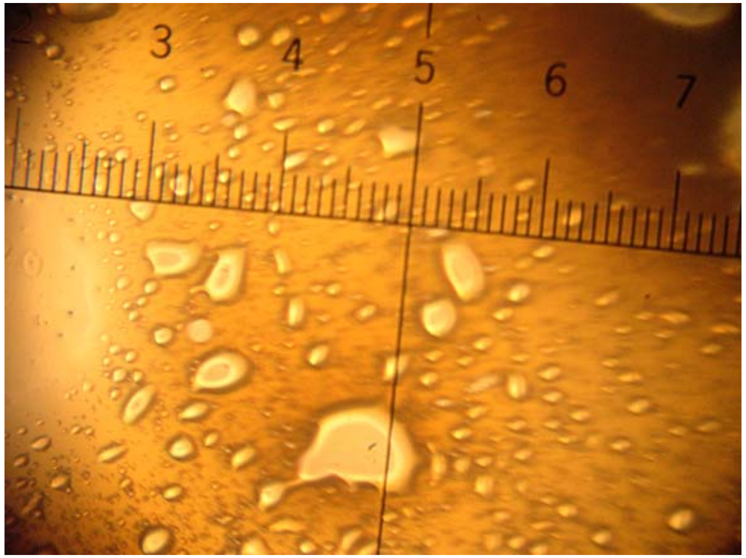
Figure B19. Progressing Cavity Pump: Endicott Crude Oil Emulsions: Slow Addition of Water



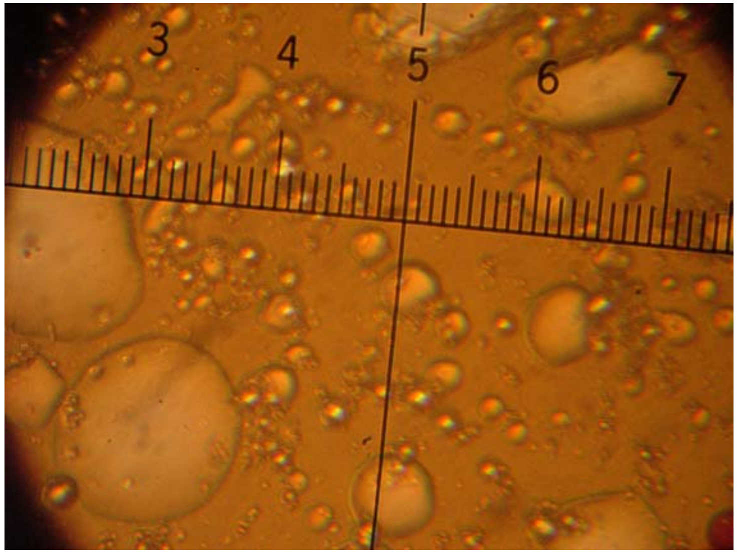
15 min 865 cP 58.1% wc (60)



30 min 825 cP 65.1% wc (70)

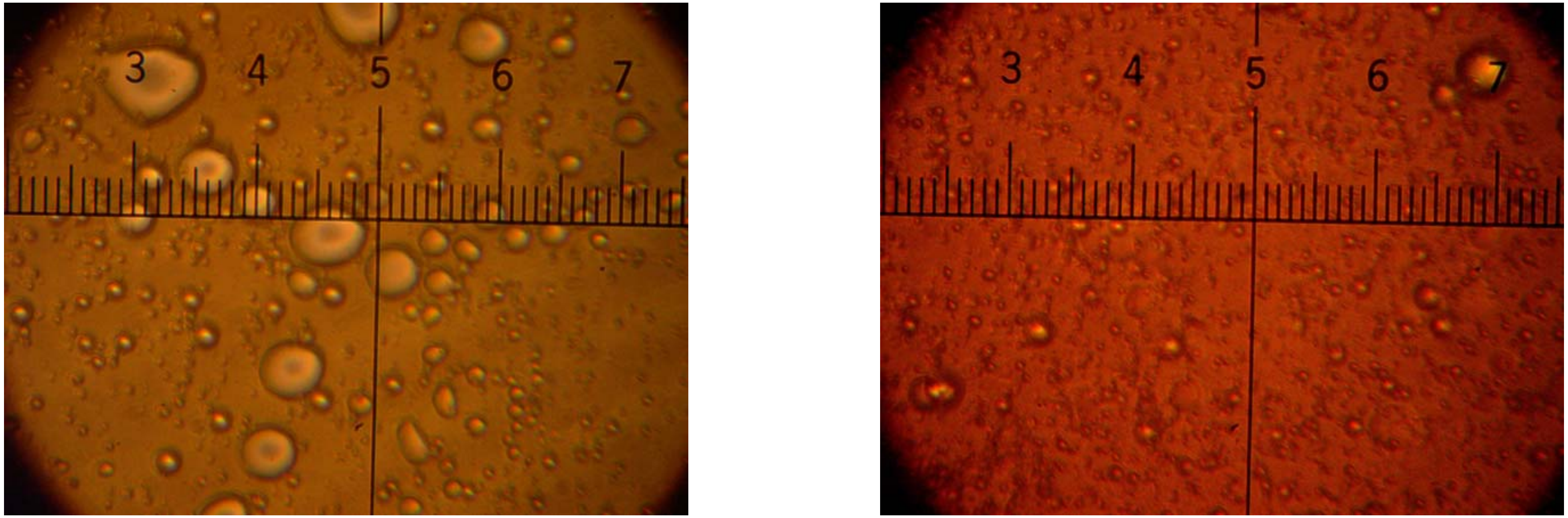


45 min 726 cP 71.7% wc (75)



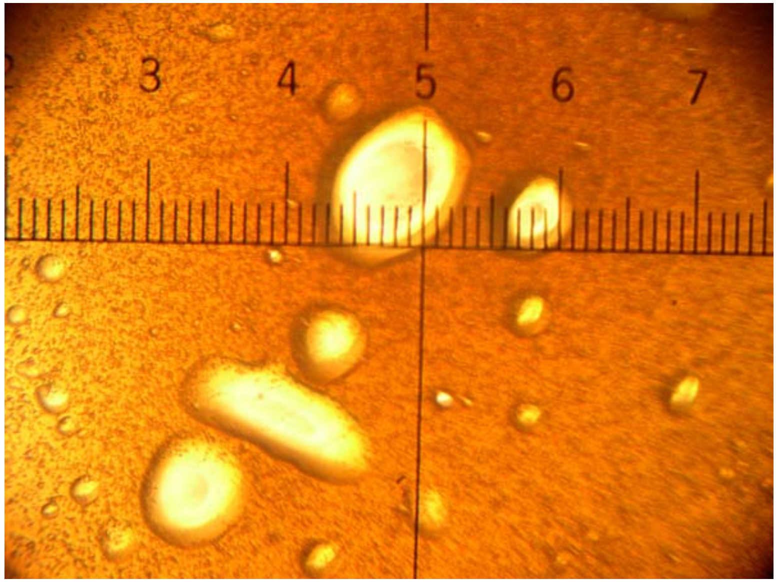
60 min 524 cP 77.8% wc (80)

Figure B20. Double Diaphragm Pump: Endicott Crude Oil Emulsions: Slow Addition of Water



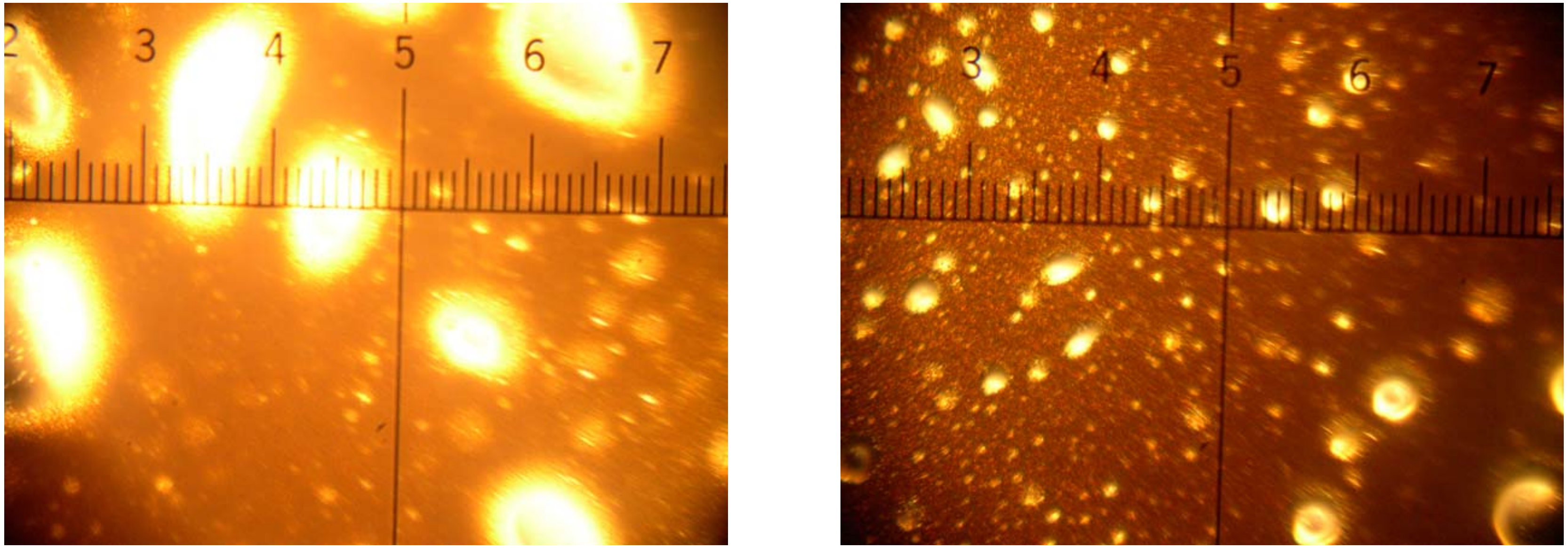
15 min 647 cP 62.2 %wc (60)

30 min 643 cP 67.3% wc (65)



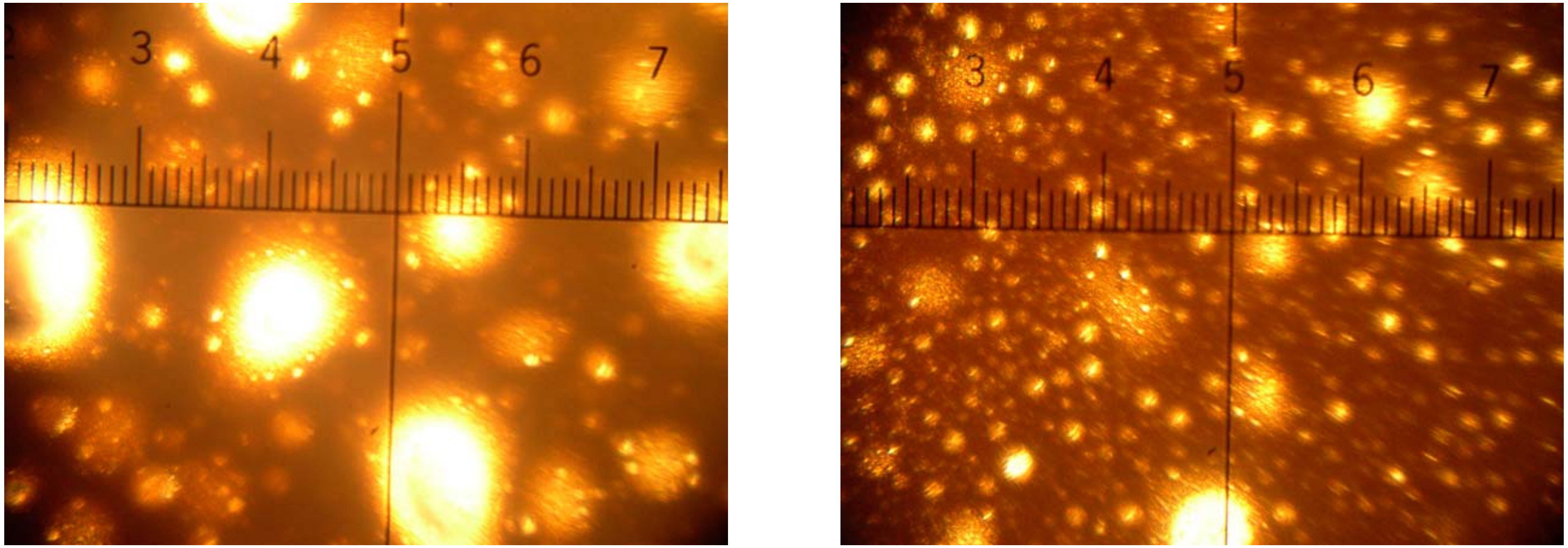
60 min 774 cP 77.6% wc (80)

Figure B21. Gear Pump: Endicott Crude Oil Emulsions: Slow Addition of Water



5 min 556 cP 61.4% wc (60)

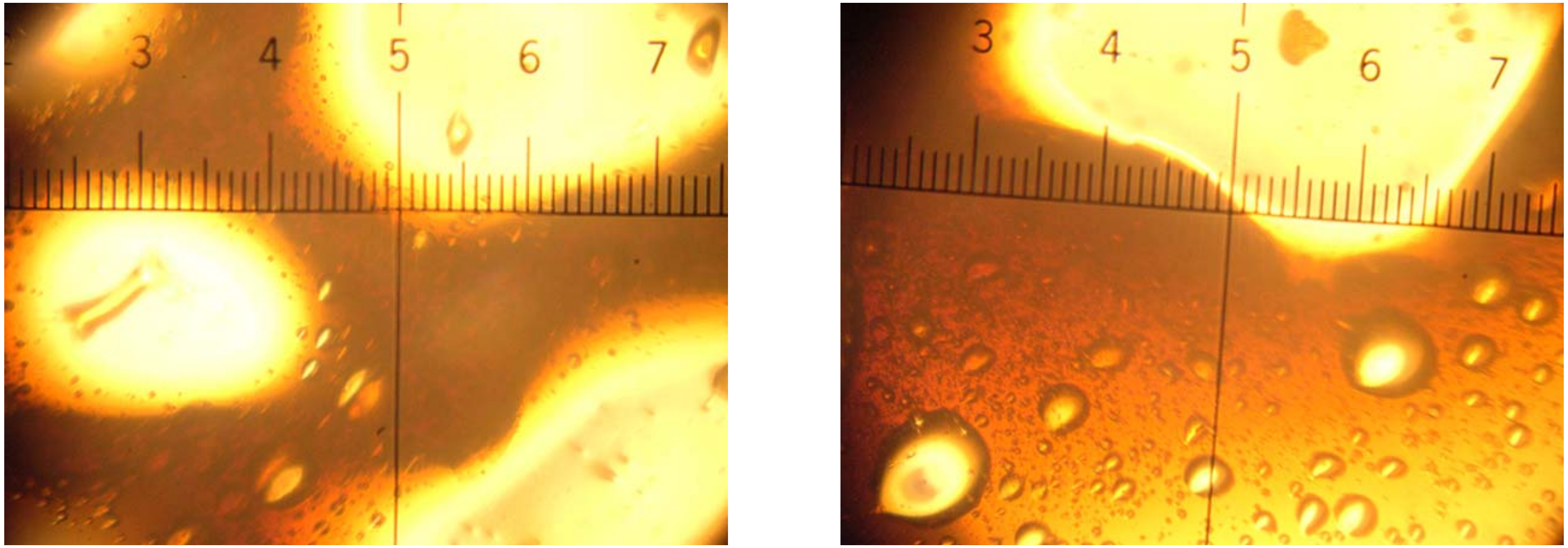
15 min 647 cP 61.4% wc (60)



45 min 667 cP 60% wc (75)

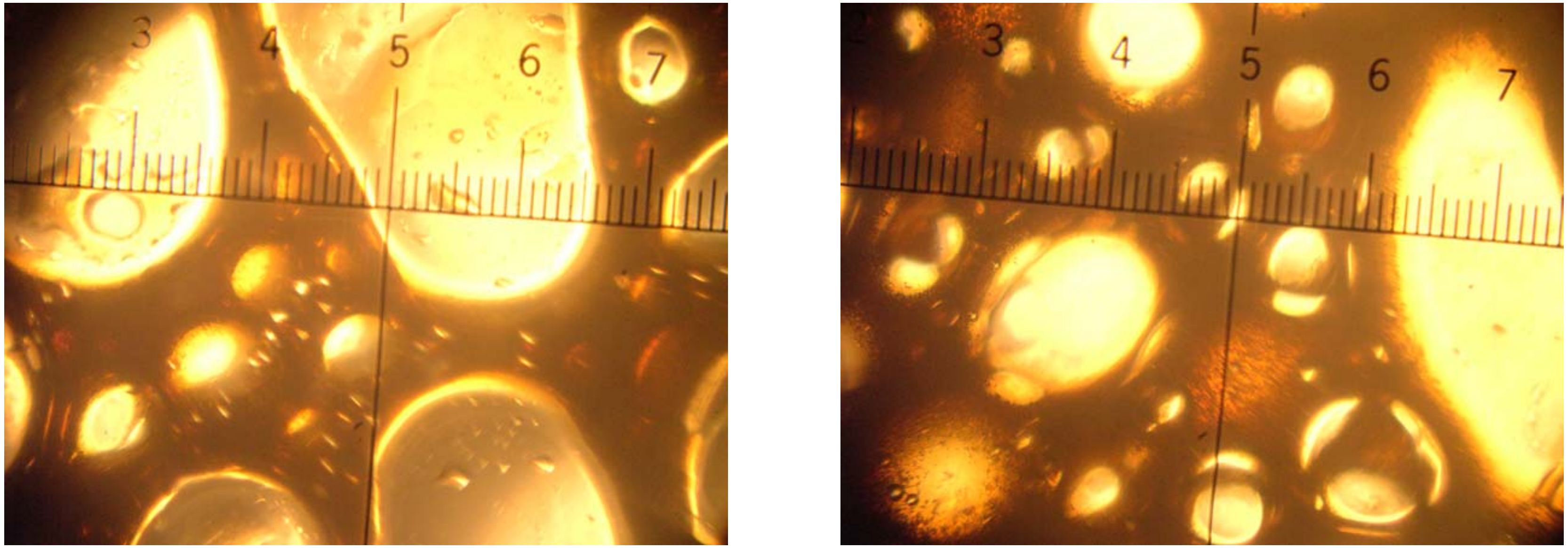
next day 1115 cP 50%wc (75)

Figure B22. Paint Stirrer (700 rpm): Endicott Crude Oil Emulsions: Slow Addition of Water



15 min 496 cP 60.5% wc (60)

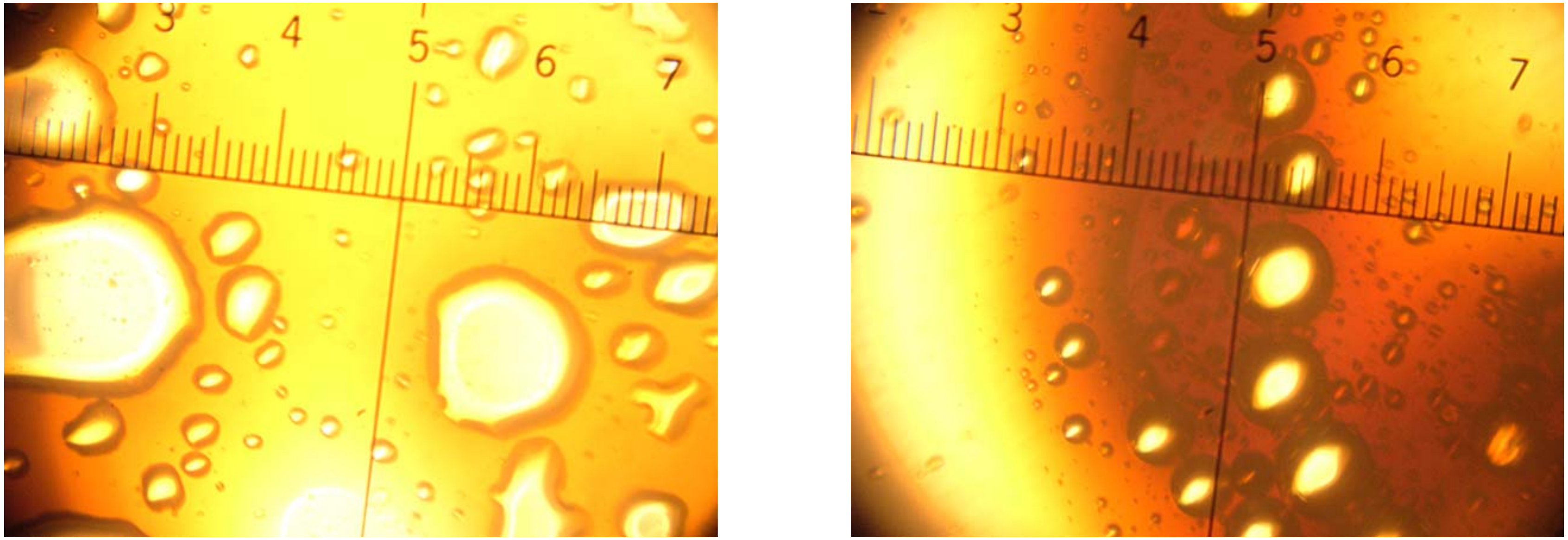
30 min 659 cP 66.7% wc (70)



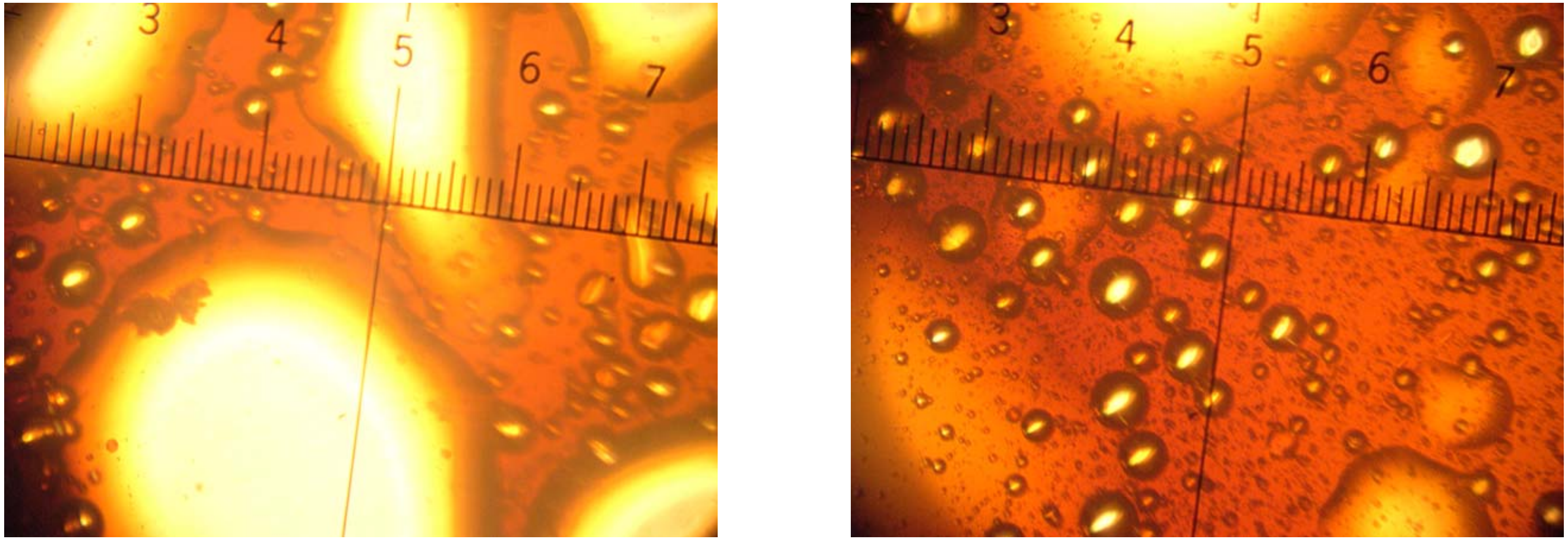
45 min 706 cP 76% wc (80)

105 min 1175 cP 71.4% wc (80)

Figure B23. Cement Mixer at 30 rpm: Endicott Crude Oil Emulsions: Slow Addition of Water

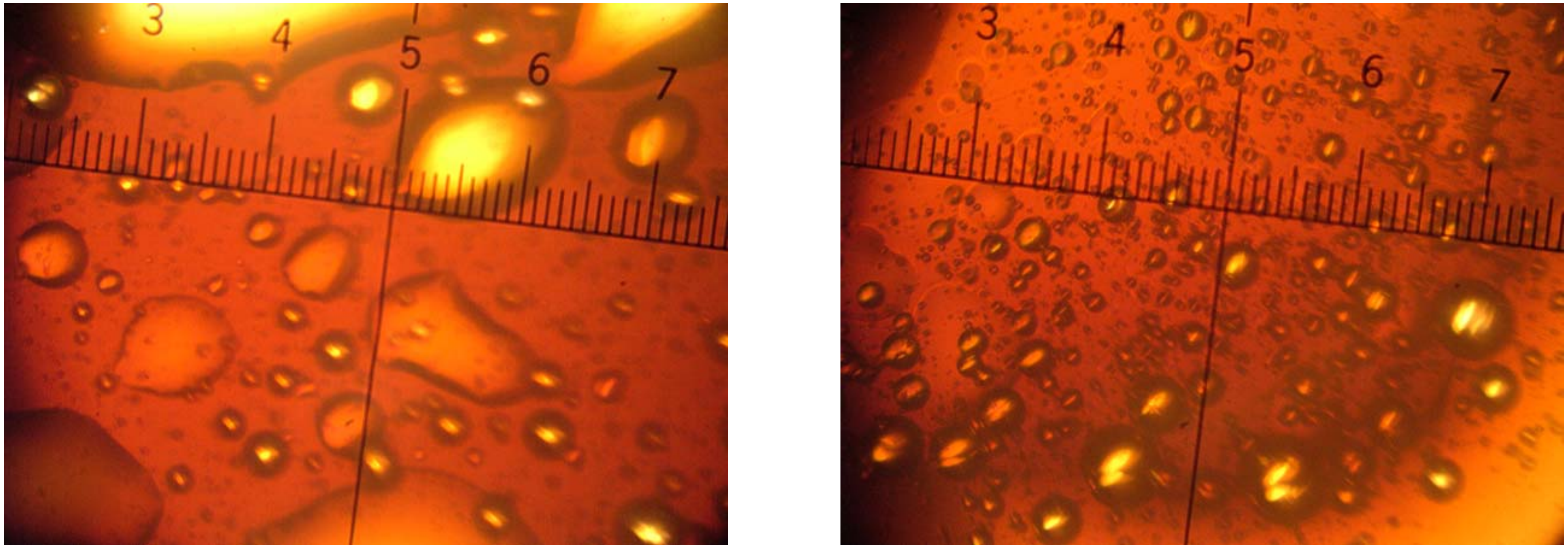


15 min 147 cP 55.5% wc (60) 30 min 262 cP 64.6% wc (70)



45 min 262 cP 65.9% wc (78.5) 60 min 329 cP 74% wc (78.5)

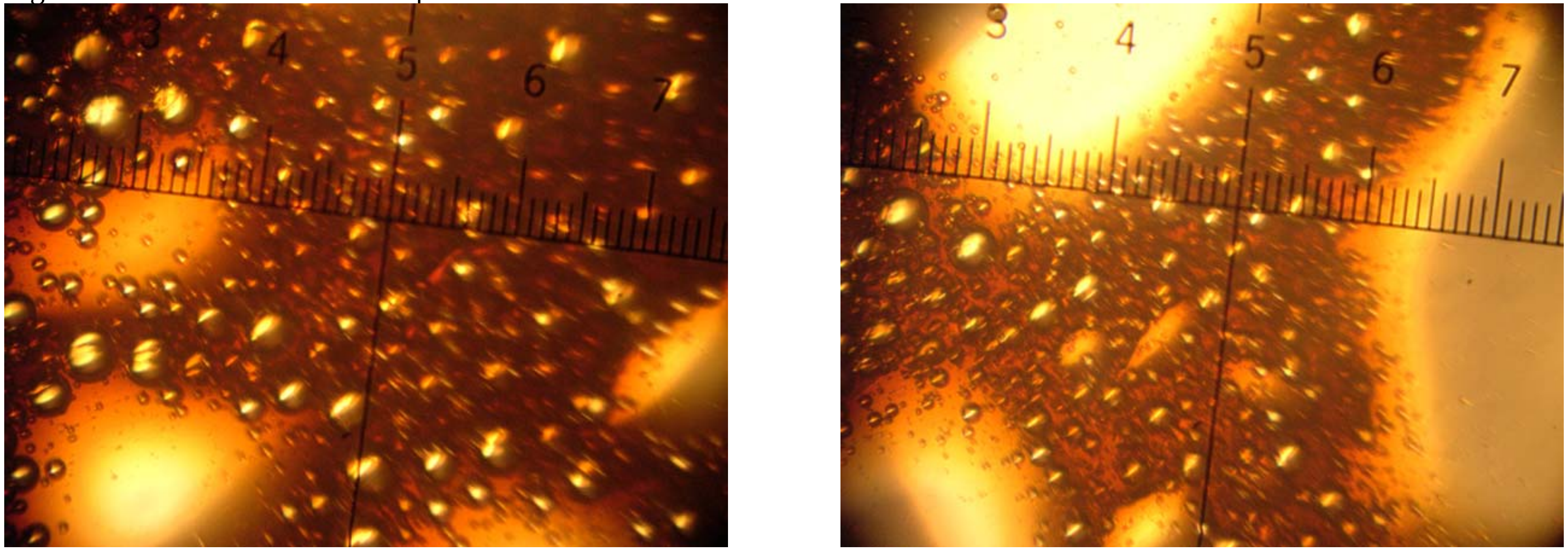
Figure B23 (cont.). Cement Mixer at 30 rpm: Endicott Crude Oil Emulsions: Slow Addition of Water



75 min 214 cP 74% wc (78.5)

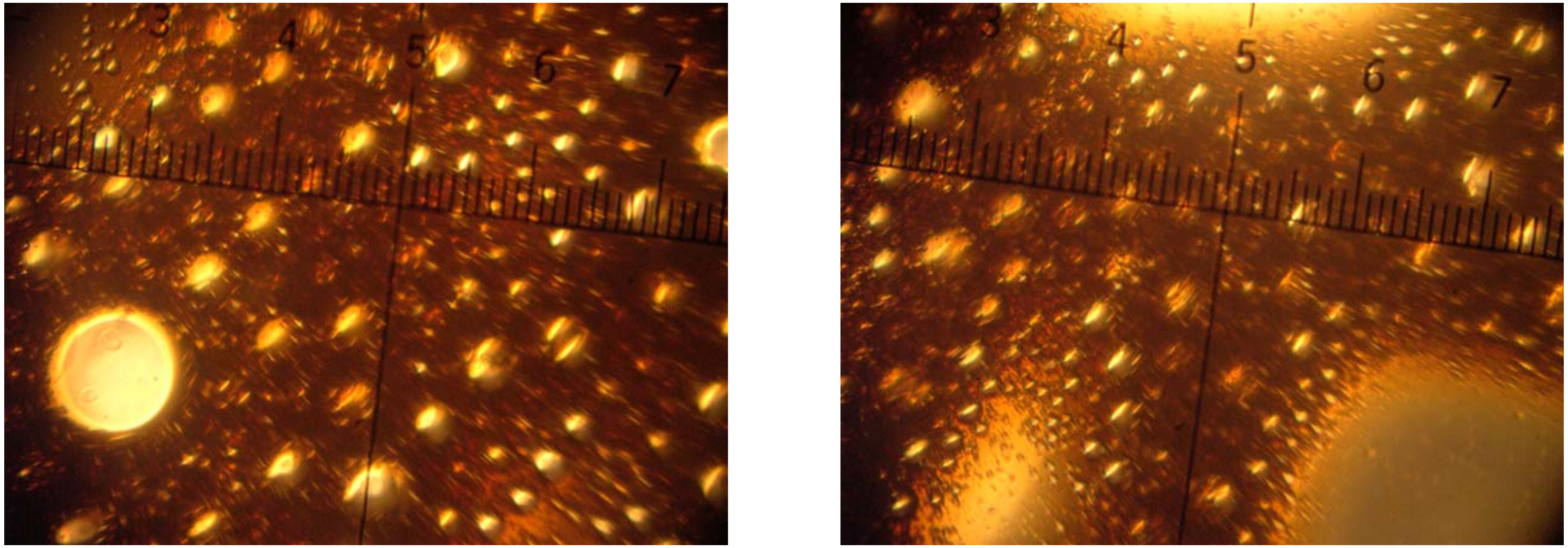
115 min 333 cP 74% wc (78.5)

Figure B24. Cement Mixer at 30 rpm: Weathered Endicott Crude Oil Emulsions: Slow Addition of Water



15 min 1334 cP 58.1% wc (60)

30 min 1568 cP 64.5% wc (70)



45 min 1742 cP 70.1% wc (75)

75 min 1897 cP 73.4% wc (80)

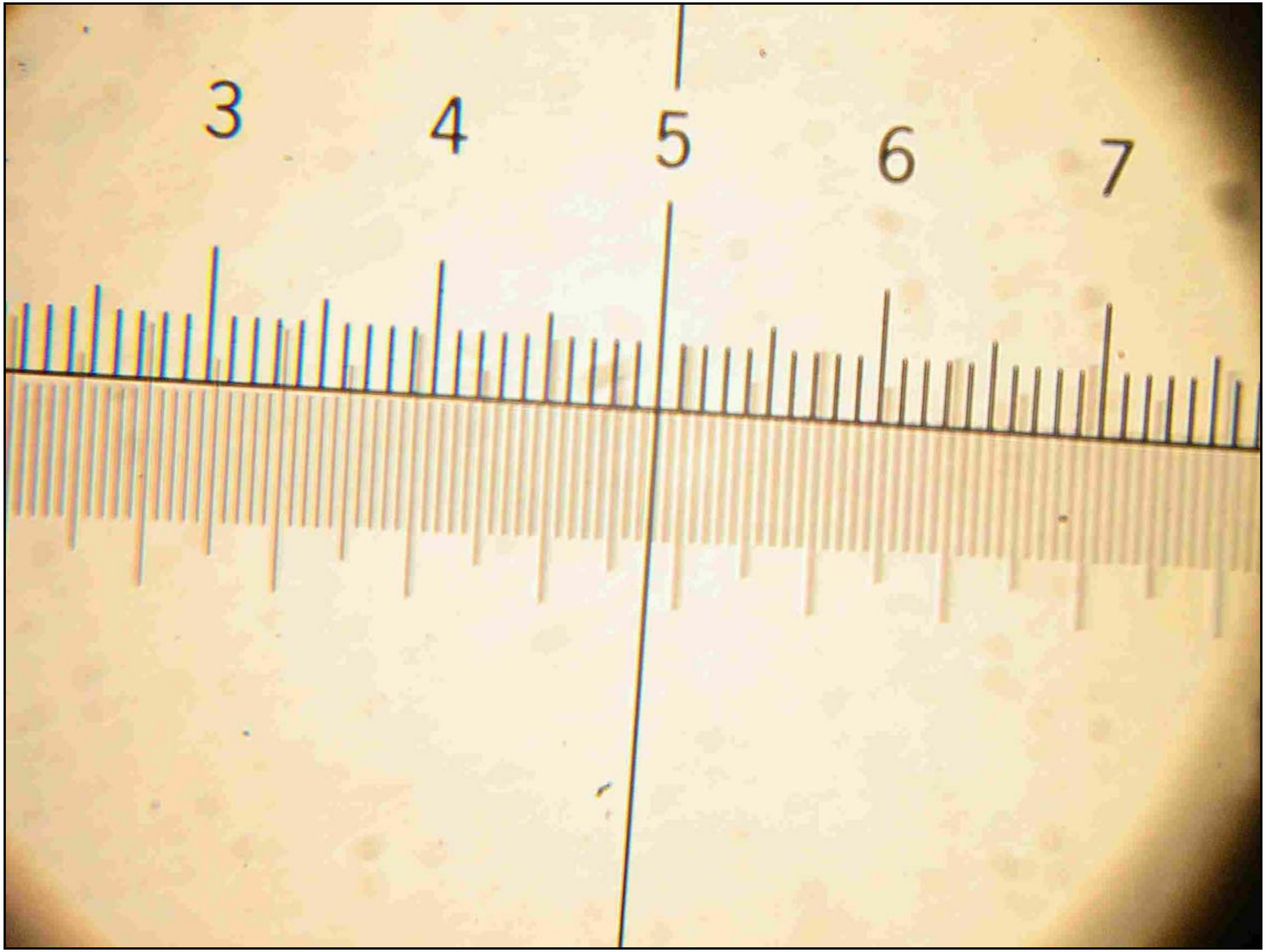
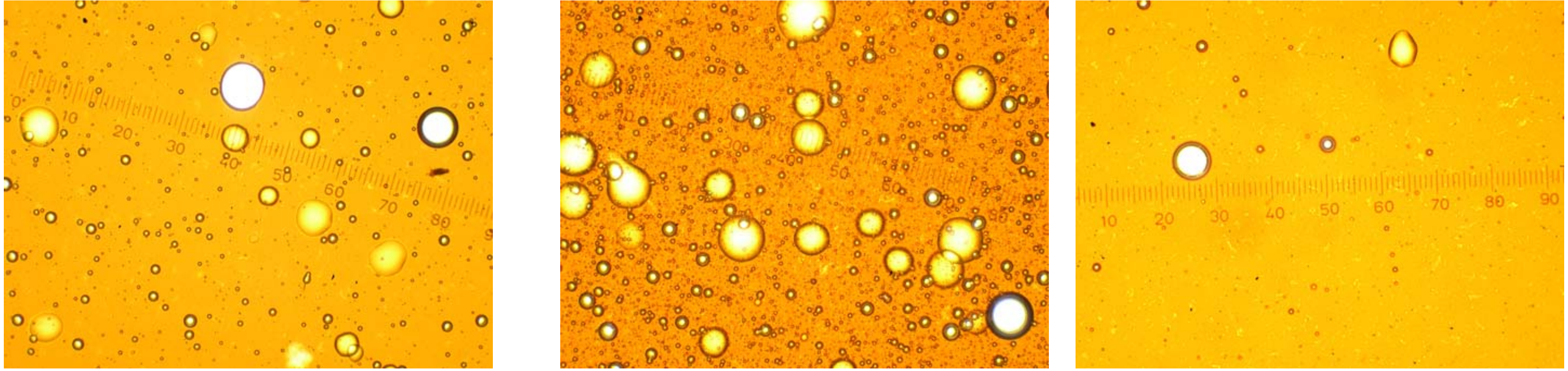


Figure B25. EyePiece Reticle Scale (100x magnification): 85 (scale: light gradations) / 51 (reticle: numbered gradations) * 10 microns = 16.7 microns per eyepiece reticle division

10. Appendix C. Example Emulsion Photos from Ohmsett Tank Tests

10.1 IFO 120: Runs 1, 2 and 4

Figure C1



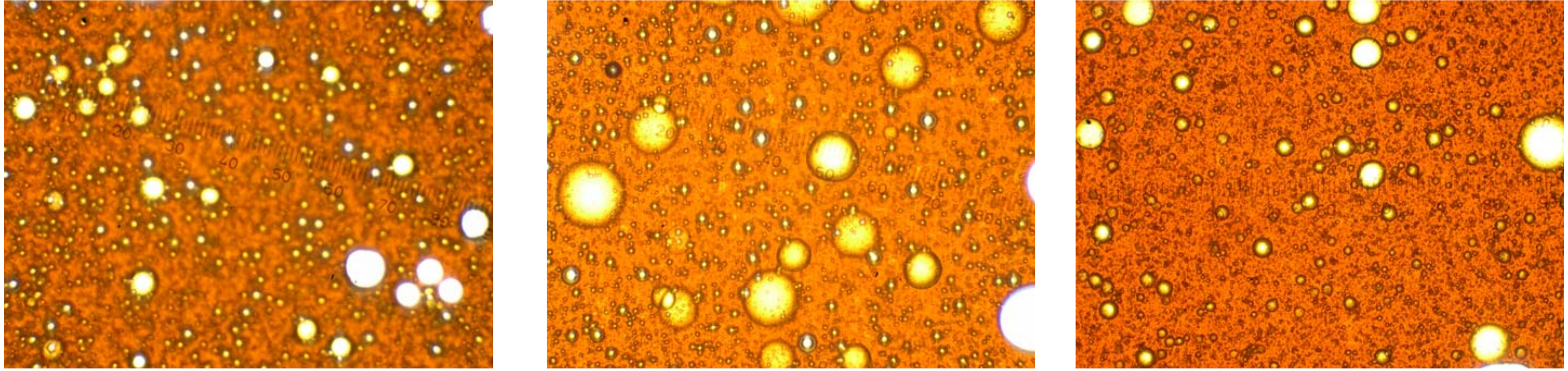
Run 1: 24 min 16% wc

33 min 2490 cP 32% wc

Run 4: 24 min 1044 cP 12% wc

Run 2:

Figure C2



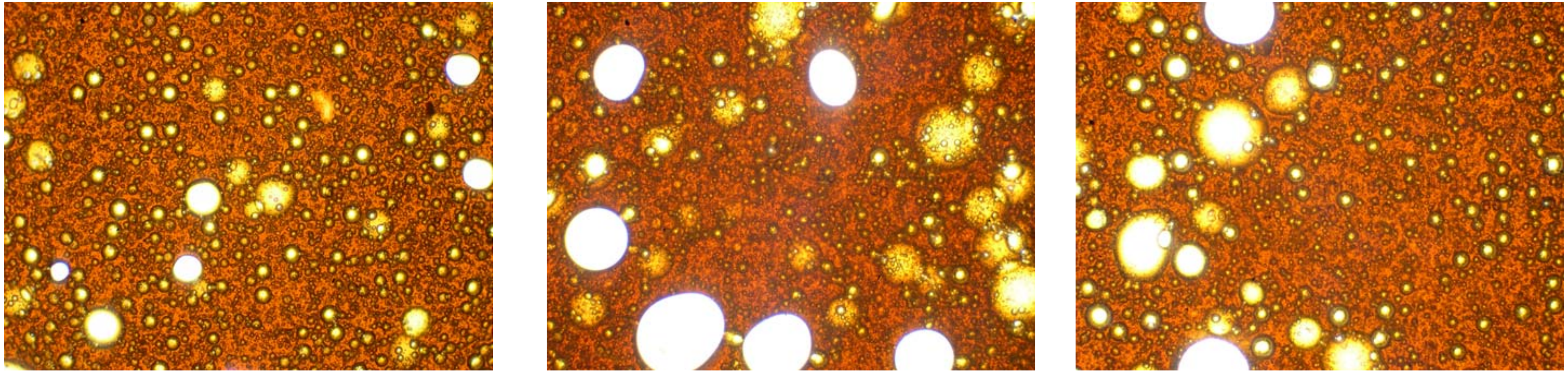
Run 1: 54 min 2600 cP 41% wc

78 min 3030 cP 40% wc

Run 4: 69 min 3863 cP 48% wc

Run 2:

Figure C3



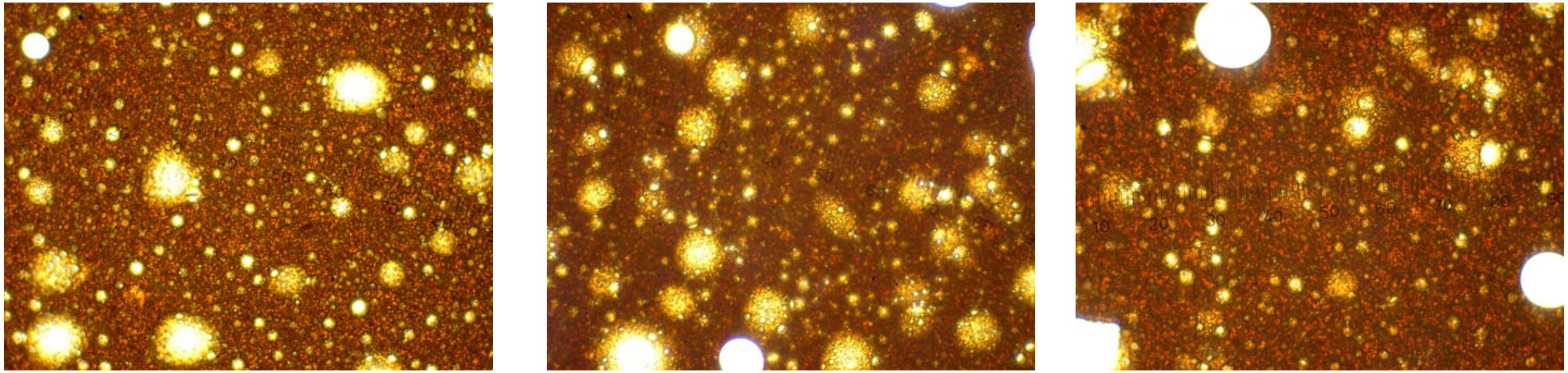
Run 1: 99 min 3300 cP 53% wc

111 min 3730 cP 50% wc

Run 4: 94 min 5060 cP 60% wc

Run 2:

Figure C4



Run 1: 264 min 7030 cP 59%

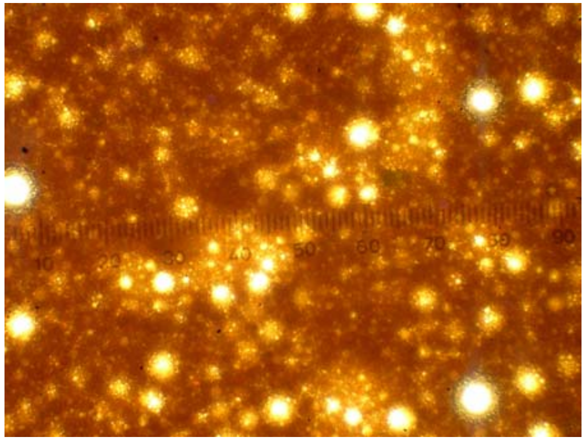
245 min 6813 cP 50% wc

161 min 7115 cP 65% wc

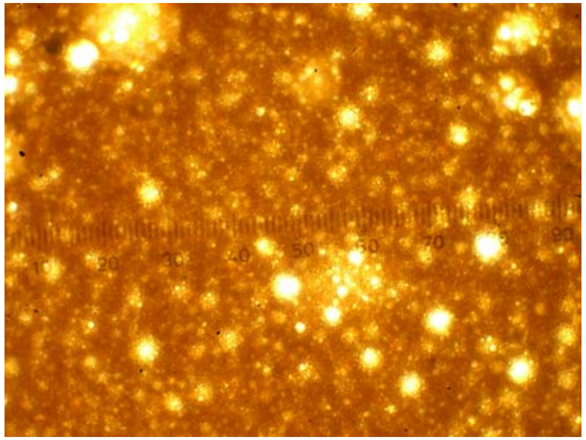
Run 4:

Run 2:

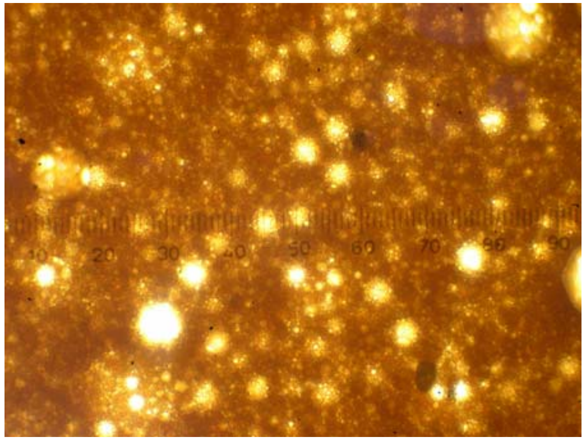
Figure C5



Run 4: 368 min 10,910 cP 75% wc



571 min 13,710 cP 60% wc



Run 4: 881 min 15,150 cP 75% wc

Run 4:

10.2 Endicott Crude Oil: Run 3

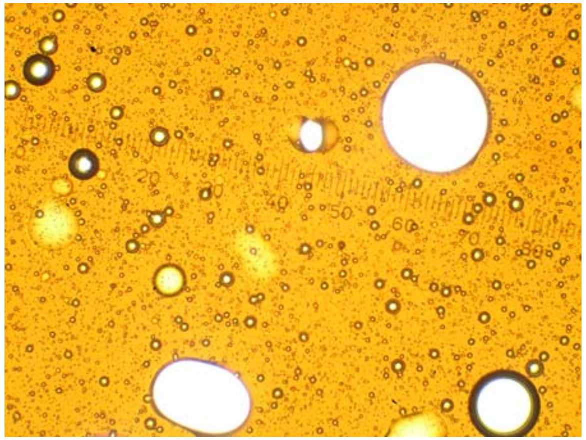


Figure C6: 22 min 178 cP 25% wc

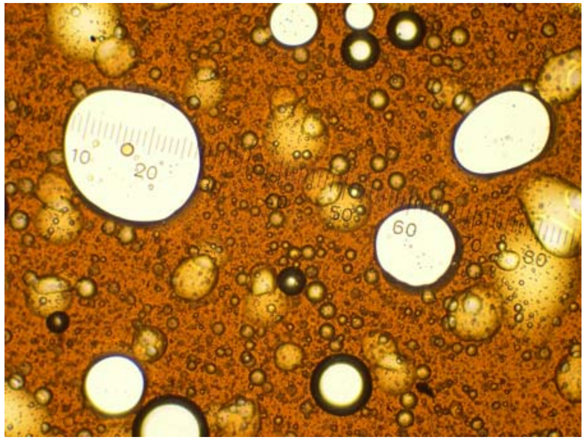


Figure C7: 51 min 940 cP 42% wc

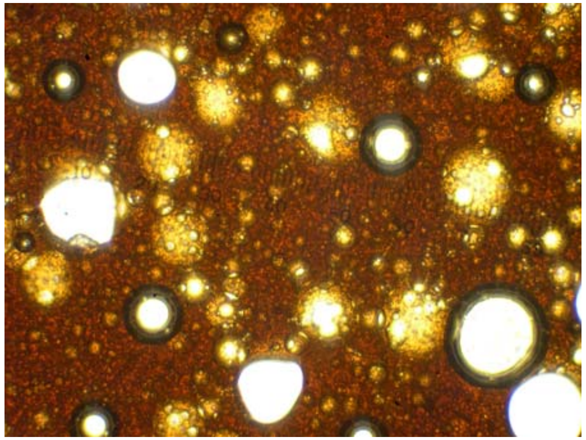


Figure C8: 99 min 2173 cP 55% wc

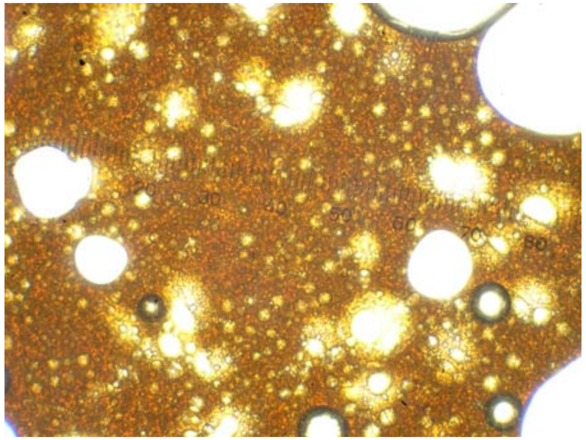


Figure C9: 171 min 3290 cP 62% wc

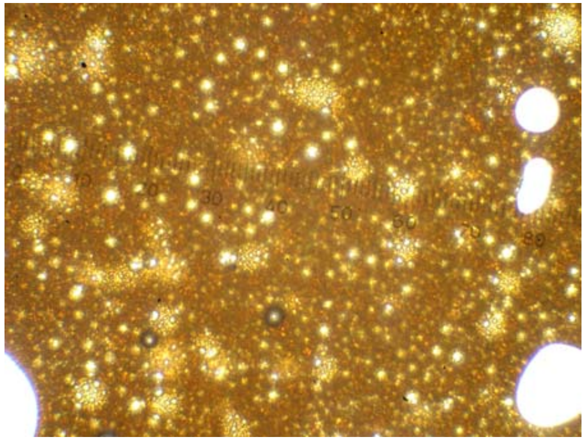


Figure C10: 236 min 4530 cP 64 % wc

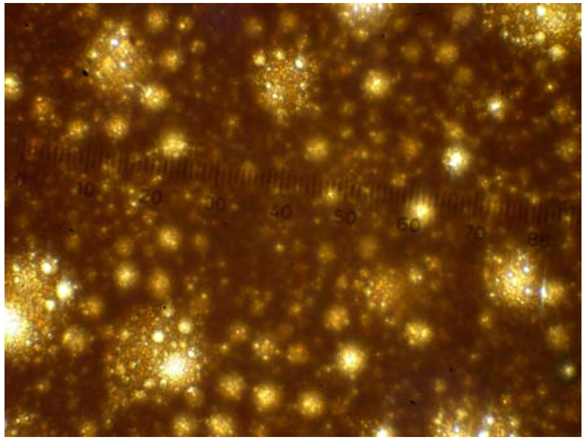


Figure C11: 328 min 4410 cP 58% wc

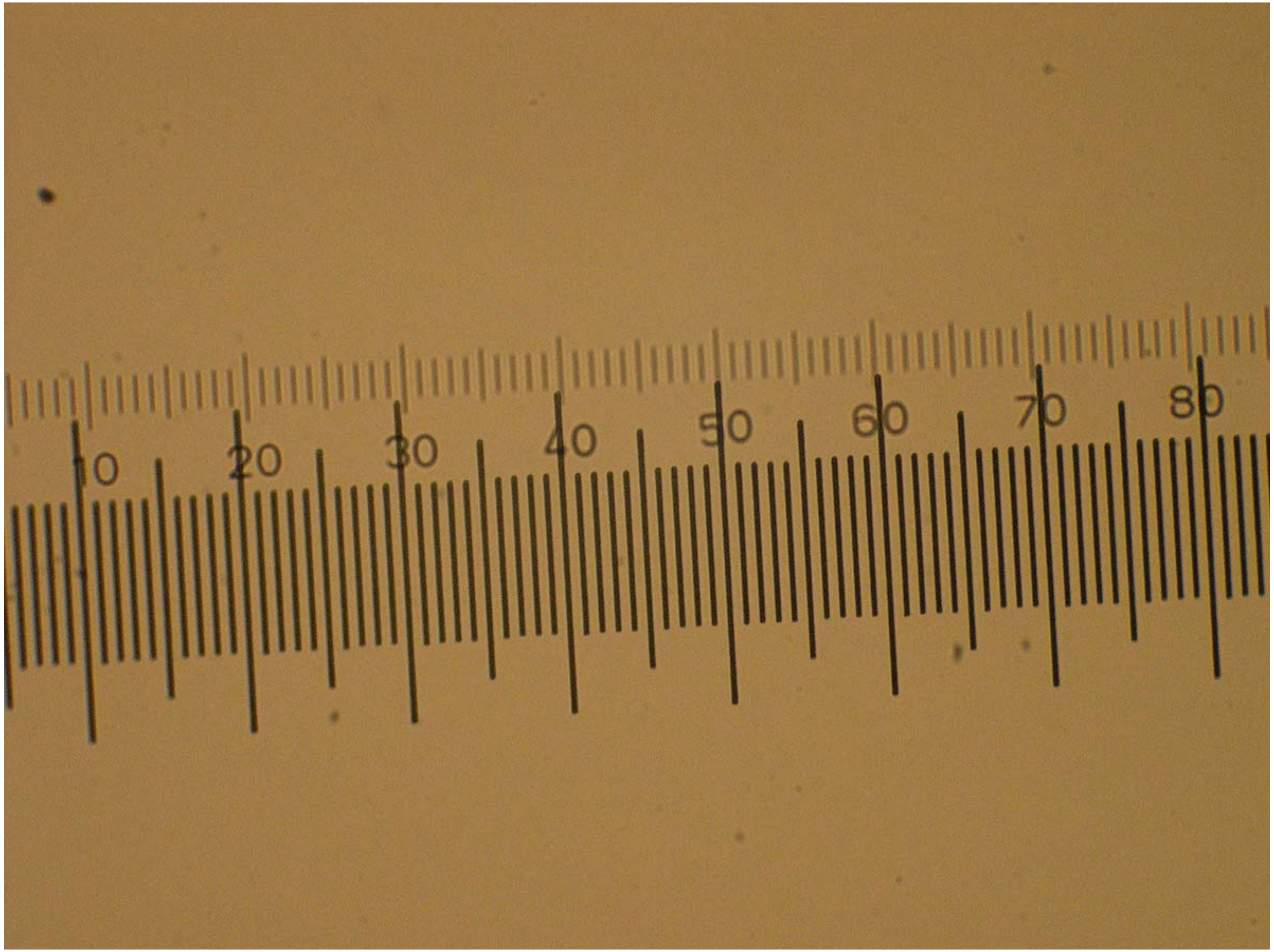


Figure C12. Photo of 1mm/100 Division Stage Micrometer with Eyepiece Reticle Installed (darker numbered scale)
(40 units on eyepiece reticle = 410 microns on Stage Micrometer or 1 unit = 10.25 microns)

11. Appendix D. Emulsion Photos from Batch-Scale Tests Compared to Ohmsett Emulsion Photos

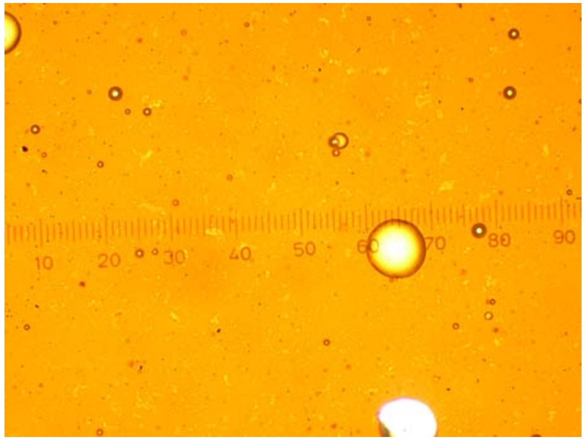
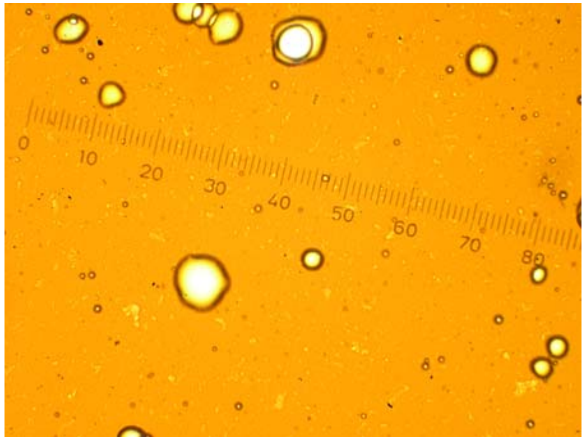
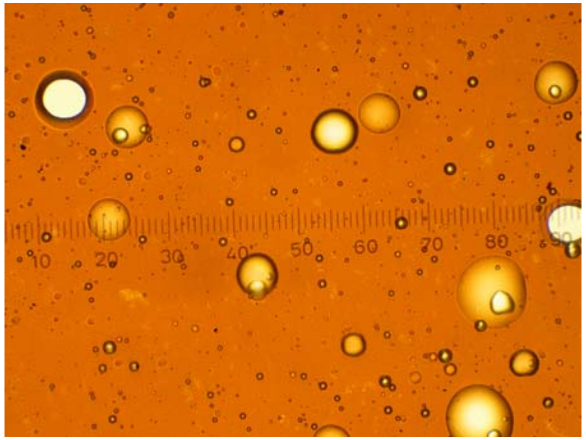


Figure D1. Ohmsett Tank 1044 cP 12% wc



BST1 1144 cP 14% wc



BST5 1187 cP 13% wc

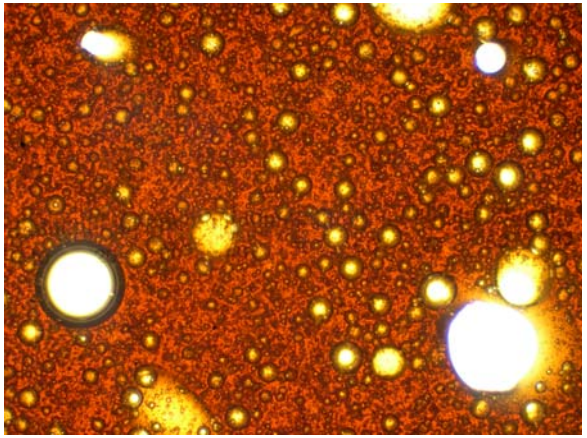
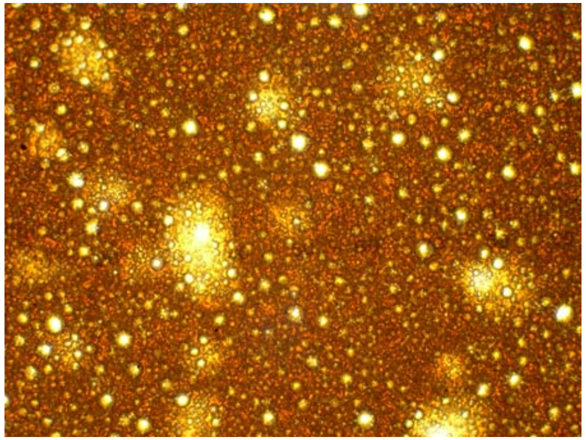


Figure D2. Ohmsett Tank 5059 cP 60% wc



BST5 3863 cP 54% wc

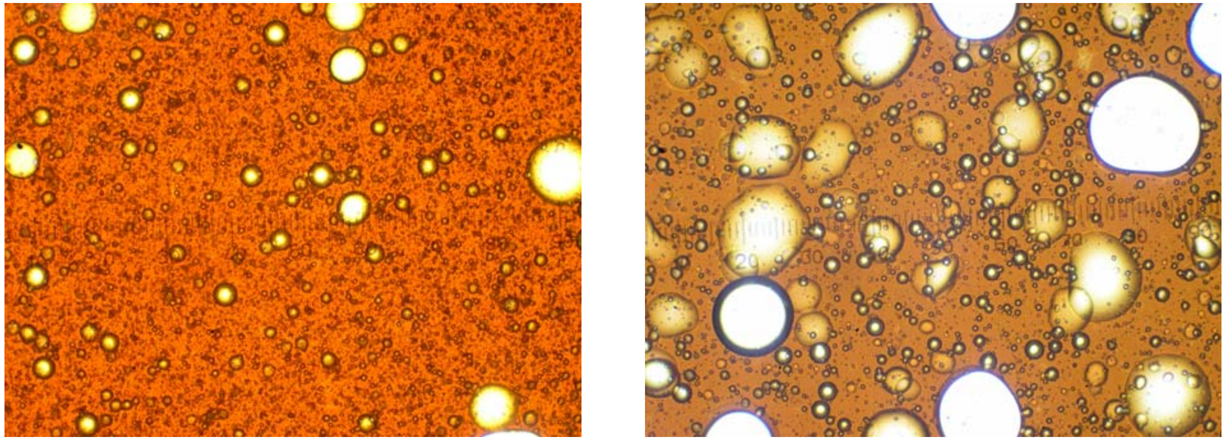


Figure D3. Ohmsett Tank 3863 Cp 48% wc BST9 3642 cP 54% wc

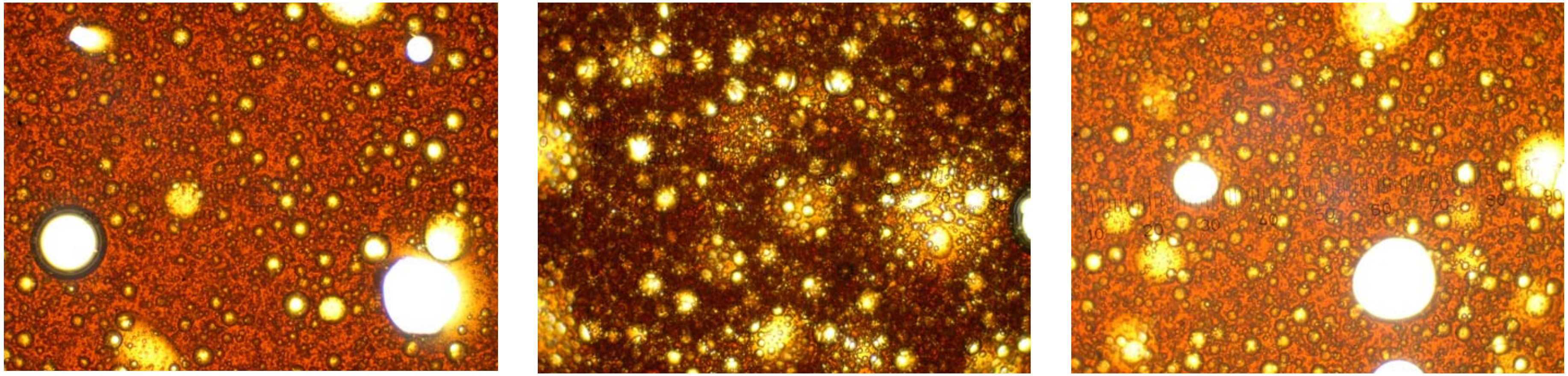


Figure D4. Ohmsett Tank 5059 cP 60% wc BST2 7981 cP 60% wc 4428 cP

BST10

60% wc

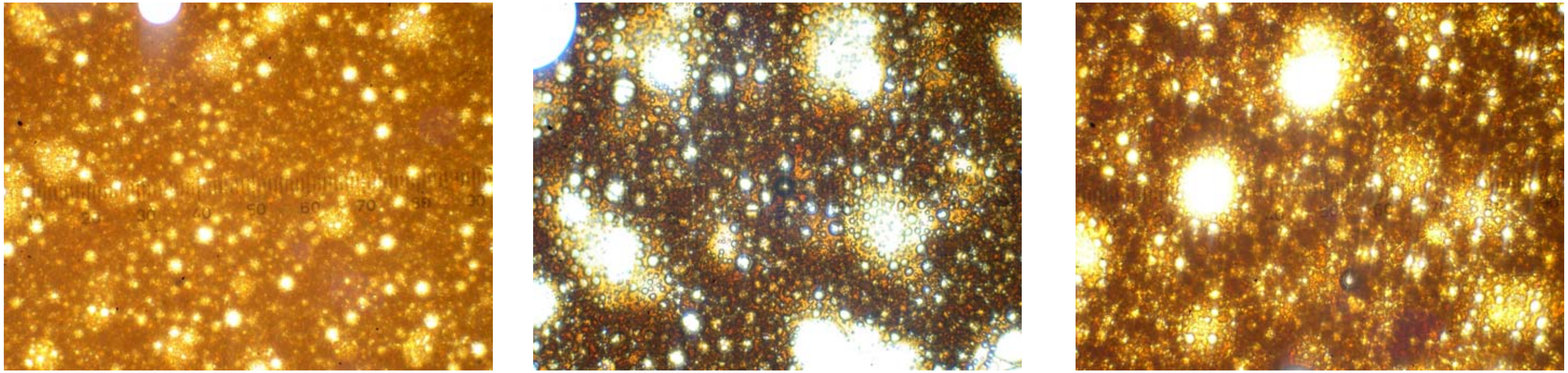


Figure D5. Ohmsett Tank 10287 cP 70% wc BST7 8567 cP 70% wc 9773 cP

67% wc

BST8

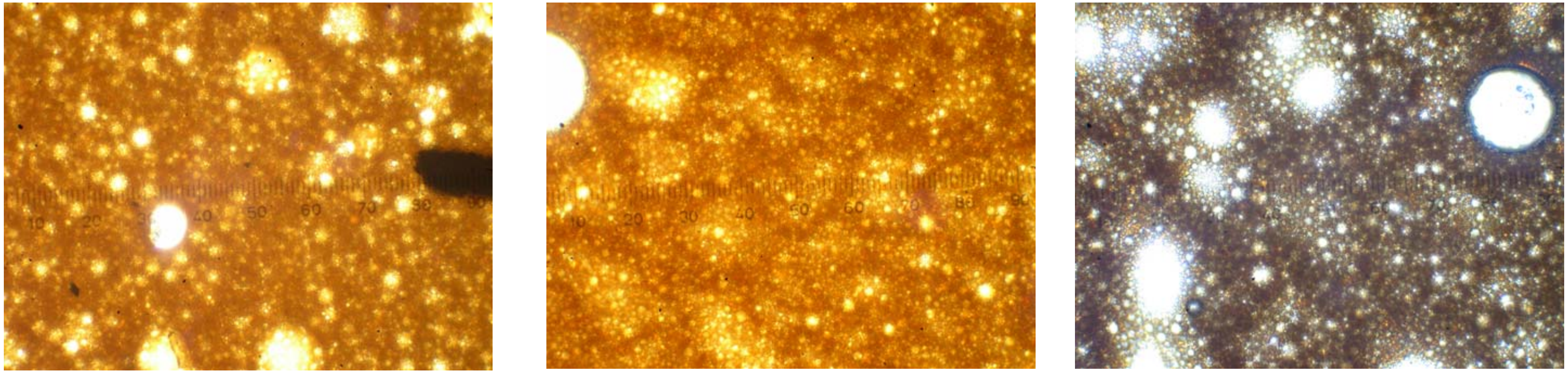


Figure D6a. Ohmsett Tank 12,658 cP 75% wc BST7 14,461 cP 72% wc 16,705 cp

73% wc

BST8

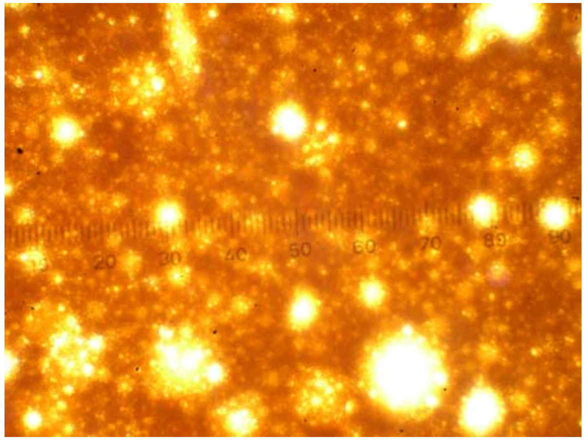
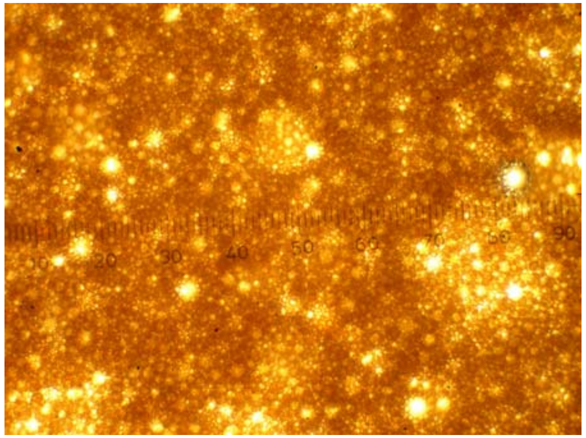
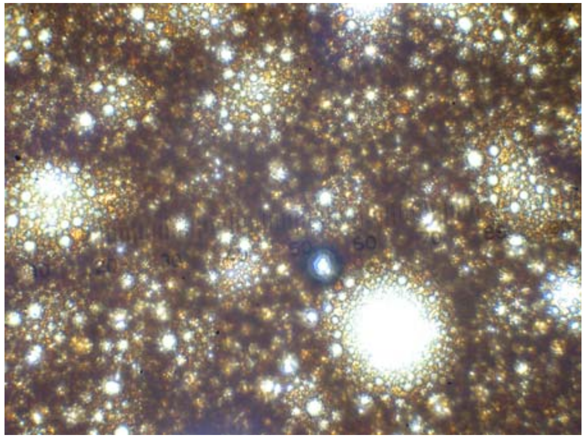


Figure D6b. Ohmsett Tank 12,684 cP 75% wc



BST9 13,777 cP 75% wc



BST10 13,784 cP 75% wc

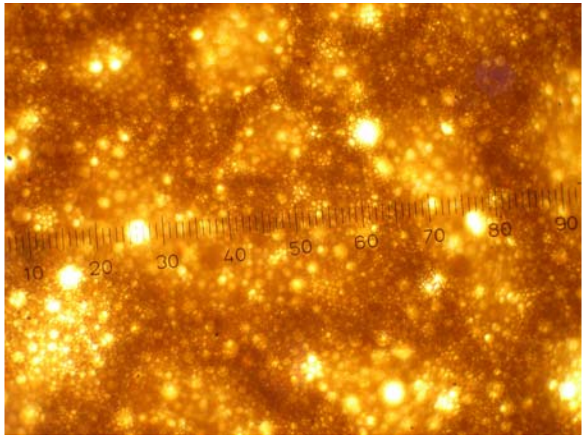
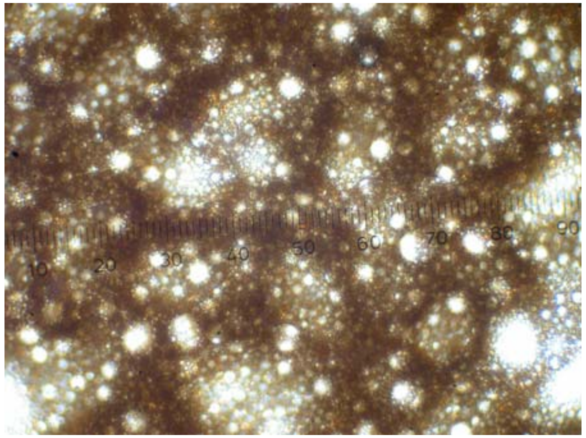


Figure D7. BST10 23,360 cP 80% wc



BST11 23,000 cP 82% wc

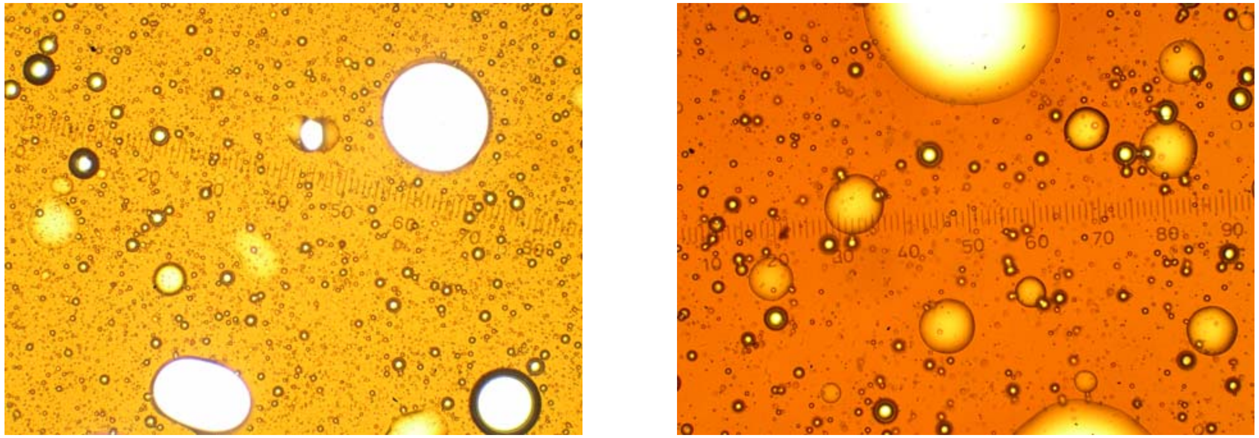


Figure D8. Ohmsett Tank 178 cP 25% wc

206 cP 28% wc
BST13

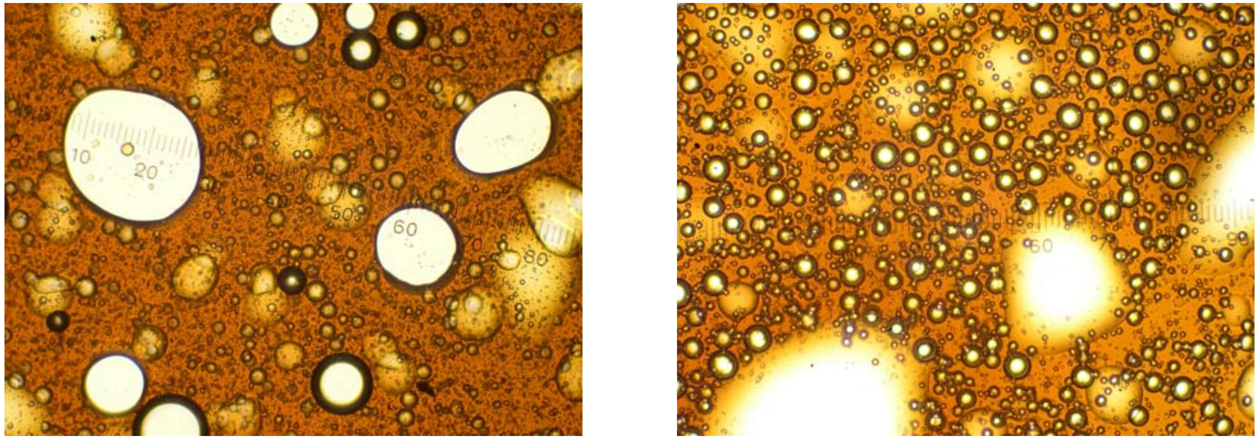


Figure D9. Ohmsett Tank 940 cP 42% wc

452 cP 45% wc
BST13

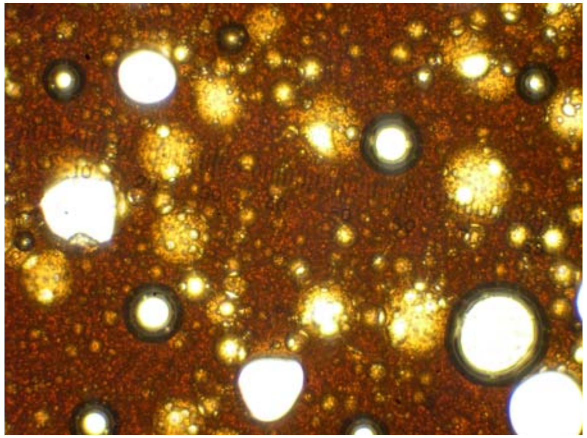
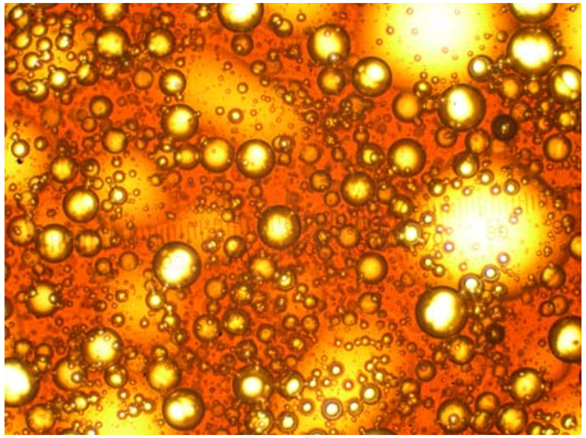
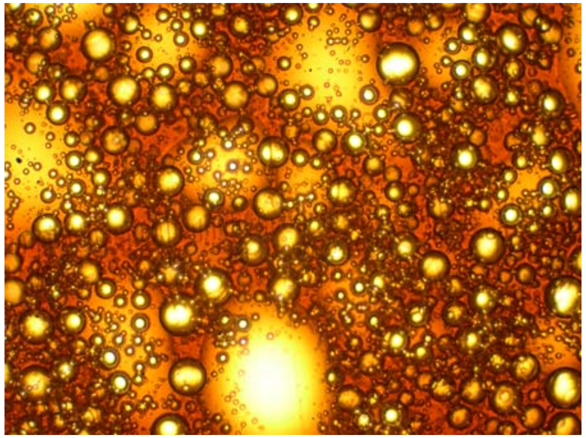


Figure D10. Ohmsett Tank 2173 cP 55% wc



557 cP 55% wc
BST12



BST12 710 cP 53% wc

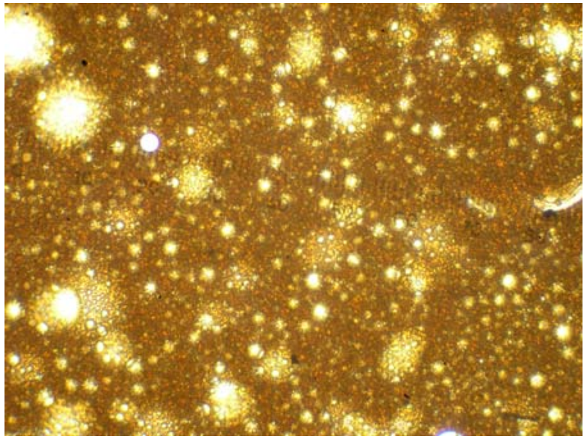
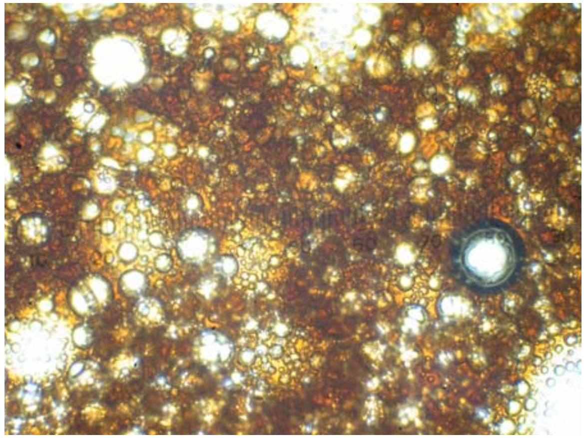


Figure D11. Ohmsett Tank 3805 cP 60% wc



1290 cP 62% wc
BST13

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