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Fluorescence Microscopy: A Technique to Study and Evaluate Spacer Fluids for Wettability Inversion

Qusai Darugar, Baker Hughes; Lirio Quintero, Baker Hughes; Chad F. Christian, Baker Hughes and Daniel R. Ellis, Baker Hughes

Abstract

It is very important that the rock and casing surfaces are rendered water-wet before cementing operations take place in oil and gas wells. Failure to efficiently displace synthetic-based mud (SBM) or oil-based mud (OBM) and to water-wet the casing and rock formation can result in poor cementing performance that can lead to casing failures, non-productive time, costly squeeze jobs, and communication between zones.

Previously, evaluation methods such as bottle cleaning tests, rheology and relative conductivity of fluid inversion from brine-in-oil (W/O) to oil-in-water (O/W) were used to qualify cement spacer efficiency. These tests do not provide information at the microscopic level and can be misleading, which can greatly affect the cement bonding process.

Microscopic techniques were used to evaluate the ability of a spacer fluid to change the surface wettability from oil-wet to water-wet during the displacement of non-aqueous fluids (NAF). Bright-field and fluorescence microscopy were used to study the mechanism of the phase inversion from brine-in-oil to oil-in-water.

This work discusses the evaluation of spacer fluid in different NAF spacer ratios and the transition from oil-continuous to water-continuous fluids using microscopy. These results increase the understanding of spacer effects on drilling fluid contamination and are in good correlation with rheology and bottle cleaning test evaluations.

Introduction

Microscopy for Spacer Evaluation

The past couple of decades have witnessed great advances in the technique and application of optical microscopy for micron and submicron level investigations in a wide variety of disciplines.[1-5] Rapid development of new fluorescent labels has accelerated the expansion of fluorescence microscopy in laboratory applications and research.[6-8] Microscopy can also be a useful tool for evaluating a spacer fluid when contaminated with NAF.

The importance of cleaning and water-wetting the rock formation and casing in order to avoid casing failures due to poor cementing job is well documented.[9-12] Water-wetting the surface is most critical when the formation is drilled using NAF based mud. Microscopy techniques can be used to evaluate and to understand the phase inversion mechanisms from oil-wet to water-wet.

Bright-field microscopy takes advantage of the differences in absorbed light by test media that have different absorption coefficients for imaging. Because of high contrast between water and oil, optical microscopy can be used to monitor the formation and the presence of O/W and/or W/O emulsions. For thin-layered samples, it can also be used to observe the presence of W/O/W and O/W/O multiple-microemulsions.

Additionally, fluorescence microscopy can be used to easily determine the presence of different phases by labeling either the aqueous phase or the non-aqueous phase with fluorescence dyes. The advantage of using fluorescence microscopy is that samples that are dense can still be investigated. This is possible because the excitation of the sample and the fluorescence emission are at the same surface. Therefore, the excitation light does not need to penetrate through the entire sample. However, it can be difficult to observe the presence of multiple-microemulsions that are only few microns in size using fluorescence microscopy, due to the bright fluorescence signal from the neighboring molecules of different phases.

Phase Inversion of Dispersed System

Phase inversion of emulsions is well documented. In practice, the phase inversion of a dispersed system or emulsion could be triggered by a change in formulation or composition, such as an increase of water or oil concentration. This kind of phase inversion is generally called dynamic inversion.[13]

A formulation such as an NAF could be altered by the continuous addition of a water-based fluid containing surfactants, stirring with low energy until inversion is detected, usually using conductivity measurements. The W/O emulsion has conductivity near zero, while the O/W emulsion has a high conductivity similar to the aqueous phase.

The phase inversion may occur suddenly or gradually, with change of composition, depending on the surfactant used in the water-based fluid. At the inversion point, the fluid system experiences its lowest interfacial tension. Under these conditions, spontaneous microemulsification occurs between the oil and water phase of the system.

When the system is approaching the phase inversion point, multiple emulsions are being formed. Multiple emulsions are the simultaneous occurrence of both emulsion types (O/W and W/O).[13-15] In most cases, the formulation transition is associated with the transition of phase behavior from Winsor type I to Winsor type II, passing through Winsor III. The phase behavior of a water-oil-surfactant system was described in the early work of Winsor.[16] The Winsor type I system is a surfactant-rich microemulsion (aqueous) phase in equilibrium with excess oil. The Winsor type II system is a surfactant-rich microemulsion (oil) phase in equilibrium with excess aqueous phase**.** The Winsor type III system contains three phases in equilibrium: a middle phase microemulsion, and two excess phases (oil and water). The three-phase behavior is associated with ultra-low interfacial tension and maximum solubilization of oil and water per unit mass of surfactant. Each phase behavior type is associated with an emulsion type at the non-equilibrium condition: oil-in-water emulsion (O/W) for Winsor I, water-in-oil emulsion (W/O) for Winsor II, and Winsor type III is associated with a microemulsion system.

Current Spacer Technologies

Good spacer fluid design, in addition to other factors such as cement composition, displacement techniques and proper job execution is critical to achieve successful well completion.[11-12]

Generally, a series of aqueous or water-continuous spacers containing surfactants, solvents, weighting materials and viscosifiers are used to displace the synthetic- or oil-based mud from the wellbore. The performance and the ultimate success of these chemical additives can be influenced by factors such as temperature, salinity, hardness, pH, solids content, oil-water ratio and oil type.

The use of inappropriate types and concentrations of chemical additives in spacer fluid can lead to incompatibility, creating a mixed interface of spacer and NAF downhole. The fluids incompatibilities can result in phase separation, settling of solids, poor cleaning, insufficient water-wetting and variations in viscosity. Significant changes in rheological properties at the interface of an NAF and an aqueous spacer can lead to channeling, which could be further exacerbated in a non-concentric wellbore.[17-19]

The use of bright-field and fluorescence microscopy has been proven to be a valuable technique to evaluate the cement pre-flush spacer technology. In addition to conventional evaluation methods, such as interfacial tension (IFT) measurements, vial tests and surfactant screening conductivity tests (SSCT),[20] the use of optical microscopy may be used to better understand the mechanism involved in displacing NAF and rendering surfaces water-wet. The microscopy study may be correlated with the vial tests and relative conductivity studies to better understand the phase inversion process.

Lab Evaluation and Results

Phase Inversion by Relative Conductivity

The phase inversion from the oil-continuous phase to the water-continuous phase can be measured using the SSCT apparatus. This device measures the relative conductivity changes (measured in microamperes) that occur as a fluid shifts from oil-wet to water-wet. Oil-based fluids exhibit zero relative conductivity, a number which increases as spacer fluid is added and the mixture shifts from oil-continuous to water-continuous. The SSCT provides a good means for measuring the ratio of spacer fluid to NAF required to invert the phases.

The type of base oil, as well as the mud weight, affects the efficacy of a spacer fluid to clean and water-wet downhole surfaces. This can be observed by the required spacer/NAF ratio for the phase inversion in this test. A good spacer design can overcome the differences in performance seen when changing NAF formulations. Many different density drilling fluids were formulated using various base oils, ranging from diesel to synthetics. The spacer fluid used in this study was a pre-flush cement spacer formulated based on mesophase technology. The component of the spacer formulation is presented in **Table 1**.

To evaluate the spacer, 300 mL of fluid is added to the mixing cup and a baseline is set, usually at 125 microamperes. The spacer is then removed and 300 mL of NAF is placed into the cup. The NAF should have a conductivity reading of zero at this point. As the NAF is mixed in the cup, spacer fluid is added in 10-mL increments, and the change in conductivity is monitored. The addition of spacer continues until the mixture reaches a ratio of 75% spacer to 25% NAF. Various spacers were evaluated. A spacer formulated with mesophase technology produced a very acute phase inversion, creating a steep slope, which levels off when the inversion is complete and the mixture is water-continuous. This phase inversion is well represented in **Fig. 1**. In this case, the mesophase spacer fluid is a 12.5 lbm/gal formulated in freshwater-based fluid. The NAF is a 12.5 lbm/gal synthetic-based drilling fluid. The relative conductivity measurements increase beyond the upper limit of the device, leveling off above the 200-microampere mark. Notice the percentage of spacer required to begin the inversion, and how quickly the inversion occurs.

As can be seen in **Fig. 1**, once the concentration of spacer reached approximately 40%, the spacer began to shift the phase from the W/O phase to the O/W phase. This is the key for the spacer's ability to clean the NAF from downhole surfaces. Upon reaching approximately 49% concentration, the microamperes reached the upper limit of the measuring device. Based upon the percentage of spacer fluid that is required to begin the phase inversion, one can draw conclusions about the volume required to turn the system water-continuous, which is a requirement to turn the system from oil-wet to water-wet. This is useful in determining how a spacer fluid is to be formulated for a particular application.

Fluorescence Microscopy and Sample Preparation

The components of a fluorescence microscope necessary for observing fluorescence signal are described in **Fig. 2**. White light passes through an excitation filter that filters out all but the wavelength of light used to excite the sample. The excitation light is reflected towards the objective by a dichroic mirror that focuses the light onto the sample under investigation. The fluorescence light from the sample is collected by the objective and refocused on to a detector or an eyepiece. The dichroic mirror is carefully chosen to reflect all wavelengths of lights and only allows fluorescence light to go through. Since dichroic mirrors are not 100% efficient, an additional emission filter is used to filter stray light not from the fluorescence signal.

Unweighted spacer fluid and solid-free NAF were prepared in order to avoid interference from the solids during microscopy imaging studies. For fluorescence imaging, an oil-soluble dye was added to the external oil phase. The dye is highly soluble in non-aqueous fluids and completely insoluble in an aqueous medium. The fluorescence signal observed under the microscope indicates the presence of oil.

Different ratios of spacer fluid to NAF mixtures were investigated to observe the type of emulsion or Winsor phases formed. The sample was immediately observed under both the bright-field and fluorescence microscope. Since a very thin layer of sample is investigated on a microscope slide, it was necessary to put a fresh sample every few minutes to minimize error due to heating of the sample by the lamp.

Wettability and Phase Inversion Studies with Microscopy

Spontaneous emulsification and coalescence of emulsion droplets are observed when the spacer fluid comes in contact with the NAF. Depending on the ratio of the spacer fluid to NAF, the presence of W/O, O/W or multiple emulsions (either O/W/O or W/O/W) are formed. The multiple emulsions can be observed using optical microscopy. The wettability of the surface changes as the fluid goes through the process of phase inversion during the displacement. In the case of W/O emulsions, the surfaces are oil-wet. At a certain proportion of spacer/NAF the inversion process begins and multiple emulsions and mixed wettability are observed. Upon achieving a high percentage of spacer in the spacer/NAF mixture, the fluid finishes the inversion to O/W and the surfaces become water-wet.

The phase inversion measured using relative conductivity testing is correlated with microscopic studies. **Fig. 3** shows the change in relative conductivity of a mixture of spacer fluid with NAF at different ratios. The conductivity is zero for the 50/50 mixture. This was also validated using vial tests, discussed in detail below. These vial tests showed poor cleaning due to oil-wet surfaces at spacer/NAF ratios of less than 50/50 (**Fig. 4**).

For a 50/50 mixture, the fluorescence image in **Fig. 5a** clearly shows the presence of water droplets inside the non-aqueous continuous phase (W/O). Figure 5a also shows the advantage of using fluorescence microscopy. The bright-field microscopy image (**Fig. 5b**) does not provide information that would indicate if the outer phase is water-continuous or oil-continuous.

In this example, after increasing the ratio of the spacer fluid to NAF to about 60/40, an increase in the conductivity is observed. This can be followed with the microscopic images shown in **Fig. 6**. Figure 6a shows an image of the process of phase inversion. This process occurs very fast once it reaches the proportion of the NAF/spacer at which the Winsor type I system has a transition to Winsor III. At this point the fluid is a microemulsion type Winsor III, which is typically characterized by ultra-low interfacial tension. **Fig. 7** shows the interfacial tension obtained when the mesophase spacer contacts the synthetic-based oil. The spacer fluid used exhibited two orders-of-magnitude lower interfacial tension with the synthetic-based oil compared to the one between the water and synthetic-based oil (17 mN/m). The microemulsification occurs between 60/40 and the 65/35 spacer/NAF ratio for this particular system. Observation under the microscope shows rapid formation and coalescence of the droplets. These emulsion droplets are free flowing and coalesce until a thermodynamically stable state is reached.

After increasing the amount of spacer fluid to 65%, the conductivity reaches close to its maximum. At this point, the microscopy images (**Figs. 8 and 9**) show virtually complete change from an oil-continuous to water-continuous phase. Because of the bright fluorescence signal from the oil droplet, it becomes difficult to clearly observe the presence of multiple-microemulsion (W/O/W) using fluorescence microscopy (**Fig. 8**). This occurs because the fluorescence signal overshadows the non-fluorescing water droplets. At this stage, bright-field imaging becomes very useful to clearly see the formation and the presence of W/O/W multiple microemulsions, as shown in **Fig. 9**.

The conductivity is at a maximum for a mixture containing 65% spacer fluid or more. With the ratio of 75% spacer fluid to NAF, optical microscopy images in **Fig. 10** show very stable O/W emulsions.

As discussed earlier, microemulsions are systems with high detergency and high solubilization of oil and are an intermediate stage of the phase inversion from W/O to O/W. Therefore, the formation of microemulsion during the displacement of NAF by the spacer is critical and results in the most efficient spacer fluid performance. If the mixture of the spacer fluid and NAF does not go through a microemulsification process at certain proportions of spacer/NAF, the total phase inversion will not occur and will produce a partial or incomplete water-wetting of the tubulars and formation.

Cleaning Efficiency and Rheology

The cleaning efficiency was evaluated using the vial test. Different ratios of spacer fluid to NAF (from 90/10 to 10/90) were prepared in a vial and tested to determine the cleaning efficiency of the spacer. Figure 4 show only the vials with 50% or higher spacer concentration. This is due to the presence of W/O emulsion at this ratio, as seen in the microscopic images in **Fig. 5**. The ratio of spacer to NAF of 75/25 and higher left no observable oil residue after the spacer treatment indicating the ability of the spacer to water-wet the glass surface.[19] The effective cleaning of the glass vial at this ratio is due to the phase inversion from oil-continuous to water-continuous, as seen under the microscope (**Figs. 8, 9 and 10**). Ease of cleaning of the vial indicates good compatibility of various spacer/NAF ratios.

Compatibility of various spacer/NAF systems were also evaluated by rheological property measurements. Often, the viscosity is greatly increased when a non-aqueous fluid is contaminated with an aqueous fluid. The increase in viscosity can reduce the efficiency of the spacer fluid to effectively displace NAF. It is critical to monitor the compatibility of the spacer fluid with NAF and to prevent drastic changes in the rheological properties at the different ratio of the two fluids. **Fig. 11** shows rheological properties at 150°F using a FANN 35 viscometer at variable speeds. The rheology of NAF by itself and when it is in contact with the spacer fluid indicates that the presence of spacer fluid does not cause undesirable changes in the rheological behavior of the spacer/mud mixture. No significant increase of plastic viscosity, yield point and low rpm readings were observed for different spacer/NAF proportions.

The results of the rheology evaluation are in good agreement with the results of the microscopy evaluation. The microcopy evaluation shows the transition from oil-continuous to microemulsification and finally to water-continuous with a minimal amount of multiple emulsion droplets. Multiple emulsions typically found in viscous emulsions are associated with the increase in plastic viscosity and other rheological properties. The increase in rheological properties can be a major problem leading to reduced cleaning and water-wetting of the casing and formation

Conclusions

- Optical microscopy imaging provides an excellent means to understand the spacer fluid technology and the phase inversion mechanism involved at a truly microscopic level. This microscopy technique is fast and provides accurate representation of the inversion process.
- Bright-field and fluorescence microscopy can be used for screening surfactants and surfactant-blend packages for developing spacer fluids by observing fluid interactions under different conditions.
- The results obtained in the bottle tests, rheology, relative conductivity and microscopy all prove that the spacer technology used in this study has the ability to totally water-wet the surfaces and produce a phase inversion of the oil-based mud from oil-continuous to water-continuous.

Acknowledgments

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Nomenclature

cP = Centipoise
NAF = Non-aqueous fluid
O/W = Oil-in-water emulsions
OBM = Oil-based mud
SBM = Synthetic-based mud
SSCT = Surfactant screening conductivity test
W/O = Water-in-oil emulsions
W/O/W = Water-in-oil-in-water emulsions

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Tables

Table 1. Additives of Pre-flush Cement Spacer

Pre-Flush Cement Spacer Components
Weighting Material
Water or low salinity brine
Surfactant package additive
Polymer

Figures

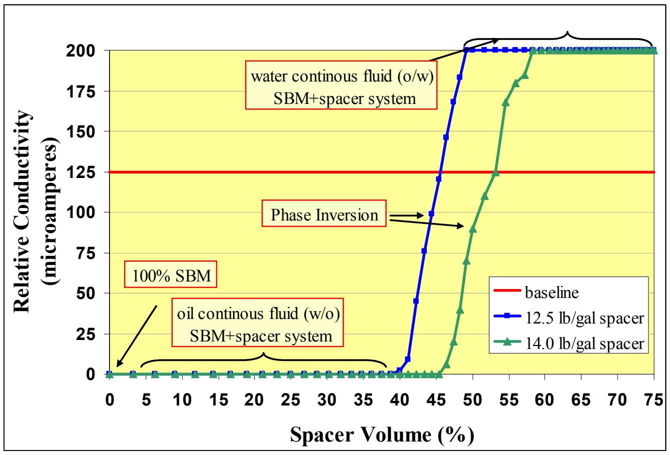

Fig. 1—12.5 lbm/gal and 14.0 lbm/gal synthetic-based mud treated with freshwater spacer fluid

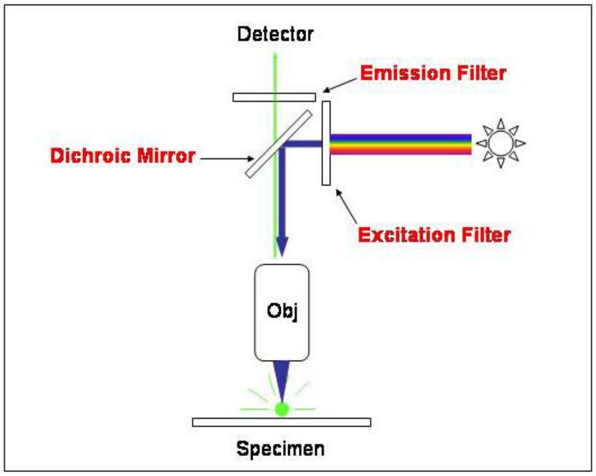

Fig. 2—Outline of a fluorescence microscope [21]

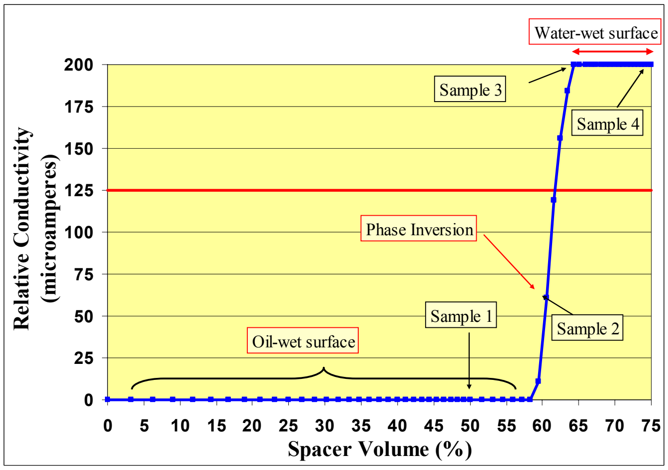

Fig. 3—Conductivity measurements of the unweighted spacer and unweighted synthetic-based mud mixture

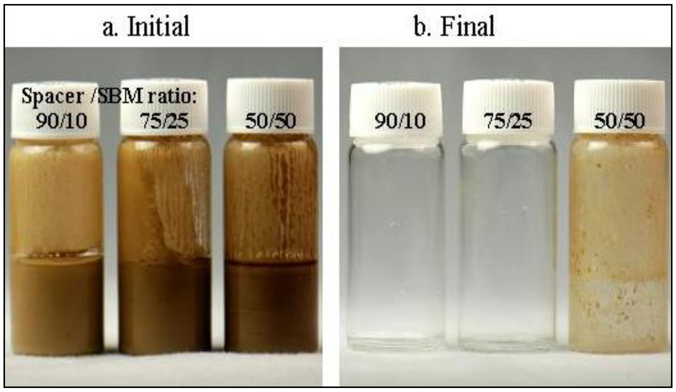

Fig. 4—Cleaning test at various ratios of spacer/ NAF in glass vials

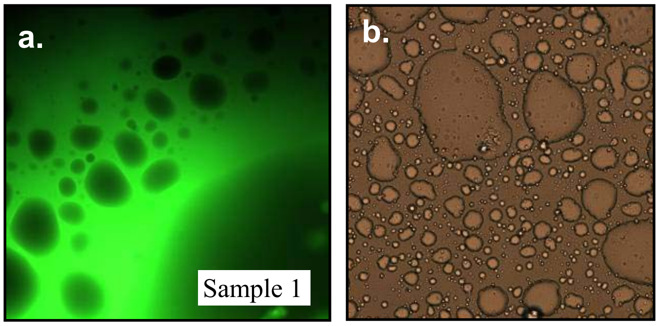

Fig. 5— Fluorescence (a) and bright-field (b) images of a 50/50 spacer fluid to NAF mixture showing W/O emulsions

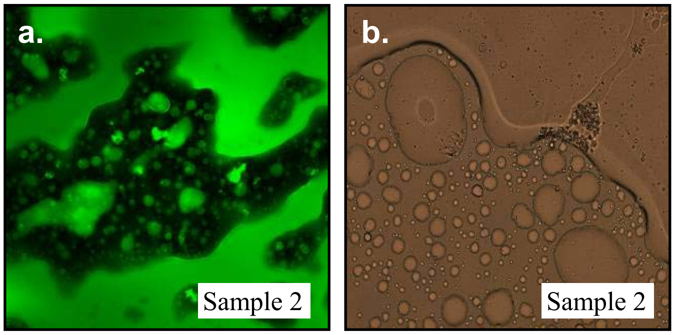

Fig. 6—Fluorescence (a) and bright-field (b) images of a 60/40 spacer/NAF mixture showing both oil- continuous and water-continuous phases

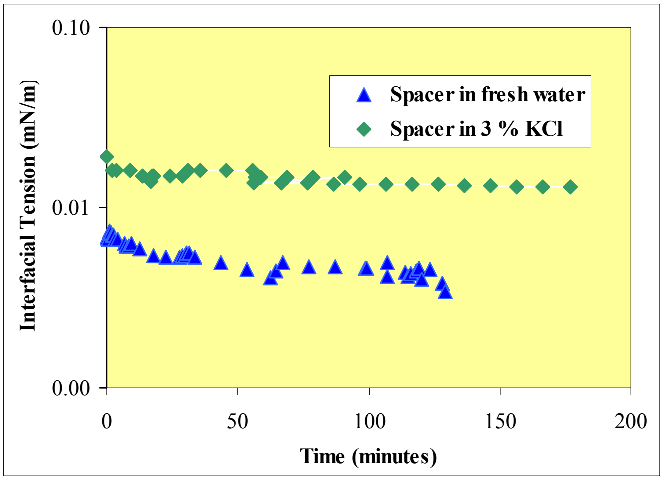

Fig. 7—Interfacial tension between spacer and synthetic-based oil

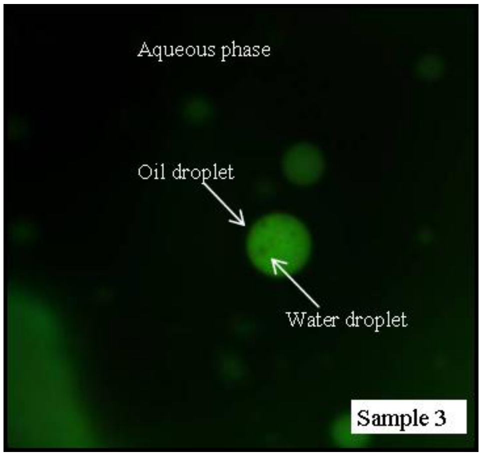

Fig. 8—Fluorescence microscopy image of a 65/35 spacer/NAF barely showing the presence of multiple emulsions

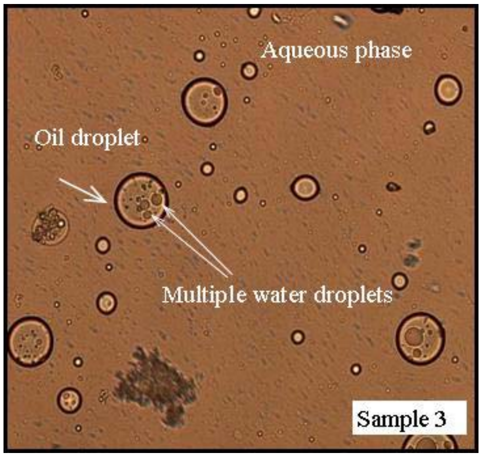

Fig. 9—Bright-field microscopy image of a 65/35 spacer/NAF clearly showing the presence of multiple emulsions

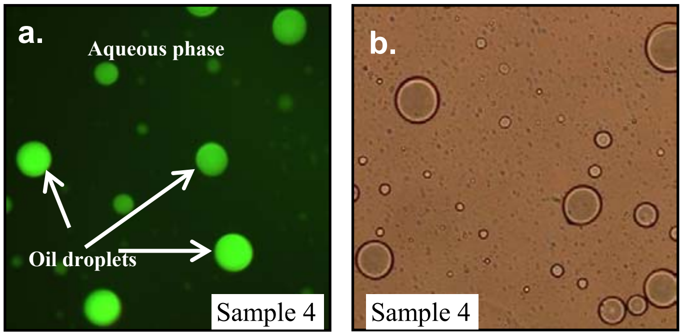

Fig. 10—Fluorescence (a) and bright-field (b) images of a 75/25 spacer/NAF mixture showing the presence of O/W emulsions

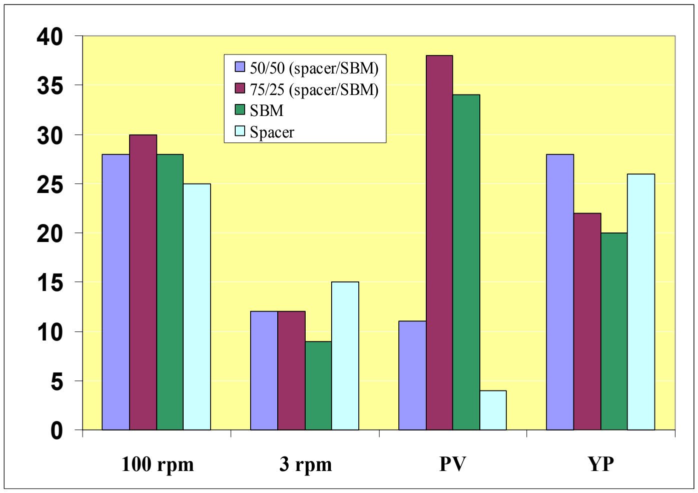

Fig. 11. Rheology of NAF and NAF/spacer dispersed system at 150°F