THESIS

IDENTIFICATION AND VALIDATION OF SCREENING METHODS FOR ASSESSMENT OF THE SHEENING POTENTIAL OF EMBEDDED OIL IN SEDIMENTS

Submitted by

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ABSTRACT

IDENTIFICATION AND VALIDATION OF SCREENING METHODS FOR ASSESSMENT OF THE SHEENING POTENTIAL OF EMBEDDED OIL IN SEDIMENTS

Sediments impacted with petroleum hydrocarbons (oil) may sheen due to ebullition-driven transport or sediment disturbance. The goal of this project was to develop a screening method that can be deployed on a small autonomous watercraft that will provide a reliable indication of sheening potential of embedded oil in shallow sediments. Different potential probes and methods were explored to penetrate sediments and determine sheening potential. Preliminary probe identification focused on development of a standardized laboratory column to test different probes and penetration methods to determine which probe has the highest probability to generate a sheen. Column tests were performed that consisted of different combinations of five crude oil types and a control (no oil embedded), seven probe candidates, two types of oil deposits, two targeted sheen levels, and with or without embedded air. Based on the data collected, a direct push rod with water injection had the greatest potential to generate a sheen.

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1.0 INTRODUCTION

Petroleum sheens are thin (0.1-100 micron) films of iridescent petroleum hydrocarbons or light non-aqueous phase liquids (LNAPL) that spreads across air-water interfaces as shown in Figure 1. Sediments impacted with embedded oil (i.e., LNAPL) in river, lake, and coastal settings can lead to sheening. Sheening in surface water can potentially cause ecological impacts and may result in regulatory violations, odors, and public perception issues.

Figure 1. Example of petroleum sheen observed in parking lot.

Under the Clean Water Act, any appearance of a petroleum sheen on a water body is a violation. The Discharge of Oil regulation [61 FR 7421, Feb. 28, 1996], more commonly known as the "sheen rule," states:

> *§ 110.3 …discharges of oil in such quantities that the Administrator has determined may be harmful to the public health or welfare or the environment of the United States include discharges of oil that:*
>
> *(a) Violate applicable water quality standards; or*
>
> *(b) Cause a film or sheen upon or discoloration of the surface of the water or adjoining shorelines or cause a sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines.*

Sheens can be classified as chronic or episodic. Episodic sheens often correlate to low or high water stages, seasonal conditions, or specific climatic events (such as changes in barometric pressure). Timing of episodic sheens is dependent on numerous factors, including mechanism of release, degradation of light or dense non-aqueous phase liquids, and specific architecture of the groundwater-surface water interface. One of the primary mechanisms for the release of sheens is ebullition, as illustrated conceptually in Figure 2a and b for a deposited-source and upgradient source scenarios, respectively. Gas bubbles can occur due to air trapped in soil and/or gases release due to biological degradation of entrapped oil or natural organic matter. Gases released from entrapped oil zones can contain a thin film of oil between the gas and the water. Often, the release of one bubble leads to the coalescing of multiple bubbles, and a resulting cascade of ebullition that yields a sheen on the water surface (Sale et al. 2018). Sheens generated from embedded oil can also be triggered when sediments are disturbed by boat traffic or other mechanical processes (such as erosion).

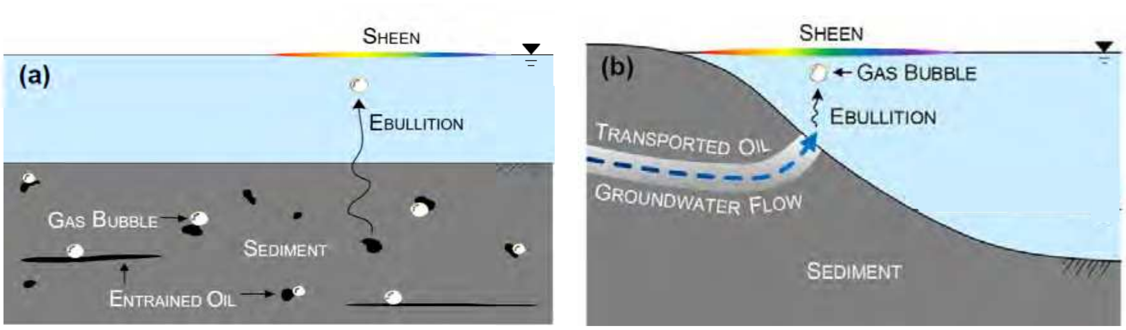


Figure 2. Conceptual models for embedded oil in (a) deposited-source setting, and (b) upland source type settings.

Identifying embedded oil that is yielding, or may yield, sheens can be difficult given the episodic nature of sheening and the requirements for expensive manual sampling of potentially contaminated subaquatic sediments. A relatively small number of locations are typically sampled, making pinpointing the location and extent of sheening potential difficult over large areas. In addition, current screening methods that can detect the presence of embedded oil in sediments (e.g., laser induced fluorescence, LIF) typically require large pontoon boats or barges to accommodate the heavy equipment needed to obtain results; pontoon boats or barges require substantial effort to relocate and may be unable to access sediments at complex, shallow [≤ 3 meters (m)], or remote sites. In addition, the presence of oil may not correlate to the potential of the embedded oil to generate a sheen. Therefore, there is a need for smaller scale screening methods that provide accurate and reliable indications of both embedded oil presence and sheening potential, that also includes improved maneuverability to allow for more effective acquisition of data. Such a method will reduce the cost of acquiring datasets with better spatial coverage to enable more informed decision making.

The overarching goal of this project is to develop a smaller scale screening methods that can be deployed on an autonomous watercraft that will provide multiple lines of evidence of both embedded oil presence and sheening potential in shallow sediments. This thesis is focused on the preliminary development of a probe to assess the sheening potential of embedded oil for future incorporation onto an autonomous watercraft, although the identified probe and method may also be deployed manually.

The objectives of the research presented herein were:

1. Generate a sheen in lab;
2. Develop a method to consistently differentiate between no sheen present, presence of a sheen, and the presence of an oil glob; and,
3. Resolve a penetration method(s) with the highest probability to generate a potential sheen from embedded oil.

2.0 BACKGROUND

This section provides a background on observing sheens and summarizes existing sheen classification systems that were used in this study.

2.1. Physics of Sheen Observation

Petroleum sheens occur when the sum of the outward force at the edge of LNAPL on surface water are greater than the sum of inward forces. The surface tension of the air-water interface is greater than the surface tensions of air-LNAPL and LNAPL-water. The greater surface tension pulls the oil in all directions until interfacial tensions (γ) at the leading edge of the sheen are balanced as shown in Figure 3 (Sale et al. 2018). Sheens do not spread as an even layer with equal thickness, but consist of thicker and thinner patches (Lewis 2007).

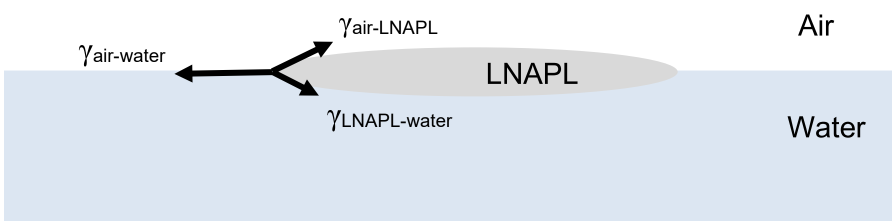


Figure 3. Forces controlling spreading of LNAPL across water-air interfaces.

The streaks of color witnessed on a sheen are the result of the interference of light by the thin film of oil on the water surface. This phenomenon is referred to as thin film interference. Any visible color is a mixture of wavelengths within the visible spectrum. “White” light contains all wavelengths in the visible spectrum and black is the absence of all light (US EPA 1972, Bonn Agreement 2017). When light hits the film of an oil sheen, some of the light is reflected off of the top of the oil surface (air-LNAPL interface), depicted as ray 1 in Figure 4, while the rest of the light is transmitted through the film. When the light hits the bottom of the film (LNAPL-water interface), a portion of the light is reflected (ray 2 in Figure 4) while the remainder is transmitted through the water (not shown in figure) (the Physics Classroom 2019).

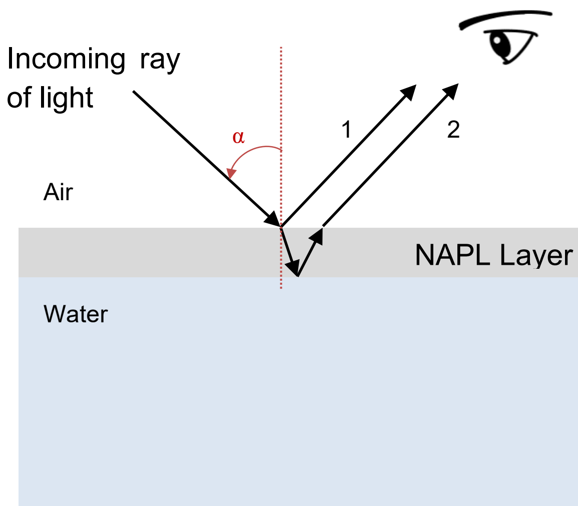


Figure 4. Interference of light on a thin film of oil.

Ray 2 must travel further compared to ray 1 (two times the thickness of the film) and as a result the two waves may be in or out of phase. If the two waves are in phase, meaning the crests and troughs of both waves match up, the interference is constructive, resulting in an enhanced color (Figure 5a). If the waves are out of phase, the combined wave is attenuated. This results in a less intense color or no color if the two wavelengths cancel each other out, known as destructive interference (Figure 5b; the Physics Classroom 2019).

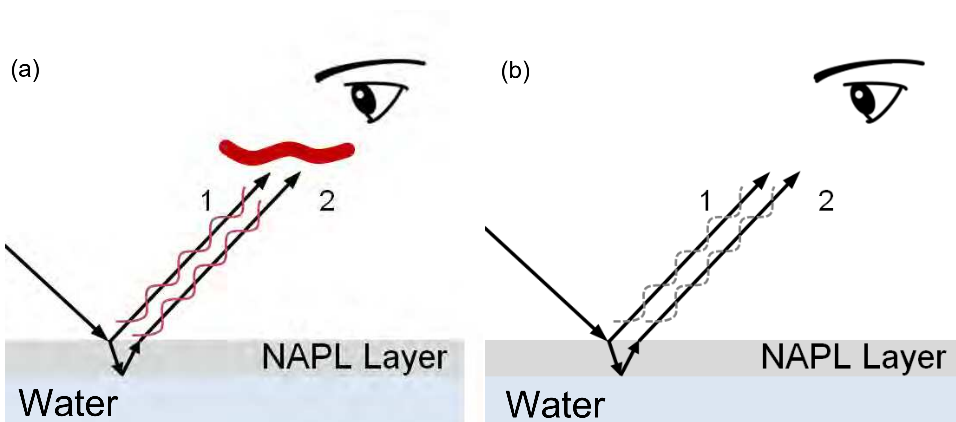


Figure 5. Example of (a) constructive and (b) destructive interference of light waves to produce color.

Light wave interference depends on the angle of incidence (from the normal, shown as α in Figure 4) and the thickness of the film. Oil films thinner than approximately 0.04 microns (μm) are invisible to the human eye (Bonn Agreement 2017, Lewis 2007). As the thickness of the oil film changes, so does the appearance. The following sheen types are classified at varying oil thicknesses.

Silver (0.04 μm – 0.3 μm)

When the oil film thickness is between 0.04 μm – 0.3 μm, no single color is constructively interfering. All wavelengths are traveling back to the eye, essentially equally. The oil film appears white or silver due to the reflection on the water beneath, shown in Figure 6a (the Physics Classroom 2019). All types of oil will appear the same if they are present in these extremely thin layers (Bonn Agreement 2017).

Rainbow (0.3 μm – 5.0 μm)

Oil layers in the range 0.3 μm to 5.0 μm are at the critical thicknesses for the wavelengths to constructively and destructively interfere, creating the appearance of a rainbow as shown in Figure 6b with bands of individual color; red, orange, yellow, green, blue, indigo, and violet (Lewis 2007). Repeating bands of color appear because the waves will constructively interfere at integer multiples of film thickness. All oil types in films with thickness between 0.3 μm – 5.0 μm will show a similar tendency to produce the 'rainbow' effect (Bonn Agreement 2017).

Metallic (5.0 μm – 50 μm)

As the film thickness increases, the increased distance allows a greater number of wavelengths (color) to interfere or mix on the way to your eye. The net color becomes a blend of colors distributed through the visible spectrum so the apparent color becomes less and less pure, degrading towards grey (US EPA 1972). This range of thicknesses acts as an imperfect mirror. The apparent color is dependent on the viewing conditions and sometimes reflects the color of the sky (blue or shades of grey). The reflectance creates a visual effect of a flat, almost uniform surface without obvious features, described as "metallic" (Lewis 207). Then, as the film become too thick to show bright colors, the color comes from self-color (browns and blacks for crudes and residuals) or from the water itself (US EPA 1972).

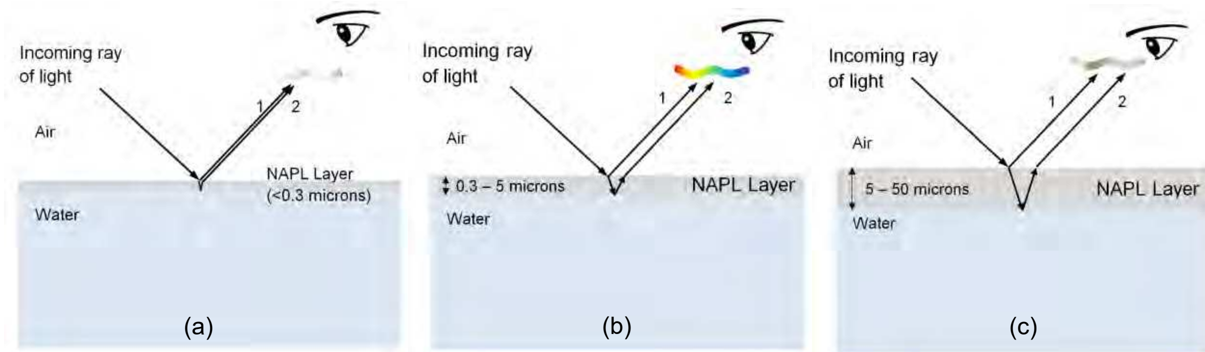


Figure 6. Interference of light on varying oil film thickness: (a) silver, (b) rainbow, and (c) metallic.

Thicker Oil (< 50 μm)

For oil films thicker than 50 μm the wavelength cannot penetrate the oil layer and is only reflected from the oil surface. The "true color" of the oil will dominate the color observed (Bonn Agreement 2017). Herein referred to as "true oil."

Sheen Dynamic Spreading

As a drop of oil spreads and the surface tensions balance, the sheen will often transition from a sliver sheen to rainbow, metallic, and then true oil if enough oil is present. Figure 7 shows a drop of oil release from a sediment clump as the oil sheen transitions from a silver sheen to metallic sheen.

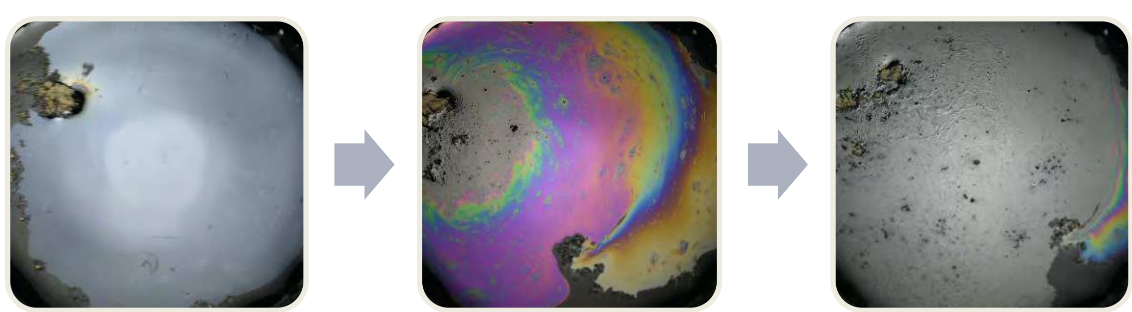


Figure 7. Transition from silver to metallic sheen.

2.2. Sheen Detection

Sensors used in sheen and oil detection are either passive or active. Passive sensors detect natural radiation emitted or reflected by the oil under observation. The most common sources of natural radiation (or electromagnetic energy) are reflected sunlight and thermal emissions and therefore passive sensors are used in detecting an oil spill on the open ocean. Active sensors emit a pulse of electromagnetic energy and then measure the signal reflected back to the sensor (API 2013).

2.2.1. Optical Sensors

Optical sensors are passive imaging devices sensitive in the ultraviolet, visible, and near-infrared spectrum. These sensors exploit differences in reflectance as the primary mechanism for detecting oil on water and rely on external sources of energy, i.e., the sun (CDFW 2017, API 2013). Obtaining useful results from these sensors requires a trained observer or photo algorithm as the results are typically visual observations. The appearance of an oil film depends on how light waves of different wavelengths are reflected off the surface of the oil, transmitted through the oil (and reflected off the water surface below), and/or absorbed by the oil, as described in Section 2.1.

For the purpose of this research, all three types of sensors were considered, as all three are currently used to detect and characterize oil spills on the ocean, but as the Clean Water Act is defined in the visible spectrum, this research focused on using a visual spectrum optical sensor. In the visible spectral range (400 to 700 nm), imagery is displayed in “true color.” This is the nearest approximation of what a human observer might view directly. In the visual spectrum range, oil has a higher surface reflectance than water and sheens are detected by color on the water surface (Fingas and Brown 2014).

2.2.2. Spectrometer (Laser-Induced Fluorescence)

A spectrometer is an active sensor used to gather information about a substance based on the visible, ultraviolet, or infrared light that the source projects. Direct push laser-induced fluorescence (LIF), originating from work by Dakota Technologies, is an *in situ* spectroscopy probe for the detection and characterization of hydrocarbons (Figure 8). When exposed to specific wavelengths, such as by a pulsed laser, most hydrocarbons will produce fluorescence (Dietrich and Leven 2009). LIF probes can measure the relative concentration of the hydrocarbons and gather a spectral product “fingerprint” to assist in identifying the hydrocarbons in the subsurface. When attached to a direct push probe, these measurements can be made continuously with depth (Robertson and Cabal 2008).

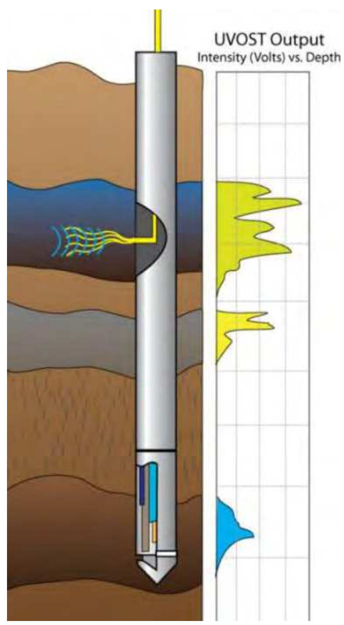


Figure 8. Schematic of LIF system and ultraviolet optical screening probe (UVOST) output (Robertson and Cabal 2008).

In situ sensing of oil using florescence techniques is the current state of practice for terrestrial sites, although the small and mobile platform of the overarching project goal adds complicating operational constraints including instrument size and sensing time. Dakota Technologies is currently evaluating existing direct and indirect LIF technologies to identify candidate technologies to be used in conjunction with the results of this research.

2.3. Visual Classification Schemes

The use of color as a guide to sheen thickness has been recognized and adapted since the 1930s (Lewis 2000). Most notability, the United States National Oceanic and Atmospheric Administration (NOAA) revised their sheen classification system for aerial observation in August 2016 (NOAA 2016). The European response community produced a set of standards, Bonn Agreement Oil Appearance Code (BAOAC) in 2004 which are still used today (Bonn Agreement Webpage). As shown in Table 1, the two most recent and most widely used classification schemes are consistent in the definitions of sheen appearance versus film thickness. These schemes use the oil thickness presented in Section 2.1 and used in this research.

Table 1. Sheen visual classification schemes comparison.

Appearance	BAOAC, 2004 Film Thickness (µm)	NOAA, 2016 Film Thickness (µm)
Almost Transparent		<0.04
Silver/Gray	0.04 to 0.30	0.04 to 0.30
Rainbow	0.30 to 5.0	0.30 to 5.0
Metallic	5 to 50	5 to 50

2.4. Hydrocarbon vs non-hydrocarbon

Sheens are commonly associated with release of petroleum liquids (petroleum sheen) or organics associated with natural breakdown of organic material (biogenic sheen). The Clean Water Act specifies that only petroleum sheens are in violation of the act, therefore the ability to distinguish between a hydrocarbon sheen and a non-hydrocarbon sheen is important. The best method to distinguish between non and true hydrocarbon sheen is to note the behavior of the sheen when disturbed. If the sheen is brittle, cracks, breaks apart, or disaggregate upon disturbance, this indicates a biogenic origin. If the sheen is non-brittle and rapidly coalesces upon disturbance, the source of the sheen is either petrogenic (e.g., petroleum hydrocarbons) or pyrogenic (e.g., combustion-related materials) (ITRC 2018).

3.0 MATERIALS AND METHODS

The appearance and color of an oil sheen can be influenced by many factors, including oil properties, sheen thickness, light conditions, and observer positioning (Ramstad 1998) all of which are discussed in the following section.

3.1. Test Oils

Five crude oils of varying viscosities were used in this study. Oils were selected to span a range of characteristics, while all having low sulfur to minimize odor during laboratory testing. The properties of the five crude oils are presented in Table 2. The oils are listed from the lowest viscosity to the highest.

Table 2 Crude oil properties (oils are color coded and the associated color is used through this thesis).

Crude Oil	API Gravity	Specific Gravity	Pour Point	Viscosity, cSt	Sulfur, weight %
OIL-1	43.8	0.8070	-15.1°C (4.8°F)	2.21 @ 40°C (104°F); 1.88 @ 50°C (122°F)	0.214
OIL-2	32.8	0.8611	-39.0°C (-38.2°F)	5.12 @ 40°C (104°F); 4.11 @ 50°C (122°F)	0.913
OIL-3	21.9	0.9224	-53.2°C (-63.8°F)	66.3 @ 40°C (104°F); 45.2 @ 50°C (122°F)	3.33
OIL-4	21.4	0.9254	-29.3°C (-20.7°F)	76.0 @ 40°C (104°F); 47.7@ 50°C (122°F)	3.63
OIL-5	15	0.9660	-22.0°C (-7.6°F)	469 @ 40°C (104°F); 230 @ 50°C (122°F)	1.21

3.2. Sheen Quantification (oil-in-dish) Tests

Before undertaking the methods to produce a sheen from embedded oil, a series of “oil-in-dish” tests were performed to reaffirm the sheening principals presented in Section 2 with the provided crude oil, and develop a set of baseline images for each oil and sheen level with which to compare column test results. A summary of the oil-in-dish tests and the results are discussed below, and a comprehensive summary and photograph log are provided in Appendix A. Oil was added in 2 microliters (µL) increments to a 10.5 centimeter (cm) diameter aluminum tray, spray painted black and filled with approximately 100 mL of water, until all three levels of sheen were observed. A still from the OIL-3 test immediately after a 2 µL drop was applied to the surface is presented in Figure 9.

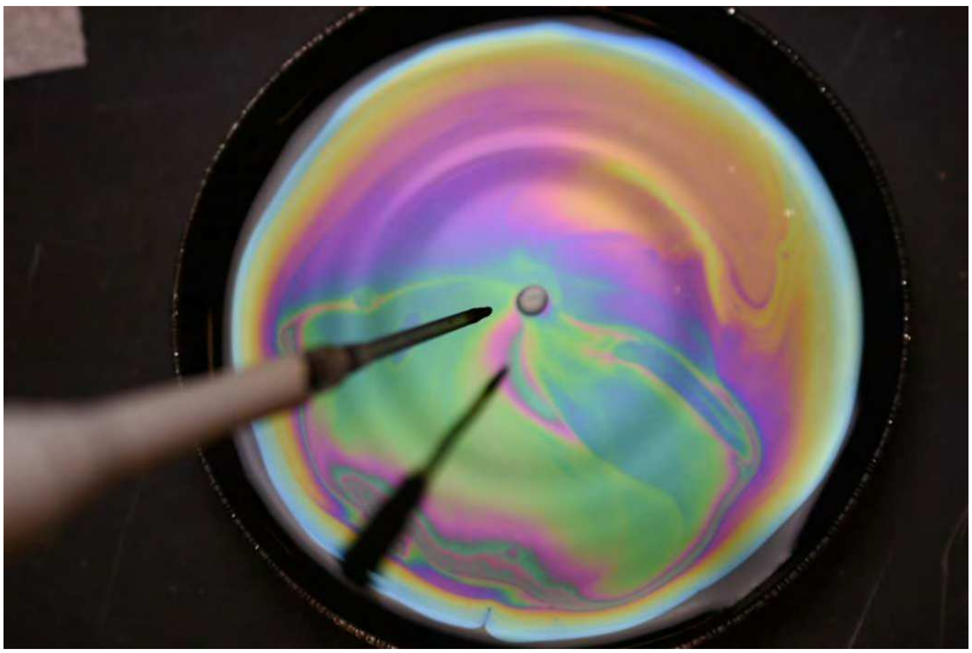
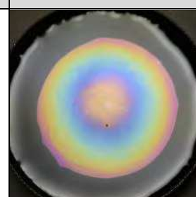
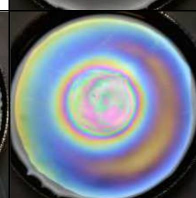
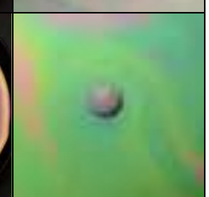
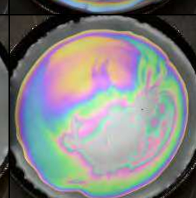
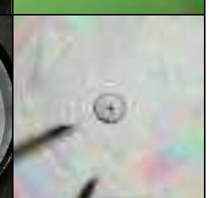
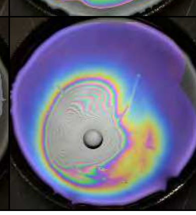
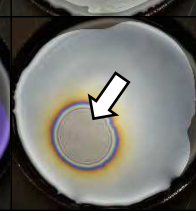
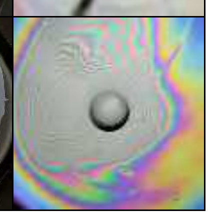


Figure 9. Application of 2 µL of OIL-3 during the oil-in-dish test.

A representative capture or still photograph ("still") of each level of sheen for each of the five crude oils was gathered from videos taken during oil-in-dish tests by manually viewing each frame from each video. The stills were used as references during the column tests (described subsequently). A comparison of the five oils at different levels of sheen are presented in Table 3. Due to the speed of the OIL-1 spreading, a silver sheen was not observed at a frame rate of 20 frames per second. The OIL-1 test was also concluded before true oil was achieved. Many of the photographs included in Table 3, show multiple sheen levels simultaneously, but all follow the pattern, silver sheen on the edge and metallic sheen in the center with a rainbow sheen separating the two. All of the photographs are in order of the test progression from left to right (silver sheen to true oil) except for OIL-5. The representative still for both OIL-5 silver and metallic sheens occurred in the same picture with the silver sheen on the edge and metallic sheen in the center. A thin band of rainbow sheen separates the two. All of the true oil photographs are zoomed to better see the representative true oil.

Table 3. Summary of the oil-in-dish tests comparing levels of sheen for each crude oil.

Oil	Silver	Rainbow	Metallic	True Oil
OIL-1	X			X
OIL-2				
OIL-3				
OIL-4				
OIL-5				

Note:
X - Sheen level not observed
- Arrows identify relevant sheen.
True Oil stills are zoomed in on the true oil.

The primary takeaway from these tests was the necessity of watching and observing (via a video instead of a single photograph) as the sheen spreads and transitions. The easiest way to qualify a sheen is to see the transition. The rainbow sheens are the easiest to visually detect and identify, and without the presence of a rainbow sheen between the silver and metallic sheens, the two could be difficult to distinguish independently.

3.3. Column Tests – Equipment

This section discusses the probes, photo equipment, and laboratory direct push apparatus used during the bench scale sheen column tests.

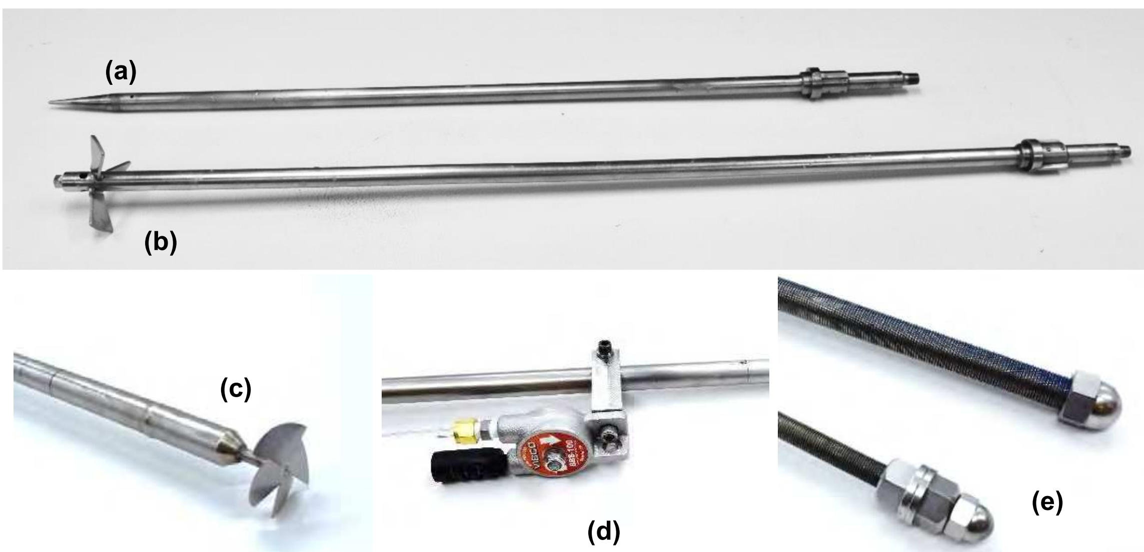


Figure 10. Probes tested: (a) direct push rod used for direct push, air injection, and water injection, (b) large propeller mixer, (c) small propeller mixer, (d) vibrator, and (e) rod drop.

3.3.1. Probes

A variety of probes were considered for this research. Only probes that had potential compatibility with small autonomous sample systems were evaluated. Seven candidate probes were identified and are presented in Figure 10: direct push, direct push with air injection (air injection), small propeller mixer, large propeller mixer, rod drop with manual agitation, direct push with light vibrating (vibrator), and direct push with water injection (water injection). For each probe, the probe description is provided below, as well as some background information, real-world uses, targeted release mechanisms, and consideration for how the probe would perform on a small autonomous watercraft.

Direct Push: The direct push probe is a 2.54 cm diameter hollow stem rod with a 9 cm long cone tip shown in Figure 10a.

Direct push technology (DPT) consists of small-diameter steel rods that are driven into the subsurface, often by hydraulic methods. Typically, the weight of the direct push rig is used as a reaction force for pushing the probe into the subsurface. By attaching sensors to the end of a steel rod, specialized DPT probes have been used for *in situ* geophysical, geochemical, geotechnical, and hydrogeological investigations. DPTs acquire a vertical profile of the subsurface with minimal disturbance. DPTs are generally the investigation method of choice when greater mobility is required and when investigation derived waste is a concern (Dietrich and Leven 2009). Conventional DPT may not be able to penetrate caliche, bedrock, or unconsolidated layers with significant amounts of gravel or cobbles but should be effective for penetration of most sediments (U.S. EPA 2005). A disadvantage of DPT is that a substantial reaction force may be required that cannot be achieved on an autonomous watercraft; additionally, pulling the rod from the subsurface may pose a challenge for the same reason.

Air Injection: The air injection probe tested is a direct push rod with air injection and uses the same probe as the direct push (only) and water injection, shown as Figure 10b. The hollow stem probe has an injection port located 10 cm from the tip of the rod. Air can be injected through the rod and released into the sediment.

Subsurface oil recovery methods such as air sparging or airlift bubblers directly inject air into the sediment and groundwater to promoting gas-liquid mass transfer and mixing. Air sparging has been used in dredging operations and to clean well bores. Airlift bubblers are commonly used for *in-situ* collection of biota and microinvertebrates. In both processes, the injected air mixes with the liquid causing the mixture to be less dense than water resulting in an upward displacement (Benson 1989). Disadvantages of this system are the requirement for compressed gas to be stored on the small autonomous watercraft that will have to be periodically refilled, and the methods are vulnerable to preferential pathways in the subsurface and therefore may miss relevant (potentially sheen generating) embedded oil.

<u>Water Injection</u>: The water injection probe is a direct push rod with water injection and uses the same rod as the direct push and air injection, shown as Figure 10c. Instead of injecting air through the rod, a water source can be attached, and water is injected.

Water injection, also known as waterflooding, is commonly used for oil recovery. Water injection uses water pressure to move oil within the reservoir rock toward the production well (Speight 2016). Water injection induces a change in the hydraulic gradient causing the liquid to flow upward or shears the soil and forces any entrapped oil upward, via the natural buoyancy of the LNAPL. Unlike direct push, an advantage of water injection is pulling the rod from the subsurface may be easier due to the positive water pressure reducing the stress of the surrounding soil. Unlike the air injection probe, water injection would not need a water source stored on the small autonomous watercraft. Installed pumps could use the water around the small autonomous watercraft, running the water through a filter before injecting the water into the subsurface.

<u>Propeller Mixers</u>: Two propeller mixers were tested. The large propeller mixer (Figure 10d) is a three-blade mixer with a diameter of approximately 10 cm. The small propeller mixer (Figure 10e) is a four-blade mixer with a diameter of approximately 4 cm.

During the first iteration of testing with this probe, an auger was considered. Augers are a rotating probe with a helical bit for boring. Auger borings are commonly used in soil exploration and sampling and are designed to bore by bringing soil cuttings up to the surface. The traditional advantages and disadvantages of augers comes from the type of material augers cut through and the goal of the drilling (e.g., subsurface exploration or monitoring well installation) (ASTM D4700). The advantages of auger methods for a small autonomous watercraft are principally the effective penetration of the subsurface without the need for a large reaction force to push against like DPT, and augers may effectively disturb the subsurface and release any entrapped air in a larger radius. The disadvantage of auger methods is the requirement of a moment reaction force to prevent the rig from spinning, a force that a small-scale lightweight watercraft rig cannot easily provide. For this project, bringing any sediments and possible contamination to the surface by drilling may pose an investigation derived waste management concern. A “propeller” blade was selected as the final probe instead of a traditional auger to reduce disturbance and waste but still retaining many of the benefits that an auger provides.

Vibrator: For this candidate probe, a Vibro® pneumatic vibrator (Vicbo, Wyoming, Rhode Island) was mounted to the direct push rod, creating a direct push with vibration, shown in Figure 10f.

Vibration is used in both concrete and geotechnical engineering to increase the density of a porous media. Vibration reduces or eliminates the effective mechanical friction between particles by temporarily increasing porewater pressure and reducing effective stress. As the particles consolidate, entrapped pore fluid (liquid and/or air) is released to the surface (Reading 1982). A vibration probe may be effective at bringing entrapped air with oil, or oil with no air, to the surface to test the potential of embedded oil to sheen. A more powerful vibrator, such as a concrete vibrator, was considered, but the power requirements made this type of vibrator unsuitable for a small autonomous watercraft. A pneumatic vibrator will require an air source that will need to be periodically refilled.

Rod Drop and Manual Agitation: For this probe, two stainless steel threaded rods with steel nuts were considered (shown in Figure 10g), but only the lower rod in the figure, a 1.9 cm (¾ in)-16 stainless steel threaded rod with two stainless steel nuts and a stainless steel nut cap was tested. The steel nuts and cap add extra weight to better drive the probe into the column.

A rod drop was selected as an alternative form of direct push when direct push failed to release oil (discussed in Section 4). DPT, known for minimal disturbance in geophysical, geochemical, geotechnical, and hydrogeological investigations, is not designed to release oil outside of the direct path of the probe. The rod drop, therefore, was selected as a probe for the greater effective radius of influence than direct push. Rod drop uses the weight of the rod to drive the probe into the subsurface instead of the reaction weight of the rig, triggering soil liquefaction due to the sudden and rapid loading. Liquefaction causes the sediment to lose frictional strength and covert to liquid like behavior. Then, like the water injection, the natural density of the embedded oil is anticipated to bring the oil to the surface. If dropping the rod does not create enough sufficient force to induce liquefaction for sufficient duration to allow oil to escape to the free water column, manual agitation (series of short up and down movements with the rod) may trigger or enhance liquefaction, but a reaction force would be required. A disadvantage to rod drop and manual agitation, similar to or even more than direct push, is that pulling the rod out of the subsurface may pose a challenge for a small autonomous watercraft.

3.3.2. Photo Equipment

A visible light, digital single lens reflex camera was used to identify mobilized sheens. All column tests were recorded in video, and then Mixilab's *Video to Photo* (Mixilab, Kharkiv, Kharkiv Oblast, Ukraine) was used to select stills from the videos. As part of the sheen quantification (Section 3.2), a variety of light bulbs types (fluorescent, light-emitting diode (LED), and halogen) and a variety of light bulb temperatures (cool versus warm) were tested, see Appendix A. Based on the test summarized in Appendix A, sheens are best detected under a cool compact fluorescent lamp (CFL) lightbulb. A circle bulb was selected so the probes could pass through and achieve 360-degree lighting.

The photographic equipment used to take videos of the oil films, shown in Figure 11, was:

- Camera: Nikon DX D7200 with AF-S NKKOR 18-140mm 1:3.5-5.6G ED XR Lens (Nikon Inc., Melville, New York);
- Light source or light bulb [Sunlite CFL 30/50K Fluorescent 30W T9 Circline Ceiling Lights, 5000K Super White Light (Sunlite, Brooklyn, New York)]; and,
- Cloth diffuser to wrap around the light bulb.

Figure 11. Typical example of the photo equipment setup.

3.3.3. Laboratory Direct Push Apparatus

A preexisting laboratory direct push apparatus and columns were used for this study. The laboratory direct push apparatus was used to control the vertical and rotational movements of the probes during testing. A detailed schematic of the direct push apparatus is shown in Figure 12. The columns, sized to fit the direct push apparatus, consisted of clear polyvinyl chloride (PVC) tubing with an inner diameter of 10.2 cm and a length of 45.7 cm.

The direct push apparatus has three key operations: 1) vertical movement of the probe, 2) rotation of the probe, and 3) air or water injection. Vertical movement is driven by a 1/3 hpAC electric motor (Dayton 5K537 right angle gear motor, Dayton Motor Co., Dayton, TX) that is mounted at the top of the direct push apparatus. This motor is geared to rotate two threaded screws that raise or lower the underlying platform at a fixed rate of 10.2 cm/min. The probes and probe rotation system are attached to this platform. The rotation system consists of a 1/12 hp variable speed DC electrical motor (Dayton 47726A permanent magnet gear motor, Dayton Motor Co., Dayton, TX) and rheostat control. The rate of rotation (reversible) is adjustable up to ~ 21 rotations per minute (rpm, Castlebaum et al. 2011). Air and water source and controls were external from the direct push apparatus mechanism and used house compressed air, a pressure gage and regulator, and an external accumulator (for water) connected to the direct push apparatus.

3.4. Column Tests - Setup

To screen potential probes, bench scale column tests were performed to represent the anticipated field conditions. The column tests consisted of oil embedded 15 cm deep in a water-sediment column made up of a synthetic sediment mixture.

3.4.1. Sediment Mixture

The anticipated deployment for candidate probes was constrained to shallow (maximum 3 m deep) rivers or harbors, and as such, the assumption was made that the subsurface will be saturated fluvial, lacustrine, estuary, littoral, etc., and the sediments would be relatively soft (i.e., not rock, riprap, asphalt, etc.; although subsurface material may contain layers of sand, gravel, and cobbles). A representative synthetic sediment mixture was created by reviewing 12 river and harbor particle size distribution reports from oil-impacted sites around the world (see Appendix B for full summary). The particle size distributions by weight from the 12 reports were tabulated and are graphically summarized in Figure 13 by coarse sand (C) (2.0 – 4.75 mm), medium sand (M) (0.425 – 2.0 mm), fine sand (F) (0.075 – 0.425 mm), silt (0.002 – 0.075 mm), and clay (< 0.002 mm). Complete particle size distributions were not provided in most reports.

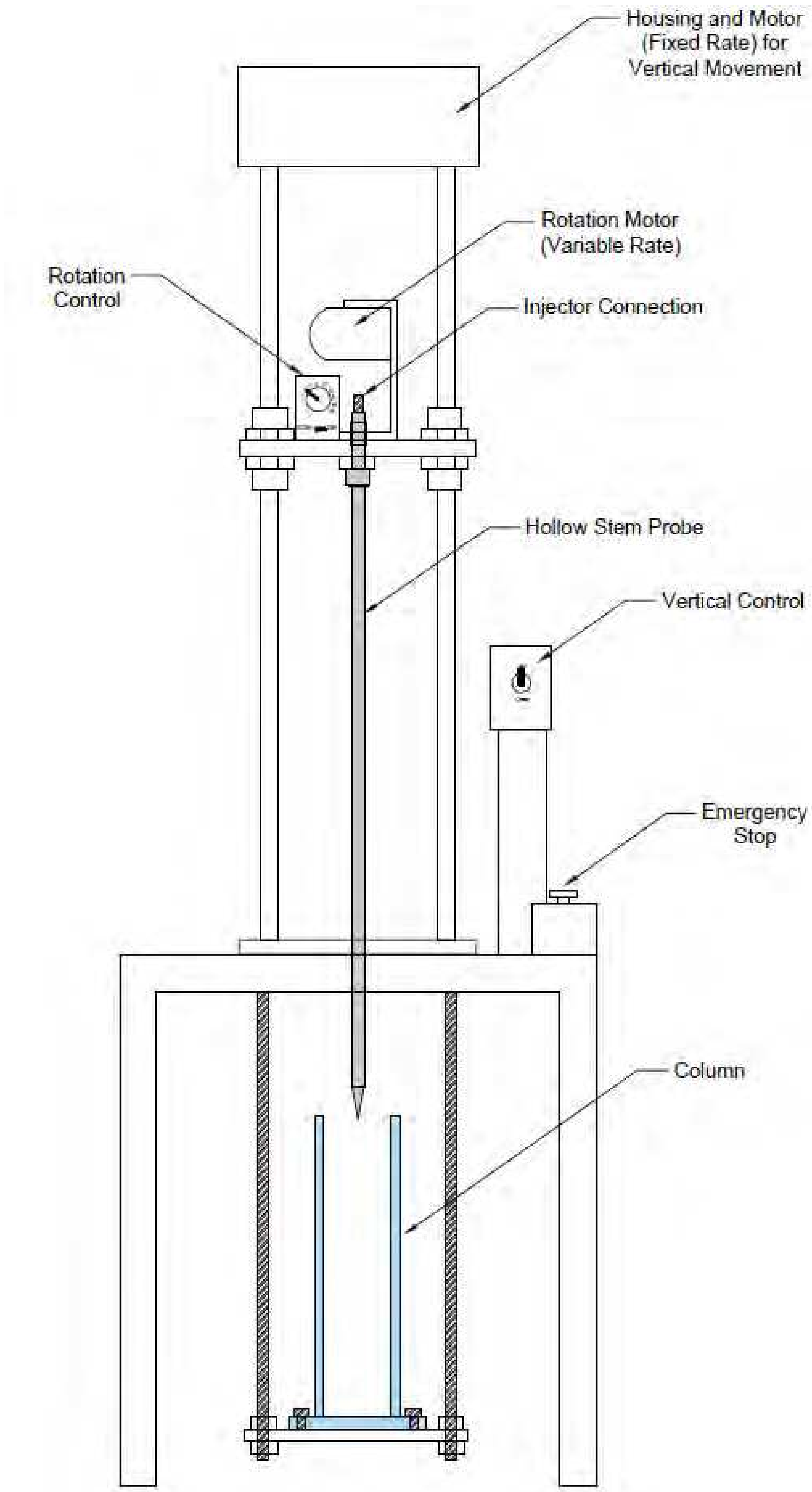


Figure 12. Laboratory direct push apparatus schematic.

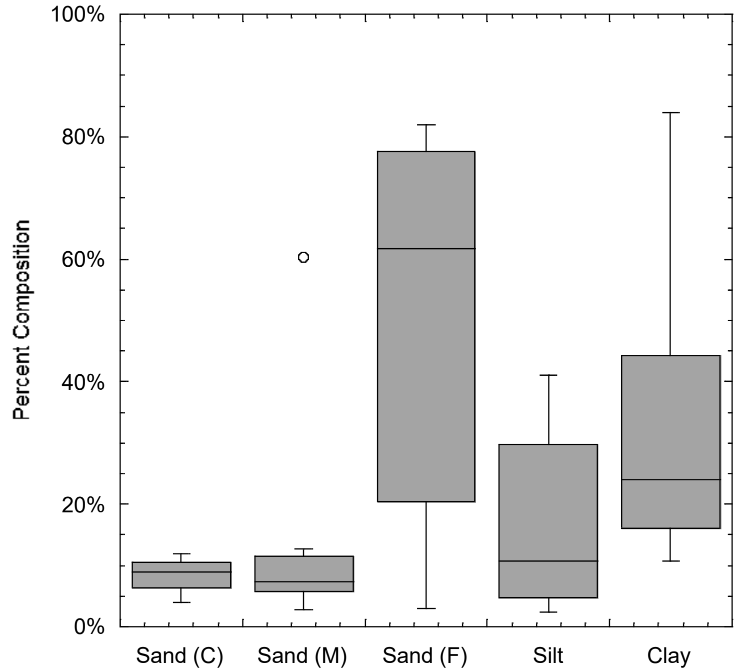


Figure 13. Particle size distributions by weight and by coarse sand (C) (2.0 – 4.75 mm), medium sand (M) (0.425 – 2.0 mm), fine sand (F) (0.075 – 0.425 mm), silt (0.002 – 0.075 mm), and clay (< 0.002 mm).

Three variations of the sediment mixture were considered, a medium and fine sand mix, a fine sand and fines (silt and clay) mix, and just fines (silt and clay) mix to test the effectiveness of the final selected probe or probes. For the initial screening and testing of probes and oil embedded methods in this study, an average fine sand and fines (silt and clay) mix was created. The sediment mixture by weight contained 59% fine sand, 13% silt, and 28% clay. A fine beach sand was used as the fine sand portion. Silica flour was selected for the silt and a clay mixture of kaolinite and bentonite (95% and 5% respectively) made up the clay percentage, see Figure 14. The individual particle size distribution charts for the four materials and the combined particle size distribution chart of the sediment mixture are provided in Appendix C.

Once weighted and blended, the sediment mixture was mixed with tap water from Fort Collins [pH of 7.30 and electrical conductivity of 8.99 mS/m @ 25ºC (Bohnhoff 2012)], Colorado, until approximately at or below the liquid limit, based on visual inspection. The soil needed to have enough strength/cohesion to aid in embedding the oil (described in Section 3.4.3, Column Assembly) but be sufficiently saturated to be representative of a river or harbor sediment.

Figure 14. The synthetic sediment mixture considered of fine beach sand, silica flour, and kaolinite and bentonite clay. Percentages by weight.

3.4.2. Oil Deposit

The goal for each column test was to produce the targeted sheen level by placing only the amount of oil needed to produce that sheen. The volumes of oil required to produce the different levels of sheens across the entire surface of a column (10.16 cm diameter) were calculated. The volume requirements for the column tests based on the visual classification scheme (Section 2.3) are presented in Table 4.

Table 4. Volume of oil required to achieve different levels of sheens in the column tests.

Sheen	Sheen Thickness (µm)	Volume of Oil (µL)
Silver	0.04 to 0.3	0.32 to 2.43
Rainbow	0.3 to 5	2.43 to 40.5
Metallic	5 to 50	40.5 to 405

An added variable in the column tests is that the embedded oil has to travel through a column of sediment to reach the water surface, thus not all of the embedded oil is likely to be released to sheen on the water surface. To be conservative, for each targeted sheen level, the higher range of the oil volume was selected for each sheen type (e.g., 40 µL for the rainbow sheen).

Oil was placed in the columns using micropipettes to control the volume and location of the embedded oil. At room temperature, OIL-3, OIL-4, and OIL-5 were too viscous to be drawn up into the pipette and were too tacky to place cleanly within the column. These three oils were placed into a water bath of 80°C to temporarily increase the viscosity and aid in embedding within the column.

Two oil deposits were used to test the effectiveness of the probes, a concentrated oil deposit, and a horizontally distributed oil deposit. The concentrated deposit, an example of which is presented in Figure 15a, was the "best-case scenario." The entire oil volume was placed in the center of the column based on the concept that, ideally, the probes would intercept the oil. The distributed deposit, an example of which is shown in Figure 15b, is more representative of the field conditions where the deployed probe may not come in direct contact with the embedded oil. The distributed deposit setup uses the same volume of oil as the concentrated deposit setup, but the oil is placed in arbitrary drop volumes around the center of the column so that the volumes of oil is separated into four or more drops. The probe may not come in direct contact with the oil, but to be considered successful, the probe still needs to release the oil to form a sheen. The distributed deposit tests the ability of probes to influence oil outside of the direct path.

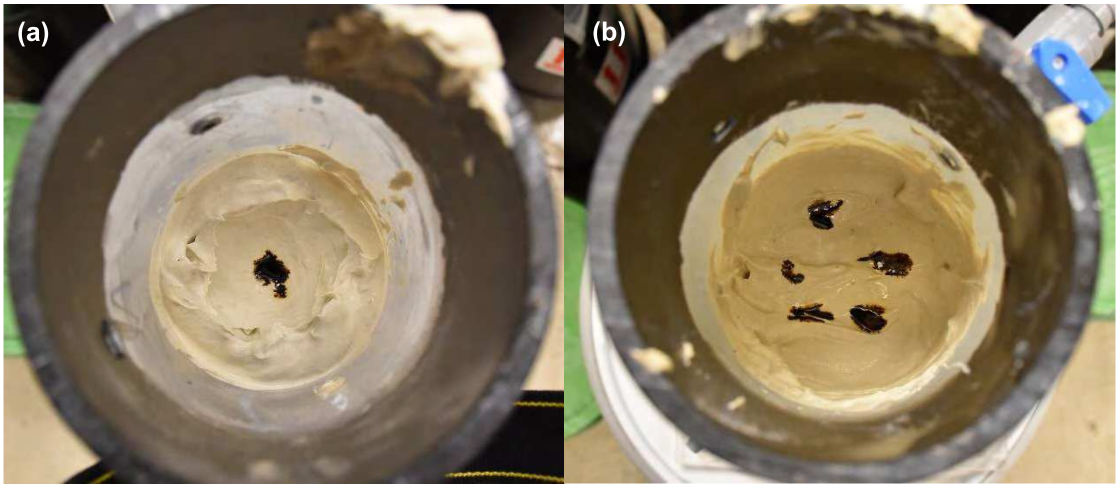


Figure 15. Examples of (a) concentrated and (b) distributed deposits of oil (40 µL of OIL-2) placed in a column.

3.4.3. Column Assembly

The columns used had an inner diameter of 10.2 cm and a length of 45.7 cm. The bottom of the columns was sealed by marine epoxy into a PVC flange bolted to an acrylic sheet. Each column had two valves installed to assist with drainage and clean up. The columns were taller than needed so as to decrease the amount of sediment volume required to fill the column, a 7.6 cm diameter, 10 cm long foam core was placed at the bottom of each column with a 10.2 cm diameter high-density polyethylene geomembrane (HDPE GM) disc on top. The HDPE GM disk was sealed in place with black 100% silicon caulk to prevent water loss to the annular space in the lower portion of the column. To act as a buffer between the probes and the HDPE GM and foam core, a base layer of sand that was coarser than the sediment mixture was placed at the bottom of the column. The inside of the top 10 cm of the columns was painted black to increase the contrast between the sheen and the PVC. A schematic and photograph of a typical column are presented in Figure 16.

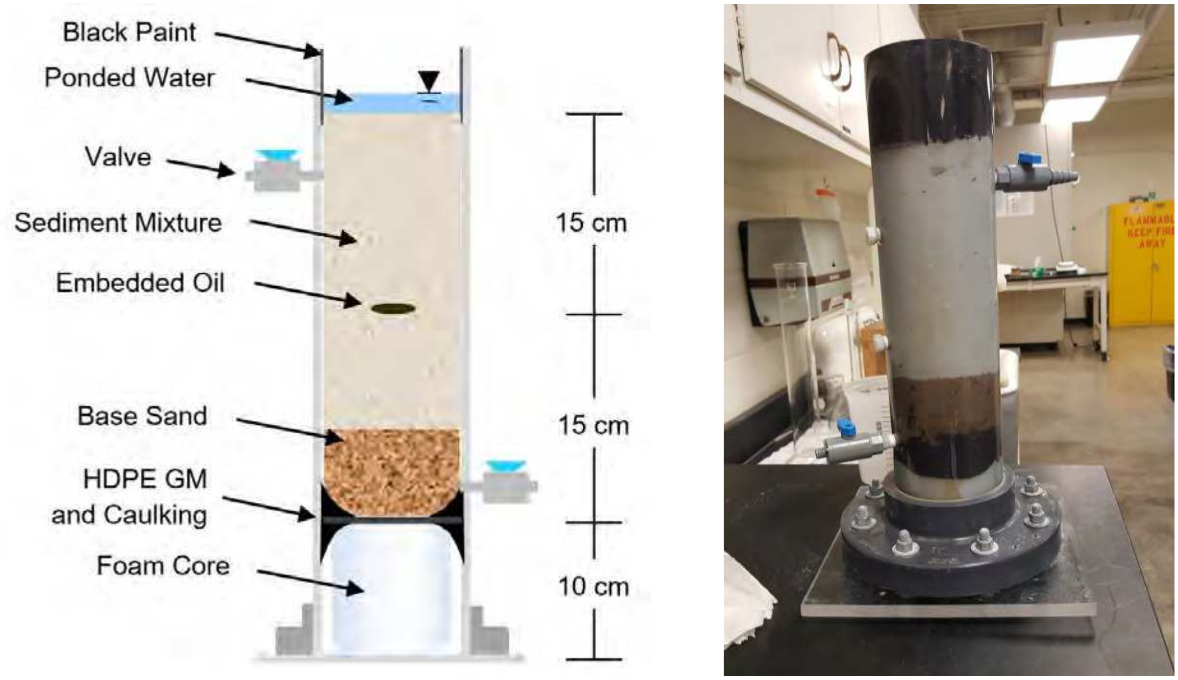


Figure 16. Schematic of typical column and example photograph of a complete column setup.

When assembling the columns for each test, the following steps were performed above the HDPE GM (internal base):

Step 1. *Base sand:* A approximate 7 cm thick base layer of dry medium-coarse sand was placed at the bottom of the column. The base layer was then saturated and excess water drained through the lower valve. Tapping the sides of the column was employed to facilitate settling of the sand and ensuring all excess water was drained.

Step 2. *Lower layer of sediment mixture:* The pre-saturated sediment mixture was placed on top of the base sand until the sediment level reached 15 cm above the geomembrane (~8 cm thick layer). The sediment mixture was placed loosely, and no extra measures were taken to compact the material beyond the self-weight of the sediment mixture.

Step 3. *Embedded oil:* For the concentrated oil deposit, a hollow depression was created in the sediment to cup the oil and keep the oil centered in the column. A micropipette was used to measure and place the oil, and the oil was then carefully covered by more sediment. The sediment mixture was water wet; therefore, careful steps were taken to keep the oil from "jumping" up the column. The walls of the hollow were carefully built up until the oil was fully encapsulated. The sediment had enough cohesion that the oil was encapsulated in a hollow ball of sediment, likely entrapping the oil with some air. For the distributed deposit, drops were placed in a circular formation around the center. The placement was similar to the concentrated deposit, except there were multiple hollow balls ensuring no oil migrated to the center or the walls of the column.

Step 4. *Upper layer of sediment mixture:* More pre-saturated sediment mixture was placed until the surface reached 30 cm above the geomembrane (15 cm thick layer).

Step 5. *Ponded water:* Depending on the probe being tested, a 1 to 3 cm thick layer of water was placed on top of the sediment mixture. Less water was placed in the column if the water injection was being tested to leave more headspace for the extra water being injected into the column. Based on preliminary tests the thickness of the water layer was not crucial, simply having a water layer thick enough that the released sheen could spread unimpeded was needed.

Alt Step 2. Sand layer: In select column tests where added air was used to simulate ebullition, an extra step was added to Step 2. Approximately 3 cm from the bottom of the lower sediment mixture layer, an approximately 3 cm thick layer of dry fine sand was placed and then covered with the sediment mixture to 15 cm above the geomembrane, see Figure 17. The water from the saturated sediment mixture would penetrate partially into the dry sand layer, but the middle of the sand layer would remain dry until penetrated by the probes. The air trapped in the sand layer was displaced by water as the probe penetrated the sand layer. The displaced air would produce a cascade of bubbles, simulating ebullition.

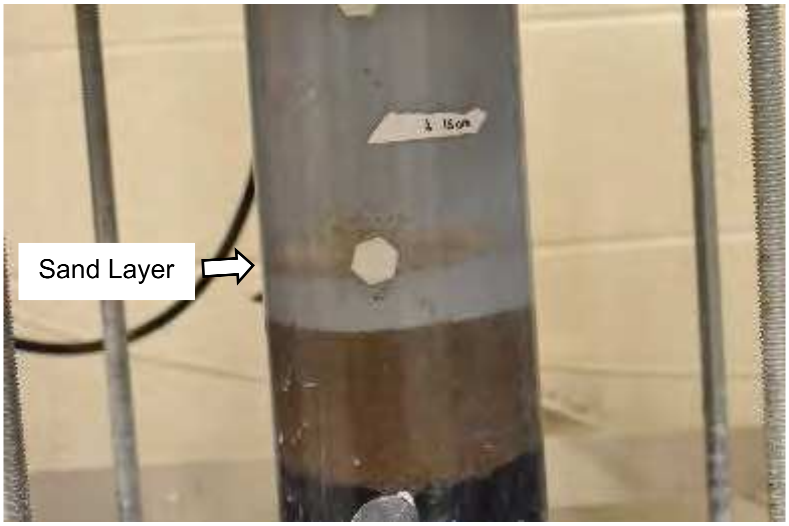


Figure 17. Example of sand layer place to embed air in the column.

3.5. Column Test – Test Runs

An example of the testing setup and a test being performed is presented in Figure 18. All the column tests were performed in the Colorado State University (CSU) Center for Contaminated Hydrology laboratory in Fort Collins, Colorado. For each column test, the column was built and then tested within an hour. The sediment with embedded oil was then treated as hazardous waste and disposed of in accordance with CSU's Environmental Health Services requirements and the column thoroughly cleaned and air dried before reuse.

For each column test, oil type, probe, sheen level target, oil deposit type, and addition of air were selected. A testing matrix presenting all combinations of column test variables is provided in Figure 19.

3.5.1. Procedure for Probes

The procedure for each of the seven probe candidates (direct push, air injection, small propeller mixer, large propeller mixer, rod drop with manual agitation, vibrating, and water injection) is described in this section.

Figure 18. Column test setup and example of an air injection test being performed.

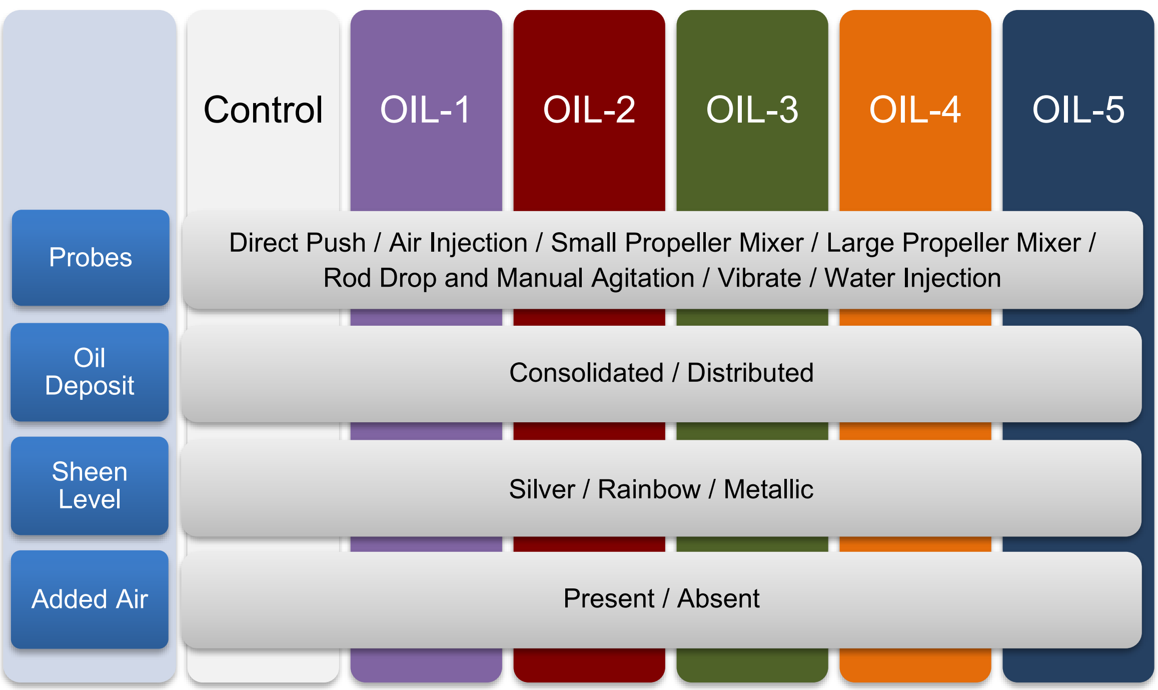


Figure 19. Testing matrix of all different column test variables used in the column tests. Note, not all experimental combinations were tested in this study.

Direct push: During this test, the probe was continuously lowered until the tip of the probe was, at minimum, 1 cm below the embedded oil and then the probe was raised until completely out of the column, see Figure 20.

Figure 20. Water surface during a typical direct push test.

Air injection: During this test, the probe was continuously rotated at approximately 8 rpm and lowered until the air injection port was, at minimum, 1 cm below the embedded oil. Air flow was continuous during the entire test (See Figure 21). The air pressure was set at approximately 140 kilopascal (kPa); however, air flow was reduced during the start of the test to prevent excessive splashing.

Figure 21. Water surface during a typical air injection test.

Small and large propeller mixers: During both tests, the mixers were continuously rotated. To protect the laboratory direct push apparatus mechanism, the mixers were rotated clockwise during the downward motion and counterclockwise during the upward motion. The large mixer is a right-handed mixer, meaning the blades are suited for clockwise rotation, and the small mixer is a left-handed mixer, suited for counterclockwise motion. The large mixer blades did extend and touch the sidewalls of the column (see Figure 22a), so to protect the column, the large mixer was rotated at approximately 8 rpm during the test. The small mixer was run at approximately 16 rpm during the downward motion (against the blades) and at max (approximately 21 rpm) during the upward motion (with the blades), see Figure 22b.

Figure 22. Propeller diameter relative to column interior diameter for the (a) large and (b) small propeller mixer.

Water injection: During this test, the probe was continuously rotated at approximately 8 rpm and lowered until the water injection port was, at minimum, 1 cm below the embedded oil. Due to limited headspace in the columns for the injected water and the fixed speed of the descent and ascent mechanism, the lowest possible water flow rate, approximately 1 mL/sec, was used during descent/ascent to conserve water. Water flow was continuous during the test to prevent the sediment mix from clogging the injection port. Once the probe reached the lowest point, the vertical movement ceased, and the water valve was opened fully (approximately 10 mL/sec) for one rotation of the probe before being choked off again for the ascent. An example of a typical water flow during the down and upward motion is presented in Figure 23a and an example of the water flow before choking off the flow presented in Figure 23b.

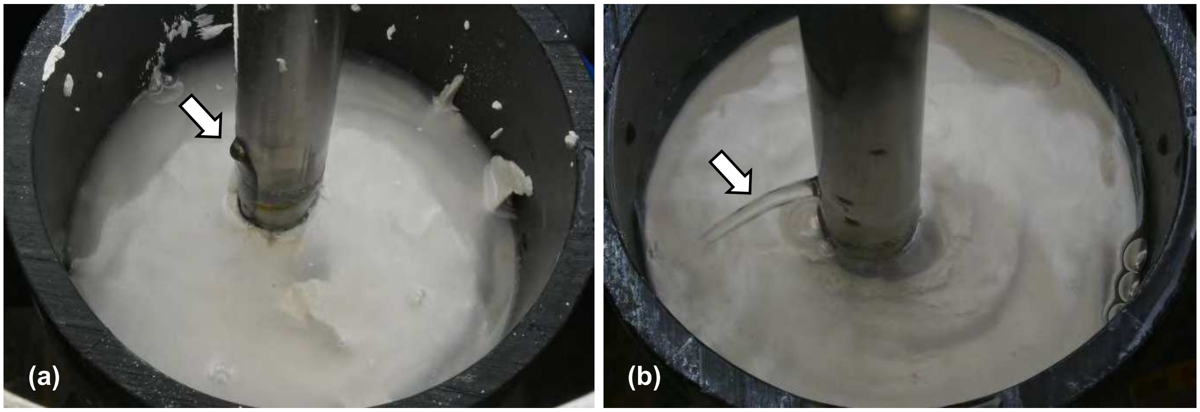


Figure 23. Examples of a typical water injection test when the water is (a) chocked off during ascent and decent and (b) full flowing at the nadir of decent.

Vibrator: For this test, the vibrator was mounted to the direct push probe at approximately 35 cm from the tip, the lowest possible position while still allowing the probe to be lowered until the tip of the cone was, at minimum, 1 cm below the embedded oil. The vibrator was mounted too high on the rod, the vibration was damped at the tip due to the mechanical connection with the direct push apparatus. This process did result in minor blocking of the water surface from the camera (see Figure 24), but not much more than the probe alone (compare to Figures 20 through 23). The vibration was continuous during the whole test applying an air pressure of 200 kPa to the vibrator.

Figure 24. Example still from a typical vibration test.

Rod drop and manual agitation: For this test, the column was set up in the laboratory direct push apparatus to keep lighting and camera setup consistent for all probes, but the motion mechanisms of the direct push apparatus were not used. The rod was dropped from a height of 91.4 cm above the top of the column, see Figure 25 for a still from a typical rod drop test. The rod rested in the column while the surface was examined before slowly being removed by hand and attempted again (one or two more times for a total of two to three drops). If the rod drops did not produce a sheen, manual agitation was performed. The rod was dropped back into the column and a series of short up and down movements with the rod for approximately 10 seconds were used to liquefy the sediment. The rod was left to rest in the column after agitation for 30 seconds to allow time for any oil to reach the surface before another round of agitation was performed or the rod removed from the column.

Figure 25. Still from a typical rod drop test.

3.5.2. Procedure for Photographing

In "*the use of colour as a guide to oil film thickness; Phase 1 – Laboratory experiments,"* Ramstad (1998) suggests that photographic equipment should be as close as possible to perpendicular (90°) to the water surface for the best sheen detection. Ramstad (1998) demonstrates that the observation angle makes a difference in sheen appearance. An observation angle of less than 45 degrees made the oil indistinguishable with the water surface (Ramstad 1998). Due to practical difficulties related to equipment placement, a perpendicular setup was not achieved during the sheen qualification or column tests. However, an effort to be as close to perpendicular as possible was made, see Figure 26 for how the sheen quantification lighting and camera equipment were set up.

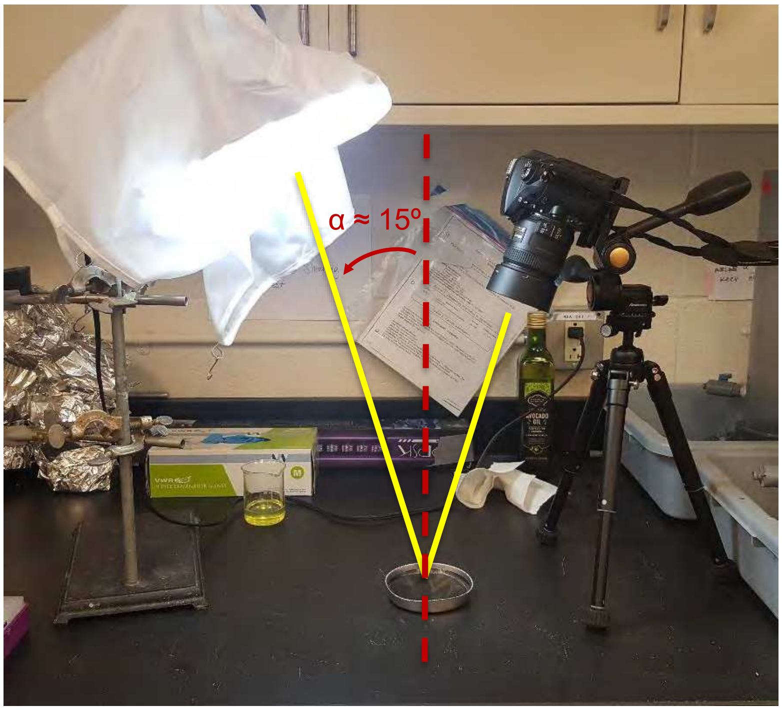


Figure 26. Light and camera setup during the sheen quantification tests.

During the sheen quantification (oil-in-dish) tests, the observation was made that the light and camera angle variables were much less complicated than anticipated. As long as the light source was not blocked, the sheen could be detected with the camera. The difficulty came from ensuring the diffusion cloth had no folds as this would cast a shadow and prevent the camera from detecting the sheen, an example of which is shown in Figure 27.

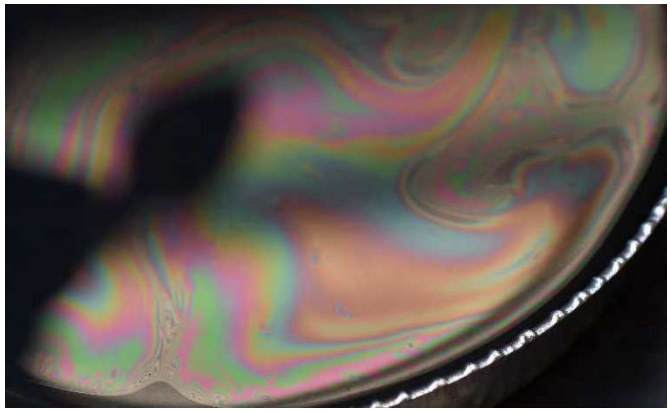


Figure 27. Close up image of how folds in the diffuser cloth creates shadows and blocks photographing the sheen.

During the column tests, the light source variable played a more significant role. As presented in Section 3.3.2, a circle bulb was used to achieve 360 degrees light coverage; however, the bulb was difficult to wrap with the diffuser cloth in a manner to prevent wrinkles and folds. The diffuser cloth was wrapped loosely around the rod to provide consistent light coverage and to allow the rod to move unrestricted. A paper towel was placed in between the rod and cloth to prevent any sediment or oil from touching the fabric. For the rod drop test, the diffuser was wrapped around a tub that allowed the rod to drop freely but prevented the rod from hitting the light, see Figure 28.

Figure 28. Typical rod drop with manual agitation column test set up.

In this column test setup, there was no way to eliminate all shadows. The wall of the column and the probes blocked the light from reaching all of the water surface (e.g., Figure 29, as an example). In Figure 29, a sheen covers the entire surface, but the sheen is indistinguishable in the upper portion of the water surface due to the shadow cast by the wall of the column and in the lower section where the probe (the large propeller mixer) blocks the light.

Figure 29. Typical example of the water surface and portions of the column where the light is blocked.

The sheen in Figure 29 also provides an example of the sheen being distinguishable versus indistinguishable to the camera. The lighting placement can also have an impact on qualifying the sheen beyond detection or not. An example of the impact the shadow cast by the probe while in the column is presented in Figures 30a and b. A blueish rainbow sheen on the edge of silver sheen is visible in Figure 30a. Similar to the sheen in Figure 31, the shadow cast by the probe makes the sheen in the lower portion of the column visually indistinguishable from the water surface. In the same column, but before the sheen spreads to the blueish rainbow, the sheen is a discernible rainbow sheen in the right side of the column as seen in Figure 30b; however, in the shadow cast by the probe, the sheen is not indistinguishable like in Figure 30a; instead the sheen is still visible and has a light brown appearance that could be mistaken as a metallic sheen. Once the sheen moved out of the shadows and into the light (with the water movement), the sheen was identifiable as a rainbow sheen instead of metallic sheen. Color is still observable in the shadow due to indirect light. In his 1998 experiments, Ramstad also distinguished the effects direct and indirect light had on sheen detection (Ramstad, 1998). He found that thinner sheens (e.g., silver and rainbow sheens) were more detectable with direct light, whereas thicker sheens (e.g., metallic and true oil) were easier to detect with indirect light (Ramstad, 1998).

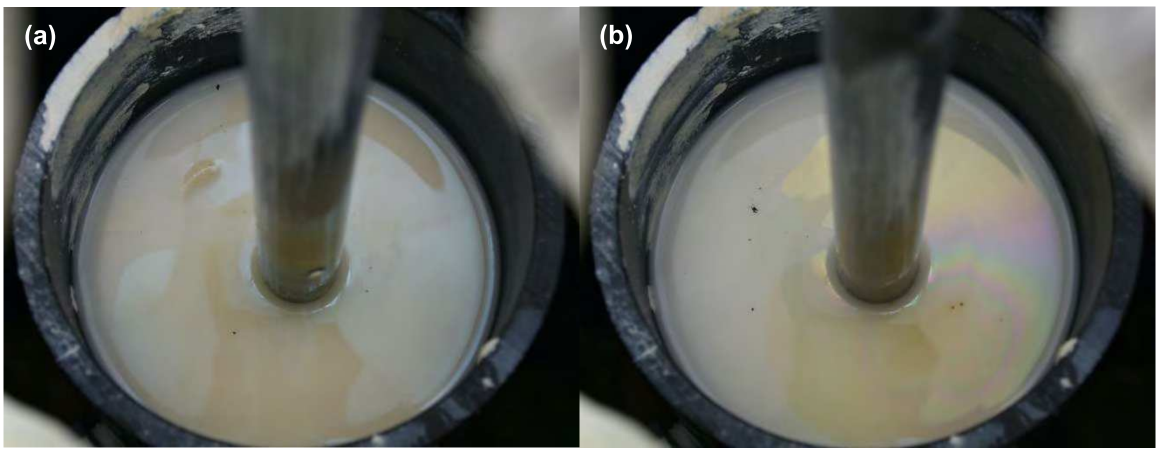


Figure 30. Example comparison of light blocking on different sheen types. The first picture (a) is a rainbow sheen of on the edge of silver. The light blocking is apparent in the patches of no sheen. The same column with more oil, (b), is harder to see as the indirect light show a brown that could be mistaken as metallic.

As this research primarily focused on producing rainbow sheens in direct light, direct versus indirect light effects were not tested further but are discussed in Appendix A. The only way around the lighting constrictions was through continuous observation as sheens tended to float in and out of light patches.

3.5.3. False Positives During Column Tests

The distinction between a hydrocarbon and a non-hydrocarbon sheen can be visually distinguished by the behavior or response when disturbed. While no non-hydrocarbon sheens were expected to occur in these laboratory tests, a false sheen detection could occur from reflective sediment floating on the water surface. Similar to non-hydrocarbon sheens, false positives were ruled out by the behavior of the floating sediment. A hydrocarbon sheen was observed to swirl and change shape, for example, elongate with the currents, whereas, a false positive (sediment sheen) tended to keep the same form or shape. False positives were typically only difficult to distinguish from specks of silver sheen as the colors were similar. An example of a false positive and a true silver sheen observed in the same column test is presented in Figure 31a and b, respectfully.

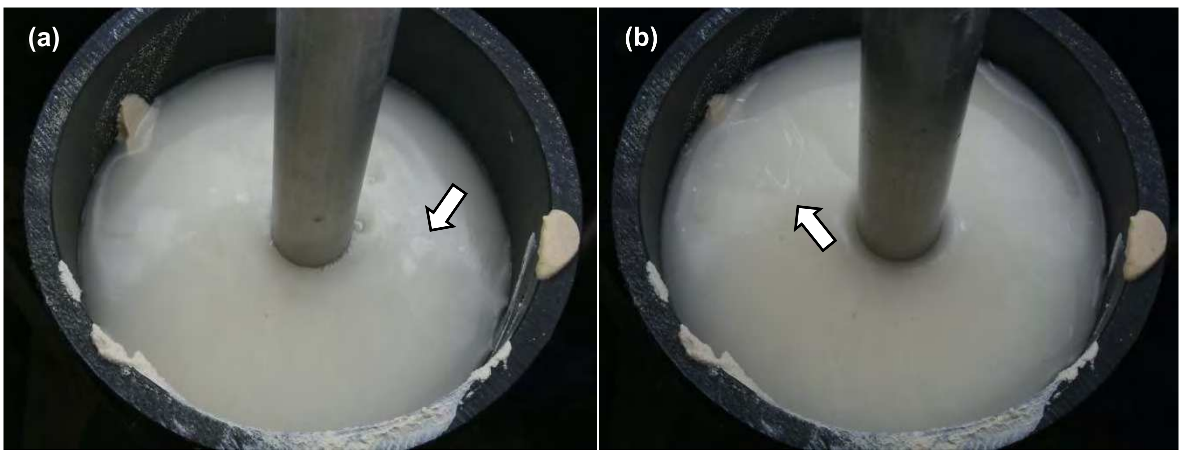


Figure 31. Example column test that has (a) false positive (reflective material that could be mistaken as a silver sheen and (b) true silver sheen (based on the sheen behavior).

4.0 RESULTS – COLUMN TESTS

Columns tests were performed to establish testing procedures and evaluate the suitability of different probes to produce sheens. Appendix D consists of a photograph log of each test, documenting the major sheen transitions observed during each test, and any test observations that were made. If the probe and setup combination was tested multiple times to establish a final test method, only the most representative test (best video quality or best representation of the sheen levels observed) is included in Appendix D. Table D.1 in Appendix D provides a list of the selected column tests performed. Column tests were performed in a series of five rounds that consisted of different combinations of the five oil types and a control (no oil embedded), seven probes, two types of oil deposits, two targeted sheen levels, and with or without embedded air, as presented in Figure 32.

The results of the column tests are presented in the following sections and Tables 5 through 11 provide a summary of the results. In each summary table, a still of each level of sheen observed is presented. For each column, success was defined as observing the targeted sheen level, and the corresponding photograph is highlighted with a green outline in the summary table.

While only rainbow and metallic sheens were targeted, sheen observations for all sheen levels from each test are included in Tables 5 through 11. Each sheen or true oil photograph is rated with one checkmark (slight sheen), two checkmarks (moderate sheen), or three checkmarks (extensive sheen). Checkmarks denote the difficulty in detecting the sheen and are based on multiple factors including extent of sheen, quantity of sheens, and sheen contrast to the water surface. Silver sheens range from almost transparent to almost rainbow sheens and are inherently difficult to visually differentiate from the water surface. Therefore, the checkmarks applied to silver sheen photographs rely more on the extent of the sheen or the quantity of specks of silver sheens. True oil has a high contrast to the water surface and therefore the checkmarks applied to these photographs also rely more on the extent and quantity of true oil specks or globs. Rainbow and metallic sheen checkmarks rely primarily on extent because at larger volumes of oil the contrast is generally greater. If the probe was not successful in producing the targeted sheen, but produced a lower level sheen, that information was used during evaluation of the probe or column setup. The photographs in Tables 5 through 11 are not necessarily in temporal order from left to right; often the sheen level observed transitioned to other levels throughout the test. In some cases, photographs are used twice if that photograph had the best representation of multiple sheen levels. The purpose of presenting the data in this method is to provide a visual representation of the test results.

	Oil Type	Probe	Oil Deposit	Sheen Level	Added Air
Round 0	Control (no oil)	Direct Push, Air Injection, Small Propeller Mixer, Large Propeller Mixer, Rod Drop, Vibrator, and Water Injection	Not Applicable	Not Applicable	None
Round 1	OIL-2	Direct Push, Air Injection, Small Propeller Mixer, Large Propeller Mixer, Rod Drop, Vibrator, and Water Injection	Concentrated	Rainbow	None
Round 2	OIL-2	Air Injection, Rod Drop, Vibrator, and Water Injection	Distributed	Rainbow	None
Round 3	OIL-1, OIL-2, OIL-3, OIL-4, and OIL-5	Air Injection, Rod Drop, and Water Injection	Concentrated	Rainbow	None
Round 4	OIL-1, OIL-2, OIL-3, OIL-4, and OIL-5	Rod Drop, Rod Drop with Manual Agitation and Water Injection	Concentrated	Metallic	Sand Layer
Round 5	OIL-2	Rod Drop with Manual Agitation	Distributed	Metallic	Sand Layer

Figure 32. Summary of the tests for each column test round.

4.1. Control Columns

The seven probes selected were run in a control column (no embedded oil) to establish laboratory procedures. Control results also provide a basis to rule out false positives from reflective clay particles. The results of the control columns are presented as photographs in Tables 5 through 11 and in Appendix D.

4.2. Rainbow Sheen

Rainbow sheens are the easiest to distinguish from the water surface and are the sheen level typically associated with identified oil sheens by observers, therefore the rainbow sheen was targeted in the first rounds of column tests. As discussed in Section 3.3, to target the rainbow sheen, 40 µL of oil was embedded in the column in both the concentrated and distributed oil deposit setups.

4.2.1. Concentrated Deposit – OIL-2

The first round of tests was conducted with concentrated deposits of OIL-2, the results are summarized in Table 5. OIL-2 was selected for this first round because of the relatively low viscosity (5.12 cSt @ 40ºC) at room temperature allowed the use of a micropipette for application, and OIL-2 behaved as expected in the oil-in-dish sheening qualification tests. The purpose of the first round of tests was to establish and standardize laboratory procedures for sediment column sheen generation. None of the columns in this first round had added embedded air.

Five of the seven probes tested produced a rainbow sheen: air injection, large propeller mixer, rod drop, vibrator, and water injection. Air injection produced a silver, rainbow, and metallic sheen, but no true oil. The large propeller mixer only produced silver and rainbow sheens. Light vibrating of a pushed rod produced all four levels of sheen. Both the rod drop and water injection produced rainbow, metallic, and true oil sheens; no silver sheen was observed. Water injection produced an extensive true oil that transitioned to a slight rainbow. Water injection was the only test that produced a sheen/true oil prior to the removal of the probe. The true oil was released when the probe was deepest in the column and then the oil transitioned to sheens during the probe ascent.

Direct push and the small propeller mixer did not produce any level of sheen and were therefore eliminated from the testing matrix as these probes proved ineffectual for sheen generation. The large propeller mixer was also removed from the testing matrix because the blades of the mixer were the same diameter as the inside of the column. The test column was not changed to accommodate this probe as a smaller propeller mixer was also tested and eliminated. The effectiveness of the large propeller mixer at releasing oil outside the direct path (distributed deposit) would not be possible to test, thus the concentrated deposit test for this probe would have limited comparability to other probes tested. To summarize the first round of column tests, and the rounds of testing later discussed, Figure 33 presents, by round, a summary of the oil and probes tested, the successful and unsuccessful probes, and the outcome of the round in terms of any decision made regarding the ability of probes to meet study objectives.

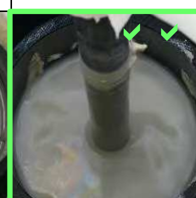
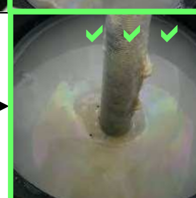
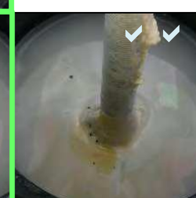
4.2.2. Distributed Deposit – OIL-2

The effective probes based on concentrated deposit tests (air injection, rod drop, vibrator, and water injection) were tested in a distributed deposit with OIL-2 and no added embedded air. The results for the air injection, vibrator, and water injection are presented in Table 6. The column setup for the rod drop test differed from the concentrated deposit, rendering the results incomparable to the concentrated deposit and the other distributed deposits and as such the results were excluded. As shown in Table 6, only the vibrator and water injection were successful in producing a rainbow sheen (both tests produced metallic sheens and true oil as well). Like the concentrated deposit, water injection produced true oil at the nadir of penetration. The true oil then transitioned to rainbow as the test continued. During the vibrator, the sheen was not produced until the probe was almost completely out of the column.

Round	Probe	Oil Type	Successful Tools	Unsuccessful Tools	Round Outcome
Round 1	Direct Push, Air Injection, Small Propeller Mixer, Large Propeller Mixer, Rod Drop, Vibrator, and Water Injection	OIL-2	Air Injection, Large Propeller Mixer, Rod Drop, Vibrator, and Water Injection	Direct Push and Small Propeller Mixer	Unsuccessful tools and large propeller mixer eliminated
Round 2	Air Injection, Rod Drop, Vibrator, and Water Injection	OIL-2	Vibrator and Water Injection	Air Injection and Rod Drop	Vibrator eliminated
Round 3	Air Injection, Rod Drop, and Water Injection	OIL-1	Rod Drop	Air and Water Injection	Air injection eliminated
		OIL-3	Water Injection	Air Injection, Rod Drop	
		OIL-4		Air, Rod Drop, Water	
		OIL-5	Water Injection	Air Injection, Rod Drop	
Round 4	Rod Drop, Rod Drop with Manual Agitation	OIL-2	Rod Drop with Manual Agitation	Rod Drop	Manual agitation added after rod drop
	Water Injection	OIL-1		Water Injection	
		OIL-2	Water Injection		
		OIL-3	Water Injection		
		OIL-4		Water Injection	
		OIL-5		Water Injection	
Round 5	Rod Drop with Manual Agitation	OIL-2		Rod Drop with Manual Agitation	Tool composition does not change

Figure 33. Candidate probe elimination decision matrix (colored font relates to oil type established in Table 2).

Table 5. Column results targeting rainbow sheen with concentrated deposit.

	Control Column	Oil	No Sheen Produced	Silver Sheen	Rainbow Sheen	Metallic Sheen	True Oil
Direct Push		OIL-2		X	X	X	X
Air Injection		OIL-2	→	 ✔✔	 ✔✔✔	 ✔✔	X
Small Mixer		OIL-2		X	X	X	X
Large Mixer		OIL-2	→	 ✔✔✔	 ✔✔	X	X
Rod Drop		OIL-2	→	→	 ✔✔✔	 ✔✔	 ✔✔
Vibrator		OIL-2	→	 ✔	 ✔✔	 ✔	 ✔✔
Water Injection		OIL-2	→	→	 ✔	 ✔✔✔	 ✔✔✔

Key:

✔ - Ease of detection. Ranges from one checkmark, slight sheen, to three checkmarks, extensive sheen.

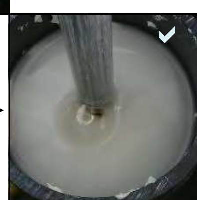
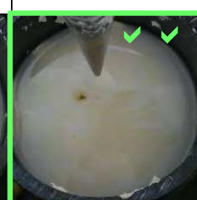
→ - Sheen produced or produced sheen skipped over lower sheen level(s).

X - Sheen level not produced.

✔ - Attempted sheen achieved. Test is considered successful.

Vibrator was tested three times in the concentrated deposit and only once in the distributed deposit and was only successful once for each application. As discussed in Section 3.4, vibrating should liquidize the sediment releasing any bubbles or oil. However, observation showed the vibrator was not strong enough to produce this sediment liquefaction and the oil that was released was due to the preferential flow path made by the probe in both the concentrated and distributed deposit. This iteration of the vibrator probe was removed from the testing matrix and vibrating as potential probe has been removed from the testing matrix until the test (column setup or probe) based on limitations in the energy required to produce a necessarily powerful vibration on a small autonomous watercraft.

Table 6. Column results targeting rainbow sheen with distributed deposit.

	Control Column	Oil	No Sheen Produced	Silver Sheen	Rainbow Sheen	Metallic Sheen	True Oil
Air Injection		OIL-2		X	X	X	X
Vibrator		OIL-2	→	 ✔	 ✔✔	 ✔✔✔	 ✔
Water Injection		OIL-2	→	→	 ✔	 ✔✔	 ✔✔

Key:

* - Sand Layer used to add air.

✔ - Ease of detection. Ranges from one checkmark, slight sheen, to three checkmarks, extensive sheen.

→ - Sheen produced or produced sheen skipped over lower sheen level(s).

X - Sheen level not observed.

✔ (green box) - Attempted sheen achieved. Test is considered successful.

4.2.3. Concentrated Deposit – Crude Oil Comparison

Probes successful at producing a sheen in the OIL-2 concentrated deposit test (air injection, rod drop, and water injection) were tested on the other four types of oil to see how oil properties affected sheen generation for a given probe. The results of the air injection, rod drop, and water injection for all five oils are presented in Tables 7, 8, and 9, respectively.

Air Injection

As shown in Table 7, the air injection only produced a rainbow sheen in the original OIL-2 test. A slight silver sheen was produced in the OIL-1 test, but because no rainbow sheen was produced, this test is not considered successful. The air injection tests suffered from a propensity to create preferential flow paths within the column that missed embedded oil. Due to the constricted nature of the column setup or perhaps the sediment blend, the air injection test failed in releasing the embedded oil and therefore this probe was eliminated from further consideration.

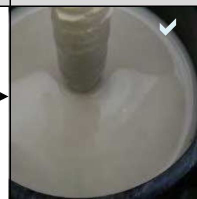
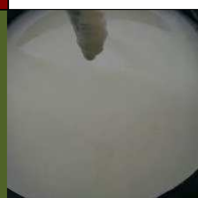
Rod Drop

The rod drop test was only successful for two of the five oils, OIL-1 and OIL-2 (Table 8). The OIL-1 test produced both slight silver and slight rainbow sheens. The OIL-3 test produced a moderate silver sheen, but no rainbow sheen. Neither OIL-4 nor OIL-5 produced a sheen.

Water Injection

The water injection test was successful for three out of the five oils, OIL-2, OIL-3, and OIL-5 (Table 9). OIL-1 and OIL-4 did not produce a sheen with water injection. OIL-2 test produced rainbow, metallic and true oil, but no silver sheen. OIL-3 produced all four levels, ranging from slight to moderate sheens. In both OIL-2 and OIL-3 tests, true oil was produced at the deepest position and then the true oil transitioned to metallic then rainbow. OIL-5 produced a slight silver and rainbow sheen.

Table 7. Air injection results by oil type targeting rainbow sheen with concentrated deposit.

	Control Column	Oil	No Sheen Produced	Silver Sheen	Rainbow Sheen	Metallic Sheen	True Oil
Air Injection		OIL-1	→	 ✓	X	X	X
		OIL-2	→	 ✓ ✓	 ✓ ✓ ✓	 ✓ ✓ ✓	X
		OIL-3		X	X	X	X
		OIL-4		X	X	X	X
		OIL-5		X	X	X	X

Key:

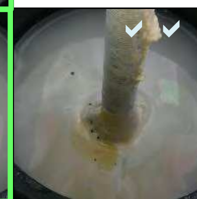
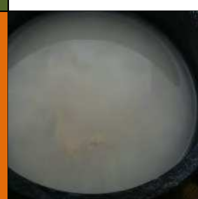
✓ - Ease of detection. Ranges from one checkmark, slight sheen, to three checkmarks, extensive sheen.

→ - Sheen produced or produced sheen skipped over lower sheen level(s).

X - Sheen level not observed.

✓ (green box) - Attempted sheen achieved. Test is considered successful.

Table 8. Rod drop results by oil type targeting rainbow sheen with concentrated deposit.

	Control Column	Oil	No Sheen Produced	Silver Sheen	Rainbow Sheen	Metallic Sheen	True Oil
Rod Drop		OIL-1	→	 ✓	 ✓	X	X
		OIL-2	→	→	 ✓✓✓	 ✓✓	 ✓✓
		OIL-3	→	 ✓✓	X	X	X
		OIL-4		X	X	X	X
		OIL-5		X	X	X	X

Key:

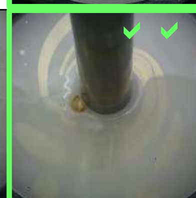
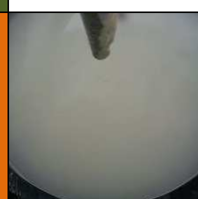
✔ - Ease of detection. Ranges from one checkmark, slight sheen, to three checkmarks, extensive sheen.

→ - Sheen produced or produced sheen skipped over lower sheen level(s).

X - Sheen level not observed.

✓ (green box) - Attempted sheen achieved. Test is considered successful.

Table 9. Water injection results by oil type targeting rainbow sheen with concentrated deposit.

	Control Column	Oil	No Sheen Produced	Silver Sheen	Rainbow Sheen	Metallic Sheen	True Oil
Water Injection		OIL-1		X	X	X	X
Water Injection		OIL-2	→	→	 ✔✔	 ✔✔✔	 ✔✔✔
Water Injection		OIL-3	→	 ✔	 ✔✔	 ✔	 ✔✔
Water Injection		OIL-4		X	X	X	X
Water Injection		OIL-5	→	 ✔	 ✔	X	X

Key:

- ✔ - Ease of detection. Ranges from one checkmark, slight sheen, to three checkmarks, extensive sheen.
- → - Sheen produced or produced sheen skipped over lower sheen level(s).
- X - Sheen level not observed.
- ✔ (green box) - Attempted sheen achieved. Test is considered successful.

4.3. Metallic Sheen

The next round of testing consisted of 400 µL concentrated and distributed deposits of all five crude oils to target a metallic sheen. During this round of testing, all columns tests had embedded air added to better simulate sheening due to ebullition. This round of testing was also used to evaluate how the probes perform with more embedded oil and evaluate if the amount of oil embedded in the column is a limiting factor. The column tests (probe and oil combination) that were successful in the targeted rainbow sheen columns were expected to be successful again. The previously unsuccessful column tests were expected to potentially exhibit a sheen because more oil was present.

4.3.1. Concentrated Deposit

The results of the concentrated deposit tests using the rod drop with manual agitation and water injection are presented in Table 10. Rod drop was tested in multiple columns with OIL-2 with no sheen produced in any of the tests. However, the addition of manual agitation resulted in sheen generation in all the tested columns. Rod drop with manual agitation was tested twice and both times an extensive metallic sheen was produced. The longer the manual agitation, the more oil, typically true oil, that would initially rise to the surface and spread into a metallic sheen.

Water injection was tested with all five crude oils and produced sheens with OIL-2 and OIL-3. The OIL-2 test produced slight silver, rainbow, and metallic sheens. The OIL-3 produced all four levels with an extensive metallic sheen. In this test, true oil did not appear when the probe was at the deepest point as in the rainbow target tests. However, a drop of true oil appeared as the probe was removed that transitioned to metallic. More true oil appeared as the probe was further removed. Both OIL-1 and OIL-5 did not produce a sheen. The OIL-4 test, which did not produce any sheens during the rainbow target tests, produced a slight silver sheen, reinforcing that the lack of success of this test is likely related to the oil properties.

Table 10. Column results targeting metallic sheen with concentrated deposit.

	Control Column	Oil	No Sheen Produced	Silver Sheen	Rainbow Sheen	Metallic Sheen	True Oil
Rod Drop*		OIL-2		X	X	X	X
RDMA*		OIL-2	→	 ✔	 ✔✔	 ✔✔✔	 ✔✔✔
Water Injection*		OIL-1		X	X	X	X
		OIL-2	→	 ✔	 ✔	 ✔	X
		OIL-3	→	 ✔	 ✔	 ✔✔✔	 ✔✔✔
		OIL-4	→	 ✔	X	X	X
		OIL-5		X	X	X	X

Key:

RDMA - Rod Drop with Manual Agitation

* - Sand Layer used to add air.

✔ - Ease of detection. Ranges from one checkmark, slight sheen, to three checkmarks, extensive sheen.

→ - Sheen produced or produced sheen skipped over lower sheen level(s).

[X] - Sheen level not observed.

[✔] - Attempted sheen achieved. Test is considered successful.

4.3.2. Distributed Deposit

Because to CSU's CCH lab closing due to Coronavirus (COVID-19) in the Spring of 2020, this round of testing was not completed. The results of the rod drop with manual agitation in a distributed deposit with embedded air, is presented in Table 11. Only OIL-2 was tested and no metallic sheen was produced. Rod drop with manual agitation and water injection will need to be tested with all five oil types in the distributed deposit to complete the comparison.

Table 11. Column results targeting metallic sheen with distributed deposit.

	Control Column	Oil	No Sheen Produced	Silver Sheen	Rainbow Sheen	Metallic Sheen	True Oil
Rod Drop*		OIL-2		X	X	X	X
RDMA*		OIL-2	→	 ✔✔	 ✔✔	X	X

Key:

RDMA - Rod Drop with Manual Agitation
* - Sand Layer used to add air.
✔ - Ease of detection. Ranges from one checkmark, slight sheen, to three checkmarks, extensive sheen.
→ - Sheen produced or produced sheen skipped over lower sheen level(s).
[X] - Sheen level not observed.
[✔] - Attempted sheen achieved. Test is considered successful.

5.0 DISCUSSION

Columns tests were performed to establish testing procedures and evaluate the suitability of seven probes to produce sheens when inserted into sediment containing embedded crude oil. The following probes were tested: direct push, air injection, small propeller mixer, large propeller mixer, rod drop with manual agitation, vibrator, and water injection. By the end of column testing, only two probes showed consistent performance, rod drop with manual agitation and water injection. Based on the data, water injection has the highest probability of generating a sheen. This section discusses the results of the column tests and the changes needed to enhance the evaluation of the suitability for the probes and to further the overarching goal of this project.

5.1. Testing Setup Review

For each column test, oil type, probe, sheen level target, oil deposit type, and addition of air were selected. The column setup, i.e., the diameter of the column, sediment mixture, method of embedding air and oil, and photograph setup, all remained constant during this probe identification study. However, to fully and confidently identify the probe that has the greatest probability of generating a sheen, every variable must be considered; therefore, this discussion includes potential weaknesses in the setup as well as the strengths.

5.1.1. Radius of Influence

The pre-existing PVC columns were sized for the laboratory direct push apparatus and to keep the generated waste at a minimum for the initial screening of the probes. Although no oil was observed migrating up the column sidewalls during testing, the probe tests would benefit from large scale testing to ensure that the oil did not find a preferential flow path along the sides of the column and to evaluate the radius of influence of the probes. While the distributed deposit tested if the probe was successful outside the direct path of the probe, the way the column tests were setup did not allow for determining the range of influence, which will be a crucial component in site characterization use.

5.1.2. Sediment Mixture

To determine the effect of the sediment mixture used for testing on the results of the column study, further tests should be performed with other sediment mixtures. The two other variations of the sediment mixture (a medium and fine sand mix and just fines mix) considered in Section 3.4 but not used during this study should be considered.

5.1.3. Added Air (Sand Layer)

During the water injection tests, the appearance of true oil that then spreads to a sheen is not mechanistically consistent with ebullition driven transport, the primary mechanism targeted in this research. If embedded air was present, the produced oil might be quicker to sheen, which is why embedded air was added to the columns that lacked naturally embedded air. The sand layer was successful in adding air to the columns. When the tip of the cone penetrated this layer, a cascade of bubbles would appear.

The sand layer was introduced into the testing matrix when targeting the metallic sheen. The oil amount embedded in the column was ten times the volume placed in the rainbow sheen target columns. The column tests (probe and oil combination) that were successful in the targeted rainbow sheen columns were expected to be successful again, but they were often unsuccessful. The lack of success could be attributed to the sand layer. The water rushing into the sand layer, displacing the air, may have pulled the oil into the sand layer as well, since oil will move to the closest air-water interface. During the targeted rainbow sheen test with a concentrated OIL-2 deposit (Section 4.2.1), water injection was successful two out of two times. This probe was tested again targeting the rainbow sheen with a concentrated OIL-2 deposit but in a column with a sand layer three times, all without success, see Figure 34. While water injection should benefit from embedded air to produce sheens by ebullition-driven transport, instead of true oil that slowly transition to a sheen, the sand layer failed. A modification to this probe would be injecting both water and air through the probe.

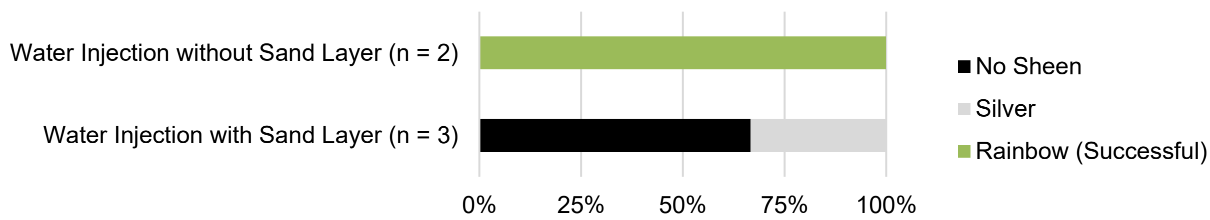


Figure 34. Probe reproducibly comparison of water injection with and without embedded air during concentrated deposits of OIL-2 targeting rainbow sheens.

5.1.4. Embedded Oil

The two deposit methods were selected as approximate representations of embedded oil. The method of embedding the oil did result in a pocket of air embedded with the oil which may have affected the behavior of the oil in the column. A variation on this type of deposit would be to place water in the depression before the oil. The oil would still be embedded with air, but the oil may be less likely to absorb to the sediment. Another option would be to freeze the oil into oil "balls" that could be embedded without any entrapped air right by the oil. By changing the method of how the oil is embedded, the probes could be tested to see how much of a variable the oil deposit method has on the results.

5.1.5. Procedure for Photographing

The column tests reinforce the importance of capturing the behavior of the produced oil on video as many sheens would have been missed if only a single still photograph at the end of the test was captured. Some of the column tests that had a distinct sheen during the test would, by the end, have a sheen so broken up due to surface disturbance or so thin that the sheen became indistinguishable from baseline. An example from a vibrator test is presented in Figure 35. The vibrations create a minimal disturbance, but the oil continued to spread until the sheen became a faint silver that was similar to the water surface at the start of the test.

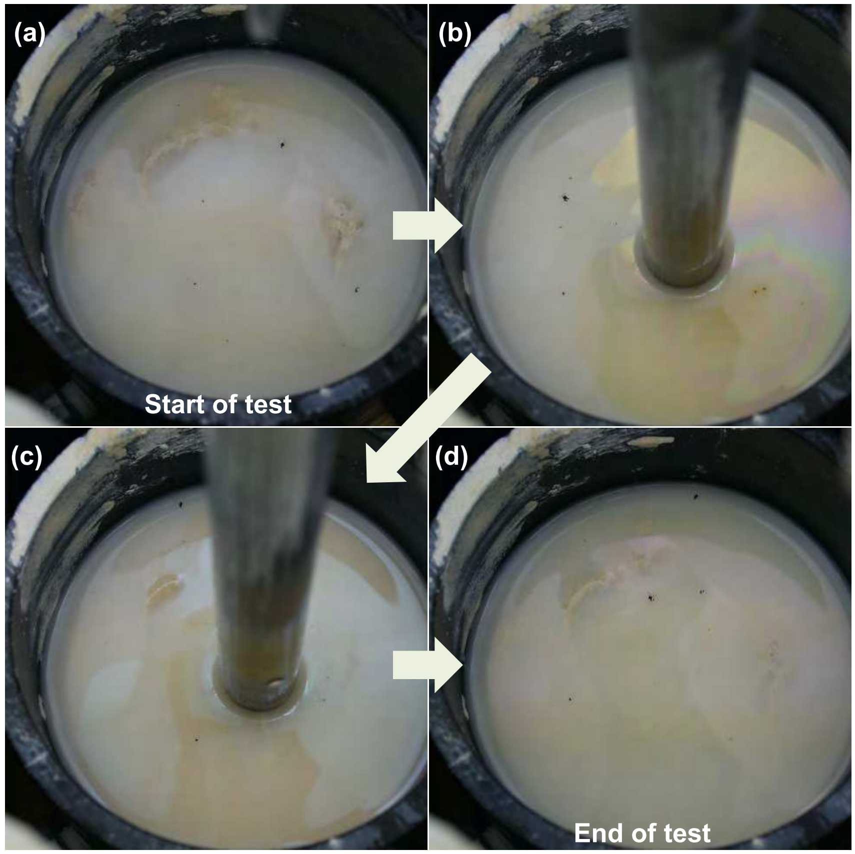


Figure 35. Example vibration test with OIL-2 targeting rainbow sheens. Figure (a) is the start of test (note black specs are paint chips from the column), in Figure (b) a rainbow sheen appears, then in Figure (c) the rainbow sheen spreads and transitions to blueish rainbow sheen on the edge of silver. Figure (d) is the end of test and the previous sheen is hard to distinguish from the water surface.

The use of ultraviolet (UV) light sensors instead of visible light photography was explored briefly during the oil-in-dish tests (discussed in Appendix B). Passive UV sensors capture the ultraviolet energy reflected from the oil sheen. Oil is highly reflective when exposed to ultraviolet radiation even at thin layers (<0.01 µm) (Brown, Fingas, Goodan 1998). Under ultraviolet light, the reflectivity of oil is 1.02, whereas water is 0.722. Since reflectivity is a surface phenomenon, any hydrocarbon on the water surface, independent of thickness, would be detected (Goodman 1994). The camera equipment used was for visible light and not effective under UV light. While one of the main goals of this research was to distinguish between sheen detection and no detection, a secondary goal was to characterize the sheen (identify sheen level), if possible, which is not possible under UV light. UV sensors are still a viable system for the small autonomous watercraft, as UV systems are simple, lightweight, and require little power and should be explored further.

5.2. Probe Comparison

All the probes, except for water injection, typically produced a sheen while the probe was being removed from the column. Only water injection consistently produced oil while the probe was deepest in the column, i.e., the water injection port was beneath the oil and the water valve was opened fully (flow rate of approximately 10 mL/sec). This observation confirms the release mechanism targeted with water injection (the hydraulic gradient promoted flow upward, releasing the oil) was achieved. Water injection typically produced true oil that would start to spread and transition into sheens, as shown in Figure 36.

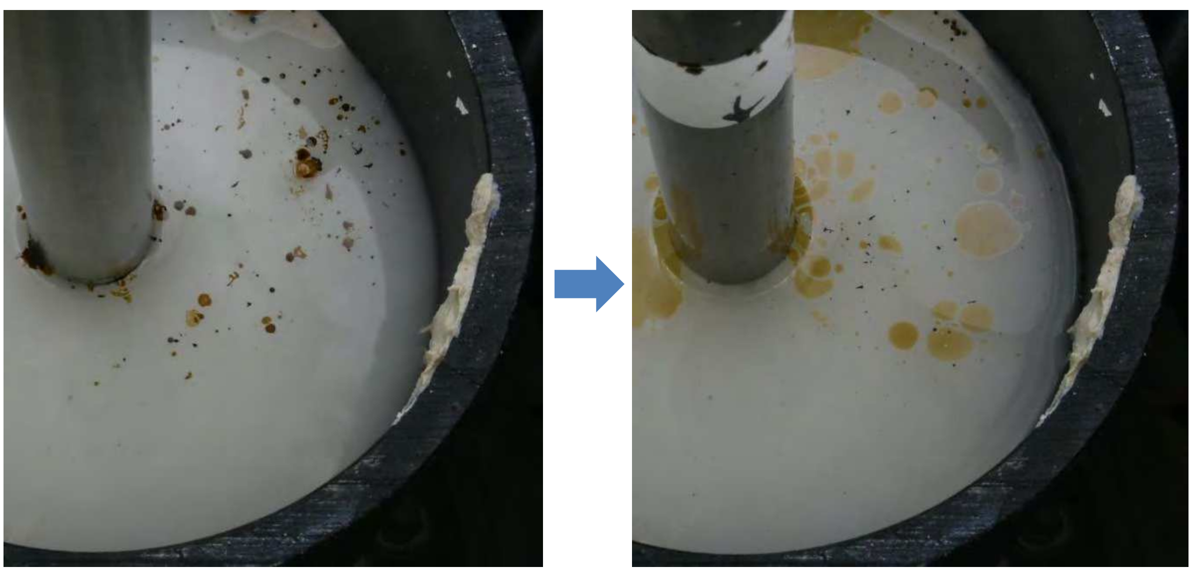


Figure 36. True oil to metallic sheen during water injection test.

Rod drop, selected as an alternative for the direct push probe, was successful during concentrated deposits of OIL-2 targeting rainbow sheens but was less successful with the other oils. Manual agitation was added when rod drop was unsuccessful in the columns with embedded air (sand layer). Manual agitation was able to liquefy the sediment more efficiently and produce oil when rod drop did not; however, the agitation resulted in partial emulsification of the oil, only true oil was observed instead of sheens. Due to external factors preventing complete testing of rod drop with manual agitation, rod drop, with and without manual agitation, was not eliminated from the testing matrix and could still be considered for further testing. However, rod drop may still pose a challenge for a small autonomous watercraft when pulling the rod out of the subsurface.

Establishing testing procedures and evaluating the suitability of candidate probes to produce sheens was the focus of this study. Most column tests (setup and probe configuration) were only performed a single time once testing procedures were codified. Three of the probes were run multiple times to dial in the procedures of the test or to ensure the test setup did not influence the results. During the targeted rainbow sheen tests with a concentrated OIL-2 deposit (Section 4.2.1), the air injection and water injection probes were tested twice, and the vibrator was tested three times, with minor adjustments to each test (such as flow rate or location of the vibrator along the rod). A comparison of the success rates (producing a rainbow sheen) of these tests are presented in Figure 37. In both tests performed for the air injection and water injection, the probes were successful during both tests. In the vibrator test, the probe was successful only once; while in the other two runs, the vibrator only produced a silver sheen, which in part led to the elimination of this probe from the testing matrix. The reproducibility of the probe results is an important factor and should be further explored.

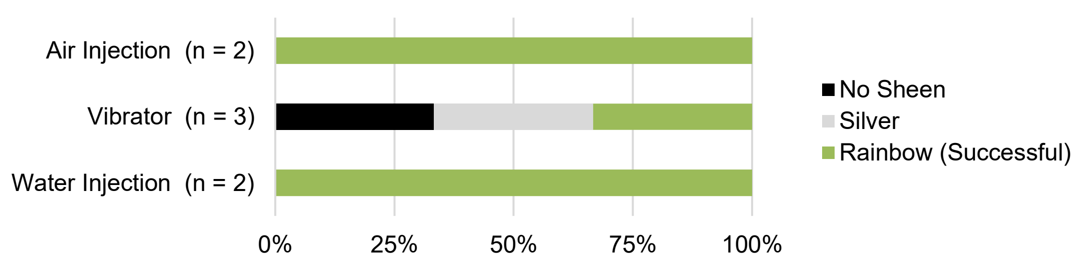


Figure 37. Probe comparison of air injection, vibrator, and water injection during concentrated deposits of OIL-2 targeting rainbow sheens.

Only probes that had potential compatibility with a small autonomous sample systems were evaluated; however, the water injection and rod drop probes could be considered for manual site characterization (i.e., without the autonomous platform) as both proved successful in releasing embedded oil to sheen. Manual application will still be expensive and have limited capabilities accessing sediments at complex, shallow, or remote sites

5.3. Oil Comparison

The properties of the embedded oil are important variables in sheen generation potential; however, the oil characteristics are likely to be an unknown in field applications. The five different crude oils were used to identify the limits of the probes capabilities and methods tested. For this discussion, only the results from the concentrated deposits targeting rainbow sheens (probes air injection, rod drop, and water injection) for all five oil types were directly compared.

For the combined results of the three probes, how often each level of sheen was observed for each oil type is shown in Figure 38. The following observations were made for each oil type:

- *OIL-2*: OIL-2 appears to be the easiest-to-sheen oil tested; however, as this oil was used as a first iteration screening oil, probes that did not produce a sheen with OIL-2 were eliminated earlier in the study.
- *OIL-3*: All four levels of sheen were observed with during the water injection tests with this oil. OIL-3 was the second easiest-to-sheen oil tested.
- *OIL-1*: In the oil-in-dish tests, OIL-1 spread too quickly to capture a representative silver sheen and transitioned to metallic quickly, but this oil never reached a distinct true oil like the other four oils. Unsurprising, no true oil was observed during the column tests. When a sheen was observed, the sheen was always classified as a slight sheen, and no metallic sheens were observed.

- *OIL-5*: OIL-5 was a hard oil to work with due to the high viscosity of the oil. The expected success of tests with this oil was low due to the high viscosity. The results of OIL-5 were similar to OIL-1. No metallic or true oil was observed during the column tests, only slight silver and rainbow sheens.
- *OIL-4*: During the oil-in-dish tests, OIL-4 behaved similarly to the other oils in that the all four sheen levels were observed and no observations were made during the test that stood out. During the concentrated deposits targeting rainbow sheens column tests, no sheen was observed during any of the three tests. The lack of success in the OIL-4 tests may be indicative of the properties of the oil, as all of the other oils produced a rainbow sheen (success) for at least 33% of tests. During the concentrated deposit targeting metallic sheen tests, a slight sheen was produced in the water injection test, but the testing setup differences (mainly the addition of the sand layer) make comparison between the rainbow tests and metallic tests ineffectual. The slight sheen was produced using the water injection during the metallic loading test could be easy to miss by visual inspection.

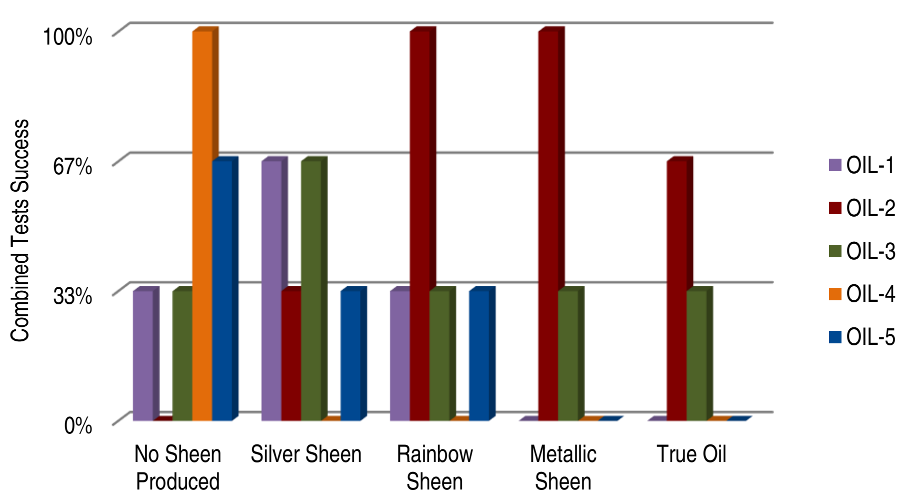


Figure 38. Percentage of tests where the rainbow sheen level was observed for each oil type in the combined air injection, rod drop, and water injection concentrated deposits tests.

OIL-4 does not appear to be able to travel through the sediment column. OIL-1 and OIL-5 appear to be somewhat impeded traveling through the sediment column but some sheening was observed. The oil mobility through the sediment could be a factor of the oil properties or the combination of the oil in the sediment mixture. The interfacial tension of each oil against water was planned to be tested for each oil type as well as the hydraulic conductivity and shear strength of the sediment mixture, but these tests were not completed due to the closing of CSU's CCH lab due to COVID-19. These tests (interfacial tension, hydraulic conductivity, and shear strength) are recommended for future work. The air-oil and air-water interface tension should also be measured to calculate the spreading coefficients of each oil.

A comparison of the ease of detection of the produced rainbow sheen, which appears to be analogous or correlated to oil mobility, versus the bulk crude oil properties (API, specific gravity, pour point, and viscosity) is presented in Figure 39. OIL-3, the second easiest-to-sheen oil, and OIL-4, the hardest-to-sheen, have similar API gravities (21.9 and 21.4, respectively), specific gravities (0.9224 and 0.9254), and viscosities (66.3 cSt and 76.0 cSt at 40°C). The differences in the oil mobility suggest that these properties do not affect the sheening results. Out of the four oil properties considered, only pour point appears correlated to the mobility of the oil. OIL-2 and OIL-3, the oils that appeared to have the greatest mobility through the columns, have the two lowest pour points. However, OIL-4, which had the most difficulty traveling through the sediment, has the third-lowest pour point. Pour point might be correlated to the mobility of the oil, but further testing should be performed to confirm and to ensure whether sediment properties might also affect this relationship.

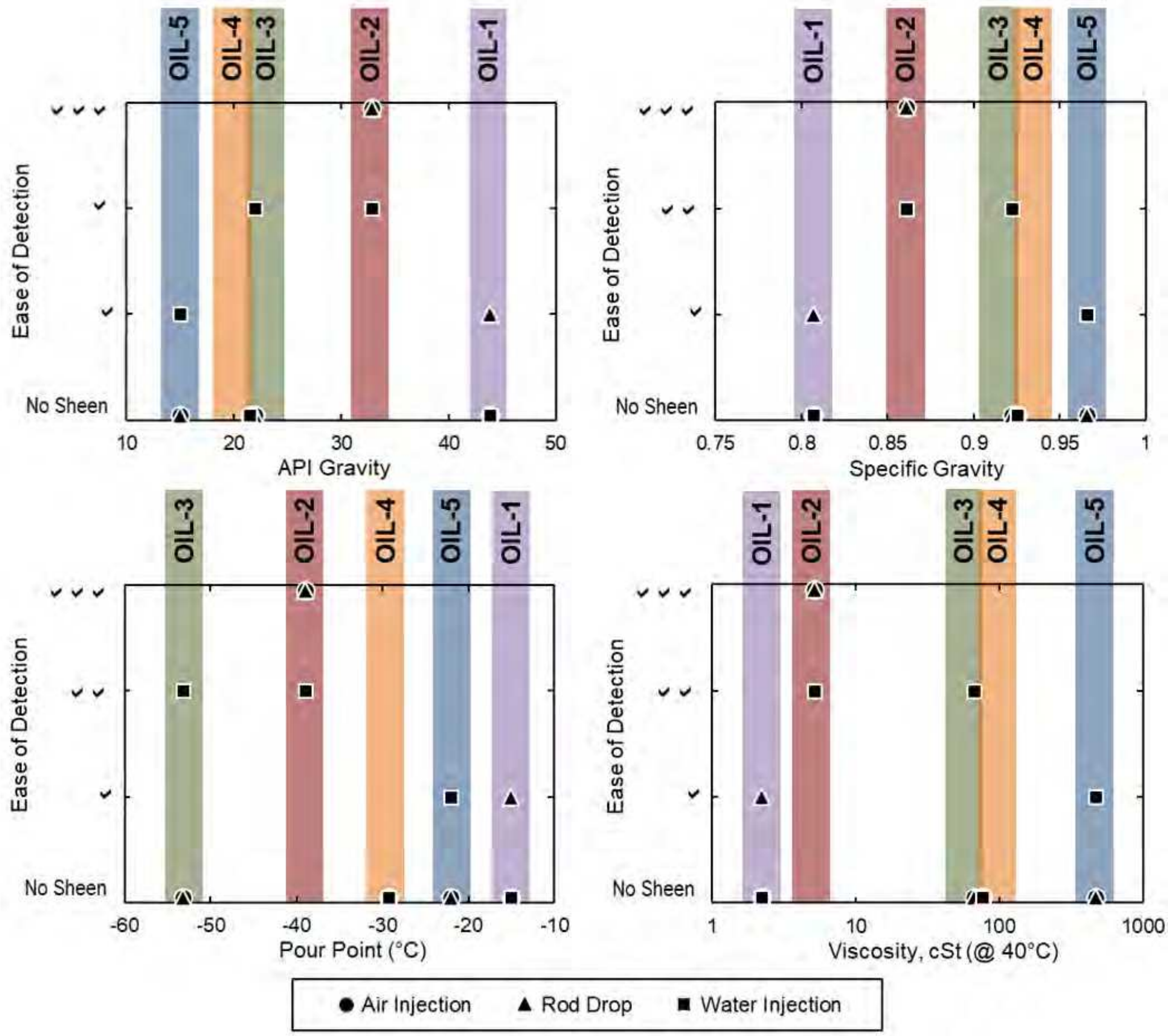


Figure 39. Oil properties versus ease of detection of produced rainbow sheen by probe during the concentrated deposits targeting rainbow sheens. Rainbow sheens were rated with one checkmark (slight sheen), two checkmarks (moderate sheen), or three checkmarks (extensive sheen). (Note, the colored bars are oil labels and do not specify a range of the oil sheening properties).

6.0 CONCLUSIONS AND RECOMMENDATIONS

The overarching goal of this project is to develop a smaller scale screening methods that can be deployed on an autonomous watercraft that will provide multiple lines of evidence of both embedded oil presence and sheening potential in shallow sediments. Such a method will reduce the cost of acquiring datasets with better spatial coverage to enable more informed decision making. Using a combination of independent lines of evidence will provide the opportunity for critical comparisons and will generate more defensible data. This thesis is focused on the preliminary development of a probe to assess the sheening potential of embedded oil. The small autonomous watercraft will be modified to incorporate the probe identified in this study to allow for more effective acquisition of sheening data as part of future work. Different potential probes and methods were explored to penetrate sediments and determine sheening potential.

Preliminary probe identification focused on the development of a standardized laboratory column to test different probes and penetration methods to determine which probe has the highest probability to generate a sheen. Column tests were performed that consisted of different combinations of five crude oil types and a control (no oil embedded), seven probe candidates, two types of oil deposits, two targeted sheen levels, and with or without embedded air. A visible light camera was used to identify sheen once mobilized. Based on the data collected, a direct push rod with water injection has the greatest potential to generate a sheen in the columns tested. Rod drop has the second highest potential to generate a sheen in the columns tested but may still pose a challenge for a small autonomous watercraft. Both probe tests would benefit from large scale testing to ensure that the oil did not find a preferential flow path along the sides of the column and to evaluate the radius of influence of the probes.

The column tests reinforce the importance of capturing the behavior of the produced oil sheens on video. The oil/sediment properties may have more influence on the results than that could be fully explored during this study. Further tests, including the interfacial tension of oil against water and hydraulic conductivity and shear strength of the sediment, are recommended for future work to identify which properties affect the mobility of the oil in sediment and the relationship between the oil and sediment. As this study is the first in an anticipated series of studies to produce a small autonomous watercraft, the next phase of testing for the probes would be to field validate and incorporate autonomous sampling and spectroscopic in situ sensing (LIF) of oil presence in the observations of this study conjunction with the probe. Both probes could also be considered for manual site characterization (i.e., without the autonomous platform) as both proved successful in releasing embedded oil to sheen.

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APPENDIX A – SHEEN QUANTIFICATION (OIL-IN-DISH) TESTS

SHEEN QUANTIFICATION (OIL-IN-DISH) TESTS

The sheen thicknesses required to produce silver, rainbow, and metallic sheens, based on the visual classification scheme, are provided in Table A.1. The area of a 10.5 cm diameter aluminum tray and the range of sheen thicknesses were used to calculate the volume range of oil required to achieve the different levels of sheen if the oil extended to the edge of the tray. The ranges of oil are presented in Table A.1.

Table A.1. Volumes of oil required to achieve different levels of sheens in the aluminum trays.

Sheen	Sheen Thickness (μm)	Volume of Oil (μL)
Silver	0.04 to 0.3	0.35 to 2.60
Rainbow	0.3 to 5	2.60 to 43.3
Metallic	5 to 50	43.3 to 433

Test Lighting

The appearance of an oil film depends on the way light waves of different wavelengths are reflected off the surface of the oil, transmitted through the oil (and reflected off the water surface below), and/or absorbed by the oil. In the visible spectral range, imagery is displayed in "true color". True color is the nearest approximation of what a human observer might view directly. Sheens are detected by color on the water surface (API 2013). In the visible spectral range, oil has a higher surface reflectance than water but does not show specific absorption/reflection tendencies like what is observed in the ultraviolet or infrared spectral ranges (Fingas & Brown 2014). As part of the sheen quantification a variety of visible light bulbs types were tested on a diesel engine oil:

- EcoSmart CFL Daylight, 5000 K Cool Bulb (Home Depot, Atlanta, Georgia);
- EcoSmart Incandescent Natural Light 3050 K Warm Blub (Home Depot, Atlanta, Georgia);

- EcoSmart Incandescent Natural Light, 2950 K Warm Blub (Home Depot, Atlanta, Georgia);
- Cree LED Daylight, 5000K Cool Bulb (Cree Lighting, Research Triangle Park, North Carolina);
- CREE LED R20 Daylight, 5000K Cool Bulb (Cree Lighting, Research Triangle Park, North Carolina);
- GE Halogen Clear Soft White Light, 3000 K Warm Bulb (GE Lighting, Cleveland, Ohio);
- GE CFL Soft White, 2700K Warm Bulb (GE Lighting, Cleveland, Ohio); and,
- Philips Incandescent Agro-Lite Plant Light, 2700K Warm (Philips, Amsterdam, Netherlands).

The difference between how 20 μL of diesel on the water surface looked under a LED (cool) and CFL (cool) light bulb is presented in Figure A.1a and b, respectively. The colors of the sheen were difficult to capture when under the LED light, often the colors of the sheen were dull or greyed out. A close up of a rainbow sheen under LED light is presented in Figure A.2. Rainbow sheens under CFL lights were distinct compared to the water surface.

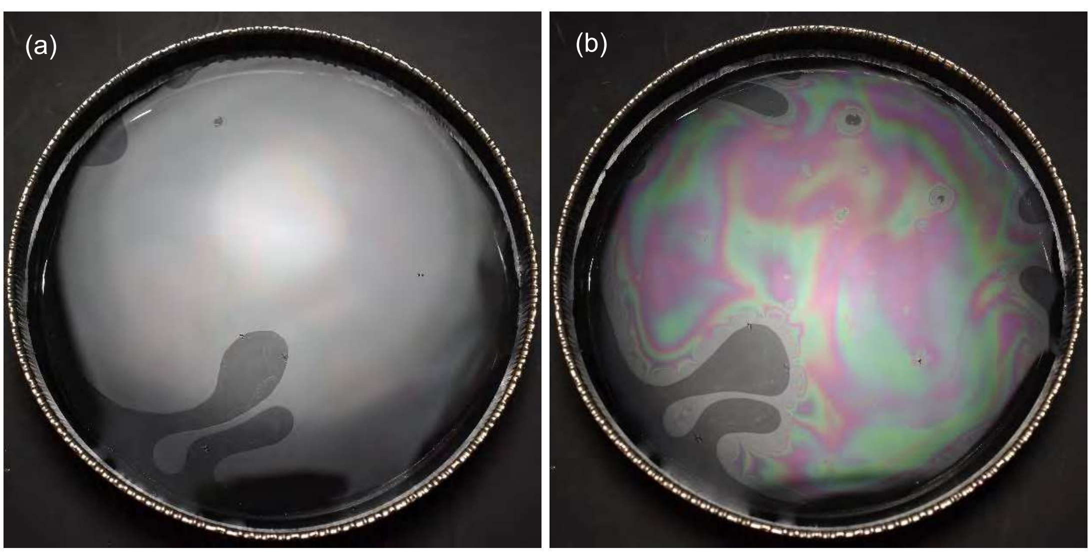

Figure A.1. Same tray with 20 μL of diesel oil on the water surface under: (a) cool LED light and (b) cool CFL light.

Figure A.2. Close up photograph of 20 µL of diesel oil on the water surface under cool LED light.

CFL light was selected for this study due to the greater contrast of the sheens under this light. A cool CFL light was selected over a warm CFL light because the color of the sheen under cool light is closer to “natural light”. This “true color” is the nearest approximation of what a human observer might view directly. An example of how 20 µL of diesel on the water surface looked under a cool CFL and warm CFL is presented in Figure A.3a and b, respectively.

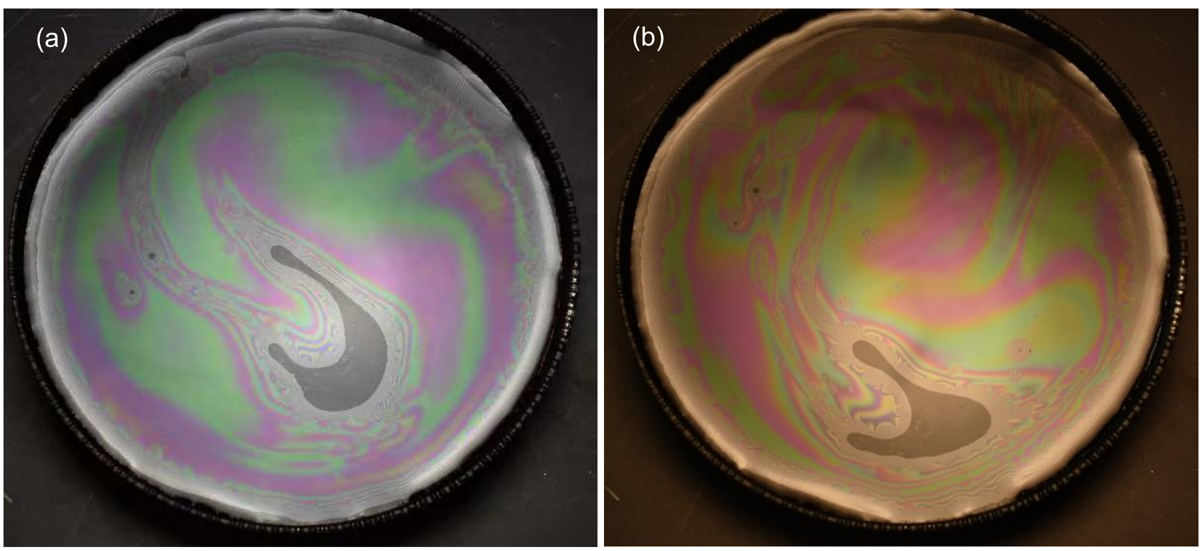

Figure A.3. Same tray with 20 µL of diesel oil on the water surface under: (a) CFL 5000K (cool) bulb and (b) CFL 2700K (warm) bulb.

In his experiments, Ramstad (1998) distinguished the effect direct and indirect light had on sheen detection. He found that thinner sheens (e.g., silver and rainbow sheens) were more detectable with direct light, whereas thicker sheens (e.g., metallic and true oil) were easier to detect with indirect light (Ramstad, 1998). An example of a metallic sheen and true oil under direct and indirect CFL light is presented in Figure A.4a and b, respectively. While this concept was not tested further during this study, as rainbow sheens were the primary target, the difference between direct and indirect light was observed. The difference was most notably the color. All of the provided crude oils were a dark brown to black-brown, but under the direct CFL, all oils appeared a metallic gray (Figure A.4a). Under indirect light, the thicker oils would appear closer to their “true color”, a dark brown (Figure A.4b).

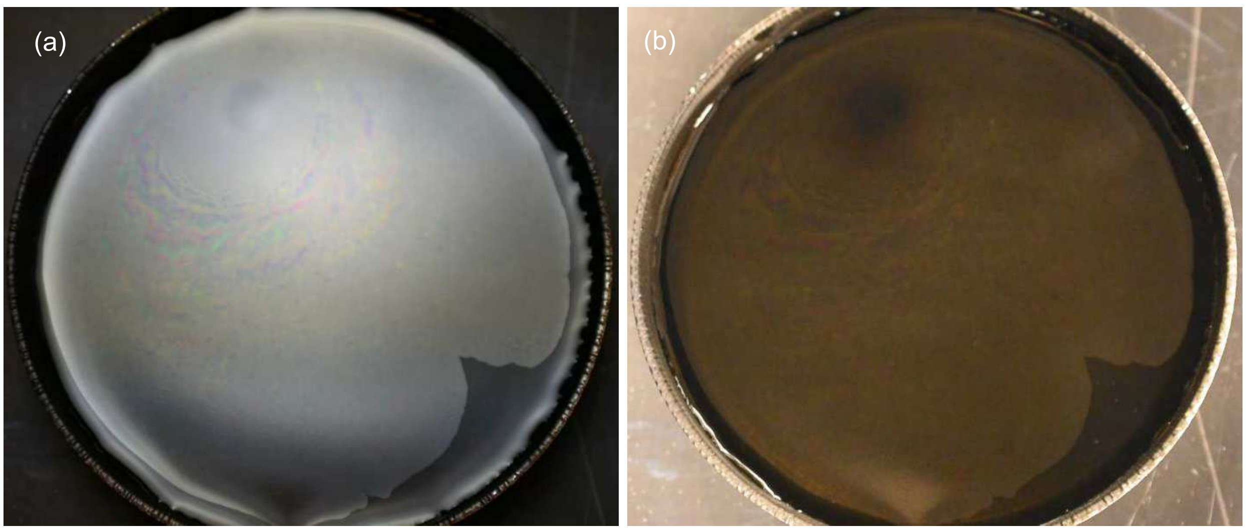

Figure A.4. Same tray with 44 µL of OIL-2 under (a) direct light and (b) under indirect light.

Sheen Observation

The five crude oils were tested to confirm that the sheens produced matched the visual classification schemes expectation under visible light. A 10.5 cm diameter aluminum tray, spray painted black, filled with approximately 100 mL of water, was loaded in 2 microliters (µL) increments of crude oil until all three levels of sheen were observed. At room temperature, OIL-3, OIL-4, and OIL-5 were too viscous to be drawn up into the pipette for measuring. Oils were placed into a water bath of 75ºC to temporarily increase the viscosity. OIL-1 and OIL-2 were tested at room temperature as well as heated. A photograph log of each test, documenting the major sheen transitions observed during each test, and any observations made, follows this discussion.

Intervals of 2 μL of oil were selected because that was the smallest pipette available at the time of testing in the CCH lab. Ideally, if the oil spread to the full extent of the tray, the sheen should have been a silver sheen on the edge of transitioning to a rainbow sheen; however, the oil never extended to the edge. A representative capture or still photograph ("still") of silver sheens was taken from the first drop of oil spreading. Most of the added 2 μL drops of oil would push the oil already sheening on the water surface outward. While this did not prevent developing a set of baseline images for each oil and sheen level, this behavior did limit the evaluation of oil volume to sheen appearance.

Due to the speed of the OIL-1 spreading, a silver sheen was not observed during either of the OIL-1 tests. The OIL-1 test was also concluded before true oil was achieved. During the OIL-5 test, a distinct transparent sheen was observed. OIL-5 was still very tacky and had difficulty releasing from the pipette and likely needs to be heated to a higher temperature (heated to 80ºC during column tests). The ability to tell true oil from metallic was very difficult as both appeared as the same color. True oil was defined, for these tests, as having a "3-D appearance." The oil would have a shadow and appear to rise out of the sheen around the true oil.

The primary takeaway from these tests was the necessity of watching and observing (via a video instead of a single photograph) as the sheen spreads and transitions. The easiest way to qualify a sheen is to see the transition. The rainbow sheens are the easiest to detect and identify visually, and without the presence of a rainbow sheen between the silver and metallics sheens, the two could be difficult to distinguish independently.

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ATTACHEMENT – CRUDE OIL-IN-DISH TEST PHOTOGRAPH LOGS

OIL-1 – Room Temperature

Oil: OIL-1
Video/Photo No: 0469 (1)

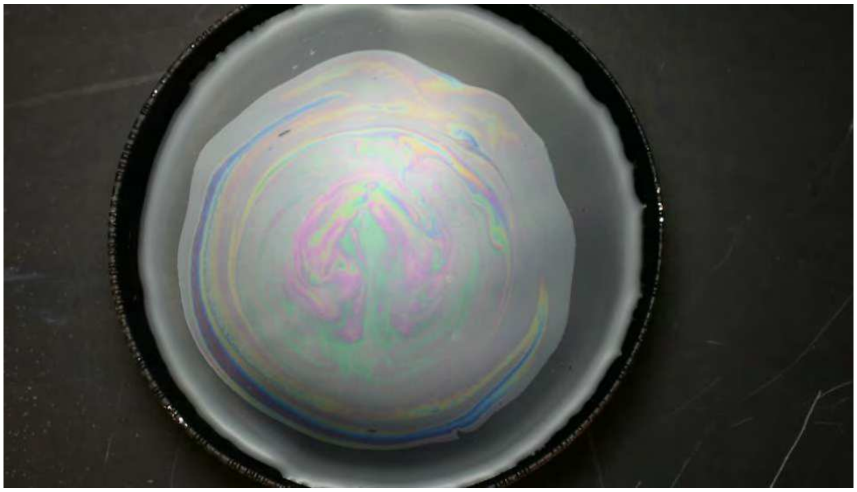
Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 0 µL
Photo Description: Start of test.

Oil: OIL-1
Video/Photo No: 0469 (2)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: Between 0 and 2 µL
Photo Description: Application of first drop. Drop of oil transitions from metallic to rainbow sheen. No sliver sheen observed.

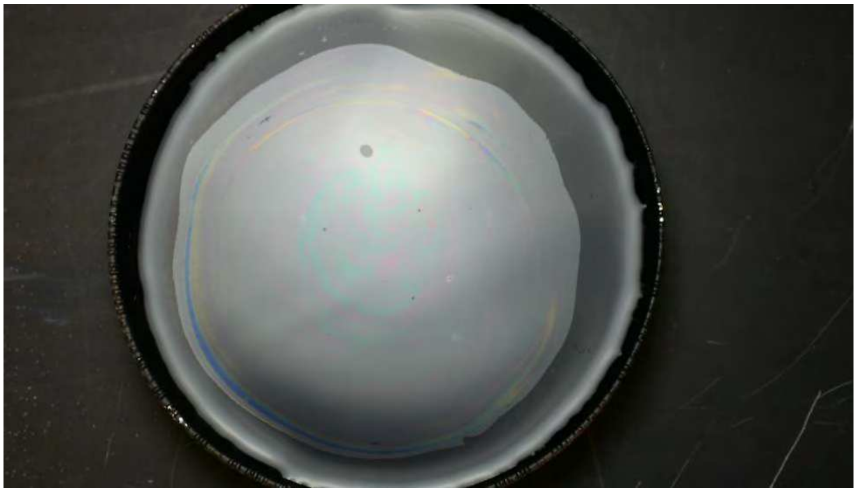
Oil: OIL-1
Video/Photo No: 0469 (3)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 2 µL
Photo Description: First drop of oil settles into a rainbow sheen.



Oil: OIL-1
Video/Photo No: 0469 (4)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 4 μL
Photo Description: Second drop of 2μL added and already sheen appears more metallic than rainbow.



Oil: OIL-1
Video/Photo No: 0469 (5)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 6 μL
Photo Description: Third drop of 2μL added to surface. Sheen appears almost completely metallic.

Oil: OIL-1
Video/Photo No: 0469 (7)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 10 μL
Photo Description: Metallic sheen.

Oil: OIL-1
Video/Photo No: 0469 (12)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 20 μL
Photo Description: Sheen appearance does not change as more oil is added. No true oil observed (two small black spots are bubbles). End of test.

OIL-1 – Heated

Oil: OIL-1
Video/Photo No: 0476 (1)

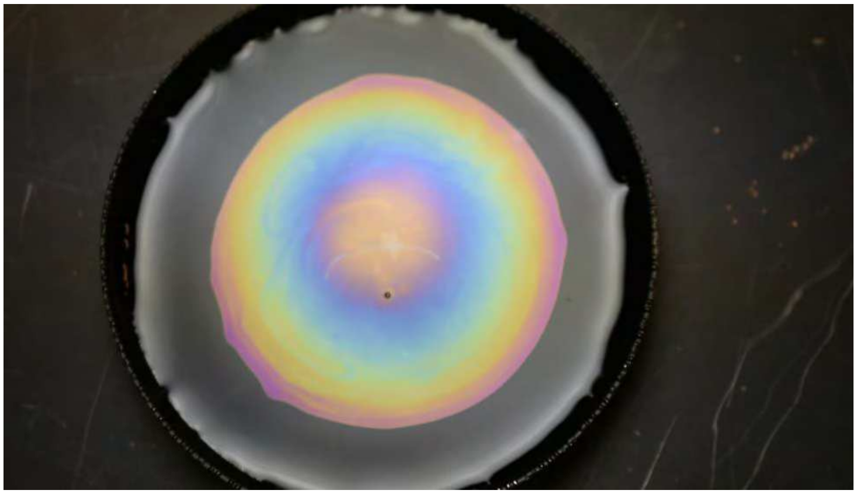
Oil Temperature: 75°C
Cumulative Oil Volume: 0 µL
Photo Description: Start of test.

Oil: OIL-1
Video/Photo No: 0476 (2)

Oil Temperature: 75°C
Cumulative Oil Volume: between 0 and 2 µL
Photo Description: Application of first drop. Drop of oil transitions from metallic to rainbow sheen. No sliver sheen observed.

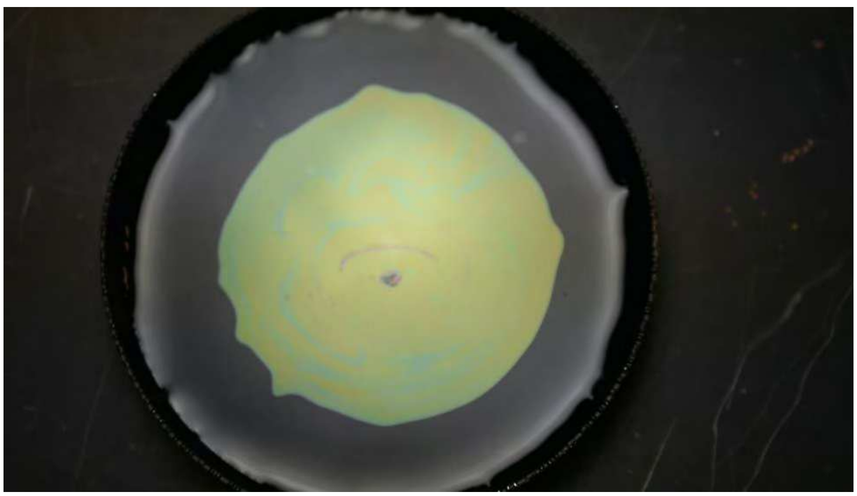
Oil: OIL-1
Video/Photo No: 0476 (3)

Oil Temperature: 75°C
Cumulative Oil Volume: between 0 and 2 µL
Photo Description: First drop of oil quickly transitions into a brighter rainbow sheen than the room temperature OIL-1 drops.



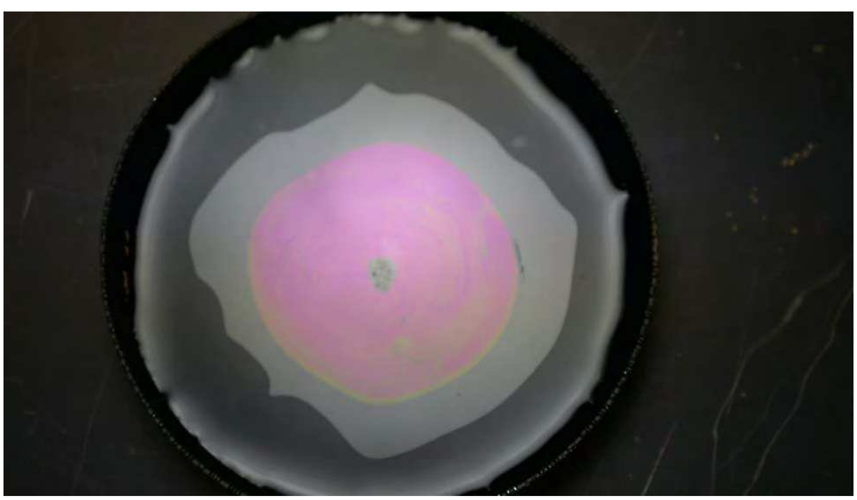
Oil: OIL-1
Video/Photo No: 0476 (4)

Oil Temperature: 75°C
Cumulative Oil Volume: between 0 and 2 µL
Photo Description: First drop of oil continues to spread.



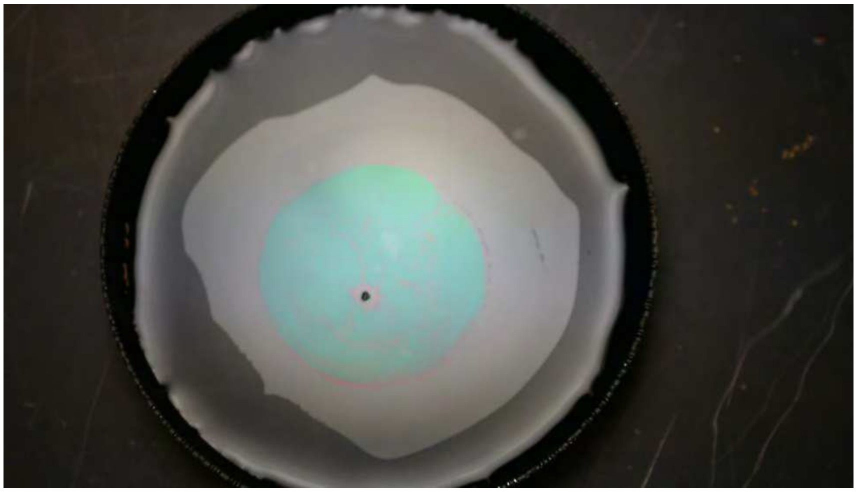
Oil: OIL-1
Video/Photo No: 0476 (5)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 µL
Photo Description: First drop of oil settles into a yellow and green rainbow sheen.



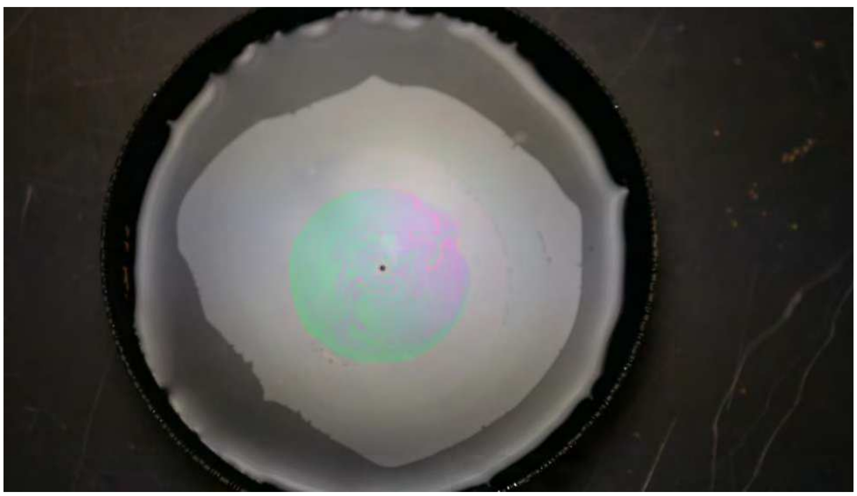
Oil: OIL-1
Video/Photo No: 0476 (6)

Oil Temperature: 75°C
Cumulative Oil Volume: 4 µL
Photo Description: Second drop of oil applied to surface and allowed to settle. New drop of oil pushes the oil on the surface outward and into a metallic sheen. Without watching the sheen behavior, the outer layer could be mistaken as silver.



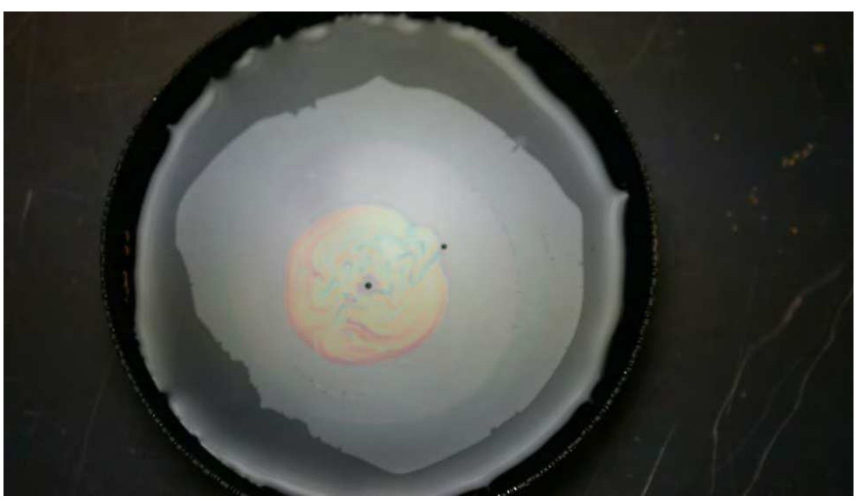
Oil: OIL-1
Video/Photo No: 0476 (7)

Oil Temperature: 75°C
Cumulative Oil Volume: 6 µL
Photo Description: New drop of oil continues to push the “old” oil outward into a metallic sheen (Center speck is a bubble).



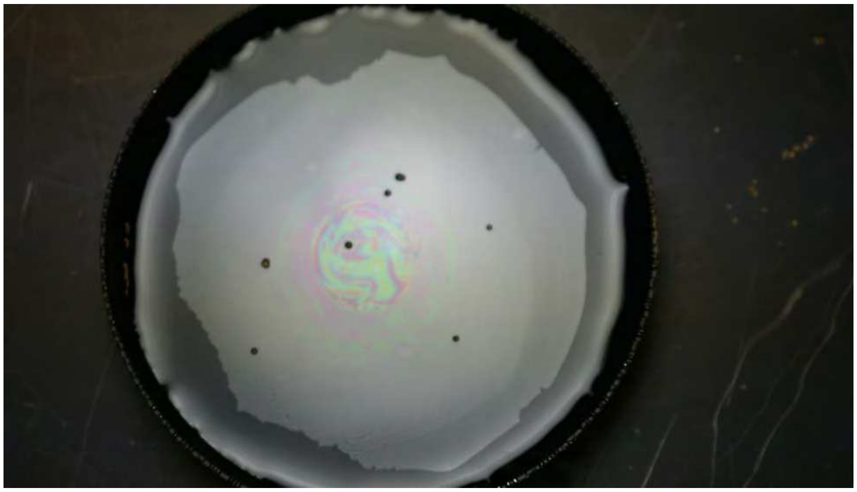
Oil: OIL-1
Video/Photo No: 0476 (8)

Oil Temperature: 75°C
Cumulative Oil Volume: 8 µL
Photo Description: New drop of oil continues to push the “old” oil outward into a metallic sheen (Center speck is a bubble).



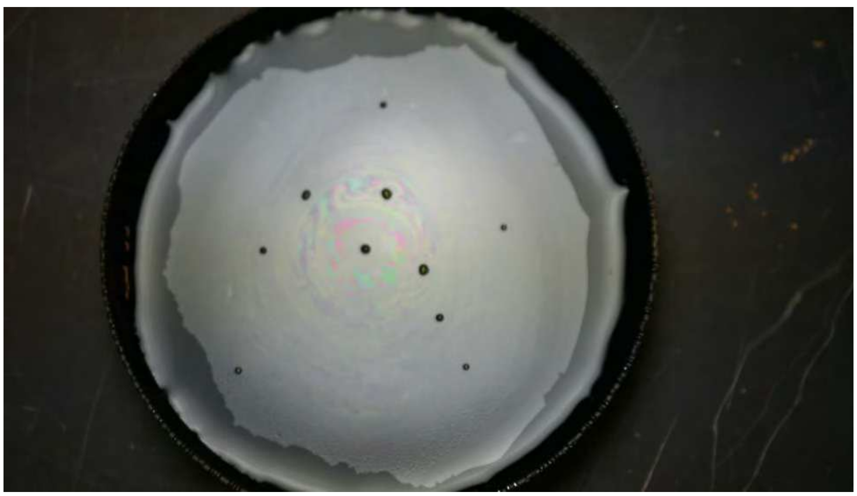
Oil: OIL-1
Video/Photo No: 0476 (9)

Oil Temperature: 75°C
Cumulative Oil Volume: 10 µL
Photo Description: New drop of oil continues to push the “old” oil outward into a metallic sheen (Center spots are bubbles).



Oil: OIL-1
Video/Photo No: 0476 (14)

Oil Temperature: 75°C
Cumulative Oil Volume: 20 µL
Photo Description: Sheen pattern continues with more bubbles present.



Oil: OIL-1
Video/Photo No: 0476 (19)

Oil Temperature: 75°C
Cumulative Oil Volume: 30 µL
Photo Description: Sheen pattern continues with more bubbles present.

Oil: OIL-1
Video/Photo No: 0476 (21)

Oil Temperature: 75°C
Cumulative Oil Volume: 34 µL
Photo Description: Complete metallic sheen and bubbles popped. No true oil observed. End of test.

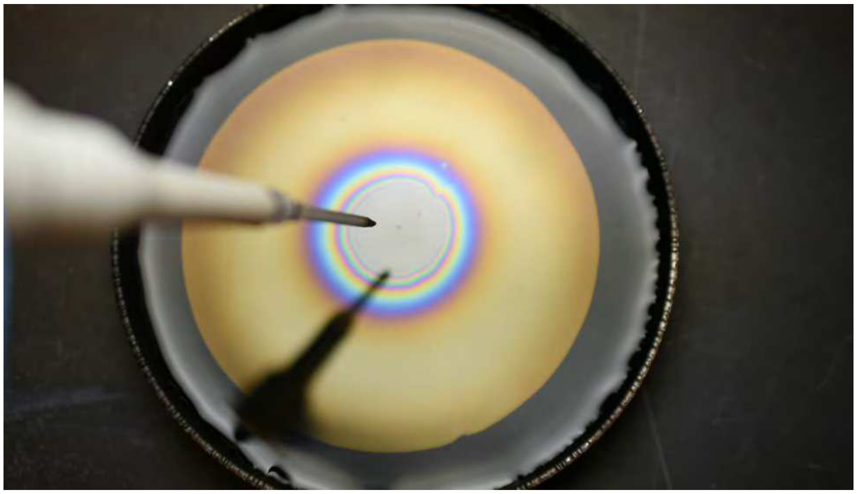
OIL-2 – Room Temperature

Oil: OIL-2
Video/Photo No: 0468 (1)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 0 µL
Photo Description: Start of test.

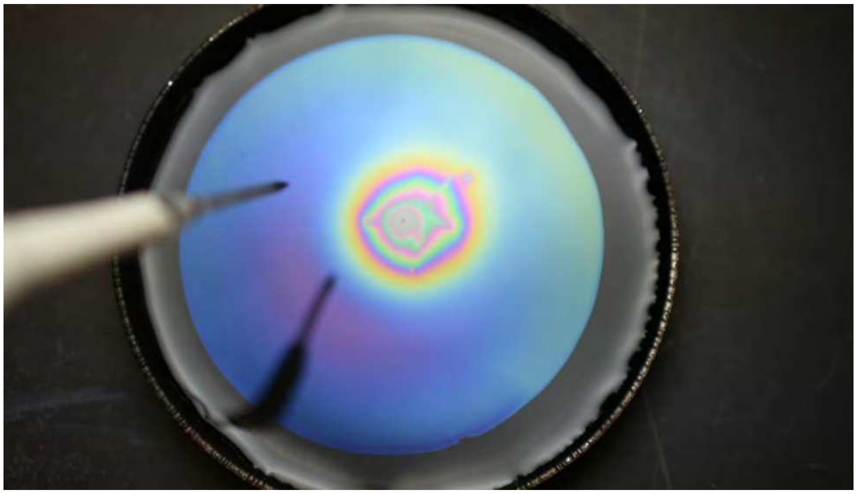
Oil: OIL-2
Video/Photo No: 0468 (2)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: between 0 and 2 µL
Photo Description: Application of first drop. Drop of oil transitions from metallic to rainbow to silver (middle to outward).



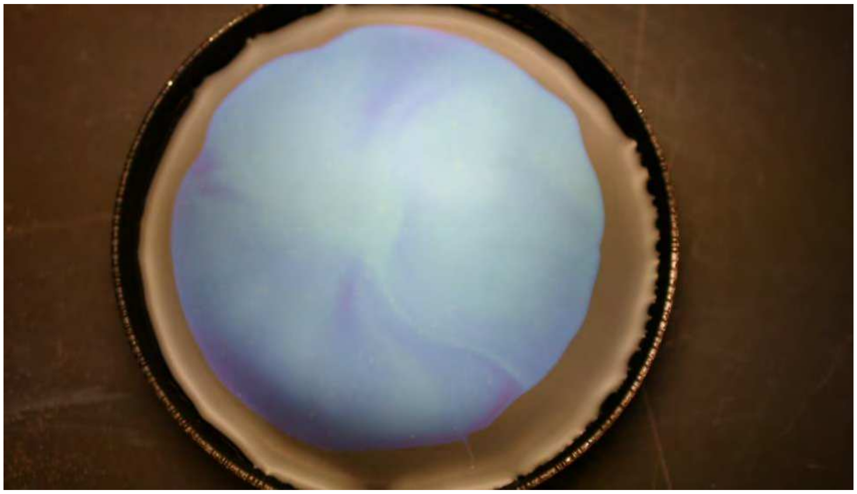
Oil: OIL-2
Video/Photo No: 0468 (3)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: between 0 and 2 µL
Photo Description: Application of first drop. Silver sheen transitions to rainbow sheen.



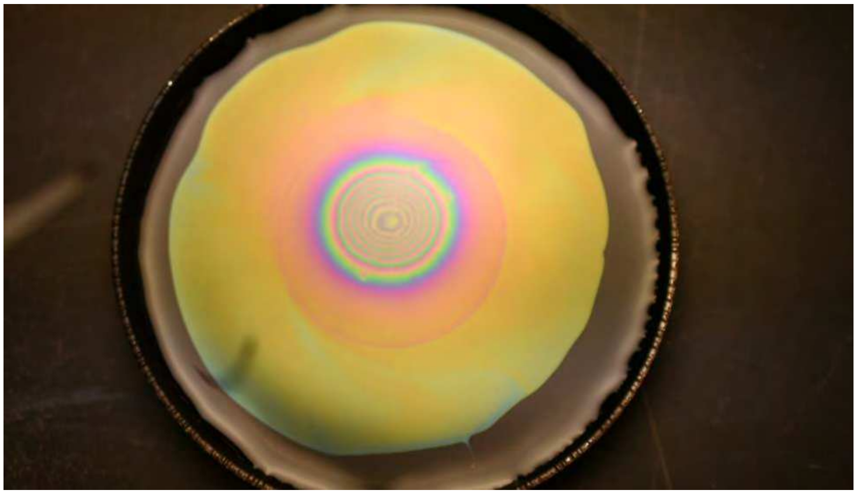
Oil: OIL-2
Video/Photo No: 0468 (4)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: between 0 and 2 μL
Photo Description: Application of first drop. Metallic sheen transitions to rainbow until only a rainbow sheen is visible.



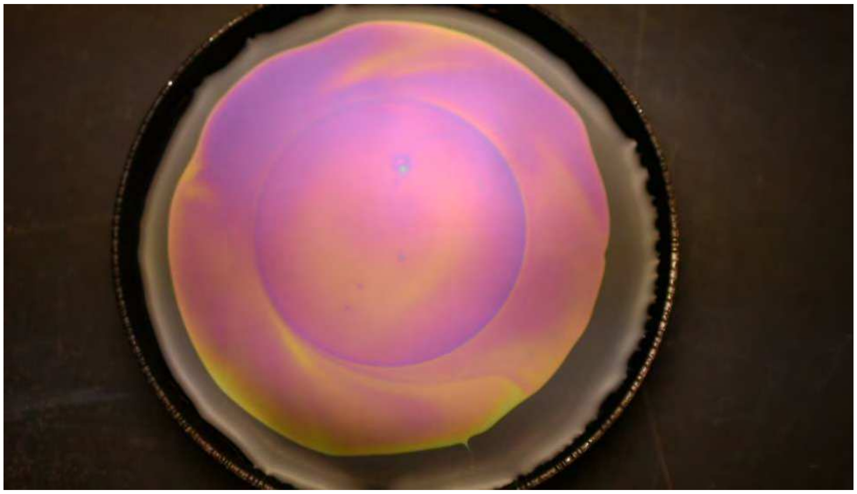
Oil: OIL-2
Video/Photo No: 0468 (5)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 2 μL
Photo Description: First drop of oil settles into a blue rainbow sheen. Lighting not changed, the camera self-adjusted light settings.



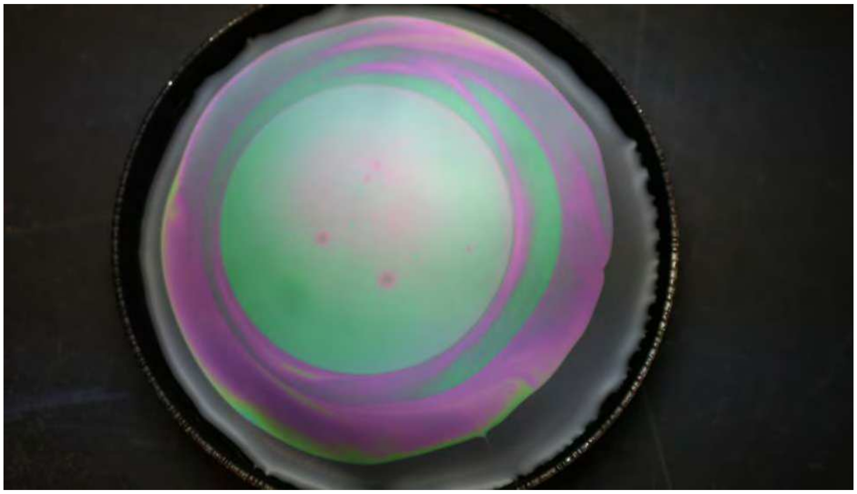
Oil: OIL-2
Video/Photo No: 0468 (6)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: between 2 and 4 μL
Photo Description: Application of second drop of oil. Good example of the bands of color. New drop of oil appears to have pushed the "old" oil outward, similar to OIL-1, but the sheen remains a rainbow sheen.



Oil: OIL-2
Video/Photo No: 0468 (7)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 4 µL
Photo Description: Though the sheen coloring is the same, there is a distinct line marking the second drop of oil applied to the surface.

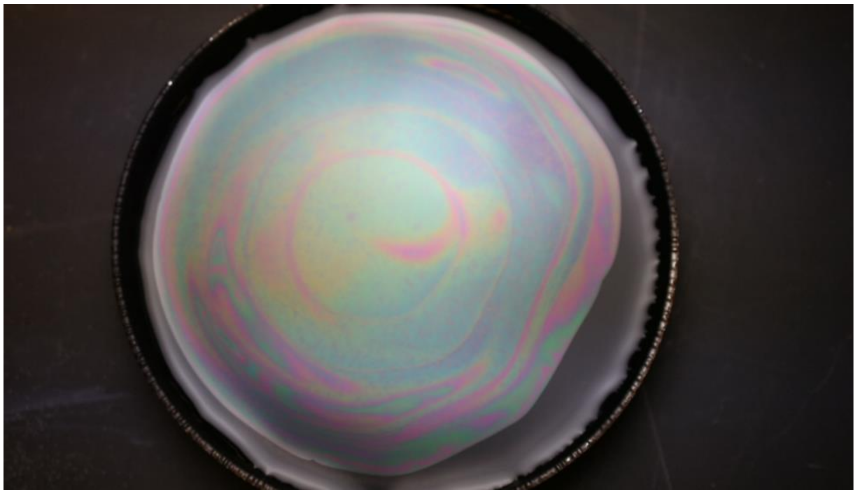


Oil: OIL-2
Video/Photo No: 0468 (8)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 6 µL
Photo Description: Third drop of oil pushes oil outward, but sheen remains a rainbow sheen.

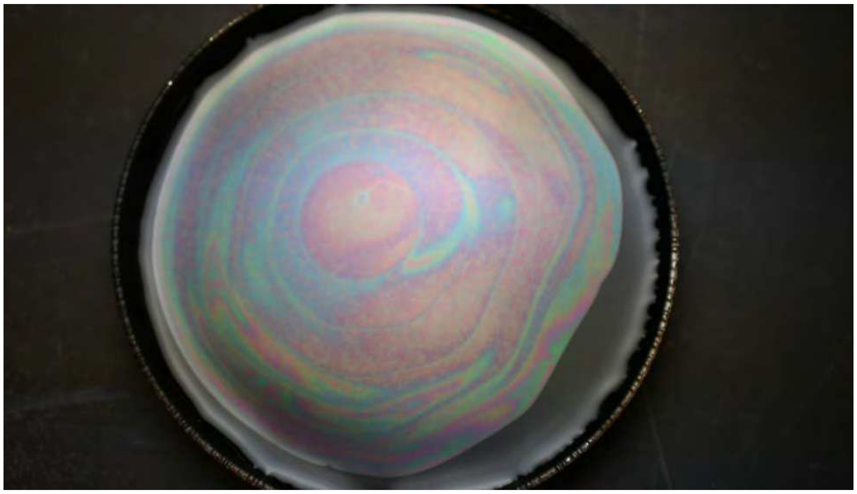
Oil: OIL-2
Video/Photo No: 0468 (9)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 8 µL
Photo Description: Still a rainbow sheen, but colors are starting to “muddy.”



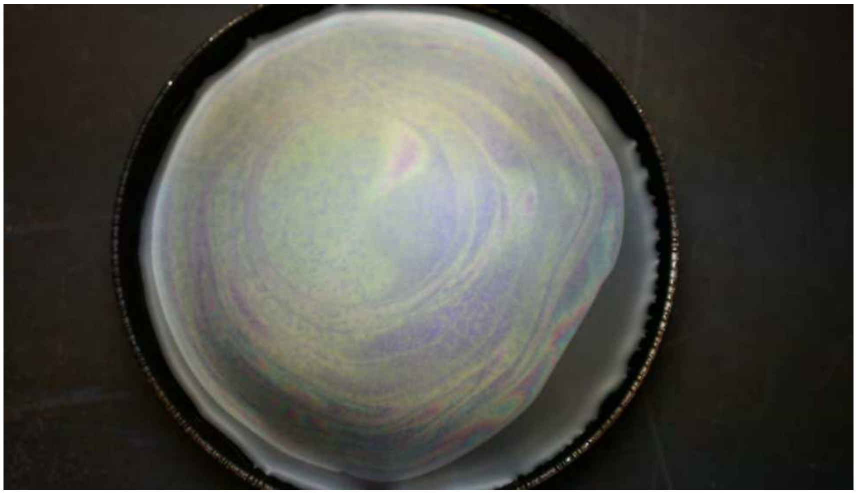
Oil: OIL-2
Video/Photo No: 0468 (10)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 12 µL
Photo Description: Still a rainbow sheen, but colors continue to “muddy.”



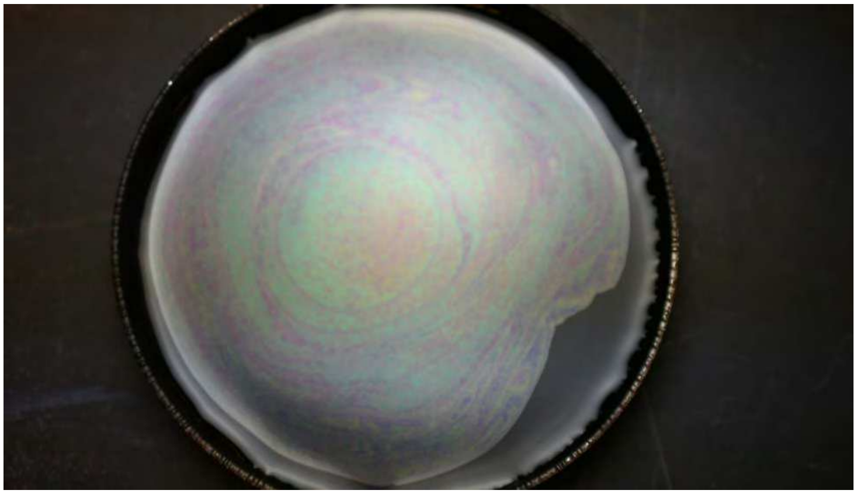
Oil: OIL-2
Video/Photo No: 0468 (11)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 14 µL
Photo Description: Still a rainbow sheen, but colors continue to “muddy.”



Oil: OIL-2
Video/Photo No: 0468 (12)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 16 µL
Photo Description: Rainbow sheen starting to transition to metallic.



Oil: OIL-2
Video/Photo No: 0468 (14)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 20 µL
Photo Description: Rainbow sheen starting to transition to metallic.

Oil: OIL-2
Video/Photo No: 0468 (14)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 34 µL
Photo Description: Outer sheen appears to be a metallic sheen, but some color (rainbow sheen) is still coming through. The added oil drops are spreading much slower now. Example of true oil.

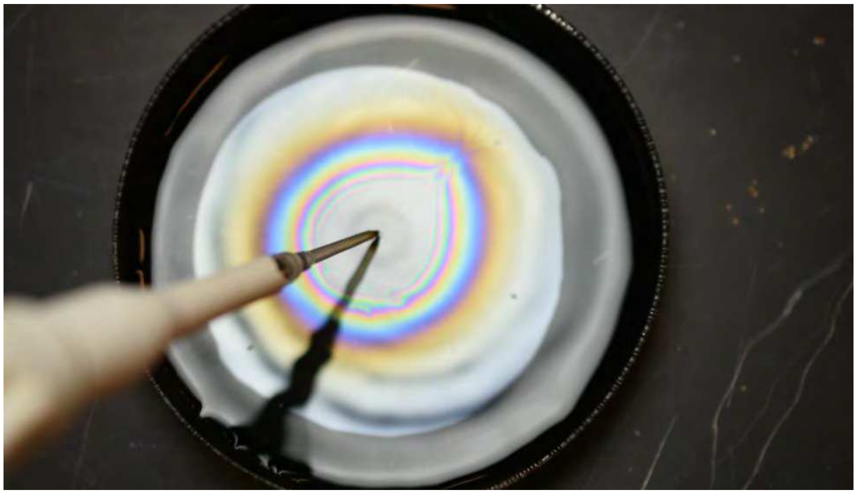
Oil: OIL-2
Video/Photo No: 0468 (15)

Oil Temperature: Room Temperature (approx. 25ºC)
Cumulative Oil Volume: 44 µL
Photo Description: For the most part, the sheen is metallic though some color (rainbow sheen) is still coming through. Where the latest drop of oil was applied, the oil looks 3D implying that drop is still true oil and not a metallic sheen though the coloring is similar. End of test.

OIL-2 - Heated

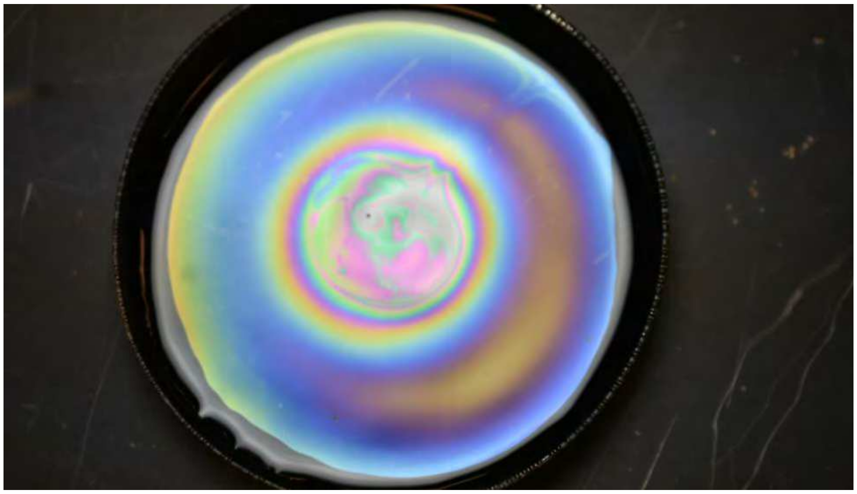
Oil: OIL-2
Video/Photo No: 047 (1)

Oil Temperature: 75°C
Cumulative Oil Volume: 0 μL
Photo Description: Start of test.



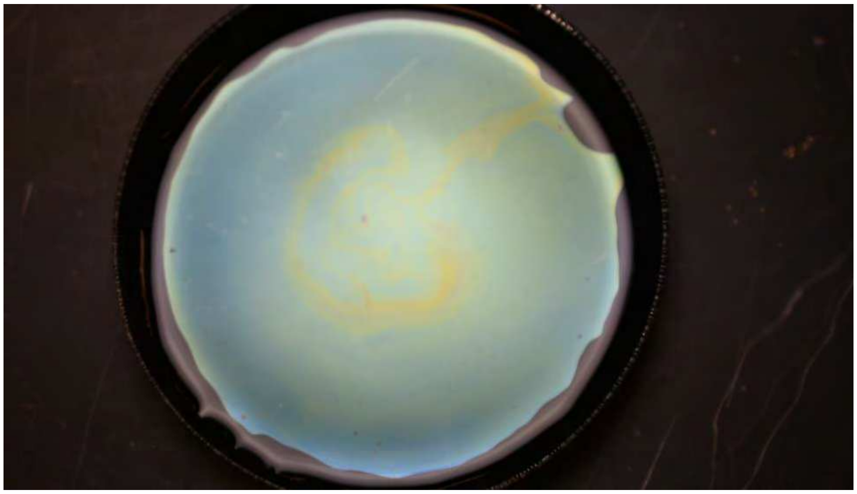
Oil: OIL-2
Video/Photo No: 0477 (2)

Oil Temperature: 75°C
Cumulative Oil Volume: 0-2 μL
Photo Description: Application of first drop. The oil spread across the water surface much quicker than the room temperature oil. Silver sheen observed in edges.



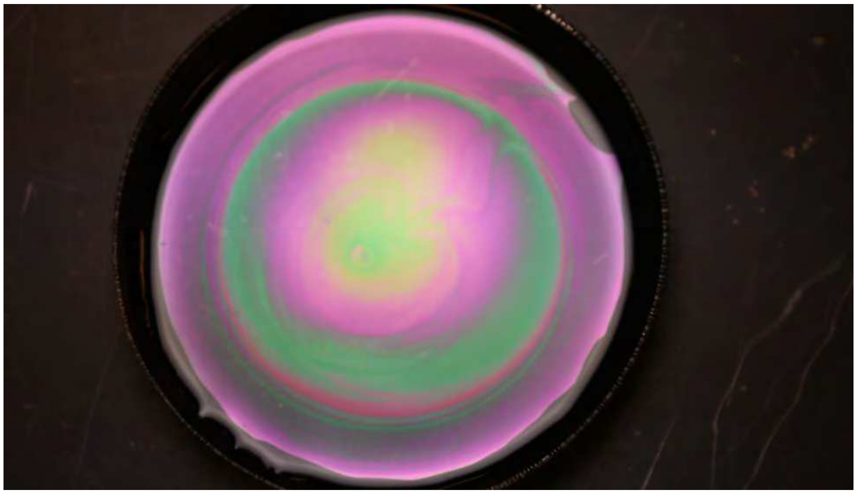
Oil: OIL-2
Video/Photo No: 0477 (3)

Oil Temperature: 75°C
Cumulative Oil Volume: 0-2 μL
Photo Description: Application of first drop of oil. As the oil spreads a bright rainbow sheen is observed.



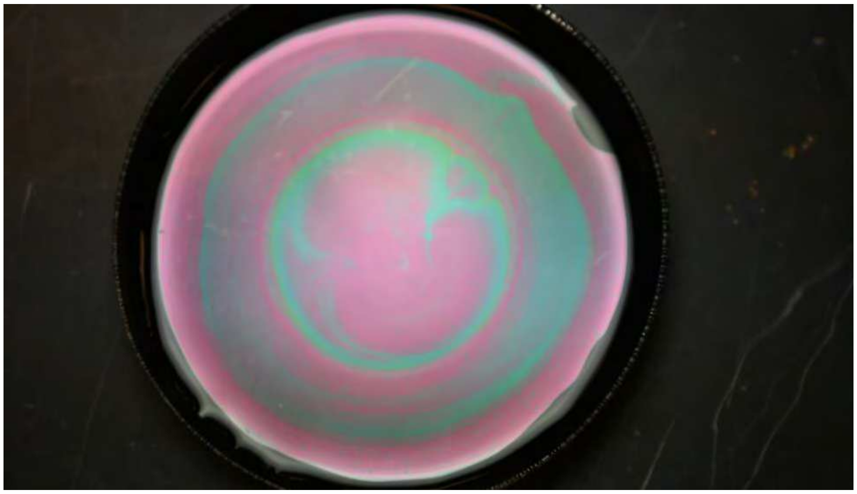
Oil: OIL-2
Video/Photo No: 0477 (4)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 μL
Photo Description: First drop of oil settles into a muddy yellow and green rainbow sheen, similar colors as the room temperature OIL-2.



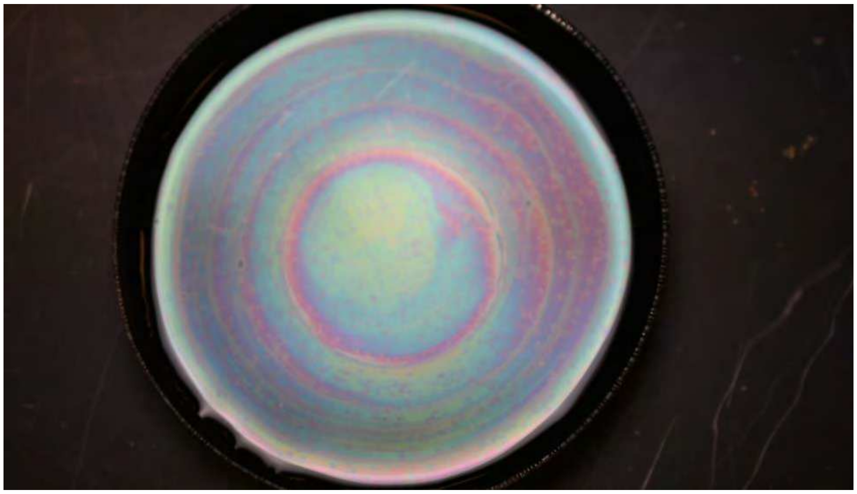
Oil: OIL-2
Video/Photo No: 0477 (5)

Oil Temperature: 75°C
Cumulative Oil Volume: 4 μL
Photo Description: New drop of oil appears to have pushed the old oil outward, but the sheen remains a rainbow sheen and again the colors are similar to the room temperature OIL-2.



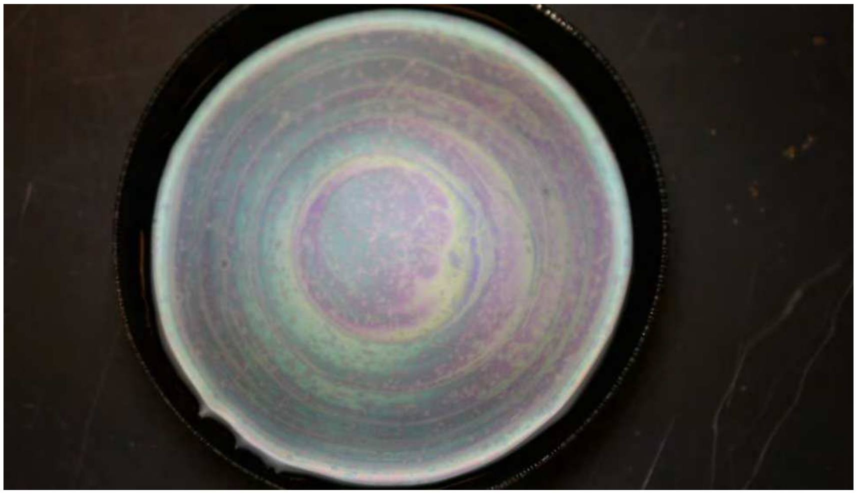
Oil: OIL-2
Video/Photo No: 0477 (6)

Oil Temperature: 75°C
Cumulative Oil Volume: 6 μL
Photo Description: Third drop of oil pushes oil outward, but sheen remains a rainbow sheen.



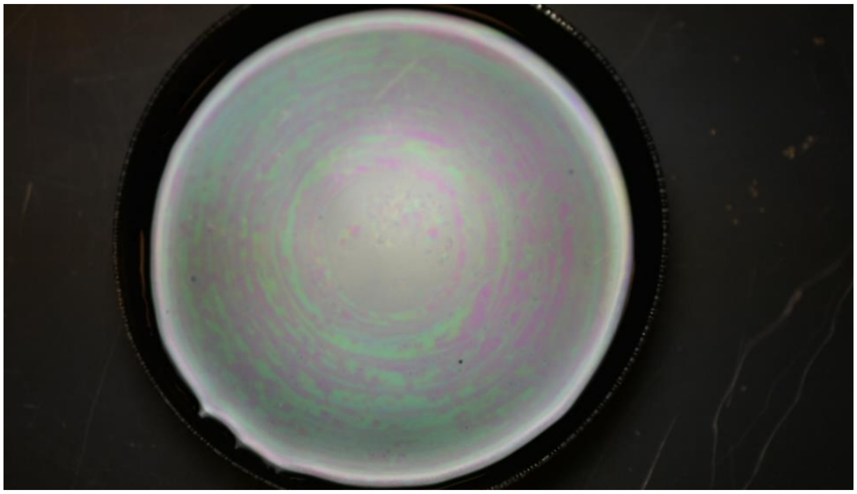
Oil: OIL-2
Video/Photo No: 0477 (7)

Oil Temperature: No
Cumulative Oil Volume: 10 µL
Photo Description: Still a rainbow sheen, but colors are starting to “muddy.”



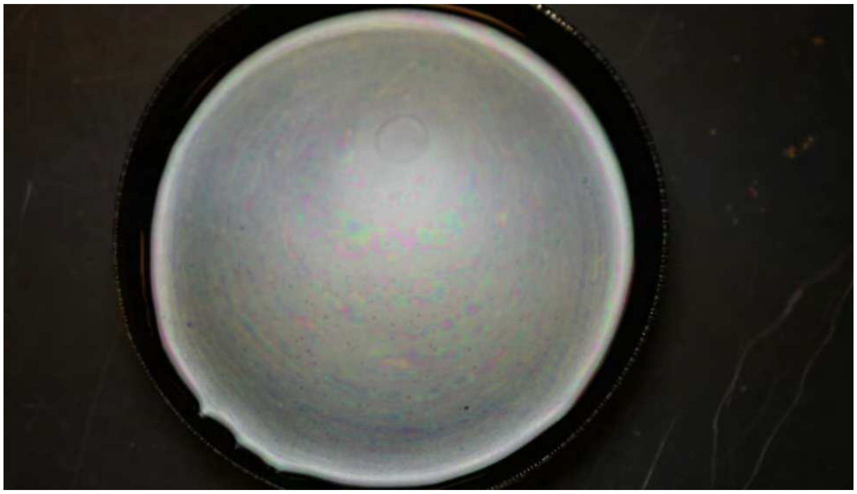
Oil: OIL-2
Video/Photo No: 0477 (8)

Oil Temperature: No
Cumulative Oil Volume: 12 µL
Photo Description: Rainbow sheen starting to transition to metallic.



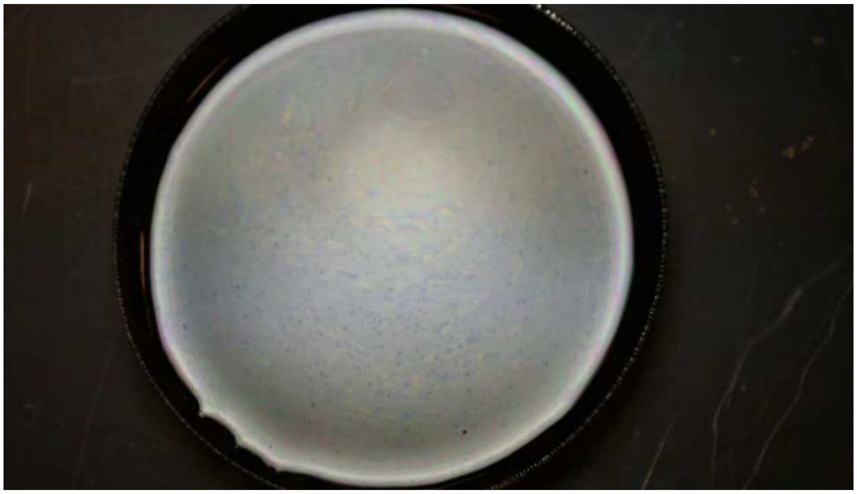
Oil: OIL-2
Video/Photo No: 0477 (9)

Oil Temperature: No
Cumulative Oil Volume: 20 µL
Photo Description: Rainbow sheen continuing to transition to metallic.



Oil: OIL-2
Video/Photo No: 0477 (10)

Oil Temperature: No
Cumulative Oil Volume: 30 µL
Photo Description: Sheen appears to be a metallic sheen, but some color (rainbow sheen) is still coming through. The added oil drops are spreading much slower now.



Oil: OIL-2
Video/Photo No: 0477 (11)

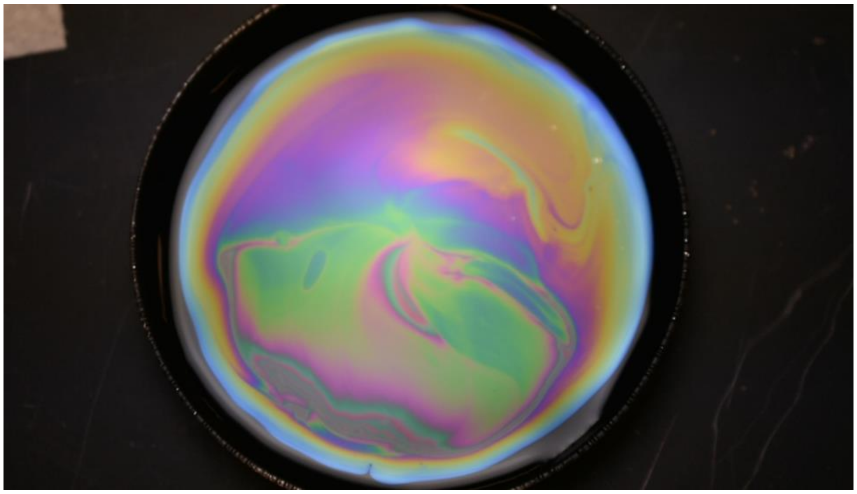
Oil Temperature: No
Cumulative Oil Volume: 38 µL
Photo Description: For the most part, the sheen is metallic though some color (rainbow sheen) is still coming through. End of test.

Oil: OIL-3
Video/Photo No: 047 (1)

Oil Temperature: 75°C
Cumulative Oil Volume: 0 μL
Photo Description: Start of test.

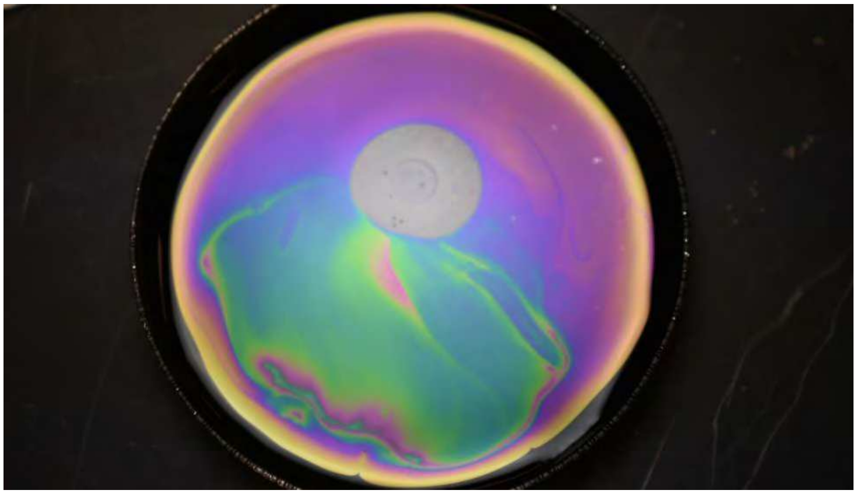
Oil: OIL-3
Video/Photo No: 0477 (2)

Oil Temperature: 75°C
Cumulative Oil Volume: 0-2 μL
Photo Description: Application of first drop. Drop of oil transitions from metallic to rainbow to silver (middle to outward).



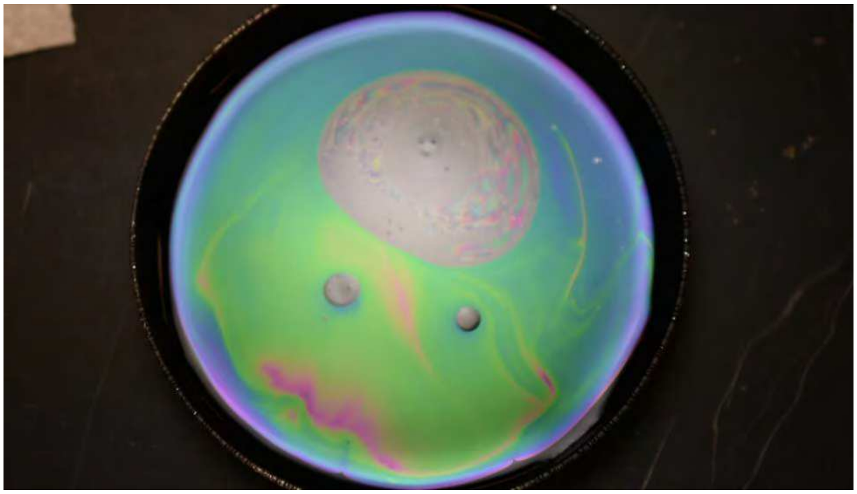
Oil: OIL-3
Video/Photo No: 0477 (3)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 μL
Photo Description: First drop of oil settles into a rainbow sheen.



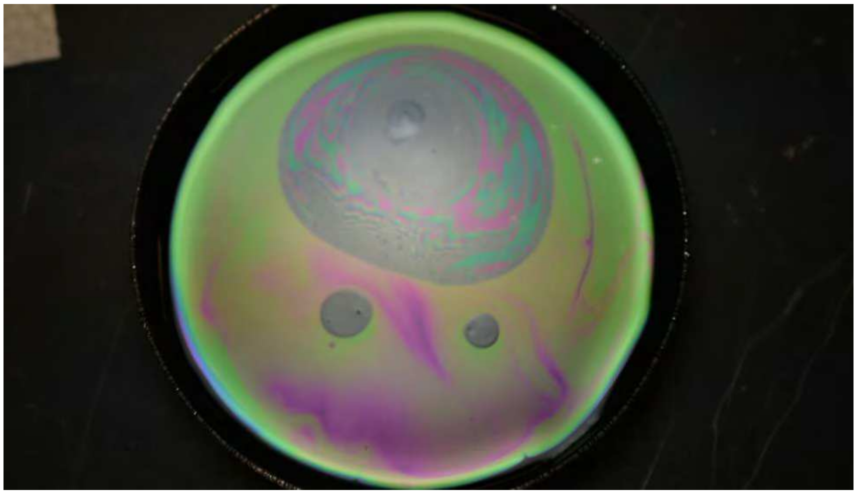
Oil: OIL-3
Video/Photo No: 0477 (4)

Oil Temperature: 75°C
Cumulative Oil Volume: 6 µL
Photo Description: Second and third drop of OIL-3 do not spread outside of metallic sheen and do not combined with the first drop of oil.



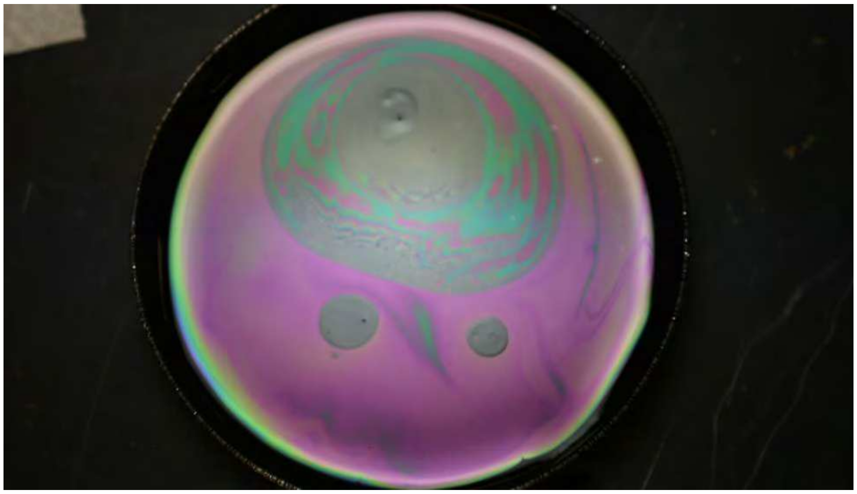
Oil: OIL-3
Video/Photo No: 0477 (5)

Oil Temperature: 75°C
Cumulative Oil Volume: 12 µL
Photo Description: More oil is added to the same spot. Fifth and sixth drop (10 and 12 µL, left and right, respectively) applied to rainbow section. Both spread very slowly and are an example of true oil in this photograph.



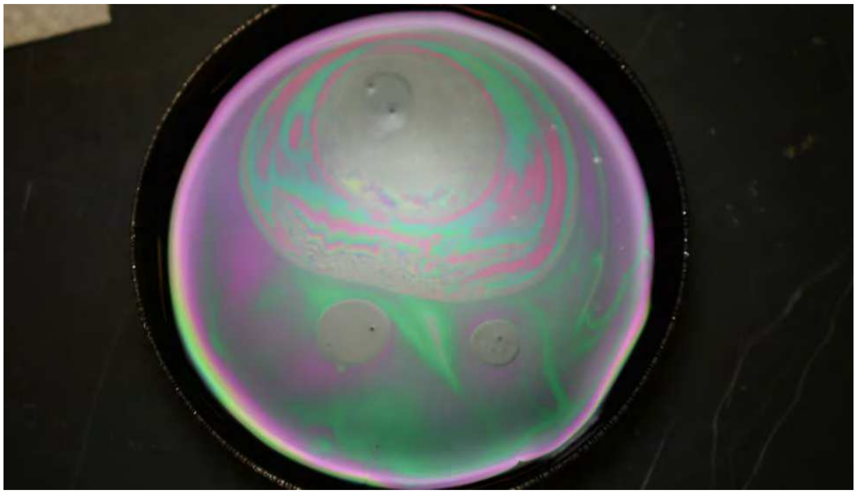
Oil: OIL-3
Video/Photo No: 0477 (6)

Oil Temperature: 75°C
Cumulative Oil Volume: 16 µL
Photo Description: Drops 7 and 8 (14 and 16 µL, respectively) added back to main patch.



<u>Oil</u>: OIL-3
<u>Video/Photo No</u>: 0477 (7)

<u>Oil Temperature</u>: No
<u>Cumulative Oil Volume</u>: 18 µL
<u>Photo Description</u>: Drop 9 added back to main patch. Metallic sheen spreads to rainbow sheen slowly.



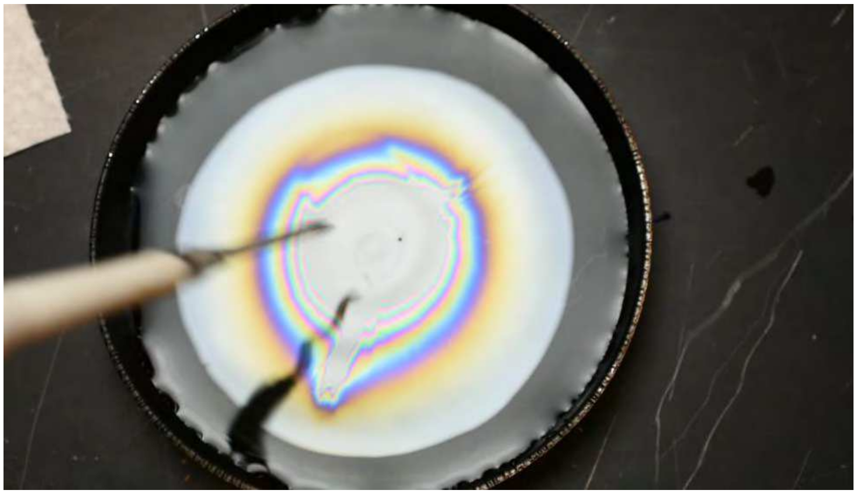
<u>Oil</u>: OIL-3
<u>Video/Photo No</u>: 0477 (8)

<u>Oil Temperature</u>: No
<u>Cumulative Oil Volume</u>: 20 µL
<u>Photo Description</u>: End of test.

OIL-4 - Heated

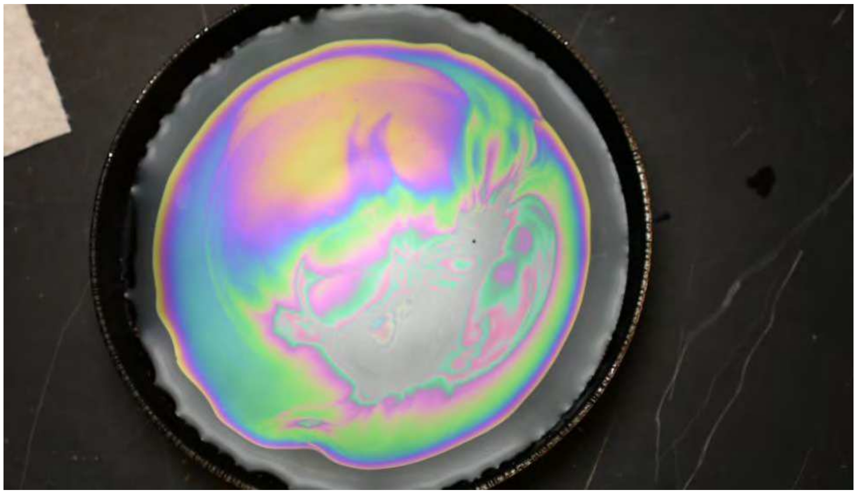
Oil: OIL-4
Video/Photo No: 047 (1)

Oil Temperature: 75°C
Cumulative Oil Volume: 0 μL
Photo Description: Start of test.



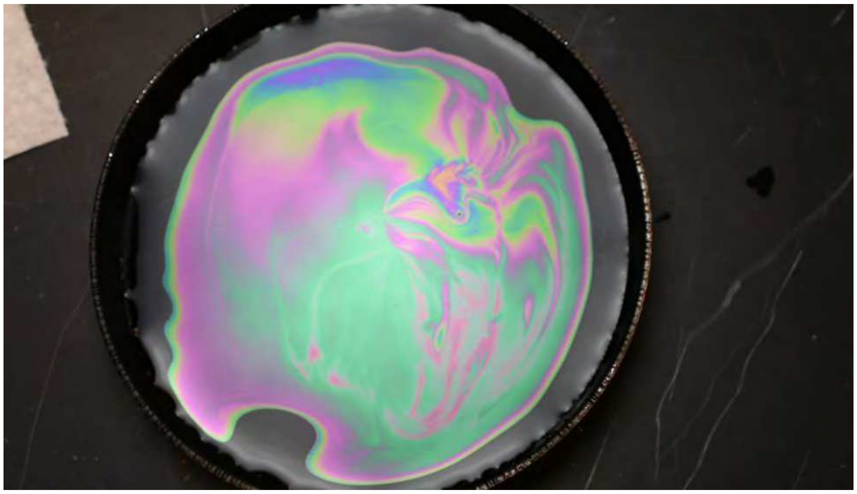
Oil: OIL-4
Video/Photo No: 0477 (2)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 μL
Photo Description: Application of first drop. Drop of oil transitions from metallic to rainbow to silver (middle to outward).



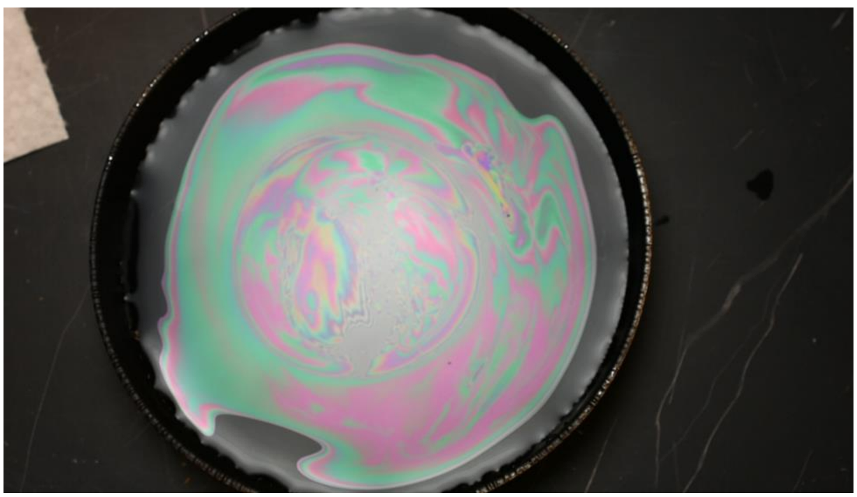
Oil: OIL-4
Video/Photo No: 0477 (3)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 μL
Photo Description: First drop of oil spreads into a rainbow sheen.



Oil: OIL-4
Video/Photo No: 0477 (4)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 μL
Photo Description: First drop of oil settles into a rainbow sheen.

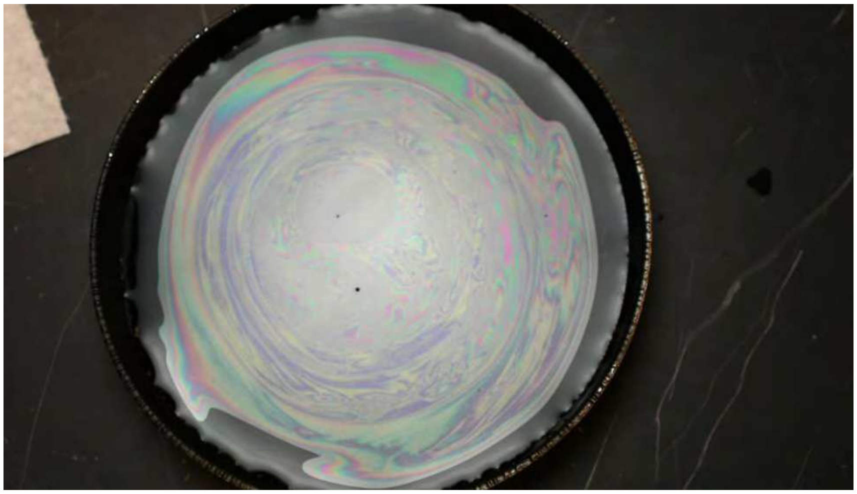


Oil: OIL-4
Video/Photo No: 0477 (5)

Oil Temperature: 75°C
Cumulative Oil Volume: 4 μL
Photo Description: Still a rainbow sheen, but colors are starting to “muddy.”

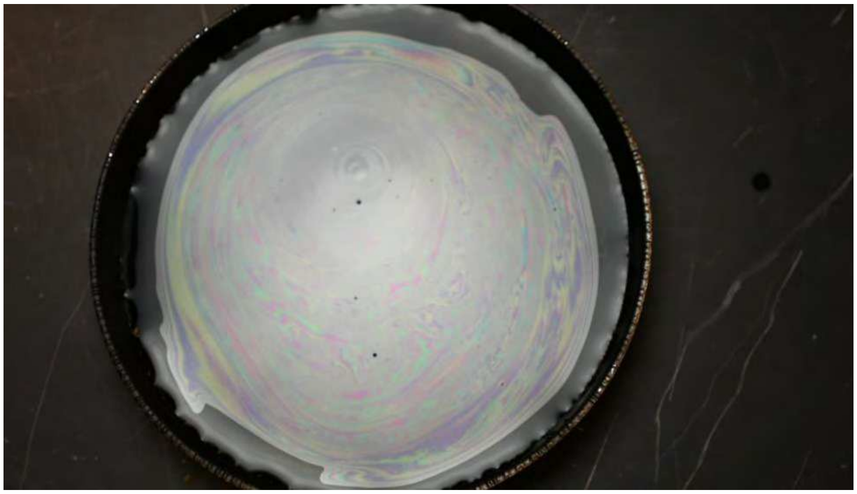
Oil: OIL-4
Video/Photo No: 0477 (6)

Oil Temperature: 75°C
Cumulative Oil Volume: 6 μL
Photo Description: Still a rainbow sheen, but colors are continuing to “muddy.”



Oil: OIL-4
Video/Photo No: 0477 (7)

Oil Temperature: No
Cumulative Oil Volume: 10 µL
Photo Description: Rainbow sheen continues to transition to metallic.



Oil: OIL-4
Video/Photo No: 0477 (8)

Oil Temperature: No
Cumulative Oil Volume: 20 µL
Photo Description: Sheen appears to be a metallic sheen, but some color (rainbow sheen) is still coming through. The added oil drops are spreading much slower now.

Oil: OIL-4
Video/Photo No: 0477 (9)

Oil Temperature: No
Cumulative Oil Volume: 24 µL
Photo Description: Sheen appears to be a metallic sheen, but some color (rainbow sheen) is still coming through. The added oil drops are spreading much slower now. End of test.

OIL-5 - Heated

Oil: OIL-5
Video/Photo No: 047 (1)

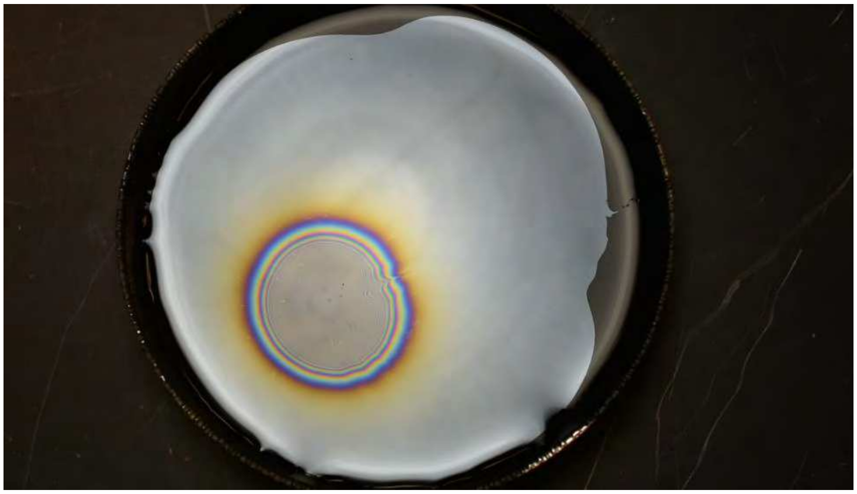
Oil Temperature: 75°C
Cumulative Oil Volume: 0 µL
Photo Description: Start of test.

Oil: OIL-5
Video/Photo No: 0477 (2)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 µL
Photo Description: Application of first drop. OIL-5, even heated is still very “sticky” and likely needs to be heated more. Oil appears to be true oil (black appearance) with silver band and transparent sheen on the outer edge.

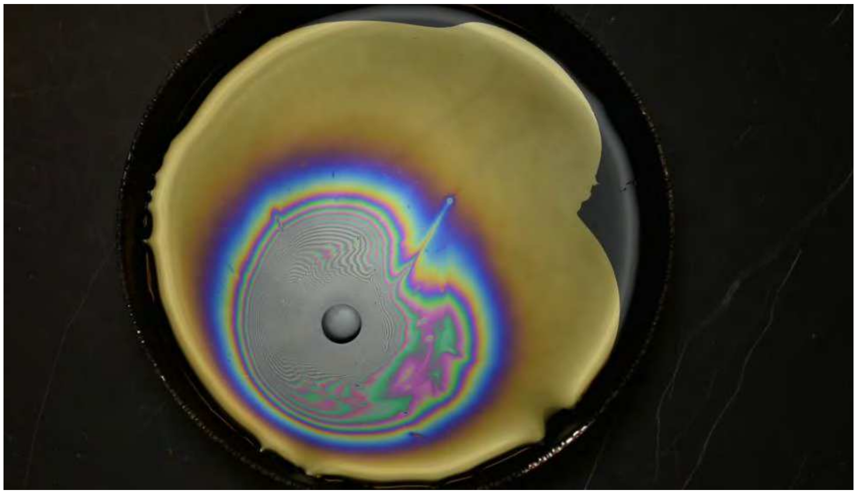
Oil: OIL-5
Video/Photo No: 0477 (3)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 µL
Photo Description: Transparent sheen spreads to the edge of the dish as the true oil spreads to metallic with silver band. No obvious rainbow sheen between the silver and metallic sheens.



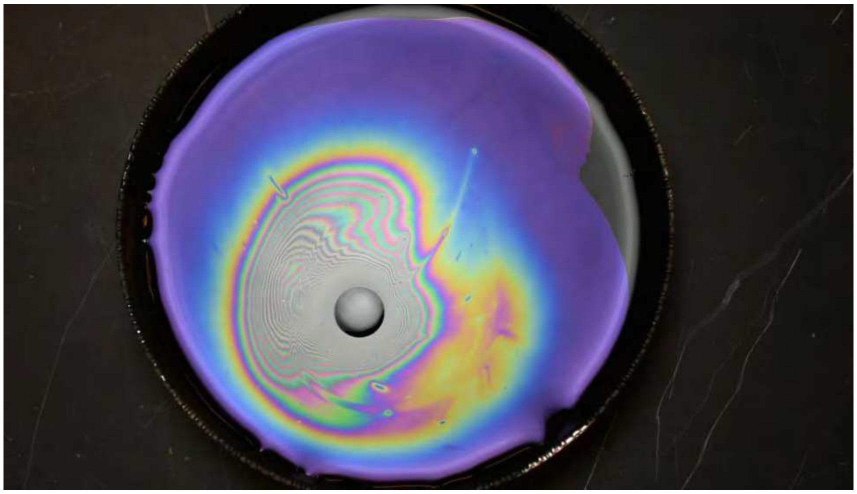
Oil: OIL-5
Video/Photo No: 0477 (4)

Oil Temperature: 75°C
Cumulative Oil Volume: 2 μL
Photo Description: First drop of oil settles into a metallic, rainbow, and silver sheen (middle to outward). Only time a silver sheen is present as sheen settles and balances.



Oil: OIL-5
Video/Photo No: 0477 (6)

Oil Temperature: 75°C
Cumulative Oil Volume: 4 μL
Photo Description: Second drop of oil applied, example of true oil. The new drop does not spread any further. Silver sheen transitioned to rainbow.



Oil: OIL-5
Video/Photo No: 0477 (7)

Oil Temperature: No
Cumulative Oil Volume: 6 μL
Photo Description: Third drop added to true oil. The two drops combine but do not spread further. Test of test.

APPENDIX B – RIVER AND HARBOR SEDIMENT SUMMARY TABLE

Table B.1. River and harbor sediment summary table.

Site	Location	Coarse Sand	Medium Sand	Fine Sand	Silt	Clay	Reference
		2.0 - 4.75 mm	0.425 - 2.0 mm	0.075 - 0.425 mm	0.002 - 0.075 mm	< 0.002 mm	
Kemaman River	Malaysia			80.8	8.6	10.8	Kamaruzzaman, et al. 2002
Charlestone Harbor	South Carolina, USA			70.9	13.3	13.8	ANAMAR 2015
Sediment Basin, Savannah River	Georgia, USA			3.0	13.0	84.0	SHEP 2009
Entrance of Savannah Harbor, Savannah River	Georgia, USA			53.7	27.6	18.5	SHEP 2009
Inner Savannah Harbor, Savannah River	Georgia, USA			34.5	41.0	24.1	SHEP 2009
Agana Boat Basin	Guam	9.0	10.2	77.0	3.8		Denton, et al. 1997
Apra Harbor	Guam	11.7	12.8	69.7	5.9		Denton, et al. 1997
Agat Marina	Guam	6.2	5.2	81.9	6.6		Denton, et al. 1997
Merizo Pier	Guam	11.9	7.4	78.3	2.4		Denton, et al. 1997
Mississippi River	Grafton, Illinois, to Head of Passes, Louisiana, USA	3.9	60.3	30.0	2.7		Gaines and Priestas 2016
Maumee River Channel	Ohio, USA	9.4	6.3	10.8	32.0	36.0	Ohio EPA
Toledo Harbor Channel	Ohio, USA	6.7	2.7	4.7	33.5	52.4	Ohio EPA

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APPENDIX C – PARTICLE SIZE DISTRIBUTION OF SEDIMENT MIXTURE

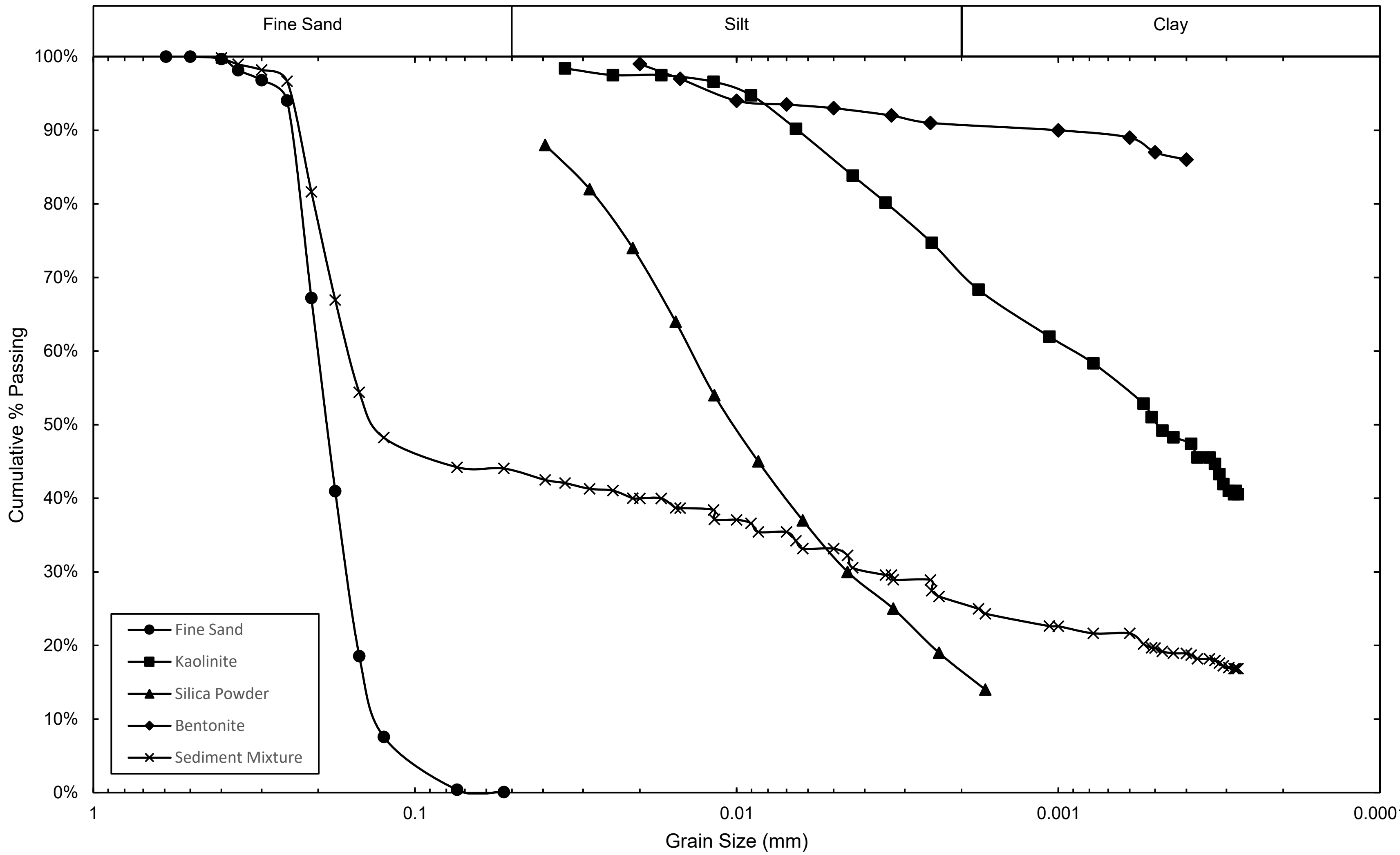


Figure C.1. Particle size distribution chart for the four individual materials and combined sediment mixture.

APPENDIX D – COLUMN TEST RESULTS

Table D.1. Column test summary table.

Tools	Oil Type	Oil Deposit	Sheen Level	Oil Volume (µL)	Added Air	Photo/Video No
Large Propeller Mixer	Control	NA	NA	0		0492
Direct Push	Control	NA	NA	0		0546
Air Injection	Control	NA	NA	0		0537
Water Injection	Control	NA	NA	0		0548
Light Vibrating	Control	NA	NA	0		0555
Small Propeller Mixer	Control	NA	NA	0		0589
Rod Drop	Control	NA	NA	0		0624, 0630
Small Propeller Mixer	OIL-1	Consolidated	Rainbow	40		0602, 601
Air Injection	OIL-1	Consolidated	Rainbow	40		0595
Water Injection	OIL-1	Consolidated	Rainbow	40		0598, 0599
Light Vibrating	OIL-1	Consolidated	Rainbow	40		0597, 0600
Rod Drop	OIL-1	Consolidated	Rainbow	40		0650
Rod Drop	OIL-1	Consolidated	Rainbow	40	Sand Layer	0656
Large Propeller Mixer	OIL-2	Consolidated	Rainbow	40		0535, 0551
Direct Push	OIL-2	Consolidated	Rainbow	40		0525
Air Injection	OIL-2	Consolidated	Rainbow	40		0540
Air Injection	OIL-2	Consolidated	Rainbow	40		0533
Water Injection	OIL-2	Consolidated	Rainbow	40		0549
Water Injection	OIL-2	Consolidated	Rainbow	40		0550
Light Vibrating	OIL-2	Consolidated	Rainbow	40		0553
Light Vibrating	OIL-2	Consolidated	Rainbow	40		0554
Light Vibrating	OIL-2	Consolidated	Rainbow	40		0555
Small Propeller Mixer	OIL-2	Consolidated	Rainbow	40		0591
Water Injection	OIL-2	Consolidated	Rainbow	40		0631
Water Injection	OIL-2	Consolidated	Rainbow	40	Sand Layer	0655
Rod Drop	OIL-2	Consolidated	Rainbow	40		0642
Rod Drop	OIL-2	Consolidated	Rainbow	40	Sand Layer	0654
Small Propeller Mixer	OIL-3	Consolidated	Rainbow	40		0603, 0605
Air Injection	OIL-3	Consolidated	Rainbow	40		0604, 0606
Water Injection	OIL-3	Consolidated	Rainbow	40		0607, 0612
Rod Drop	OIL-3	Consolidated	Rainbow	40		0646, 0651
Air Injection	OIL-4	Consolidated	Rainbow	40		0613, 0608
Water Injection	OIL-4	Consolidated	Rainbow	40		0614, 0611
Rod Drop	OIL-4	Consolidated	Rainbow	40		0647, 0652
Air Injection	OIL-5	Consolidated	Rainbow	40		0617, 0621
Water Injection	OIL-5	Consolidated	Rainbow	40		0616, 0618
Rod Drop	OIL-5	Consolidated	Rainbow	40		0649, 0653
Small Propeller Mixer	OIL-2	Distributed	Rainbow	40		0587, 0588
Air Injection	OIL-2	Distributed	Rainbow	40		0579
Air Injection	OIL-2	Distributed	Rainbow	40		0581
Air Injection	OIL-2	Distributed	Rainbow	40		0584
Water Injection	OIL-2	Distributed	Rainbow	40		0585
Light Vibrating	OIL-2	Distributed	Rainbow	40		0583
Rod Drop with Manual Agitation	OIL-2	Distributed	Rainbow	40	Sand Layer	0685
Water Injection	OIL-1	Consolidated	Metallic	400	Sand Layer	0662
Water Injection	OIL-2	Consolidated	Metallic	400	Sand Layer	0663
Rod Drop with Manual Agitation	OIL-2	Consolidated	Metallic	400	Sand Layer	0684
Water Injection	OIL-3	Consolidated	Metallic	400	Sand Layer	0664
Water Injection	OIL-4	Consolidated	Metallic	400	Sand Layer	0665
Water Injection	OIL-5	Consolidated	Metallic	400	Sand Layer	0666
Rod Drop with Manual Agitation	OIL-2	Distributed	Metallic	400	Sand Layer	0686, 0687

ATTACHMENT: COLUMN TEST PHOTOGRAPH LOGS

CONTROL COLUMNS
Air Injection

Control Column
Tool: Air Injection
Video/Photo No: 0537 (1)

Photo Description: Start of test.

Control Column
Tool: Air Injection
Video/Photo No: 0537 (2)

Photo Description: End of test.

Control Column
Tool: Direct Push
Video/Photo No: 0546 (1)

Photo Description: Start of test.

Control Column
Tool: Direct Push
Video/Photo No: 0546 (2)

Photo Description: End of test.

Small Propeller Mixer

Control Column
Tool: Small Propeller Mixer
Video/Photo No: 0589 (1)

Photo Description: Start of test.

Control Column
Tool: Small Propeller Mixer
Video/Photo No: 0589 (2)

Photo Description: End of test.

Large Propeller Mixer

Control Column
Tool: Rod Drop
Video/Photo No: 0630 (1)

Photo Description: Start of test.

Control Column
Tool: Rod Drop
Video/Photo No: 0630 (2)

Photo Description: End of test.

Rod Drop

Control Column
Tool: Rod Drop
Video/Photo No: 0630 (1)

Photo Description: Start of test.

Control Column
Tool: Rod Drop
Video/Photo No: 0630 (2)

Photo Description: End of test.

Vibrator

Control Column
Tool: Vibrator
Video/Photo No: 0555 (1)

Photo Description: Start of test.

Control Column
Tool: Vibrator
Video/Photo No: 0555 (2)

Photo Description: End of test.

Water Injection

Control Column
Tool: Water Injection
Video/Photo No: 0548 (1)

Photo Description: Start of test.

Control Column
Tool: Water Injection
Video/Photo No: 0548 (2)

Photo Description: End of test.

RAINBOW SHEEN – CONSOLIDATED DEPOSIT
OIL-2 – Air Injection

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0551

Photo Description: Oil deposit.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0540 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0540 (2)

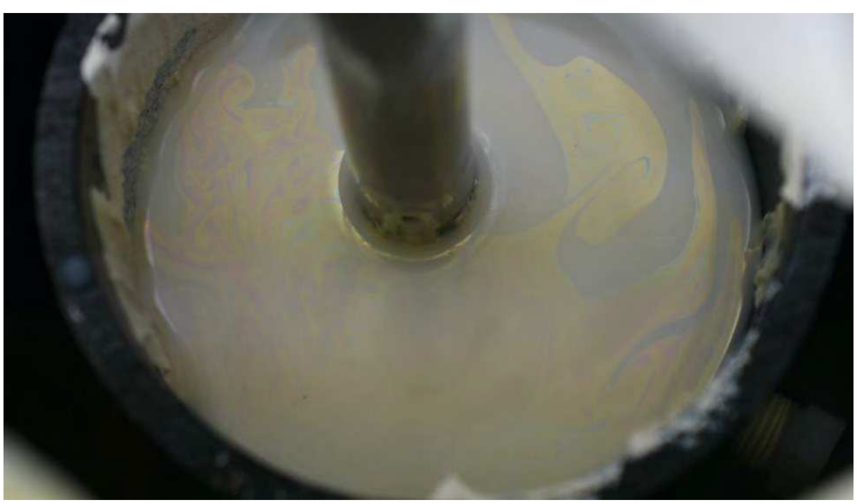
Photo Description: Silver sheen released while tool is ascending.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0540 (3)

Photo Description: Oil released right after air injection port was lifted above the water surface.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0540 (4)

Photo Description: Oil spread to metallic and then rainbow sheen.



Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0540 (5)

Photo Description: More oil released and spread until surface is approximately 80% covered by rainbow sheen.

OIL-2 – Air Injection (continued)

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0540 (6)

Photo Description: End of test.

OIL-2 – Direct Push

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Direct Push
Video/Photo No: 0525 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Direct Push
Video/Photo No: 0525 (2)

Photo Description: End of test. No sheen observed.

OIL-2 – Small Propeller Mixer

<u>Oil</u>: 40 µL OIL-2
<u>Deposit</u>: Consolidated
<u>Tool</u>: Small Propeller Mixer
<u>Video/Photo No</u>: 0591 (1)

<u>Photo Description</u>: Start of test.

<u>Oil</u>: 40 µL OIL-2
<u>Deposit</u>: Consolidated
<u>Tool</u>: Small Propeller Mixer
<u>Video/Photo No</u>: 0591 (2)

<u>Photo Description</u>: End of test. No sheen observed.

OIL-2 – Large Propeller Mixer

Oil: 40 μL OIL-2
Deposit: Consolidated
Tool: Large Propeller Mixer
Video/Photo No: 0535 (1)

Photo Description: Start of test.

Oil: 40 μL OIL-2
Deposit: Consolidated
Tool: Large Propeller Mixer
Video/Photo No: 0535 (2)

Photo Description: Ebullition brings up rainbow sheen.

Oil: 40 μL OIL-2
Deposit: Consolidated
Tool: Large Propeller Mixer
Video/Photo No: 0535 (3)

Photo Description: Rainbow sheen start to spread and swirl around tool rod.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Large Propeller Mixer
Video/Photo No: 0535 (4)

Photo Description: Rainbow sheen start to spread and swirl around tool stem (continued). Majority of surface is covered in silver sheen with a thick band of rainbow.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Large Propeller Mixer
Video/Photo No: 0535 (5)

Photo Description: End of test.

OIL-2 – Rod Drop

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0625

Photo Description: Oil deposit.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (2)

Photo Description: After rod drop, no sheen observed.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (3)

Photo Description: Oil released as rod was removed.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (4)

Photo Description: The oil started spreading immediately upon reaching the surface or remained in a ball.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (5)

Photo Description: Oil spread to rainbow sheen. Oil balls still present.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (6)

Photo Description: More oil balls and sheens were released as rod removal continued.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (7)

Photo Description: Couple of drops of oil captured on tool.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (8)

Photo Description: Oil continued to be released after rod was removed from column.

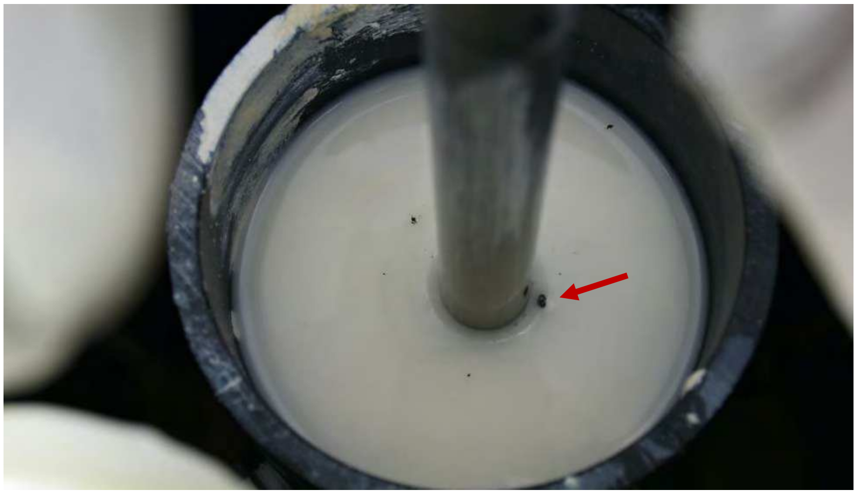
OIL-2 – Rod Drop (continued)

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop – Test 1
Video/Photo No: 0642 (9)

Photo Description: End of test.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Vibrator
Video/Photo No: 0554 (1)

Photo Description: Start of test. Sediment or paint chips fell into column during set up, not oil.



Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Vibrator
Video/Photo No: 0554 (2)

Photo Description: Glob of oil released.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Vibrator
Video/Photo No: 0554 (3)

Photo Description: Glob started spreading upon reaching the surface.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Vibrator
Video/Photo No: 0554 (4)

Photo Description: Oil glob transitioned from a metallic sheen to rainbow sheen.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Vibrator
Video/Photo No: 0554 (5)

Photo Description: Sheen spreads to a thin rainbow on the edge of silver.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Vibrator
Video/Photo No: 0554 (6)

Photo Description: End of test, the black specks are the original dust from before the start of the test.

OIL-2 – Water Injection

Oil: 40 μL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0550 (1)

Photo Description: Start of test.

Oil: 40 μL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0550 (2)

Photo Description: True oil released when tool was at its lowest point.

Oil: 40 μL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0550 (3)

Photo Description: True oil slowly starting to spread to metallic sheens.

OIL-2 – Water Injection (continued)

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0550 (4)

Photo Description: Metallic sheen spreads to rainbow sheen.

Oil: 40 µL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0550 (5)

Photo Description: End of test.

OIL-1 – Air Injection

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0595 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0595 (2)

Photo Description: Drop of silver sheen appeared when tool was almost completely removed (air injection port was over an inch above water surface).

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0595 (3)

Photo Description: End of test.

OIL-1 – Water Injection

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0598

Photo Description: Oil deposit.

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0599 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0599 (2)

Photo Description: End of test. No sheen was observed.

OIL-1 – Rod Drop

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0645

Photo Description: Oil deposit.

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0650 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0650 (2)

Photo Description: First rod drop produced silver sheen on the left and either an ebullition bubble or oil ball that drifts off camera (column wall cuts off water surface) and started to sheen.

OIL-1 – Rod Drop (continued)

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0650 (3)

Photo Description: Silver sheen from (2) is broken up when sediment falls off the drop rod. The oil ball had started spreading and began swirling as the surface was disturbed.

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0650 (4)

Photo Description: Second rod drop broke up original sheen and produced drop of rainbow sheen.

Oil: 40 µL OIL-1
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0650 (5)

Photo Description: End of test.

OIL-3 – Air Injection

Oil: 40 μL OIL-3
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0604

Photo Description: Oil deposit.

Oil: 40 μL OIL-3
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0606 (1)

Photo Description: Start of test.

Oil: 40 μL OIL-3
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0606 (2)

Photo Description: End of test. No sheen was observed.

OIL-3 – Rod Drop

Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0646

Photo Description: Oil deposit.

Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0651 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0651 (2)

Photo Description: After first rod drop, oil bubble appeared.

OIL-3 – Rod Drop (continued)

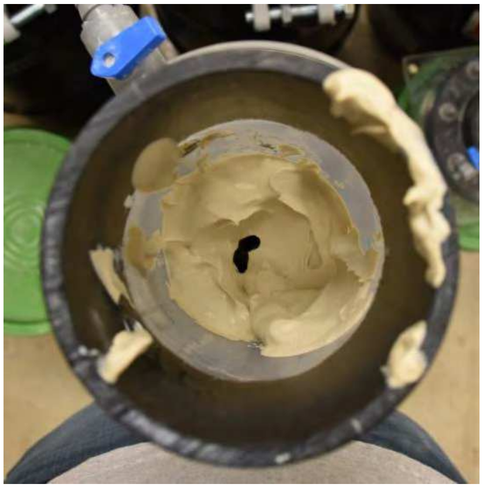
Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0651 (3)

Photo Description: The oil bubble from (2) popped and a silver sheen covered approximately 75% of the water surface.

Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0651 (4)

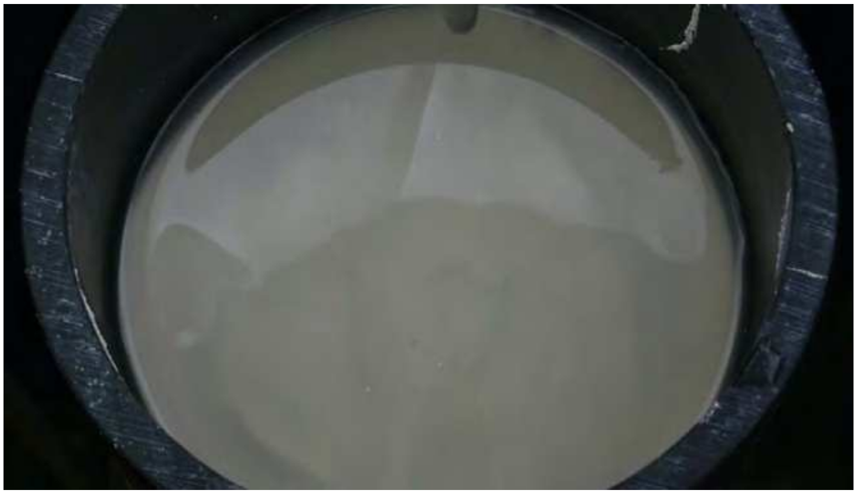
Photo Description: Second rod drop was preformed, breaking up the silver sheen until the sheen was too faint to make out. End of test.

OIL-3 – Water Injection



Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0607

Photo Description: Oil deposit.



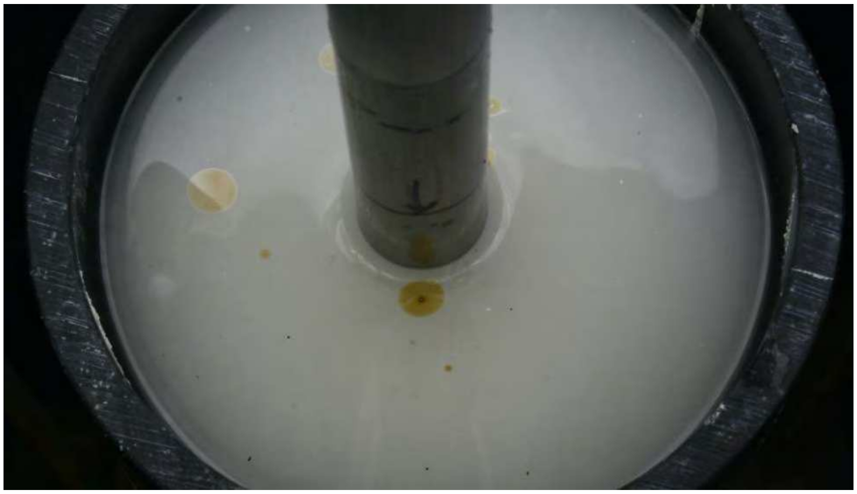
Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0612 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0612 (2)

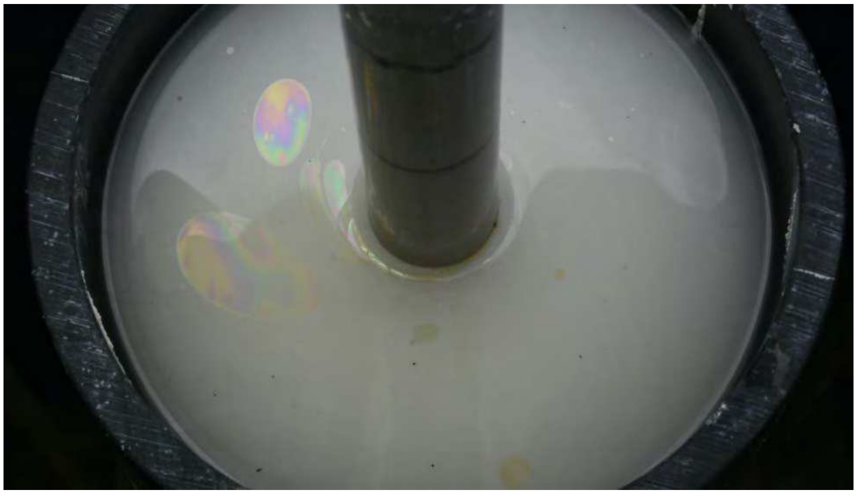
Photo Description: Oil globs brought to surface as tool ascends.

OIL-3 – Water Injection (continued)



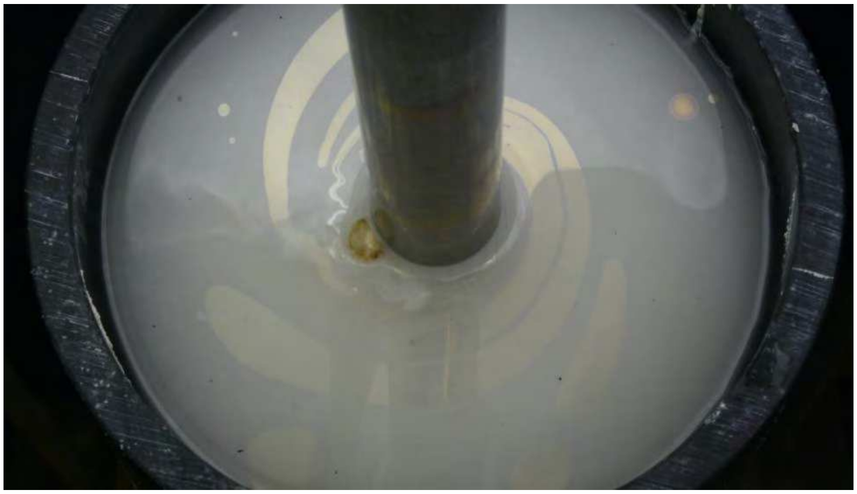
Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0612 (3)

Photo Description: Oil globs started to spread to metallic sheens.



Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0612 (4)

Photo Description: Metallic sheen transitioned to rainbow as the oil spreads further.



Oil: 40 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0612 (5)

Photo Description: The rainbow sheens spread more with the water current. More oil is brought to the surface with ebullition.

OIL-3 – Water Injection (continued)

Oil: 40 μL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0612 (6)

Photo Description: End of test. The sheen was broken up into silver and metallic sheens.

OIL-4 – Air Injection

Oil: 40 µL OIL-4
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0608

Photo Description: Oil deposit.

Oil: 40 µL OIL-4
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0613 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-4
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0613 (2)

Photo Description: End of test. No sheen was observed.

OIL-4 – Rod Drop

Oil: 40 μL OIL-4
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0647

Photo Description: Oil deposit.

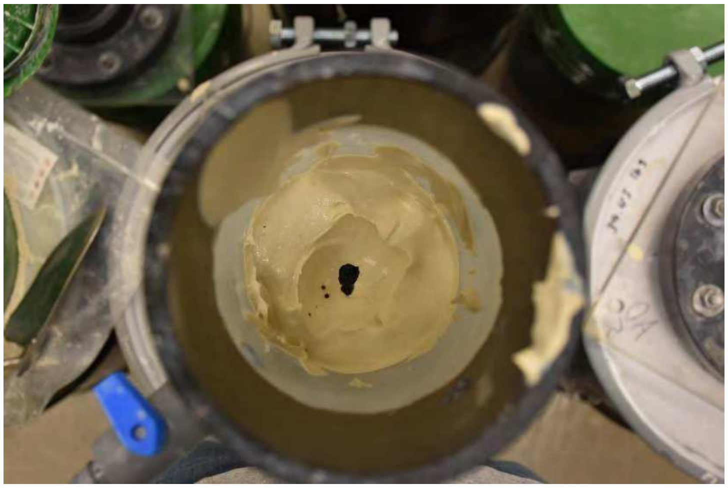
Oil: 40 μL OIL-4
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0652 (1)

Photo Description: Start of test.

Oil: 40 μL OIL-4
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0652 (2)

Photo Description: End of test after two rod drops. No sheen was observed.

OIL-4 – Water Injection



Oil: 40 µL OIL-4
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0611

Photo Description: Oil deposit.

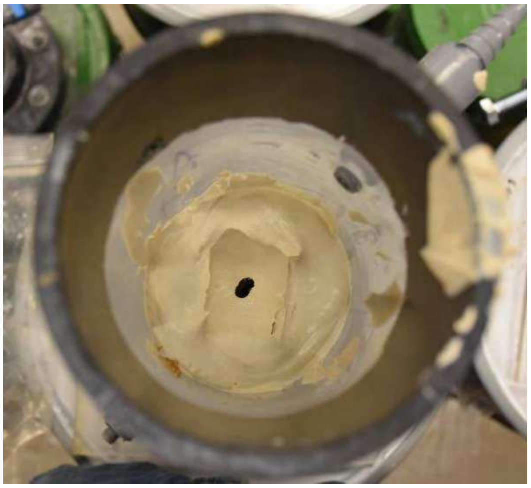
Oil: 40 µL OIL-4
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0614 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-4
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0614 (2)

Photo Description: End of test. No sheen was observed.

OIL-5 – Air Injection



Oil: 40 μL OIL-5
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0617

Photo Description: Oil deposit.

Oil: 40 μL OIL-5
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0621 (1)

Photo Description: Start of test.

Oil: 40 μL OIL-5
Deposit: Consolidated
Tool: Air Injection
Video/Photo No: 0621 (2)

Photo Description: End of test._No sheen was observed.

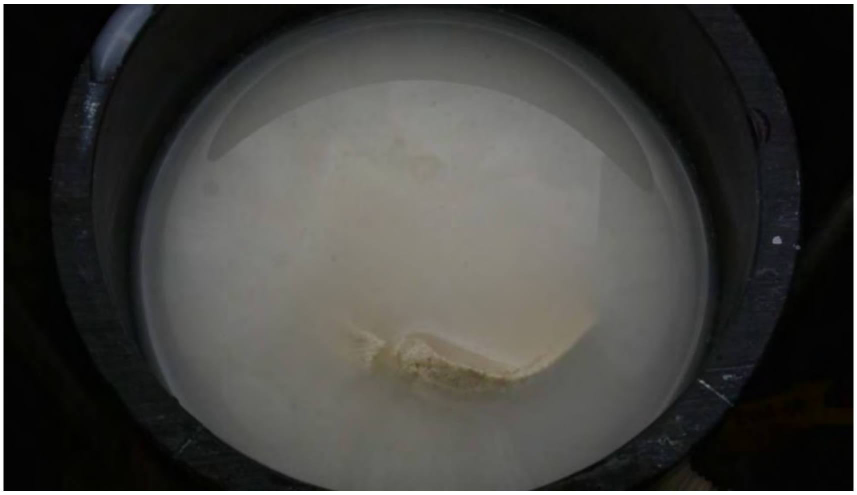
OIL-5 – Rod Drop

Oil: 40 µL OIL-5
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0649

Photo Description: Oil deposit.

Oil: 40 µL OIL-5
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0653 (1)

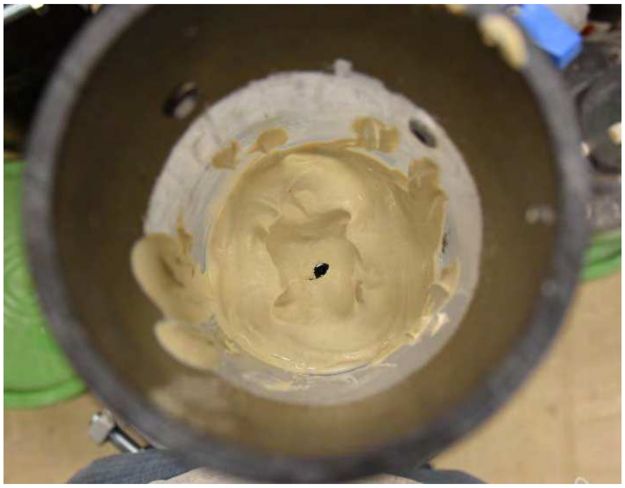
Photo Description: Start of test.



Oil: 40 µL OIL-5
Deposit: Consolidated
Tool: Rod Drop
Video/Photo No: 0653 (2)

Photo Description: End of test after three rod drops. No sheen observed.

OIL-5 – Water Injection



Oil: 40 µL OIL-5
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0616

Photo Description: Oil deposit.

Oil: 40 µL OIL-5
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0618 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-5
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0618 (2)

Photo Description: Drop of rainbow sheen appeared.

OIL-5 – Water Injection (continued)

Oil: 40 μL OIL-5
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0618 (3)

Photo Description: Rainbow sheen from (2) spread into silver sheen.

Oil: 40 μL OIL-5
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0618 (4)

Photo Description: End of test (video cut off before water overflowed).

RAINBOW SHEEN – DISTRIBUTED DEPOSIT
OIL-2 – Air Injection

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Air Injection
Video/Photo No: 0577

Photo Description: Oil deposit.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Air Injection
Video/Photo No: 0581 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Air Injection
Video/Photo No: 0581 (2)

Photo Description: End of test. No sheen was observed.

OIL-2 – Rod Drop with Manual Agitation

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Rod Drop
Video/Photo No: 0685 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Rod Drop
Video/Photo No: 0685 (2)

Photo Description: No sheen observed after two rod drops.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Rod Drop
Video/Photo No: 0685 (3)

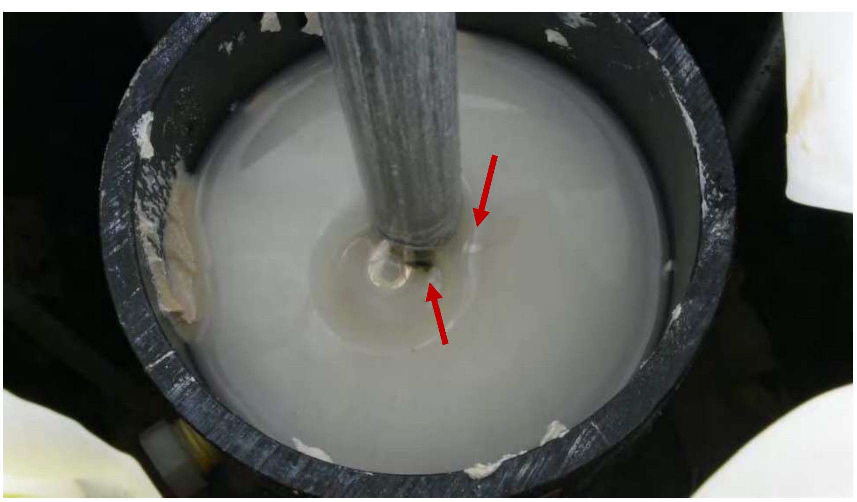
Photo Description: No sheen observed after manual agitation.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (2)

Photo Description: Bubbles released while tool was ascending. Oil appears beneath and slowly moves around bubble.



Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (3)

Photo Description: A drop of true oil appeared beneath the bubble and drop of silver appeared on the water surface.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (4)

Photo Description: The oil from (3) spread across water-air interface inside the bubble.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (5)

Photo Description: The oil from (3) spread across water-air interface inside the bubble (continued).

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (5)

Photo Description: The oil from (3) spread across water-air interface inside the bubble (continued).

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (6)

Photo Description: Once the bubble popped, the sheen began to spread across water surface.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (7)

Photo Description: True oil spread to a metallic sheen.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (8)

Photo Description: Sheen spread from metallic to rainbow sheen.

Oil: 40 μL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (9)

Photo Description: Another drop of true oil was released and started spreading once the oil reached the surface.

Oil: 40 μL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (10)

Photo Description: Another drop of true oil was released and started spreading once the oil reached the surface (continued).

Oil: 40 μL OIL-2
Deposit: Distributed
Tool: Vibrator
Video/Photo No: 0683 (11)

Photo Description: End of test.

OIL-2 – Water Injection

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Water Injection
Video/Photo No: 0578

Photo Description: Oil deposit.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Water Injection
Video/Photo No: 0585 (1)

Photo Description: Start of test.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Water Injection
Video/Photo No: 0585 (2)

Photo Description: True oil released at maximum decent of tool.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Water Injection
Video/Photo No: 0585 (3)

Photo Description: True oil slowly spread to metallic sheen.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Water Injection
Video/Photo No: 0585 (4)

Photo Description: Oil sheen transitioned into rainbow as the sheen swirled around the ascending tool.

Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Water Injection
Video/Photo No: 0585 (5)

Photo Description: Release of new metallic sheen.

OIL-2 – Water Injection (continued)

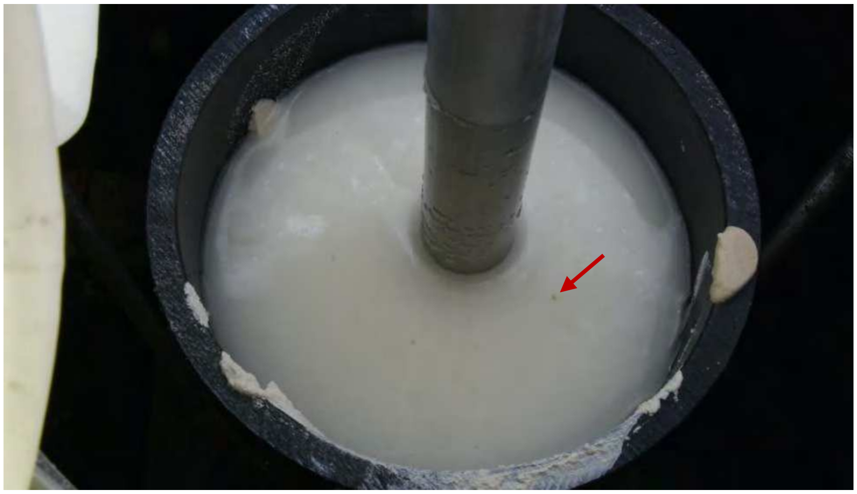
Oil: 40 µL OIL-2
Deposit: Distributed
Tool: Water Injection
Video/Photo No: 0585 (6)

Photo Description: End of test.

METALLIC SHEEN – CONSOLIDATED DEPOSIT
OIL-2 – Water Injection

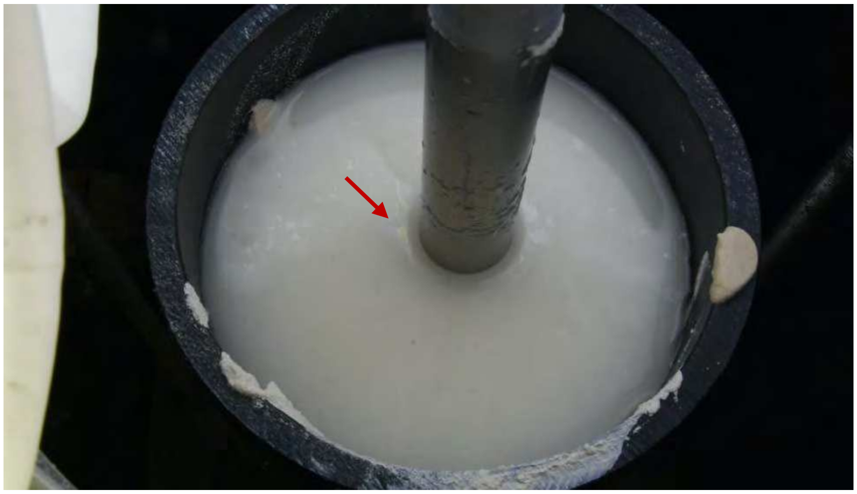
Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0663 (1)

Photo Description: Start of test.



Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0663 (2)

Photo Description: Drop of oil released and immediately started to spread once the oil reached the surface. Oil transitioned from metallic sheen to rainbow as sheen moved around the tool.



Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0663 (3)

Photo Description: Small amount of rainbow sheen observed moving around tool stem.

Oil: 400 μL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0663 (4)

Photo Description: Swirls of silver observed.

Oil: 400 μL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0663 (5)

Photo Description: More swirls of silver observed.

Oil: 400 μL OIL-2
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0663 (6)

Photo Description: End of test.

OIL-2 – Rod Drop with Manual Agitation

Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0658 (1)

Photo Description: Oil deposit.

Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0684 (2)

Photo Description: Start of test.

Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0684 (3)

Photo Description: After two rod drops, no sheen was observed.

Oil: 400 μL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0684 (4)

Photo Description: During manual agitation, a rainbow and silver sheen appeared along with drops true oil (oil did not start spreading even after reaching surface).

Oil: 400 μL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0684 (5)

Photo Description: After the manual agitation (tool allowed to rest in column as surface was observed), more picks of true oil and oil sheens appeared covering approximately 75% the surface in rainbow sheens.

Oil: 400 μL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0684 (6)

Photo Description: A second round of manual agitation releases larger globs of true oil; some of which started to spread into metallic sheens.

Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0684 (7)

Photo Description: After the second round of manual agitation (column allowed to rest), more true oil was released.

Oil: 400 µL OIL-2
Deposit: Consolidated
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0684 (8)

Photo Description: After the second round of manual agitation more oil was released and started to spread. End of test.

OIL-1 – Water Injection

Oil: 400 µL OIL-1
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0662 (1)

Photo Description: Start of test.

Oil: 400 µL OIL-1
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0662 (2)

Photo Description: End of test. No sheen was observed.

OIL-3 – Water Injection

Oil: 400 μL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0664 (1)

Photo Description: Start of test.

Oil: 400 μL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0664 (2)

Photo Description: Specks of silver and rainbow sheens or reflective sediment appeared as tool was removed. Very small amount of either miniscule spots of true oil or oil-particle aggregate also appeared.

Oil: 400 μL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0664 (3)

Photo Description: True oil appeared and began spreading.

OIL-3 – Water Injection (continued)

Oil: 400 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0664 (4)

Photo Description: True oil appeared and began spreading (continued).

Oil: 400 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0664 (5)

Photo Description: More true oil appeared and began spreading. Original true oil spread into metallic and rainbow sheens.

Oil: 400 µL OIL-3
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0664 (6)

Photo Description: More true oil appeared. End of test.

OIL-4 – Water Injection

Oil: 400 µL OIL-4
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0665 (1)

Photo Description: Start of test.

Oil: 400 µL OIL-4
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0665 (2)

Photo Description: Drops of silver sheen appeared upon removal of tool.

Oil: 400 µL OIL-4
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0665 (3)

Photo Description: End of test.

OIL-5 – Water Injection

Oil: 400 µL OIL-5
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0666 (1)

Photo Description: Start of test.

Oil: 400 µL OIL-5
Deposit: Consolidated
Tool: Water Injection
Video/Photo No: 0666 (2)

Photo Description: End of test. Ran out of water during tool removal, therefore water injection did not occur during the whole duration of test. No sheen observed.

METALLIC SHEEN – DISTRIBUTED DEPOSIT
OIL-2 – Rod Drop with Manual Agitation

Oil: 400 µL OIL-2
Deposit: Distributed
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0687

Photo Description: Oil deposit.

Oil: 400 µL OIL-2
Deposit: Distributed
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0688 (1)

Photo Description: Start of test. Reflective sediment on the surface.

Oil: 400 µL OIL-2
Deposit: Distributed
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0688 (2)

Photo Description: No sheen observed after two rod drops.

OIL-2 – Rod Drop with Manual Agitation (continued)

Oil: 400 µL OIL-2
Deposit: Distributed
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0688 (3)

Photo Description: Multiple drops and swirls of silver appeared after manual agitation.

Oil: 400 µL OIL-2
Deposit: Distributed
Tool: Rod Drop with Manual Agitation
Video/Photo No: 0688 (4)

Photo Description: Multiple rainbow sheen drops appeared after another round of manual agitation.