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Update on Developing and Commercializing Oil Herders for In-Situ Burning

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ABSTRACT 300009:

Since the 2011 Conference (Buist *et al*. 2011 and Buist and Nedwed 2011), work on advancing oil herding agents for in-situ burning (ISB) has focused on three areas:

1. Obtaining regulatory approvals for their use in North America;
2. Developing an application system for use in a helicopter; and,
3. Researching the effectiveness of herders for rapid-response ISB in open water.

Desmi-AFTI worked in conjunction with S.L. Ross Environmental Research to get approval to use herders in North American waters. The proscribed test data from an accredited laboratory in Louisiana on three candidate herding agents (also called surface collecting agents) was submitted to the U.S. EPA for approval to list them on the National Contingency Plan (NCP) Product Schedule. Two herders have been placed on the list and are now commercially available. These two can be used, with the FOSC's concurrence, for spill response operations in U.S. waters. Samples of all three herders have been sent to Environment Canada, along with all the EPA test data, for their consideration. Quantities (200 L) of the two herders listed on the NCP Product Schedule have been produced and are stockpiled at Desmi-AFTI in Buffalo, NY.

An application system, consisting of a pump, controls and reservoir has been designed to be placed inside an appropriate helicopter. It incorporates a reel-able hose that is used to lower the application nozzle to the correct height above the water for herder application. Dry land, static trials were conducted in September 2013 and helicopter flight trials are planned for summer and fall 2014. A back-pack sprayer system for herder application from a small vessel is available off-the-shelf, with only minor modifications required for cold-temperature use.

The US Department of the Interior's Bureau of Safety and Environmental Enforcement sponsored a series of laboratory and Ohmsett experiments to see whether herders could contract oil slicks in wave conditions in open water. The results showed that the monolayer of each of the two best herders will survive for more than 45 minutes in a calm sea. The presence of breaking or cresting waves rapidly disrupts the herder monolayer and the oil slick resulting in the production of many small slicklets from the herded slick and the re-spreading of the oil to thin

slicks. The monolayer survives for considerable periods of time in a swell condition, but the constant stretching and contracting of the herded slick results in elongating the oil slick and slowly breaking the slick into smaller segments.

Testing of the helicopter application system with a herding agent on a 10 m^3 experimental crude oil release in drift ice is planned for spring 2015. Further laboratory study of the approved herders is also planned with the goals of better understanding their toxicity and biodegradation and the window of opportunity for their effective use on weathered, emulsified and waxy oils.

INTRODUCTION:

The key to effective *in situ* burning is thick oil slicks. Concentrated pack ice can enable *in situ* burning by keeping slicks thick. In loose drift ice conditions oil spills can rapidly spread to become too thin to ignite. Fire-resistant booms can collect and keep slicks thick in open water; however, field deployment tests of booms and skimmers in pack ice conditions in the Alaskan Beaufort Sea in 2000 (Bronson *et al.*, 2002) and fire boom testing in the Barents Sea in 2009 (Potter and Buist, 2010) highlight the limitations of booms in even very open drift ice. Research over the last 10 years has indicated that chemical herding agents can thicken free-drifting, fluid oil slicks enough that they can be ignited and burned successfully in drift ice conditions (SL Ross, 2007, Buist *et al.*, 2010a). This paper describes recent research and development projects to:

- Obtain regulatory approvals for the use of herders;
- Develop the technology to apply herders from helicopters; and,
- Determine if herders could be a rapid-response tool for oil spills in calmer open water conditions.

BACKGROUND:

The use of specific surface-active chemicals (surfactants), sometimes called oil herders or oil collecting agents, to clear and contain oil slicks on the surface of water is well known. Two commercial products were developed and tested in the 1970's and 80's: Shell Herder and Corexit OC-5 Oil Collector, and both were listed on the U.S. National Oil and Hazardous Substances Pollution Contingency Plan (NCP) Product Schedule at the time. These agents have the ability to spread rapidly over a water surface into a monomolecular layer as a result of their high spreading coefficients, or spreading pressures. Herders sprayed onto water surrounding an oil slick result in formation of a monolayer of surfactants on the water surface. These surfactants reduce the surface tension of the surrounding water considerably (from about 70 mN/m to 20-30 mN/m). When the surfactant monolayer reaches the edge of a thin oil slick it changes the balance of interfacial forces acting on the slick edge and allows the interfacial tensions to contract the oil into thicker layers. Herders do not require a boundary to "push against" and work even in unbounded open water. A conceptual drawing of the herding process in pack ice is shown in Figure 1. Although commercialized in the 1970s herders were not used offshore because they only worked in very calm conditions: physical containment booms were still needed to hold or divert slicks in wind speeds above 2 m/s (4 knots), and breaking waves quickly disrupted the herder layer. For application in loose pack ice, the intention is to herd freely-drifting, fluid oil slicks among the ice floes to a burnable thickness, then ignite them. The herders will work in conjunction with the wave dampening and partial containment provided by the ice to allow an extended window of opportunity for burning.

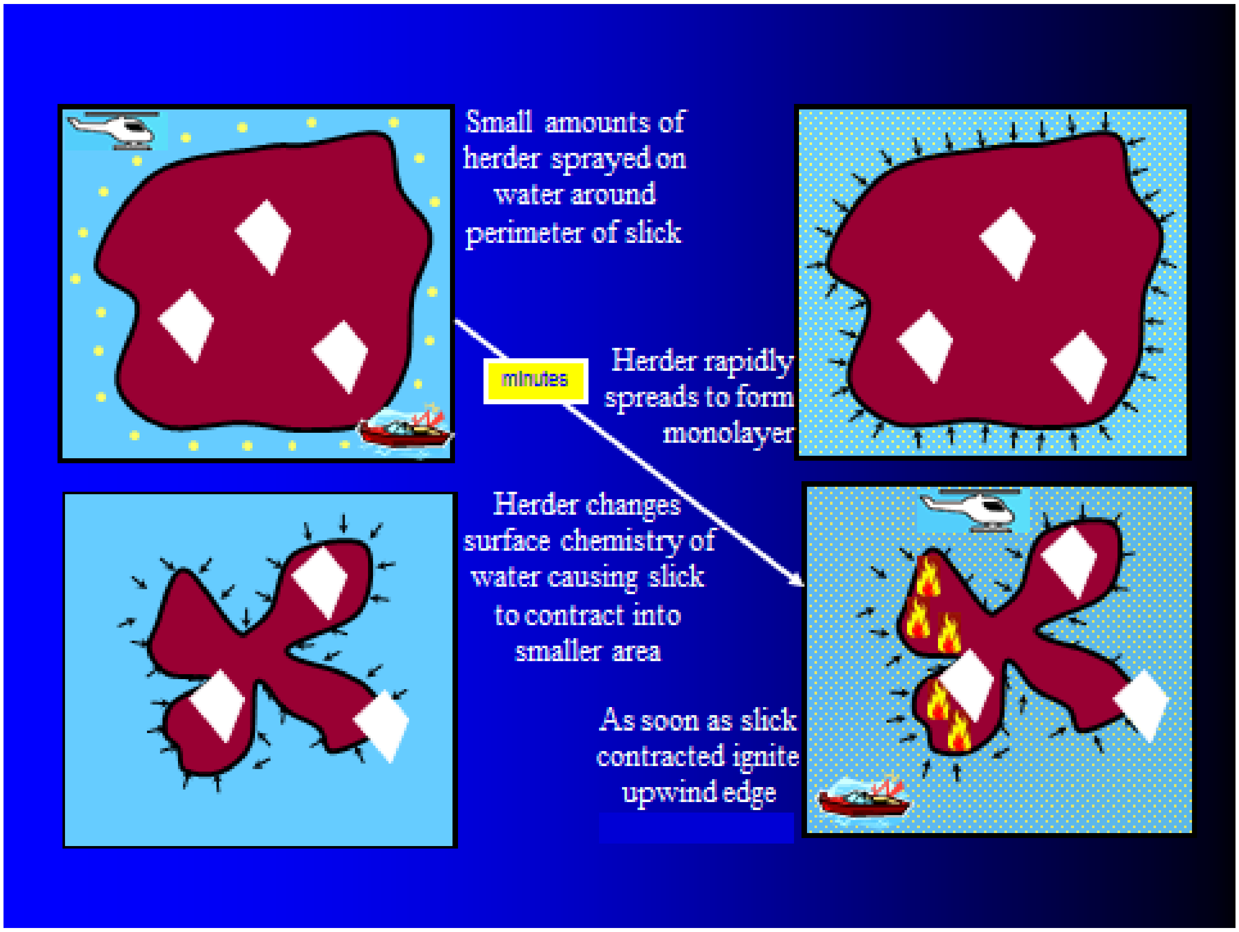

Figure 1. Concept for use of herders to contract oil slicks in drift ice for ignition and burning

A research program began in 2003 to advance oil spill response in ice found that herding agents persisted long enough to enable in-situ burning of relatively fresh, fluid oils in broken or drift ice. This multi-year, multi-partner program (Buist *et al.* 2011) involved:

- A very small scale (1 m^2) preliminary assessment of a shoreline-cleaning agent with oil herding properties was conducted in 2003 to assess its ability to herd oil different oils on cold water and among ice (SL Ross 2004).
- Additional small-scale (1 m^2) experiments were carried out next in 2005 to explore the relative effectiveness of three hydrocarbon-based herding agents in simulated ice conditions; followed by larger scale (10 m^2) quiescent pan experiments to explore scaling effects; small-scale (2 to 6 m^2) wind/wave tank tests to investigate wind and wave effects on herding efficiency; and finally, small ignition and burn tests in a wave tank (SL Ross 2005). These tests identified ThickSlick 6535 as an effective herding agent on cold water and in ice conditions.
- Experiments were done next with the ThickSlick 6535 herder at the scale of 100 m^2 in the indoor Ice Engineering Research Facility Test Basin at the US Army Cold Regions

Research and Engineering Laboratory (CRREL) in November 2005; at the scale of 1000 m^2 at Ohmsett in artificial pack ice in February 2006; and finally, a series of 20 burn experiments (Figure 2) were carried out in 2006 with the ThickSlick 6535 herder at the scale of 30 m^2 in a specially prepared test basin containing broken sea ice in November 2006 at the Fire Training Grounds in Prudhoe Bay, AK with fresh crude oil (SL Ross 2007).

- Field tests in pack ice in the Barents Sea were performed in 2008. One experiment involved the release of 630 L of fresh Heidrun crude in a large lead. The free-drifting oil was allowed to spread for 15 minutes until it was far too thin to ignite (0.4 mm), and then ThickSlick 6535 herder was applied around the slick periphery. The slick contracted and

Figure 2. Burn test with ThickSlick 6535 at Prudhoe Bay, AK in 2006

thickened for approximately 10 minutes at which time the upwind end was ignited using a gelled gasoline igniter. A 9-minute long burn ensued (Figure 3) that consumed an estimated 90% of the oil (Buist *et al.*2010a).

- Studies on better herding surfactants were completed between 2008 and 2010 (Figure 4). It was during this testing that the OP-40 silicone-based herder was identified as being more effective than the ThickSlick 6535 at herding (Buist *et al.* 2010b).

- Work on developing techniques for applying herding agents to slicks in ice-affected water commenced in 2010 (Buist and Belore 2011).

Figure 3. Burn of herded slick in Barents Sea ice lead (near start on left, near end on right)

Figure 4. Testing of silicone-based herding agents at CRREL (far left shows oil release, centre shows oil spread at equilibrium, right shows contraction to new equilibrium after herder addition to water).

REGULATORY APPROVALS:

In the fall of 2011 work began on getting experimental herders listed in the U.S. EPA's National Contingency Plan (NCP) Product Schedule so that they could be used during spill response operations in U.S. waters. This process involved submitting samples to a certified laboratory for proscribed testing and the submission of the data required for listing (U.S. CFR 300.915 Subpart J).The proscribed testing includes a *Test to Distinguish Between Surface Collecting Agents and Other Chemical Agents*. For a herder to be listed as a Surface Collecting

Agent, at least 75% of 5 mL of the candidate herder must resurface after being rotated in a graduated cylinder with 95 mL of distilled water and then allowed to settle for one hour.

A 4-L sample of the ThickSlick 6535 and a 4-L sample of the silicone herder Siltech OP-60, were sent to an accredited laboratory in Louisiana and subjected to the required tests, plus some additional cold-weather rheology measurements.

The ThickSlick 6535 passed the *Test to Distinguish Between Surface Collecting Agents and Other Chemical Agents*; however, the Siltech OP-60 did not, forming a cloudy suspension/solution that did not separate in the specified hour of settling. A second silicone surfactant (OP-40) was then chosen as a substitute for Siltech OP-60 (it passed the *Test to Distinguish between Surface Collecting Agents and Other Chemical Agents* in the manufacturer's laboratory and has been lab-tested previously and shown to be a good herder - SL Ross, 2008).

Table 1 presents the laboratory test results for the ThickSlick 6535, Siltech OP-60 and OP-40. The ThickSlick 6535 had a significantly lower toxicity than both the Siltech OP-60 and OP-40. The ThickSlick 6535 had a much lower toxicity than No. 2 fuel oil (i.e., had a much higher LC50); however, the 1:10 mix of the ThickSlick 6535 and the No. 2 fuel oil was more toxic than the No. 2 fuel oil by itself. The 1:10 mixtures of Siltech OP-60 and OP-40 exhibited the same trend. These herders are not intended to be applied onto the oil; rather, they are intended to be applied to the water around the perimeter of the oil and shouldn't mix with the oil. Even if herders were accidentally sprayed onto a slick, the dosage would be considerably less than 1:10 (the recommended application rate for herders is 150 mg/m^2, more than 30 times less than the design application rate for dispersants that the toxicity test was originally designed for).

Table 1. Summary of EPA NCP Listing Required Test Results

TEST		**ThickSlick 6535**	**Siltech OP-60**	**Siltech OP-40**
	Units	**Results**	**Results**	**Results**
NCP Category		Surface Collecting Agent		Surface Collecting Agent
Toxicity				
Product				
M. bahia 48-hr LC50	ppm	286	4.76	6.83
M beryllina 96-hr LC50	ppm	138	15.9	3.33
No.2 Fuel Oil				
M. bahia 48-hr LC50	ppm	2.43	2.43	6.43
M beryllina 96-hr LC50	ppm	37.6	37.6	40.5
10:1 No.2 Fuel Oil / Product				
M. bahia 48-hr LC50	ppm	1.53	4.38	3.27
M beryllina 96-hr LC50	ppm	5.91	10	9.7

Reference Toxicant- Sodium Dodecyl Sulfate				
M. bahia 48-hr LC50	ppm	8.23	8.23	8.68
M beryllina 96-hr LC50	ppm	3.02	3.02	2.33
Analytical				
Key Findings Summary				
Flash Point		>180 °F (82°C)	>180 °F (82°C)	>180 °F (82°C)
Pour Point		21.2 °F (-1.7°C)	37.4 °F (3°C)	-74.2 °F (-59°C)
Viscosity	cSt	24.7	38.55	8.27
Viscosity @100°F	SUS	118	184	53
Specific Gravity@60°F		0.974	1.056	0.988
Surface Collecting Agent Test		PASS	FAIL	PASS
Phase Separation		None	None	None
Freezes at		11.2°F (-24°C)	12.2°F (-11°C)	-95.8°F(-71°C)
Solubility		Partial Miscibility	Total Miscibility	Partial Miscibility
pH		6.45	7.5	10.1

The analytical results for the two herders that passed the *Test to Distinguish Between Surface Collecting Agents and Other Chemical Agents* (ThickSlick 6535 and OP-40) show that both will float on water and are relatively low viscosity fluids at room temperature. When cooled, the ThickSlick 6535 will congeal at -2°C and freeze at -24°C: the OP-40 will congeal at -59°C and freeze at -71°C. Neither undergoes any phase separation during cooling. Both ThickSlick 6535 and OP-40 are partially miscible in water. Both of their flash points exceed 180°F (82°C).

HERDER APPLICATION SYSTEM DEVELOPMENT:

The usage being considered for herders is the thickening of relatively small individual slicks of oil (on the order of 10’s to 100’s of meters in size) in an Arctic environment in the presence of drift ice where wave conditions are relatively calm. To be effective the herders need to be applied at about 15 liters per kilometer of slick perimeter (SL Ross, 2007). An important characteristic of delivery systems will be good droplet size control in order to limit the production of fines that might drift onto the slick. The herder should be applied onto the water surface around a targeted slick, as contamination of the slick with herder will reduce its ability to contract into a thicker patch for efficient burning.

To meet these basic requirements, two primary modes of application are considered feasible. The herder could be applied from a small boat that travels slowly around the perimeter of the oil slick at a speed that does not mix the herder into the water or, it could be applied from a helicopter at a speed and altitude that minimizes rotor downwash influences on the herder spray and nearby slick. For the purpose of application system design it was assumed that small boat application would be completed at a speed of 2 to 5 knots (i.e., no wake).

When applying dispersant from a bucket slung under a helicopter the recommended altitude is 10 to 15 m and the recommended speed is 25 to 50 knots directly into the wind, in order to minimize effects of the rotor wash on the droplets of dispersant (Fiocco and Lewis, 1999). When applying herder, the helicopter would fly at a forward speed of approximately 10 to 20 knots, slower than when applying dispersant, because of the need to maneuver around individual slicks. The altitude of the helicopter while applying herder would likely be higher than while applying dispersant in order to reduce the rotor wash effect on the water surface. Field tests will be required to confirm these assumptions.

To achieve minimal over-spray and negligible penetration of product into the water column the herder will have to be applied with a large enough drop size to curtail crosswind drift and small enough drop size to limit penetration into the water column. Experience with chemical dispersant application systems has shown that spray drops smaller than about 0.3 mm tend to drift significantly and drops in excess of 1 mm tend to penetrate through oil slicks into the water below.

In dispersant application a wide spray-swath is desired whereas with herders, a narrow spray width is preferred. Dispersants are also usually applied at higher aircraft or boat speeds than those assumed for the herder application. The slower speeds envisioned for herder application by helicopter and the different air flow patterns from a helicopter platform versus a fixed-wing aircraft should result in less herder atomization due to wind shear and a tighter drop distribution from a nozzle positioned beneath the helicopter.

A “straight stream” type of nozzle is well suited to this purpose. At the low speeds proposed for application from a small surface boat the flow from a straight stream nozzle should not atomize into small droplets and will result in a very narrow spray band striking the water with negligible herder drift.

The required application flow rates for the range of application speeds that would likely be used for the boat and helicopter application modes are summarized in Table 2. The SSC 0002 nozzle appears to be a reasonable choice based on flow rate and likely drop size characteristics. Multiple nozzles (five to ten) would be required for the helicopter spray system but a single nozzle would be adequate for the boat application system at 2 knots.

Table 2. Application Speeds and Nozzle Requirements versus Spray Speed

Spray Speed [knots] (m/s)	Required Flow [gpm] (L/s)	# of 0002[a] nozzles @60 psi
Boat Application		
[2] (1.0)	[0.24] (0.015)	1.0
[5] (2.6)	[0.61] (0.039)	2.5
Helicopter Application		
[10] (5.1)	[1.2] (0.077)	4.9
[20] (10.2)	[2.4] (0.154)	9.8

[a]The first two digits of the nozzle identifier refer to the fan angle (00 or 0° in this case). The remaining digits refer to the flow rate of the nozzle in tenths of gpm when operated with water at 40 psi (0002 refers to 0.2 gpm of water at 40 psi).

Experiments conducted at the SL Ross lab, simulating spraying from a helicopter and a small boat confirmed that the SSC 0002 straight stream nozzle was suitable for herder application (Buist and Belore, 2011). A commercial backpack sprayer (Figure 5) was deemed to be appropriate for small boat application in temperate conditions: heating and insulation of the backpack sprayer will be required for Arctic use.

Herder Application System Initial Testing

The DESMI AFTI herder application system (Figure 6) has been designed to transport and apply either OP-40 or ThickSlick 6535 from the open rear door of a commercial helicopter. The storage tank is insulated and carries up to 20 gallons (75 L) of herder. Its features include:

- 28 V electrical system using aircraft quality components

Figure 5. Commercial backpack sprayer recommended for small-boat application system.

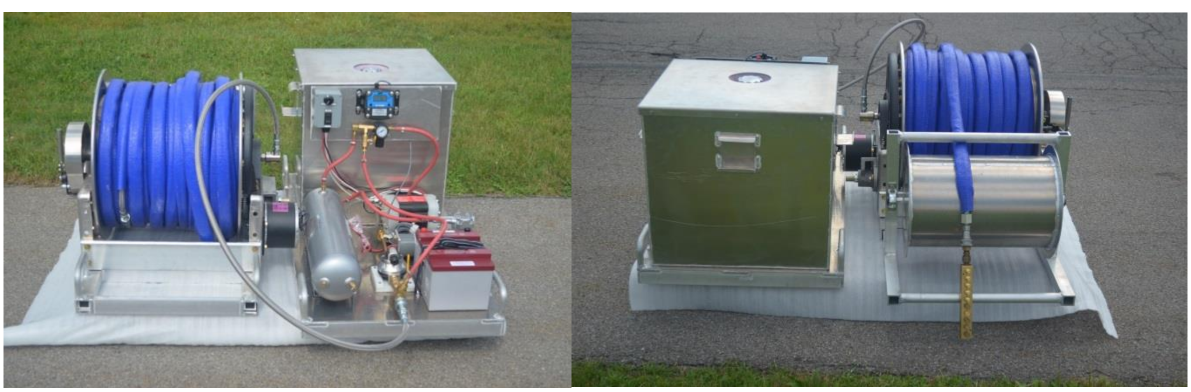

Figure 6. Mark I Helicopter Herder Application system

- Two modules which are easily handled by two or 3 persons
- Aluminum frames with the reel module having an extendible reel
- 100 feet (30 m) of insulated Stratoflex stainless steel hose with Teflon liner

- Powered reel
- Air powered pump and air compressor for purging of lines
- Self-contained 28 V battery plus 28 V accessory cord for attachment to aircraft power
- Complete electrical circuit protection with integral circuit breakers.
- Multiple nozzles (up to seven) to adjust flow rate

The first series of tests involved deploying the full length of the 100-foot hose on the ground, operating the pump with water and measuring the flowrates through the nozzles. Figure 7 shows the nozzle body with seven SSC 0002 nozzles spraying water. Proper operation of the air purge system, storage reel and other components was also confirmed.

Figure 7. Applicator spray nozzle configuration.

The second series of tests involved lifting the Mark I Helicopter Herder Application system and an operator to a height of 46 feet using a person lift (Figure 8). These tests involve operating the pump with tap water and recording the spray pattern generated by the nozzles. The winds at this time had increased to 21 mph (34 km/h), gusting to 29 mph (47 km/h), which is the upper limit for safe operation of the person lift. The third series of tests involved a short test from a 15-foot height (due to the gusty winds) of the application system spraying a surrogate fluid. Canola oil (with a viscosity of ≈ 70 mPas at 20°C) was determined to be a good substitute for the OP 40 herder at colder temperatures. This test involved operating the pump with the surrogate fluid drawn directly from a small drum and recording the spray pattern generated by the nozzles on Kromecoat cards. In order to minimize the spray of Canola onto the surrounding area, all but one of the nozzles was wrapped in a garbage bag placed in a bucket suspended from the nozzle body. The flow from the one uncovered nozzle was directed into an inflatable plastic swimming pool.

Figure 8. Applicator raised 46 feet above ground

As can be seen from Figure 9, the flow from the one nozzle (on the order of 0.4 L/min, or 0.12 gpm) began to break up into droplets within a foot or two of the nozzle. Comparison of Kromecoat cards passed through the Canola spray and from laboratory tests in 2010 spraying ThickSlick 6535 in a 20-knot crosswind revealed roughly similar drop sizes.

Figure 9. Flow of Canola oil from single nozzle.

HERDERS FOR RAPID RESPONSE ISB IN OPEN WATER:

In 2011 a research program was started to explore the use of herding agents for in situ burning in open water conditions as a rapid-response technique for oil spills offshore. The research was conducted in two parts: the first involved laboratory testing to identify the best herding agent(s) for warmer water conditions; the second involved experiments at Ohmsett to quantify the persistence of the herder monolayer in waves (Buist and Meyer, 2012).

Warmer Water Laboratory Testing

A series of comparative experiments was undertaken at the SL Ross lab with five different hydrocarbon-based and silicone-based herding agents in 1-m^2 pans, a 10-m^2 pan, small pans mounted on a rocking shaker and the SL Ross wind/wave tank to determine the best of several candidate herders for use on warmer water. Overhead digital photographs were taken and analyzed by computer to determine the herder effectiveness in the pan tests. The wind/wave tank tests were videotaped. The following conclusions were reached (SL Ross 2012):

- In the laboratory herding tests the Siltech OP-60, Silsurf A004-D and ThickSlick 6535 herders performed best.
- The two silicone-based herders retained a small burning crude oil slick and achieved burn efficiencies as good as or better than the USN herder.

Ohmsett Testing in Waves

Surfactant film persistence (i.e., how long the monolayer generated by a specific herding agent will last as a function of sea state) and to what degree periodically replenishing the film can counteract this was investigated in an 8-day test program at Ohmsett. The experiments took advantage of the facility's newly upgraded wave making capabilities. Overhead digital video and photographs were taken to qualitatively compare and determine the persistence of three herding agents in calm conditions, a swell and breaking waves.

A total of 11 experiments were completed with three herding agents (ThickSlick 6535, Siltech OP-60 and Silsurf A004-D). All the tests were conducted with fresh Endicott crude oil. Table 3 gives the matrix for the tests. The control tests were scheduled last to maximize the available weather window for the experiments. Figure 10 shows typical swell waves and Figure 11 shows typical breaking waves.

Table 3. Matrix of Tests at Ohmsett.

Test Number	Wave Condition	Herder
1	Calm	ThickSlick 6535
2	Calm	Siltech OP-60
3	Calm	A004-D
4	Breaking	ThickSlick 6535
5	Breaking	Siltech OP-60
6	Breaking	A004-D
7	Swell	ThickSlick 6535
8	Swell	Siltech OP-60
9	Swell	A004-D
10 (Dup 8)	Swell	Siltech OP-60
11	Swell, then Breaking	None


Figure 10. Typical herded slick in swell conditions.

Figure 11. Typical breaking wave conditions during a herder test.

Based on visual observations and review of test video the following observations were made:

- The monolayer of each of the two best herders will survive for more than 45 minutes in a calm sea (the Ohmsett tests were terminated when the slicks reached the end of the tank).
- The presence of breaking or cresting waves rapidly disrupts the herder monolayer and the oil slick resulting in the production of many small slicklets from the herded slick and the re-spreading of the oil to thin slicks. The implications of this for using herders in open water conditions offshore will depend strongly on the frequency and coverage of breaking waves at the time; the ability of the oil slick and/or herder to suppress wave breaking; and, the ability to rapidly herd and ignite a slick with helicopters. Further work will be necessary to understand these factors.
- The monolayer survives for considerable periods of time in a swell condition, but the constant stretching and contracting of the herded slick results in elongating the oil slick and slowly breaking the slick into smaller segments.
- The Siltech OP-60 herder performed noticeably better than the other two herders in all test conditions.

NEXT STEPS

Field tests of the helicopter application system with a herding agent on a 10 m^3 experimental crude oil release in drift ice is planned for spring 2015. Further laboratory study of the approved herders is also planned with the goals of better understanding their toxicity and biodegradation and the window of opportunity for their effective use on weathered, emulsified and waxy oils.

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