

Standard Guide for Use of Herding Agents in Conjunction with In-Situ Burning¹

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1. Scope

1.1 This guide relates to the use of herding agents in conjunction with in-situ burning of spilled oil.

1.1.1 Although the focus is on the use of herders in conjunction with in-situ burning, herders may also be used to aid in mechanical recovery of spilled oil.

1.2 The purpose of this guide is to provide information that will enable oil-spill responders to select the appropriate techniques and devices to successfully collect and ignite oil spilled on water.

1.3 The focus of this guide is on the in-situ combustion of marine oil spills in drift ice conditions. The use of herding agents on calmer ice-free water is also possible.

1.4 This guide is one of several related to in-situ burning. Other standards cover specifications for fire-containment booms and the environmental and operational considerations for burning.

1.5 The storage, transport, and use of herding agents may be subject to regulations that will vary according to the jurisdiction. While guidance of a general nature is provided in this document, users of this guide should determine regulations that apply to their situation.

1.6 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.

1.7 This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

2. Referenced Documents

2.1 ASTM Standards:²

D971 Test Method for Interfacial Tension of Oil Against Water by the Ring Method

F631 Guide for Collecting Skimmer Performance Data in Controlled Environments

3. Terminology

3.1 *herding agent* (also known as *surface collection agent*)—chemical product that can be applied to the water surface surrounding an oil slick to concentrate the slick and thicken it to enhance countermeasures such as in-situ burning or recovery.

3.2 *ice concentrations*—ice cover expressed as tenths, that is, $\frac{5}{10}$ ths is equivalent to 50 % ice coverage by area.

4. Significance and Use

4.1 This guide describes the use of herding agents for the purpose of in-situ burning. It is intended to aid decision-makers and spill-responders in contingency planning, spill response, and training, and to aid manufacturers in developing effective herding agents.

4.2 This guide is not intended as a detailed operational manual for the use of herding agents or the burning of spilled oil.

5. Overview of the Use of Herding Agents for Burning Spilled Oil on Water

5.1 The main requirement for the effective use of in-situ burning of a marine oil spill is an adequate slick thickness to support combustion. Slicks of greater than 1 mm are required to allow ignition and sustain combustion. Thicknesses of 2 to 3 mm or greater will ensure effective in-situ burning.

5.2 For spills that are not naturally contained against a shoreline, ice edge, or amongst ice pieces, artificial containment will be required to achieve burnable slick thicknesses.

5.3 Collection and containment using fire-resistant boom is possible in open water and drift ice concentration up to 3 to $\frac{5}{10}$

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

ths, but is slower than in open water. In drift ice concentrations of 7_{10} ths and greater, natural containment may be adequate for in situ burning. Herding agents (also known as herders) may be useful when ice concentrations do not allow the use of booms and when natural containment is not afforded. Herding agents can be used to contain and concentrate oil for the purpose of in-situ burning.

5.4 Herding agents sprayed onto the water surrounding an oil slick result in the formation of a monomolecular layer of surfactants on the water surface (Fig. 1). These surfactants reduce the surface tension of the surrounding water significantly. When the surfactant reaches the edge of a thin oil slick it changes the balance of interfacial forces acting on the slick edge and causes the oil/water and oil/air interfacial tensions to contract the oil into thicker layers.

5.5 Herding agents were initially developed in the 1970s as a method of thickening oil slicks on open water prior to mechanical recovery. Unfortunately, it was discovered during field tests that herded slicks resumed spreading within tens of minutes in all but relatively calm seas and cannot resist winds in excess of 2 m/s (4 knots). Herders have limited effectiveness in breaking waves which rapidly disrupt the herder layer. Recent research has re-examined the use of herding agents in the context of in-situ burning in drift ice conditions, where breaking waves are generally less of an issue and the ice and oil tend to drift downwind at the same velocity.

5.6 When applied correctly, herding agents do not affect the physical or chemical properties of the oil, and will not affect the ability to subsequently disperse or mechanically recover the oil, beyond any effect related to thickening the oil slick.

5.7 The ultimate fate of herding agents will generally be dispersion and dissolution into the water column due to wave action. Given the low application rate, the concentration of herding agent in the water will generally be very low.

5.8 A more thorough description of herding agent development is contained in Appendix X1.

5.9 Although not the focus of this standard, herders may also be used in other applications, such as: concentrating oil to enhance recovery operations; and clearing thin films of oil from under piers and among wetlands where marine access may be difficult.

6. Guidelines for Use

6.1 The use of specific chemical surface-active agents, sometimes called oil herders or surface oil collection agents, to clear and contain oil slicks on an open-water surface is well known.

6.2 Herding agents are applied to the water surface around the periphery of a slick, not onto the slick itself. Herders can be applied in a low-volume and low-pressure stream, for example, using simple backpack sprayers.

6.3 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. The most effective herding agents have spreading pressures in the mid-40 mN/m range, whereas most crude oils have spreading pressures in the 10 to 20 mN/m range.

6.4 Consequently, small quantities of these surfactants (approximately 15 L per kilometre, equivalent to 7 gal per nautical mile, as measured along the perimeter of a slick) will quickly clear thin films of oil from large areas of water surface, contracting the oil into thicker slicks. Additional applications may be required.

6.5 For example, a 10 m³ (63 barrels, equivalent to 2640 gal) spill with an average thickness of 0.1 mm would have a perimeter of approximately 1100 ml (3600 flt), and would require approximately 16 L (4 gal) of herding agent. In this example the herding agent to oil ratio is 1:600.

6.6 Depending on the scale of the application, herding agent may be applied dropwise or in low volume streams. In either case, care should be taken to avoid mixing the herding agent into the water column or spraying it onto the slick.



Small amounts of herder sprayed on water around perimeter of slick

Herder rapidly spreads to form monolayer



Herder changes surface chemistry of water causing slick to contract into smaller area

FIG. 1 Depiction of Herding Agent Application

6.7 Following application of the herder, a period of 30 to 60 min may be required for it to have its full effect and maximize the thickness of the slick.

6.8 Another potential advantage of using herders in drift ice conditions is the possibility that the entire operation could be carried out using helicopters, or possibly even remote-control aircraft, to spray herders on the water around slicks and then ignite the thickened oil with aerially-deployed igniters. This type of totally aerial response could be much faster, more effective, safer and less complicated than conventional icebreaker-based countermeasures in Arctic waters.

6.9 This type of aerial- based response could be much safer, faster, more effective, and less complicated than conventional countermeasures in arctic waters.

6.10 Herding agents in common use may gel at sub-freezing temperatures. Gelling can be avoided by limiting the exposure of herding agent to ambient conditions, the use of insulated application containers, and the use of heat.

7. Herding Agent Effectiveness Test

7.1 With renewed interest in the use of herding agents there has been renewed interest in developing and evaluating new and existing products. To be accepted as a spill control agent in US waters, a herding agent must pass a floating persistence test and have its toxicity test results published

7.2 The test parameters are intended to reflect minimum conditions for acceptable performance. More stringent conditions such as higher wind speed or the use of weathered or emulsified oils may be considered for some herding agents, depending on the application.

7.3 The recommended oil for the effectiveness test is a light to medium viscosity crude oil. (See Guide F631, Table X1.1 and select a Type I or II oil.) Diesel could be used, but should be tinted to aid in visual measurement techniques.

7.4 The following test can be performed using fresh water underlying the oil. Present-day herding agents work equally well in fresh water and in seawater. For new products, depending on the intended application, the inconsequence of water salinity should be confirmed or, preferably, both conditions tested.

7.5 The general procedure for a $1-m^2$ pan experiment is:

7.5.1 Place 20 L (a depth of 2 cm) of room-temperature water in each $1-m^2$ pan lined with freshly rinsed (using tap water) new plastic film.

7.5.2 Take a sample of the water from the surface using a Petri dish and measure the water-air interfacial tension (IFT) using a DuNuoy Ring Tensiometer (Test Method D971-12). If the IFT reading is less than 65, replace the water and film and retry.

7.5.3 Carefully pour 500 mL of the test oil on the water; making sure that it doesn't stick to the plastic on the bottom of the tray while being poured.

7.5.4 Allow the oil to spread to equilibrium and take a digital photograph from overhead, preferably directly overhead the center of the pan, for subsequent oil area coverage analysis.

7.5.5 Apply prescribed amount (150 μ L) of herding agent to open water area with micropipette.

7.5.6 Allow the oil to contract and take another digital photograph after one minute, 10 min, 30 min and 1 h.

7.5.7 Empty water from pan, remove plastic film, and dry the tray.

7.5.8 The slicks (including any oil sheen) in the photographs must be corrected for perspective and the area measured. Average slick thickness is estimated by dividing the volume of oil by the calculated area.

7.5.9 The error in estimating area should be quite small, less than 5 % taking into account parallax errors at the sides of the pans. Errors in average slick thickness would increase as time progresses, unless evaporation losses are taken into account, but in a quiescent lab environment over the period of an hour would not likely exceed 10 %.

7.6 An effective herder will thicken a light to medium crude from an initial equilibrium thickness of approximately 0.5 mm to a thickness greater than 3 mm in a few minutes and maintain the herded slick thickness at 3 mm or greater for the one hour test.

8. Regulatory Considerations

8.1 In most jurisdictions, application of a chemical product in a marine environment is subject to regulatory approval.

8.2 Few jurisdictions have established approval criteria for the acceptance of herding agents for spill response. In the U.S., the Environmental Protection Agency would approve or disapprove of such a product based on one criteria: tendency for the product not to mix into the water column. Should a product meet this criteria EPA will list it on the National Contingency Plan (NCP) Product Schedule along with the results of standardized toxicity tests.

NOTE 1—Accepting a product for listing in the NCP Schedule does not constitute approval for use in a spill.

9. Safety

9.1 SDS information should be consulted prior to the use of any herding agent.

9.2 In general, the use of herding agents does not present any particular safety concerns to response personnel. Standard Personal Protection Equipment should be used to avoid ingestion, inhalation, and prolonged contact.

10. Shipping and Storage

10.1 In general, the currently available herding agents do not present any particular concerns regarding shipping and storage regulations.

10.2 For some herders, the solvent may present a flammability hazard and may have restrictions with regards to commercial air shipment.

10.3 Herding agents should be stored in sealed containers in a warm facility, shielded from sunlight and avoiding extreme temperatures (that is, avoid freezing temperatures and temperatures greater than 35 $^{\circ}$ C).