NRT-RRT Factsheet

February 2007

Prepared by the
National Response Team
Science & Technology Committee

FEMA

USDA

APPLICATION OF SORBENTS AND SOLIDIFIERS FOR OIL SPILLS

NOTE: ALL solidified oil must be removed from the environment. No product can be left in the environment unless it is classified as a bioremediation agent by U.S. EPA.

Regional Response Teams and Area Planners are tasked with developing planning documents to allow for the use or prohibition of solidifiers listed on the U.S. EPA National Contingency Plan, Subpart J Product Schedule (Schedule) for mitigation of oil spills.

Solidifier and sorbent manufacturers often contact oil companies, response contractors, state and federal agencies to promote the use of their products. Most sorbents do not have to be on the Schedule, while solidifiers, classified as a *chemical agent* by definition in 40CFR300.5, must be on the Schedule. Solidifiers are considered an alternative or can be used in conjunction with sorbents to recover small amounts of oil.

This guide will also assist product manufacturers and members of the response community in distinguishing a sorbent from a solidifier for purposes of listing such products on the Schedule and applying them in the field**.**

Manufacturers should contact the EPA Product Schedule Manager with any questions they have before proceeding with testing or marketing of their sorbents and or solidifiers. For a current listing of solidifiers on the NCP Product Schedule go to www.epa.gov/oilspill.

What Are Sorbents?

Definitions under Subpart J of the NCP

Section 300.915(g) ...materials consisting of, but not limited to the following materials:

i) Organic products
   a. Peat moss or straw; Cellulose fibers or cork; Corn cobs; Chicken, duck, or other bird feathers.

ii) Mineral compounds
   a. Volcanic ash or perlite; Vermiculite or zeolite.

iii) Synthetic products
   a. Polypropylene; Polyethylene; Polyurethane; Polyester.

Sorbents are essentially inert and insoluble materials that are used to remove oil and hazardous materials from water through adsorption, in which the oil or hazardous substance is attracted to the sorbent surface then adheres to it; absorption, in which the oil or hazardous substance penetrates the pores of the sorbent material; or a combination of the two. Sorbents are generally manufactured in particulate form for spreading over an oil slick or as sheets, rolls, pillows, or booms.

ASTM Definitions: ASTM F726-99 Standard Method of Testing

Sorbent – an insoluble material or mixture of materials used to recover liquids through the mechanisms of absorption or adsorption, or both.

Absorbent – a material that picks up and retains a liquid distributed throughout its molecular structure causing the solid to swell (50% or more). The absorbent is at least 70% insoluble in excess fluid.

Adsorbent – an insoluble material that is coated by a liquid on its surface including pores and capillaries without the solid swelling more than 50% in excess fluid.

Type I adsorbent (roll, film, sheet, pad, blanket, web) – a material with length and width much greater than thickness and which has both linear form and strength sufficient to be handled either saturated or unsaturated.

Type II adsorbent (loose) – an unconsolidated, particulate material without sufficient form and strength to be handled except with scoops and similar equipment.

Type III adsorbent (enclosed): pillows – adsorbent material contained by an outer fabric or netting which has permeability to oil, but with openings sufficiently small so as to substantially retain the sorbent material within the fabric or netting. adsorbent booms–adsorbent material contained by an outer fabric or netting which has permeability to or is permeable to oil but with openings sufficiently small so as to substantially retain the sorbent material within the fabric or netting.

What are Solidifiers?

Most solidifiers available in today's market are products composed of dry high molecular weight polymers that have a porous matrix and large oleophilic surface area. Solidifiers form a physical bond with the oil.

Oil's viscosity increases to the point that the oil becomes solidified into a rubber-like solid.
End product can range from a firm cohesive mass to a non-cohesive granular material. Solidifiers are available in various forms, including dry powder, granules, semi-solid materials (e.g., pucks, cakes, balls, sponge designs), and contained in booms, pillows, pads, and socks.

Solidifiers Should Meet the Following Criteria

- Insoluble in water;
- Specific gravity of less than 1.0;
- Composed primarily of polymers (with few other additives);
- Contain less than 5 ppm of heavy metals and chlorinated hydrocarbons;
- Have a physical reaction with oil whereby, at the prescribed application rate, the oil is sorbed by the product in a manner where the oil is resistant to leaching;
- Do not release solidified liquids under pressure; and
- Product itself is non-toxic to wildlife and other species

What are the Mechanisms of Actions for Solidifiers?

Solidifiers are polymers that have a physical attraction to oil that is enhanced by van der Waals forces, which are based on the theory that molecules are attracted to those that have similar structures. Non-polar hydrocarbon polymers are attracted to non-polar petroleum hydrocarbons, thus they prefer to be oil-wet rather than water-wet. They consist of long chains of hydrocarbons that have a loose molecular structure and a very porous matrix. They are soluble

in excess liquid (solvent) but with continued application will increase the viscosity of the oil to the point that it forms a solid mass.
One analogy is how Styrofoam behaves when mixed into gasoline. Initially the Styrofoam pieces will dissolve in the excess gasoline (a solvent); however, continued addition of Styrofoam pieces will thicken the gasoline, increase it's viscosity, and eventually form a solid mass.

The reaction time is primarily controlled by the grain size (and thus surface area) of the product. Fine-grained powders solidify faster than granules because of the higher surface area of the product and the higher diffusion rate of the oil. Light, low viscosity oils are solidified more readily compared to heavy, high viscosity oils. Heavy, viscous oils result in a lower effectiveness and longer solidification time.

Oil bonds strongly with solidifiers but the exact solidification mechanisms have not been studied in depth. Experiments by Ghalambor (1996) showed that solidifiers tend to absorb energy (endothermic reaction) in their reactions with crude oil. This initial decrease in temperature is due to the partial dissolution of the polymer in the oil, and it indicates the lack of a chemical reaction between the oil and polymer.

It appears that most large molecules are firmly held, implying an aggressive interaction with the polymers. However, light compounds, such as in gasoline, are able to vaporize, albeit more slowly, from the solidified mass, indicating that there is only a physical bonding and not a chemical reaction.

What are the Environmental Concerns Associated with Solidifiers?

Whether the product and/or treated oil may sink, either initially or over time. Solidifier products currently listed (May 2006) on the Product Schedule have a specific gravity less than 1.00 and should float in both fresh and salt water. The treated oil should float as well. Pre-authorized products should be tested to document that they do not sink or cause treated oil to sink initially or after 24 hours of floating on the water surface. These tests could be conducted with oil types to be included in the pre-authorization.

Fate and bioavailability of unreacted product in the environment. Under certain conditions, the product could be released to the environment (e.g., wind-blown powder, failure of containment booms and pillows). Polymers degrade very slowly, thus residues may be highly persistent. There are concerns that the product could be ingested by wildlife feeding on the water surface or in fauna living in sediments. Currently, there are no standard oil-spill treating agent toxicity tests for an ingestion pathway for birds or mammals. Pre-authorization stipulations should require recovery of all materials, both untreated product and treated oil.

Fate and behavior of treated, unrecovered oil. There is concern about exposure to solidified or partially solidified oil that remains in the environment after recovery efforts are terminated. Treated oil is expected to weather more slowly, compared to untreated oil, thus it may be more persistent. If the oil is solidified into a cohesive mass, it will be less bioavailable; if it is sticky, it could adhere to soils, vegetation, and animal body parts (including skin, fur or feathers) that come into contact with the solidified mass.

Pre-authorization stipulations should require application only under situations where containment and recovery would be most effective.

Acute aquatic toxicity is not a major concern. Solidifiers, by definition, are solids that are insoluble in water. Thus, LC_{50} values are generally high, based on nominal exposures where most of the product remains as a solid on the water's surface; however the NCP requires toxicity testing. Solidifiers that are left in the water may have impacts that need to be evaluated.

The chart on the following pages shows the benefits and shortcomings of, and comparisons between sorbents and solidifiers.

What are the Benefits/Shortcomings/Comparisons of Using Solidifiers versus Sorbents?

Issue	Benefits	Shortcoming	Comparison with Sorbents
Effectiveness with Light Oils	Work best with light oils.	None	Effective in recovering light oils spread into thin slicks and are difficult to recover with sorbents.
Effectiveness on Sheens	Can remove even light sheens.	Tend to over-apply on sheens.	Effective in recovering sheens that are very difficult to pick up with sorbents.
Effectiveness with Heavy, Viscous Oils	*Little*	Longer solidification time with emulsified, viscous oils due to poor mixing.	Not very effective. Sorbent effectiveness is dependant on type; oil snare is very effective with viscous oil.
Low Temperature	Could be applied in ice conditions.	Longer solidification time or reduced effectiveness at low temperatures due to increased oil viscosity.	Temperature has little effect on most sorbents.
Flash Point	Treated oil is less flammable.	None	Both solidifiers and sorbents may lower flammability.
Worker Training	Increases effectiveness	Need training in proper use of new products.	Sorbents are a very familiar product, but there is often overuse.
Access Limitations	NA	NA	Same requirements for access to deploy/retrieve.
Application Considerations	Likely to be used by trained individuals in specific response conditions.	General broadcasting of loose material could be a problem in open areas and in high wind conditions that would inhibit effective containment and recovery.	In contained form (booms, pillows and socks), would be the same as for sorbents. In loose form, both have problematic containment and recovery issues.
Recovery Methods	Manual recovery of both contained and loose product from effective containment should be straightforward.	Effective containment of loose product is an issue- especially in conditions of currents, tides, and wind. Recovery of all material is highly desirable due to product persistence.	In contained forms, recovery of solidifiers should be the same as sorbents.

Monitoring Considerations	Can monitor visually for effectiveness during both tests and application.	When used in loose form, constant visual monitoring should ensure: 1) proper and complete containment and recovery; 2) no adverse wildlife or fish impacts. Use should be modified or stopped if either condition is not met.	Basically similar to sorbents, but less passive, especially when using loose material. All material should be recovered as soon as it is no longer effective at removing oil.
Pickup Time for Treated Oil	NA	Can be slow with loose product.	About the same when products are contained as booms, socks, etc.
Application on Solid Surfaces	Effective on solid surfaces (land); treated oil is a dry solid that can be swept up. Also can form a containment barrier.	None	Likely more effective than sorbents.
Waste Volume	Will increase volume proportional to application rate.	None	Sorbents create large waste volumes.
Waste Weight	NA	Generates waste weight equal to the weight of added solidifier.	When properly applied, sorbents themselves add little to the waste weight, but can pick up water.
Waste Disposal - Landfill	More likely to pass leach test for landfill.	None	Sorbents less likely to pass leach test for landfill.
Waste Disposal - Incineration	High BTU value; Need preplanning to assess waste to energy options and management as separate waste stream.	None	Sorbents can also be incinerated but may have lower BTU compared to solidifiers, depending on the product.
Waste Disposal Industrial intermediate for recycling of encapsulated product and oil	Can be recycled via introduction into other industrial processes, including: asphalt modification; rubber additive, etc.	Must meet TCLP and EPA/state testing procedures.	Not applicable for most traditional sorbents.

What are Application and Monitoring Issues with Use of Solidifiers?

Application Rate: Recommended rates are from 10-50 percent by weight of the liquid to be recovered. In practice, even higher application rates are used because of the difficulty of estimating oil spill volume, use on thin sheens, worker unfamiliarity with the product (particularly if solidification is not immediate), and general attitude that more is better. Higher application rates can lead to increased wastes and product costs; similar to what occurs when sorbents are overused.

Application Method: Application of loose product by hand or blowers under even light wind conditions can result in product being blown out of the treatment area. This issue is particularly true for fine powders. Thus, product in some sort of containment is preferred.

Mixing Energy: Most solidifiers require some degree of physical mixing with floating oil, which can be achieved with water spray, boat wakes, or hand-held devices. Booms, pillows, pads, and filter packs can be used like similar sorbent products.

Solidification Time: Most solidifiers act quickly, solidifying the oil in less than 1 minute up to 1 hour. Some products continue working for over a number of hours. Fast-acting products can be problematic because they react with that portion of the oil they first contact, potentially resulting in a mix of solidified and un-solidified oil. This behavior can be beneficial where the solidifier can be applied to the perimeter of the oil, forming a solidified barrier to prevent further spreading, rather than treating the entire spill volume.

Oil Type: Solidifiers work best with light to moderate oils. For highly volatile oils such as gasoline, it should be noted that the oil will continue to evaporate, albeit slowly. Solidifiers are less effective on heavy or emulsified oils. At a spill, preliminary tests should be conducted with the spilled oil to determine overall application rate, effectiveness, and character of the treated oil (consistency, cohesiveness, stickiness). See the effectiveness test procedure in the Selection Guide for Oil Spill Applied Technologies.

Solidifier Products Need to Be Listed on the NCP as Miscellaneous Oil Spill Control Agents Because:

Solidifiers can vary in chemical composition, including additives, although the actual composition of each product is proprietary. Listing is necessary so information on their chemical composition, physical properties (e.g., density), and toxicity are made available in a standard format.

References:

Dahl, W., Lessard, R.R, Cardello, E.A., Fritz, D.E., Norman, F.S., Twyman, J.D., Clayton, E.W., Knight, B.L., Crane, R.D., Johnson, S.J., and Martin, B.R., 1996. Solidifiers for oil spill response. Proceedings of the Society of Petroleum Engineers Conference on Health Safety and Environment, SPE paper No. 35860, pp. 803-810.

Fingas, M., R. Stoodley, N. Stone, R. Hollins, and I. Bier, 1991. Testing the effectiveness of spill-treating agents: Laboratory test development and initial results. Proceedings of the 1991 Oil Spill Conference. American Petroleum Institute, Washington, D.C., pp. 411-414.

Ghalambor, A., 1996. The effectiveness of solidifiers for combating oil spills. Louisiana Applied Oil Spill Research and Development Program, OSRADP Technical Report Series 96-006, 68 pp.

Walker, A.H., J. Michel, G. Canevari, J. Kucklick, D. Scholz, C.A. Benson, E. Overton, and B. Shane, 1994. Chemical oil spill treating agents: herding agents, emulsion treating agents, solidifiers, elasticity modifiers, shoreline cleaning agents, shoreline pre-treatment agents, and oxidation agents. Marine Spill Response Corporation, Wash., D.C., Tech. Report 93-015, 328pp.