Review of Solidifiers: An Update 2013

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Abstract

This paper is a review and update of oil spill solidifiers and summarizes data on solidifier effectiveness, composition, and application.

The prime motivation for using solidifiers is to recover very small oil spills or to protect wildlife. A major issue is the actual effectiveness or advantage over sorbents or mechanical recovery. Once solidifiers are used, other recovery methods are difficult, if not impossible. Use of skimmers is precluded once oil is treated with solidifiers.

There are three types of solidifiers, polymer sorbents (not truly solidifiers), cross-linking agents and polymers with cross-linking agents. Each type has unique characteristics. Polymer sorbents, common at this time, simply adsorb oil into spaces between polymers. Oil is only held by weak forces into these spaces. Strictly speaking, these products should be classified as sorbents. Cross-linking agents form chemical bonds between molecules in the oil. Polymers with cross-linking agents also form chemical bonds. Reaction time and reactivity are issues. Some solidifiers react so quickly that they solidify the first oil they contact and may form a crust on the oil surface. This prevents solidifier from reaching underlying oil. Other proposed solidifiers react so slowly that they are not of use. Some agents will cross-link or react with other materials such as oil boom, docks and other organic materials.

Another motivation for using solidifiers is to reduce the spread of oil and protect wildlife and receptor areas. To accomplish this, the solidifier application must be well targeted and effectiveness high. Furthermore, the recovery of the solidified oil must occur rapidly and efficiently. Recent solidifier use on very small and thin spills near shore have been reported as effective. Past tests on the use of solidifiers offshore have not had the same success. Solidifiers might be best restricted to small spills on water near shore. Land-based spills might be treated, however there are several data gaps on this type of application.

Only limited effectiveness testing has been carried out on solidifiers, mostly in the past. Laboratory testing requires re-examination. More laboratory work is needed on the stability of solidified oil and other aspects of the solidifier issue.

Few environmental studies have been done on solidifiers. Data gaps include: the fate and effects of solidifiers and solidified oil in the environment, toxicity other than aquatic toxicity, the biodegradation of solidifiers and solidified oil, the long term fate and effects of solidified oil in landfills, studies on mixing of solidifiers with oil (by type), and studies of optimal application of agent and recovery of solidified oil. Further studies on the applicability of the technology and its limitations are advised.

1 Introduction to solidifiers

The use of solidifiers was never widespread since the 1960's when the concept started. The motivations for using solidifiers are: to recover oil from smaller areas quickly, to prevent the spread of slicks, to recover thin sheens and to protect areas and wildlife on a rapid basis. The issues surrounding solidifiers also remain the same; effectiveness, problems mixing of the solidifier with the oil, long-term considerations, possible toxicity, and most importantly that solidifying the oil precludes most other countermeasures. It is an important point to recognize that most other countermeasures, especially booms and skimmers, are designed to recover liquid oil. Oil weathering and oil becoming more viscous and even solid, are major problems in the oil spill business. So unless solidified oil can be easily and quickly recovered, solidification compounds the oil spill problem. This, and other factors, may restrict the use of solidifiers to small, thin and nearshore spills.

There are serious research gaps which have not been addressed over 40 years since solidifiers were first proposed.

1.1 Motivations for using solidifiers

The prime motivation for using solidifiers is to reduce the spread of oil and protect wildlife and receptor areas. To accomplish this, the solidifier application must be highly successful and effectiveness high. Furthermore, the recovery of the solidified oil must occur rapidly and efficiently - before the oil leaves the immediate vicinity.

The second motivation for using solidifiers is to reduce the impact on birds and mammals on the water surface. No research at all has been carried out on this aspect of treating agent use. This is remarkable because this is one of the prime motivations for use.

1.2 Solidifier issues

Utility remains a major issue with oil spill solidifiers. If solidifiers are used, this precludes the use of other mechanical countermeasures. It is important to recognize that booms and skimmers are designed to deal with liquid oil. The big problem with these recovery methods are the weathering of oil or dealing with heavier oils. More viscous and heavy oils are a major problem. Solidifying the oil, without recovering it immediately, can cause major problems. Thus solidifiers must never be used on large spills or where the oil cannot be recovered immediately.

Another major issue is the completeness of solidification and mixing of the solidifier with the oil mass. Large scale tests notes two situations where this issue was raised.[1] A solidifier can potentially react with the oil it first comes into contact with, leaving the remaining oil untreated. Mixing of the agent is always an issue and the resulting ‘solidified’ oil is often a heterogenous mixture of both liquid and solid.[2,3]

The last issue to be raised in this section is that of long-term fate and effects. The long-term effects of treated or partially-treated oil have not been studied and therefore remain largely as a topic for speculation.

1.3 Solidifier chemistry

It is important to understand how solidifiers work as there are several different kinds. Some of them form chemical bonds, others work only by adsorbency into polymer chains. The exact details of most products are proprietary and thus only a general presentation can be made here.

1.3.1 Polymer sorbents

This is currently the most common type of ‘solidifier’. These types are sometimes called super-sorbents, but would be best called polymer sorbents. Strictly speaking, these are not solidifiers, but sorbents. There is no chemical bonding, van der Waals forces hold the oil between polymer strands. Figure 1 shows a scheme of how these work. Many polymers have spaces between them that can hold oil. The oil can be adsorbed into these spaces. The oil is held into these spaces by van der Waals forces, which are weak attraction forces between molecules. If there was little solidifier of some types, the oil could be removed by applying pressure to the completed solid. The success of this reversal would depend on the time, as the solidified oil becomes more stable with time.

Many polymers are capable of this action. Generally, block co-polymers are more efficient and hold oil better. Currently the most commonly used materials are styrene-butadiene and related polymers. Others which have been used in the past include: polytertiary-butylstyrene, polyacrylo-nitrile butadiene, polyisoprene (rubber), polyethylene and polypropylene, poly isobutylene and related polymers.

The advantages of these types of sorbents are that they are relatively simple, probably of low toxicity and are slower to react and thus mix better - given a similar density to oil. Further, these products do not link to other materials such as booms, docks, organic material or stone. The disadvantages of these type of solidifiers are that they are more like sorbents and oil can be released from these products, especially under some pressure.

1.3.2 Cross-linking agents

Cross-linking agents are chemical products that chemically form bonds between two hydrocarbons to solidify the oil. The reaction is that of a chemical one and typically can release a small amount of heat depending on the chemical used.

When solidifiers were popular in the 1980's, cross-linking agents were more commonly used than polymer sorbents. One must be careful about interpreting some of the literature then as some of the tests may refer only to cross-linking agents or only to polymer sorbents or products that are a combination of both as will be described in the next section.

The schematic of how these products function is shown in Figure 2. Figure 2 shows that the starting reagent, shown as X's, mixed with the black oil to form the cross links as shown by the jagged line. Also it might be noted that with thick oil, the cross-linking product reacts with the first oil that it comes in contact with. Most cross-linking agents react quickly and thus do not penetrate very thick oil.

Cross linking agents that have been used include norbornene and anhydrides.

Pelletier and Siron made a new series of oil treating agents which solidify oil.[4] These agents were prepared by reacting surfactants, alcohols or carboxylic acids with alkychlorosilanes in light hydrocarbon solvents.

The advantages of cross-linking agents are that the final product is truly solidified (if mixed before the product reacts completely). If fully solidified, the product leaches little oil and forms a durable mat which is easy to recover. The disadvantages of this technology as that it is difficult to get complete solidification, especially of a thicker slick as the product is reactive and reacts with the first hydrocarbon it comes into contact with. Cross-linking agents also have the disadvantage of linking with other hydrocarbons such as in containment booms, docks, organic matter, etc.

1.3.3 Cross-linking agents and polymeric sorbents combined

This type of agent combines a polymeric sorbent with a cross-linking agent. Often the cross-linking agent is attached to a polymer end. The purpose of this combination is to gain the advantages of both types of agent. A schematic of how this agent type works is shown in Figure 3.

The polymers used are those described above, while the cross-linking agents are typically anhydrides.

A product called RigidOil made by British Petroleum, that was an agent of this type, is of interest because the composition was widely disclosed.[5] The agent consisted of two liquids which were generally mixed shortly before applying to the oil. One liquid consisted of a 10% maleinized polybutadiene of molecular weight 8000 with 50% of odourless kerosene plus ester, as a diluent. The other liquid consisted of a cross-linking agent, zinversate diethanolamine also in 50% kerosene/ester (9:1). Extensive testing was carried out on this product as reported in this paper.

The advantages of this type of solidifier agent are that the product mixes with oil better than cross-linking agent alone and that solidification, if achieved, is better than for polymeric sorbents alone. The disadvantages of this type of agent are that generally it has two components which must be mixed immediately before application and that solidification may be difficult to achieve because the product may form a crust on the top of the oil. This type of agent may also adhere to booms, docks and other carbon-containing materials.

2 Review of major solidifier issues

This section will explore the sub-topics of solidifier use, section by section. Information is drawn from the papers summarized in the back of this report, with emphasis on the reviewed literature.

2.1 Effectiveness

Solidifier effectiveness is defined as the amount of agent that is required to solidify oil under standard conditions. Many factors may influence solidifier effectiveness, including oil composition, sea energy, state of oil weathering, the type of solidifier used and the amount applied. The most important of these is the composition of the oil, however there is very little data on testing with these factors.

While it is easier to measure the effectiveness of solidifiers in the laboratory than in the field, laboratory tests may not be representative of actual conditions. Important factors that influence effectiveness, such as sea energy and mixing, may not be accurately reflected in laboratory tests. Results obtained from laboratory testing should therefore be viewed as representative only and not necessarily reflecting what would take place in actual conditions. However, laboratory testing is useful in establishing chemical and physical relationships.

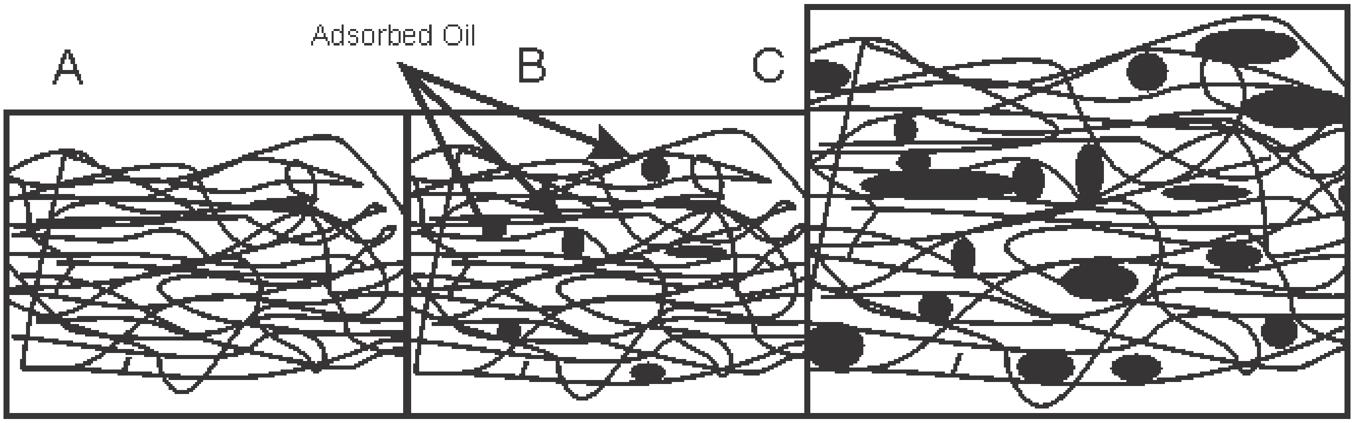

Figure 1 Schematic of the Process of Polymeric Adsorption. Figure 1A shows a schematic of a typical polymer which on a micro-scale has spaces. If added to oil these polymers start absorbing oil as shown in Figure 1 B. The final product is shown in Figure 1C where the polymer matrix swells with the absorbed oil.

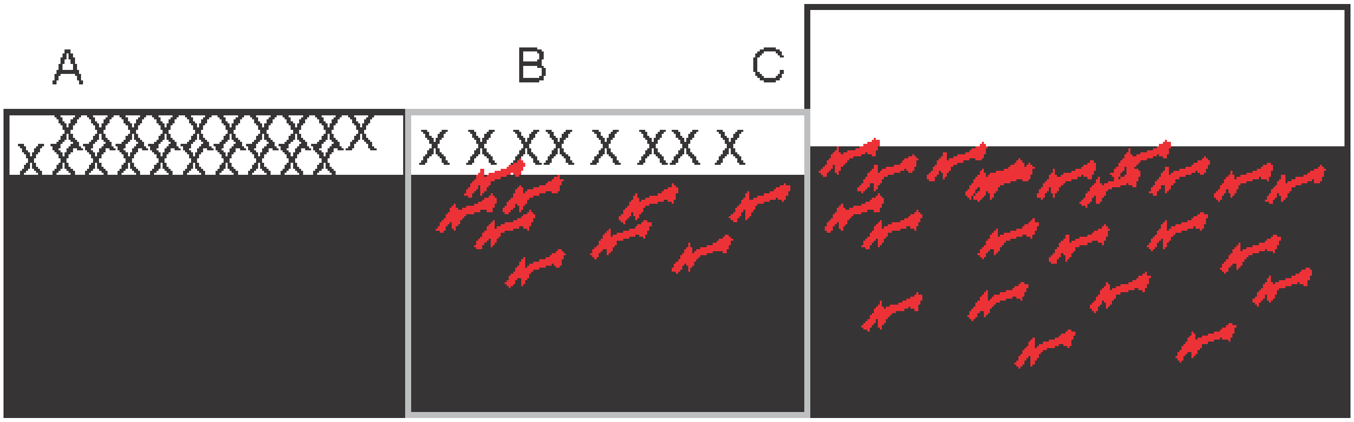

Figure 2 Schematic of the Process of Cross-Linking. Figure 2A shows a schematic of oil with the X's being the cross-linking agent. If added to oil these agents start to cross-link various oil components as shown in Figure 2 B by the jagged lines. The final product is shown in Figure 2C where the agent has cross-linked a portion of the oil.

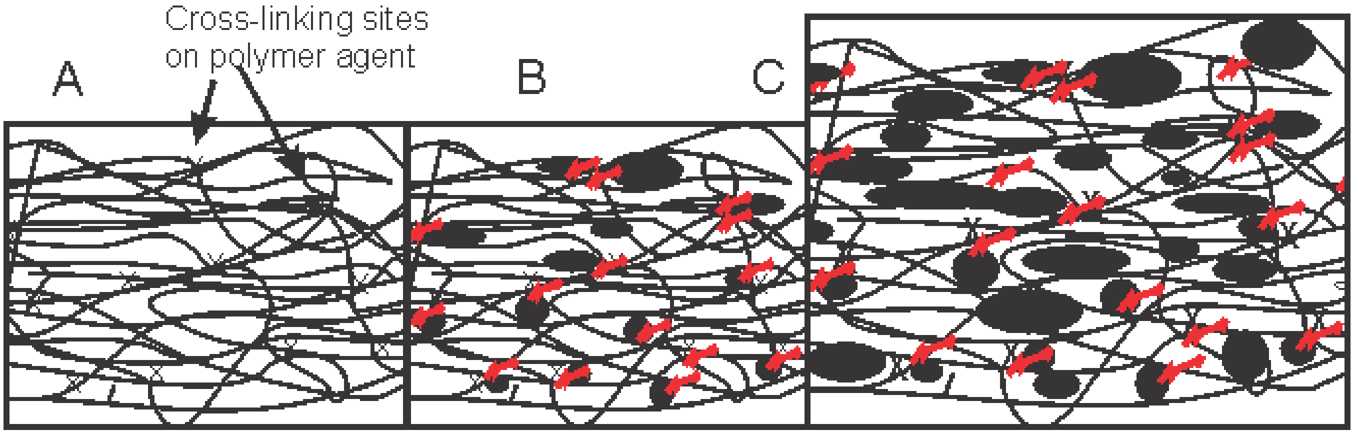

Figure 3 Schematic of the Process of Polymeric Sorption Combined with Cross-Linking. Figure 3A shows a schematic of oil with the X's being the cross-linking agent on the ends of polymers. If added to oil these agents start to adsorb oil and cross-link various oil components as shown in Figure 3 B by the jagged lines. The final product is shown in Figure 3C where the agent has adsorbed and cross-linked a portion of the oil.

2.1.1 Field trials

Several field trials were carried out on the British Petroleum product, RigidOil.[6] . In 1981, 11 tests were carried out using RigidOil on 205 L light fuel oil and topped crude. The product was applied using spray booms. The North Sea was choppy throughout the tests, and thus promoted mixing. Several tests resulted in what appeared to be completed solidified oil. Some tests, however, resulted in partially-solidified oil with some free oil floating beside. In two tests the oil emulsified with water after solidifier was applied.

In that same time period, a trial of RigidOil was carried out on oil-under ice in the Canadian Beaufort Sea.[6] The application resulted in some solidification and some free oil. It was felt that the lack of mixing was the cause of this.

A test on oil on shoreline was carried out at BIOS (Baffin Island Oil Spill Study).[6] The agent was mixed and then applied with a hand sprayer. This resulted in the formation of a crust with little solidification of oil under the crust. It was judged that this application had little benefit. The cause was felt to be a too-rapid reaction of the agent and lack of mixing.

In the mid 1980's, the BP agent was tested in larger scale by the Canadian Coast Guard and the Canadian oil industry offshore Newfoundland.[7] In these large scale tests, even more agent was required to partially solidify the oil, in fact up to 40% of the actual volume of the oil itself. This is double the laboratory requirement. Both requirements were deemed to be far in excess of what was actually practical in the event of a real spill. Crude oil was released and a ship with spray booms applied the solidifier to the oil, which was partially contained in a boom. The agent again reacted with the oil on the surface and when the oil was sampled at a later time, it was soft with some portions almost liquid. What appeared to have happened is that the surface solidified and was later mixed by waves with the liquid oil underneath. It was concluded that this technology was not practical for offshore oil spills.

Delaune et al. tested the solidifier product, Nochar A 650, by putting the granular product on oiled test plots near a shoreline.[8] Four days after the application, the oil was removed by hand. The findings were that the solidifier did react with the South Louisiana crude forming a cohesive solid mass with no dripping. The solidified oil had a rubber-like consistency that retained its shape and could be removed by mechanical or hand means. The recovery of oil in the 3 plots ranged from 70 to 76%.

The findings from the field tests are that more solidifier was required to achieve the end result than from laboratory tests. Further, in many cases, complete solidification was not achieved. This appears to be particularly the case when the oil was thick and when there was insufficient mixing energy. Near-shore tests or use appears to be more successful, especially when the slicks were thin and mixing was achieved.

Caution must be used, however, in translating the test findings of one type of solidifier to another type as the three types of solidifiers behave somewhat differently. Polymeric sorbents are less likely than the other two types to form a crust and thus inhibit further solidification. Cross-linking agents are the most likely to form a crust.

2.1.2 Laboratory tests

Laboratory tests were carried out by Environment Canada, by Exxon, by Rea, by Pelletier and by Ghalambor. Most used a procedure similar to that noted in Appendix A with the end point being the disappearance of free oil. Some tested with penetrometers and viscometers, however no consistent results were found.

Fingas et al. reported on the testing of three solidifiers: the BP (British Petroleum) product, Rigid Oil, which consisted of polymer in deodorized kerosene and a cross-linking agent; a Japanese product consisting of an amine which forms a polymer; and the solidification agent proposed by Professor Bannister of the University of Lowell, an agent which used liquefied carbon dioxide and an activating agent.[9] During tests conducted in the laboratory, all three agents functioned, but required large amounts of agent to effectively solidify the oil (render the oil to a viscosity of greater than 1,000,000 cSt). Under some situations the oil became a viscous semi-solid which would not aid in recovery. The BP agent worked better than the other agents and was tested in larger scale by the Canadian Coast Guard and the Canadian oil industry. In these large scale tests even more agent was required to solidify the oil, in fact up to 40% of the actual volume of the oil itself. Both requirements were deemed to be far in excess of what was actually practical in the event of a real spill.

A standard test was developed to assess new solidifiers. The test consists of adding solidifier to an oil while being continuously stirred until the oil is solid.[9] The test results were found to be repeatable within 5%, despite the fact that visual observation was used. Results of testing some solidifiers are given in Table 1 with the procedures in Appendix A. The aquatic toxicity of these products was measured and in all cases for the products listed, exceeded the maximum test value, in other words all products listed were relatively nontoxic to aquatic species. It should be noted that some products such as the wax are poor sorbents and solidifiers and have little interstitial spaces in which sorption can occur. This is why such products require over 100% of the material to solidify.

Rea tested seven pure polymer or cross-linking chemicals with diesel fuel.[10] Mixing was carried out and then the products tested with a penetrometer and the products tested for diesel fuel vaporization as well as leachability. The products tested were norbornene (in two forms), styrene-ethylene butylene-styrene block copolymer (in two forms), and styrene-butadiene block copolymer in 3 forms. The testing was carried out over 3000 hours with the properties of the gelled substance tested at each point and either 5 or 10% of the polymer added. There was little differentiation between the various polymers in terms of penetrometer data over the time. Findings include that the gelled fuel continued to solidify over time, but eventually approached a constant level. The ratio of solidification was proportional to the mass of agent added. All the gelled fuels emitted volatile organics at a declining rate over time. The leachability of BTEX was however, lowered by gelation. Test results are summarized in Table 2.

Table 1 Environment Canada's Testing of Solidifiers

AGENT	PERCENT [1] TO SOLIDIFY	TOXICITY[2] (AQUATIC)
A610 Petrobond (Nochar)	13	>5600
Rawflex	16	>5600
Envirobond 403	18	>5600
Norsorex	19	>5600
Jet Gell	19	>5600
Grabber A	21	>3665
Rubberizer	24	>5600
SmartBond HS	25	>5600
Elastol	26	>5600
CI Agent	26	>5600
Gelco 200	29	>5600
Oil Bond100	33	>5600
Oil Sponge	36	>5600
Spill Green LS	43	>10000
Petro Lock	44	>5600
SmartBond HO	45	>5600
Molten wax	109	>5600
Powdered wax	278	>5600

1 Values are the average of at least 3 measurements,

average standard deviation is 6

2 Values are LC50 to Rainbow Trout in 96 hours

this shows that all are insoluble and less than can be measured

Table 2 Agents Used in Rea's Solidifier Testing

Designation	Active Agent	Type - According to This Report	Physical Description	Apparent Density g/mL	Relative Effectiveness*
A	Norbornene	cross-linker	green clumped flakes	0.2	10
B	Norbornene (with solvents)	cross-linker	white powder	0.32	7
C	Styrene-ethylene butylene-styrene block copolymer	polymeric sorbent	white small flakes	0.22	1
D	Styrene-butadiene block copolymer	polymeric sorbent	off-white powder	0.4	3
E	Styrene-butadiene block copolymer	polymeric sorbent	white rough flakes	0.18	3
F	Styrene-butadiene block copolymer	polymeric sorbent	white large flakes	0.31	no data
G	Styrene-ethylene butylene-styrene block copolymer	polymeric sorbent	white powder-flakes	0.21	2

** The author (Rea) did not have a table of Effectiveness, these are values calculated approximately from the graphs using the reciprocal of the penetration times the percentage used, a bigger number is better*

Ghalambor tested 23 available solidifiers.[11] These solidifiers were: Elastol 1, Elastol 2, Envirobond # 403, Nochars A 610, Nochars A 650, OARS, OSSA, Omni-Zorb #2000, Omni-Zorb # AZ1N, Omni-Zorb # BZ, Omni-Zorb # PZ, Petro-Lock, Rubberizer, Seamate - 3mm, Seamate - 4 mm, Seamate fine, SPI particulate 1, SPI particulate 2, Spill Gel (Fractech), Waste-set PS # 3200, and Waste-set PS # 3400. It should be noted that there are only 13 unique types, the remainder are variations of the same product. It might also be noted that some of these products are elasticizers or sorbents. The results of testing did not reveal the product names. Various test oils were used. The laboratory test was similar to that noted in Appendix A, with somewhat different quantities of water and the end points were chosen to be the same. The 'consumption level' of solidifier or the quantity of agent needed to solidify varied from 25 to 120%. The viscosity of the resulting products varied from about 1000 Poise to about 8000 Poise. Calorimetry was carried out on the reactions and the heats of reaction varied from 0.9 to 4.3 Cal/g. Values less than 1 would indicate an endothermic reaction and values greater than 1 would be an exothermic, or heat-releasing value. Values very close to 1 could be considered as neither endothermic or exothermic. All three types of reactions were found.

The Exxon laboratory test included application of solidifier to oil until no visible oil remained on the water surface.[12] The oils tested were gasoline, diesel, Bunker C and 3 different crude oils. Most of the products were able to solidify some of the oils into a firm mat, however, none of the solidifiers formed a firm solid mat with all of the oils tested. The solidifiers used range from a ratio of about 1:5 to about 1:20. Dahl et al. also report on testing of several agents.[13] The laboratory test included a modification of the Environment Canada test (described in Appendix A) and included application of solidifier to oil until no visible oil remained on the water surface. The 14 solidifiers tested included: Micro-Set, SPI, Omni-Zorb, Inipol, Nochar A-610, GTS-modified Elastol, Seamate, MWE, Envirobond, Petrosorb, Petro-Lock, PetroGuard, Rubberizer and Petro-Capture. The salt level did not have an effect on solidification.

Pelletier and Siron tested their new silicone solidifier using a light crude oil, Brent. A procedure similar to that in Appendix A was used.[14] The ratio needed to solidify was 1:7, agent to oil. The solidified oil contained water up to 85% by weight of the total mass. These agents are prepared by reacting surfactants, alcohols or carboxylic acids with alkychlorosilanes in light hydrocarbon solvents. A trichlorosilane of a general formula, Cl_3SiR, where R is H or CH_3, is used as the primary reactant. The reaction proceeds as:

$Cl_3SiR + R\text{-}OH \rightarrow SiOR + HCl$

Two silanes, octadecyltrichlorosilane ($CH_3(CH_2)_{17}SiCL_3$) and trimethyoxysilane ($((CH_2))_3SiH$) are added to the solution along with a surfactant, silicone grease and a petroleum ether solvent. The mixture of the final solution was a ratio, by molar weights, of one part Brij 76, the surfactant, one part of trichlorosilane, 5 parts of the octadodecyltrichlorosilane, 5 parts of the trimethoxysilane and 0.05 g/mole of silicone grease in petroleum ether. The treatment solution is rapidly sprayed over the surface. Laboratory testing was carried out using a light crude oil, Brent. The ratio needed to solidify was 1:7, agent to oil. The solidified oil contained water up to 85% by weight of the total mass. It was found that the silicone coated solid surfaces and rendered them less adhesive to oil. The solidification process was found to be independent of temperature and salinity effects. The solidifier could easily be reformulated as an oil herder as well. The product was thought to be nontoxic, but no tests were carried out. The application of this solidifier was thought to be useful for application to very small spills and not to larger spills. The use of the petroleum ether as a solvent rendered this mixture, flammable, however a substitute solvent could be found.

Fieldhouse and Fingas tested a number of agents for effectiveness using the method in the Appendix and also using rheology.[3] The test results and observations are summarized in Table 3. The conclusions from this part of the study are that the optimum oil layer thickness for ASMB and marine diesel is between 2 to 5 mm. In this range, the product treatment was virtually complete and the treated oil could be recovered as a single mat. Below 1 mm, the layer is not sufficiently thick to provide contact between product grains to remain cohesive; this is true below 2 mm for some agents which are more granular. At 100 µm, the treating agent must be applied in excess and the individual grains or small agglomerations tend to repel each other. At 10 mm, the endpoint is misleading as the treatment is still incomplete, especially for the more granular, floating and reactive agents. Some agents have a tendency to crust at the surface and are only driven down by the weight of additional product on top. Some products more easily entered the oil layer, especially those which is denser than the oil and thus there were fewer issues with incomplete treatment. Allowing the sample to sit overnight greatly improved recovery, but the resulting mat was less firm and tended to flow.

Table 3 Testing by Environment Canada

Product	Oil	Oil Thickness (mm)	Dose (%w/w)	Description
SmartBond HO	Diesel	0.1	222	Excess product, separate
		1	79	Clumps
		10	42	Incomplete, oil released
		10	46	Overnight, cohesive layer
	ASMB	0.1	273	Excess product
		1	92	Clumps
		2	68	Cohesive layer
		5	50	Cohesive layer, res. sheen
		10	42	Cohesive layer, res. sheen
		10	37	Cohesive layer, res. sheen
	Arab Heavy	2	60	Cohesive layer, brittle
	Fuel Oil #5	1	31	Crust
SmartBond HS	Diesel	0.1	129	Clumps
		1	44	Cohesive layer
		10	30	Additional
		10	32	Overnight, cohesive
	ASMB	0.1	129	Clumps
		0.5	59	Clumps
		1	49	Cohesive layer
		2	38	Cohesive layer
		5	38	Cohesive layer
		10	28	Cohesive layer, res. sheen
		10	25	Cohesive layer, excess oil
	Arab Light	2	51	Cohesive layer, brittle
		2	23	Cohesive layer
	Arab Heavy	2	45	Cohesive layer, brittle
		2	20	Clumps, res. slick
	Sockeye	2	32	Sits on top, brittle, res. slick
CI Agent	Diesel	0.1	117	Clumps
		1	40	Cohesive layer
		10	24	Cohesive layer, sags
	ASMB	0.1	91	Clumps
		1	52	Cohesive layer, brittle
		2	47	Cohesive layer
		5	29	Cohesive layer, res. sheen
		10	19	Cohesive layer, res. slick
		10	19	Cohesive layer, res. slick
	Arab Heavy	2	50	Cohesive layer, brittle
		Temperature (ºC)		
SmartBond HO	Diesel	-5	77	Separate grains
	ASMB	-5	56	Clumps
	ASMB	0	79	Clumps
SmartBond HS	Diesel	-5	52	Clumps
	ASMB	-5	30	Clumps
	ASMB	0	50	Cohesive layer, brittle
CI Agent	Diesel	-5	47	Cohesive layer
	ASMB	-5	35	Clumps
	ASMB	0	56	Cohesive layer, brittle

Fieldhouse and Fingas also tested at, two of the agents were tested on marine diesel and ASMB at a thickness of 2 mm in -5ºC conditions, and at 0ºC on ASMB only.[3] Results are also provided in Table 3. One of the products was far less cohesive at the lower temperatures, but dose rates were similar. Another product appeared to be less affected, perhaps due to smaller grain size. Only one of the treatment combinations had an outcome similar to the test result at 15ºC. It appears that temperature is a limiting factor for generating a cohesive mass. It is interesting that when moved to room temperatures, the treated material adhered and became a cohesive mass.

Another issue identified during these tests is the density of the solidifier. If the agent was lighter than the oil, which is the case with most agents, the top surface of the oil was solidified and the agent did not penetrate the remaining oil. Mixing of the agent with the oil was always the issue and the resultant solidified masses were often quite heterogenous.

Throughout this testing few end points other than the disappearance of free oil were used. Measurement of viscosity and penetration was used, but an acceptable procedure was not found. This is probably because of the heterogeneity of the solidified mass. Sampling error may also be a cause. It should be noted that all researchers felt that the disappearance of free oil method resulted in good repeatability. Further discussion on this will be given in the analytical section below.

Rosales et al. tested the effectiveness of five solidifiers to remove Prudhoe Bay crude oil from artificial seawater in the laboratory by UV-Vis and GC/MS.[15] The performance of the solidifiers was determined by UV-Vis as a function of solidifier-to-oil mass ratios (SOR), water volume and surface area, and contact time. An SOR of 1:4 solidified crude oil from 58% to 84%. Under more severe test conditions (SOR 1:16) the material with better performance solidified 28% of the oil initially added to water. The percent mass of free oil remaining on the seawater at the end of the contact time was the same when measured by either UV-Vis or by GC/MS. Analyses performed using GC/MS revealed that oil solidification is not a selective process; n-alkenes and polycyclic aromatic hydrocarbons reacted at a similar rate for each solidifier. Infrared Spectroscopy was used to investigate the functional groups in the solidifiers.

Jadhav proposed a sugar to selectively gel oil on water.[16,17] Phase-selective gelling agents or solidifiers (called by the authors ‘gelators’) were synthesized from sugar alcohols using biocatalysis. The solidifiers showed an ability to phase-selectively gel only organic liquids including crude-oil fractions in the presence of water at room temperature.

Calorimetry and vapor suppression testing methods were used by Solomon to optimize the screening and selection of solidifiers.[18] The optimum dosage of the solidifiers and hydrocarbon liquids were determined. A solution calorimeter (Parr Instruments, Model No.6755) was used to measure the heat evolved or absorbed during solidification. A thermogram obtained from the calorimeter gave the temperature change and heat of solidification values of the commercially available solidifiers with the hydrocarbon liquids, e.g., gasoline, diesel, and transformer oil. A method for testing the VOC concentration of various solidifiers with the hydrocarbon liquids was developed. The speed of solidification and the integrity of the byproduct were determined from the heat of solidification values. The vapor suppression data was used to provide the comparisons between the different solidifiers to aid in solidifier selection in an oil spill scenario.

2.1.3 Tank tests

Only one tank test was carried out, that by Exxon in 1995.[13] Field application studies were carried out in the Imperial tank and a specialty insulation blower was used. The oils tested were gasoline, diesel, Bunker C and 3 different crude oils. The primary purpose was to assess the overall applicability of the technology on larger scale. The findings of the field application were that: the blower performed well, the application rate was about 1:1; waves of about 12 to 20 cm had little effect but the material broke into clumps; solidification increased with time and if the leading edge was treated and approached the shore, little retention on the shore was noted. Solidification increased with time and if the leading edge was treated and approached the shore, little retention on the shore was noted. Tests of recovery were carried out and fish netting was found to work well, containment booms also worked and the solidified oil could be removed to drums using shovels or wire-screen nets Disposal was found to be an issue and solidified diesel was still flammable and it was noted that vapours were released from the solidified oils.

2.1.4 Actual use

One of the producers of a micro-sorbent product provide recent use on their web-site.[19] These results are summarized in Table 4

Table 4 Uses of CI Agent (from CIAGENT website)

Waterway	Place	Product	CI used	Product Removed	Approx. Ratio*	Time**
McAlpine Dam	Louiseville, KY	hydraulic oil	25 gals	35 gal	0.3	4 hr
Ohio River	Louiseville, KY	oily sludge	962 lbs	534 gals sludge	0.2	6 hr
unidentified	Clewiston, FL	diesel fuel	55 lbs	55 gals	0.5	3 hr
manhole	Mid-Atlantic	vault oil	70 lbs	35 gals	0.2	2 hr
Creek	New Town Creek, NY	unspecified	boom	sheen only		na
Juniper Beach	Louisville, KY	diesel fuel	30 lbs	15 gal	0.2	3 hr
Channel	Jacksonville, FL	diesel fuel	boom	sheen only		na
Channel	St. Petersburg, FL	gasoline	boom	sheen only		na
Storm drain	Louisville, KY	diesel fuel	70 lbs plus booms	40 gals	0.2	3 hr
Highway	Jeffersonville, IN	diesel fuel	60 lb	40 gals	0.2	4 hr
Drain	Simpsonville, KY	hydraulic oil	35 lbs plus boom	15 gals	0.3	2 hr
Retention pond	Shelbyville, KY	diesel fuel	40 lb plus boom, pads	150 gals	0.1	8 hr
Channel	Reddington Shores, FL	diesel fuel	1 lb plus booms	sheen only		1 hr
Cooling Tower	Albama	lube oil	filter	reduce discharge		na
Secondary Containment	London, Ohio	transformer oil	containment			na

** ratio estimated by this author using the data on web site*

*** given on the web site as the time to clean up*

2.1.4 Analytical methods

Analytical means in any test system is a major concern. As noted, almost all tests were carried out using visual means, that is noting the presence of liquid oil. Most researchers also noted that this was repeatable. This is probably the reason that this means continued. Several researchers used penetrometers and viscometers to try to determine an end point.[7,10] These methods did not yield consistent results. One of the problems with these methods is that a sample must be removed for analysis, disrupting the test. Further, sampling a heterogeneous material often results in varying results..

The method used by Environment Canada (see Appendix A), uses visual testing and repeatability within less than 5% has been found. It has been found, however, that changing operators initially results in slightly greater discrepancy, but this is remedied with practice. This is an unsatisfactory situation, however, as a test should always be operator independent. Research on other end points were unsuccessful, although more effort could be applied.[7] Rea noted similar findings.[10]

2.2 Toxicity

The second important issue when discussing solidifiers is toxicity, both of the solidifier itself and of the treated oil.

A standard aquatic toxicity test is to measure the acute toxicity to a standard species such as the rainbow trout. The LC_{50} of a substance is the 'Lethal Concentration to 50% of a test population', usually given in mg/L, which is approximately equivalent to parts per million. The specification is also given with a time period, which is often 96 hours for larger test organisms such as fish. The smaller the LC_{50} number, the more toxic the product. The aquatic toxicity of solidifiers has always been low ($LC_{50} << 1000$) or not measurable as the products are not water-soluble.

There are some studies departing from the traditional lethal aquatic toxicity assay and also some that focus on the longer-term effects of short term exposures. There certainly is need for more of these types of studies. There is also a need to leave the traditional lethal assays and use some of the newer tests for genotoxicity, endocrine disruption and others.

2.2.1 Toxicity of solidifiers

The results of solidifier toxicity testing are similar to that found in previous years, namely that solidifiers have little aquatic toxicity. There are no studies departing from the traditional lethal aquatic toxicity assay and none that focus on the longer-term effects of short term exposures. Further there is a need to test the effects of the solidifier and treated oil on wildlife such as may come into contact with the products. Of particular concern is the potential for enhanced adhesion of the product.

2.2.2 Toxicity of the treated oils

No studies of the toxicity of solidifier-treated oils were found.

2.3 Biodegradation

No studies of the biodegradability of solidifiers or of solidifier-treated oil were found.

3 Other issues

3.1 Spill size

A review of the limited work to date shows that solidifiers appear to work only on very small and thin spills.[9,12] This is because the solidifiers mix poorly on large and thick spills. Further it is difficult to apply solidifiers at controlled rates on larger spills and to provide adequate mixing.

3.2 Solidifier use in recent times

Because of the pre-authorization of use in USA EPA region 4, several uses in that area have occurred.[19,20] These uses have limited documentation and no independent reviews. All of the spills have been very small as is the specification of the pre-authorization.

3. 3 Solidifiers or sorbents

One of the serious issues that must be dealt with is the difference between true solidifiers and sorbents.[20] Many of the products on the market today are polymer sorbents as noted above. It may not be satisfactory to classify these as solidifiers, however, there is a very fine line between these and similar products. These form a continuum to regular sorbents such as polypropylene pads, peat moss, etc. This question needs to be addressed by regulatory authorities because the leachability of the oil and disposal issues are quite different at the opposite ends of the sorbent spectrum. One of the specifications might be the oil leachability using a specific test.

3.4 Potential for sinking

There are concerns that solidified oil might sink.[20] No studies of the density of the final products have been performed, although no observations of sinking have been made in the limited testing and use to date.

3.5 Modeling solidifier and solidified oil behaviour and fate

There are no models that incorporate solidification nor are there any algorithms to incorporate into models. Since the use of solidifiers may be restricted to very small spills, this may not be a concern.

3.6 Solidified oil stability

No studies of the long-term stability of solidified oil have been made. Rea studied the solidified oil for 160 days, but did not conclude anything in particular about the stability of these products.[10]

3.7 Fate of un-reacted solidifier

No studies of the fate of un-reacted solidifier have been carried. Concerns are not that great, however, with many of the current polymer sorbents.

3.8 Recovery of solidified oil

In recent uses, most solidified oil was recovered using hand tools such as shovels, ranks and pool nets. Dahl et al. suggest the use of fishing nets or nets that were developed for the recovery of heavy oil. Recovery is another factor that may restrict the use of solidifiers to small, nearshore spills.[13]

3.9 Solidification time

Solidification time is very important and is partially dependent on the reactivity of the treating agent itself. If the reaction time is very fast, crusting occurs and the oil will not be completely solidified. If the reaction time is too slow, the product is not useful. It is suggested that solidification time might best occur between 10 to 60 minutes to have optimal use on typical small spills.

3.10 Application systems

Only Dahl et al. developed systems to apply solidifier by modifying an insulation blower. Since current applications are to small, nearshore spills, manual application is carried out.[13]

3.11 Reduction of flash point

Limited testing by some researchers showed that fuel flash points were not reduced by solidification.[10,13] There is no chemical or physical reason to assume that flash points would be altered by the use of typical solidifiers.

Solomon et al. used calorimetry and vapor suppression testing methods to optimize the screening and selection of solidifiers.[18] A method for testing the VOC concentration of various solidifiers with the hydrocarbon liquids was developed. The speed of solidification and the integrity of the byproduct were determined from the heat of solidification values. The vapor suppression data was used to provide the comparisons between the different solidifiers to aid in solidifier selection in an oil spill scenario. No evidence that solifidifiers actually reduced real flash point was given.

3.12 Assessment of the use of solidifiers

Several authors have assessed the use of solidifiers from a non-technical perspective.[21-29] The general conclusions of these documents are that solidifiers could be safely used on small spills. None of the documents addressed the operational definition of solidifiers.

3.13 Disposal Methods or Recycling

Little work has been carried out on disposal of used solidifiers and the solidified mass of oil. Leachate testing carried out on some products reacted with oil, suggest that these products could be safely disposed of in a landfill. Incineration is also possible in some jurisdictions. Recycling has not been tried or at least has not been mentioned in the literature.

4 Summary on the considerations for the use of solidifiers

Solidifiers have not been used or studied to the extent that operational considerations or uses can be definitively stated. Considerations include:

- Solidifiers may be useful on very small spills, close to shore where product can be recovered,
- The long-term fate of solidifiers and solidified oil in the environment has not been studied,
- Some of the products currently touted as solidifiers are actually sorbents,
- Mixing of solidifiers with oil is very difficult due to high reactivity with first oil encountered, and density difference problems,
- There is no reduction of flash point or other inherent chemical properties of the oil.

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Appendix A - Testing Procedures from Environment Canada

Solidifier Test Procedures Used in Early Years

1.a. Equipment: Stirrer stop watch analytical balance
1.b. Supplies: Jar ASMB (Alberta Sweet Mixed Blend) standard oil saltwater spatula
1.c. Procedure: 200 mL of seawater is placed into jar and 20 mL of the standard oil is weighed and placed on the water. A stirrer (Labline model 200 or equivalent) is placed at the oil-water interface and is turned on. After one minute, quantities of the solidification agent are added at 1-minute intervals from a pre-weighed container. A plastic spatula is used to test the solidity of the oil. When the oil is solid as determined by a viscosity of 1,000,000 or the visual equivalent, the weight of solidifier added and weight of the oil are used to calculate the percentage required to solidify.

Oil Solidifier Effectiveness Test Used 1998 to Present

Purpose – The purpose of the test is to determine the effectiveness of a solid Spill Treating Agent (STA) in solidifying a standard oil under specific laboratory conditions. This allows for the assessment of an STA product as a spill countermeasure, as well as comparison with other products of the same class.

Brief Description of the Test

The product is added in weighed increments to a known mass of standard oil with mixing. The end point is reached when the oil mass no longer moves freely, and the exposed water surface lacks a sheen of oil. The effectiveness value is reported as the percentage required to solidify.

Equipment and Supplies

500 mL 3.3% (w/v) sodium chloride solution
20 mL standard oil
1 litre beaker, 10 cm ID
Mixer with 3 blade impeller, 1.5 cm width and 3 cm radius
Balance, min. 10 mg accuracy
Weighing boat
Scoop or spoon
Timer

Procedure

1. All materials are allowed to reach room temperature prior to starting. The oil is mixed thoroughly and the agent homogenized as required.
2. Add 500 mL of 3.3% sodium chloride solution to a 1 litre beaker.
3. Weigh a syringe containing 20 mL of standard oil. Carefully add the 20 mL of oil to the surface of the salt water. Weigh the empty syringe to determine the mass of oil.
4. Insert a 3-blade mixer into the beaker, adjusting such that the impellers are just at the surface. Begin mixing at 75 RPM and continue for 1 minute.
5. Weigh 1.0 g of solidifier agent into a weighing boat. Record the mass to at least two decimal places.
6. Add the solidifier agent to the oil slick between the mixing blades and the beaker walls and observe.
7. Continue adding solidifier agent in 1.0 g increments at 1 minute intervals until there is a

significant change in oil properties.

8. Continue adding solidifier agent in 0.1 g increments at 1 minute intervals until the end point is reached.

9. The end point is defined by an immobile oil slick and the lack of a sheen on exposed water surfaces.

10. The contents are continuously stirred for a minimum 20 minute period, regardless of the time required to reach the end point.

Calculation

The sum total of solidifier agent added is divided by the initial mass of the oil to provide the ratio of solidifier-to-oil. The result of the test is reported in percentage form.