A Review of Literature Related to Oil Spill Solidifiers
1990-2008

for

Prince William Sound Regional Citizens' Advisory Council (PWSRCAC)
Anchorage, Alaska

by

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Abstract

This report is a review of the limited literature on oil spill solidifiers published from 1990 to August 2008. The report identifies and summarizes data on solidifier effectiveness, composition, and application.

The prime motivation for using solidifiers is to recover very small oil spills. A major issue is the actual effectiveness or advantage over sorbents or mechanical recovery. Once solidifiers are used, the 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, 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. 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 these 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 better protocols. More laboratory work is needed on the stability of solidified oil and other aspects of the solidifier issue.

Few 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.

Executive Summary

Overall

The literature on oil spill solidifiers between 1990 and 2008 is very scarce, consisting of only about 10 reviewed papers. For this reason, secondary sources, web sites and private communications were also used. Solidifier literature largely focuses on potential uses, rather than actual experience. Recent use of solidifiers on very small spills appears to be successful, however, this has not been critically reviewed by independent outside parties. There are many research gaps on solidifiers, almost every aspect remains unknown. It is important to recognize that at least three fundamental types of solidifiers have been marketed. Each of these types has somewhat different advantages and different characteristics.

Types of Solidifiers

There are three types of solidifiers, polymer sorbents, cross-linking agents and polymers with cross-linking agents. The types have unique characteristics and properties. Polymer sorbents, common at this time, simply adsorb oil into spaces between polymers. Oil is only held into these spaces by weak forces. Cross-linking agents form chemical bonds between molecules in the oil. Polymers with cross-linking agents also form chemical bonds. The latter two agents may react quickly and thus result in incomplete solidification if not rapidly mixed.

Reactivity and Reaction Time

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. If this is mixed after the solidifier is expended, chunks of solidified oil will be mixed with liquid 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. Therefore reaction time and agent reactivity are of concern.

Effectiveness Testing Overall

Effectiveness is an issue with oil spill solidifiers. Many factors influence solidifier effectiveness, including oil composition, sea energy, state of oil weathering, the type of solidifier used and the amount applied. Temperature and salinity of the water may not be as important as with dispersants. More emphasis might be put on monitoring effectiveness on real applications to provide real information for assessment.

Laboratory Effectiveness Tests

Bench scale testing has been conducted on a limited basis several years ago, only three past series of tests were recorded and only one continuous test program. A major disadvantage is that it is difficult to scale the results of these tests to predict performance in the field. Several factors that are difficult to extrapolate include application ratio, time to solidification and completeness of solidification. Bench scale tests are very useful for determining the effectiveness of various solidifier-oil combinations, effects of oil composition and effects of oil weathering.

Tank Testing

Tank testing was only conducted once in the literature reviewed. The tests were useful for examining the effectiveness of some application methods and determining the field amounts of solidifier needed, typically about twice that of the laboratory tests.

Analytical Methods for Effectiveness

Analytical methods are an essential for effectiveness testing. Current methods rely on visual means, namely the presence of liquid oil. Some parties have used penetrometers and viscometers, but the data base is not broad enough to know if this will be repeatable and accurate.

Toxicity of Solidified Oil and Solidifiers

The results of solidifier toxicity testing have been restricted to looking at aquatic studies. Since the present generation of solidifiers are not water-soluble, it is no surprise that all products appear nontoxic. Other forms of toxicity have not been investigated. Further the effects of solidified oil, partially-solidified oil and raw solidifier on various wildlife has not been investigated. Included in this should be ingestion, contact, adhesion and inhalation of particulate matter.

Spill-of-Opportunity Research

Accurate and precise data from real spills would be most useful in making assessments for future use. Essential data needs include: effectiveness values, time to solidify, percentage solidified given wind and water conditions, long-term data and detailed component analysis of the solidified oil with time. Effectiveness monitoring at actual solidifier operations could provide very useful information for future assessment, modeling and basic understanding of solidification. Emphasis must be placed on obtaining accurate and precise data.

Solidifier Use in Recent Times

Solidifier use in recent times is not well-documented. There is some web-site data by venders. Scientific assessment of solidifier effectiveness at spill scenes is often not carried out.

Mixing Required to Solidify

An important issue is the thoroughness of mixing. Reports show that early tests revealed that the solidifier reacted with the first oil it contacted, then formed a harder layer which prevented penetration of further agent. The end result was solidified outer crusts on liquid interiors. In some cases, subsequent mixing broke the crusts and turned the oil into a mixture of liquid and solidified oil. This may also relate to the thickness of the oil treated. Thin sheens would be more homogeneously mixed without the addition of much or any energy.

Stability of Solidification

No real tests have been carried out on the long term stability of solidified oil. In the limited uses that have been carried out, treated material was disposed of. The fate of unrecovered solidified oil is also relatively unknown.

Ability of Solidifiers to Reduce Flash Point

Specific tests on flash point have shown that the flash point of fuels is not reduced by the use of solidifiers.

Efficacy of Solidification in Alaskan Waters

The efficacy of solidifiers in Alaskan waters remains an issue. There are few data available on applications that would be relevant to offshore waters and as this report shows, this would not be a good use of solidifiers. Use of solidifiers for nearshore and very small, thin spills might be effective. Temperature does not appear to be a major issue, however, testing to date is very limited.

Weather and Application of Solidifiers in Alaska

Weather including temperature, winds and waves may be an important consideration for oil spill solidification. Effective solidifier use will probably not occur in Prince William Sound areas. Use of solidifiers for nearshore and very small, thin spills might be effective, however winds will certainly restrict application of solidifiers.

Fate of Unrecovered and Solidified Oil

There are few, if any, thoughts on what the long-term fate of solidified oil is. There are no studies on this matter.

Application Technology and Issues

There was some work on application issues in earlier times, however in recent times the solid agents are simply applied by hand.

Correlation of Oil Properties with Effectiveness

There are no detailed studies on this matter. Some early studies indicated that heavy oil might be difficult to solidify.

Recommendations for Further Research

All aspects of solidification require study, particular the fate of un-recovered and solidified oil and the effect of this on the environment.

List of Acronyms

ANS - Alaska North Slope - Usually referring to the crude oil mixture at the end of the pipeline

EPA - U.S. Environmental Protection Agency

GC - Gas chromatography - a separation technique that is very common

GCMS - Gas chromatography Mass Spectrometry - the mass spectrometry is a powerful analytical technique

IFO - Intermediate Fuel Oil - A mixture of Bunker C and diesel used for ship propulsion - eg. IFO 180 and 380 refer to the viscosity of the oil at about 38ºC.

LC50 or LC_{50} - Lethal concentration to 50% of the test population

LOEC - Lowest Observable Effect Concentration - the lowest concentration that produces a noted effect

NOEL - No-Effect Level

PAH - Polynuclear Aromatic Hydrocarbons

∑PAH - the sum of PAHs in a given sample

PWSRCAC - Prince William Sound Regional Citizens' Advisory Council

TPH - Total Petroleum Hydrocarbons - a measure of total hydrocarbons in a sample, usually by GC - FID

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1. Introduction

1.1 Objectives

The objectives of this review are to summarize the literature on solidifiers from 1990 to the current date (2008) and to synthesize the literature to answer key questions relevant to the Prince William Sound Regional Citizens' Advisory Council (PWSRCAC).

1.2 Scope

This review covers the literature from 1990 and to mid 2008. Solidifier literature is not abundant and because of such information from web-sites and government sources are also included. There are few peer reviewed scientific tests carried out on solidifiers and mostly in the very early 1990's and some of these were noted as preliminary. Much of the literature on solidifiers consists of speculative information on possible uses and effects.

1.3 Organization

The report begins with a summary and then provides a detailed review of the literature. A review of the overall solidifier situation is presented in Section 2 Further, the chemistry and types of solidifiers are presented. In Section 3, the major issues of on effectiveness and possible uses, are discussed. In Section 4, other issues, particularly those relevant to PWSRCAC, are summarized as drawn from the literature review. Section 5 presents summaries of recommendations and this report's recommendations. Section 6 is a detailed review of the new literature, reference by reference. The literature is divided into peer-reviewed literature, reviewed conferences and 'grey' literature, that is literature which may not have undergone external review. Finally, Appendix A gives information on Environment Canada testing and Appendix B gives more details on methodology for this report and observations.

2 Overview of Solidifiers

The use of solidifiers was never widespread and occurred infrequently about every 10 years since the 1960's when the notion 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, 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. Many of the questions asked about solidifiers have never been addressed by tests or research.

2.1 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. Similar to dispersants, 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.

2.2 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 meant 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. Large scale tests notes two situations where this issue was raised (Walker et al., 1994). A solidifier can potentially react with the oil it first comes into contact with, leaving the remaining oil untreated.

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 well studied and therefore remain largely as a topic for speculation.

2.3 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. Exact details of most products are proprietary and thus only a general presentation can be made here.

2.3.1 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. There is no chemical bonding, van der Waals forces hold the oil between polymer strands. Figure 1 shows a scheme on 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.

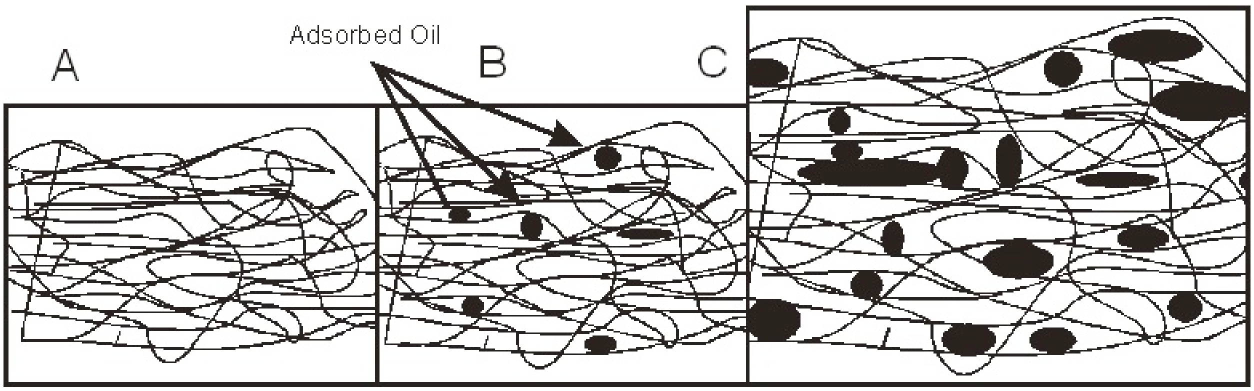

Figure 1 Schematic of the Process of Polymeric Adsorption. Figure 1A shows a schematic of a typical polymer which on a micro-scale has spaces. If added to oil these polymers start absorbing oil as shown in Figure 1 B. The final product is shown in Figure 1C where the polymer matrix swells with the absorbed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

Many polymers are capable of being solidifiers. Generally, the 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. 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.

2.3.2 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 or absorb that 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 below:

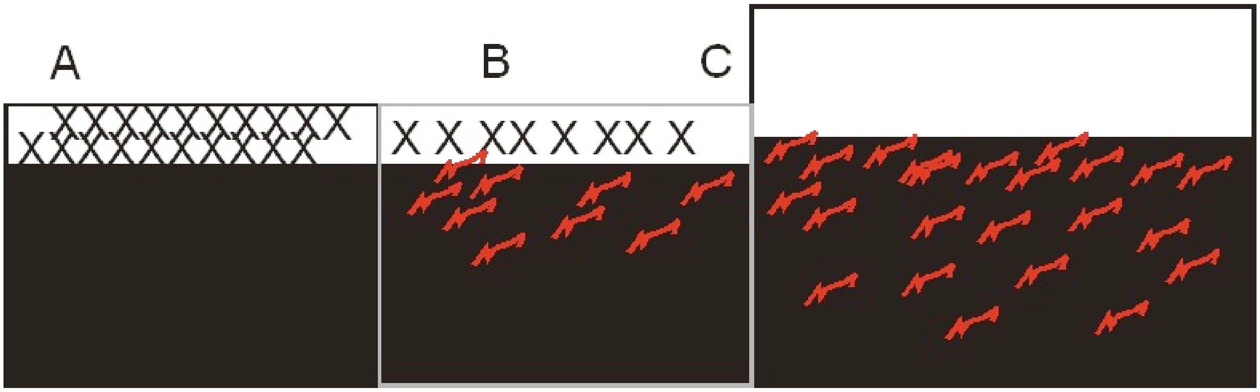

Figure 2 Schematic of the Process of Cross-Linking. Figure 2A shows a schematic of oil with the X's being the cross-linking agent. If added to oil these agents start to cross-link various oil components as shown in Figure 2 B by the jagged lines. The final product is shown in Figure 2C where the agent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

Figure 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 mostly 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 (1999) made a new series of oil treating agents which solidify oil. 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.

2.3.3 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 below.

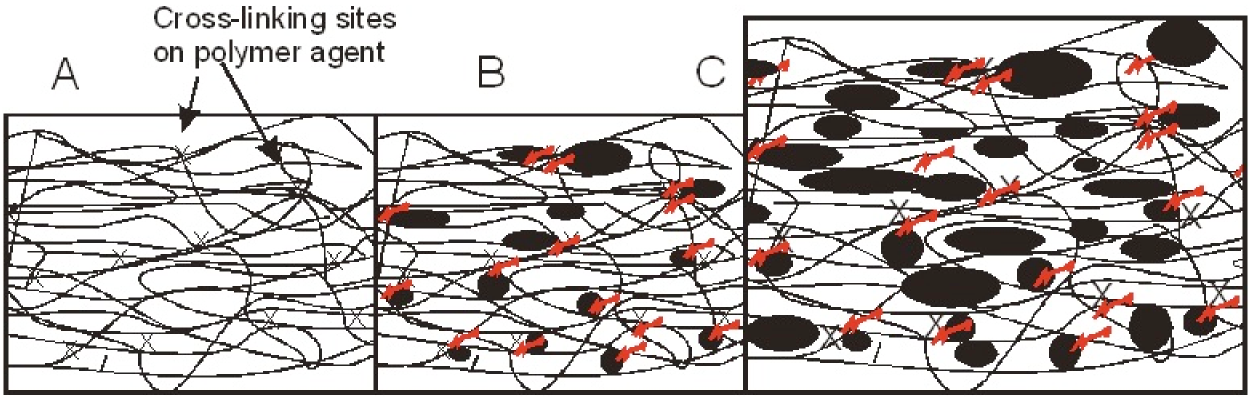

Figure 3 Schematic of the Process of Polymeric Sorption Combined with Cross-Linking. Figure 3A shows a schematic of oil with the X's being the cross-linking agent on the ends of polymers. If added to oil these agents start to adsorb oil and cross-link various oil components as shown in Figure 3 B by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

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

A product called RigidOil by British Petroleum that was an agent of this type, is of interest because the composition was widely disclosed (Meldrum et al., 1981). The agent consisted of two liquids which were generally mixed shortly before applying to the oil. The one liquid consisted of a 10% maleinized polybutadiene of molecular weight 8000 with 50% of odorless 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 report.

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 with the oil on the top. This type of agent may also adhere to booms, docks and other carbon-containing materials.

3 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.

3.1 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, and phenomena.

3.1.1 Field Trials

Several field trials were carried out on the British Petroleum product, RigidOil (McGibbon et al., 1982). 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 (McGibbon et al., 1982). 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) (McGibbon et al., 1982). 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 (Fingas et al., 1994). 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. (1999) tested the solidifier product, Nochar A 650, by putting the granular product on oiled test plots near a shoreline. 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.

3.1.2 Laboratory Tests

Laboratory tests were carried out by Environment Canada over several years (see Appendix A), 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.

Rea (1991) tested 7 pure polymer or cross-linking chemicals with diesel fuel. 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.

Ghalambor (1996) tested 23 available solidifiers. 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 (Dahl et al., 1996). 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 3.5.

Pelletier and Siron (1999) tested their new silicone solidifier using a light crude oil, Brent. A procedure similar to that in Appendix A was used. 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.

Throughout this testing no end point other than the disappearance of free oil was used. Measurement of viscosity and penetration was used, but an acceptable procedure was not found. It should be noted that all researchers felt that the disappearance of free oil method did result in good repeatability.

3.1.3 Tank Tests

Only one tank test was found, that by Exxon in 1995 (Dahl et al., 1997). 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. Tests of recovery were carried out and fish netting was found to work well, containment booms also work 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.

3.1.4 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 (Fingas et al., 1994; Rea, 1991). 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 is difficult.

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 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 (Fingas et al., 1994).

Rea (1991) noted similar findings.

One method that requires investigation is the use of a modified viscometer which is applied in a similar manner as the Environment Canada test. The end point would be the apparent viscosity of a certain value for a given oil.

3.2 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 (LC50 << 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.

3.2.1 Toxicity of Solidifiers

The results of solidifier toxicity testing are similar to that found in previous years, namely that solidifiers have no 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.

3.2.2 Toxicity of the Treated Oils

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

3.3 Biodegradation

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

4 Other Issues

4.1 Spill Size

A review of the limited work to date shows that solidifiers appear to work only on very small and thin spills (Fingas et al., 1991; Dahl et al., 1996). 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.

4.2 Solidifier Use in Recent Times

Because of the pre-authorization of use in EPA region 4, several uses in that area have occurred (Michel et al., 2008; CI Agent website and others). 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.

4. 3 Solidifiers or Sorbents

One of the serious issues that must be dealt with is the difference between true solidifiers and sorbents (Michel et al., 2008). Many of the products on the market today are polymer sorbents as noted above. It may 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 newly-defined test.

4.4 Spills-of-Opportunity Research

There is need for real data on actual treatments. Because of the nature of solidifier use - rapid and on small slicks, this may be difficult to collect. Independent research on actual use is needed.

4.5 Potential for Sinking

There are concerns that solidified oil might sink (Michel et al., 2008). 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.

4.6 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 an issue.

4.7 Solidified Oil Stability

No studies of the long-term stability of solidified oil have been made. Rea (1991) studied the solidified oil for 160 days, but did not conclude anything in particular about the stability of these products.

4.8 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.

4.9 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. (1997) 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.

4.10 Overall Effects of Weather on Solidification

Solidification is very dependent on mixing. Application of the agent is dependent on the presence of low winds. This also restricts the use solidifiers to small, nearshore spills.

4.11 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.

4.12 Monitoring Solidifier Application at Actual Spills

The purpose of monitoring is to determine if a solidifier application was relatively effective or not; to provide information to the responders and to provide scientific information for solidification. Emphasis must be placed on obtaining accurate and precise data.

4.13 Correlation of Solidifier Effectiveness with Oil Properties.

No specific scientific studies have been carried out.

4.14 Use of Solidifiers on Land or Shore

Specific studies are needed to determine the benefits, fate and applications of solidifiers on land or shorelines. Questions about adhesion of plants and other biota arise. Other questions such as the ability of the solidifier to slow or stop penetration downwards, should be answered.

4.15 Application Systems

Only Dahl et al. (1997) developed systems to apply solidifier by modifying an insulation blower. Since current applications are to small, nearshore spills, manual application is carried out.

4.16 Reduction of Flash Point

Limited testing by some researchers showed that fuel flash points were not reduced by solidification (Rea, 1991, Dahl et al., 1997). There is no chemical or physical reason to assume that flash points would be altered significantly by the use of typical solidifiers.

5 Recommendations for Further Research

This study shows that there are several important data gaps such as:

1. What is the long term fate of solidifiers and solidified oil in the environment given that they may be released?
2. What are the other wildlife toxicological implications of using the technology such as ingestion and adhesion?
3. Data of all types from several real applications should be collected and assessed.
4. Data must be correlated to the exact type of solidifier as each of the three types is different and there may be even more variations.
5. More exacting comparisons of different cleanup techniques are needed.
6. Analytical methods should be developed for laboratory tests.
7. Laboratory tests should be conducted to examine the many chemical and physical aspects of solidification including stability, long-term stability, etc.
8. Much of the emphasis at this point of time should be placed on fundamental studies, such as careful chemical, physical studies, toxicological mechanism studies, etc.
9. Studies on the biodegradation of solidifiers and solidified oil are needed.
10. Studies on the fate of solidified oil in landfills are needed.
11. A study on the density changes upon solidification with various oil types should be carried out.
12. A small study on optimizing hand application of solidifier agent is needed. and,
13. Studies on mixing and solidification of oil should be carried out.

6 Detailed Literature Review

6.1 Peer-Reviewed Literature

Delaune, R.D., C.W. Lindau, and A. Jugsujinda, "Effectiveness of "Nochar" Solidifier Polymer in Removing Oil from Open Water in Coastal Wetlands" *Spill Science and Technology Bulletin*, *Vol. 5*, pp. 357-359, 1999.

A solidifier product, Nochar A 650, was tested by putting the granular product on oiled test plots near the shoreline. Four days after the application, the oil was removed by hand. The findings were that the solidifier reacted 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%.

Fingas, M.F., R. Stoodley and N. Laroche, "Effectiveness Testing of Spill-Treating Agents", *Oil and Chemical Pollution*, *Vol. 7*, pp. 337-348, 1991.

Solidifiers are those agents that often consist of polymerization catalysts and cross-linking agents. Three solidifiers were tested by Environment Canada in the past without using standard procedures: 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. 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. 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.

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. 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 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.

Pelletier, E., and R. Siron, "Silicone-based Polymers as Oil Spill Treatment Agents", *Environmental Toxicology and Chemistry, Vol. 18*, pp. 813-818, 1999.

A new series of oil treating agents which solidify oil was made and tested. 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.

Walker, A.H., J.H. Kucklick and J. Michel, "Effectiveness and Environmental Considerations for Non-Dispersant Chemical Countermeasures" *Pure and Applied Chemistry*, *Vol. 71*, pp. 67-81, 1999.

Various treating agents are reviewed including solidifiers. Solidifiers are divided into two categories, traditional solidifiers and gelling agents. The latter are so-called because they form a gel-like substance, do not solidify and sometimes can be returned to the former state. Older effectiveness tests are reviewed. Solidifiers are said to be nontoxic and a LC_{50} value of > 10,000 to Artemia is quoted.

6.2 Reviewed Conference Proceedings

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

This paper reviews the potential of solidifiers, beginning at laboratory tests and ending with tank tests with full-scale application equipment. The laboratory test included application of solidifier to oil until no visible oil remained on the water surface. 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 ranged from a ratio of about 1.5 to about 3.5. Field application studies were carried out in a field tank and a specialty insulation blower was used. 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. Tests of recovery were carried out and fish netting was found to work well, containment booms also work and the solidified oil could be removed to drums using shovels or wire-screen nets. Disposal was found to be an issue and several disposal options were evaluated.

Dahl, W.A., R.R. Lessard and E.A. Cardello, "Recent Research on the Application and Practical Effects of Solidifiers" in *Proceedings of the1997International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 391-395, 1997.

This paper reviews a series of studies that were carried out on solidifiers, beginning at laboratory tests and ending with tank tests with full-scale application equipment. The laboratory test included a modification of the Environment Canada test (described in Appendix A in this report) 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 oils tested were 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 form a firm solid mat with all of the oils tested. The salt level did not have an effect on solidification. The solidifiers used range from a ratio of about 1.5 to about 3.5. Field application studies were carried out on a field tank and a specialty insulation blower was used to apply the product. 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. Tests of recovery were carried out and fish netting was found to work well, containment booms also work 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.

Fingas, M.F., D.A. Kyle, N.D. Laroche, B.G. Fieldhouse, G. Sergy and R.G. Stoodley, "The Effectiveness Testing of Spill Treating Agents," *The Use of Chemicals in Oil Spill Response*, *ASTM STP 1252*, Peter Lane, Ed., American Society for Testing and Materials, Philadelphia, pp. 286-298, 1995.

Solidifier agents often consist of polymerization catalysts and cross-linking agents. Three solidifiers were tested by Environment Canada in the past: 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. During tests conducted in the laboratory, all three agents functioned, but required large amounts of agent to effectively solidify the oil. 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. 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.

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. 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 Appendix A. The aquatic toxicity of these products was measured and in all cases for the products listed, exceeded the maximum test value.

Michel, J., P. Keane and B. Benggio, "Pre-authorization for the Use of Solidifiers-Results and Lessons Learned" in *Proceedings of the 2008 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 345-348, 2008.

The RRT for EPA region 4 has allowed the use of solidifiers, as listed on the National Products Schedule in the USA, to be used as an alternative to sorbents or mechanical recovery for the removal of small or thin sheens from water, or small amounts of oil from land. Guidelines were developed for conditions where solidifiers could be pre-authorized for use, specifying type so oil, on spill of less than 500 gallons. For this condition, no more than 1000 pounds of solidifier in loose form could be applied during a spill event. There were requirements for complete containment and recovery of material.

One lesson learned was the difference between a sorbent and a solidifier and these definitions, it was felt, require much more work. According to some definitions, a sorbent is inert and insoluble and is a material which picks up the spilled materials and retains it through its molecular structure by adsorption or adsorption. A solidifier, on the other hand, has some form of chemical reaction with the target liquid. Chemical agents could include agents that coagulate, emulsify, congeal, entrap, fix, make the mass more rigid or viscous.

Some solidifiers have been shown to be effective on many types of oil, and as mixing with viscous oils is difficult, solidifiers are considered to be more effective with lighter oil types. Examples of sources of spills where solidifiers might be used include: 1) Spills to water in marinas, ports, harbors, and industrial areas where: spills occur frequently; spills are mostly light refined products; water currents are slow; products could be stored at likely spill sources and facility staff can be trained in proper use, recovery and disposal; 2) Spills on land where; spill oil could flow into ditches or creeks; oil could soak into the ground; facility staff can be trained in proper use, recovery and disposal; and example facilities include fueling and loading stations, rail yards and fuel storage sites.

Environmental concerns appear low as solidifiers are insoluble and thus have no acute aquatic toxicity. Other concerns include: toxicity associated with ingestion of unreacted product; ingestion or fowling of treated oil or partially treated oil; treated oil interaction with sensitive habitats and if treated oil could be persistent in the environment and possible sink over time.

The pre-authorization conditions include: product information to be given to be listed on the NCP product schedule; amount of oil to be treated would not exceed 500 gallons for loose product; no restriction on contained product in booms or pillows or pads; restriction on the amount of product used in a single treatment, a maximum of 1000 pounds; and several application recovery and disposal requirements as noted below. On water, recovery must be conducted as soon as the product is no longer effectively removing oil. The loose product must be applied directly onto the oil; booms and pads can be deployed in flowing waters but must be monitored and replaced if containment is an issue; loose product can only be applied by trained personnel; loose product cannot be applied directly to wildlife; and all product and treated oil will be recovered. On land the restrictions are similar and include: loose product can be applied only directly onto oil or to create a barrier ahead of an oil flow; booms or pads can be placed in drain areas to intercept oil and authorization does not extent to aquifers or areas where recovery is not possible. There are monitoring requirements covering the effectiveness and effects of the application including; the product to oil ratio needed to solidify the oil; the properties of the treated oil; the efficiency of treated oil recovery; and the degree of damage to the substrate and vegetation during the operation. The reporting requirements are: the amount of loose solidifier used; type and amount of oil treated; weight and/or volume of treated oil recovered; and evaluation of the application effectiveness. A placard is proposed to provide some of this information for training or near use areas.

Scholz, D., J. Boyd, A.H. Walker and J. Michel, "Using the Selection Guide for Spill Countermeasures Technologies in Response Decision Making and Planning" in *Proceedings of the 2001 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 797-803, 2001.

The paper is a review of decision-making on treating agents using the NCP guide. It is noted that for solidifiers that they are applicable at the start of a spill to surface oils of most types and for spills no large than 1000 gallons (4000 L). They would be useful for most weather conditions given low winds.

Walker, A.H., J.H. Kucklick, A. Steen and D. Fritz, "Oil Spill Chemicals in Freshwater Environments: Technical Issues" in *Proceedings of the 1995 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 15 p., 1995.

This is a review of the use of oil spill treating agents in a freshwater environment. The basic questions to be asked include: Does the product produce the desired result? That is, does the product do what it is intended to do? Does the test mimic field conditions? Is the products's effectiveness influenced by variables such as oil type, oil amount and air and water temperature? What application method(s) are necessary to achieve effectiveness.

Walker, A.H., J.H. Kucklick, J. Michel, D. Scholz and T. Reilly, "Chemical Treating Agents: Response Niches and Research and Development Needs" in *Proceedings of the 1995 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., 14 p., 1995.

A variety of treating agents and their possible niches in oil spills are reviewed. Solidifiers are speculated to have potential to stop rapid oil spreading. Benefits have not really been evaluated at this point in time but are thought to be applied to lighter oils and also might protect wildlife. There are concerns about the amount of product required to solidify oil and the practicality of mixing the oil and product, particularly if the solidifier has two components. Research needs include: the mechanism of action; effectiveness determination; mesoscale and field effectiveness tests; need to develop a conceptual model of the fate and toxicity of treated versus untreated oil; and the need to develop field effectiveness criteria.

Walker, A.H., R.G. Pond, and J.H. Kucklick, "Using Existing Data to Make Decisions About Chemical Countermeasure Products" in *Proceedings of the 1997 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 403-408, 1997.

The paper is a review of decision-making on treating agents. It is noted that for solidifiers there are not sufficient data to decide on use in an open environment, and that there is a very limited need to do so. An effectiveness test is needed as well as laboratory and field data.

Walker, A.H., D. Scholz, J.N. Boyd, E. Levine and E. Moser, "Using the Pieces to Solve the Puzzle: A Framework for Making Decisions About Applied Response Technologies" in *Proceedings of the 2001 International Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp. 503-508, 2001.

The paper is a review of the NCP Applied Response Tool Evaluation System (ARTES) and the selection guide as decision-making tools for the use of oil spill treating agents.

6.3 ‘Gray’ Literature (not formally peer-reviewed)

CI Agent Website, http://www.ciagent.com/,Accessed 2008.

The following is a list of CI Agent uses listed on their website. The results are theirs, however the ratio of agent to recovered product was estimated from their data.

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	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	15 gals	0.3	2 hr
Retention pond	Shelbyville, KY	diesel fuel	40 lb plus l	150 gals	0.1	8 hr
Channel	Reddington Shores, FL	diesel fuel	1 lb plus b	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*					

The following is a table of their toxicity testing results:

Toxicity Measures of CI Agent		
Species	**Time**	**Result**
Red Abalone Development Test	48 hr.	LOEC >1000 mg/L
Fathead Minnow	96 hr.	LOEC >1000 mg/L
Rainbow Trout	96 hr.	LOEC >1000 mg/L
note the product is largely insoluble therefor tests are of limited value		

EPA, Environmental Protection Agency National Contingency Plan Product Schedule, http://www.epa.gov/OEM/content/ncp/product_schedule.htm, August, 2008.

This includes a listing of approved solidifiers under “Other Treating Agents” along with products such as sorbents and elasticizers.

Ghalambor, A., *The Effectiveness of Solidifiers for Combatting Oil Spills*, Louisiana Applied and Educational Oil Spill Research and Development Program, 68 p., 1996.

Tests on 23 available solidifiers were performed. 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.

A test was similar to that noted in Appendix A, with somewhat different quantities of water, however, 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. It was found that all three types of reactions were present.

Internet Search for Solidifiers Generally, 2008

Some Solidifier Products Noted on the Internet		
Product Name	**Internet Address**	**Past Use Info or Details**
Aqua N-Cap	http://www.tepcoproducts.com/public/productInfo.cfm?prodid=4	some
CI Agent	http://www.ciagent.com/	yes
Dawg	http://www.dawginc.com/spill-control-absorbents/gelling_agents_ar12.php	some
Nochar	http://env.loyola.com/products/granular/petro-lock.html	some
Petrobond	also Petrolock see Nochar	
Rubberizer	http://rubberizer.com/how.htm	yes

NRT-RRT, *Factsheet on Application of Sorbents and Solidifiers for Oil Spills*, USA EPA National Response Team, 6 p., 2007.

This is a fact sheet on sorbents and solidifiers, attempting to differentiate these two products. Solidifiers are 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. Sorbents, on the other hand are materials such as organic products, mineral compounds or synthetic fibrous products. Solidifiers are polymers that have a physical attraction to oil that is enhanced by van der Waals forces. Oil bonds with solidifiers, but the exact mechanisms have not been studied in depth. There may be heat absorbed (endothermic) in the reaction.

Solidifiers should meet the following requirements: insoluble in water, specific gravity of less than 1.0; comprised primarily of polymers; contain less than 5 ppm of heavy metals and chlorinated hydrocarbons; have a physical reaction with the oil such that the oil resists leaching; do not release the liquids under pressure and the agent itself is nontoxic to wildlife. The environmental concerns with solidifiers include: possible sinking of the product or the treated oil over time (24 requirement); fate and bioavailability of unreacted product in the environment; and fate and behaviour of treated but unrecovered oil. Aquatic toxicity is not a concern because solidifiers are, by definition, insoluble.

The recommended application rates are from 10 to 50 percent by weight of the liquid to be recovered. The application should avoid product loss from winds. Some degree of physical mixing with the product is required. The reaction time is typically fast, 1 minute to 1 hour. It is noted that solidifiers work best with light to moderate oils.

Rea, B., *Analyses of Solidification and Fixation Parameters of Diesel Fuel when Blended with Chemical Polymer Gelling Agents*, New Mexico State University, 138 p., 1991.

Tests were performed on 7 pure polymer or cross-linking chemicals with diesel fuel. 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 is 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 approaches a constant level. The ratio of solidification was proportional to the mass of agent added. All the gelled fuels emit volatile organics at a declining rate over time. The leachability of BTEX was however, lowered by gelation. There is uncertainty about the long-term shelf life of the agents. Results are summarized in the following table:

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*

RRT III and IV, Selection Guide for Oil Spill Applied Technologies: Volume I: Decision-Making, Scientific and Environmental Associates, Ltd. For RRT III and IV, 367 p., 2003.

This is a decision-making document and provides a few general comments about solidifiers with extensive non-specific items about treating agents in general. The general requirements for solidifiers include: the fact that most products are granular and require broadcast systems to apply; mixing is generally needed; application rates vary from 10 to 50%; solidification times vary from immediate to 18 hours; and hand tools or nets can recover the solidified oil. Limiting factors include: effectiveness is likely to be low for emulsified, weathered or heavy oils; salinity has little effect; temperature may slow reaction; most agents float before and after reaction and must do so; if waves are present, clumps form rather than a large mass; solidifiers have relatively low toxicity; use of solidifiers require physical access to the spill scene; solidifiers will inhibit natural dispersion and evaporation; unrecovered solidified oil weathers slowly; use of solidifiers will impair the operation of conventional recovery equipment; and disposal options may be limited for solidified oil.

RRT Team IV, "Regional Response Team IV, Pre-Authorization Policy for the Use of Solidifiers", Regional Response Team IV, 33 p., 2006.

This is a policy document stating how solidifier might be used and under what conditions. Solidifiers are noted as have the following benefits: immobilize the treated oil so it will not spread further or down; solidifiers can be added to the perimeter of the oil and thus prevent spreading; solidified oil can be removed with readily-available hand tools; solidifiers are effective on thin sheens whereas some sorbents do not pick up sheens; and solidifiers may be more effective on slow continuous releases than other methods.

Some solidifiers have been shown to be effective on many types of oil. Mixing with viscous oils is difficult, thus solidifiers are considered to be more effective with lighter oils. Examples of sources of spills where solidifiers might be used include: 1) Spills to water in marinas, ports, harbors, and industrial areas where: spills occur frequently; spills are mostly light refined products; water currents are slow; products could be stored at likely spill sources and facility staff can be trained in proper use, recovery and disposal; 2) Spills on land where; spilled oil could flow into ditches or creeks; oil could soak into the ground; facility staff can be trained in proper use, recovery and disposal; and example facilities include fuelling and loading stations, rail yards and fuel storage sites.

Environmental concerns appear low as solidifiers are insoluble and show no acute aquatic toxicity. Other concerns include: toxicity associated with ingestion of un-reacted product; ingestion or fowling of treated oil or partially treated oil; treated oil interaction with sensitive habitats and if treated oil could be persistent in the environment and possible sink over time.

The pre-authorization conditions include: product information to be given to be listed on the NCP product schedule; amount of oil to be treated would not exceed 500 gallons for loose product; no restriction on contained product in booms or pillows or pads; restriction on the amount of product used in a single treatment, a maximum of 1000 pounds; and several application recovery and disposal requirements as noted below. On water, recovery must be conducted as soon as the product is no longer effectively removing oil. The loose product must be applied directly onto the oil; booms and pads can be deployed in flowing waters but must be monitored and replaced if containment is an issue; loose product can only be applied by trained personnel; loose product cannot be applied directly to wildlife; and all product and treated oil will be recovered. On land the restrictions are similar and include: loose product can be applied only directly onto oil or to create a barrier ahead of an oil flow; booms or pads can be placed in drain areas to intercept oil and authorization does not extent to aquifers or areas where recovery is not possible. There are monitoring requirements covering the effectiveness and effects of the application including; the product to oil ratio needed to solidify the oil; the properties of the treated oil; the efficiency of treated oil recovery; and the degree of damage to the substrate and vegetation during the operation. The reporting requirements are: the amount of loose solidifier used; type and amount of oil treated; weight and/or volume of treated oil recovered; and evaluation of the application effectiveness.

Walker, A.H., J. Michel, G. Canevari, J. Kucklick, D. Scholz, C.A. Benson, E. Overton, and B. Shane, *Chemical Oil Spill Treating Agents: Herding Agents, Emulsion Treating Agents, Solidifiers, Elasticity Modifiers, Shoreline Cleaning Agents, Shoreline Pre-treatment Agents, and Oxidation Agents*, prepared for the Marine Spill Response Corporation, Washington, D.C., Technical Report Series 93-015, 328 p., 1994.

A variety of treating agents and their possible niches in oil spills are reviewed. Solidifiers are speculated to have potential to stop rapid oil spreading. Benefits have not really been evaluated at this point in time but are thought to be applied to lighter oils and also might protect wildlife. There are concerns about the amount of product required to solidify oil and the practicality of mixing the oil and product, particularly if the solidifier has two components. Some early laboratory tests are reviewed. Questionnaires were sent to 8 manufacturers and questions also included lead times and quantities of products available.

Notes on information received noted that several testers had found that solidifiers react with the first portion of the oil slick and continue to react there. Often, full solidification on a thicker slick does not occur, rather an object with a hard outer surface and liquid inside, is formed. Other items noted that the treated oil or agent is often very adhesive. This tendency is noted by the authors as being beneficial if one were to treat a rapidly spreading slick and might serve to contain it. Other limitations noted are the amount of product needed to treat a slick.

Workshop, Workshop Proceedings on *The use of Chemical Countermeasures Product Data for Oil Spill Planning and Response*, Xerox Document University and Conference Center, Leesburg, VA., 26 p., 1995.

This is a report on a workshop held to discuss the use of oil spill treating agents. With respect to solidifiers, the consensus is stated as: solidifiers may have uses but further study is recommended; there may be conditions where solidification may be beneficial to wildlife; solidification may prevent oil from penetrating a beach; solidifiers may not be beneficial to tidal flats and wetlands; and there may be site-specific concerns about the amount of product required for each application.

6.4 References

Meldrum, I.G., R.G. Fisher, and A.J. Plomer, “Oil Solidifying Additives for Oil Spills”, in *Proceedings of the Fourth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 325-352. 1981.

McGibbon, G., R.G. Fisher, I.G. Meldrum, and A.J. Plomer, “Further Developments in Oil Spill Solidification”, in *Proceedings of the Fifth Arctic and Marine Oil Spill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, pp. 199-216, 1982.

Appendix A - Testing Results from Environment Canada

Fingas, M.F. and B. Fieldhouse, Private Communication, Results from Environment Canada Testing on Solidifiers, testing conducted 1986 to 2008, Results given 2008.

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.

Test Results Table

The results of testing solidifiers over 20 years is shown in the following table. The results show that the effectiveness of the products vary widely, however the aquatic toxicity of all products tested is below the threshold of measurement.

Environment Canada's Testing of Solidifiers

AGENT	PERCENT [1] TO SOLIDIFY	TOXICITY[2] (AQUATIC)
A610 Petrobond	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
Petro Lock	44	>5600
SmartBond HO	45	>5600
Molten wax	109	>5600
Powdered wax	278	>5600

1Values are the average of at least 3 measurements, average standard deviation is 6

2 Values are LC_{50} to Rainbow Trout in 96 hours this shows that all are insoluble and less than can be measured

Appendix B Comments on the Methodology and the Literature

Methodology - Emphasis was placed on peer-reviewed literature in this report. Secondary emphasis was placed on papers in reviewed conference proceedings. The division of papers was on this same basis, ie. peer-reviewed papers, reviewed conference proceedings and then all others, or 'grey' literature. It should be noted that scientific quality does not reside only in the peer-reviewed literature and that there are some quality papers in the other two categories. There are perhaps also some questionable papers in the peer-reviewed literature. It should also be noted that several authors have similar papers in two or more of these categories. This is usually because their sponsor required a 'final' report and the authors also submitted a paper to a conference or a journal.

Papers that did not contain a significant amount of new information were summarized briefly. Many papers contain a lot of repetitive (compared to other papers) introductory material, as a necessity for their particular forum or venue. This introductory material was not repeated here.

Comments - The author has noted some points in preparing this summary:

1. Several papers do not contain modern references. Unfortunately some authors relied on out-dated (sometimes by 30 years) references. In many cases this was inappropriate since there was new, verified, differing information. This reflects on the oil spill field, that often very poor literature searches are carried out. Further, there are a lot of self-references which often are not useful.
2. Introductions to many of the papers contain many conventional or speculative statements on what solidifiers might be or do. These introductions were not useful in preparing this report.