

Effectiveness and environmental considerations for non-dispersant chemical countermeasures*

Ann Hayward Walkert†, Janet H. Kucklick¹ and Jacqueline Michel²

¹Scientific and Environmental Associates, Inc., 868 Robert E. Lee Blvd., Charleston, SC 29412, USA; ²Research Planning, Inc., 1200 Park St., Columbia, SC 29201, USA

Abstract: Mechanical countermeasures for oil spill response have various effectiveness and operational limitations under certain spill situations. This has led to an interest in and use of alternative treatment methods. This chapter reviews the potential utility of one such group, nondispersant chemical countermeasures, in controlling the adverse impacts from marine oil spills. The types of nondispersant chemical countermeasures presented here include: herding agents, emulsion treating agents, solidifiers, elasticity modifiers, and shoreline cleaning agents. Each countermeasure group is discussed separately to provide a definition, mechanism of action, and effectiveness and environmental considerations for the group. Where ever possible, examples are given of countermeasure use during an actual spill. In addition to the groups mentioned above, a few other treating agents are briefly described under the section ‘Miscellaneous Agents’ to illustrate other, less prominent types of chemical countermeasures.

Non-dispersant chemical countermeasures appear to have discrete *response niches*, i.e. situations where the countermeasures are well-suited and offer potential benefits. The key is matching conditions for optimal effectiveness with the appropriate incident-specific characteristics and window of opportunity. The practical aspects of logistics are not addressed because, if their potential utility can be demonstrated, the resolution of these issues would follow.

INTRODUCTION

The adverse impacts from marine oil spills are widely considered unacceptable therefore various actions are implemented to control and reduce the spread, movement, and environmental effects of spilled oil. For countermeasures to be effective, they must be strategically employed, given response objectives and the circumstances characterizing the specific spill incident. Timing is especially critical during the early stages of the spill when countermeasures are intended to control the spread of spilled oil. Figure 1 presents an overview of the various types of marine oil spill countermeasure strategies in relation to the phases of a marine oil spill (from a tanker or barge in open waters), that is, it indicates the windows of opportunity for their use.

Mechanical technologies have various limitations which have yet to be overcome. As public intolerance for oil spill impacts has grown, the interest in identifying other techniques to supplement and/or provide alternatives to mechanical countermeasures, has increased substantially over the last decade. This chapter reviews the potential utility of one of the groups of alternative oil spill treatment methods, i.e. nondispersant chemical countermeasures, in controlling the adverse impacts from marine oil spills. **Chemical countermeasures (or treating agents) are chemical substances which are added to spilled oil to change its physical or chemical properties so the oil is easier to control in a desired manner.** Most chemical countermeasures change the physical properties of the oil, e.g. dispersants which break up the oil into small droplets to reduce the threat of surface slicks, but some actually change the

*Pure Appl. Chem. 71(1) (1999). An issue of special reports reviewing oil spill countermeasures.

†Corresponding Author: Scientific and Environmental Associates, Inc., 325 Mason Avenue, Cape Charles, VA 23310, USA. E-mail: seahq@erols.com

<div style="display: flex; justify-content: space-around; border-bottom: 1px solid black;"> <div style="border: 1px solid black; padding: 2px;">Incident start (window of opportunity)</div> <div style="border: 1px solid black; padding: 2px;">...hours... (very early)</div> <div style="border: 1px solid black; padding: 2px;">...hours/days/weeks... (early)</div> <div style="border: 1px solid black; padding: 2px;">...months... (later)</div> </div>			
Phase Strategy	Stabilize/Secure Source	On-water Contain/ Recover/Protect	Shoreline Treatment/Cleanup
Mechanical	Close Valves Patch Pump/Offload	Boom, Skimmers Sorbents Vacuum trucks Dikes	Sorbents Manual Mechanical Equipment
Chemical		Dispersants Emulsion Treating Agents Solidifiers Herding Agents Elasticity Modifiers	Shoreline Cleaning Agents Solidifiers Bioremediation (nutrients)
Other Countermeasures		<i>In situ</i> Burning	Bioremediation (organisms) <i>In situ</i> Burning
Waste Management		On-site Storage Recycle Incineration	On-site Storage Recycle Landfill Incineration Bioremediation

Fig. 1 Potential roles of chemical treating agents during response to a major oil spill (after [1] as modified by [45]).

oil's chemical composition, e.g. bioremediation. Bioremediation is excluded from this section because it, like dispersants, is addressed separately. Those chemical treating agents which change the oil's physical properties do so through an interaction with the oil; those that change the oil's chemical composition actually promote a chemical reaction.

The types of nondispersant chemical countermeasures discussed here include: herding agents, emulsion treating agents, solidifiers, elasticity modifiers, shoreline cleaning agents, and miscellaneous agents. Only titanium dioxide beads, discussed under Miscellaneous agents, promote a chemical change in the oil; all others change the oil's physical properties.

There have been, and may be in the future, other types of chemical countermeasures. Most of the nondispersant chemical countermeasure types discussed in this chapter are those which are currently available, either in the U.S. or overseas. In addition, under the Miscellaneous Agents section, a few other treating agents are briefly described to illustrate other, less prominent types of chemical countermeasures. These agents, some of which have been considered in the past, as well as those that are currently being developed, have not yet faced the scrutiny of trial in major oil spill applications. As technology advances, it is likely that additional types of nondispersant chemicals, beyond the types discussed here, will be developed and considered for treating marine oil spills.

The information presented is largely based on research performed during a study [1] for the Marine Spill Response Corporation (MSRC), during which a world-wide survey of existing non-dispersant chemical countermeasures was conducted. This chapter updates the earlier study with recent data from field use of nondispersant countermeasures. Specific product names are mentioned only to provide examples of actual data; for details on a broad range of products, refer to the earlier MSRC study.

HERDING AGENTS

Definition and mechanism of action

Oil herding agents, sometimes referred to as collecting agents, are chemicals that have the ability to push or compress the oil on the water surface into a smaller area, to form thicker slicks that are more readily recovered [2]. These products work by exerting a spreading pressure on the water surface greater than the oil slick. They contain special types of surface-active agents to reduce the surface tension of water, thus increasing the spreading pressure.

Spreading pressure of a liquid is measured with a film balance, which measures the force exerted against a fixed barrier as the liquid is compressed into a smaller surface area. The two-dimensional spreading pressure or spreading force is expressed as newtons per meter (10^{-7} dynes/cm) on the boundary experiencing that force.

Effectiveness

An effective herding agent must have the following characteristics [2]:

- Remain a liquid at temperatures of potential use, i.e. 5–35 °C (41–95 °F);
- Spread spontaneously into a thin surface film on water;
- Have a low evaporation rate;
- Exhibit a spreading pressure generally $>35 \times 10^{-7}$ N/m, which is greater than most oils, but should be greater than the oil being treated;
- Be stable against forming emulsions;
- Have a low (less than 1%) oil and water solubility; and
- Does not disperse oil into the water during use.

Herders are most effective where they have something to push against (e.g. docks or semienclosed areas). Their use in the open sea is more limited.

Barger [3] tested 47 commercially available chemicals capable of controlling oil and found five passed the requirements outlined above. Several of those five were further tested in field trials where the surface area of the slick was reduced by more than 50% of the initial coverage. In the 1970s, one product was tested in subarctic waters and showed that it could keep an oil slick herded for at least 5 h [4]. In another study, three products were tested in temperate and Arctic conditions on three fresh crude oils. The products reduced areal coverage of thin oil layers by 85–95% within 1 minute. Their efficiency decreased only slightly with air temperatures below 0 °C [4]. In 1983, an oil herder was used in the Panama Canal during response to the *Texaco Connecticut* oil spill incident, however, results proved inconclusive [5].

Environmental effects

Herding agents are applied directly to the water surface, not on the oil, and do not disperse the oil or increase its solubility. Thus, the greatest environmental risk is the aquatic toxicity of the product alone to microlayer organisms and contact toxicity to intertidal vegetation. Because of their low application rates (2.5–35 L per linear kilometer), acute toxicity of these products is of concern only under special conditions, such as very shallow waters with limited flushing rates and abundant organisms of early life stages. There are no data on contact toxicity of these products to vegetation.

EMULSION TREATING AGENTS

Definition and mechanism of action

The purposes of emulsion treating agents, also known as demulsifiers, are to either: (i) prevent the formation of an emulsion (emulsion inhibitors); or (ii) break the emulsion into separate oil and water phases (emulsion breakers). Most emulsion treating agents are composed of hydrophilic surfactants which modify the properties of the oil/water interface, by displacing, mixing with, or chemically

neutralizing the naturally occurring emulsifying surfactant in the oil, thus inhibiting or destabilizing the emulsion.

The formation of stable water-in-oil emulsions has many effects on the physical behavior of spilled oil. Two effects are of particular concern to responders: (i) emulsions can contain between 50 and 80% water, thus increasing the volume of oil liquid to be recovered; and (ii) the viscosity of the emulsified oil increases dramatically, reaching up to 100 000 centistokes (cSt). Emulsions reduce the efficacy of skimming systems and are also difficult to burn or disperse.

Effectiveness

To be effective as an emulsion treating agent, a product should [6]:

- Possess a large enough free energy of adsorption; i.e. be more surface active than the emulsifying surfactant associated with the oil, so that the emulsion treating agent modifies the interfacial properties and promotes oil/water separation; and
- Decrease the emulsion tendencies of the original oil/water system to either prevent the formation of or break a water-in-oil emulsion.

Based on use of emulsion treating agents in petroleum production, different formulations are required for different oils. However, matching a product with an oil is more of an empirical process rather than a scientifically based evaluation of an oil's properties. Emulsion treating agents tend to be emulsion-specific.

Emulsion treating agents have been found to be effective in a number of laboratory and field trials. At the *Amoco Cadiz* oil spill in 1978 off the coast of France, demulsifiers were successfully applied in the vacuum trucks or storage tanks to increase the pumping efficiency [7,8]. Another product was tested following a spill of Basra Light crude oil in 1980, where it was added to drums of the collected oil. Immediately the collected oil became less viscous so that it could be pumped into waste disposal trucks [9]. Laboratory studies have indicated that emulsion treating agents applied in small amounts to fresh oils can inhibit or retard the formation of emulsions [10,11].

In 1989 field trials, the demulsifier premixed with the oil, as well as the demulsifier applied directly to the oil (via aerial spraying), increased slick spreading and reduced emulsion viscosity. In 1992 field tests with combined use of dispersants and demulsifiers [11,12] results indicated that 'treatment with demulsifier slowed down or reversed the formation and stabilization of emulsion. This led to a reduced slick area which dispersed faster than the control slick' [12].

Under laboratory and mesoscale conditions [13] a product, Vytac DM, was found to break emulsions and prevent their formation at concentrations as low as 500 p.p.m. During field trials, the product was shown to reduce viscosity (from 105 000 to 22 600 cSt) within 30 min after application [14]. During development of laboratory methods for testing of emulsion treating agents, Environment Canada found that several products were effective on stable emulsions with an agent to oil ratios as low as 1:500 [15].

Environmental effects

Environmental considerations can be divided into two categories: (i) direct toxicity of the product to water-column organisms and to birds and mammals on the water surface in the treatment area; and (ii) indirect effects of the product on oil behavior.

Using the same procedure as used for dispersants, the French Petroleum Institute concluded that demulsifiers were generally more toxic than dispersants. Further studies were conducted to determine the partition of demulsifier between oil and water. They concluded that 'taking into account the natural dilution of the settled water in the sea or the possibility of diluting it before its release to the sea, one can consider that the environmental impact related to the use of demulsifier in connection with skimming operations is limited' [8].

In laboratory studies, a crude oil (Galeota Mix crude from Trinidad; API gravity = 31.4) treated at the production platform with only 20 p.p.m. of emulsion treating agent was highly prone to breakup and

natural dispersion under moderate sea conditions [16]. The treated oil did not form stable emulsions until 23% of the oil evaporated, whereas the fresh, untreated oil formed stable emulsions. Lunel & Lewis [12], in field tests on oil slicks treated with an emulsion treating agent, showed that dispersed oil concentrations below treated slicks were five times higher than untreated slicks and covered a much larger area. They concluded that the treated slicks dispersed more readily. How emulsion treating agents, applied to inhibit emulsification of slicks at sea, affect the dispersion of the oil and increase the aquatic toxicity needs to be further evaluated in large-scale tests.

Another possible indirect effect of using emulsion treating agents to break emulsions of recovered oil is enhanced solubility of oil in the separated water relative to conventional recovery approaches. The presence of dispersed oil and greater solubility of the aromatic compounds could produce discharge water more toxic than that normally generated during gravity separation. Toxicity tests on the product alone, product plus oil, and separated water from both treated and untreated emulsions would allow comparisons of the relative changes in toxicity.

SOLIDIFIERS

Definition and mechanism of action

Solidifiers are products which, when mixed with oil, turn the oil into a coherent mass. They are usually available in dry granular form. Unlike sorbents that physically soak up liquid, solidifiers bond the booms, pads, or liquid into either a solid carpet-like mass or solid granular material with minimal volume increase. The bonded material also eliminates a dripping-sponge effect by not allowing the material to be squeezed out [17]. Most polymers can actually convert the oil to a solidified rubber-like substance. There is usually little change in the specific gravity of the treated oil. Products that are essentially sorbents are not discussed here because they are considered to be mechanical countermeasures.

Gelling agents, a subclass of solidifiers, are usually two or more compounds applied as separate entities that react and form a gel-like structure. The components are composed of polymerization catalysts and cross-linking agents [18] and must be mixed uniformly for gelling to occur. The mechanical strength of gels is weak, thus they often (depending on the dose rate) can be broken down and the oil returned to its original liquid state. Gelling agents do not solidify and therefore do not have the potential that commercially available solidifier products have as an oil spill response tool.

Effectiveness

The effectiveness of a solidifier is based on the amount of product and time it takes to 'fix' a given volume of oil. Fingas *et al.* [15] found in laboratory tests that 13–44% by weight of the product to oil was required to solidify Alberta Sweet Crude over a 30-min period. Effectiveness is likely to decrease for emulsified, weathered, thick, or heavy oils because of the difficulty of mixing the product into viscous liquids.

An extensive study on solidifiers was conducted by the Petroleum Environmental Research Forum (PERF) in 1993–95 [17]. In laboratory tests, solidifiers were applied to oil (gasoline, diesel, Bunker C, and three crude oils) in both fresh and salt water and the application was continued until no visible oil remained. Fourteen solidifiers were tested, and final classification of each was based on the consistency of the solidified material as well as the application ratio. All of the solidifiers were able to form a solid mat (usually within one hour after application) with some but not all of the oils tested. Generally, the lighter the oil, the greater the tendency to solidify. Final consistencies ranged from a firm, solidified mass to an incomplete, gel-like substance. The average application rate was 25% solidifier by weight. Salinity did not have an effect on solidification [17].

The PERF project also studied effectiveness of the solidifiers in large-scale wave basin tests [17]. Solidification increased with time; solidification of diesel was complete within an hour, however, crude oil took longer but did form a coherent mass. If the leading edge of the slick was sprayed, the oil solidified and came 'ashore' with no noticeable oiling of the simulated shoreline. Waves of 15–20 cm had little effect on solidifier performance, however, the material formed small clumps and not one large mass.

Environmental effects

Solidifiers have relatively low toxicity, and many products are considered to be nontoxic, with LC₅₀ values for *Artemia* higher than 10 000 p.p.m.

The primary environmental concern, which is more difficult to evaluate, regards the fate and secondary effects of treated and unrecovered oil and unreacted product. The treated oil can be very sticky at first; the issue is how long it will take for the oil to become inert. It appears that these products biodegrade slowly, however, it is difficult to evaluate the ultimate fate of treated oil or product residues in the environment.

Additional secondary environmental concerns regarding treatment of stranded oil are related to physical disturbance of habitats during application and a potential smothering effect. Workers would have to enter the treatment area twice—once to apply the product and again to recover the solidified oil. Repeated foot traffic will likely disturb soft substrates, trampling vegetation and biota. At the recommended application rates, large amounts of the product would have to be applied to oil on shorelines. Intertidal fauna and flora could be smothered by the treated oil (if it is not recovered), or by the product alone. If the product is applied in dry, granular form, however, smothering seems less likely.

ELASTICITY MODIFIERS

Definition and mechanism of action

Elasticity modifiers are inert substances that increase the viscoelasticity of spilled oil to improve the efficiency of removal by skimmers or other methods. They are composed of long-chained, oil-soluble organic polymers such as polyisobutylene (PIB). They are preferentially soluble in oil, modifying the physical properties of the oil. The PIB dissolves in oil during the application process (e.g. no additional physical mixing is usually required). These products appear to be most useful for treating lighter oils, e.g. gasoline, diesel, JP-8, JP-5, kerosene, and fuel oil, to increase their recoverability from the water's surface.

Effectiveness

One particular product, Elastol, has been demonstrated to be effective for open-water application during field tests and actual spills. Two forms of elasticity modifiers, slurry and liquid, have been extensively tested by Environment Canada [13,14,19] and used during several oil spills in the USA [20–22]. Application rates of 100–5000 p.p.m. (product to oil) are recommended for the slurry formulation and have been observed to be effective [13]. The liquid formulation has not been extensively tested, although the only apparent difference between the products is that the liquid application rate is 2500–50 000 p.p.m. by weight. Improved skimmer performance has been described in various tests and applications [23], but no specific comparisons or rates have been reported.

In field tests, Elastol was applied to 10 test slicks of Alberta Sweet Crude and a mixture of the crude and Bunker A oils (Bunker C cut with 20% diesel fuel) off the coast of Nova Scotia. Based on field observations and laboratory measurements of the treated slicks, the researchers concluded that Elastol increased the viscoelasticity of the oil to a greater extent than found in previous laboratory tests [14].

Elastol slurry was tested on a spill of crude oil in Port Neches, Texas in 1993 [20]. The agent was applied to small pockets of floating oil in shallow areas adjacent to marshes where workers could not reach the oil. It was hoped that once Elastol was applied, it would modify the viscosity of the oil enough that the treated oil could be pulled out with rakes. Three hours after application, the treated oil appeared thicker, more viscous and stickier compared to untreated oil; however, it was not possible to physically 'pull' the treated oil as a coherent mass or sheet. In this case, Elastol had been over-applied, at about 75 times the recommended rate; it is not known what effect over-application had on the increased stickiness of the treated oil. The treated oil was recovered with a small, double drum skimmer specially designed for use with Elastol-treated oil.

Elastol was used to recover a chronic oil discharge from an underground source in the Port of New York [21]. The treated oil was rapidly recovered with drum skimmers, whereas the untreated oil spread

too thin to skim, requiring recovery with sorbent material. The treated oil was reprocessed, whereas sorbent use generated large amounts of waste.

During a 1994 spill of unleaded gasoline into the Mississippi River near St. Louis, Missouri, Elastol slurry was used on a small test area. Due to a number of application problems and lack of trained personnel, the product was only applied for 20 min before the test was terminated. It could not be determined if the product was effective [22].

Environmental effects

The two forms of Elastol pose few direct environmental concerns. Both are classified by the manufacturer as insoluble in water, and have very low acute aquatic toxicity (96-h LC₅₀ for *Artemia* for Liquid Elastol $\geq 100\,000$ p.p.m.; for Slurry Elastol = 18 000 p.p.m.). There have been no reported impacts to water-column organisms during use of these products. Elastol passed the California Toxicity Tests on abalone larvae.

There are environmental concerns, however, about the fate and subsequent effects of unrecovered product and unrecovered, treated oil. Questions have been raised on the effect of the unbound Elastol on fish and bivalves [22]. Treated oil spreads less, so it may be more persistent. Also, treated oil can be very sticky and could be more likely to adhere to fur, feathers, vegetation, and dry shorelines. Treated oil is less likely to adhere to wetted shorelines, such as mudflats [24]. Although these concerns have been raised in the USA, there are insufficient data on which to evaluate the real significance of these issues.

SHORELINE CLEANING AGENTS

Definition and mechanism of action

Shoreline cleaning agents are chemicals which enhance removal of oil from substrates and may contain surface-active agents that promote water wetting, thereby helping the water to displace the oil from the surfaces. There are two basic types of shoreline cleaners:

- Non-surfactant-based solvents—the purpose of the solvent is to soften, or lower the viscosity of the oil. After treatment, the surface is flushed with water to release the oil and float it to the water surface, where it can be contained and recovered by mechanical methods; and
- Surface-active agents—these products contain surfactants, additives, and solvents. The main active ingredients, however, are the surfactants which have two functions: removing the oil from the substrate, and preventing its redeposition. The additives promote certain functions, such as dissolution in the oil. The solvents are designed to increase the solubility of the surfactants in the products.

The products composed of nonsurfactant based solvents are primarily petroleum distillates similar to kerosene or vegetable oils. The original formulations, which are no longer used, contained a significant amount of aromatic compounds and were highly toxic to biota. Recent formulations have a low aromatic content.

Products composed of surface-active agents can be divided into two categories: those that do not promote the dispersion of the oil after release, and those that do. The first type consists of surface-active wetting agents formulated to effectively remove the weathered oil from the shoreline surface and refloat the treated oil in a film to be recovered from the water surface. The surfactants are often more hydrophilic, that is, they have a tendency to dissolve preferentially in the water phase, permitting sufficient 'water compatibility' of the chemical so that it can be delivered in a water stream. Once the oil is released from the substrate, the surfactant dissolves into the adjacent water, the oil/water interfacial tension increases, and the released oil droplets re-coalesce and form slicks on the water surface that can be recovered [25].

With the surfactant-type cleaners, oil is removed from the substrate by the change in contact angle between the oil and substrate, causing the oil to roll up. After removal of the oil film, the displaced oil droplets are prevented from redepositing or coalescing by the presence of the oriented surfactant at the oil droplet–water interface. If the oil coating is highly weathered, the washing step may have to be

preceded by a soak with a solvent-based shoreline cleaner to penetrate the oil film and reach the solid surface.

The second category of shoreline cleaning agents lifts the oil coating from the shoreline surface permitting it to be flushed from the surface with minimal energy. They consist of wetting agents and oil/water interfacial tension depressants that stabilized the removed oil as fine dispersed droplets. These droplets are not intended to be recovered, but rather are dispersed into the water column.

In most cases, shoreline cleaners should allow recovery of the released oil rather than dispersion into shallow, nearshore waters. One exception may be along high energy shorelines where recovery is not possible and the released oil should not be allowed to re-strand.

Effectiveness

The effectiveness of a shoreline cleaning agent on intertidal areas depends on many factors [26]:

- Properties and chemistry of the spilled oil;
- Composition of the cleaning agent;
- Type of substrate that is oiled;
- How the agent is applied;
- Ratio of the amount of agent used to the amount of the oil to be cleaned;
- Air temperature; and
- Water salinity.

Another consideration in evaluating products for effectiveness is the time required for soaking before flushing with water. For spills in tidal environments, the soaking time needs to be less than one tidal cycle (6–8 h) because of rapid loss of the product to the overlying water column during high tide. Other important field parameters to measure effectiveness include flush water volume, temperature, and pressure needed to remove the stranded oil.

Shoreline cleaners have been tested in the laboratory with several demonstrating good effectiveness. Environment Canada [18] tested a number of products, using a slightly weathered crude oil on a stainless-steel substrate; effectiveness ranged from 3 to 53% removal (over washing with water alone). The US Environmental Protection Agency tested three products during the development of a standard laboratory test for estimating the performance of shoreline cleaners and found an effectiveness range from 33 to 53% oil removal [27].

Corexit 9580, PES-51, and CytoSol are three shoreline cleaners that have been tested in field trials. In field trials in 1989 and 1990 [28] Corexit 9580 was shown effective in removing oil, thereby preventing plant mortality from oiled mangrove roots [29] and *Spartina alterniflora* plants [30,31]. Corexit 9580 was tested on salt marsh vegetation (*Spartina alterniflora*) during the response to the September 1997 *Julie N* spill of IFO 180 in Portland, Maine [32]. The salt marshes had been heavily coated by the oil, and there were concerns that wintering waterfowl would be contaminated by using the marsh. Approval was obtained to test Corexit 9580 on the vegetation, particularly since earlier studies had shown little contact toxicity to plant tissues. The test was conducted 9 days after the oil came ashore, using ambient water, low pressure flushing after a soak of 15 min. Observations of the test were: (i) The top sides of the vegetation showed evidence of 40–50% removal but the undersides remained heavily oiled; and (ii) It appeared that a significant amount of the released oil was not immediately recoverable. Further use was not considered because the test site represented perhaps the best operational conditions in term of good access on the landward side, where both application and flushing would be more effective. Even then, the effectiveness was limited.

Both PES-51 and Corexit 9580 were tested on natural beach rock and man-made structures during the response to the *Morris J. Berman* spill of no. 6 fuel oil in 1994. Both proved more effective than water alone in removing the oil from the substrate, with Corexit 9580 slightly more effective than PES-51. Based on the effectiveness and toxicity data (see discussion below), Corexit 9580 was used on several hundred meters of highly visible beach rock where high pressure water damaged the rock [33,34].

PES-51 was also tested in 1993 on a cobble/gravel shoreline in Prince William Sound, Alaska containing residual oil from the *Exxon Valdez* oil spill [35]. Observers concluded that oil was mobilized from the surface following application by air knives and coldwater flushing. Based on these results, PES-51 was used on a portion of the shoreline to remove residual oil from important subsistence areas around a native village. The product was compared with hot water on a cement walkway on top of a riprap bulkhead following oiling from the Bouchard 155 spill of no. 6 fuel oil in Tampa Bay. Based on visual observations, PES-51 and hot-water washing were both effective [35].

CytoSol has been demonstrated in field and spill applications in California. CytoSol contains methyl esters derived from vegetable oil and bioremediation enhancers. It is applied at a ratio of 1:1, product to oil, requiring a soaking period of at least one hour prior to flushing with ambient water at low pressures. CytoSol dissolves the oil, decreasing the viscosity of the released oil; the mixture of oil and CytoSol is a true mixture which has to be refined to separate the two components. The released oil is highly hydrophobic, increasing the rate of recovery of the released oil.

Laboratory experiments with both CytoSol and Corexit 9580 were conducted on marsh grasses (pickleweed, cordgrass, and tules) using North Slope crude oil applied to the vegetation at a rate of 1 L of oil per pool (1.6 m in diameter) and 1 L of each product applied two days after oiling [36]. The results showed high rates of oil removal for both products (90–95% removal). The Corexit 9580-treated pools showed some dispersion of the oil in the water during and following rinsing of the plants, but the plants that were oiled and treated with Corexit 9580 remained mostly healthy for the 6-week monitoring period. The plants treated with CytoSol after oiling showed significant mortality, particularly the upper, unoiled part of the vegetation in contact with the product. It appears that CytoSol has significant contact mortality to plant tissue, since the CytoSol-only treated vegetation experienced 30–50% mortality.

In 1995, CytoSol was applied at a rate of 7.5 L/m to 250 m² of an oiled pebble beach in San Francisco Bay [37]. Compared to water flushing alone, more oil was released from the treated area down to depths of 0.5 m. The released oil was readily recovered. In a June 1997 spill of Bunker C in Long Beach, California, both PES-51 and CytoSol were tested on oiled concrete pilings with heavy coverage of mussel beds. PES-51 was used only as a wipe on the concrete surfaces, whereas CytoSol was sprayed on the concrete and mussel beds. Use of CytoSol did not require scraping of the mussel beds to release the oil trapped in the mussels.

Environmental effects

Shoreline cleaning agents pose unique problems in the evaluation of environmental concerns because there are few field data on toxicity from the direct application of these products on shoreline biota, or on the secondary toxic effects from the product and treated oil released into shallow, nearshore waters. Corexit 9580 was extensively tested and evaluated for acute and chronic toxicity during laboratory and field trials in Alaska during the first year of shoreline cleanup of the *Exxon Valdez* [28]. This product underwent toxicity testing of the product alone and mixed with weathered Alaska North Slope crude oil for five Alaskan species of concern. Toxicity tests were also run on water samples collected at high tide from water overlying the treated areas. During field trials, hundreds of water samples were collected for bioassay and to document whether the oil was dispersed into the water column or remained on the water surface. These data showed no significant added environmental risk associated with the use of Corexit 9580, compared with the standard water washing technique [28,38]. However, wide-scale use was never approved because Alaska state agency representatives determined that ‘...increased operational effectiveness with the use of Corexit 9580 had not been well enough documented at that time...’ [28].

During operational use of Corexit 9580 at the *Morris J. Berman* spill, study sites were surveyed before, immediately following, and one day after treatment and no significant nearshore effects were observed. Organisms transplanted into the treatment site also showed few exposure-related effects compared to oil only and control sites [39].

Comparison of toxicity test results for products which are insoluble (i.e. PES-51 and Corexit 9580) is misleading because the toxicity tests were conducted using nominal concentrations. The insoluble components float on the surface and do not contribute to the exposure.

Given this caveat, PES-51 contains *D*-limonene, a naturally occurring chemical derived from oil of

orange. Limonene has relatively high toxicity; Environment Canada reported the toxicity (96-h LC_{50}) of D-limonene to rainbow trout to be 35 p.p.m. [15]. PES-51 has a higher acute toxicity compared with Corexit 9580 [33]. CytoSol has a water solubility of 43 p.p.m. at 12 °C and 230 p.p.m. at 18 °C, and immediate aquatic toxicity (578–738 p.p.m. for *Menidia beryllina* and 121 p.p.m. for *Mysidopsis bahia*).

Evaluation of the toxicity of shoreline cleaning agents is further complicated by the issue that toxicity should be considered in a broader context by comparing the relative ecological risk of the use of the chemical with a no-use alternative. To address this issue, Clayton *et al.* [40] developed a portable test kit using two oils (Bunker C and Bonny Light crude oil) and two agents (PES-51 and Corexit 9580). The effectiveness tests are designed to test removal efficiencies on oiled substrates, and to compare the amount of oil dispersed into the water column with use of an agent compared with washing alone. Four toxicity tests protocols are included, with three designed for use with resident organisms (fertilization success with echinoderms; byssel thread attachment in mussels; and righting/escape ability in snails). The fourth method uses MicrotoxTM. These tests were designed to provide reproducible data for comparing effectiveness and effects among agents and with water-only treatments.

MISCELLANEOUS AGENTS

There are three additional types of nondispersant chemical countermeasures which can be considered in the range of chemical countermeasure concepts for marine oil spills. They include shoreline pre-treatment agents, oxidation agents, and chemically selective sorbents. Because their utility as oil spill response countermeasures is less well-defined than the others already discussed, only a descriptive synopsis is provided for each.

Shoreline pre-treatment agents

Shoreline pre-treatment agents are applied to the substrate prior to oil landfall to prevent oil from adhering to or penetrating the substrate. Also known as shoreline protection agents, chemical products used as shoreline pre-treatment agents were investigated by the American Petroleum Institute (API) in the 1970s in a series of three studies [41]. Two subclasses of products were considered: film-forming and wetting agents. Film-forming agents are chemicals that form a physical barrier which prevents the oil from adhering, staining, absorbing, and contaminating the shoreline. Some were polymers that formed a thin film surface that is not wettable or compatible with oil [42]. Wetting agents affected the oil/water interface and help the water displace the oil from the substrate.

One of the most important considerations for using these agents is the critical timing for their effective use. They have to be applied at or near the oil/shoreline interface just prior to the stranding of oil. Consequently, their window of opportunity is very narrow and dependent upon a near-perfect trajectory (to predict where the oil would strand) and ready availability of prestaged product, application devices, and trained crews.

Assuming these operational impediments could be overcome, one promising use of these agents would be to reduce adherence of oil on vegetated shorelines, such as marshes and mangroves, which are difficult to clean without causing additional harm. Toxicity effects would need to be considered for the product on vegetation, compared with the oil.

Oxidation agents

Titanium dioxide beads have been considered for use as photocatalysts to accelerate sunlight-assisted oxidation of aliphatic and aromatic components of crude oil. Because these hollow ceramic, titanium coated microbeads float at the oil–air interface, the titanium dioxide (the photocatalyst) is able to accelerate the oxidation of the oil [43].

Small-scale laboratory test results estimated that with 45 kg of beads per barrel of spilled oil, photo-oxidation will be complete within one week (under moderate seas). Under calm seas, photo-oxidation is estimated to take two weeks [44]. These results suggest that the beads may be effective in preventing mousse formation. No toxicity data is available for the beads, and colorless glass microbeads are left as a residue after photo-oxidation. Concerns regarding the toxicity of the residue and its potential physical adverse effects, along with poor aesthetics of thousands of beads left on the shoreline.

Chemically selective sorbents

While sorbents have traditionally fallen into the mechanical countermeasures category, recently some products have been developed which appear to have chemically selective mechanisms of action and this prompts their consideration as a chemical countermeasure.

As an example of this type of countermeasure, one product, the Oil Aquatic Recovery System (OARS), consists of cylindrically shaped polymer capsules. These capsules are contained in mesh bags and blankets and provide the sorbent-type of oil encounter area. The polymer capsules have a very high internal surface area, much like a sponge, which is extremely oil-selective and water-avoidant; oil is wicked inside the internal pore space where the polymer and the oil chemically interact. This interaction causes the oil to dissolve into the polymer, which locks up the oil into the structure and precludes water from interacting with the oil. However, unlike a sponge, this chemical interaction prevents the oil from being squeezed back out, even under pressure; recovered oil does not rub off upon contact or drop-off the material when the product is removed from water as is the case with common polyethylene-type sorbents. The recovered oil/polymer capsules, which over time can become a gelatinous mass inside the bags or blankets, are recyclable using a low-temperature catalytic distillation.

Based on laboratory tests and limited field tests, including OHMSETT (a US national oil spill response test facility), this chemically selective type of sorbent may be useful in situations when all oil, including sheens and vapors, needs to be recovered and where the mesh bags and blankets can be easily recovered, e.g. small spills at waterfront facilities or portions of larger spills along shorelines with good access. The

Table 1 Summary of potential uses of chemical treating agents*

Situation	Applicable to treating agent	Anticipated conditions for use	Possible disadvantages
Rigid oil spreading with no control options	Herding agents	Thin oil; calm water only	Multiple applications may be needed; need to recover oil
	Solidifiers	Requires thorough mixing	Solidified oil may not be recoverable
Oil heading to shoreline	Herding agents	Thin oil; calm water only	Multiple applications may be needed; need to recover oil
Oil will form an emulsion	Emulsion inhibitors	Agent must contact unemulsified oil	Agent may not stay with the oil; treated oil may be less recoverable
Oil has formed an emulsion	Emulsion breakers	Agent must contact emulsified oil	At sea, oil may be less recoverable; may impact other countermeasures; discharge of separated water may be restricted
Light oil difficult to recover/skim	Elasticity modifiers	Most effective on light oils	Critical dose requirements; will leave sticky residue
Oiled shoreline needs cleaning; oil remaining on shoreline difficult to remove	Shoreline cleaning agents	Oil still must be recovered; requires flushing	Requires manpower; oil not always recoverable

*After [1].

Table 2 Potential use of chemical treating agents by oil type*

Agent	Oil Type/Degree of Weathering		Remarks
	Light	Heavy	
Herding			calm water, no wind, no currents, thin oil
Emulsion Inhibitor	? 		? early application
Emulsion Breaker	? 		? open water or in containers
Solidifier			use if easier to handle a solid; sticking to equipment an issue; do not overdose
Elasticity Modifier			do not overdose
Shoreline Cleaning			must act within tidal cycle

Most effective	
Moderately effective	
Least effective/appropriate	
Ineffective	
Lack of data	?

*After [1].

oil must be fairly nonviscous to be wicked up by the product. Consequently, heavy oils or heavily weathered oils may not lend themselves to effective recovery with this countermeasure.

CONCLUSIONS

The role and practicality of using nondispersant chemical countermeasures during marine oil spill response is a continuing issue since these agents have been used at so few oil spills. Given the need to have alternatives to mechanical countermeasures and dispersants, especially in coastal areas where most marine oil spills occur, nondispersant chemical countermeasures have been examined, in most cases, on the basis of laboratory data and, when available, field data. Non-dispersant chemical countermeasures appear to have discrete *response niches*, i.e. situations where the countermeasures are well-suited and offer potential benefits. The key is matching conditions for optimal effectiveness with the appropriate incident-specific characteristics and window of opportunity. The practical aspects of logistics are not addressed because, if their potential utility can be demonstrated, the resolution of these issues would follow.

The most likely response niches for nondispersant chemical countermeasures are defined by their potential applications in various response situations and by the types of oil which they are likely to effectively treat. Table 1 summarizes the potential uses of chemical treating agents during marine oil spill response. The first column identifies specific problems for which conventional countermeasures have been ineffective and identifies the types of chemical countermeasures to alleviate those problems. This table also indicates the spill conditions under which products are likely to be most effective, along with their anticipated use limitations. Table 2 illustrates the types of oil that are expected to respond well to treatment by the different types of chemical treating agents. This table uses a relative scale, i.e. light to heavy, to indicate oil type, which takes into account the weathering of various types of oil, given that oil becomes heavier as it weathers. Also displayed are conditions that favor effectiveness.

Chemical oil spill treating agents offer potential distinct utility in certain situations. Yet, like all

countermeasures, they possess limiting characteristics. At this time, the primary benefit of these agents, assuming they can be applied effectively and within the window of opportunity, appears to be in strategically treating portions of large slicks, or smaller spills, on water or after the oil has stranded, alone or in combination with other countermeasures. For example, emulsion treating agents may be suitable for treating large open water slicks to prevent emulsion formation, thereby extending the window of opportunity for dispersants, *in situ* burning, and/or mechanical recovery. Chemical countermeasures are the *specialty* tools in the oil spill responder's toolbox.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge AbTech Industries for sponsoring the preparation of this manuscript. We sincerely appreciate Edward Overton of Louisiana State University, Alun Lewis of AEA Technology, and William Dahl of Exxon Research and Engineering Company for their review of the manuscript. The efforts of Debra Scholz of SEA were most helpful in gathering background information and providing copy editing of the document.

REFERENCES

- 1 A. H. Walker, J. Michel, G. Canevari, J. H. Kucklick, D. Scholz, C. A. Benson, E. Overton, B. Shane. *Chemical oil spill treating agents*. Marine Spill Response Corporation, Washington, DC. MSRC Technical Report Series 93-015 (1993).
- 2 W. D. Garrett, W. R. Barger. *Control and confinement of oil pollution on water with monomolecular surface films*. US Coast Guard, Washington, DC (1971).
- 3 W. R. Barger. *Proceedings of the 1973 Conference on Prevention and Control. of Oil Spills, 13–15 March, Washington, DC*, pp. 241–246. American Petroleum Institute, Washington, DC (1973).
- 4 P. Pope, A. Allen, W. G. Nelson. *Proceedings of the 1985 Oil Spill Conference, 25–28 February, Los Angeles, CA*, pp. 199–201. American Petroleum Institute, Washington, DC (1985).
- 5 C. Von, J. C. Chong, J. R. Gutierrez. *Proceedings of the 1983 Oil Spill Conference, 28 February–3 March, San Antonio, TX*, pp. 369–370. American Petroleum Institute, Washington, DC (1983).
- 6 G. P. Canevari. *Proceedings of the 1979 Oil Spill Conference, 19–22 March, Los Angeles, CA*, pp. 443–446. American Petroleum Institute, Washington, DC (1979).
- 7 R. N. Bocard, P. Renault, J. Croquette. *Proceedings of the 1979 Oil Spill Conference, 19–22 March, Los Angeles, CA*, pp. 163–168. American Petroleum Institute, Washington, DC (1979).
- 8 G. Peigne. *Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings* (A. H. Walker, D. L. Ducey Jr, J. R. Gould, A. B. Nordvik, eds). Marine Spill Response Corporation, Washington, DC. MSRC Technical Report Series 93-018 (1993).
- 9 A. L. Bridié, T. H. Wanders, W. Zegveld, H. B. van der Heijde. *Mar. Pollut. Bull.* **11**, 343 (1990).
- 10 P. S. Daling, J. N. Hokstad, P. J. Brandvik. *Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings* (A. H. Walker, D. L. Ducey Jr, J. R. Gould, A. B. Nordvik, eds). Marine Spill Response Corporation, Washington, DC. MSRC Technical Report Series 93-018 (1993).
- 11 A. Lewis, M. Walker, K. Colcomb-Heiliger. *Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings* (A. H. Walker, D. L. Ducey Jr, J. R. Gould, A. B. Nordvik, eds). Marine Spill Response Corporation, Washington, DC. MSRC Technical Report Series 93-018 (1993).
- 12 T. Lunel, A. Lewis. *Proceedings of the Sixteenth Arctic and Marine Oil Spill Program Technical Seminar, 7–9 June, Calgary, Alberta*, pp. 955–972. Environment Canada, Ottawa, Ontario (1993).
- 13 M. Bobra, P. Kawamura, M. Fingas, D. Velicogna. *Mesoscale applications and testing of an oil spill demulsifying agent and Elastol*. Environment Canada. EE-105 (1988).
- 14 Seakem Oceanography Ltd. *Field test of two spill treating agents*. Environment Canada, Ottawa, Canada, EE-124 (1990).
- 15 M. F. Fingas, D. A. Kyle, N. D. Laroche, B. G. Fieldhouse, G. Sergy, R. G. Stoodley. *The Effectiveness Testing of Spill-Treating Agents*. Emergencies Science Division, Environment Canada, Ottawa, Canada (1994).
- 16 S. Ross. *Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings* (A. H. Walker, D. L. Ducey Jr, J. R. Gould, A. B. Nordvik, eds). Marine Spill Response Corporation, Washington, DC. MSRC Technical Report Series 93-018 (1993).

- 17 W. A. Dahl, R. R. Lessard, E. A. Cardello. *Proceedings of the 1997 Oil Spill Conference, 7–10 April, Ft. Lauderdale, FL*, pp. 391–395. American Petroleum Institute, Washington, DC (1997).
- 18 M. Fingas, R. Stoodley, N. Stone, R. Hollins, I. Bier. *Proceedings of the 1991 Oil Spill Conference, 4–7 March, San Diego, CA*, pp. 411–414. American Petroleum Institute, Washington, DC (1991).
- 19 M. Bobra, P. Kawamura, M. Fingas, D. Velicogna. *Laboratory and Tank Test Evaluation of Elastol*. Environment Canada, Ottawa. EE-94 (1987).
- 20 J. Michel, C. B. Henry, J. M. Barnhill. *Use of Elastol during the Unocal spill on the Neches River, 24 April 1993*. NOAA Hazardous Materials Response and Assessment Division, Seattle, WA (1993).
- 21 E. Levine. Personal communication. National Oceanic and Atmospheric Administration (NOAA) SSC, New York, NY (1993).
- 22 J. M. Hartley, D. F. Hamera. *Proceedings of the 1995 Oil Spill Conference, 27 February–2 March, Long Beach, CA*, pp. 453–458. American Petroleum Institute, Washington, DC (1995).
- 23 E. J. Tennyson, H. Whittaker. *Proceedings of the 1989 Oil Spill Conference, 13–16 February, San Antonio, TX*, pp. 101–103. American Petroleum Institute, Washington, DC (1989).
- 24 E. Scambos. Personal communication. Environmental Recovery Resources Inc., South Salem, NY (1994, 1997).
- 25 G. P. Canevari. *Mar. Poll. Bull.* **13**, 49 (1982).
- 26 J. R. Clayton. *Chemical shoreline cleaning agents for oil spills: Update state-of-the-art on mechanism of action and factors influencing performance*. Environmental Protection Agency, EPA/600/R-93/113b (1993).
- 27 J. R. Clayton, S.-F. Tsang, V. Frank, P. Marsden, N. Chau, J. Harrington. *Evaluation of performance for chemical shoreline cleaning agents: Laboratory testing of two protocols for removing oil from substrate surfaces*. Risk Reduction Engineering Laboratory, Office of Research and Development, US EPA (1992).
- 28 R. J. Fiocco, G. P. Canevari, J. B. Wilkinson, H. O. Jahns, J. Bock, M. Robbins, R. K. Markarian. *Proceedings of the 1991 Oil Spill Conference, 4–7 March, San Diego, CA*, pp. 395–400. American Petroleum Institute, Washington, DC (1991).
- 29 H. J. Teas, R. R. Lessard, G. P. Canevari, C. D. Brown, R. Glenn. *Proceedings of the 1993 Oil Spill Conference, 29 March–1 April, Tampa, FL*, pp. 146–151. American Petroleum Institute, Washington, DC (1993).
- 30 S. R. Pezeshki, R. D. DeLaune, J. A. Nyman, R. R. Lessard, G. P. Canevari. *Proceedings of the 1995 Oil Spill Conference, 27 February–2 March, Long Beach, CA*, pp. 203–209. American Petroleum Institute, Washington, DC (1995).
- 31 S. R. Pezeshki, R. D. DeLaune, A. Jugsujinda, G. P. Canevari, R. R. Lessard. *Proceedings of the 1997 Oil Spill Conference, 7–10 April, Ft. Lauderdale, FL*, pp. 397–402. American Petroleum Institute, Washington, DC (1997).
- 32 J. Michel, S. Lehmann. *Oiling and cleanup of salt marshes at the Julie N spill, Portland, Maine*. NOAA Hazardous Materials and Assessment Division, Seattle, WA (in preparation).
- 33 J. Michel, B. Benggio. *Proceedings of the 1995 Oil Spill Conference, 27 February–2 March, Long Beach, CA*, pp. 197–209. American Petroleum Institute, Washington, DC (1995).
- 34 G. Petrae, eds. *Barge Morris J. Berman NOAA's scientific report*. HAZMAT Report 95-10. NOAA Hazardous Materials and Assessment Division, Seattle, WA (1995).
- 35 R. Hoff, eds. *Chemistry and environmental effects of the shoreline cleaner PES 51*. National Oceanic and Atmospheric Administration, Hazardous Materials Response and Assessment Division, Seattle, WA. Report Number 94-2 (1994).
- 36 G. McGowan, J. Vollmar, R. von Wedel. *5th International Conference on the Effects of Oil on Wildlife, 3–6 November 1996*. Monterey, CA (1996).
- 37 J. Tarpley. Personal communication. California Office of Oil Spill Prevention and Response, Sacramento, CA (1997).
- 38 D. C. Lees, J. P. Houghton, W. B. Driskell. In *Proceedings of the 1993 Oil Spill Conference, 29 March–1 April, Tampa, FL*, pp. 345–354. American Petroleum Institute, Washington, DC (1993).
- 39 G. Shigenaka, V. Vicente, M. A. McGehee, C. B. Henry. *Proceedings of the 1995 Oil Spill Conference, 27 February–2 March, Long Beach, CA*, pp. 177–184. American Petroleum Institute, Washington, DC (1995).
- 40 J. R. Clayton Jr B. C. Strasky, M. J. Schwartz, D. C. Lees, J. Michel, B. J. Snyder, A. C. Adkins. *Development of protocols for testing cleaning effectiveness and toxicity of shoreline cleaning agents (SCAs) in the field*. Marine Spill Response Corporation, Washington, DC, MSRC Technical Report Series 95-020.1 (1995).

- 41 R. J. Seltzer. *Chem. Engng News* **30** (1975).
- 42 Tracor, Inc. *Beach protection study*. American Petroleum Institute, Washington, DC (1974).
- 43 A. Heller, M. Nair, L. Davidson, J. Schwitzgebel, Z. Luo, J. L. Norrell, J. R. Brock, J. G. Ekerdt. *Proceedings of the 1993 Oil Spill Conference, 29 March–1 April, Tampa, FL*, pp. 623–627. American Petroleum Institute, Washington, DC (1993).
- 44 A. Heller. Personal communication. Letter dated 5 March 1993. Heller Environmental, Austin, TX (1993).
- 45 American Petroleum Institute, United States Coast Guard and the National Oceanic and Atmospheric Administration. *Marine oil spill response options for minimizing environmental impacts* (in preparation).