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CHEMICAL TREATMENT OF OIL SPILLS

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Abstract

This paper is a review of 10 types of chemical treatments for oil spills. Gelling agents change oil to a solid or semi-solid form, but are not used because of the large amount of agent required. Biodegradation agents consist of bacteria, enzymes, fertilizers or combinations of these and are found to have low effectiveness in open water and on soils. Degradation is limited to a small fraction of the oil. Sinking agents cause the oil to be sunk to the bottom. They are not used because of ineffectiveness and because of the increased oil exposure caused by resurfacing of oil. A number of recovery aids have been proposed, but only Elastol has been tested and proven to function well under a variety of conditions. A number of water-in-oil emulsion preventers and breakers have been proposed, but none are commercially-available. Demoussifier developed by Environment Canada has been recently tested and found to be effective. Surface washing agents contain surfactants and because they are soluble in water, can only effectively be used on solid surfaces and as such have little application to oil spills. Dispersants contain surfactants which break up oil into small droplets in the water column. Dispersants are the most common treating agents and have been extensively tested and used. No undisputed documentation exists to show that dispersants have been very effective in field situations, but analytical means to measure effectiveness are poor. Dispersant action mechanisms are poorly understood and there exist a number of interferences to field effectiveness. A number of other treating agents have been proposed, but none are in current use. The main problem with most treating agents is their effectiveness and this is often dependent on molecular size and type. Oil has many molecular types and sizes, thus rendering treatment much less than totally effective.

Introduction

A number of chemical agents have been commercially sold over the 20 years since the TORREY CANYON incident during which some of these chemical treatment concepts were first tried on a large scale. These chemical spill control agents can be classified as the following:

1. Dispersants,
2. Gelling agents,
3. Biodegradation agents,
4. Sinking agents,
5. Recovery aids,
6. Emulsion breakers and preventers,

7. Surface washing agents,
8. Herding Agents,
9. Combustion Promoters, and
10. Miscellaneous agents.

During the past twenty years many agents have come and gone. During the seventeen years of the life of the Environmental Emergencies Technology Division over 100 dispersants were tested for toxicity and/or effectiveness. Only 8 products still remain on the accepted list and only about 15 products are still being produced. The compendium on oil Spill treating agents prepared for the American Petroleum Institute in 1972 lists 69 dispersants and 43 beach clean-up agents, most of which are dispersants.[1] Only two of these are current commercial products, but both are produced in different formulations. Four gelling agents were tested by EETD and others; none remain on the market. The API compendium listed four different gelling agents. Over 50 biodegradation agents, including bacterial mixtures, enzymes or fertilizers have been proposed and only 5 of these, all very recent inventions, remain on the market. Ten sinking agents have been examined with none remaining commercial. The API compendium lists 18 sinking agents. One recovery aid of the several proposed, Elastol, still remains. Ten emulsion breakers and preventers have been on the market. None are commercially available at this time. Over 100 surface washing agents have been sold in the North American market. About 12 of these are still commercially available. A number of agents which have been sold for various purposes, but do not fit into the above categories, include those that help trace or detect an oil, those which are combinations of the categories described above, and those very vague items that are claimed to make oil disappear, become non-toxic, etc. It is estimated that over 100 of this category of agent has been offered at one time or another on the North American market. The total number of agents proposed world wide is estimated to be 600, of which only about 200 were ever tested in lab or field, even in a limited way. It is also estimated that only 35 agents actually are commercially available at this time. The bustle of activity in this field has left the buyer confused and skeptical of treating agents.

Many agents are offered to the potential buyer as a magic cure and some buyers expect miracles from the product. Demonstrations are often presented which show the product to work very effectively. One firm recently had an oil-disappearing demonstration, which they would only do in their own plant "to ensure proper conditions". Oil was poured into a glass of water, and the magic solution was added; this caused significant fizzing, and then the demonstrator drank the clear liquid, the oil supposedly having been reduced to elemental gas. Interestingly, this demonstration would not work in other laboratories. The firm is no longer in business.

The history of chemical agents and oil spills have left many, and especially the experienced, oil spill worker skeptical about any oil spill chemical control agent. Rarely a week goes by in EETD laboratories where we aren't approached by someone offering a new magic cure. The same is true of the potential customers of such products. Any new agents, even if it may have potential is treated with the same sort of skepticism, perhaps even disdain, reserved for the weekly 'snake oil'. A number of agents do however offer assistance in dealing with oil spills. No agent is a magic cure nor is there any agent that has wide applicability. All agents suffer from limited effectiveness with oil, especially with certain types of oil.

Effectiveness will remain the major problem with most treating agents. Effectivness is generally a function of molecular size and type. Crude and refined oil products have a wide range of molecular sizes and composition. What is often effective for a small asphaltene is ineffective on the large asphaltene. What is effective on an aromatic compound may not be effective on a polar compound. Additionally, the composition of crude oils varies widely. This leaves little scope for a universally-applicable and effective spill control chemical.

Gelling, Biodegrading and Sinking Agents

Gelling agents are those agents which change liquid oil to solid. Also known as solidification agents, these agents consist of polymerization catalysts and cross-linking agents. Agents which are actually sorbents are not considered to be gelling agents. Three significant gelling agents were tested by Environment Canada and others in recent years:

1. The BP (British Petroleum) product which consisted of deodorized kerosene and a cross-linking agent,
2. A Japanese product consisting of an amine agent which formed a polymer, and
3. 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 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.

Because of the large amount of agent required, gelling agents are not used nor stocked for use by spill responders.

Biodegradation agents are of four basic types:

1. those that contain mutant bacteria,
2. those containing enzymes,
3. those containing nutrient materials to foster biodegradation, and
4. those containing two or more of the above.

Laboratory tests on products utilizing mutant bacteria have shown an increased degradation rate. Treatments in impoundments or sewage-treatment facilities appear to have been effective. The rate of biodegradation is dependent on concentration and type of oil as well as temperature. Field tests have shown no beneficial effect, on water or on soil. In water, the bacteria is far too dilute to have significant effect. On soil, degradation is limited to certain components of the oil, and thus has no significant overall benefit. Again, the fact that oil consists of a large variety of chemical groups and a large variety of molecular sizes, is very significant in determining effectiveness.

Although a large number of enzyme agents have been examined, none of these survived initial laboratory assessment. None showed any effect on oil even under optimal conditions. Examination of some of these products showed that they were actually domestic laundry soap with enzymes. It is not certain at this time if any specific enzymes were ever designed for crude or refined oil breakdown, or even if this is possible.

Many agents have been proposed for assisting the microbial breakdown of oil. Most of the agents contain an oil-soluble fertilizer, others an ordinary fertilizer. Tests of these products in water have shown no benefit. However, on shorelines, the results are mixed. During the course of the BIOS experiments, oiled supratidal sediments were treated with fertilizer and these plots showed no increased degradation through five years of monitoring.[2] A test of one product on a real spill in British Columbia showed no increased degradation on oiled rocks treated with a fertilizer.[3] Tests on Arctic shorelines in Norway showed increased biodegradation.[4] A novel product which uses a surfactant to suspend fertilizer and make it more available to the oil has been tested on oiled plots and favorable results reported.[5] None of the tests have reported significant oil removals with fertilizer-enhanced biodegradation.

The variable but generally poor results have discouraged widespread use of biodegradation agents.

Sinking agents were used at the time of the TORREY CANYON with disastrous environmental results.[6] The use of lime to sink the oil en masse led to smothering of many bottom-dwelling organisms. In addition, the use of the agent actually increases exposure to oil. As the oil moves through the water on the sinking agent it dissolves in the water and also a certain percentage frees itself from the sinking mass and rises to the surface. During the passage through the water column the sinking oil mass and the resurfacing oil can encounter marine life. The increased hydrocarbons in the water increases exposure. The sinking mass causes suffocation to bottom life and also exposes many bottom-dwelling organisms to oil. Problems do not end here. None of the agents are effective in holding the oil for a long period of time and the slowly leaching oil recontaminates the water and the water surface over the few days after the initial sinking. A study on several sinking agents by Environment Canada showed that most agents retained only 20 to 40% of the oil after one hour and much less after 72 hours.[7]

No sinking agents are commercially available at this time and their use is generally forbidden by environmental regulatory agencies.

Burning agents are also not commercially available at this time. They consisted of two generic types, sorbents and pyrotechnical compositions. The sorbent types operated by collecting oil in thicknesses sufficient to burn and the pyrotechnical compositions release large amounts of heat on combustion, thereby aiding in flame propagation. Neither type functioned well in actually practice and were limited by the large amount of material needed to actually cause a beneficial effect.

Herding agents were proposed to stop or reverse oil spill spreading. Commercially-successful types such as Shell Oil Herder employed large-chain alcohols which have a greater spreading coefficient than oil on water and thus push oil films together. Tests and actual use of these products showed that utility was limited to absolutely calm waters.[8] There is little remaining use of herders at this time due to their limited application and operating spectrum.

Recovery Aids and Demoussifiers

A number of agents have been sold throughout the years for assisting in the recovery of spilled oil. None have been widely known or promoted except for Elastol. Earlier agents were not well tested nor were they sophisticated. One product was shredded peat moss and was claimed to improve the recovery efficiency of sorbent-surface devices. None of these earlier agents offered enough promise to warrant testing.

A number of agents were also available to break or prevent emulsions. Most agents were hydrophilic surfactants, that is with surfactants with an HLB (hydrophobic-lipophilic balance) of 12 to 19. Such surfactants have the ability to reverse the emulsion from water in oil to two separate phases. The problem with a surfactant with an HLB in this range is that the surfactant is more soluble in water than in oil and will quickly leave the system if there is sufficient water. Obviously such products cannot be successfully used on open water. Some recent products avoided this problem by using a lower HLB surfactant and accepting the resulting decrease in effectiveness. One recent product developed by Environment Canada does not use surfactant in the normal sense of the word. This product does not suffer the limitations noted above.

One study reviewed two commercial products, Exxon Breaxit and the Shell product, LA 1834 and a surfactant, sodium diooctyl sulfosuccinate.[9] All three products functioned in a limited way, but only the Shell product prevented the formation of emulsions over a wide range of oils and conditions. The Shell product and the Exxon product are not commercially available, but have been obtainable in small quantities for testing.

The United States Minerals Management Service and Environment Canada joined forces to evaluate two new and promising treating agents, Elastol, a recovery-enhancement agent, and Demoussifier, an emulsion breaker and preventer. Results of the extensive testing on these products have been widely published.[10-15]

Elastol is a white powder and renders oil visco-elastic making it adhesive to oil spill recovery surfaces. Elastol is composed of a non-toxic polymer, polyisobutylene. Demoussifier is a mixture of long-chain polymers which again have no measurable toxicity to humans or aquatic life. This product was developed at Environment Canada's River Road laboratories and functions both to break emulsions and prevent their formation.

The laboratory work on Elastol involved several different tests. The effect on a suite of different oils was determined by measuring the time to initiate change and the degree of elasticity formed. These oils included: Prudhoe Bay, Alberta Sweet Mix Blend, Norman Wells , Bent Horn, Hibernia, Tarsiut, Atkinson, Amauligak crudes, diesel fuel and a Bunker C Mix. All oils displayed viscoelastic properties when treated with doses of 600 to 6000 ppm Elastol. In general, more viscous oils tended to attain a higher degree of elasticity than non-viscous oils, but did so over a longer period of time. No simple correlation could be established between an oil property and Elastol effectiveness. Elastol effectiveness is enhanced by mixing and by higher temperatures, although the latter may be the effect of decreasing oil viscosity.

Under low mixing energy conditions, oils exhibited some degree of elasticity within 15 minutes of Elastol application. A high degree of elasticity was not observed until after one hour. Less viscous oils took less time to reach maximum elasticity and viscous oils more time. If left to weather, Elastol-treated oil became more elastic with the increasing viscosity of the oil. In fact, some samples left for 30-day periods became as elastic as rubber bands sold for stationery purpose. This effect has been ascribed to the effect of the increasing viscosity of the oil with weathering (evaporation) and not the progressive reaction of the Elastol.

Elastol causes a minor reduction in the rate of oil evaporation, but not significant enough to reduce its flash point. Elastol reduces slick spreading to a limited degree, especially at high concentrations. This effect, about 20%, is not believed to have a significantly useful benefit by itself in real applications. When Elastol is applied in very large doses, >1%, the slick would actually contract somewhat, but again, the effect is too small to have any practical benefit. The addition of Elastol either had no effect or an inhibiting effect on the formation of water-in-oil emulsions, except in the case of the Amauligak and Tarsiut oils from the Beaufort Sea region. In two cases, the application of Elastol to emulsified oil actually led to some measurable de-emulsification. Application of Elastol to stable water-in-oil emulsions sometimes had little effect. Testing with the Demoussifier showed the Elastol has no effect on its operation and that both products could be used together.

Elastol reduces chemical dispersant effectiveness by as much as one order of magnitude. Elastol also reduces natural dispersion of oil into water by as much as 3 orders-of-magnitude. This property, while superficially appearing negative, is actually quite useful. If Elastol was used in situations where the aquatic life is very sensitive and important, it could reduce oil concentration in the water to threshold values.

Both Elastol and Demoussifier were tested on a large scale using the Esso test tank in Calgary, Alberta. Funding for this part of the program was provided by the U.S. Minerals Management Service, Environment Canada and Esso Resources. An application device was developed for both products as commercial ones did not exist. The application devices were tested in larger vessels before proceeding to the larger Esso facility, to ensure that application did not affect results.

In the large scale tests, two slicks were put out simultaneously in parallel booms. This permitted the simultaneous testing of a control and a treated slick under identical conditions. The first two days were devoted to the testing of demoussifier. The demoussifier prevented the formation of water-in-oil emulsions on both slicks and did so at treatment ratios as low as 1:2000 (500 ppm). Elastol was tested on the final two days. In the first of these tests, Elastol was added to a test crude oil at 4000 ppm and the test slick was released several hours later when the oil was highly elastic. Although not thick enough to burn, the high elasticity increased the recovery rate by a rotating disk skimmer. On the fourth day of testing, crude oil was treated with 2000 ppm of Elastol and recovered with a skimmer. The recovery rate was again high and exceeded the capacity of the pump to remove it. On this particular day, the oil in the untreated slick had formed an emulsion. This was treated with demoussifier as was the Elastol-treated slick. The demoussifier broke the emulsion in the untreated slick and no emulsion formed in the treated slick, nor were any other effects noted. It was concluded that Demoussifier and Elastol could be used together to enhance recovery and eliminate emulsion.

The tank scale tests showed that there were no scaling effects for either the Elastol or the Demoussifier. Both products worked well for the intended purpose. Elastol increased the visco-elasticity of the oil and greatly increased the skimmer recovery rate. Elastol, however, did not reduce the spreading or increase the thickness of the slick sufficiently to allow insitu burning. Demoussifier prevented the formation of water-in-oil emulsion and also broke emulsion already formed. Although demoussifier causes the oil to be less adhesive and lowers the recovery rate of skimmers, the two products can be applied together to achieve positive results.

The two products were then tested on a large scale offshore. The sponsors of this test included; U.S. Minerals Management Service, Environment Canada, Esso Resources and the Canadian Coast Guard. The field trail was conducted 50 miles offshore Nova Scotia. Five slicks of five-barrels each were laid for each of the products and each product was tested both pre-mixed and by application-at-sea, to confirm that application effects were not a factor. The treatments and results are summarized in Table 1.

TABLE 1 TREATMENTS AND RESULTS OF TRIALS

			Sample 1					Sample 2				
Trials	Slick	Treatment (ppm)	Time (min.)	Viscosity (cSt)*	Water Content	Elasticity	Comments	Time (min.)	Viscosity (cSt)*	Water Content	Elasticity	Comments
Demoussifier	1	1000	60	10 000	84%		No mousse formed	300	84 250	90%		No mousse noted
	2	250	60	2 700	54%		No mousse formed	300	62 250	93%		No mousse noted
	3	control	60	6 350	88%		Heavy mousse	270	320 000	95%		Heavy mousse
	4	post-4000	60	2 200	72%		Moderate mousse	pre-240 post-270	105 000 22 600	90% 78%		Heavy mousse Treatment broke mousse
	5	pre-1000	15	970	32%		No mousse formed	280	38 500	80%		No mousse formed
Elastol	6	3000	130	29 300		1.33	Moderately elastic	280	300 000		1.35	Highly elastic
	7	1000	145	32 250		1.28	Low elasticity	280	228 000		1.33	Moderately elastic
	8	control	135	187 000		0.99	No elasticity, widespread	290	242 000		0.99	No elasticity, widespread
	9	9000	120	93 000		1.99	High elasticity	330	696 000		2.63	Super elastic
	10	pre-3000	115	170 500		1.35	Moderate elasticity	315	156 000		1.57	Highly elastic

* 1 cSt = 1 x 10^{-2} cm^2/s

The demoussifier trials were performed by laying down a five-barrel oil slick, treating it with the product at the specified ratio, taking samples at subsequent intervals and measuring the water content and the viscosity. One slick was left untreated and then treated at the 240-minute interval to test the demoussifier's ability to break emulsion at sea. As can by seen by the large reduction in viscosity (105,000 to 22,600 cSt) over the 30-minute period between samples, the product worked well to break the emulsion. The product continued to work well over the five-hour test period to prevent the formation of emulsions. This is illustrated in Figure 1, by the strong correlation between the viscosity and the amount of treatment.

The water content of slicks was universally high, even in those slicks that did not form water-in-oil emulsions. Although water content is indicative of the formation of water-in-oil emulsions, the stability of the mixture would have to be determined because the unstable emulsions lose water over time. All slicks laid over the two-day period rapidly took up water, although only slicks not treated with demoussifier during the first day formed stable emulsions.

The Elastol tests were performed in an analogous manner to that of the Demoussifier, with one control slick laid and one slick being pretreated to test the effect of at-sea treatment. The slicks were sampled periodically and both viscosity and elasticity were measured immediately on board ship. The elasticity of the treated slicks was significantly higher than that of the untreated slicks and corresponded to that experienced in the laboratory. In fact, as shown in Figure 2, it actually exceeded laboratory results at higher doses. This unexpected result is probably due to the better mixing achieved in the field situation.

Both agents functioned well in large-scale tests offshore. Both agents were shown to have beneficial effects when used for their intended purpose under all conditions tested.

Surface Washing Agents and Dispersants

The most common and most suggested treating agent are those containing surfactants as the major ingredient. These agents have been divided into two groups, dispersants and surface washing agents. The reason for this division will become readily apparent.

Surfactants have varying solubility in water and have varying actions toward oil and water. One parameter that has been used to characterize surfactants is the HLB or the hydrophilic-lipophilic balance.[16] A surfactant with an HLB of about 1 to 8 promotes the formation of water-in-oil emulsions and one with an HLB in the range of 12 to 20 promotes the formation of oil-in-water emulsions. Dispersants have HLB's in the range of 9 to 11. The HLB range as defined is only applicable to non-ionic surfactants, however ionic surfactants can be rated using an expanded scale and often have HLB's ranging from 25 to 40. They are strong water-in-oil emulsifiers, very soluble in water, relatively insoluble in oil, and generally work from the water to any oil present.

Such products have little applicability to oil on water because they rapidly disappear in the water column, having little effect on oil. However, because of their commonality and cheapness many ionic-surfactants are proposed as dispersants. It is these agents, that should be better classed as surface-washing agents.

Surface-washing agents then are surfactant-containing mixtures with high HLB's and are best suited to removing oil from solid surfaces such as roads and parking lots. EETD has been trying to develop an effectiveness test for such agents, but has had no success to date; no agent has performed better than water. Many such agents come onto the market each year, many are re-packaged industrial cleaners and have little utility in spills. Use on heavily oil-encrusted concrete has shown some value, but such applications are not typical of spills.

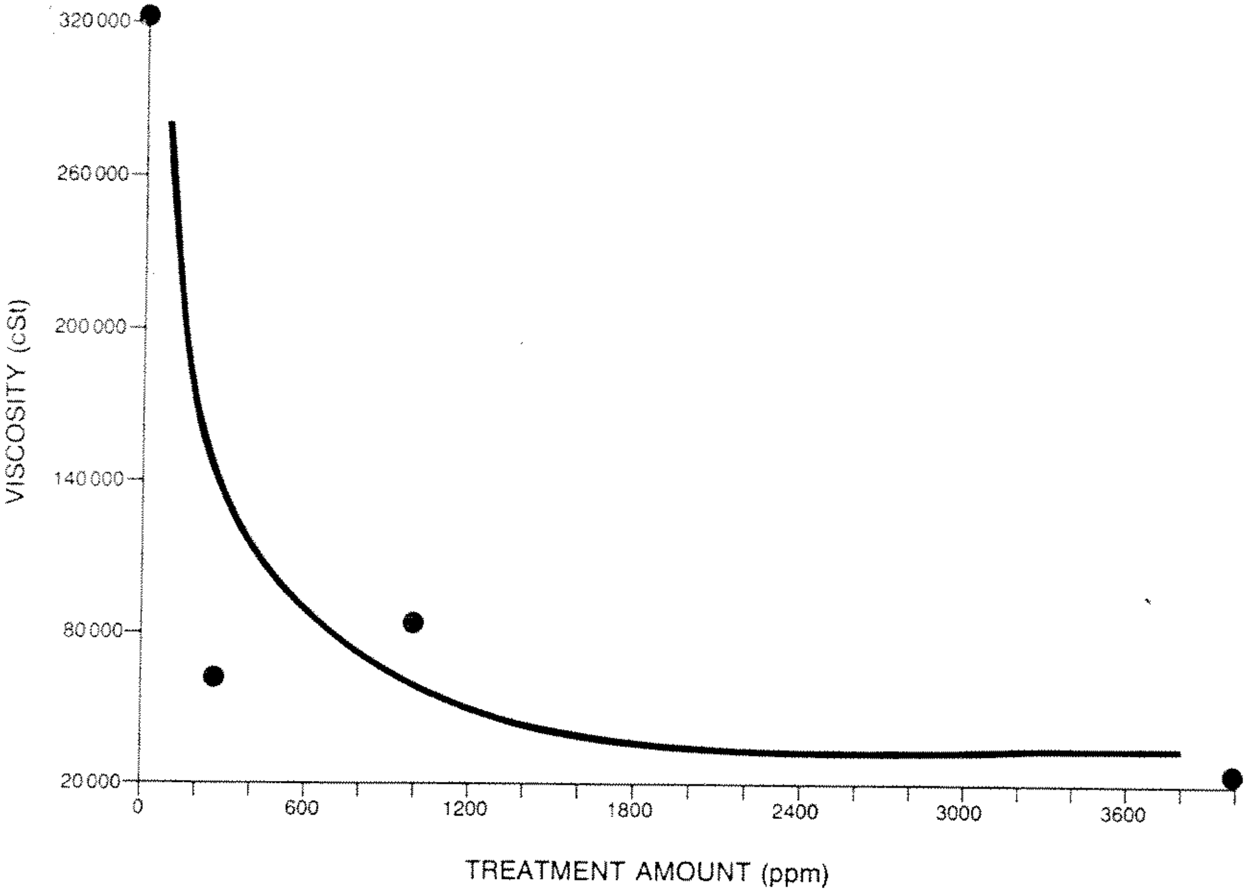

FIGURE 1 THE EFFECT OF DEMOUSSIFIER APPLICATION ON VISCOSITY

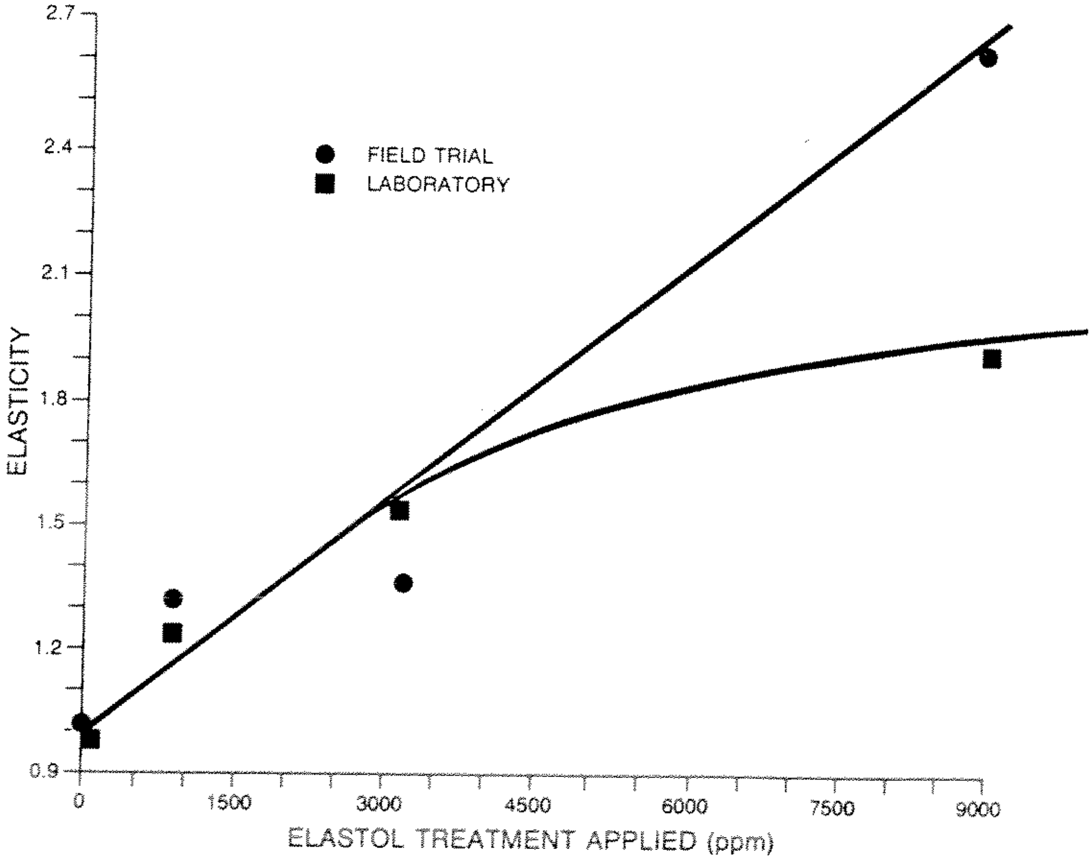

FIGURE 2 ELASTICITY OF OILS AFTER ELASTOL TREATMENT

Dispersants are the biggest class of oil spill treating agents and have perhaps generated the greatest amount of studies and discussion since the birth of the oil spill industry twenty years ago after the TORREY CANYON incident. Discussion is still as lively today and there still exists a polarization between dispersant proponents and opponents. Little has changed in the way of documentation. There is still no undisputed documentation on large-scale experiments or use to show that dispersants are effective or not. Similarly, no large scale biological experiments have convinced all environmentalists that the use of dispersants is safe in all conditions, although the evidence is becoming increasing clear that dispersants cause little ecological damage above that by un-treated oil and that they could in fact minimize ecological damage if they were effective.

The U.S. Minerals Management Service led the support of a National Academy of Science study of the dispersant situation. The study, which began two years ago and used literature up to that point, has recently released its conclusions and will shortly release the entire report.[17] Two main questions were first answered about dispersants. The first, "do they do any good", is answered with a resounding "maybe". The reason is that only in a few tests were dispersants shown to be effective; in most others they were not. The two pages containing this answer are a politician's dream in circumlocution, but the fact remains that there is still no undisputed and well-documented case where dispersants have been shown to have effectiveness values above 50%.

The second major question, "Do they do any harm", was answered in a shorter, but similarly circumlocutory manner. The best interpretation of the answer is that dispersants will not cause harm.

A number of recommendations were also made:

1. That dispersants might be considered as a first-response option along with mechanical clean-up,
2. That a rapid decision-making process be put into place to allow use while oil is still dispersable,
3. That ecological assessments of dispersants be made at sites where the water is shallow to clarify differences between dispersed and untreated oil,
4. A large number of physical studies be undertaken to determine the physics and chemistry of dispersant action and interaction,
5. That biological research should employ realistic field concentrations,
6. That dispersant formulations should be made readily available to researchers,
7. That methods be developed to compare field and laboratory exposures,
8. That degradation rates of dispersed versus non-dispersed oils be examined,
9. That additional ecological studies in shallow waters

with defined circulation be conducted,

10. That studies of fur and feather insulation after exposure to dispersed oil, hatchability of eggs and effects of ingested oil be made, and

11. That remote sensing and other analytical equipment is needed to determine field effectiveness.

While useful, the recommendations should be taken in the context of the process by which they were developed. The weaknesses of the NAS recommendations include the following:

1. They are largely based on studies at least two years old,
2. They presume that the dispersant is intrinsically effective and that effectiveness problems are only in the use of the "effective" product,
3. Recommendations are somewhat based on consensus among committee members,
4. Personal biases and desires for funding of personal projects are evident, and
5. Few data are available for the application and effectiveness of dispersants, thus personal recollection and other less reliable sources had to be used.

The main report contains much useful information and represents a good collection of data on dispersants.

Dispersants - Field Effectiveness Trials

Over the past 12 years, 107 test spills have been laid out to test the effectiveness of oil spill dispersants.[18] These spills are summarized in Table 2. A number of smaller tests or other tests which were not documented have taken place but are not included here. Of the 107 slicks documented, 23 are controls used to establish a comparison. Percentage effectiveness is reported in 25 spills and the average for these is 30%. Values range from 0 to 100%. Most experimenters have not assigned effectiveness values because, as will be demonstrated in more depth later, effectiveness values are hard to assign.

The test results show clearly that dispersants are not highly effective, even under highly controlled experimental situations. Of greater concern than this is the methodology used to estimate effectiveness. Some experimenters simply estimated effectiveness, but most based their measure on integrations of water column concentrations relative to surface slick dimensions. This is not a correct means to perform the measure because the underwater concentrations have little positional relationship to the surface slick. Underwater dynamics of the ocean are very different than surface dynamics. Extreme cases of the positional variances between surface and sub-surface slicks have been illustrated by Brown and Goodman in controlled tank testing.[19] Their work has shown that the underwater plumes move in highly random fashions with respect to the surface slick and even two trials conducted on the same day will not have similar movement patterns.

TABLE 2 SUMMARY OF EFFECTIVENESS TRIALS

TRIAL NUMBER	YEAR	LOCATION	OIL TYPE	APPLICATION VEHICLE	CLAIMED EFFECTIVENESS
1	1976	NORTH SEA	EKOFISK	SHIP	0%
2			KUWAIT	SHIP	100%
3	1978	NEW JERSEY	MURBAN	HELICOPTER	-
4			LA ROSA	HELICOPTER	-
5			MURBAN	HELICOPTER	50%
6			LA ROSA	HELICOPTER	100%
7	1978	CALIFORNIA	NORTH SLOPE	HELICOPTER	-
8				AIRPLANE	-
9				HELICOPTER	-
10_11				SHIP	-
12				AIRPLANE	-
13-14				SHIP	-
15				ABOVE 3	-
16-18	1978	VICTORIA	NORTH SLOPE	SHIP	-
19	1979	LONG BEACH	PRUDHOE	CONTROL	0.50%
20				SHIP	8%
21				SHIP	5%
22				AIRPLANE	78%
23				AIRPLANE	45%
24				CONTROL	1%
25				AIRPLANE	60%
26				SHIP	11%
27				SHIP	62%
28-41	1979	FRANCE-PROTECMAR 1	LIGHT FUEL	ALL 3	-
42-49	1980	FRANCE-PROTECMAR 2	LIGHT FUEL	ALL 3	-
50	1981	FRANCE-PROTECMAR 3	LIGHT FUEL	AIRPLANE	50%
51				AIRPLANE	-
52				CONTROL	-
53	1981	NEWFOUNDLAND	ASMB	CONTROL	-
54				AIRPLANE	-
55	1982	NORWAY	STATFJORD	CONTROL	0.60%
56				SHIP	6%
57				SHIP	17%
58				CONTROL	3%
59				SHIP	19%
60				SHIP	22%
61				SHIP	2%
62	1982	NORTH SEA	ARABIAN	CONTROL	-
63-64				AIRPLANE	-
65-67	1982	FRANCE-PROTECMAR 5	LIGHT FUEL	SHIP	-
68-69				AIRPLANE	-
70				HELICOPTER	-
71				PREMIXED	-

TABLE 2 ctd. SUMMARY OF EFFECTIVENESS TRIALS

TRIAL NUMBER	YEAR	LOCATION	OIL TYPE	APPLICATION VEHICLE	CLAIMED EFFECTIVENESS
72				CONTROL	-
73-74	1983	HOLLAND	LIGHT FUEL	CONTROL	2%
75-76			STATFJORD	CONTROL	2%
77-79			STATFJORD	AIRPLANE	2%
80			LIGHT FUEL	AIRPLANE	2%
81			STATFJORD	PREMIXED	100%
82-83	1983	HALIFAX	ASMB	CONTROL	1%
84				HELICOPTER	2.50%
85				HELICOPTER	13%
86				HELICOPTER	10-41%
87				CONTROL	7%
88-89	1984	NORWAY	STATFJORD	CONTROL	-
90-92				AIRPLANE	-
93				PREMIXED	-
94	1985	FRANCE-PROTECMAR 6	LIGHT FUEL	CONTROL	-
95				SHIP-SPRAY	-
96				SHIP-AEROSOL	-
97				HELICOPTER	-
98-99	1985	NORWAY	STATFJORD	CONTROL	-
100				PREMIXED	-
101			EMULSION	PREMIXED	-
102-104	1986	BEAUFORT SEA	FEDERATED	CONTROL	-
105-107				HELICOPTER	-

Furthermore, all of the experimenters who used underwater concentrations to estimate field effectiveness also used the method of dividing the water into different compartments and averaging concentrations. Mathematically this is not appropriate and can result in effectiveness values that are much larger and range from twice to ten times greater than the actual values. Because of these factors underwater estimates of oil spill dispersant effectiveness are highly inaccurate and misleading.

Surface measures are also inadequate. Remote sensing does not provide a thickness measure and thus calculating volume is impossible. Numerous surface phenomena also interfere with the process of estimating slick volume. These have been detailed in a recent paper by Goodman and Fingas.[20]

In summary, field trials of dispersant effectiveness have not shown any quantitative or qualitative proof of high (>50%) dispersant effectiveness. Analytical means do not exist to accurately quantify dispersant effectiveness at field trial situations.

Dispersants - Actual Usage

Table 3 lists dispersant usage during some notable large spills.[21,22] Results are summarized from the noted references. The problem with actual spill data is that some observers may have reported seeing evidence of effectiveness and others directly the opposite. In none of the cases were any analytical means tried to quantify effectiveness or even to provide better estimates. Dispersants are used on a routine basis in countries like Great Britain and in many Arabic counties. Again no quantitative results are available to show effectiveness nor lack of such.

TABLE 3 HISTORICAL USE OF DISPERSANTS

SPILL EVENT	YEAR	COUNTRY	AMOUNT SPILLED(t)	DISPERSANT AMOUNT(t)	RESULTS
TORREY CANYON	1967	ENGLAND	119000	10000	LITTLE EFFECTIVENESS, ADVERSE ECOLOGICAL
OCEAN EAGLE	1968	PUERTO R.	12000	60	NO EFFECT
SANTA BARBARA	1969	USA	1000	32	NO EFFECT
ARROW	1970	CANADA	5000	12	NO EFFECT
PACIFIC GLORY	1970	ENGLAND	6300	?	LITTLE EFFECT
SHOWA MARU	1975	SINGAPORE	15000	500	LITTLE EFFECT
JAKOB MAERSK	1975	PORTUGAL	88000	110	LITTLE EFFECT
OLYMPIC ALL.	1975	ENGLAND	2000	220	LITTLE EFFECT
URQUIOLA	1976	SPAIN	100000	2400	LITTLE TO NO EFFECT
AMOCO CADIZ	1978	FRANCE	220000	2500	LITTLE EFFECT
ELENI V	1978	ENGLAND	7500	900	NO EFFECT
CHRISTOS BITAS	1978	ENGLAND	3000	280	LITTLE EFFECT
BETELGEUSE	1979	IRELAND	1000	35	NO EFFECT
IXTOC I	1979	MEXICO	500000	5000	LITTLE EFFECT
SIVAND	1983	ENGLAND	6000	113	LITTLE EFFECT

Dispersants - Laboratory Studies

Few laboratory studies have been done on the process of dispersant action. The Mackay studies of recent years are the exception, but only begin to answer many of the questions which arise.[23,24] Recent studies have also indicated that dispersant action is very complicated and poorly understood.[16] In particular, we do not understand the mechanisms behind dispersant mixing with oil, its alignment at the oil/water interface, its subsequent partitioning from oil to water and its dynamics at the interface. These studies have also shown that there exist interferences to dispersant effectiveness including; dispersant herding of the oil, complete lack of mixing in some situations, accelerated weathering of oil by dispersant, and resurfacing of dispersed oil. Until some of these problems and mechanisms are understood or overcome, it will be difficult to assess the effectiveness potential of dispersants.

A number of laboratory studies have been performed to compare the test results from different apparatus and procedures. A review of these results show that there is poor correlation in effectiveness results between the various test methods.[25] A recent study by the present author has shown that lack of correlation is primarily a function of settling time allowed between the time that the energy is no longer applied and the time that the water sample is taken from the apparatus.[26] Another important factor is that of the oil-to-water ratio in the apparatus. When these two parameters are adjusted to be the same and to larger values, test results from most apparatus are similar. Results from more energetic dispersant effectiveness tests, such as the Mackay test and the Labofina or Warren Springs test, are somewhat higher, but when corrected for natural dispersion, these results are nearly identical to those from less energetic apparatus. Results from a series of tests and after having performed these corrections are shown in Table 4. The effectiveness results from all tests are nearly identical, especially when considering that the errors for measurement in the Mackay and Labofina tests are 10 percent or more. The fact that these values are nearly identical may imply that they have some meaning. Just the fact that this phenomena occurs also indicates that energy plays a lesser role than was previously thought. The high energy in the Mackay and Labofina tests only increases the dispersant effectiveness for those oils that disperse naturally.

Dispersants - Summary

The state-of-the-art in dispersants is summarized as follows:

1. Effectiveness is the main issue of dispersant usage and it is increasingly evident that dispersant effectiveness may range in practice from about 10 to 30 %,

2. Analytical means for measuring oil dispersant effectiveness at sea is poor,

3. Dispersant effectiveness cannot be measured accurately using the oil slick as reference because of the different

TABLE 4 EFFECTIVENESS IN DIFFERENT APPARATUS

AFTER CORRECTION FOR NATURAL DISPERSION

OIL	DISPERSANT	DISPERSABILITY IN PERCENT			
		SWIRLING FLASK	FLOWING CYLINDER	LABOFINA MODIFIED	MNS MODIFIED
ADGO	9527	61	52	60	60
	CRX-8	42	40	59	61
	EN 700	67	59	58	70
AMAULIGAK	9527	48	38	56	44
	CRX-8	56	46	43	71
	EN 700	54	39	39	59
ASMB	9527	22	21	20	19
	CRX-8	28	31	22	41
	EN 700	43	43	51	56
ATKINSON	9527	7	18	20	7
	CRX-8	9	10	10	10
	EN 700	8	18	18	12
BENT HORN	9527	29	46	29	29
	CRX-8	27	37	27	51
	EN 700	44	51	19	42
FEDERATED	9527	39	35	41	35
	CRX-8	23	31	25	76
	EN 700	38	42	60	76
GEAR OIL	9527	29	18	18	12
	CRX-8	40	25	27	10
	EN 700	10	6	15	30
HIBERNIA	9527	6	12	12	6
	CRX-8	9	10	8	9
	EN 700	7	8	12	14
ISSUNGNAK	9527	24	22	21	20
	CRX-8	42	76	35	76
	EN 700	42	60	35	76
LAGO MEDIO	9527	7	8	18	14
	CRX-8	11	15	8	10
	EN 700	10	23	13	24
LUBE OIL	9527	13	19	20	24
	CRX-8	14	24	20	28
	EN 700	13	23	20	56
MOUSSE MIX	9527	9	15	22	30
	CRX-8	11	25	13	26
	EN 700	24	32	18	32
NORMAN WELLS	9527	41	55	43	39
	CRX-8	60	47	49	57
	EN 700	63	53	53	81
PANUK	9527	100	100	89	100
	CRX-8	93	100	85	100
	EN 700	100	100	87	100
PRUDHOE BAY	9527	7	13	27	14
	CRX-8	5	16	18	23
	EN 700	17	14	28	27
SYNTHETIC CRUDE	9527	57	50	58	63
	CRX-8	69	55	40	62
	EN 700	61	39	56	62

movement regimes of the surface slick and the plume, because of the unknown distribution of the plume and because a large number of data points are required to define the plume,

4. Remote sensing means to determine dispersant effectiveness do not yet exist nor is there a slick thickness-measuring capability,

5. Effectiveness of actual dispersant usage is not quantitatively documented and reports of effectiveness are very contradictory,

6. The toxicity, both short and long-term, of dispersants and dispersed oil does not seem to be a major problem or issue,

7. The operating processes of dispersants are poorly understood as are a number of competing processes, and

8. Laboratory effectiveness measures may be meaningful if done at high water-to-oil ratios and with settling times of 10 minutes or greater, such correction produces identical results except in highly energetic devices where correction for natural dispersion is also required, and

9. Dispersant effectiveness is not as energy-dependent as formerly thought.

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CHEMICAL TREATMENT OF OIL SPILLS

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Table Of Contents

List of Figures

List of Tables