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# Project Summary

# Three New Techniques for Floating Pollutant Spill Control and Recovery

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**Three new techniques were investigated for controlling and recovering oil and floating hazardous material (HM) spills in water bodies: amine carbamate gelling agents, fluorescent agents for nighttime operations, and environmental sonic sensing. The last two methods are aimed at solving the serious problems posed by the poor visibility that often accompanies spill situations. Operational capability is nonexistent at night or during other periods of low visibility. But fast, continuous action is essential to recovery operations, since cleared areas can be covered again in just a few hours as the unharvested contaminant drifts back over the cleared track. Moreover, skimmer operations are most efficient with thicker pollutant films. Thus, the spreading of the material both increases the operational area and decreases cleanup efficiency.**

**Amine carbamate gelling agents can be used to gel oil and floating HM spills quickly and completely to a solid consistency. This gel is much more visible than the liquid pollutant, does not readily flow or spread, is very easily, quickly, and completely recovered by nets or sieves, is much less volatile (and thus less hazardous with regard to fire and toxicity), does not permeate sand or other porous materials, and can be easily regenerated into the original pollutant and gelling components.**

**Cheap, nontoxic, and highly efficient fluorescent agents can be applied in low (50 ppm) concentrations onto spill areas by conventional crop dusting or spraying techniques. In open water with no floating pollutant cover, the fluorescer is dissipated into the water column; but it is preferentially retained without extraction into the water wherever there are pollutant patches. At night, commercial UV (ultraviolet, or "black" light) display lights (or modified ordinary mercury vapor street lights) can be beamed over the spill area. Vivid fluorescent illumination occurs only from pollutant spill patches, thereby making such areas easily visible and extending spill control and recovery operations into nighttime hours.**

**Underwater sonic sensing techniques were shown to be excellent means of locating near-surface pollutants. In typical spill situations, a large portion of the pollutant is in a floating globule near the water surface as a result of surface wave action. This condition is particularly common for high-density materials. Sonic sensing can also provide much-needed information on the rate of dissipation of pollutant into the water column. Sonic sensing and fluorescent techniques also have excellent synergistic capabilities when used together, though both techniques are excellent alone.**

***This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

Large quantities of oil and hazardous materials (HM) are constantly being handled by inland and marine transportation and support equipment. Spills during transit or at producer and user storage facilities pose a serious threat to the health and welfare of the general public and the environment. This study investigates improved techniques for controlling and recovering spills of oil and floating, immiscible HM, particularly during periods of poor visibility. Several concepts were considered feasible: The use of amine carbamate gelling agents, fluorescent agents, and environmental sonic sensing equipment.

Amine carbamate gelling agents have advantages over presently used absorbent or gelling agents as a means of immobilizing the pollutants. They also considerably increase visibility and greatly facilitate recovery with unconventional equipment such as nets, sieves, etc.

The use of fluorescent agents provides nighttime operational capabilities in which long wave length ultraviolet (UV) light causes floating patches of pollutant to stand out vividly in the darkness. This advantage could be extremely important in high latitudes where winter nights are quite prolonged and there is little or no daylight. The system would also be quite advantageous in tracking pollutant slicks at night in any area of the world and enabling spill control and recovery operators to maintain round-the-clock working hours.

Environmental sonic sensing equipment can be used to track near-surface pollutant dispersed below the water surface by wave action. This technique has also proved invaluable for determining the rate of dissipation of the pollutant into the water column.

Combinations of the above techniques can also be used to afford synergistic effects.

The purpose of this study was to investigate the effectiveness and practicality of these concepts in simulated and actual field environments. Tests were performed at (1) the U.S. Environmental Protection Agency (EPA) Oil and Hazardous Material Simulated Environmental Test Tank (OHMSETT) at Leonardo, NJ; (2) Bay F test facilities in Edison, NJ; (3) the U.S. Naval Submarine Base at New London, CT; and (4) aboard EPA's ocean survey vessel *Antelope* in Cape Cod Bay south of Boston, MA.

## Description of Techniques

### *Amine Carbamate Gelling Agents*

Recovery and control of pollutants on inland and open waters is an environmental problem of prime importance. One of the greatest difficulties in such efforts is the inability to attain complete recovery of the pollutant, largely because of the spread of unharvested pollutant back on the track previously cleaned by skimmer or similar equipment. Thus continued passage of the recovery craft over the contaminated water surface only reduces the film thickness. Each time the craft passes, the pollutant tends to flow back over the cleaned track, seriously limiting recovery efficiency.

Additives have been used in the past to facilitate collection of pollutant spills by gelation or other agglomerative processes. But invariably problems have arisen with viscous interfaces between the pollutant and the gelant that tend to prevent complete and rapid distribution.

This project has developed an amine gelling agent that can gel oil and HM spills to a solid consistency quickly, safely, and economically using readily available amines. The latter are first added as a spray to the pollutant to form a complete solution before gelation, thus avoiding the formation of viscous interfaces. Carbon dioxide is then added to react with the amine and form a zwitterionic carbamate salt that sets up a gelling matrix within the spill:

$$R\text{-}NH_2 + CO_2 \rightarrow R\text{-}\overset{+}{N}H_2\text{-}CO_2^-$$

A three-component solution is used, consisting of 70% dehydroabietylamine (Amine D™, Hercules Corp.*), 15% ethanol, 15% 6,6-dimethylbicyclo [3.3.1] hept-2-ene-2-ethanol ("Nopol"). The ethanol is used to decrease the viscosity of the amine, and the Nopol increases the uptake of water into the gel, providing increased gel strength. A dose rate of approximately 15% of the gelling agent formulation in the pollutant is required for good gel consistency to occur.

This process provides several other significant advantages in addition to enabling fast and complete mixing before carbonation to form the gel. The visibility of the spill is greatly enhanced. The vivid white color of the gelled pollutant makes harvesting much easier, particularly in conditions of low visibility. The rigidity of the gel drastically reduces its mobility and greatly lessens its tendencies to spread back over previously cleaned tracks or over ever-increasing areas. The rigidity of the gelled pollutant also enables easier and safer transportation after recovery since free surface ("sloshing") effects are eliminated. Thus solidified pollutant can be transported by barge or other recovery vessels much more quickly and safely, particularly under adverse weather conditions. Furthermore, simple containers such as fiber pack drums, cardboard boxes, and plastic or burlap bags can be used for transporting and storing the gelled pollutant. Should gelled pollutant wash up on a beach or be accidentally spilled onto a wood or other porous surface, this solid form will not readily permeate, whereas liquid pollutant will be absorbed readily. Gelled pollutant also has greatly reduced evaporation rates and correspondingly increased flash points. Thus flammability and toxicity are also reduced.

Recovery of the gelled pollutant is virtually complete, and there is no residual sheen. The gelled pollutant is very compatible with conventional harbor skimmer craft in spill control and recovery operations. Furthermore, it is relatively immobile, with little or no tendency to move away from the recovery craft or to drift back over previously cleared areas.

Upon completion of the recovery procedure, the gelled pollutant can be subjected to pressure filtration, and more than 90% of the original pollutant (oil or HM) can be extracted, uncontaminated by gelling agent. The filter cake can then be heated to about 100°C to drive off the carbon dioxide and regenerate the amine and Nopol for reuse.

Some limitations exist for this process. Since a concentration of about 15% of the amine mixture is needed to effect gelation of pollutant, this process would probably not be practical for very large spills. Assuming that it would be feasible to stockpile and transport twenty-five 55-gal barrels of gelling agent, spills of about 10,000 gal could be handled by this process. Also, high-viscosity pollutant spills are probably poor candidates because of poor mixing of the gelling agent. A few important types of pollutants are not easily gelled—some lubricating oils, vegetable oils, and highly acidic materials, for example, which preferentially react with the basic amine gelling agent. But the great majority of floating pollutant spills (including all organic materials cited in Table 1) are compatible with this gelling system.

The principle problem that remained upon entering the final development work in this phase of the overall project was the means of delivering the gelling agents (the liquid amine and Nopol combination

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

on the one hand and the carbamating $CO_2$ in a subsequent treatment) onto the spill. Preferably the method would involve a single pass with one recovery and control craft.

## Fluorescent Agents for Nighttime Operations

Because considerable advantages were derived from the enhanced visibility of gelled oil and floating HM pollutants, fluorescent agents were studied for their ability to provide operational visibility at night for pollutant spills (gelled or ungelled). The early work on this project showed that commercially available, nontoxic, and highly efficient fluorescent agents with both oil and water compatibility could be applied in very low concentrations to pollutant spills with excellent results. Under laboratory conditions, such fluorescent agents were retained exclusively in the patches of pollutant floating on water surfaces, with little or no extraction of the agent into the water column over weeks or even months. With illumination only by relatively low intensity, long-wave UV irradiation, very vivid fluorescent illumination from the floating patches made them readily visible. Moreover, the organic materials most frequently involved in spill situations (Table 1) were all shown to be compatible with the fluorescence system. All that remained was to demonstrate the process in the field, with the main problems being the delivery of the agent over such contaminated water surfaces and the means of providing adequate UV illumination safely and efficiently.

## Environmental Sonic Sensing Techniques

A large proportion of pollutant spills are found near rather than at the water surface. Such is particularly true of high-density, low-viscosity, and/or high-polarity (and thus more soluble) materials, and of course it is especially the case in turbulent waters. The rate of pollutant dissipation into the water column is of great importance from the standpoint of ecology as well as recovery. Recently in the IXTOX-1 oil spill, underwater sonic sensing techniques were very useful in locating near-surface pollutant.

The possible use of underwater sonic sensing in association with fluorescent agents was also investigated to determine the capability of the systems.

*Table 1. Chemicals Most Frequently Involved in Transportation Incidents*

| Commodity | All Modes | | | Highway | | | Railway | | |
|---|---|---|---|---|---|---|---|---|---|
| | Deaths | Injuries | Incidents | Deaths | Injuries | Incidents | Deaths | Injuries | Incidents |
| Paints, enamel, lacquer | 0 | 28 | 13,304 | 0 | 26 | 13,075 | 0 | 0 | 57 |
| Corrosive liquids | 12 | 306 | 7,959 | 10 | 263 | 7,660 | 2 | 35 | 235 |
| Wet batteries | 0 | 23 | 5,429 | 0 | 20 | 5,334 | 0 | 0 | 29 |
| Flammable liquid[a] | 5 | 211 | 3,076 | 5 | 188 | 2,763 | 0 | 19 | 224 |
| Paint remover | 0 | 60 | 2,828 | 0 | 59 | 2,781 | 0 | 1 | 17 |
| Sulfuric acid | 2 | 422 | 2,218 | 2 | 212 | 1,555 | 0 | 210 | 639 |
| Hydrochloric acid | 0 | 104 | 1,760 | 0 | 76 | 1,502 | 0 | 28 | 237 |
| Electrolyte battery fluid | 0 | 5 | 1,310 | 0 | 5 | 1.273 | 0 | 0 | 17 |
| Plastic and resin solutions | 0 | 12 | 1,206 | 0 | 11 | 1,138 | 0 | 0 | 30 |
| Flammable or poisonous insecticides | 0 | 28 | 894 | 0 | 25 | 876 | 0 | 3 | 13 |
| Ink | 1 | 0 | 829 | 1 | 0 | 819 | 0 | 0 | 3 |
| Alcohol[a] | 0 | 13 | 760 | 0 | 8 | 626 | 0 | 4 | 92 |
| Phosphoric acid | 0 | 32 | 671 | 0 | 11 | 278 | 0 | 21 | 384 |
| Sodium hydroxide | 2 | 178 | 635 | 2 | 120 | 451 | 0 | 54 | 173 |
| Acids[a] | 1 | 79 | 573 | 1 | 35 | 537 | 0 | 44 | 25 |
| Anhydrous ammonia | 13 | 404 | 470 | 12 | 265 | 129 | 1 | 139 | 336 |
| Nitric acid | 4 | 82 | 437 | 1 | 76 | 395 | 0 | 2 | 31 |
| Solvents[a] | 0 | 4 | 374 | 0 | 4 | 349 | 0 | 0 | 13 |
| Corrosive solids[a] | 0 | 56 | 370 | 0 | 28 | 350 | 0 | 0 | 15 |
| Compressed gases[a] | 2 | 62 | 512 | 2 | 61 | 465 | 0 | 1 | 28 |
| Radioactive materials | 0 | 2 | 377 | 0 | 0 | 262 | 0 | 0 | 7 |
| Methanol | 0 | 10 | 350 | 0 | 7 | 236 | 0 | 3 | 106 |
| Rust preventers and removers | 0 | 1 | 266 | 0 | 1 | 265 | 0 | 0 | 0 |
| Acetone | 0 | 4 | 219 | 0 | 0 | 171 | 0 | 3 | 38 |
| Xylene | 1 | 7 | 216 | 1 | 3 | 178 | 0 | 0 | 29 |
| Subtotal | 43 | 2,133 | 47,043 | 37 | 1,504 | 43,468 | 3 | 567 | 2,778 |
| All other hazardous materials | 168 | 3,180 | 22,988 | 128 | 1,740 | 19,790 | 39 | 1,264 | 2,671 |
| Total | 211 | 5,313 | 70,031 | 165 | 3,244 | 63,258 | 42 | 1,831 | 5,449 |

[a]Not otherwise specified. Note: Data are for reported incidents, 1971-78. Source: Department of Transportation.

## Procedures

A number of tests were performed during the course of the investigation. Their characteristics and objectives were as follows:

1. Preliminary investigations were sponsored by the U.S. Navy (1975-76). These were conducted primarily in the laboratories of the University of Lowell and in the test facilities of the JBF Company at Wilmington, MA, to determine the tentative feasibility of the amine gelation system.
2. Preliminary extrapolation of the amine gelation system was made to larger-scale situations by EPA in 1976-77. These were conducted initially at the University of Lowell and then extrapolated to OHMSETT. This facility has a water surface 203 m long and 20 m wide, with moving bridges for towing floating equipment at speeds up to 3 m/s and wave-making equipment capable of imposing regular or harbor chop waves up to 1.2 m high.
3. Tests at the EPA indoor tank (Bay F) facility at Edison, NJ, were conducted in 1978 to determine the feasibility of using liquid or gaseous $CO_2$ rather than the solid dry ice previously used.
4. Prototype floating pollutant spill control and recovery equipment was designed, constructed, and tested in 1978. This series of tests at OHMSETT involved a control and recovery craft that would affect gelation of HM spills by simultaneous spraying and carbonation of the spill in a single pass.
5. Prototype portable pollutant spill control and recovery equipment was designed, constructed, and tested in 1979. This testing was performed at the Bay F tank and involved preliminary design of a recovery and control craft that could be easily stored and transported to remote spill sites.
6. Field tests of the recovery and control craft were conducted at the U.S. Naval Submarine Base in New London, CT (1980-81). These tests indicated the need for improvements in design of the craft. As a result, a prototype trimaran (three-hulled) raft was constructed to meet the criteria and requirements for a portable recovery and control craft for use in amine gelation work.
7. Fluorescent agents and acoustic sensing were used for nighttime floating pollutant spill control and recovery operations (1978 to present). These tests were performed at the EPA OHMSETT facility, the University of Lowell, Sias Laboratories of the Lahey Clinic Foundation, Datasonics, Inc., Massachusetts Maritime Academy, and on board the EPA ocean survey vessel *Antelope* at sea in Cape Cod Bay. The objectives of these tests were to demonstrate full operational capabilities of these systems.

## Results and Conclusions

### *Amine Carbamate Gelling Agents*

1. Amine D (70%) /Nopol (15%) /ethy alcohol (15%) is an optimum gelling agent for pollutant spills. The extractability of amine from a pollutant spill into the water column affords low concentrations in the water (about 1 ppm). The toxicity of Amine D to marine life is low—of the same order as that of ordinary hydrocarbons. Gelled pollutant compositions are not readily emulsified under ordinary turbulent water conditions.
2. Commercially available, liquified $CO_2$ (pressurized in cylinders or tanks) is the optimum carbamating agent.
3. Conventional motor whaleboats or similar craft or trimaran-type rafts can be used as a single-pass, amine-spraying/carbamating craft. On either type of craft, a 1,700-lb $CO_2$ transit tank can be installed along with suitable containers of amine gelling agent (e.g., kegs or barrels). The amine is sprayed at the bow of the vessel into the oncoming floating pollutant spill, which is directed either into carbonator chutes (on either side of the boat) or between the hulls (in the case of the trimaran). $CO_2$ is directed from the transit tank shortly behind the amine sprayers, and the gelled oil is ejected astern. Large spill areas (an acre or more) could be gelled quickly—within 10 min or less. For relatively calm water conditions, the trimaran design is considered superior in terms of its increased load of gelling agent, larger crew, and easier equipment handling. For waters with considerable harbor chop conditions, the whaleboat design may be required.

### *Fluorescent Agents for Nighttime Operations*

1. Fluorescent agents can be applied by spraying on liquid solutions or by dusting with powder formulations. Current tests strongly suggest that dusting operations would be more feasible, but both techniques have proved extremely promising.
2. Very small concentrations of fluorescer (about 50 ppm) in HM spills provide excellent nighttime visibility.
3. The best dust formulations appear to be intimate mixtures of the fluorescer in powdered gypsum ($CaSO_4$). The optimum spray formulation appears to be a solution of the fluorescer in di-or tri-propylene glycol monomethyl ether solvents.
4. Uvitex OB™ (Ciba-Geigy Corp.) and Yellow 131SC™ (Morton Chemical Co.) have proved to be excellent, nontoxic, cheap, and highly efficient fluorescers.
5. The gypsum powder base is entirely nontoxic and has no fire or other hazards associated with it. Glycol ether solvents have very low fire and toxicity effects, and in the concentrations contemplated for use, they would probably present no significant hazard.

### *Environmental Sonic Sensing Techniques*

1. Underwater sonic sensing techniques were shown in an actual sea trial to provide excellent synergistic effects when used with the fluorescence technique. But both techniques are also excellent when used alone.
2. Sonic sensing is particularly invaluable when a need exists to determine the rate of pollutant dissipation into the water column.

## Recommendations

In view of the successful results of the research discussed here and in the full report, further work is proposed to extrapolate these results to full-scale operational situations. Construction, testing, evaluation, and full use of appropriate equipment and procedures are recommended with the following objectives:

1. A prototype trimaran craft for use in spill recovery and control operations

in inland waters and in harbor situations should be designed, constructed, tested, and used. The craft must be portable, easy to assemble and disassemble, and capable of supporting a load of approximately 12,000 lb for control and recovery operations over an area of about an acre in about 5 min, (gelling up to 2,200 gal of pollutant in a track up to 17 ft wide and 1-1/2 miles long). Equipment for operations with fluorescent agents under nighttime conditions will be available. When disassembled, the craft could be stored and transported in a truck trailer space of about 8 x 12 x 6 ft along with all required chemicals and supplies.

2. Full-scale tests should be performed with applications of fluorescer from aircraft or ships onto floating spills in open water. Subsequent illumination at night by UV light should be provided by modified conventional highway lighting equipment to permit full-scale nighttime recovery and control operations. Acoustic sensing gear operated from recovery vessels should be used to help locate and track such spills and determine the course of recovery and control work.

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*The complete report, entitled "Three New Techniques for Floating Pollutant Spill Control and Recovery," (Order No. PB 84-123 694; Cost: $16.00, subject to change) will be available only from:*
*National Technical Information Service*
*5285 Port Royal Road*
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