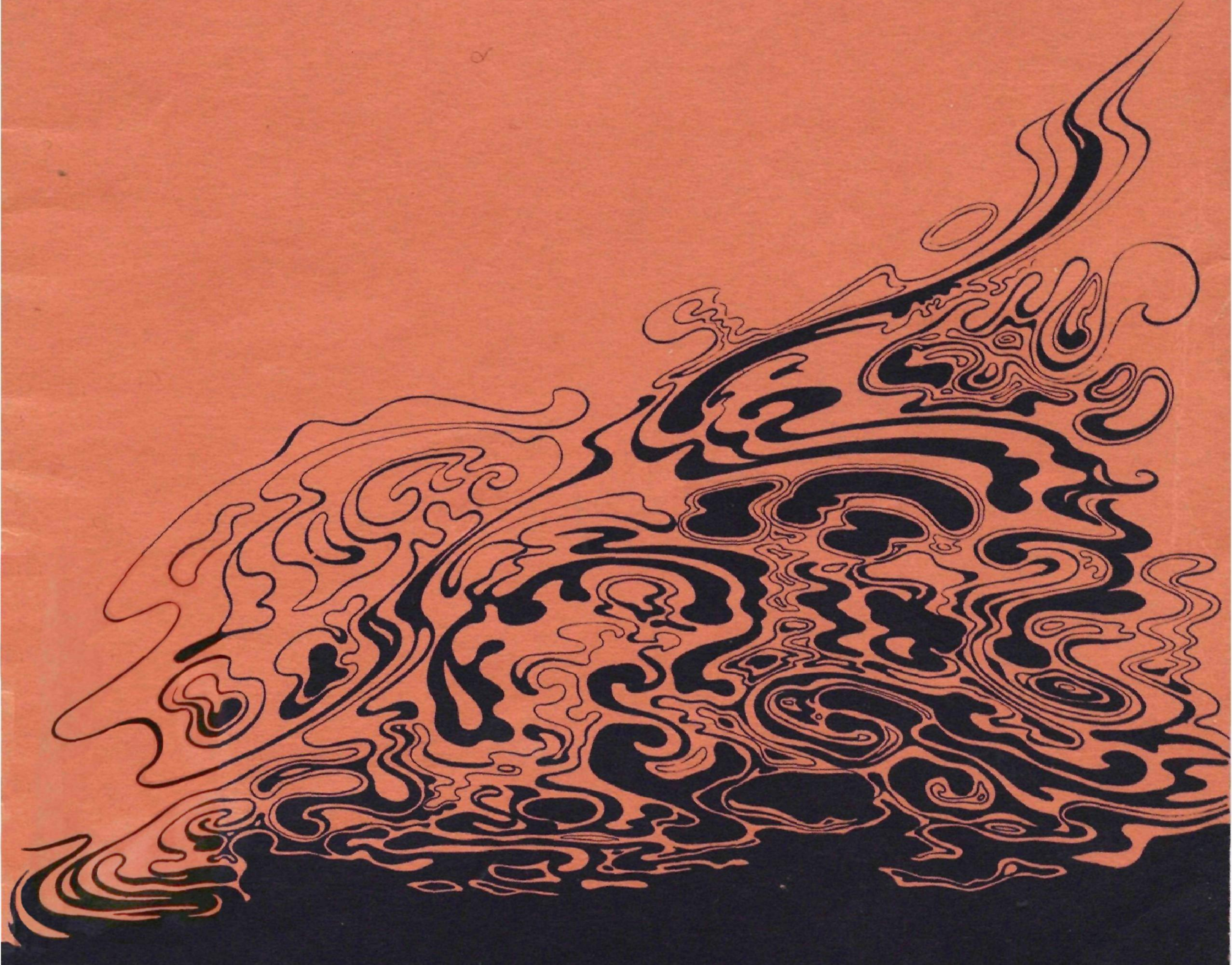
CLEAN WATER

WATER POLLUTION CONTROL RESEARCH SERIES • ORD-3

Chemical Treatment of Oil Slicks



U.S. DEPARTMENT OF THE INTERIOR • FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

CHEMICAL TREATMENT OF OIL SLICKS

A STATUS REPORT

ON THE USE OF CHEMICALS AND OTHER

MATERIALS TO TREAT OIL SPILLED ON WATER

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

DEPARTMENT OF THE INTERIOR

BY

WATER QUALITY LABORATORY

NORTHEAST REGION

EDISON, NEW JERSEY 08817

MARCH 1969

ABSTRACT

The effectiveness and potential pollutional effects of chemicals and other materials used to disperse, sink, burn or otherwise dissipate oil slicks are discussed.

Agents considered are classed as; dispersants, floating sorbents, sinking agents, gelling agents and burning agents.

Since many dispersants are presently available, much experience has been gained with the use of dispersants. However, dispersants should not be used indiscriminately, they may have deleterious effects on the ecology. It is necessary to determine the toxicity and the effectiveness of dispersants viz-a-viz the same characteristics of the oil without dispersants. Practical experience with gelling burning, floating and sinking agents is limited.

Some of the many commercial products and natural materials used in connection with recent large oil spills are reported.

KEY WORDS: Oil spills, oil spills-chemical treatment, dispersants, detergents, sorbents, floating sorbents, burning agents, sinking agents, gelling agents, dispersant toxicity, dispersant effectiveness chemical use, effects.

C O N T E N T S

INTRODUCTION

The disastrous effects of significant oil spills into the water environment, together with required remedial measures, are described in "Oil Pollution: A Report to the President," submitted early in 1968. Chemical compounds are intended to assist in the control of oil on the water and facilitate cleanup operation. Basically, chemicals are employed to disperse, gel, sink, absorb, and facilitate the burning of oil. Present knowledge has resulted primarily from experience with the major spills from the tankers TORREY CANYON and OCEAN EAGLE and the offshore oil platform at Santa Barbara, California. In addition, the FWPCA is gaining valuable experience through giving technical assistance on actual spill incidents and is conducting broad research and development programs relating to the cleanup and control of oil in the water environment.

With the exception of gelling agents, chemicals have been used during the three major incidents, singly and in combination, with varying results. Each major incident differed as to causes and immediate control of the sources of oil, the type and use of the water environment, and the nature and proximity of the shoreface. The resulting damage has been waterfowl fatalities, deposition of oil upon recreational beaches, and adverse effects to marine life.

SUMMARY

This report provides a statement by the Research Program of the FWPCA on the use of various chemicals to treat oil on water. Basically, methods employed are designed to disperse, absorb, sink, gel, and facilitate burning of oil on the water surface and affected shorelines. A number of factors must be carefully evaluated in the use of chemicals most important of which are toxicity and overall effects upon the water environment, effectiveness of the methods utilized, and cost of obtaining and applying chemicals together with recovery and disposal operations.

Dispersants theoretically serve to increase the surface area of an oil slick and disperse oil globules throughout the larger volume of water thereby aiding in accelerated degradation of oils by microbiological means. The chemical dispersants do not themselves destroy oil. They vary considerably in toxicity, effectiveness and ability to stabilize the oil after extended periods of time. Technology for proper application of dispersants over large oil slicks with necessary mixing is currently lacking. Use appears far more critical in harbor and estuary areas and in proximity to shore. Particular care must be exercised where water supply might be affected. The desirability of employing dispersants in the open sea remains doubtful although their use here is potentially more promising pending additional field data. After widespread dispersant use, reports led to the conclusion that dispersants on the dispersant-oil mixture cause much more damage to aquatic life than oil alone. For beaches, they actually compound the problem by adding to the amount of pollutants present, by

causing the oil to penetrate more deeply into the sand, and by disturbing the sand's compactness, so as to increase beach erosion through tidal and wave action.

Floating absorbents include a wide range of materials with oil-attracting and water-repelling characterisitics. Absorbents have unique advantages over other methods of oil cleanup, such as limiting the rate of slick spreading or facilitating cleanup, but it also has a number of disadvantages including delivery and application of the material, and collection and disposal of the oil-absorbent mass. Straw is extensively used as an absorbent because of availability, cheapness and accepted effectiveness; large investment in equipment and manual labor for removal of oil soaked straw is however required. Natural products or those modified by heat and chemical treatment are currently used as absorbents. An additional group of absorbent products, which hold potential promise, are those derived from the synthetic or plastic manufacturing field; of these, polyurethane and polypropylene are in greatest use. Considerable mixing or interaction between the oil and the absorbent is very desirable for maximum uptake of oil. Absorbent application and their overall use become increasingly complex with the larger oil spills. Collection and disposal of the oily mass poses greater problems than disposal of oil-water emulsions due to the relatively large bulk and due to the lack of disposal techniques that can handle the conglomerate.

Sinking agents properly applied onto an oil slick adhere to the oil, and there is subsequent absorption and sinking of the oily mass. Sinking absorbents should be evenly mixed with the slick and allowed time to react before the mass eventually sinks. For optimum effectiveness, there should also be little or no tendency for release of the oils back to the water environment. Care should be exercised in its use as the oil mass can form a layer or "blanket" on the bottom causing adverse effects on fixed shellfish beds and bottom feeding organisms. The only large-scale use of sinkants was that made by the French following the TORREY CANYON. Opinion is still divided as to efficency, cost, application, and possible environmental effects. It appears the utilization of sinking agents would be most advantageous in deeper ocean waters outside the heavier fishing zones and where there will be minimum adverse effects to productive biological life in the coastal zones.

Gelling agents applied over the surface or periphery of an oil slick show promise as another approach for containing and cleaning up oil spills. The gelled mass would still require removal from the water surface perhaps with specialized equipment developed for that purpose. Further development is necessary for this class of chemicals.

Burning agents offer an attractive and inexpensive means of disposing of large amounts of oil over the water surface. This course of action is inadvisable except in situations where the oil is sufficiently distant from the shoreline or other property subject to fire damage. Past attempts to burn oil have been largely unsuccessful due to the fact that the light ends of the oil usually are no longer present, raising the flame temperature, plus the ability of the water to remove the heat faster than it can be created. Because of the potential value of this method, however, further consideration should be given for improving and refining these procedures.

In considering the use of chemicals with oil spills, a number of factors must be carefully borne in mind. Of prime importance is the effect of the chemical or oil-chemical mixture on the water environment. The introcution of toxic chemicals in the water or on the shoreface can destroy the delicate balance of aquatic ecology and result in long-lasting damage or destruction of valuable species intended to be protected by the removal of the oil. The ability of the chemicals to accomplish the assigned task is a critical factor. The type of oil involved, the physical and chemical nature of the water body, and the particular products used will relate to the effectiveness of the method. In major incidents involving spills of oil, the cost of obtaining and applying chemicals may range into millions of dollars.

The purpose of oil removal is not to eliminate its visibility but to minimize its effects upon water shore and near shore resources. The most effective means for eliminating visible oil could destroy the very resources intended to be protected; conversely, the most visible and tedious means for removal can be the most effective in resource protection. The objective of adequate oil pollution control is to minimize the removal and minimize the short and long range adverse effect.

DISPERSANTS

Scores of products are sold in this country for the purpose of emulsifying oils. Many have been developed for such uses as clearing residual oil from cargo tanks before loading of fresh cargo. Of these, at least 70 have been claimed useful for dispersing oil from the surface of water. These products are known by a variety of names: emulsifiers, detergents, degreasers, dispersants, etc. For consistency, they will be referred to as dispersants since this term describes what they are intended to accomplish - the dispersion of oil from the surface into and throughout the body of water.

The primary components in most dispersants are surfactants, solvents, and stabilizers. Surfactants, by their affinity for both oil and water, alter the interaction between oil and water so the oil tends to spread and can be more easily dispersed into small globules - or what is commonly called an emulsion. Soap does the same thing to oil on our hands, allowing it to be emulsified or dispersed and washed away in water.

Solvents enable the active agent or surfactant, to mix with and penetrate into the oil slick and thusly form the emulsion. The solvent usually comprises the bulk of the dispersant product and may range from petroleum solvents such as kerosene to water solvents. Petroleum based and chlorinated hydrocarbon solvents represent the most toxic component in the dispersant product but also dissipate rapidly in thewater environment. Stabilizers,which are the third major component in most dispersants, fix the emulation once it is formed.

The use of dispersants in oil pollution incidents is intended to separate the slick into miniscule particles and thus provide a means of accelerating the rate of natural degradation of oil. We know that oil is degraded naturally at sea at a rate depending upon the surface area of the oil available to the microorganism populations. Increasing the surface area of the oil by dispersion is thought to accelerate this biological degradation.

Dispersants have been used for a number of years, for dispersing small oil slicks in several harbors in this country and abroad. Because of the small quantities involved, the environmental effects were minimal and the complaints limited. Few alternatives exist for handling oil spills and dispersants are easily obtained, transported and applied. They furthermore offer visible evidence of "doing something" about pollution incidents.

Their first major test came during the TORREY CANYON incident where 15,000 tons of dispersants were used to treat 75,000 tons of oil. Two-thirds of this amount was used for cleaning oil from contaminated shores and resulted in severe adverse effects on the aquatic life. The areas of the shore where dispersants were not used, but heavily polluted with oil alone, showed very minor damage according to J. E. Smith, Director of the Plymouth Laboratory of the Marine Biological Association of the United Kingdom, who studied the biological effects of the TORREY CANYON spill. These observations led to the conclusion that dispersants cause much more damage to aquatic life than oil alone.

The dispersants used during the TORREY CANYON incident were mostly solvent-based and highly toxic, killing marine organisms at concentrations around 10 parts per million.

The biological damage during the TORREY CANYON appeared to be limited to the shore areas. In the open sea where they were also used, there were no detectable effects on marine life. Officials from the United Kingdom took samples by trawling directly beneath slicks treated with emulsifiers and observed no deaths and no tainting of the flavor of commercial species. Procedures for this type of sampling are not notably precise, however.

Current information indicates that dispersants vary considerably in toxicity. Various reports state that dispersants used during the TORREY CANYON incident were highly toxic. Since then, other less toxic dispersants have been developed. Fifty percent of marine test fish are killed within 24 hours by exposure to concentrations as low as 4 parts per million of one product, and as high as 10,000 parts per million of another.

Moreover, the combination of oil and dispersant may conceivably increase the toxicity of either the oil, the dispersant chemical, or both. The possibility of this "synergistic" action must be carefully examined before wholesale and widespread use of dispersants is permitted. Dispersing the oil (which is toxic) may also compound the damage.

But toxicity is not the only consideration in the use of dispersants. Of equal significance is their effectiveness. Experience at San Juan, Puerto Rico, and field tests conducted by research personnel at Edison, N.Y., indicate that they are generally ineffective for cleaning oil from beach sand of the type found along our east coast. They actually compound the problem by adding to the amount of pollutants present and by causing the oil to prenetrate more deeply into the sand. The "TORREY CANYON Pollution and Marine Life" report also noted that "quicksand," occurred as the result of using these materials, resulting in beach erosion from tidal and wave action.

Evaluation of the effectiveness of dispersants on water is much more difficult in cases of accidental spills. Lack of adequate methods for measuring the amount of oil on water and the rate of natural dispersion make precise evaluation difficult. Their effectiveness during the TORREY CANYON is still being debated. Subsequent incidents which are claimed to have demonstrated their effectiveness have been at remote locations and without impartial, qualified observers. Application methods of dispersants and subsequent agitation, which are critical for effective performance, have not always been optimal.

The cost of dispersants ranges from two to four dollars per gallon. Using recommended doses, the cost of chemicals for dispersing a relatively small 500 barrel spill would be about $20,000. The cost for chemicals used on the TORREY CANYON oil exceeded $5 million. Adequate technology for their massive application to major spills is lacking. Slicks from large spills spread in micro-thin layers over hundreds of square miles. Efficient use of dispersants to treat a complete slick would require proper density application and agitation of large areas of the sea surface. Such methods and the required scale of equipment have not been developed.

Thus, the desirability of using dispersants on the open sea remains unresolved. The FWPCA is conducting research to help provide the answers. As an initial step an interim standard procedure has been developed for measuring the comparative acute toxicity of dispersants to selected aquatic organisms. This will allow the assessment of relative toxicity among equally effective dispersants. We are continuing to refine this procedure and refine our capability for predicting the effect of dispersants on the water and near shore environment. Our research personnel are also developing a standard test for measuring the effectiveness of dispersants, so they may be rated on a common basis.

DEPARTMENT OF THE INTERIOR

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

POLICY ON THE USE OF CHEMICALS TO TREAT FLOATING OILS

1. Chemicals should not be used to emulsify, disperse, solubilize, or precipitate oil whenever the protection or preservation of (a) fresh water supply sources, (b) major shellfish or fin fish nurseries, harvesting grounds or passage areas, or (c) beaches is a prime concern.

   Such chemicals should only be used in those surface water areas and under those circumstances where preservation and protection of water related natural resources is judged not to be the highest priority or where a choice as to resource preservation may make the use of such materials a necessary alternative.

2. Examples of areas and circumstances where the use of such chemicals might be acceptable are:

   a. where fire or safety hazards are presented by the spill of a petroleum product;

   b. where large numbers of waterfowl may perish because of the proximity of floating oil;

   c. under certain conditions, as a "polishing" or final clean-up of light slicks of oil following mechanical removal of floating oils.

3. Chemicals that emulsify, disperse, solubilize or precipitate oil should be used only under the immediate supervision of the Federal Water Pollution Control Administration except where it is judged that fire or safety hazards require the immediate application of such chemicals.

4. When chemical compounds are used in connection with oil clean-up, only those compounds exhibiting minimum toxicity toward the aquatic flora and fauna should be used. The Federal Water Pollution Control Administration is now developing and will soon issue a standard procedure for determining the toxicity of such chemicals.

5. Materials which aid in the collection of floating oils such as sorbents, gellants and viscosity control additives are considered to be generally acceptable providing that these materials do not in themselves or in combination with the oil increase the pollution hazard.

6. Research and development to improve chemicals which emulsify, disperse, solubilize or precipitate oil is encouraged. Whenever it is demonstrated to the complete satisfaction of the Federal Water Pollution Control Administration, that such a chemical, by itself and in combination with oil is non-toxic its use may be approved in the areas where the protection or preservation of a) fresh water supply sources, or b) major shellfish or fin fish nurseries, harvesting grounds or passage areas is a prime concern.

July 5, 1968

FLOATING SORBENTS

Absorbent is a broad term defining in this report a type of material used in oil pollution control and clean-up. Most absorbents are described as oil-attracting (oleophilic) and water-repelling (hydrophobic). The use of absorbents requires placement in the oil slick, attraction of the oil to this material, and subsequent removal and disposal of the resulting oily materials. Such materials include straw, hay, sawdust, rope, sisal, tree bark, peat moss, perlite, vermiculite, talc, pumice, various clays, sea weed, kelp, chrome leather wastes, rock wool sheets, glass wool, rayon floss, polymer beads and copolymers, polyurethane and polypropylene sheets, fibers and foam, rubber or latex, and cotton or textile wastes. Any of the above materials may also be specially treated in one or more ways to improve its absorbtive properties and handling characteristics. Furthermore, these materials may be used as integrallpart of oil recovery-pickup devices, booming systems, beach clean-up methods and other.

Absorbents are advantageous in that they generally do not add materials in solution and thereby contribute to the existing problem. They are also capable of picking up oils in large ratio to the amount of absorbent used. Major difficulties, particularly for large-scale spills, are in calculating and delivering sufficient absorbent in the proper form at the proper place and time, applying the materials over the water body, adequately collecting and transporting the oil-soaked mass to shore, recovering the oil and securing ultimate disposal of the mass. Fire hazard may also be increased by use of many of these materials in confined places if ignition sources are present.

Many absorbents have performed quite well, particularly in small-scale spills, and may have high potential for moderate and even large-scale spills. Toxicity is far less a problem than with dispersants since the absorbent material generally remains in solid state; however, certain absorbent products may need further evaluation in this respect. Comparison of the relative effectiveness between various products together with relative cost is presently lacking. Evaluation must be conducted both within the laboratory and under realistic field conditions. The FWPCA Research facility has initiated limited studies in this direction.

Straw is widely used as an oil absorbent because of ready availability, cheapness and accepted effectiveness. It can be distributed manually or mechanically with or without shredding. Straw is most effective when used on shore or close to shore. Although straw can be effective in clean-up it must be adequately worked into the oil and its retrieval and disposal is a dirty, slow and tedious job, requiring equipment and considerable manual labor. In certain areas, soaked straw may not be burned because of air pollution codes and may not be buried because of potential groundwater pollution.

Far less use has been made of other absorbents compared to straw. Concerning natural absorbents, sea weed, kelp and indigenous grasses have been capable of absorbing appreciable oil in the TORREY CANYON, OCEAN EAGLE and Santa Barbara incidents. Production of powdered pine bark has been initiated by a Swedish pulp and paper mill. It is reported that two pounds of bark will absorb about one gallon of oil with indicated costs around $5 per 33 pound bag of powdered bark. Preliminary data received from Sweden on peat moss show about two pounds of absorbent required per gallon of oil.

Natural products can be heated or chemically treated to provide modified materials for oil pollution control. Perlite, a naturally occurring volcanic rock receiving subsequent pulverization and thermal expansion, has received favorable reports in aiding oil recovery on San Juan beaches; however, its action was less certain in Santa Barbara and in FWPCA research studies conducted on New Jersey beaches in 1968. Cost is approximately $75.00 per 100 cubic feet of absorbent. Vermiculite after treatment to render it expandable and hydrophobic has received mixed reports in its ability to absorb oil. Certain vermiculite products are reported to rapidly absorb floating oils whereas others do not have the required affinity.

Absorbents derived from synthetics or plastics represent an additional group of products with potential promise. These materials are generally high-molecular weight polymers or polyethylene, polystyrene, polypropylene and polyurethane. These agents may be applied as a light foam or plastic network by spraying, as a solid-state in the form of pillows, sausage shapes, or otherwise shredded and distributed over the oil slick. It is reported in theoretical terms that polyurethane foam can ultimately absorb over 90 percent of its own volume of oil or 100 times its own weight. Polypropylene is also reported as absorbing six times its weight in oil with one cubic yard capable of retaining 100 pounds of oil. These data represent extremely low cost to clean-up large volumes of oil but such figures likely reflect laboratory conditions which can be far different from those experienced in the field. Difficulties have been experienced with absorbing heavy and weathered oils. Effectiveness appears dependent upon prolonged time interaction, temperature, and other factors which must be better understood before many of the observed limitations can be overcome.

No absorbent appears truly effective when merely distributed over the oil slick. Agitation and increased interaction between the oil and the absorbent is necessary whether induced by natural wind, wave or tidal forces or by mechanical means. Absorbent application becomes increasingly complex with the larger oil spills. In massive oil spills, the logistics and equipment required to acquire and properly apply sufficient amounts of absorbents and the consequent collection and disposal of the resultant oily mass, become enormous due to the sheer bulk of the conglomerate and the lack of adequate methods for handling and disposal.

SINKING AGENTS

Sinking agents are granular solids of high density and generally of fine structure. When applied over the surface of a slick, they adhere to the oil, absorb it and ultimately sink. Typical oil-sinking agents include sand, brick dust, fly ash, slaked lime, stucco, cement, china dust, omya clay, vlocanic ash, chalk, crushed stone, coal dust and specially-produced materials such as carbonized-siliconized-waxed sands and fly ash.

Sinking agents can be efficiently employed on thick heavy or weathered oil slicks. If the oil is widely dispersed on the surface in disassociated masses, quantities of materials required are prohibitive. It is doubtful that sinkants may be profitably used with thin films and light crudes. The absorbent must be evenly mixed with the slick and have proper time for interaction before the ensuing mass eventually sinks. Furthermore, bonding of the agent with the oil must be nearly permanent; or else there will be eventual release of the entrapped and sunken oils back to the water environment.

The single known large-scale application of sinking agents was undertaken by the French during the TORREY CANYON incident. Some 3,000 tons of calcium carbonate with about one percent of sodium stearate added were reportedly used to treat and sink about 20,000 tons of oil found in the Bay of Biscay and originating from the TORREY CANYON. Although good scientific data are generally lacking particularly as to the precise amount of oil acutally treated, the oils were reported sunk in 60-70 fathoms and coastal pollution was minimized. The French success was attributed to good spreading and mixing of the chalk into the oil body and the high density of the weathered slick, thereby requiring considerably less absorbent as compared to fresher oils. Subsequent reports state that 14 months after the incident no sign of oil was found over the water surface. On the basis of French experiences above, oil-sinking agents have subsequently become more attractive and promising.

Opinions on the use of oil sinkants still remain divided as to efficiency, cost, application and detrimental environmental effects. Advantages of this type of treatment are that it tends to confine the spilled oil and the concommitant damage to a fixed place on the sea and probably minimizes toxicity to free floating plants and animals. Opposition to these agents are ascribed to the potential damage to sea bottom life, the problems associated with transporting and properly applying large amounts of the agents to the oil slicks plus the possibility of the oil resurfacing following biological degradution of the conglomerate.

Economics of this treatment method varies widely because practically all data have been obtained from laboratory testing rather than from application under field conditions. Early Department of Interior studies suggest three pounds of carbonized sand are required to sink one pound of oil whereas other studies indicate ratios of one or less of sinker weight to oil weight, depending upon density of oil slick and other factors. Large-scale application generally envisions spraying a slurry of sand or other mixture over the slick from a large vessel, hopper dredge, or equivalent. The cost of sinking agents is generally in the range of $20 to $80 per ton, depending upon quantity purchased, and location and type of material required.

The use of sinking agents would be most advantageous in deeper ocean waters outside the heavy-fishing zones. If resurfacing of the oils does occur, it should be gradual and far less objectionable in the event weathered oils were washed ashore at a later time.

GELLING AGENTS

The use of special gelling or congealing materials applied over the surface or periphery of an oil slick is another approach for containing and cleaning up oil spills. The gelling concept is also in the process of development for stabilizing liquid cargo aboard a stranded or heavily-damaged vessel at sea.

One patented product when applied in spray form, is reported to form a stiff gel with oil on water. When placed around the perimeter of an oil slick, the gel is said to form an effective chemical boom which prevents the oil from further spreading. The oil contained within the inner circle may be removed by mechanical means or the total slick may be gelled to facilitate removal. The developers also claimed that the oils recovered in this manner may be profitably reclaimed. For example, the gelled mass may be mixed with fuel oil and burned as replacement bunker fuel.

Possible toxicity of this class of chemical is unknown but under current evaluation. Data from the manufacturer indicate approximately one part chemical is necessary per part of oil to be gelled, thereby giving an estimated cost of about $1.50 per gallon oil treated. However, these costs very likely reflect laboratory testing and assuredly would be lower then for field application.

BURNING AGENTS

The concept of setting afire oils which have spilled and spread over the surface of a water body is potentially attractive principally because this appears to offer an inexpensive means of disposing of the problem. Past attempts to burn oils upon the sea have been almost completely unsuccessful, especially in the case of the TORREY CANYON. There, addition of thousands of gallons of aviation fuel, Napalm and sodium chlorate, together with aerial bombing of the vessel, failed to produce sustained burning. Spilled oil may possibly be burned by using catalytic or combustible agents or inducing "wicking" action between the oil and water.

The "wick" theory, assumes that capillary action is induced in the oil slick and a portion of the oil is drawn up to air (oxygen) interface to promote burning. Concurrently, the surface oil is partially insulated from the cooling effect of the sea water underneath. Wood, debris and flotsam emmeshed with the spilled oil apparently also insulates this layer from the colder water body and sustains burning. Since freshly spilled crude oil contains a relatively high proportion of volatile components, its ignition is more feasible than for weathered crude where the volatiles have already evaporated. Besides potential materials such as felting and asbestos-like agents, two commercial products are known which promote the burning of oils on water. One employs both a liquid and powder. The other is reported to consist of a specially-treated fine silica which increases capillary action aiding in sustained and controlled burning. Neither product, so far as is known, has been applied in large-scale, and therefore factors of logistics, application and amount of residue are unknown.

Controlling the burning oil mass, ensuing air pollution and disposal of residue would appear to preclude the use of this course of action except in those situations where the oil mass is sufficiently distant from the shore face and off shore facilities. The possible loss of the vessel or drill platform that is the source of the spill, is another factor which must be recognized. Because of the potential value of burning, additional and refined procedures should be further investigated.

GPO 879-485