

A DECISION-MAKER'S GUIDE TO DISPERSANTS

A REVIEW OF THE THEORY AND OPERATIONAL
REQUIREMENTS

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
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American Petroleum Institute

Environmental, Health, and Safety Mission and Guiding Principles

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- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

A Decision-Maker's Guide to Dispersants

A Review of the Theory and Operational Requirements

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4692

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BACKGROUND ON THIS BOOKLET SERIES

Beginning in 1994, the Marine Spill Response Corporation (MSRC), and later the Marine Preservation Association (MPA), sponsored a study to examine the reasons for the apparent differences between the science of dispersant use and perceptions of ecological effects. Using a prescribed risk communication methodology, the study compared the mental models (an individual's thought processes in making a decision regarding a particular issue) of US dispersant decision-makers and other stakeholders to an expert model (expert consensus of the relevant decision concepts that might be used), specifically looking at untreated, spilled oil in comparison to chemically-dispersed oil. Through a series of interviews and written questionnaires, a number of dispersant misperceptions were identified. These misperceptions were translated into topics for booklets that would provide dispersant information in a concise and reader-friendly format. For more information on the MSRC/MPA study, please see Bostrom *et al.*, 1995, Bostrom *et al.*, 1997, and Pond *et al.*, 1997a.

As a result of the MSRC/MPA work, in 1996, the American Petroleum Institute (API) commissioned the preparation of three dispersant booklets:

1. Fate of Spilled Oil in Marine Waters: Where Does It Go? What Does It Do? and How Do Dispersants Affect It?
2. A Decision-maker's Guide to Dispersants: A Review of the Theory and Operational Requirements.
3. Defining the Links Between Fate and Transport Processes with Exposure and Effects of Oil and Chemically Dispersed Oil in the Environment.

This booklet is the second in the series.



Documents

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OVERVIEW

- The American Petroleum Institute (API) commissioned the preparation of three booklets to help bridge the gap in the understanding of dispersant use, effectiveness, and effects.
- This booklet (second in the series) focuses on chemical dispersant technology and the information needs of decision-makers when attempting to make informed decisions regarding the use of chemical dispersants, their potential benefits and risks.
- Crude oil is a complex mixture of thousands of different compounds, composed primarily of carbon, hydrogen, sulfur, nitrogen, and oxygen. Hydrocarbons (composed solely of carbon and hydrogen atoms in various combinations) are the most abundant compounds found in crude oils.
- Dispersants are chemicals composed of surface-active agents (surfactants) and solvents. The surfactants in the dispersants reduce the interfacial tension of the water and promote the break-up of the slick into fine droplets, facilitating the dispersion of the oil into the water column. They act to prevent the recoalescence of suspended, chemically dispersed oil droplets.
- The solvent component of chemical dispersants assists surfactants in the penetration and alignment within the oil.
- Dispersants are designed to break up surface slicks and disperse the oil as fine droplets into the water column immediately under the slick. These chemically dispersed droplets will be further diluted within the water column as the droplets are subjected to natural dispersion through advection forces. Chemical dispersants lower the water interfacial tension, thus enabling wave action to transfer the oil from one location (the water surface) to another (spread out within the water column).
- An energy source (often in the form of wave action) is required to mix the chemically dispersed oil droplets into the water column. Some of the smaller oil droplets can remain dispersed in the water column for a long time.
- Use of dispersants is considered a viable response technique as they may:
 1. reduce the overall impact of oil on many habitats;
 2. prevent oil from stranding on sensitive shorelines and other economically important resources (e.g., boats, marinas, shellfish beds);
 3. reduce potential damage to birds, marine mammals, and other natural resources that could be impacted by oil on the water surface;
 4. provide a clean-up option when other response techniques are less effective (e.g., waves too high for booms and skimmers);
 5. enhance microbial degradation and evaporation by increasing the surface area of the oil droplets;
 6. remove the oil from the action of the wind that may ultimately bring the oil ashore; and
 7. reduce the formation of tarballs and mousse.

- There is a greater potential that resources that exist in the water column (e.g., fish) will be exposed to chemically dispersed oil droplets than if the slick were to remain untreated on the water surface (note that there are exceptions to every generalization). Exposure potential is greatest directly under the slick and would diminish with depth and distance from the oil source.
- Chemically dispersed oil droplets (generally less than 10 to 20 microns in diameter) will remain in the water column for extended periods of time, where the chemically dispersed droplets will undergo natural weathering processes (dissolution, biodegradation).
- Concentrations of oil dispersed under slicks are typically greater when oil is chemically dispersed than if left to naturally disperse. Naturally dispersed oil concentrations are typically measured in the 100–500 ppb (0.1–0.5 ppm) range for the upper three meters of the water column under freshly spilled and/or released oils. Peak concentrations of chemically dispersed oil in the upper three meters of the water column are typically less than 10 ppm, but have been measured for brief periods in the 20–50 ppm range; these concentrations are generally greater than those measured for natural dispersion, by a factor of 40 or more.
- Pre-spill planning is necessary to facilitate the use of chemical dispersants during actual spill response decision-making.
- The decision to use chemical dispersants is based on several factors affecting each incident, including:
 1. environmental issues: sea state, salinity, water temperature, and specific issues related to the ecosystem at risk;
 2. oil issues: chemical composition of the oil, the degree of weathering the oil has undergone; and
 3. dispersant issues: federal and state approval for use, availability, and application personnel and strategy.
- Application rates are important; the average recommended dispersant-to-oil ratio is 1 to 20. However, during recent spills off Great Britain, dispersant-to-oil application ratios averaged from 1 to 65 to as little as 1 to 80. In order to disperse heavy or weathered oils, a dispersant to oil ratio greater than 1 to 20 may be necessary.
- Several application systems have proven to be effective in applying chemical dispersants (vessel-based, fixed wing aircraft or helicopter systems). Applying chemical dispersants effectively requires trained and skilled personnel.
- Following a dispersant application, it is valuable to monitor the application to determine if the dispersant was applied at the appropriate dosage in the correct locations, if the dispersant is working effectively, and if there are any obvious (qualitative) ecological effects. Data obtained from monitoring are used to improve future dispersant use decision-making through long-term data gathering.

INTRODUCTION

Consider this...an oil tanker has grounded offshore, releasing some or all of its cargo. It is your job to recommend response options to protect the sensitive nearshore environment. One of the recommendations that you are considering is the use of chemical dispersants on the already expanding surface slicks. You need a concise, complete, and easy-to-use summary of dispersant technology, to refresh your memory and support your decisions. This booklet is designed to fill that need.

Purpose of Section

- Introduce the subject.
- Discuss the purpose and organization of the booklet.

PURPOSE OF BOOKLET

This booklet was developed for oil spill response decision-makers, to provide an accurate summary of chemical dispersant technology. To make informed decisions on using dispersants, or any countermeasure, it is important first to have a clear understanding of the potential benefits and risks.

- How do these chemicals work?
- Are they safe to use?
- Why should they be used?
- Under what conditions are chemical dispersants appropriate?
- What are the operational issues involved with chemical dispersant applications?

All of these answers are found in this booklet, in an easy-to-use format supplemented with diagrams and figures. To address chemical dispersant technology fully, this booklet has been divided into three parts.

Part I provides a brief review of oil chemistry: more details can be found in the first booklet in this series, "Fate of Spilled Oil in Marine Waters: Where Does It Go, What Does It Do, and How Do Dispersants Affect It?"

Part II provides a detailed discussion on chemical dispersants and their mechanism of action. This section briefly compares and contrasts chemical dispersion with natural dispersion and dissolution.

Part III comprehensively reviews the operational issues associated with chemical dispersant applications, including: application rates and variables that affect these rates, equipment needs, effectiveness issues, monitoring issues, and application limitations and restrictions.

Purpose of Part I

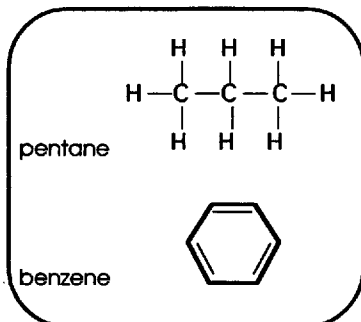
- To review information on general oil properties.

Hydrocarbons are chemical compounds found within crude oils and refined products that are composed solely of carbon and hydrogen atoms in various combinations. Hydrocarbons are the most abundant compounds found in crude oils; up to 85 percent.

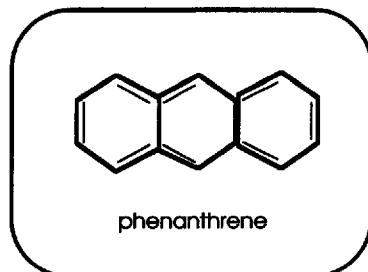
Trace Metals, such as nickel, vanadium, iron, aluminum, sodium, calcium, copper and others, are chemical elements typically found in small quantities in petroleum.

Asphaltenes and Waxes are complex hydrocarbons that contain trace elements in their structure; these compounds are considered relatively inert and resistant to most weathering processes.

Examples of Light-weight Molecules Found in Oil



Example of Medium-weight Molecules Found in Oil



PART I: OIL CHEMISTRY REVIEW

The chemical components and characteristics of crude and refined oils are reviewed in this section. An individual oil's chemistry influences dispersion processes and dispersant effectiveness. Being familiar with oil chemistry will help you interpret the specific data for your response decisions. General properties are reviewed below. A more detailed discussion, especially concerning physical oil properties and oil classification, can be found in the first booklet in this series "Fate of Spilled Oil in Marine Waters: Where Does It Go, What Does It Do, and How Do Dispersants Affect it?"

WHAT IS OIL?

Oil is not one "thing"; it is a complex and highly variable mixture of compounds (Lewis and Aurand, 1997). Crude oil is a complex mixture of mainly HYDROCARBONS, and to a smaller extent compounds containing TRACE METALS. Hydrocarbons (including ASPHALTENES and WAXES) are the most abundant compounds in crude oil (NRC, 1989; Gilfillan, 1993). In general, there are essentially three groups of hydrocarbons in every oil:

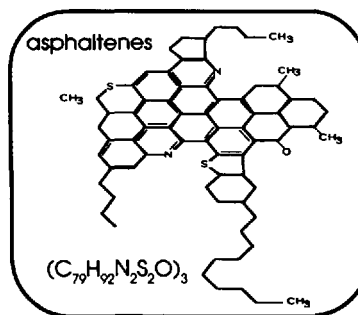
- **Light-weight components** (low molecular weight)
 - 1 to 10 carbon atoms (C1 to C10);
 - small number of atoms in each molecule;
 - evaporate and dissolve rapidly (hours) and leave little or no residue because they are simple in molecular structure;
 - many of these components (e.g., benzene) are thought to be readily absorbed by animals through the skin or through inhalation; and
 - potentially flammable and readily inhaled by people, and so are of concern for human health and safety.
- **Medium-weight components** (medium molecular weight)
 - 11 to 22 carbon atoms (C11 to C22);
 - more complex molecules;
 - evaporate or dissolve more slowly, over several days, with some residue remaining;

- sometimes regarded as more toxic than the light-weight components (Clark, pers. comm.); and
 - not as bioavailable as lower-weight components, so less likely to affect animals.
- **Heavy-weight components** (high molecular weight)
 - 23 or more carbon atoms ($\geq C_{23}$);
 - undergo little to no evaporation or dissolution; and
 - can cause chronic (long-term) effects via smothering or coating as residue in the water column and sediments (tar balls, etc.) (Helton, 1996).

Crude oils are composed of various combinations of the three hydrocarbon categories. When comparing crude oils, the concentration of the larger molecular compounds (medium- and heavy-weight relative to the amount of light-weight components) within the oil affects PERSISTENCE; oils with greater concentrations of medium- and heavy-weight components will typically result in increased persistence (Table 1). Oils composed primarily of the light-weight components are usually considered NON-PERSISTENT.

Refined products are typically composed of a narrow range of processed components, usually containing the lighter-weight components (e.g., gasoline, condensates, and diesel-like products). RESIDUAL or LOW API GRAVITY OIL PRODUCTS are primarily composed of heavy-weight components sometimes mixed with a blending agent (No. 2 fuel oil is a common blending agent) in the development of these heavy re-

Examples of Heavy-weight Molecules Found in Oil



Persistence refers to an oil or refined product's tendency to remain in the environment following a discharge for a long period of time.

Persistent Oils are those crude and refined oil products that cannot be completely removed from an affected environment as a result of weathering processes; some residue remains. In general, an oil with a weathering half-life of months to years is considered persistent.

Non-persistent Oils are refined oil products that will be completely removed from the affected environments through natural weathering processes. Only short-term impacts are expected from these refined products. In general, an oil is considered non-persistent if it requires days to weeks before natural weathering processes decrease the volume of the oil to half its original volume.

Residuals (or residue) are compounds left when crude oils are processed at refineries for the extraction of gasoline, diesel fuel, and other oil products. Residue is often blended with lighter-weight refined products for the development of residual fuels (often referred to as **Low API Gravity Oils** (LAPIO), or Group V oils) that are sold to utilities for the generation of electricity (Scholz et al., 1994).

Table 1. Persistence as defined by US 33 CFR, Section 155.1029.

Category	Persistence	Specific Gravity	Typical Examples
Group I	Non-persistent*	N/A	Gasoline products, condensates
Group II	Persistent **	< 0.85	Diesel-like products and light crude oils
Group III	Persistent	$0.85 \leq 0.95$	Medium-grade crudes & intermediate products
Group IV	Persistent	$0.95 \leq 1.00$	Heavy crude oils and residual products
Group V	Persistent	> 1.00	Low API gravity products [heavier than pure (fresh) water]

* Non-persistent: a petroleum-based oil that, at the time of shipment, consists of hydrocarbon fractions

-At least 50% or which by volume, distills at a temperature of 340°C (645 °F); and
 -At least 95% of which by volume, distills at a temperature of 370°C (700°F).

** Persistent: a petroleum-based oil that does not meet the distillation criteria for a non-persistent oil.

Purpose of Part II

- To discuss chemical dispersants and to answer the following questions:
 - what are they?
 - how do they work?
 - why would you want to use them?
 - what happens to the chemical dispersant once it is applied to the oil?
 - what are the differences/similarities between chemical dispersants and natural dispersion and dissolution weathering processes?

Surfactants are naturally occurring and chemically manufactured molecules often referred to as surface active agents or "detergents." Surfactant molecules contain both water compatible (hydrophilic) and oil compatible (oleophilic or hydrophobic) portions that orient themselves at the oil-water interface so that the oil compatible portion of the molecule attaches to the oil and the water compatible portion of the molecule faces outward into the surrounding water.

Solvents are chemical compounds that are included in dispersants to assist the surfactants in penetrating the oil.

Oleophilic refers to a chemical structure which has an affinity or attraction for oil or oil-like substances.

Hydrophilic refers to a chemical structure which has an affinity or attraction for water; these substances naturally repel oil and oil-like substances.

finer oils, etc. There are also several naturally occurring crude oils that are considered low API gravity oil products (Scholz *et al.*, 1994).

PART II: CHEMICAL DISPERSANTS

SECTION I: WHAT ARE THEY?

Chemical dispersants are mixtures that contain "surface-active" chemicals (SURFACTANTS) and SOLVENT(s). It is the surfactants that actually cause the oil to "disperse" into tiny droplets that remain suspended in the water column due to wave action. The molecules in surfactants are double ended, with one end having an affinity for oil (OLEOPHILIC) and the other an affinity for water (HYDROPHILIC) (NRC, 1989; Canevari, 1978) (Figure 1). The surfactant molecule attaches itself to an oil droplet with the oleophilic end while the hydrophilic end remains outside, on the surface of the oil where it adheres to water and repels other oil droplets. Once the dispersant is applied to the spilled oil on the water, the surfactants enhance the formation of oil droplets and reduce the oil's tendency to stick to other droplets or surfaces (e.g., beaches, animals, etc.).

Historically, the first large scale use of "dispersants" to clean oil spilled in the environment occurred in 1967 and involved heavy-duty detergent and/or degreaser solutions (refer to page 12 for more information); the detergents used were developed to clean oily residue on machinery, boiler rooms, workshop floors, and tanker compartments. These early "dispersants" were a mixture of toxic solvents and surfactants, but were effective in cleaning. The solvent was used to penetrate the oil (which could have become hardened by age or heat, or be mixed with a variety of other substances) and the surfactant was included to keep the now-softened oil suspended as an emulsion in the water used for cleaning. No one really worried about the relative toxicity of the solvents or the natural removal of the surfactants from the environment as they were not meant to be used directly in the environment (Lindblom, 1978; Lewis and Aurand, 1997). Use of these products in the 1967 *Torrey Canyon* spill was unfortunate and led to more damage than if they had not been used.