

FATE OF SPILLED OIL IN MARINE WATERS:

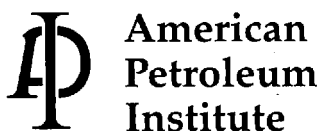
WHERE DOES IT GO?

WHAT DOES IT DO?

HOW DO DISPERSANTS AFFECT IT?

AN INFORMATION BOOKLET FOR DECISION-MAKERS

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4691
MARCH 1999





American Petroleum Institute Environmental, Health, and Safety Mission and Guiding Principles

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The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. We recognize our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to the following principles using sound science to prioritize risks and to implement cost-effective management practices:

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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.



Fate of Spilled Oil In Marine Waters:

Where Does It Go?

What Does It Do?

How Do Dispersants Affect It?

An Information Booklet for Decision-Makers

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4691

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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, this 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 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 of the dispersant booklets:

- Fate of Spilled Oil in Marine Waters: Where Does It Go? What Does It Do? and How Do Dispersants Affect It?
- A Decision-maker's Guide to Dispersants: A Review of the Theory and Operational Requirements.
- 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 first in the series.

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OVERVIEW

- The American Petroleum Institute commissioned the preparation of three booklets to help bridge the gap in the understanding of dispersant use, effectiveness, and effects.
- This first booklet focuses on oil chemistry and oil weathering, two concepts that spill response decision-makers need to interpret dispersant information more effectively. This booklet then presents information on how dispersants alter or affect the weathering process
- Oils are typically described in terms of physical properties, used to determine, in part, how an oil spilled on water will react under various ambient conditions:
 - ⇒ Specific gravity – ratio of the mass of a given material to the mass of fresh water. For most crude oils and refined products, specific gravity is usually between 0.78 and 1.0.
 - ⇒ API gravity – scale for measuring fluid specific gravities based on an inverse relationship with specific gravity. For instance, an oil with a low specific gravity (0.73) will have a high API gravity (62). This scale was developed so that larger values are used.
 - ⇒ Pour point – the temperature below which oil will not flow.
 - ⇒ Viscosity – an oil's internal resistance to flow. A highly viscous oil will not flow easily.
 - ⇒ Asphaltene and wax content – non-hydrocarbon portions of the oil which are defined in terms of solubility. An oil with a high asphaltene and wax content is generally heavier.
 - ⇒ Trace constituent content – these include nickel, vanadium, iron, aluminum, sodium, calcium, and copper. Oils with large concentrations of these trace constituents tend to emulsify easily.
- Oil is a complex mixture of thousands of different compounds, composed primarily of carbon, hydrogen, sulfur, nitrogen, and oxygen. Hydrocarbons (composed solely from carbon and hydrogen atoms) are the most abundant compounds found in crude oils
- After oil is discharged into the environment, a wide variety of physical, chemical, and biological processes begins to transform the discharged oil. Collectively called “weathering,” the rate and significance of these processes are dependent on the type of oil spilled, spill location, and weather conditions at the time of the spill.
- Ten weathering processes are discussed:
 - ⇒ Spreading and advection – spreading is the movement of the entire slick horizontally on the surface of the water due to effects of gravity, friction, viscosity, and surface tension. Advection is the movement of the oil due to the influence of overlying winds and/or underlying currents. Neither is uniform, and large variations in oil thickness occur within the slick. Spreading dominates the initial stages of a spill and involves the whole oil, that is, it does not partition the various components of the oil or affect its chemical composition. Spreading and advection continue for approximately one week to ten days following the discharge, or until the oil is contained by shorelines, collection efforts, or other obstructions.

- ⇒ Evaporation – the preferential transfer of light- and medium-weight components of the oil from the liquid phase to the vapor phase. It is the primary weathering process involved in the natural removal of oil from the sea surface. During the first 24 to 48 hours of the spill, it is the single most important weathering process, from the standpoint of volume reduction. Evaporation starts immediately following the spill and continues for approximately two weeks.
- ⇒ Dissolution – the transfer of oil components from a slick on the surface into solution in the water column. It is a relatively insignificant weathering process in terms of reducing the volume of the spills and typically occurs within the first 24 hours of a spill.
- ⇒ Natural dispersion – the process of forming small oil droplets that become incorporated into the water column in the form of a dilute oil-in-water suspension. Dispersion reduces the volume of the slick at the surface but does not change the physiochemical properties of the oil. Following evaporation, it is the most important process in the breakup and disappearance of a slick. It begins soon after the spill occurs and reaches a maximum rate in approximately 10 hours following a spill.
- ⇒ Emulsification – the mixing of water droplets into oil spilled on the water's surface. Water-in-oil emulsions are highly viscous and have densities approaching seawater. Once the oil has emulsified, the weathering of oil can be significantly reduced. Emulsification begins during the first day of the spill and can continue to occur throughout the first year. The largest volume of emulsions is typically formed within the first week of the spill.
- ⇒ Photo-oxidation – sunlight, in the presence of oxygen, transforms hydrocarbons through photo-oxygenation into new by-products. It occurs at the very surface of the oil and directly on components which have physically separated from the whole oil. It plays a fairly minor role in the overall weathering of the oil, and can last for several weeks to a month following a spill.
- ⇒ Sedimentation and shoreline stranding – sedimentation is the incorporation of oil within both suspended and bottom sediments. Sedimentation is a very important process in shallow, rough sea conditions where bottom sediments are repeatedly resuspended. It begins soon after the spill occurs and peaks several weeks into the spill. Shoreline stranding is the visible accumulation of oil on shorelines following a spill. It is affected by the proximity of the spill to the shore, intensity of current and wave action on the affected shoreline, and the persistence of the spilled product.
- ⇒ Biodegradation – process where naturally occurring bacteria and fungi consume hydrocarbons to use as a food source. Carbon dioxide and water are excreted as waste products. It is a significant but slow process. It begins several days following a spill and will continue as long as hydrocarbons persist.
- These weathering processes occur simultaneously with each other, as they overlap through the course of a spill. The processes interact and affect each other and in turn affect the properties of the spilled oil.
- Dispersants are chemicals composed of surface-active agents (surfactants), solvents, and stabilizing agents. The surfactants in the dispersants reduce the interfacial tension at the water:oil interface and promote the break-up of the slick into fine droplets, facilitating the dispersion of the oil into the water column. They also act to prevent the recoalescence of suspended, chemically dispersed oil droplets.

- Dispersants affect natural weathering processes in the following ways (please note these are generalities):
 - ⇒ Spreading is enhanced.
 - ⇒ Evaporation will primarily occur as a secondary weathering process following dispersant application.
 - ⇒ Natural dissolution will probably be increased.
 - ⇒ Natural dispersion will probably be enhanced.
 - ⇒ Emulsification will decrease.
 - ⇒ Photo-oxidation will probably be slowed.
 - ⇒ Sedimentation and shoreline stranding is reduced.
 - ⇒ Biodegradation is enhanced.

SECTION 1: INTRODUCTION

Consider this scenario...an oil tanker has had an offshore accident and is releasing its cargo. It is your job to recommend response options to protect the sensitive nearshore environment. One of the response options you are considering is chemical dispersants. Although you have worked on oil spills in the past, dealing with these spills is only one facet of your job which has wide-ranging responsibilities. You want to have a good understanding of what happens to the oil when it is spilled and how dispersants can change that, but you may not be a biologist or chemist by training, and much of the information you have available is very technical.

This scenario is all too common. As a decision-maker involved in oil spill response, you have received extensive on-the-job training, but you don't live and breathe oil spills and don't use your oil spill training every day. Consequently, much of the literature and information available to assist you during planning and actual response operations is too technical, too long, and does not help resolve your questions and concerns. You need short summary reports which accurately but concisely provide the answers you need to help make a decision regarding the use of dispersants during an oil spill. This booklet, the first in a series of three, helps fill that need.

Purpose of Section I

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

PURPOSE OF BOOKLET

This booklet was developed for oil spill response decision-makers. It summarizes what happens to oil that spills on marine waters. To make informed decisions on using dispersants, or any countermeasure, it is important first to have a clear understanding of the overall fate of the oil entering the environment: What will the oil do once it is spilled? Where will it go? Once the fate of the oil alone is understood, we can then examine how the addition of dispersants will affect that fate.

All of these answers are found in this booklet, in an easy-to-read format supplemented with diagrams and figures. Each fate process involved is reviewed independently, including a discussion of how significant the process is, when it occurs following a release, and what properties or ambient conditions influence it. The booklet then presents information on how dispersants affect or alter the various fate processes.

This booklet is also designed to identify and explain unfamiliar terms associated with oil that may be used by technical experts during planning or response operations. The first time a new technical term is used

within this booklet, it will appear in an ALL CAPS format; this signifies that a more detailed explanation or definition is present in the right or left narrow margin at or near where the word(s) is first used within the main text.

Purpose of Section II

- To review information on oil properties, composition and classification systems.

SECTION II: OIL CHEMISTRY REVIEW

An oil's physical properties and chemical composition are important factors that influence fate processes.

PHYSICAL PROPERTIES OF OIL

Oils are typically described in terms of their physical properties [e.g., SPECIFIC GRAVITY and API GRAVITY, POUR POINT, VISCOSITY, ASPHALTENE and WAX CONTENT, and the presence of TRACE CONSTITUENTS (Payne, 1994)]. These parameters (combined with various environmental information, e.g., wave height, wind speed, currents, etc.) are used to determine how oil spilled on water will react under ambient conditions.

DENSITY

The density of oil relative to fresh water is typically expressed in terms of specific gravity or API gravity. Density can help the decision-maker determine if an oil is likely to sink or float in the water column following a discharge.

Specific Gravity

Specific gravity is defined as the ratio of the mass of a given material (e.g., oil) to the mass of freshwater, for the same volume and at the same temperature. Clark and Brown (1979) determined that the majority of crude oils and refined products have specific gravity values (SG) between 0.78 and 1.00. As these values are less than the SG for fresh water (1.0 at 4°C), they will float on the water surface.

Weathering is the combination of physical and chemical changes in oil composition. It may result in the removal of oil from the water's surface to the atmosphere, water column, sediments, and shorelines.

Most oils and refined products have a specific gravity of less than 1.0; oils with a specific gravity greater than 1.0 tend to sink or be neutrally buoyant (neither sink nor float on top, but stay as a unit within the water column). When these products are released onto the water, they typically float unless they gather sediment, undergo additional WEATHERING, or are consumed by various marine animals. The specific gravity of most crude oils and refined products lies between 0.78 and 1.00 (Table 1) (Overstreet and Galt, 1995). As an oil or refined product weathers (components are lost to the environment), the specific gravity of that oil will increase. With an oil that has a specific gravity near 1.00 (in freshwater) or 1.03 (in saltwater), weathering may result in the oil having a specific gravity value greater than or equal to the surrounding water. The weathered oil may sink or it may become neutrally buoyant (Scholz *et al.*, 1994).

Product	Specific Gravity	API Gravity	Pour Point (°F)	Boiling Point Range (°F)	Viscosity cSt @ 68 °F	Relative Persistence
Gasoline	0.74 to 0.73	59 to 62	NA	104 to 302	~0.5	1
Jet Fuel (JP-4)	0.75 to 0.80	44.3 to 56.7	NA	203 to 518	0.94	~2
Kerosene	0.80 to 0.88	43 to 29	0	392 to 572	2.0 to 3.5	NA
Fuel Oil No. 2 (Diesel)	0.88	29	20	93 to 365	2.25 to 5.0	8
Lube Oil (crankcase)	0.87	29	-35	710 to 822	79 to 86	~55
Kuwait Light Crude Oil	0.83	37.8	-50	NA	13.8	~320
Fuel Oil No. 6 (Bunker)	0.96 to 0.97	10 to 17.5	60	615 to 826	>500	400
North Slope Crude Oil	0.89	17.5 to 35	-	NA	58.4	~450
San Ardo (CA) Crude Oil	0.99	5 to 17.5	80	NA	4754	~590
Residual Asphaltene	-	< 10	-	> 752	-	1600

Table 1. A comparison of oil properties for a variety of crude oil and refined oil products. All numbered persistence data are based on the relative persistence of the product in the environment, divided by the least persistent oil product (gasoline). Adapted from Curl and O'Donnel (1977), Gilfillan (1993), API (1990), and Markarian *et al.*, (1993).

API Gravity

This scale (ranging from essentially 0 to more than 60; Table 1) can provide insight as to the type of oil spilled and how it will generally react in the environment. In general, the larger the API gravity value, the greater amount of light-weight components an oil or refined product has (Figure 1). With decreasing API gravity values (less than 17.5), which means increasing the amount of medium and heavy-weight components, the oil or refined product is likely to remain in the system. As an oil or refined product weathers (components are lost to the environment), the API gravity of that oil will decrease. With an oil that has an API gravity at or near 10, additional weathering may result in the oil having an API gravity value less than or equal to the surrounding water. The weathered oil may sink, or it may become neutrally buoyant (neither sink nor float on top, but stay as a unit within the water column) (Scholz *et al.*, 1994).

POUR POINT

If the temperature of the water is as cold or colder than the oil's pour point, the oil will stiffen up and no longer flow. In cold climates and cold waters, many of the heavy refined products which have high temperature pour points must be heated during transport and pumping. When these types of oils are spilled into the water, they will not flow readily or

API gravity is a scale for measuring fluid specific gravities based on an inverse relationship with specific gravity. This scale was primarily developed to expand the scale for specific gravity so that larger values are used. An oil with a low specific gravity (e.g., gasoline; SG = 0.73) will have a high API gravity ($^{\circ}\text{API} = 62$); inversely, an oil with a high specific gravity (e.g., very heavy crudes; SG = 0.98) will have a low API gravity value ($^{\circ}\text{API} = 13$).

$$\text{API gravity} = (141.5 / \text{SG}) - 131.5$$

* at 60 °F

Pour point is the temperature below which oil will not flow.

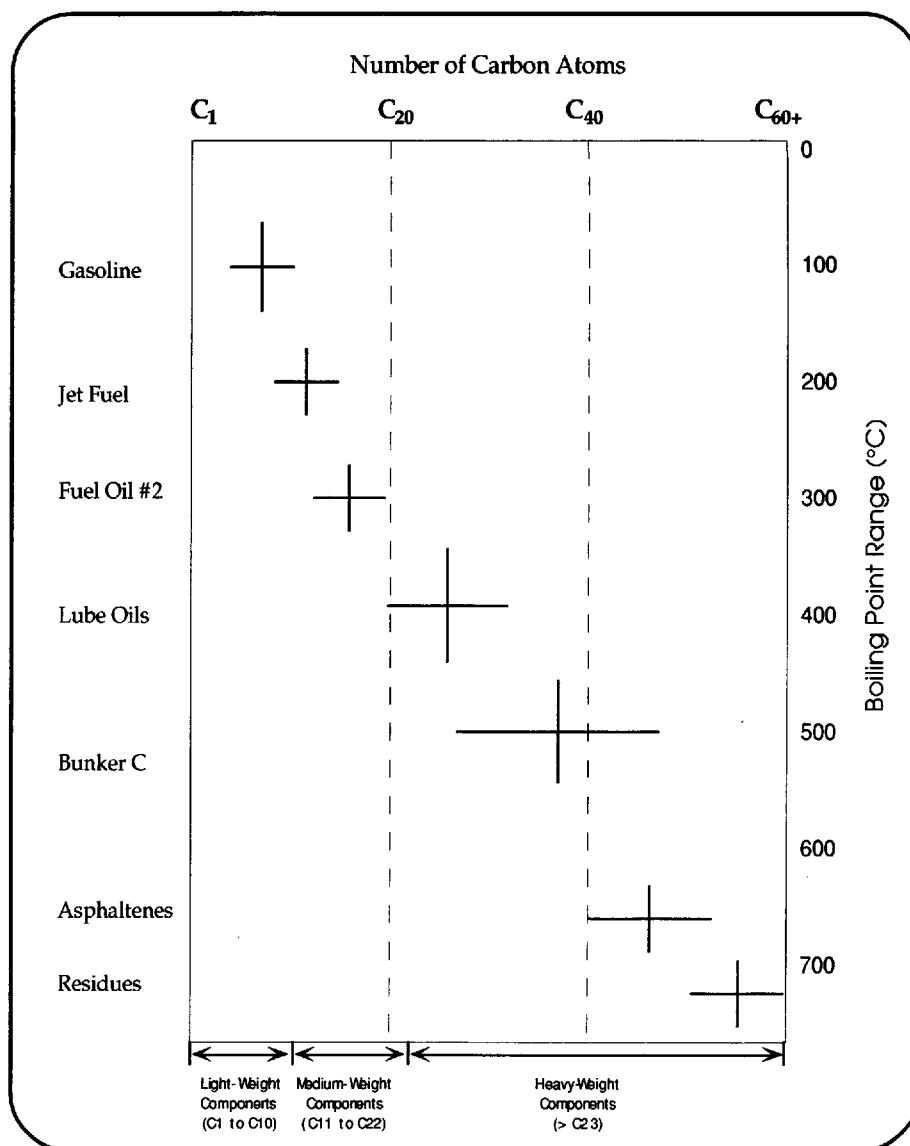


Figure 1. Distribution of various refined petroleum products as developed from a "generic" crude oil. No concentration data are provided because the exact composition of the oil product will vary due to the source and refinery. Adapted from Markarian *et al.*, (1993).

Viscosity is an oil's internal resistance to flow. A highly viscous oil will not flow easily. This physical property of the oil or refined product is important to understand as it helps determine the oil's behavior during a spill.

Centistoke (cSt) is a unit of measurement used in defining the KINEMATIC VISCOSITY of a fluid. $cSt = 1/100 St$.

Kinematic viscosity is a unit of measurement used to define an alternative viscosity measurement. This alternative viscosity measurement is simply the fluid's dynamic viscosity divided by its density. Measured in St or stoke.

spread. In these instances, the oil can move "like semi-submerged strands of thick rope or 'icebergs'; the majority of the bulk oil resid[ing] just below the water surface" (Lewis and Aurand, 1997). For refined oil products, pour point values can vary between -60 °C for jet fuels to +46°C for waxy No. 6 fuel oils (Overstreet and Galt, 1995).

VISCOSITY

Viscosity is measured in CENTISTOKES (cSt). An oil's viscosity influences or controls the success of cleanup operations, since very viscous oils are difficult to recover with conventional technologies (e.g., disc skimmers) (Overstreet and Galt, 1995). As oil spilled on the water un-