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THE LOGISTICS OF OIL SPILL DISPERSANT APPLICATION
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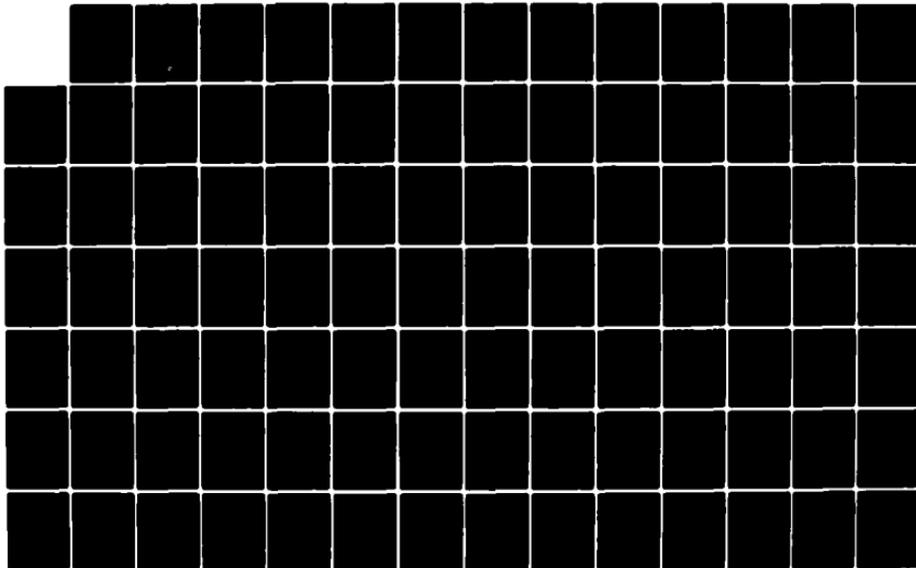
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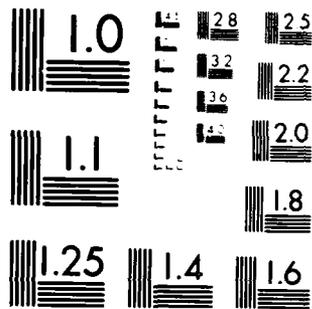
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The Logistics of Oil Spill Dispersant Application

Volume I: Logistics -Related Properties of Oil Spill Dispersants

Transportation Systems Center
Cambridge MA 02142

November 1982
Final Report

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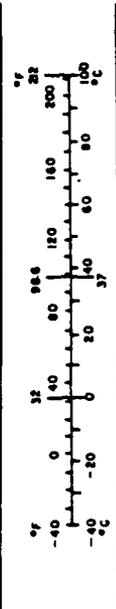
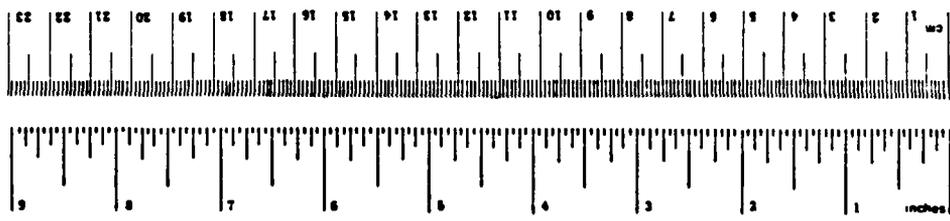
The data and this report are presented solely for the guidance of the Coast Guard on-scene coordinator in accordance with the National Oil and Hazardous Substances Pollution Contingency Plan. The conclusions and recommendations of this report are those of the author and do not represent conclusions, recommendations, or policy of the United States Coast Guard, or any other part of the U.S. Government.

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16. Abstract <p>The use of chemicals for oil spill dispersal, while not presently widespread in the U.S., would have implications for the U.S. Coast Guard's Marine Environmental Protection program. This report explores the logistics of oil dispersant application by the U.S. Coast Guard.</p> <p>Volume I: <u>Logistics-Related Properties of Oil Spill Dispersants</u></p> <p>Data were reviewed for the 13 dispersants for which data had been submitted to the EPA as of October 1979. Manufacturer's data and published test results were also examined and information summarized with regard to classification, handling and storage, application, availability and cost.</p> <p>Volume II: <u>Application Techniques, Stockpiling, Dispersant Selection, Strategies</u></p> <p>Formulae and charts are developed for analyzing single and multiple-pass application; factors in stockpiling, and present inventories are examined; the factors in dispersant selection from Volume I are summarized. Six operational strategies, consisting of choices of vehicles, stockpiles and dispersant, are formulated and evaluated.</p>					
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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures			Approximate Conversions from Metric Measures		
When You Know	Multiply by	To Find	When You Know	Multiply by	To Find
LENGTH					
inches	2.5	centimeters	millimeters	0.04	inches
feet	30	centimeters	centimeters	0.4	inches
yards	0.9	meters	meters	3.3	feet
miles	1.6	kilometers	kilometers	1.1	yards
AREA					
square inches	6.5	square centimeters	square centimeters	0.16	square inches
square feet	0.09	square meters	square meters	1.2	square yards
square yards	0.8	square meters	square kilometers	0.4	square miles
square miles	2.6	square kilometers	hectares (10,000 m ²)	2.6	acres
acres	0.4	hectares			
MASS (weight)					
ounces	28	grams	grams	0.035	ounces
pounds	0.45	kilograms	kilograms	2.2	pounds
short tons (2000 lb)	0.9	tonnes	tonnes (1000 kg)	1.1	short tons
VOLUME					
teaspoons	5	milliliters	milliliters	0.03	fluid ounces
tablespoons	15	milliliters	liters	2.1	pints
fluid ounces	30	milliliters	liters	1.06	quarts
cups	0.24	liters	liters	0.26	gallons
pints	0.47	liters	cubic meters	35	cubic feet
quarts	0.96	liters	cubic meters	1.3	cubic yards
gallons	3.8	liters			
cubic feet	0.03	cubic meters			
cubic yards	0.76	cubic meters			
TEMPERATURE (exact)					
Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature



* In a 256 (exact), for other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Length and Measures, Price \$2.25, SD Catalog No. C13 10 286.

PREFACE

The use of chemicals for the dispersal of oil spilled on water has been the subject of discussion (and of disagreement) since their first major use in the Torrey Canyon disaster in 1967. The net adverse ecological effects produced by dispersants in that spill raised serious questions about their use. Although dispersant formulations have since been developed that are more effective and less toxic than those used on the Torrey Canyon spill, their use is not universally accepted. In the United States, in particular, a cautious approach has been taken; use of dispersants is governed by the National Oil and Hazardous Substances Pollution Contingency Plan, which requires that approval be obtained from the Regional Response Team before chemical dispersion is undertaken. This approval has been sought and employed in relatively few cases in the United States compared to other countries.

Despite their infrequent use at present in the United States, the implications of chemical dispersion of oil would be substantial for the US Coast Guard if it became common. Accordingly, the US Coast Guard Office of Marine Environment and Systems (USCG/G-W) requested the Transportation Systems Center to analyze the logistics of handling, stocking, transporting and applying chemical oil dispersants. The study was carried out by the Transportation Systems Center Office of Air and Marine Systems (DOT/DTS-500) in Fiscal Year 1980.

The project was initiated under the sponsorship of CDR J. Valenti, USCG/GWEP, and completed under CDR. R Rufe Jr. of the Pollution Response Branch, Environmental Response Division. Technical guidance and assistance were provided by LCDR W. Jurgens and CDR J. Paskowich of the US Coast Guard. Numerous Coast Guard personnel provided assistance and information, as did many individuals in the Environmental Protection Agency and industry.

The report is in two volumes. Volume I deals with the logistics properties of dispersants, and Volume II deals with their application.

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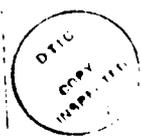


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INTRODUCTION

Research and discussion concerning the use of chemicals for the treatment of oil spills has risen substantially in the last three years.⁽¹⁾ While it is still not clear that the use of dispersants in US waters will be expanded⁽²⁾, it must be assumed that their widespread use will have important impacts on the Coast Guard's Marine Environmental Response Program. These impacts would occur in the areas of operational procedures, programs, planning, funding, and effectiveness. In order to assess these impacts the Coast Guard has initiated a study of the logistic requirements of oil spill dispersal by chemicals. The first part of the study, covered in the present volume, deals with the classification of dispersants,⁽³⁾ storage and handling properties, application characteristics, availability, and cost. The second volume deals with the application, stockpiling, and overall strategy of dispersant use by the Coast Guard.

The dispersants covered in this volume are the thirteen for which test data have been accepted by the Environmental protection Agency (EPA) as of October 1979, in accordance with Annex X of the National Contingency Plan. (Reference 2.) This Plan specifies that dispersants employed by the On-Scene Coordinator (OSC) must have been accepted by the EPA in accordance with that Annex. The data on which this report is based have been obtained from the tests and product information submitted by the manufacturer to the EPA (contained in the EPA Technical Product Bulletin), from the

(1) See, for example, the Introduction of Reference 1. The number of papers dealing with dispersants in the 1977 and 1979 Conferences on the Prevention and Control of Oil Spills was about double that in the 1973 and 1975 meetings.

(2) After their use in the Santa Barbara Spill in 1969, dispersants were not used under Annex X of the National Contingency plan until 1978 (dredge Pennsylvania) and again in 1979 (Sea Speed Arabia).

(3) Oil collecting agents and biological additives are excluded.

manufacturer's product data sheets, and from the technical literature. Information with regard to cost and availability was obtained directly from the manufacturers, distributors and oil spill cooperatives.

The following sections of this volume will deal with the general classification problem, the handling and storage characteristics of dispersants, with their application characteristics and their availability. The final section of the volume will present the conclusions to be drawn from the investigation.

The 13 subject dispersants are:

<u>Product #</u>	<u>Brand Name</u>	<u>(Manufacturer)</u>
1	PROFORM Pollution Control Agent	(Proform Products Corp.)
2	CONCO DISPERSANT K	(Continental Chemical Co.)
3	SLIK-A-WAY	(MI-DEE Products, Inc.)
4	Corexit 7664	(Exxon Chemical Company)
5	SEA MASTER NS555	(Whale Chemical Co.)
6	"COLD CLEAN" #500	(Adair Equipment Co.)
7	ATLANTIC-PACIFIC OIL DISPERSANT	(GFC Chemical Co.)
8	Gold Crew Dispersant	(Ara Chem., Inc.)
9	Corexit 9527	(Exxon Chemical Company)
10	Corexit 8667	(Exxon Chemical Company)
11	BP1100X	(BP North America, Inc.)
12	BP1100WD	(BP North America, Inc.)
13	Ameroid OSD/LT	(Drew Chemical Corp.)

CLASSIFICATION OF DISPERSANTS

Oil dispersants consist of a surface active agent (surfactant) in a suitable solvent. The surfacant is a molecular chain with both oil-soluble and water-soluble groups. When applied to an oil and water mixture this multiple solubility acts to reduce the interfacial tension at the oil-water surface, thus aiding the formation of oil droplets in the water. Surfactants, and hence dispersants, have been classed as water-based or hydrocarbon-based, depending on whether the water-soluble (hydrophilic) or oil-soluble (lipophilic) group is dominant in the molecule. In 1974 dispersants were introduced (Reference 3) in which the concentration of surfactant was greater than the 1:7 to 1:10 range previously employed. These so-called concentrates, although individually classifiable as water- or hydrocarbon-based, have substantially different characteristics from either so that they are often considered to be in a separate category.

The categories described above may be more academic than practical. The UK Ministry of Agriculture, Fisheries and Food (UKMAFF) recently tested 10 dispersants that they classed as concentrates, (Reference 1, Norton et. al.) along with 12 that they classed as "conventional." The Canadian Environmental Protection Service (CEPS) tested 13 dispersants (Reference 1., Doe and Wells) in four groups: (1) "self mix", (2) concentrates, (3) water-immiscible conventional, and (4) water-miscible conventional. ("Self-mixing" here refers to a dispersant that functions without the addition of mechanical agitation.) The situation is further confused by the fact that some dispersants are considered by their producers to be both self-mixing and concentrate. Moreover, the terms "self-mixing" and "concentrate" are relative, the underlying parameters being (1) quantity of mixing energy required to achieve a given dispersion under given conditions, and (2) percent surfactant contained in the product.

Clearly, any classification is a one-dimensional view of a multi-dimensional situation. A dispersant classification scheme

based on any one characteristic may be completely different from classifications based on other equally important characteristics. In that case no simple classification is possible and the products must be described individually with regard to each characteristic.

With the above possibility in mind, a water-based/hydrocarbon-based/concentrate classification was chosen primarily to provide a preliminary framework within which all relevant characteristics could be tabulated. Those characteristics fall into three groups:

1. Handling and Storage Properties
2. Application Characteristics
3. Availability and Cost

These characteristics are each examined in the following sections and the generalizations and conclusions that may be drawn from the data are presented in the last section.

One should note that the water-based/hydrocarbon-based/concentrate classification is made from manufacturer's own description of his product. This is necessary since classification depends on detailed knowledge of the composition of the product, which information is handled as trade secrets under Annex X and the Administrative Procedures Act. As will be seen in the next section, however, some products classed as water-based have physical properties remarkably similar to hydrocarbon-based dispersants. In general, the limitations and uses of this classification will become clear in the remainder of the report.

HANDLING AND STORAGE PROPERTIES

Annex X requires the following handling and storage data to be submitted for EPA acceptance:

1. Pour Point
2. Flash Point
3. Minimum Storage Temperature
4. Maximum Storage Temperature
5. Phase Separation
6. Shelf Life

(The pour point also affects application methods, and shelf life influences cost as well as storage.)

A tabulation of the above six items is given in Table 1 for the thirteen subject products. In addition, Annex X requires that the technical data include special handling and worker precautions. These are shown in Table 2, with supplementary information taken from the manufacturer's literature, if different from the Annex X data.

HANDLING

Some of the major considerations in handling are:

- (1) Fire or explosive hazards
- (2) Toxicity and causticity
- (3) Pumpability
- (4) Reactivity

(1) Fire or explosion hazard is of concern if vapors escape during indoor storage or use in a confined area, or if applied in a fine mist, to cite typical circumstances. Combustibility is undesirable for use aboard ship and in aircraft as well as during storage. One general indicator of fire and/or explosion hazard is the flash point. A minimum closed-cup flash point of 150°F is called out in the Department of the Navy specification for oil-slick emulsifiers. (Reference 4.) Eleven of the 13 dispersants meet this requirement,

TABLE 1. DISPERSANT HANDLING AND STORAGE DATA

Product #/Type	Handling Points		Storage Points		Phase	Shelf
	Pour °F	Flash °F	Min °F	Max °F	Separ. °F	Life Months
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1/W	5	218	7	212	14	18
2/W	15	325	-20	200		indefinite
3/W	25	>212	none	160	none	>24
4/W	7*	116	10	130		unlimited
5/W	23*	>215	30	130	<30,>130	>36
6/W	24	>212	0	212	<0,>212	indefinite
7/W	21	none	24	155	16,170	24to60
8/W	22	none				indefinite
9/C	<-30	172	+30 ⁽²⁾	120 ⁽²⁾		unlimited
10/H	<-30	172	-30*	170		unlimited
11/H	0	154	14		14	>60
12/C	-90	148	23	140	23	>60
13/H	-78	160	-50	150	<-78,>160	>60

Source: EPA Technical Product Bulletins, if stated therein.
by *.

* Data from manufacturer's technical application literature.

- (1) W = water-based
H = hydrocarbon-based
C = concentrate

- (2) Manufacturer's technical literature shows -30 and +170
as min and max storage temperatures.

TABLE 2. SPECIAL HANDLING PRECAUTIONS FOR DISPERSANTS

Dispersant #/Type	
1/W	No special requirements, should be kept away from eyes and flushed with water in the event of contact with the eyes.
2/W	No special handling or worker precautions required
3/W	No special handling required for storage field applications. (Sic)
4/W	Avoid contact with skin or eyes. In case of contact flush exposed area with water. [Causes skin irritation/combustible/ May cause eye irritation/Vapors irritant/keep away from heat, sparks and open flames. Avoid eye contact/ Use with ventilation equal to unobstructed outdoors in moderate breeze. Keep container closed. Wash thoroughly after handling]
5/W	Prolonged exposure may cause eye and skin irritations. Avoid prolonged contact with skin or eyes. Protective glasses, gloves and hats should be worn during extensive use. To remove from eyes or skin, a fresh water rinse for at least fifteen minutes is recommended. [Non-toxic]
6/W	No special precautions are required for workers during storage or field application; Non-flammable, non-toxic, and non-corrosive. [If contacted with eyes, simply rinse with water]
7/W	No special precautions are necessary. If dispersant gets into eyes, simply rinse off with water; Non-flammable, non-corrosive, no toxic vapors.
8/W	Avoid contact of concentrate with eyes or open cuts. In case of contact, flush with plenty of water.
9/C	Avoid contact with skin or eyes. In case of contact flush exposed area with water. [May cause eye burns/combustible/ Causes skin irritation/Vapors irritant/Keep away from heat, sparks and open flame. Do not get in eyes. Wear chemical safety goggles. Avoid contact with skin or clothing. Avoid breathing mists or vapors. Use with ventilation equal to unobstructed outdoors in moderate breeze. Keep container closed. Wash thoroughly after handling.]
10/H	Avoid contact with skin or eyes. In case of contact flush exposed area with water. [Causes skin irritation on prolonged contact/Combustible/May cause eye irritation/Vapors irritant/

TABLE 2. SPECIAL HANDLING PRECAUTIONS FOR DISPERSANTS (CONT.)

Keep away from heat, sparks and open flames. Avoid eye contact. Avoid contact with skin and clothing. Avoid breathing mists or vapors. Use with ventilation equal to unobstructed outdoors in moderate breeze. Keep container closed. Wash thoroughly after handling]

- 11/H It is advisable to protect the eyes when it is being sprayed and to avoid inhalation of spray droplets.
- 12/C Prolonged contact between the skin and undiluted dispersant should be avoided. It is recommended that plastic gloves be worn when handling the product and eye protection as well if splashing is likely to occur. Avoid inhalation of spray droplets. In case of splashes onto skin or eyes, rinse well with plenty of water.
- 13/H Avoid prolonged breathing of mist or vapor. Avoid contact with skin and eyes. Keep away from heat, open flames, and strong oxidizing agents. For protection wear goggles and rubber gloves. [Combustible/Breathing of vapors may cause narcotic or anesthetic effects. Keep away from open flames and sparks]

Source: EPA Technical Product Bulletin. Statements in brackets are from the manufacturer's technical product literature. Warnings against ingestion have been omitted from this Table.

while one of them comes close (148°F)*. The State of California requires a flash point of at least 170°F for licensing of dispersants. In the U.K., Warren Spring Laboratory (WSL) specifies a minimum flash point of 142°F. The Federal Hazardous Substances Act requires that the label "combustible" be applied "to any substance which has a flash-point above 80°F to and including 150°F."

The flash point test methods called out by Annex X are: ASTM test D92 (Cleveland Open Cup, for petroleum products, except fuel oils, having flash points below 175°F); ASTM test D93 (Pensky-Martens Closed Cup, for fuel oils, lube oils, suspensions, and liquids that form a surface film); and ASTM test D56 (Tag Closed-Cup, for liquids with viscosity below 45 SUS at 100°F and flash point below 200°F, except those that form a surface film). Unfortunately these are not the same as the tests called for under the Federal Hazardous Substances Act, (Tagliabue Open Cup Test, 16CFR1500.42, for volatile flammable materials). The Navy spec, however, is based on ASTM D93, one of those called for in Annex X. The State of California regulations do not specify the flash point test to be used.

Considering the differences in test methods, it is not surprising that some of the dispersants with flash points above 150°F in Table 1, as per Annex X, are labelled combustible by the Federal Hazardous Substances Act, Table 2. These are products 9, 10 and 13. Further, Federal labelling is not available for the UK dispersants, products #11 and #12; they have Annex X flash points close to 150°F.

The water-based products (except #4) have Annex X flash points above 212°F and hence present virtually no fire hazard in ordinary use. Products #9 and #12 are similar to the hydrocarbon-based dispersants, having Annex X flash points between 150°F and 212°F. The concentrates and hydrocarbon-based products, as a group, require some caution in use: the containers should be kept sealed when not in use, and they must be protected from fire and heat. A full assessment of the fire and explosion hazard presented by the hydrocarbon-based and concentrate products, should be made before any

*The manufacturer's literature for this product (product #11) shows a closed cup flash point of 188°F rather than 148°F, but the test method is not stated.

large-scale deployment is undertaken. A full assessment would include data on: (1) upper and lower limits of concentration for explosion, (2) burning rate, (3) vapor pressure, (4) reactivity. It is also relevant to determine whether the products of combustion are toxic.

It should be noted that product #4, although classed as a water-based dispersant by the manufacturer, displays a flash point of 116°F, which is well below the Navy specification and any other of the 13 products, including the concentrates and hydrocarbon-based ones. Moreover, the manufacturer's data sheet indicates that the product is combustible and should be kept away from heat, sparks and open flame (See Table 2.) This illustrates the difficulty of relying categorically on any classification.

(2) Toxicity and Causticity. Toxicity here refers to adverse physical effects on humans due to ingestion of the product or inhalation of its vapors or mists. Causticity here refers to adverse effects when the product or its vapors come in contact with skin or eyes.

The usual protective measures are gloves, goggles, hats, masks and other protective clothing. Often, the exposure period is an important variable in assessing toxicity and causticity; application of a dispersant by hand or back-pack or from marine vessel can bring personnel in contact with the chemical over an extended period of time; also, long-term effects should be assessed for strike-team members who may deal with the product over a period of years.

Table 2 allows a comparison of the EPA Technical Product Bulletin data on handling precautions with that [in brackets] provided by the manufacturer in his product application data sheets. The latter fall under the Federal Hazardous Substances Act (CFR 16, Part 1500), just as container labels, and must describe the product, if applicable, according to the following definitions (among others):

Corrosive* "means any substance which in contact with living tissue will cause destruction of tissue by chemical action, but shall not refer to action on inanimate surfaces".

Irritant "means any (non-corrosive) substance" - "which on immediate, prolonged, or repeated contact with normal living tissue will induce a local inflammatory reaction."

Toxic applies "to any substance... which has the capacity to produce personal injury or illness to man through ingestion, inhalation, or absorption through any body surface."

The Federal Hazardous Substances Act also provides supplementary alternative definitions of the above terms in the form of quantitative test procedures. These tests are:

16 CFR1500.40 Method of testing toxic substances.

16 CFR1500.41 Method of testing Primary Irritant Substances.

16 CFR1500.42 Test for eye irritants.

The Hazardous Substances Act requirements are not only better-defined than the Annex X requirements with regard to toxicity and causticity but they also carry penalties for violation. Thus it is seen in Table 2 that technical product literature is often more explicit than the information submitted under Annex X. Considering this difference in information it appears that better toxicity and causticity data can be gotten directly from the product labels or application literature than from the Annex X submissions. This will provide complete, well-defined statements on all products in a uniform format.

(3) Pumpability. Most application methods of value require the dispersant to be pumped or drawn through one or more orifices into a spray form. At low temperatures, the operation may be impeded by thickening, freezing, or crystallization of the dispersant. The two primary indicators of pumpability examined in this study are pour point and viscosity.

Note: *"Corrosive" as here defined is the same as "caustic" defined above.

Pour point is defined as the lowest temperature at which the product will pour under specified conditions; Annex X prescribes ASTM-D-97-66 as the test procedure for pour point. The pour point, however, is only a general guide to pumpability of a dispersant, indicating a lower limit to its usable temperature range. Many dispersants thicken substantially at temperatures well above their pour point. The data of Table 1 show that most (but not all) dispersants classed as water-based have pour points above 20°F, and all concentrate and hydrocarbon-based products have pour points of 0°F or less.

A more meaningful indicator of pumpability is viscosity. Table 3 shows viscosity of the 13 dispersants as submitted to the EPA. Unfortunately almost all data pertain to 100°F, which is well out of the range of interest, 0°F to 35°F. Also, since the viscosity is given at only one temperature, 100°F, it is not possible to extrapolate it into the temperature range of interest. The EPA Product submissions simply do not provide adequate data to assess viscosity at temperature of interest. Judging from the 100°F data, however, it can be inferred that the water-based dispersants and the concentrate #9 have higher viscosity than the hydrocarbon-based dispersants and concentrate #12. Product #3 is a low-viscosity water based dispersant.

The question of viscosity requirements for dispersants, however, is more easily answered. MIL-E-22864 (Navy) specifies 400 centistokes (1820 SSU) at 20°F for oil-slick emulsifiers. Many pumps operate well with fluids of viscosity in the 3000 SSU to 5000 SSU range, so that the Navy specifications will allow pumpability well below 20°F in most cases. Warren Spring Laboratory specifies no more than 330 SSU at 32°F for undiluted hydrocarbon-based dispersants and no more than 1137 SSU at 32°F for concentrates. (Reference 1, p. 242).

A rough guide to what temperature can be expected in some of the major oil-movement areas of the United States is given in Table 4. The Great Lakes and Northern Alaskan slope are the most conspicuous omissions from this Table. Dispersants need to be

TABLE 3. DISPERSANT VISCOSITY DATA

<u>Product #</u>	<u>Type</u>	<u>VISCOSITY</u>
1	W	441.4 SUS at 100°F (1)
2	W	706.3 SUS at 100°F (2)
3	W	72.3 SUS at 100°F
4	W	117.9 SUS at 100°F
5	W	675.9 SUS at 60°F
6	W	168.1 SUS at 100°F
7	W	142.4 SUS at 100°F
8	W	126.0 SUS at 100°F
9	C	117.5 SUS at 100°F
10	H	43.4 SUS at 100°F
11	H	34.8 SUS at 100°F
12	C	61.3 SUS at 100°F
13	H	40.5 SUS at 100°F

Source: EPA Technical Product Bulletins, except as noted.
Noted items obtained from manufacturer's product literature.

Notes: (1) Listed as 96.8 Set in Technical Product Bulletin
(2) Temperature not given in Technical Product Bulletin
(3) Viscosities converted to SUS when given in centistokes or centipoise.

TABLE 4. LOWER 5th PERCENTILE OF ALL RECORDED OFFSHORE TEMPERATURES, °F

	Air Temp		Water Temp	
	January	Annual	January	Annual
Cape Cod to Nova Scotia	18	27	34	35
Delaware Bay Coastal Area (38°N-40°N)	26	34	37	40
Gulf Coast	50	58	62	67
San Francisco Coastal Area	44	49	49	51
Puget Sound Coastal Area (48°N-50°N)	33	39	42	44

Notes:

Kodiak, AK: Average January air temperature: 25°F
 Anchorage AK: Average January air temperature: 13°F
 Average January daily high: 19°F
 Average January daily low: 5°F

pumpable at the temperatures shown in the first 5 lines of the Table in order to be usable in 95% of coastal spills that occur in the month of January. Air temperature presents a more stringent requirement than water temperature. It appears from Table 4 that a lower pumping temperature limit of 20°F would insure that a dispersant can be applied in January in almost all U.S. locations except Alaska and the Great Lakes, with 95% probability. The requirement for Alaskan use is probably in the 0°F to -10°F range, as may be seen from the last two lines of the Table.

Considering the pronounced difference in pumpability of water-based and hydrocarbon-based dispersants, the question of operating temperature specification can have great significance in stockpiling strategy.

(4) Reactivity is here taken to mean the chemical action of the dispersant on storage containers, spray gear, spray vehicles, and protective clothing. None of the 13 dispersants have any serious adverse effects on equipment or clothing, according to the Technical Product Bulletins and manufacturers' literature. One precaution, however, was commonly issued in the manufacturers' literature: prolonged contact with rubber-based materials, such as hoses and gloves, should be avoided. This caution should not be difficult to observe in the field, if operating procedures call for flushing or rinsing of equipment after each use.

STORAGE

The major storage considerations are temperature and shelf life.

TEMPERATURE

Minimum storage temperature, as given in Table 1, is usually specified by the manufacturer as the minimum temperature at which the dispersant can be stored for prolonged periods. The basis on which it is specified is not usually stated in the Technical Product Bulletins. It is seen that in some cases this temperature is

below the phase separation temperature. It is also possible that for some dispersants it is below the freezing temperature, if such data were available. Freezing not only can cause bursting of the container, but can induce phase separation and chemical change. It also retards return to normal temperature because of the latent heat of fusion of the material. Now, it must be considered impractical to heat any dispersant or to agitate it to remove a phase separation, in the event of a spill emergency, especially if this must be done to a large number of 55 gallon drums. Therefore, the practical lower limit to the storage area temperature is set by the phase separation and freezing temperatures as well as by the minimum storage temperature designated in Table 1. Unfortunately, freezing data and the phase separation temperature are not always available in the Technical Product Bulletin or manufacturer's literature.

The function of a specification on minimum storage temperature is to insure that the dispersant is still usable and effective after having been cycled, perhaps more than once, down to the minimum storage temperature and back to its use temperature. The cycling is that which would occur in an unheated storage area near the point of use, and is necessarily to a lower temperature than the minimum use temperature. While the minimum use temperature specification is set in reference to the distribution of all air temperatures, the minimum storage temperature is selected from the distribution of daily low temperatures. For example, if the minimum use temperature is taken at the 5th percentile of all air temperatures (Table 4), and the minimum storage temperature taken to be the lowest recorded air temperature in the same region, then they differ by about 15°F off the New England Coast (Cape Cod to Nova Scotia) and by 15°F in the Puget Sound area. The differences are less for the other three regions in Table 4, but more for Alaska.

In addition to freezing, phase separation, and chemical change, there may occur a reduction in dispersant effectiveness due to storage at low or high temperature. It is for that reason, presumably, that Annex X requires the manufacturer to submit "optimum

ranges as well as temperature that will cause phase separation, chemical changes or otherwise damage effectiveness of the chemical agent". In some cases the manufacturer indicated a minimum recommended storage temperature instead of a minimum "optimum" storage temperature.

Table 5 summarizes the relevant available data on minimum storage temperature for the thirteen subject dispersants. Column (1) shows the Annex X minimum storage temperature or the phase separation temperature, whichever is greater. Unfortunately, freeze point data are not explicitly included. Column (2) shows pour point, as the best available indicator of use temperature. If pumpability data were available they would afford much better indications of minimum use temperature. Similarly, complete information on freezing point would improve the estimated minimum practical storage temperatures of column (1). The manufacturer's recommended or optimum storage temperature lower limits are shown in columns (3) and (4). Generally, these points are well above those of columns (1) and (2). It is not possible to determine whether it is economic to heat the storage area so as to achieve these "optimum" temperatures without knowing the variation of dispersant effectiveness with storage temperature.

The utility of Table 5 in indicating a minimum storage temperature is limited by the factors described. In particular, they are

- (1) Lack of statements as to the specific nature of the limiting factor in the minimum storage point temperatures submitted under Annex X.
- (2) Lack of complete data on freezing points, chemical change, and phase change.
- (3) The lack of viscosity and other pumpability data necessary to establish minimum use temperature.
- (4) The lack of indication of variation of effectiveness or other optimized quantity with storage temperature.

From Table 5 it appears that seven products go into phase separation or some other disabling condition at a storage

TABLE 5. MINIMUM STORAGE TEMPERATURES FOR THIRTEEN SUBJECT DISPERSANTS, °F

<u>Product #/Type</u>	<u>Minimum Practical</u> (1)	<u>Pour Point</u> (2)	<u>Minimum Recommended</u> (3)	<u>Minimum Optimum</u> (4)
1/W	14	5		
2/W	-20	15		
3/W	None	25		32
4/W	10	7		40
5/W	30	23		
6/W	0	24	24	
7/W	24	21		
8/W		22	15	
9/C	30	< -30		40
10/H	-30	< -30		40
11/H	14	0		32
12/C	23	-90		32
13/W	-50	-78		0

(1) Maximum of columns (4) and (6) of Table 1.

(2) From Table 1., column (2).

(3) From EPA Technical Product Bulletin

(4) From EPA Technical Product Bulletin, as per Annex X.

temperature above the pour point. The disabling condition, in such cases, cannot be freezing, since the freezing point is below the pour point. Three of the remaining products cease to pour at temperatures above the minimum storage or phase separation point. The remaining three products have minimum storage temperatures equal to the pour points, or inadequate data.

SHELF LIFE

Storage shelf life impacts on efficiency and cost. Although the number of spills per year is relatively consistent, the total amount of oil spilled per year varies substantially (Reference 27., p.4). If the stockpile life is N years, then the fluctuations are averaged over N years, and the percent variance in the expected spillage is reduced proportionately. Since stockpiles must be increased to allow for the variance in expected spillage, less dispersant need be stocked per year of planned use if the time to replenishment is longer. For example, if it is decided that a one-year stock pile requires a 100% buffer above the expected spill volume (not unrealistic, as seen from Reference 27), then a three-year stockpile needs only a 57% buffer, and a five-year stockpile needs only a 45% buffer, to achieve the same assurance of adequate supply. In addition to the reduction in buffer stocks, which reduces the amount of unproductive capital investment, longer shelf life reduces the amount of dispersant that is discarded because its shelf life is exceeded.

In practice, restocking depleted stores could occur on short notice, i.e., the restock time could be much less than the shelf life, in that case the stockpile could be relatively smaller and the probability of shelf life expiration before use also would be small. The above savings on long-term stockpiles would be much less important. Therefore, the value of a long shelf life product depends on production capability and lead time, as well as on the statistics of spill frequency and volume.

The Warren Spring Laboratory specifies a shelf life of at least five years. (See, for example, Reference 28).

APPLICATION CHARACTERISTICS

The effectiveness of any dispersant or group of dispersants in a given spill situation depends on many parameters. The most important ones are given in Table 6. They are divided into two general groups:

- (1) Parameters that describe the spill conditions
- (2) Parameters that describe the method of dispersant application

Although the influence of these parameters on dispersant effectiveness is poorly understood in many cases, an attempt will be made to summarize the available information for the 13 subject dispersants.

SPILL CONDITIONS

The effectiveness of dispersants is strongly affected by the type of oil that has been spilled, its condition, and the weather and geographic conditions of the spill. These parameters affect the type and quantities of dispersants that will be required, and the locations at which they are likely to be needed.

The spill condition parameters are listed in Table 6, items 1 through 8. While the evidence is good that these parameters strongly affect the suitability of a dispersant for a particular spill (as will be discussed), specific information for the subject dispersants is not plentiful.

Oil Type, Weathering and Emulsification

The effectiveness* of a dispersant is generally considered to vary with the type of oil, not all products functioning in the same manner. For example, Doe (Reference 1, p. 59) found that in

*The term effectiveness when applied to dispersants is generally used to denote (1) the dispersant-oil ratio required to achieve dispersion of a fixed percentage of the oil, or (2) the percentage of the oil dispersed by a given dispersant-oil ratio. Usage varies among authors, and other definitions are common.

TABLE 6. PARAMETERS DESCRIBING THE APPLICATION CHARACTERISTICS OF DISPERSANTS

SPILL CONDITION PARAMETERS

1. Oil Type
2. Oil Weathering
3. Oil Emulsification
4. Slick Thickness
5. Water Temperature
6. Water Salinity
7. Wave Conditions
8. Shoreline Type

APPLICATION METHOD PARAMETERS

9. Equipment Type
10. Dilution Ratio
11. Mixing Ratio
12. Agitation Energy Level
13. Application Ratio

seawater Corexit 9517 was one-third as effective against Heavy Bunker Fuel as against Medium Bunker Fuel, whereas Corexit 9527 was considered ineffective against both. A synopsis of some of Doe's results (for seawater) follows:

Mean Minimum Dispersant-to-Oil Ratio

	°C	#2	VC	MB	HB
Corexit 9517	5	1:10	1:1	1:3	1:1
Corexit 19-L-50	5	-	1:1	1:10	1:10
Corexit 9527	1	-	1:27	IE	IE
BP1100WD	5	-	1:27	1:1	IE
BP1100X	5	-	1:3	IE	-
Corexit 8666	5	1:10	1:1	IE	-
Drew OSE 71	1	-	1:3	IE	-
Drew OSE 72	1	-	1:3	IE	-
Oilsperse 43	1	-	1:3	-	-
Shell LTX	5	-	1:3	IE	-
Corexit 7664	15	-	IE	-	-
Linco-6	5	-	-	-	-
Sugee #2	5	-	IE	-	-

Legend:

- #2: No. 2 Fuel Oil
- VC: Venezuelan Lago Media Crude Oil
- MB: Medium Bunker Fuel Oil
- HB: Heavy Bunker Fuel Oil
- IE: ineffective under the particular set of conditions.

In addition to the incompleteness of these data, there are several test conditions that need to be varied: degree of weathering, degree of emulsification, degree of agitation, contact time, all of which factors can be expected to influence the relative performance of different dispersants on different oil types.

Although one would expect dispersants to be uniformly less effective on heavier oils, the preceding data do not confirm this for Corexit 9517 and Corexit 19-L-50, but do so partly for the other dispersants.

Cormack and Nichols (Reference 1, p. 244) recognize "that oil viscosity determines the ease with which oils may be dispersed by chemicals." They state that "lighter oils present fewer problems, whereas heavier oils may require more than one treatment." These observations are based, presumably, on the authors' familiarity with the UK Warren Spring Laboratory tests of dispersant efficiency.

Murphy and McCarthy (1969 Reference 23, p. 199 ff) tested four dispersants on six oils. Three of the oils were relatively low viscosity, three were relatively high. The average dispersion of the four products is plotted against the log of the viscosity in Figure 1. Although the percent dispersion achieved on the heavier oils was less than on the lighter ones, the difference was not (37% vs 49%) very large. Substantial differences in performance exist among the four dispersants.

A rough guide to matching dispersant types to oil types is given by Castle and Schrier (Reference 6, p. 459) in work performed for the EPA. This guide (Table 7) recommends water-based products for light or low viscosity oils, hydrocarbon-based products for heavy or waxy oils, and concentrates for both. The sources of the guide are not given.

The manufacturer's recommendations for the thirteen subject dispersants are summarized in Table 8, with regard to the types of oil on which they are effective and recommended dilution. Only the vaguest descriptions of oil and slick types are found in this table, reflecting the very broad range of applications possible or, perhaps, the lack of test data covering the range of oils.

The relatively small amount of data discussed above can be supplemented by intuition. Since dispersants work by reducing interfacial tension of the oil and water, they must penetrate to the oil-water interface to do so. It would be expected that more

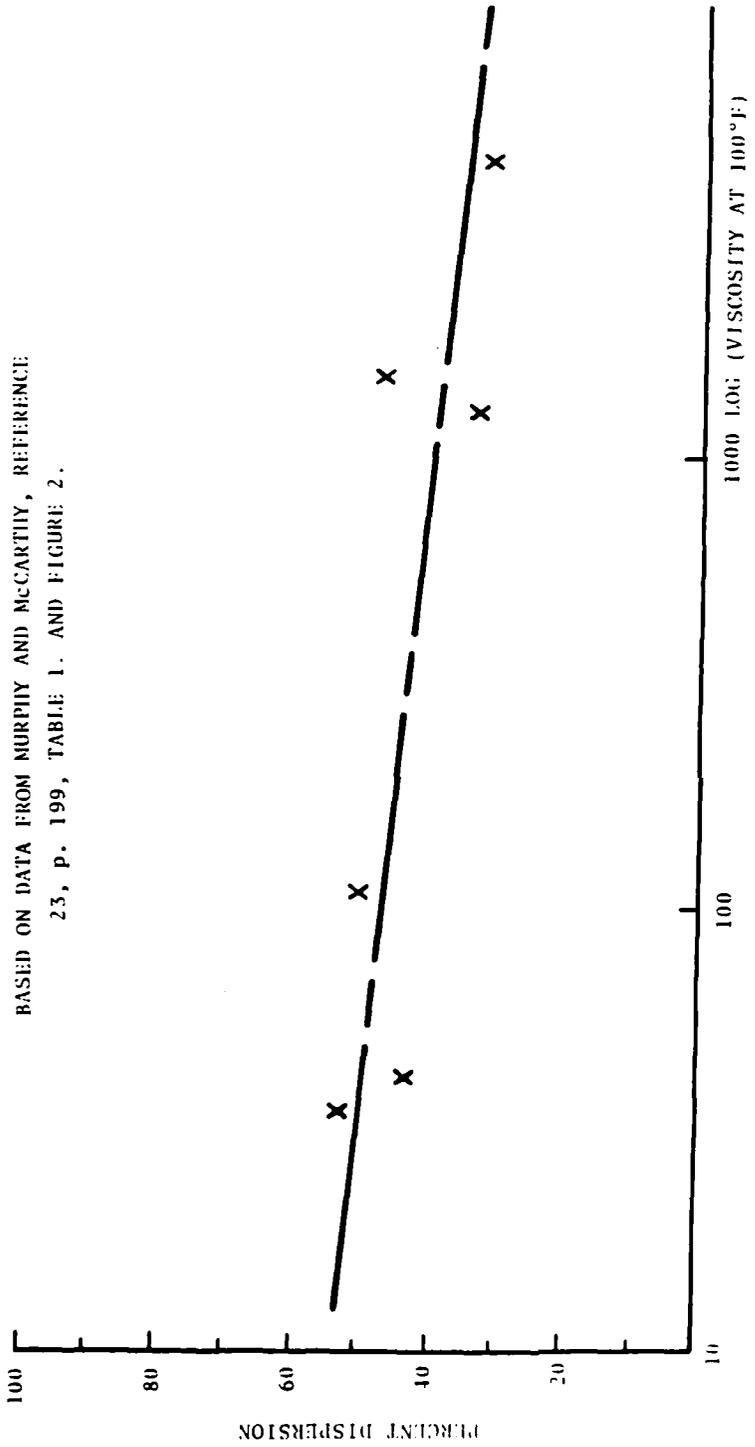


FIGURE 1.: AVERAGE DISPERSION VS. OIL VISCOSITY

TABLE 7. GENERAL COMPATIBILITY OF OIL TYPES WITH DISPERSANT TYPES (1)

	Dispersant Type		Concentrates
	Water-Based	Hydrocarbon-Based	
Light Distillate fuel oils	x		x
Low Viscosity Distillates & Crudes	x		x
High Viscosity Asphaltic crudes, residuals and weathered oil		x	x
Waxy Crudes		x	x
Well-developed Water-in-Oil Emulsions		Diminished Effectiveness, not well documented	
Non-Spreading Oils		Dispersion not effective	

(1) Adapted from Reference 6., Castle, R.W., and E. Schrier "Decision Criteria for the Chemical Dispersion of Oil Spills", p. 460, Table 1.

TABLE 8. RECOMMENDED DILUTION⁽¹⁾ RATIOS FOR VARIOUS
TYPES OF SPILLED OIL

<u>Product #/Type</u>	<u>Type and condition of Oil and Slick Thickness</u>	<u>Recommended Ratio Dispersant/Diluent</u>
1/W	Bunker C Fresh or weathered Crude or distillate fuel spill Diesel Fuel spill	1:0 1:5 (F or S) 1:5 (F or S) 1:40 (F or S)
2/W	Crude oil; light, medium and heavy	1:40 to 1:80
3/W		1:0 or 1:10 to 1:40
4/W	Floating Oil	1:0 to 1:5 or more
5/W	Light Oils (API gravity over 30) Heavier Oils	1:0 1:0
6/W	Fuel Oils Heavy Crude Oil	1:500 (F or S) 1:300 (F or S)
7/W	Light accumulations of oil Heavy accumulations of oil	1:50 (F or S) 1:15 to 1:20 (F or S)
8/W	Spills at sea Semi-solid, tar or weathered oil Medium spills Small spills	1:80 (F or S) not effective 1:40 1:20
9/C	Not very heavy oil Viscous crude or petroleum products Small spills Spills accessible by air	1:10 to 1:20 (F) 1:5 or more (AS) 1:10 (F) 1:0
10/H	Floating oil, heavy, viscous or waxy crude, or a product such as Bunker C or No. 6 fuel oil	1:0
11/H	Liquid oil, most types	1:0
12/C	Most types of oil	1:9 (S)
13/H	Fresh spills Unusually thick or heavy slick	1:0 1:0

(F): fresh water

(S): sea water

(AS): kerosene or other aliphatic solvent

(1) Both pre-dilution and dilution at time of application.

viscous oils would be more resistant to penetration and dispersion. Mackay [Reference 1, p. 44] has, in fact found that percent dispersion decreases as oil viscosity increases for one combination of dispersant and oil. It certainly would be of value to explore this relationship for various oils and dispersants. The relative effectiveness of hydrocarbon over water-based dispersants is based on the supposition that the hydrocarbon solvent more easily penetrates the oil layer and diffuses at the interface. Comparative test data, however, are not easily located, because most manufacturers produce either a water-based or hydrocarbon-based dispersant. One manufacturer of both types (Exxon, reference 25, p. 12) recommends pre-softening weathered or viscous oil or rocks or seawalls with his hydrocarbon based product or his water-based concentrate diluted in a low-aromatic hydrocarbon, before applying his water-based dispersant. Data on which this recommendation is based have not been published. In the absence of such data, however, generalizations such as that of Castle and Schrier must rest as much on intuitive as on evidential grounds.

Finally, the EPA effectiveness test data on the thirteen subject dispersants were examined. The tests, as prescribed in Reference 15, are performed for No. 2 and No. 6 oil under similar conditions and may be expected to provide an indication of relative effectiveness on the two types. The results for the 13 dispersants at a 1:10 dispersant-oil ratio are analyzed in Appendix A. The rankings based on No. 2 oil have no significant correlation with the rankings based on No. 6 oil, but initial dispersion is highly correlated with final dispersion.

In summary, it seems that there is evidence that heavier oils on water are less easily dispersed than light oils, but the difference, on average, may not be very great and there is a great deal of variability among oils and dispersants. The conjectures of Castle and Schrier regarding water-based, hydrocarbon-based, and concentrates seem plausible, but are not borne out by statistical tests on the EPA data for final dispersion on No. 6 oil.

Slick Thickness

Mackay (Reference 1, p. 45) states that "the thickness of the oil slick drastically affects the dispersion process. Laboratory tests showed that by decreasing the slick thickness from 0.91 to 0.73 mm, the percent dispersion increased from 35 to 70 percent with the same dispersant-to-oil ratio in each case. A further decrease in the slick thickness to 0.20 mm resulted in 100 percent dispersion." The tests were performed on a laboratory apparatus using two dispersants and a particular Alberta crude. The mechanisms at work in the tests are (1) reduced wave action and (2) increased penetration difficulty. Both are due to increased slick thickness. It is to be expected that these mechanisms would act similarly for most dispersants and oils.

Water Temperature

Gill (Reference 5, p. 391) has reported reduced efficiency of BP1100X, Oilsperse 43, BP1100WD, Corexit 9527 and Finasol OSR5 with reduced water temperature. The average end point oil/dispersant ratio at 40°F was about 23 percent lower than at 62°F in sea trials using light Tia Juana crude. The results are summarized as follows:

	End point oil/dispersant ratio		
	62°F	40°F	% Drop
BP1100X	2.9	2.3	21
Oilsperse 43	3.8	2.8	26
BP1100 WD	7.8	6.0	23
Corexit 9527	8.5	-	-
Finasol OSR5	-	5.4	-
Average	5.8	4.1	23

The above dispersants are concentrates or hydro-carbon-based. Zitko and Carson (Reference 7) as reported by Mackay, Nadeau and Ng, found that on Bunker C oil, one water based dispersant increased in efficiency with lower temperatures, and one oil-soluble

dispersant reduced in efficiency. The reason for this apparently maverick behavior of the water-based dispersant was not understood. It might also be noted here that microbial degradation of oil droplets proceeds more rapidly at higher temperatures. (Reference 7.)

Doe (Reference 1, p. 59) reports that effectiveness varied with water temperature in tests in a simulated environmental tank. (He defined effectiveness as the dispersant-oil ratio required to disperse 65 percent of the test oil.) Results agreed with those of Gill (above) in that Corexit 8666, Oilsperser 43, and BP1100 WD, were less effective in lower temperatures in seawater. Results in fresh water were similar for BP1100 WD, BP1100 X, Oilsperser 43, Shell LTX, Linco-6 and Sugee #2. However, Corexit 9517 was found to be more effective in lower temperatures in fresh water. Unfortunately, complete data are lacking in these tests.

It seems likely from the above that effectiveness of most dispersants drops with temperature, despite the contrary data on one dispersant obtained by Zitko and Carson and Corexit 9517 in fresh water. The available data also suggest that the drop is uniform from dispersant to dispersant.

The temperature required for effective dispersant use is stated by the manufacturer in some cases of the 13 dispersants submitted under Annex X:

<u>Product #</u>	<u>Recommendations on Temperature of use</u>
5	May be used between "30°F and 215°F"
6	"Water temperature will have little or no effect on the efficiency."
7	"Reaches its greatest efficiency at 65°F and over."

The scarcity of these data on temperature effects is not surprising, since Annex X does not require such information to be submitted.

Water Salinity

About 30 percent of US waterborne petroleum movement takes place in fresh water, about 5 percent in brackish water, and the remaining 65 percent in seawater (See Table 9). Accordingly, effectiveness of a dispersant in fresh water is an important characteristic for its use.

Theoretically, it is known that the presence of electrolytes in aqueous solution modifies interfacial tensions and influences the effectiveness of the dispersant. (References 8, 9, and 10.) It is not surprising, then, to find differences of effectiveness of the same dispersant in salt and fresh water, since they have very different electrolytic properties. Doe, for example, (Reference 1, p. 58) found that some dispersants were more, and some less, effective in salt water. (See Table 10.) In particular, Shell LTX, Corexit 9527, Corexit 8666, and BP1100 WD, were more effective in salt than in fresh water, while Drew Chemical OSE71 and 72 were less effective. BP1100X and Corexit 7664 were equally effective in salt and fresh water.

Manufacturer's recommendations were regard to effectiveness in salt and fresh water are summarized in Table 11. It should be noted that Annex X effectiveness tests are prescribed for salt water only. No statement is required by the Annex with regard to fresh water use.

Wave Conditions

The formation of oil droplets in water requires energy. A dispersant aids droplet formation by reducing the interfacial tension at the oil-water interface, thus reducing the amount of energy required to form droplets. The required energy may be supplied by mechanical means but for some dispersants (termed "self-mixing") wave action alone is adequate to produce dispersion. It is of primary importance, then, to relate dispersion effectiveness to energy input, and to relate energy input to various wave conditions. Mackay (Reference 1, p. 40) discusses the relation of dispersion to sea state, as produced in his laboratory apparatus

TABLE 9. US OIL MOVEMENT IN FRESH AND BRACKISH WATER, 1976

<u>Fresh Water</u>	<u>300.63</u>	<u>30.6%</u>
Hudson River ⁽¹⁾	16.73 million tons	1.7%
Delaware River		
Philadelphia Harbor ⁽²⁾	34.22	3.4
Above Philadelphia	7.39	0.7
Mississippi River		
Port of N. Orleans	47.48	4.7
Baton Rouge to N. Orleans	90.32	9.0
Lower Mississippi ⁽³⁾	25.50	2.6
Upper Mississippi	22.50	2.3
Illinois River	5.90	0.6
Ohio River	30.60	3.1
Great Lakes	14.49	1.4
Columbia River	5.44	0.5
<u>Brackish Water</u>	<u>55.97</u>	<u>5.6</u>
Gulf Intra-Coastal WW	55.97	5.6
<u>Total US Movement⁽⁴⁾</u>	<u>983.41</u>	<u>100</u>

(1) Above Spuyten Duyvil Creek

(2) Maximum salinity at Philadelphia is 200 mg/l

(3) Above Baton Rouge Only

(4) Excludes Alaska, but includes Hawaii and Puerto Rico.

TABLE 10. EFFECTIVENESS OF SOME DISPERSANTS IN FRESH AND SEAWATER⁽¹⁾

<u>Product Name</u>	<u>Mean Minimum Dispersant-to-Oil Ratio⁽³⁾ on Venezuelan Lago Medio Crude Oil⁽⁴⁾</u>		
	<u>°C</u>	<u>in Fresh Water</u>	<u>in Salt Water</u>
Corexit 9527	1	1:10	1:27
" 10% dilution	1	1:1	1:3
BP 1100WD	5	1:1	1:27
" 10% dilution	5	IE ⁽²⁾	1:1
BP 1100X	1	1:3	1:3
	5	1:3	1:3
Corexit 8666	5	IE	1:1
Drew chemical OSE71	1	1:10	1:3
" " OSE72	1	1:9	1:3
Shell Dispersant LTX	5	1:1	1:3
Corexit 7664	15	IE	IE

(1) This table is adapted from Table 4 of Reference 1, p. 58 (Doe et.al.)

(2) IE indicates ineffective under the particular set of conditions

(3) Required to disperse at least 65% of the test oil

(4) API gravity 32.2 to 33. at 60°F, 55 SUS at 100°F.

TABLE 11. MANUFACTURER RECOMMENDATIONS ON DISPERSANT USE
IN SALT AND FRESH WATER

<u>Product #/Type</u>	<u>Manufacturer's Recommendation</u>	<u>Source (1)</u>
1/W	"can be used in both salt and fresh water"	L
2/W	"may be sprayed on oil slicks at sea, in harbor waters and coastal waterways..."	L
3/W	"water salinity and water temperature are not important factors"	B
5/W	"stable in salt, brackish, or fresh water"	B,L
6/W	"water...salinity will have little or no effect on the efficiency..."	B
7/W	"works equally well in salt or fresh water"	B
8/W	"works equally well with fresh water or sea water"	L
9/C	"not recommended for use on freshwater" "properly used, it causes rapid, complete dispersion of oil films on salt or brackish water..."	B L
11/H	"most effective when used in sea water (salinity equals 3.0 to 3.5%), but will also work in waters with salinity as low as 0.1% NaCl."	B
12/C	"intended primarily for dispersing oil at sea, but may also be used on beaches."	L
13/H	Dispersible in Seawater, Fresh Water	L

- (1) L = Manufacturer's product application literature
B = EPA Technical Product Bulletin

and it is clear from his experiments and from other considerations (Wiegel, Reference 11) that energy input from wind to water surface increases exponentially with wind speed. The possibility must be allowed, however, that sea conditions other than wind, such as wave period and velocity, and extent of "choppiness" are influential in the dispersion process.

Canevari (Reference 1, p. 16) points out that in a "self-mixing" dispersant, part of the surfactant has an inherent tendency to diffuse into the water at the interface, taking fine oil droplets with it, thus making it possible for them to function in almost calm water.

Although the level of wave action is acknowledged to be an important factor in dispersant effectiveness, data are not generally available to indicate effectiveness as a function of wave conditions. This is especially critical for aerial application, since the need for addition of mixing energy by a surface craft can completely void any benefit that may be derived from aerial application.

The major source of information regarding wave energy and agitation requirements for the subject dispersants is the manufacturers' recommendations, which usually are qualitative in nature. Nevertheless, the information is shown in Table 12.

Further discussion of wave conditions for dispersion is postponed to the sections (below) on aerial application and mechanical agitation.

Shoreline Type

The use of dispersants on shorelines can be categorized as either (a) protective application before the oil comes ashore (b) clean-up after oil impacts the shore. The questions relevant to logistics are: which types of dispersants are suitable for these applications, and to what type(s) of shore line may they be applied.

(a) Protective Application of Dispersants: The use of dispersants to treat uncontaminated shorelines is currently considered

TABLE 12. MANUFACTURER RECOMMENDATIONS ON WAVE CONDITIONS AND AGITATION REQUIRED FOR DISPERSAL

<u>Product #/Type</u>	<u>Recommendations Regarding Wave Conditions, & Agitation</u>
1/W	Agitation of the surface will quicken the dispersion. [Agitation is an important factor in effective application. The manufacturer has found in application to oil spills at sea that the natural agitation of the sea is sufficient, however, additional agitation will increase the effectiveness]
2/W	[External energy such as high velocity water hoses or powerboat propellers may be helpful. Aerial application: In calm waters, additional agitation may be needed.]
3/W	Manufacturer recommends spray application from aircraft or vessel. [Vigorous agitation is required when water is calm]
4/W	Properly applied, it renders an oil slick dispersible by wave action or mechanical agitation. For aerial spraying use undiluted. May be sprayed from helicopters or fixed-wing aircraft. [In all cases some agitation or mixing energy must be applied to treat the oil. Usually the normal motion of the sea will suffice]
5/W	After the oil and dispersant have combined, strong agitation should force the mixture to disperse. This agitation can be supplied by high pressure water jets or boat propellers.
6/W	Vigorous action, either natural wave action or by mechanical means, will greatly increase dispersion. If sprayed by aircraft, dilution of 20 parts water (fresh or salt) to one part dispersant is recommended. [Agitation of slick with high pressure hose, beater boards, boat props or wave action is vital for rapid oil dispersion. When applied by aircraft dilute approximately 10 parts water to one part dispersant]
7/W	After the oil dispersant is applied to the water surface, it is necessary to agitate and mix the dispersant, oil and water thoroughly in order to obtain the most efficient dispersion. In open, unconfined areas, use of ship's propeller has proven to be a practical way of providing the necessary agitation. Mixing with high shear tends to break the particles into smaller sizes. The greater the shear, the smaller the particles and the greater the likelihood of a stable dispersion.

TABLE 12. MANUFACTURER RECOMMENDATIONS ON WAVE CONDITIONS AND AGITATION REQUIRED FOR DISPERSAL (Continued)

- 8/W Apply with a hard, coarse spray.
- 9/C The usual application methods include aircraft, dispersant applied undiluted during aerial spray. [Properly used, it causes rapid, complete dispersion of oil films... with minimum mixing requirements. The normal motion of the sea is usually adequate]
- 10/H Natural wave or wake action normally provides adequate mixing energy. Aerial spraying (undiluted) is recommended for very large spills or those not easily accessible to workboats.
- 11/H Vessel employed must be capable of vigorously agitating the treated oil to insure its complete dispersion. [Best results are obtained by using a trailing agitator of the type developed by Warren Spring Laboratory. For small spills in relatively confined waters the turbulence of the spraying vessel's screws or even a high pressure hose may suffice. Vigorous agitation following application is essential to ensure good dispersion.]
- 12/C Each vessel employed must be capable of vigorously agitating the treated oil to ensure its complete dispersion.
- 13/H Allow 15 minutes to penetrate, then vigorously agitate the treated surface by one of the following methods: (1) Delivering a jet of water onto the treated oil from a fire hose (2) Backing a lightly loaded launch through the treated slick, (3) Allowing the solution spray to strike the oil ahead of the vessel's bow wave. (4) Towing a five-bar gate or modified five-bar gate, as specified by Warren Springs Laboratory, through the treated slick at 2-4 meters/second.

Source: EPA Technical Product Bulletins and [Manufacturer's Technical Application Literature]

to be experimental and is not recommended by the EPA. Oil collecting agents and certain surface treatment agents (Reference 12) however, also have potential for pre-treatment of shorelines; these are not considered dispersants.

(b) Clean-up after Oil Impact on Shoreline: The primary approach to shoreline clean-up is mechanical. Secondly, natural processes can remove oil from the shoreline, sometimes with little ecological impact. If mechanical clean-up and natural processes are inadequate, dispersants can be considered.

It is generally believed that hydrocarbon-solvent dispersants, because they are applied undiluted and contain a strong solvent, should not be applied to oil on a sand beach since they would disperse the oil into fine droplets which would be driven down into the sand by wave action. This actually occurred during the Brazilian Marina incident in January 1978 near Sao Paulo, Brazil. (Reference 13.) This penetration action was also found to greater or lesser extent in simulated shoreline tests by Mackay et al. (Reference 14) using Corexit 9527, BP1100WD, Corexit 7664, Corexit 8667 and BP1100X. In general, they found that the more effective the dispersant the greater the sand penetration. It is possible, however, that a mild dispersant such as Corexit 7664 may be used to flush off oil layers from the top of a sand beach into the water or into a collecting basin, if applied with a stream of water from a hose as suggested by Canevari (Reference 6, p. 444). The net value of such cleansing is yet to be assessed, however.

The inadvisability of dispersant use of sandy beaches, discussed above, is due to their penetrability. Dispersants are better suited for clean-up on impervious surfaces such as rock cliffs, seawalls, docks and to some extent, on steep cobble beaches. Oil deposits on such surfaces are often weathered into a viscous encrusted state by the time the decision has been made to employ dispersants. Effectiveness depends on contact time and abrasion as well as the dispersant itself. Gelling agents can be mixed with the dispersant and sea water at the time of application. They increase the contact time and thereby are expected to increase the effectiveness of the dispersant, especially on

vertical surfaces. It is applied as soon as the oil is exposed by an ebbing tide to maximize the contact time. The surface is brushed and/or hosed down after several hours.

The match of dispersant to shore clean-up task is often phrased in terms of hydrocarbon-based, water-based, and gels. This is done on the assumption that water-based dispersants are less effective and/or toxic than hydrocarbon-based ones. As will be seen subsequently, this is not always true; some water-based dispersants are more effective than some hydrocarbon-based dispersants. Moreover, the use of a low toxicity dispersant may result in greater ecological damage if larger quantities are required to clean a given length of shoreline. A better basis for selection is an effectiveness-to-toxicity ratio, if such information is available. Generally, it is not.

The types of shoreline on which dispersants are most likely to be used, as described above, have certain geographic implications (Reference 16):

<u>Shore Type</u>	<u>Locations</u>
1. Exposed, steep, rocky cliffs	- Northern New England, along the Pacific Coast, Alaska, Hawaii
2. Exposed rocky shoreline	- Alaska, New England, parts of Pacific Coast, Hawaii
3. Sheltered rocky coasts	- New England, Nova Scotia, parts of the Pacific Coast, Alaska
4. Steep, gravel and coarse grained beaches	- Along most coasts of the United States
5. Rock walls, breakwaters and jettys	- Along most of coasts in the United States, more commonly in New England and the Atlantic Coast
6. Piers, pilings, structures	- Along all United States Coasts, especially in ports

Although little experience has been acquired on real coastal clean-up with the thirteen dispersants for which data have thus

far been accepted by the EPA, most are recommended by the manufacturer for rock walls, piers, docks, and structures.

APPLICATION METHODS

The parameters of concern here are dilution ratio, mixing ratio, equipment type, and agitation requirements (Table 6, items 9-11). These parameters are closely interconnected, many dispersants having been developed for a specific combination of them.

First, the major types of equipment for applying dispersants will be summarized. Then dilution ratio, mixing ratio, and agitation requirements will be discussed in the light of the various equipments.

Application Equipment

It is convenient to distinguish five general classes of equipment for applying dispersants:

- (1) Hand-carried spray tanks
- (2) Motor-operated dispersant-pump systems
- (3) Pump-Eductor systems
- (4) Dual Pump systems
- (5) Aerial Spray systems

Several sub-classes exist under each class, as will be seen. The significance of the classification lies in the different principles of operation for each class.

Hand-carried spray tanks: These are typified by the Walter Kidde pump tank and pressurized units in the US, and by the Cooper-Pegler Falcon Sprayers in the UK. The capacities available range from 2 to 5 USG (US gallons), being constrained by the amount that can be carried by backpack. They are usually fitted with spray wands (that's a 'lance' in the UK) having changeable tips. Such units look much like fire extinguishers. They are most useful in confined areas, such as around piers and structures

and on shore areas inaccessible to motor vehicles, such as breakwaters and rock walls. They may be used from boats as well as on foot.

Because of their limited capacity these units are best suited to concentrated or low-dilution dispersants. Agitation or abrasion, if required, must be applied separately by high pressure hoses on land and breaker boards or props on water.

Motor-operated pump systems: In this type of equipment the dispersant is moved from its container by a gasoline- or diesel-driven pump into a wand or boom where it is emitted in a spray directly onto the oil. The dispersant may be undiluted or pre-diluted, but water is not added during application. These units usually operate at low pressures and volumes, but need not be so restricted. They vary from small, portable one-man units suitable for post-spill shore clean-up to large ship-mounted units capable of delivering 24 USG/min, e.g., the original Warren Springs Laboratory Spraying Equipment. A smaller 'Inshore' version, also developed by WSL, is capable of 6 to 7 USG/min. This unit is capable of driving a boom on either side of a boat or two manually-operated wands on shore. A similar 'Inshore' unit developed for the Canadian Coast Guard (CCG) is described by Gill (Reference 6, p. 465).

The dispersant pumping systems are designed to apply dispersant alone, i.e., without a stream of water. The dispersant stream itself provides some of the required mixing energy, approximately equal to the nozzle pressure times the total spray volume. Thus, the advantage of a higher efficiency dispersant is partly offset by the reduced volume of its spray, at the same nozzle pressure.

While dispersant-pump systems were originally developed by WSL for applying hydrocarbon-based material which can not be diluted with water, the pump systems can also be used with water-based dispersants applied neat or pre-diluted. They have the advantage of being suitable for application of concentrates,

which allows the vessel to disperse a much larger quantity of oil per trip than non-concentrate formulations.

Pump-Eductor Systems: These systems are based on the dispersant being educted into a high-speed water stream which is sprayed onto the oil slick through a nozzle or boom. The water stream provides some of the required mixing energy. Because the dispersant is educted, rather than pumped, into the water stream the maximum concentration of dispersant achievable is limited to about 5 percent. (1 part dispersant to 20 parts water.) The amount of dispersant can be adjusted from 0 to the limit by a metering valve at the dispersant inlet line. There are several sub-classes of the pump-eductor system.

(1) Fire Hose or Fire Monitor: Most land or ship-based fire fighting equipment can be fitted easily with an eductor and flow metering valve. Many have eductors for fire-fighting foam insertion and the only addition needed is a metering valve for the dispersant, which takes the place of the foaming agent. The first use of dispersants in the US under Annex X was accomplished by the fire-fighting equipment on a USCG 32-ft Port Security boat. Both a fire hose and fire monitor were employed, driven from on-board pumps.

The use of fire-fighting equipment has the advantages of simplicity and availability. It has the disadvantage of a single stream or spray which produces a less uniform coverage than a boom. Also, dispersant concentrations are limited, as described above.

(2) High-Pressure Pump Systems: These differ from the fire fighting equipment in that they are specially designed, portable, and have several adjustments for the water and dispersant flow. In addition, many are fitted with spray booms rather than hose nozzles. Pressures are usually above 80 psi and flow rates over 80 GPM (dispersant plus water). Although some systems have an auxiliary dispersant pump, the dispersant is still injected by eduction and so its concentration is thereby limited to 1:20 or less.

Dual Pump Systems: If both the dispersant and water are pumped separately into a common junction before distribution, the mixing does not depend on eduction and hence need not involve high pressures and volumes. A larger range of dilutions is possible through the use of metering valves in both water and dispersant lines.

When concentrates were introduced, the original WSL spray system, which was a dispersant-pump type, was easily adapted into a dual-pump type system. In this adaptation the Rotan pump which was employed to pump dispersant is used instead to pump seawater at 25 GPM and the dispersant concentrate is injected at 1/10th that rate by means of a small gear pump driven by the Rotan. (See Reference 1, p. 239-240.) It may be noted that all UK DOT (United Kingdom Department of Trade) dispersant stocks have been converted to concentrate and all spray equipment have been modified as just described.

In the United States, the equipment designed by Halliburton Services for Clean Atlantic Associates is a high volume, high pressure dual-pump system designed for open water work. It can deliver 300 USG/min of a variable dispersant-seawater mixture at 90 psi to two 25 ft spray booms mounted at the bow of a work boat. A single 45 hp diesel drives both pumps. Swath widths up to 60 ft are possible; dispersant/water ratio is typically 1:33. Mixing energy is supplied by the bow wake, the nozzle pressure, and the propeller turbulence. Dispersant injection to the seawater stream is controlled by a pressure-compensated flow valve, allowing relatively precise control of the amount of chemical added. At 8 knots the 60 ft swath covers 67 acres/hour. A single 500 USG dispersant tank will last about an hour at a 1:33 dilution ratio, and provide dispersant at about 8 USG/acre, at 8 knots. (Reference 1, p. 266 ff.)

Aerial Spray Systems: Aerial systems are essentially dispersant pumping systems for airborne use. Restricted payload makes the use of concentrates or full-strength dispersants most attractive,

and lack of a means of agitation other than wave action* makes a "self-mixing" or low energy dispersant essential. There are two general types of fixed-wing aircraft and two types of helicopter equipments available.

Light Fixed-Wing: WSL conducted early tests with a Piper Pawnee, a typical light agricultural spraying aircraft. It carried about 140 to 180 USG over a 200 mile range, spraying from 7 to 124 USG/min at from 10-60 psi. These and other tests using Kuwait crude led to selection of the following nominal parameters for airborne application from the Pawnee:

Drop Size:	700-1000 microns
Altitude:	3 meters
Speed:	90 knots
Nozzle size:	3/16 inch, core removed
Nozzle spacing:	18 cm
Pressure:	20 psi
Boom width:	8 meters
Swath width:	16 meters
Application density:	10 USG/acre

The nominal flow rate corresponding to the above parameters is 114 USG/min, well within the range of the pump. Reduction of the application density to 5 USG/acre is also within the range of the pump.

In tests performed for the Southern California-Petroleum Contingency Organization (SC-PCO) and the American Petroleum Institute (API) in 1978, a small agricultural spraying aircraft, Cessna Ag-Truck, was employed to disperse slicks of Alaskan crude. The application parameters were (Reference 6, p. 475 ff).

Drop size:	500 microns
Altitude:	1.6 to 4.8 meters
Speed:	90 mph
Nozzle type:	T-Jet flat fan No. 8020

*Pursuing the spraying aircraft with a boat pulling breaker boards is not practical. . .

Nozzle spacing:	6 inches
Pressure:	40 psi
Boom width:	16 feet (apx)
Swath width:	50 feet (apx)
Application density:	7 USG/acre

The nominal flow rate corresponding to the above parameters is 63 USG/min. A flow rate of 90 USG/min was also tried.

A common pump scheme for small agricultural aircraft is a wind-driven propeller-pump mounted under the fuselage. The pumping rate is automatically varied with the air speed, thus helping to maintain a more uniform application density of dispersant.

Single-engine, light, aircraft have limited payload, range and safety compared to large fixed-wing aircraft.

Heavy, Fixed Wing: Tests have been performed by WSL (Reference 6, p. 469) and by SC-PCO (Reference 1, p. 169) using a DC-4. In addition extensive experience was acquired by Conair Aviation Ltd. Abbotsford, B.C., in applying over a million gallons of Corexit 9527 by DC-6 on slicks in the Gulf of Mexico from IXTOC I. Although some data were taken from the operation, results are not yet published.

The parameters that emerged from the WSL/SC-PCO tests with a DC-4 are as follows (Reference 6, p. 469).

Drop size:	700-1000 microns
Altitude:	50 feet
Speed:	170 knots
Nozzle Type	.25 inch barrel, 3" length
Nozzle Spacing:	17 cm
Pressure:	40 psi
Boom Width:	66 feet
Swath Width:	25 meters
Application Density	>5 USG/acre

The flow rate corresponding to the above parameters is 400 USG/minute. The WSL/SC-PCO tests employed 6 concentrates: Corexit 9527, Corexit 9600, Finasol OSR5, Shell Concentrate,

BP1100WD, Dasic Slickgone LTC. They found that Corexit 9600 was effective in dispersing the topped Kuwait crude but was much less effective on the 50 percent water-content topped Kuwait emulsion.

The DC-4 tests found that the droplets produced were slightly larger and more uniform when the nozzles were directed straight aft on the wing. This agrees with the theory (Reference 19) in that the theoretical upper and lower bounds for mean drop size converge as velocity relative to the air increases, being equal at about 75 knots (See Figure 2). Below that speed mean drop size increases. A large drop size is desirable for aircraft application because it has lower surface area per unit volume, thus reducing evaporation and the effects of cross winds. It also has a higher terminal velocity, adding to the mixing energy. Orienting the nozzles aft can be expected to reduce the relative velocity of the drops, and result in a heavier, more uniform coverage, as observed in the WSL tests. An increased nozzle pressure should have the same effect.

The effects on droplet size of dispersant viscosity and surface tension have yet to be investigated.

Helicopter-Bucket: Helicopter application has the advantage over fixed-wing aircraft in that lower speeds are possible. The helicopter is also more maneuverable at low altitudes.

Use of a belly-hung spray bucket suspended from the helicopter was tried in 1978 in the API/SC-PCO tests mentioned above (Reference 6, p. 475 ff). In 1977, Exxon, SC-PCO, and Clean Caribbean Associates also tried out the helicopter-bucket method (Reference 1, p. 170). The parameters employed in the two tests are shown in Table 13.

Helicopter - Fuselage - Mounted Boom: The slung-bucket method has disadvantages that are overcome by mounting the canister and boom directly on the fuselage. This prevents bucket sway in high winds, gives greater maneuverability and speed, and allows better altitude judgement by the pilot. Its disadvantage is that it requires special hard-point mountings on the fuselage.

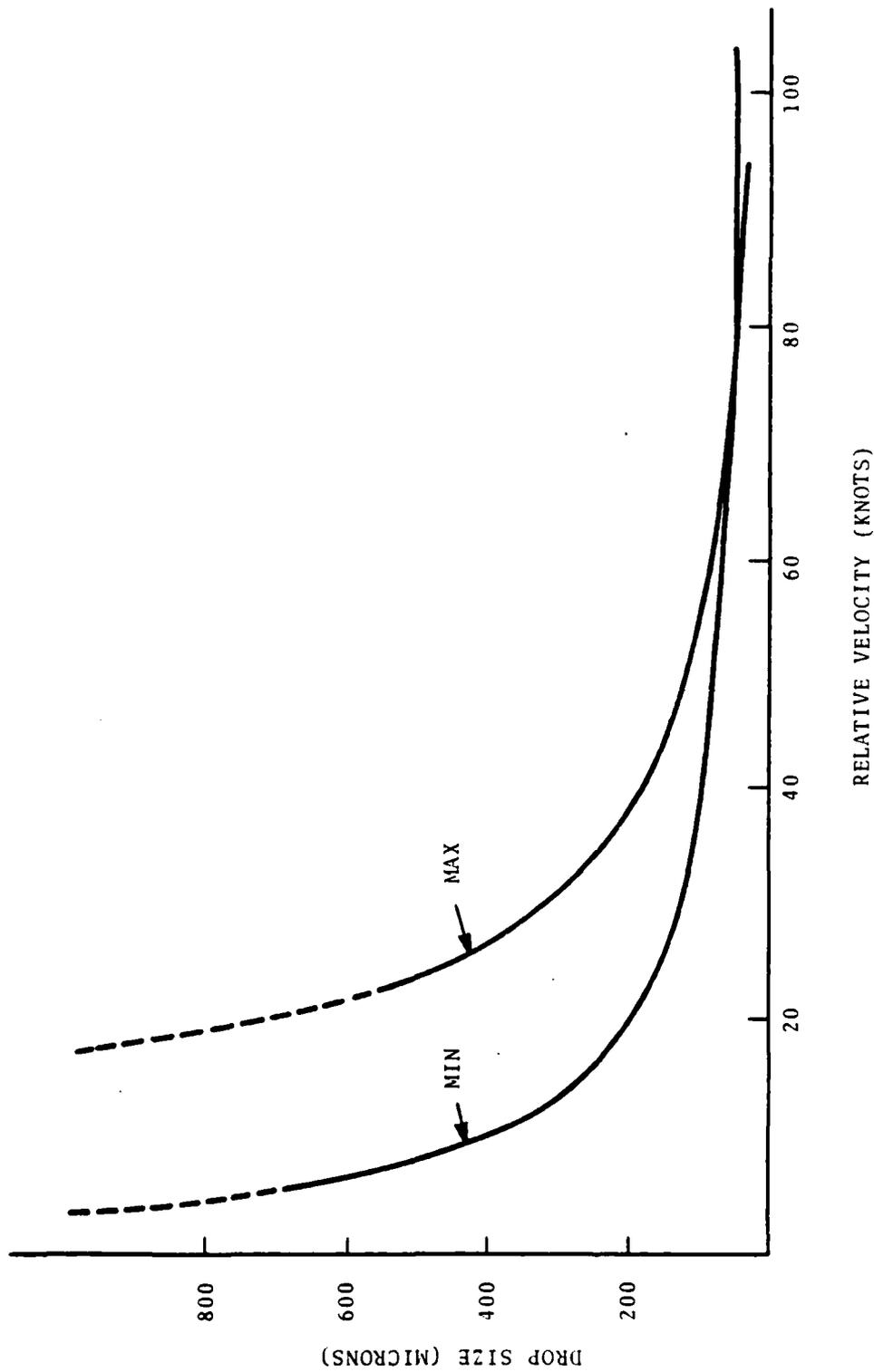


FIGURE 2. MINIMUM AND MAXIMUM FOR MEAN SIZE, WATER DROPS IN AIR
SOURCE: REFERENCE 20.

TABLE 13. 1977 AND 1978 HELICOPTER-BUCKET TESTS

	1977 tests ⁽¹⁾				1978
	1	3	5	7	
Run:					-
Aircraft:	← Hughes 500C →				Bell 206B
Speed, mph	60	60	25	40	35
Bucket:	← Spray King Assembly →				Simplex
Nozzle Type(2):	D6-45	← D8-45 →			D8-45
# Nozzles:	48	48	48	48	52
Pump, psi	40	40	40	40	40
Altitude, ft(3):	25	45	30	30	40-50
Swath, ft:	50	70	75	95	53
Density, USG/acre:	4.4	4.6	10.2	5.0	10
Flow, USG/min	27	39	39	39	35

(1) Runs 2,4,6 not tabulated here.

(2) All nozzles were Spray Systems Co., Tee-Jet diaphragm type. Each nozzle contained a strainer, a core for rotating the fluid and an orifice disk, producing a hollow cone spray.

(3) Aircraft altitude. Release altitude was about 8 feet less for 1977 tests and about 20 feet less for 1978 tests.

The fuselage-mounted boom was employed in the 1978 application of dispersant to a slick from the Sea Speed Arabia spill in New York Harbor. The aircraft employed, a Bell 206, carried a 172-gallon (USG) tank and spray rig. Typical application data are as follows:

Aircraft Type:	Bell 206
Altitude:	50 feet
Speed:	60 knots
Pressure:	40 psi
Swath width:	125 feet

The spray equipment takes about 1.5 hours to install, (provided the aircraft has the proper mounting fixtures). A concentrate was employed (Corexit 9527), the usual amount being about 100 gallons per flight, which required about 10 minutes to load into the belly tank.

Dilution, Mixing and Agitation

From the preceding summary of dispersant application methods, it is clear that each method involves a certain range of dilution, mixing and agitation, summarized in Table 14. Each manufacturer recommends application techniques, and dilution/mixing/agitation conditions to which his product is best suited. Table 8 shows the recommendations on dilution and Table 12 those on agitation. Table 15 shows which application methods are recommended by the manufacturer for his dispersant when applied to spills in salt water. These recommendations are not always accurate guides. In particular, since documented experience in aerial application is scarce, the manufacturer's recommendation is neither necessary nor sufficient information in that regard. Some manufacturers recommend aerial application but also recommend vigorous agitation. Others do not mention aerial application even though tests have shown their product to be a prime candidate for such methods.

TABLE 14. DILUTION, MIXING, AND AGITATION CONDITIONS SUITABLE FOR VARIOUS DISPERSANT APPLICATION METHODS

Method	Dilution (1)	Mixing (2)	Agitation
1. Hand-carried spray tanks-land	neat or moderate dilutions (1:0 to 1:10)	none	high pressure, low volume hoses
2. Hand-carried spray tanks-boat	neat or moderate dilutions (1:0 to 1:10)	none	fire hoses, ship's props, breaker board
3. Dispersant-pump equipment	neat or any dilution	none	fire hoses, ship's props, breaker board
4. Pump-educator systems	none	high mixing ratios, >20 parts water	ship's props, breaker boards
5. Dual-pump systems	none	any ratios from about 0.1 to 20.0 parts water	breaker boards ship's props
6. Aerial spray systems	neat or slightly dilute	none	none

Notes: (1) Refers to pre-dilution

(2) Refers to mixing with seawater at time of application

TABLE 15. APPLICATION METHODS RECOMMENDED BY
DISPERSANT MANUFACTURERS

<u>Disp. Product #/Type</u>	<u>Hand-carried Spray Tanks</u>		<u>Disp. Pump Syst.</u>	<u>Pump- Eductor Syst.</u>	<u>Dual Pump Syst.</u>	<u>Aerial Spray Syst.</u>	<u>Note</u>
	<u>-land</u>	<u>-boat</u>					
1/W	- no specific application methods recommended -						
2/W	X	X	X	X		X	(1)
3/W	X			X	X	X	
4/W	X	X	X	X	X	X	
5/W	X	X	X				
6/W				X		X	(2)
7/W			X	X			
8/W				X			
9/C		X	X	X	X	X	(3)
10/H	X	X				X	
11/H	X	X	X				
12/C					X		(3)
13/H	X	X	X	X	X		

(1) In calm waters additional agitation may be needed for aerial application.

(2) Dilution with 20 parts fresh or salt water recommended for aerial application.

(3) Has been applied by air in tests or actual spill or both.

Agitation

The question of agitation requirements is not adequately addressed in most cases. EPA effectiveness data are taken at only one agitation level, supplied by a water stream. Adjectives such as "vigorous," "strong," "thorough," "some," etc. abound in the manufacturers' product application literature, as seen in Table 12, but are of no use in quantitative comparisons. Therefore, unless highly subjective judgments are made, it is difficult to estimate the effectiveness of any of the dispersants when applied by any one of the methods, even if it is apparently suited in terms of dilution, mixing and agitation.

The question of agitation measurement is particularly acute for aerial application. Although it would seem that the "self-mixing" dispersants are ideally suited for aerial use, it is difficult to define a self-mixing dispersant except by an effectiveness test at various wave conditions. The EPA effectiveness tests do not cover the case of natural wave mixing, and hence do not adequately evaluate self-mixing dispersants.

The addition of agitation by means of breaker boards, although brought to a high level of refinement in the UK, may possibly be eliminated. Tests (Cormak and Parker, Reference 6, p. 469 and Smith and Holliday, Reference 6, p. 475) seem to indicate that "self-mixing" dispersants are effective without breaker boards or other additional energy. Actual measurement data, however, have not yet been published. The tests mentioned above (Cormak and Parker) concluded that all 6 concentrates tested were "effective in promoting the dispersion of Kuwait crude oil when used at the ratio of one part dispersant to twenty parts oil... Corexit 9527 and Finasol OSR5 tending to produce dispersion more rapidly than others." The other products were Corexit 9600, Shell Concentrate, BP1100WD and Dasic Slickgone LTC.

Mixing

Some dispersants are obviously designed to be mixed into a high-pressure seawater stream or spray at time of application. Such designs were probably influenced by the ready availability

of fire-fighting hoses on ships and tugs; the water stream not only covers a large radius circle, but provides some mixing energy as well. These dispersants are distinguished by recommended dilution ratios of 1 part dispersant to 20 or more parts water, as seen in Table 16. It does not follow that these dispersants would not be effective at lower dilutions, particularly if agitation is provided.

As an alternative to fire hose application, the high-pressure, high-volume spray systems have been developed (see, for example, Reference 1, p. 266). These systems cover a 60-ft wide swath by spray booms. The uniformity of coverage is superior to what can be achieved by hoses, and the application ratio is better controlled, particularly in the dual-pump systems. As dispersant agitation requirements are reduced so is the need for high-pressure, high-volume water streams. The newer, low agitation dispersants require less energy from the spray, allowing reduction in spray pressure and/or volume. The lower limits to volume and pressure, however, are set by the need to achieve a uniform spray.

Dilution

Pre-dilution of the dispersant is probably less critical than mixing (i.e., dilution at time of application). From a logistics point of view a pre-diluted dispersant is similar to an undiluted dispersant of the same effectiveness. Diluents may be hydrocarbons, fresh water, or even seawater; as long as dilution is done by the manufacturer prior to shipment the complete solution may be treated as ready-to-use dispersant. For this reason it is important that different dilutions of the same dispersant be considered as separate products in effectiveness and toxicity tests.

Application Ratio

Application ratio refers to the ratio of dispersant to oil. The application ratio required to disperse a specified percentage of the oil is sometimes employed as a measure of effectiveness,

TABLE 16. MANUFACTURER'S MIXING⁽¹⁾ RECOMMENDATIONS

<u>Product/Type</u>	<u>Neat</u>	<u>Mixed, Type of Water</u>	<u>Mixing Ratios</u>
1/W	Yes	Yes, Fresh or Salt	1:5 - 1:40
2/W	Yes	Yes, Fresh or Seawater	1:40 - 1:80
3/W	Yes	Yes, Fresh or Salt	1:10 - 1:40
4/W	Yes	Yes, Fresh or Seawater	1:5 +
5/W	Yes	No	
6/W	No	Yes, Fresh or Salt	1:20 - 1:500
7/W	Yes	Yes, Fresh or Salt	1:15 - 1:50
8/W	No	Yes, Fresh or Seawater	1:20 - 1:80
9/C	Yes	Yes, Seawater	1:10 - 1:20
10/H	Yes	No	
11/H	Yes	No	
12/C	Yes	Yes, Seawater	1:9
13/H	Yes	Yes, Fresh or Seawater	

(1) Mixing here means dilution at time of application

(e.g., Reference 1, Doe and Wells). For a given dispersant, the application ratio required to achieve a specified percentage dispersion is affected strongly by some of the parameters previously discussed: oil type and weathering; slick thickness; wave energy and applied agitation; and water temperature. It is also affected by dilution ratio, mixing ratio and application method.

The logistic implications of the application ratio required for full dispersion are significant. The lower the required ratio, the less dispersant that must be stored, transported and applied. Each application vehicle can disperse more oil per trip, hence reducing the time and cost of application. This is particularly important for aircraft, which are limited by payload rather than by time or speed.

The Warren Spring Laboratory tests referred to above found that the six concentrates they tested were "effective in promoting the dispersion of Kuwait crude" when used in a 1:20 ratio, on a slick of about 1.45 mm, without agitation. The tests included BP1100WD and Corexit 9527, both of which have data accepted by the EPA. The Canadian Coast Guard, however, (Gill, Reference 5) found in similar tests that these two dispersants had end points (100 percent dispersion) of 1:8.5 and 1:7.8 respectively when followed by breaker boards. An exact comparison of test conditions has not been made, but it appears that the 1:20 ratio is only a rough guide, and that a ratio closer to 1:10 may be required in some cases. Tests similar to the UK and Canadian ones have not been conducted by the EPA in the United States.

EFFECTIVENESS

From the preceding discussions, it should be clear that the parameters describing the spill conditions and application method derive their importance from their controlling influence on dispersant effectiveness. They are most important factors in determining effectiveness other than the dispersant formulation itself. In general, for a given set of spill conditions, the dispersant and application method should be selected so as to maximize

effectiveness and minimize the total effects toxicity. Although these two objectives are both contributors to the over-all objective of minimizing the total environmental impact, it is necessary at the present state of knowledge to treat them individually. The following touches on measures of effectiveness, the EPA tests for effectiveness, with a brief discussion of its relation to toxicity.

Measures of Effectiveness

The quantity of oil dispersed per gallon of dispersant is not the only, or necessarily the best, measure of effectiveness. It is likely that microbial degradation of the dispersed oil, which is the end objective, proceeds in proportion to the surface area of the oil droplets dispersed into the water. (Reference 21.) Hence a dispersant that produces small oil droplets is more effective than one that produces large droplets, (and more toxic, as pointed out by Canevari, Reference 22., p. 239) if they both disperse the same amount of oil, since smaller droplets have a higher surface-to-volume ratio.

The most common definitions of effectiveness, as pointed out, are (1) the percent of oil dispersed for a given dispersant: oil application ratio, agitation level, slick thickness, and oil type; and (2) the dispersant : oil ratio required to achieve a given percent dispersion, for given agitation level, slick thickness, and oil type. Ideally, effectiveness data might be obtained in the form of a family of plots of percent dispersion vs application ratio, with agitation level or oil type as parameter. (Murphy and McCarthy, Reference 23, p. 203). Such information is generally unavailable, even for laboratory conditions.

EPA Effectiveness Tests

The EPA effectiveness tests required by Annex X of the National Contingency Plan are laboratory tests intended to provide relative rankings of dispersant effectiveness. Due to the limited number and range of variables allowed for in the test procedure, the EPA tests are not useful in establishing effectiveness

under field conditions (See Reference 15, p. 3 and Reference 1, p. 302). Their value in determining relative rankings, however, is also limited. As shown in Appendix A, the rankings obtained on No. 2 oil have no correlation with those obtained on No. 6 oil. Neither ranking can be expected to be correlated with effectiveness on crude oils (Murphy and McCarthy, Reference 23 Figs. 2 and 6). Variability of effectiveness with slick thickness, agitation level, temperature, salinity, dilution and other conditions that affect ranking, as discussed previously, are not included in the EPA test procedure. The EPA effectiveness tests are of main use in establishing the mean percent dispersion after 2 hours at 1:10 application ratio on No. 2 and No. 6 oils with agitation from hosing. Ranking in the cases of greatest interest (e.g., crudes on open water without agitation) are not covered by the tests and cannot be inferred from them.

Relation to Toxicity

Effectiveness data are needed to carry out meaningful toxicity tests. If its effectiveness is low, substantial amounts of a dispersant may be needed to disperse a given slick; a dispersant of high toxicity may also be highly effective and thus require lower application ratios. Toxicity of the dispersant alone is of interest for that portion of the dispersant that misses the slick and is applied to the water. For the most part one is interested in the toxicity of the dispersant/oil combination taken at the ratio required to produce dispersion. Toxicity should be measured at that ratio, rather than extrapolated from measurements at other ratios, or from the toxicity of the dispersant alone, because there may be a synergistic effect between oil and dispersant, as mentioned by Connor (Reference 24) and as appears from the EPA data for the thirteen subject dispersants. In particular droplet size of the dispersed oil also affects toxicity, the smaller droplets being more toxic, but more subject to microbial degradation. Temperature is another parameter that affects microbial degradation rate, as well as droplet size through viscosity. For these reasons it would seem desirable to run toxicity

tests at the dispersant : oil ratios and other conditions most likely to be found in practice, as determined by the effectiveness tests. For example, if an application ratio of 1:15 is found to be required to disperse a given oil under expected agitation and temperature conditions, then the toxicity should be determined for the resultant 1:15 dispersant-oil suspension for the same agitation and temperature conditions. If toxicity data are gathered for all products in a similar way, then effectiveness is automatically accounted for in the toxicity rankings, and selection of a dispersant for a given spill would be substantially simplified. The On-Scene Coordinator and EPA Representative need only compare toxicities directly as given in the test data, without having to allow for effectiveness, provided the test data covered the oil type, temperature, and agitation conditions they face at the time.

AVAILABILITY AND COST

AVAILABILITY

Dispersant availability is described by the quantities and locations of present stockpiles, and by the manufacturer's ability to produce the product on short notice. The latter is affected by raw material supplies as well as by plant capacity. Plant capacity depends on how many 8-hr shifts per day are employed and on availability of feedstock. It is possible that several producers employ the same feedstock, which could limit the total productive capacity to less than the sum of the manufacturers' capacities. The existence or nature of such raw material constraints could not be determined.

Availability data, as obtained from the manufacturers, distributors and response organizations, is shown in Table 17. This Table also includes stockpiles listed in the Coast Guard Spill Cleanup Equipment Inventory System (SKIM).

At an application ratio of 1:20, one drum of dispersant can treat about 3.7 tons of oil. The application ratio required for a given percentage dispersion, however, may vary substantially from dispersant to dispersant, and is not known under actual field conditions for many dispersants. The 1:20 ratio, however, would indicate that the largest stockpile (product #9) can treat from about 3,400 to 6,800 tons of oil, with a production capacity to treat from 1,400 to 3,300 tons per day (10,000 to 24,000 BBL per day).

COST

Table 18 shows price per gallon in small quantities. Quantity discounts are usually available, typically reaching 15% off for 100 drums. Just as significant, however, is the cost of emergency air shipment to the spill debarkation point. Bulk air cargo from coast to coast is of the order of \$.10 to \$.20 per pound, or \$.90 to \$1.80 per gallon plus handling at each end.

TABLE 17. INVENTORY AND PRODUCTION CAPABILITY AS OF
 FEBRUARY 1980 - THIRTEEN EPA-ACCEPTED
 DISPERSANTS

Product #	Location in US	Present Inventory (Drums) ⁽¹⁾	Production Capability	
			Lead Time (days) ⁽²⁾	Quantity (Drums)
1	Oloh, MS	100	0	250/day
2	Clifton, NJ	50	0	100-150/day
3	Hayward, CA	25	0	150/day
	Philadelphia, PA	0	0	150/day
4	Houston, TX	50	2	90
	Houston, TX	0	1-10	200/day
	Boston, MA	15	0	0
5	New York, NY	50-100	0	40/day
	Houston, TX	10	0	0
6	Houston, TX	250-300	1	125
	Houston, TX	0	<7	200-300/day
7	W. Palm Beach, FL		30-60	450-500/day
8	San Diego, CA	200	0	100/day
	Richmond, CA	4	0	0
	Seminole, FL	≥100	0	0
9	Houston, TX	200 ⁽³⁾	3	200
	Houston, TX	0	6	200-600/day
	(Licensee)	0	0	200-300/day
	Boston, MA	250	0	0
	Harvey, LA	55-72	0	0
	San Pedro, CA	8	0	0
	Providence, RI	50	0	0
	Homer, AK	90	0	0
	Kenai, AK	192	0	0
Yakutak, AK	80	0	0	
10	Houston, TX	0	2	50
	Houston, TX	0	1-10	200
11,12	- no inventory or production in US -			

TABLE 17. INVENTORY AND PRODUCTION CAPABILITY AS OF
 FEBRUARY 1980 - THIRTEEN EPA-ACCEPTED
 DISPERSANTS (CONT.)

<u>Product #</u>	<u>Location in US</u>	<u>Present Inventory</u> (Drums) ⁽¹⁾	<u>Production Lead Time</u> (days) ⁽²⁾	<u>Capability Quantity</u> (Drums)
13	Carney, NJ	100-150	.1-.3	53/day
	N. East Coast	59	0	0
	S. East Coast	26	0	0
	Gulf Coast	62	0	0
	W. Coast	26	0	0
	Great Lakes	25	0	0

(1) 55-USG per drum. Generally these are sealed, non-returnable steel. Some of Product #13 inventory is contained in 25 liter pails, which have been converted to equivalent number of 55-USG drums.

(2) Lead Time is the time to supply the quantity shown, or the time to start up production at the quantity/day shown. Production rates are based on a single 8-hour shift per day.

(3) Up to 1000 drums additional can be borrowed by manufacturer, delivery time not specified.

TABLE 18. PURCHASE COSTS AS OF FEBRUARY
1980 - THIRTEEN EPA-ACCEPTED
DISPERSANTS

<u>Product #/Type</u>	<u>\$US per US Gallon (1)</u>	<u>F.O.B.</u>
1/W	4.55	Oloh, MS
2/W	9.80	Clifton, NJ
3/W	8.25	Hayward, CA
4/W	7.04	Houston, TX
5/W	7.50	New York, NY
6/W	6.90	Houston, TX
7/W		
8/W	8.73	San Diego, CA
9/C	10.90	Houston, TX
10/H	5.20	Houston, TX
11/H	about 4.00	UK
12/C	about 8.00	UK
13/H	9.84	Carney, NJ

(1) In quantities of one non-returnable 55-USG drum.

The prices shown in the Table do not indicate that water-based products are cheaper than hydro-carbon based products. The concentrates (products #9 and #12) are, on average, not more expensive than some of the water- or hydrocarbon-based products.

Cost data, just as availability data, are meaningless without information on effectiveness. As pointed out, that information is lacking in many cases, so that a meaningful cost comparison is not possible. If, however, a 1:20 ratio is assumed, the materials cost to treat a ton of oil is about \$150 for the average-priced dispersant.

SUMMARY AND CONCLUSIONS

HANDLING PROPERTIES

The handling and storage properties of the 13 subject dispersants are summarized in Table 19, under the three categories: water-based, hydrocarbon-based, concentrate. The major considerations are:

(1) Fire or Explosion Hazard: Of the several indicators of fire or explosion hazard, the most useful is flash point, which is given in the Annex X data submissions. The eight water-based products all have flash points above 212°, rendering them virtually free of fire hazard, with one exception. The hydrocarbon and concentrate products had flash points above or close to 150°F, but less than 200°F, requiring caution in handling and storage. Only one dispersant (Product #4) has a flash point low enough to cause serious concern. It is necessary to fully assess the fire/explosion hazard of this and any other products with flash point below 150°F.

Differences exist in flash point specification and test method for dispersants among the US Navy, the State of California, the Federal Hazardous Substances Act, and Annex X. The Federal Hazardous Substances Act requirements result in at least three of the hydrocarbon and concentrate types, and one of the water-based dispersants, being labelled combustible (flash point below 150°F by Tagliabue Open Cup Test).

(2) Toxicity and Causticity: The best guide available to these properties is the labelling requirements of the Federal Hazardous Substances Act. Most of the hydrocarbon and concentrate products, and one of the water-based products, are labelled irritant. Hence it would seem that the use of gloves, goggles and clothing to cover the skin are more important for those products. However, prolonged exposure would make precautions advisable even for the other products.

TABLE 19. SUMMARY OF STORAGE AND HANDLING PROPERTIES OF THREE DISPERSANT TYPES

Product #	W								H			C	
	1	2	3	4	5	6	7	8	10	11	13	9	12
<u>Pour Point</u>													
H: >20°F			✓		✓	✓	✓	✓					
M: 0°- 20°F	✓	✓		✓									
L: < 0°F									✓	✓	✓	✓	✓
<u>Flash Point</u>													
H: >212°F	✓	✓	✓		✓	✓	✓	✓					
M: 150°-212°F									✓	✓	✓	✓	
L: <150°F				✓									✓
<u>Viscosity @100°F</u>													
H: >100 SSU	✓	✓		✓	✓	✓	✓	✓				✓	
L: <100 SSU			✓						✓	✓	✓		✓
<u>Min Storage Temp</u>													
H: >20°F					✓		✓					✓	✓
M: 0°-20°F	✓			✓		✓				✓			
L: < 0°F		✓	✓						✓		✓	*	
<u>Shelf Life</u>													
H: >60 mos		✓		✓		✓		✓	✓	✓	✓	✓	✓
M: 36-60 mos					✓		✓						
L: <36 mos	✓		✓										
<u>Combustible</u>													
				✓					✓	?	✓	✓	?
<u>Irritant</u>													
				✓					✓	?		✓	?

Notes: W = waterbased, H = hydrocarbon-based, C = concentrate
H,M,L = high, medium, low

* Manufacturer's literature

(3) Pumpability: Pumpability is indicated approximately by pour point, but cannot be determined adequately without viscosity data. Annex X data on pour point shows that all the hydrocarbon and concentrate products have pour points of 0°F or below, making them good candidates for use in Alaska. It is doubtful that any of the water-based products can serve in Alaska, and some of those with pour points above 20°F may be unsuitable for use in New England, the Great Lakes or the Northwest. The Annex X data on viscosity is inadequate to resolve those questions.

(4) Reactivity: The chemical action of the subject dispersants on equipment does not appear to offer any serious problems or limitations on their storage, application methods, or use.

STORAGE PROPERTIES

(1) Temperature: The question of minimum required storage temperature is of more concern than that of maximum storage temperature. Although Annex X requires data on minimum allowable storage temperature, the basis on which such temperatures are determined is not usually stated and consequently they must be modified by phase separation and/or freezing points where available. The relation of minimum storage temperature and minimum use temperature is such that either one can limit the climatic conditions in which the dispersant may be employed. If pour point is used as surrogate for minimum usable temperature, then Table 5 shows in columns (1) and (2) that there are very large differences, both positive and negative, between minimum storage and minimum use temperatures. Moreover, there is no consistency among water-based, hydrocarbon-based and concentrate dispersants with regard to minimum storage temperatures.

(2) Shelf Life: The thirteen subject dispersants show shelf lives from 18 months to "unlimited". (Table 1). The economic value of a long shelf life depends on restock policy and production lead time and capability. Although Warren Spring Laboratory specifies 5 years minimum shelf life, the value of that specification needs to be assessed for US stockpiles and production capabilities.

APPLICATION CHARACTERISTICS

The major characteristics bearing on dispersant application are described in Table 6 by thirteen parameters, eight pertaining to spill conditions, and five pertaining to application methods. Information for the subject dispersants relative to four of the parameters is summarized in Table 20. Little information could be obtained on the other nine parameters.

SPILL CONDITIONS

(1) Oil Type, Weathering and Emulsification: There is evidence that dispersants vary in effectiveness on different types of oil. Some results are available from the Canadian Environmental Protection Service, covering 4 of the subject dispersants and four types of oil. The US EPA effectiveness tests cover the 13 subject dispersants for No. 2 and No. 6 oils. These results show a great deal of variability among dispersants and from oil to oil. Although the EPA data show water based dispersants to be significantly less effective than the hydrocarbon or concentrate dispersants after 2 hours on No. 2 oil they show no significant difference on No. 6 oil. (See Appendix A).

(2) Slick Thickness: Thicker oil slicks impede the penetration of dispersant and retard dispersion. Differences among dispersants in slick penetration, however, are largely unknown.

(3) Water Temperature: Two of the 13 subject dispersants showed about a 23% drop in effectiveness in 40°F water compared to 62°F water, based on Canadian Coast Guard tests on a crude oil. Similar results have been reported by the Canadian EPS. The results seem to suggest that the drop in effectiveness is similar for most dispersants, but full comparative data do not yet exist.

(4) Water Salinity: About 30% of US oil movement is in fresh water (e.g., the upper Delaware River). Eight of the 13 products are recommended by their manufacturers for use on fresh water spills; four bear no explicit recommendation, and one product is recommended only for salt or brackish water spills. Actual

TABLE 20. SUMMARY OF APPLICATION CHARACTERISTICS⁽¹⁾
OF THREE DISPERSANT TYPES

Product #	W								H			C	
	1	2	3	4	5	6	7	8	10	11	13	9	12
<u>Salinity</u>													
Fresh	✓	?	✓	?	✓	✓	✓	✓	?	✓	✓	x	
Brackish	✓	?	✓	?	✓	✓	✓	✓	?	✓	✓	✓	
Salt	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
<u>Equipment Type</u>													
Hand Tanks		✓	✓	✓	✓				✓	✓	✓	✓	
Dispersant Pump		✓		✓	✓		✓			✓	✓	✓	
Eductors		✓	✓	✓		✓	✓	✓			✓	✓	
Dual Pump			✓	✓							✓	✓	✓
Aerial		✓	✓	✓		✓						✓	
<u>Extra Agitation⁽²⁾</u>													
Essential					✓		✓	✓		✓	✓		✓
Desirable	✓	✓	✓	✓		✓			✓			✓	
<u>Mixing Ratios</u>													
Neat	✓	✓	✓	✓	✓		✓		✓	✓	✓	✓	✓
<1:20	✓		✓	✓			✓					✓	✓
>1:20		✓	✓	✓		✓	✓	✓					

Notes: (1) Based on manufacturer's recommendations

(2) See Table 12 for specific statements.

W = water-based, H = hydrocarbon-based, C = concentrate
✓ = recommended, X = not recommended, ? = not clear

effectiveness comparisons for salt and fresh water, however, are available for only four of the 13 dispersants.

(5) Wave Conditions: Many dispersant manufacturers imply in their literature that wave action alone can produce effective dispersion in some cases. An interpretation of their literature (Table 12) can be taken (Table 20) showing that six of the 13 producers consider agitation other than wave action to be essential to dispersion with their product, while all state that external agitation will improve the dispersion.

(6) Shoreline Type: It is generally recommended by the EPA that dispersants not be used for beach protection (i.e., application before the fact). Further experience has shown that effective dispersant application on an oiled beach can drive the oil into the sand, thus delaying its microbial degradation. This reduces the likely uses of dispersants on shorelines to the cases of rocks, cobbles and other impenetrable surfaces. It is not proven that hydrocarbon-based dispersants are superior to water-based dispersants for such use.

APPLICATION METHODS

Five different application methods were considered, each having restrictions with regard to dispersant dilution, mixing, and agitation (Table 14). Dispersant manufacturer recommendations on application method (Table 15) and mixing (Table 16) and agitation (Table 12) lead one to typify the methods/dispersant matches as follows:

(1) Hand carried pumps: These are useful on shorelines and in boats near piers, rocks, etc. Because capacity is limited, dispersants selected should be effective when applied neat or only slightly diluted. All product manufacturers, except four, recommend their product for such application, as shown in Table 15, but even those four products may be suitable for hand carried use.

(2) Dispersant-Pump Systems: When used on shore, these devices are similar in requirements to (1). When used on a vessel, dispersants requiring higher dilution ratios, say up to 1:20, are possible in addition to neat application. The suitable dispersants are products #2, #4, #5, #7, #9, #11, #13 as shown in Table 15., although the other products also may be found to be suitable.

(3) Pump-Eductor Systems: These are high-pressure/high-volume water pump systems. Several water-based products (#2, #3, #6, #7, #8) were apparently designed primarily for this type of equipment (See Tables 15 and 16). The hydrocarbon-based products, except #13, are not intended for this type of application. One of the concentrates is recommended for eductor use (specifically, by fire hose).

(4) Dual Pump Systems: These systems allow better control of the dispersant : water ratio. The method is recommended for the two concentrates but is also advantageous for dispersants that are effective at low dilutions, such as product #1, #3, #4, #7 and #13.

(5) Aerial Application: Aerial application is suitable only for dispersants that are effective (a) when applied neat, and (b) without the addition of agitation. Six manufacturers describe their products as suitable for aerial application, but the effectiveness of these products without agitation is generally not documented.

(6) Agitation: Most dispersants are increased in effectiveness if agitation is applied, provided adequate contact time is allowed. The so-called "self-mixing" dispersants (products #9 and #12) have been found to be "effective in promoting the dispersion of Kuwait crude" at a 1:20 application ratio.

(7) Mixing, Dilution: Products designed for pump-eductor systems (see above) are more effective when mixed with large amounts of water at time of application. Pre-dilution of dispersants, if done before storing, effectively creates a new dispersant product.

(8) Application Ratio: This is a critical parameter in dispersant operations. Manufacturer recommendations range from 1:1 to 1:80 or more, but the available sea trial data seems to indicate 1:20 to 1:8 for Corexit 9527 and BP1100WD, used on Kuwait or Tia Juana crude.

EFFECTIVENESS

The application characteristics described determine effectiveness, i.e., the dispersant : oil ratio required to achieve a given percent dispersion, or percent dispersion achieved by a given dispersant : oil ratio. The greater the effectiveness, the fewer the problems of stockpiling, transporting, and applying the dispersant. The present EPA tests for effectiveness are of limited use in establishing effectiveness rankings among the subject dispersants because they are limited to No. 2 and No. 6 fuel oils, which give significantly different rankings. They do not cover any crude oils, which are of major interest. Also, the EPA tests do not allow for effectiveness variation with agitation level, temperature, or salinity.

AVAILABILITY

The total US inventory of the subject dispersants was about 2050 drums, as of February 1980. Total productive capacity is about 2500 drums/day. At a 1:20 application ratio, the above inventories could treat about 7,500 tons of oil plus 9,000 tons per day. The largest single product inventory in the US can treat at least 3,400 tons of oil, plus at least 1,400 tons per day, at a 1:20 application ratio.

COST

Prices of the subject dispersant ranged from \$4 to \$11 per gallon in February 1980. Water-based dispersants averaged \$7.57/gallon and hydrocarbon-based dispersants averaged \$6.34/gallon. Concentrates averaged \$9.45/gallon. At a 1:20 application ratio, the materials cost of treating a ton of oil is .

about \$115 using the average-priced dispersant. But significant differences in cost can occur because of variations in effectiveness.

CONCLUSIONS

The conclusions are drawn from EPA Technical Product Bulletins, published reports, and manufacturer's literature for the thirteen dispersants for which the EPA has accepted data as of October 1979.

1. Although full hazard assessment data should be obtained for all products, it appears that all the dispersants but one have adequately high flash points for normal use.
2. Toxicity, causticity and reactivity information indicates that no handling problems can be expected from those sources, assuming normal precautions are observed. These precautions include, for some products, use of gloves, goggles and protective clothing.
3. Data are generally inadequate to determine minimum practical storage temperature. The most significant deficiencies occur in regard to viscosity, freezing points, and phase separation points.
4. Shelf life requirements need to be established in the context of inventory data, inventory strategy, and production capability.
5. There are no published data on effectiveness for most of the dispersants applied to crude oil. Canadian and UK sea tests on Kuwait and Tia Juana crude showed full dispersion at 1:20 to 1:8 ratios for two of the dispersants, with and without agitation.
6. EPA-accepted data for effectiveness on No. 2 oil show no significant correlation with data on No. 6 oil. They also show water-based dispersants to be significantly less effective than hydrocarbon-based on concentrates on No. 2 oil, but not on No. 6 oil. They do not cover variation of effectiveness with water

temperature, slick thickness or agitation level.

7. Dispersants can differ substantially in effectiveness on fresh vs salt water. A significant part of US oil movement (over 30%, takes place in fresh or brackish water.

8. Pre-dilution requirements have little impact on logistics. Requirements for mixing with water at the time of application have a strong impact on application method.

- Three dispersants are recommended only for neat application (no mixing). They are suitable for hand carried tanks, dispersant pump systems and, possibly, aerial application.
- Four dispersants are recommended primarily for high mixing ratios (>20 parts water to 1 part dispersant). They are best suited to eduction systems.
- Six dispersants are recommended for a range of mixing ratios from 1:0 (neat) to about 1:20 (or more). They are suitable for all types of application methods.

9. Although a dispersant may be suitable for application by a particular method, it may have low effectiveness when so applied. This is particularly true for aerial application which precludes externally applied agitation.

10. Application ratio required for effective dispersion is a critical parameter but seems to have been established in part for only two of the dispersants.

11. Present inventories of all manufacturers in the US can treat about 7,500 tons of oil plus 9,000 tons/day: The largest single product inventory can treat at least 3,400 tons of oil, plus at least 1,400 tons/day. These estimates assume a 1:10 dispersant : oil application ratio, a highly variable quantity.

* * * * *

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APPENDIX A

ANALYSIS OF EPA DISPERSANT EFFECTIVENESS TEST DATA

The EPA effectiveness tests (Reference A.1) are carried out in a laboratory test tank at 23°F and dispersant : oil ratios of 1:10, 1:4, 1:2 and 1:1. Both No. 2 and No. 6 fuel oils are employed. The oil is applied to the surface of the synthetic seawater, followed by the dispersant. After 1 minute of contact the surface is hosed at 20 psig nozzle pressure and 4.0 USG/min for 1 minute. The mixture is recirculated and samples taken at 10 minutes and 2.0 hours to determine "initial" and "final" dispersions. The mean percent dispersion is calculated from five consistent runs, for each combination of oil type and dispersant: oil ratio.

While the validity of this and other laboratory tests for field conditions is generally rejected, it is substantially agreed that such tests are reasonable for preliminary screening and ranking (Reference A.2, p. 302). The utility of the tests for establishing rankings, in particular, are direct concern to the US Coast Guard in selecting a dispersant for field use. Accordingly, the rankings of the thirteen dispersants for which effectiveness data have been accepted by the EPA were compared for the two types of oil and for initial and final dispersion.

Rank Correlation

The rankings of the thirteen dispersants based on mean percentage dispersion are shown in Table A.1, for the four possible oil and dispersion-time combinations. The rankings based on initial dispersion were plotted against those based on final dispersion (See Figure A.1) for the No. 2 oil tests and for the No. 6 oil tests. Similarly, the rankings obtained for No. 2 oil were plotted against those for No. 6 oil, using both initial and final dispersion data (Figure A.2.). For each graph the rank correlation coefficient was calculated by the formula

TABLE A-1. RANKINGS BASED ON MEAN PERCENT DISPERSION
AT 1:10 APPLICATION RATIO

<u>Dispersant Product</u>	<u>With No. 2 Oil</u>		<u>With No. 6 Oil</u>	
	<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>
A	12	11	8	4
B	4	4	11	11
C	9	8	2	3
D	*	*	*	*
E	6	7	3	2
F	11	12	10	9
G	8	9	4	6
H	10	10	5	5
I	2	2	*	*
J	1	1	1	1
K	7	6	7	7
L	5	5	9	10
M	3	3	6	8

* Data not taken

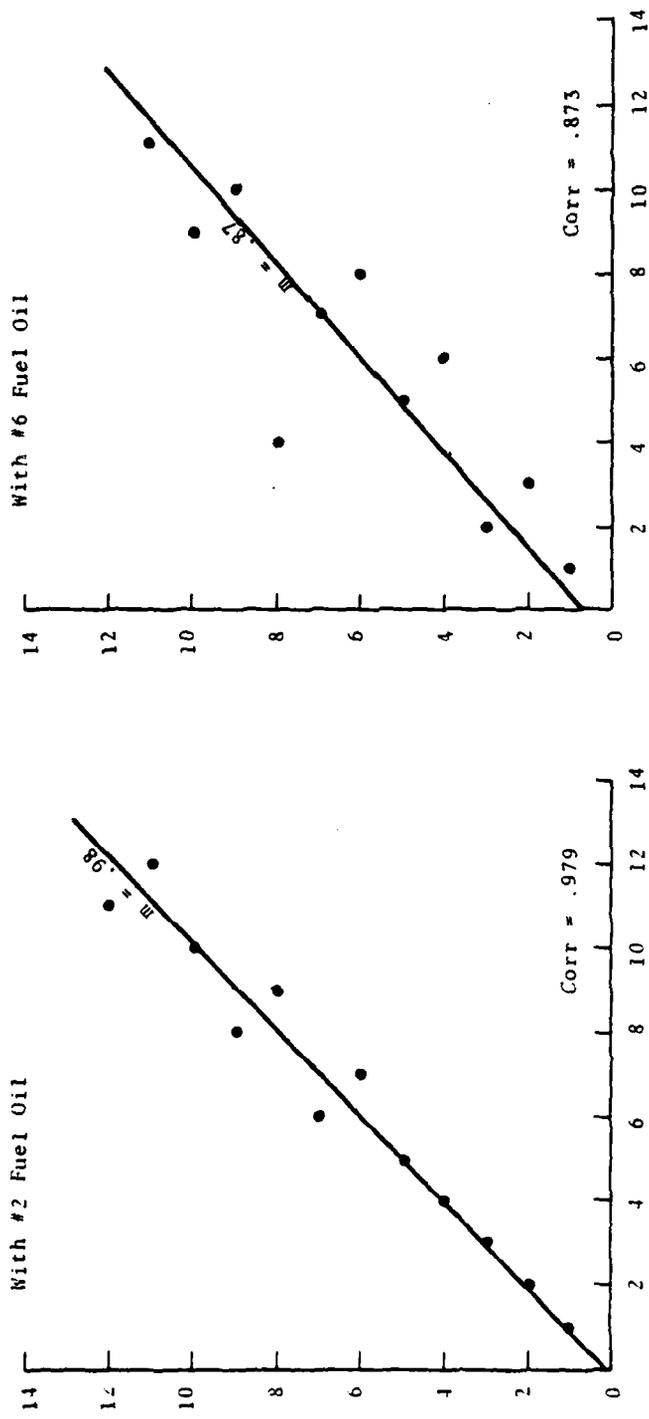


FIGURE A.1. STANDARD EFFECTIVENESS: MEAN DISPERSION PERCENTAGE RANKINGS Initial (10 min.) Vs. Final (2 hrs.) (vertical scale) (horizontal scale)

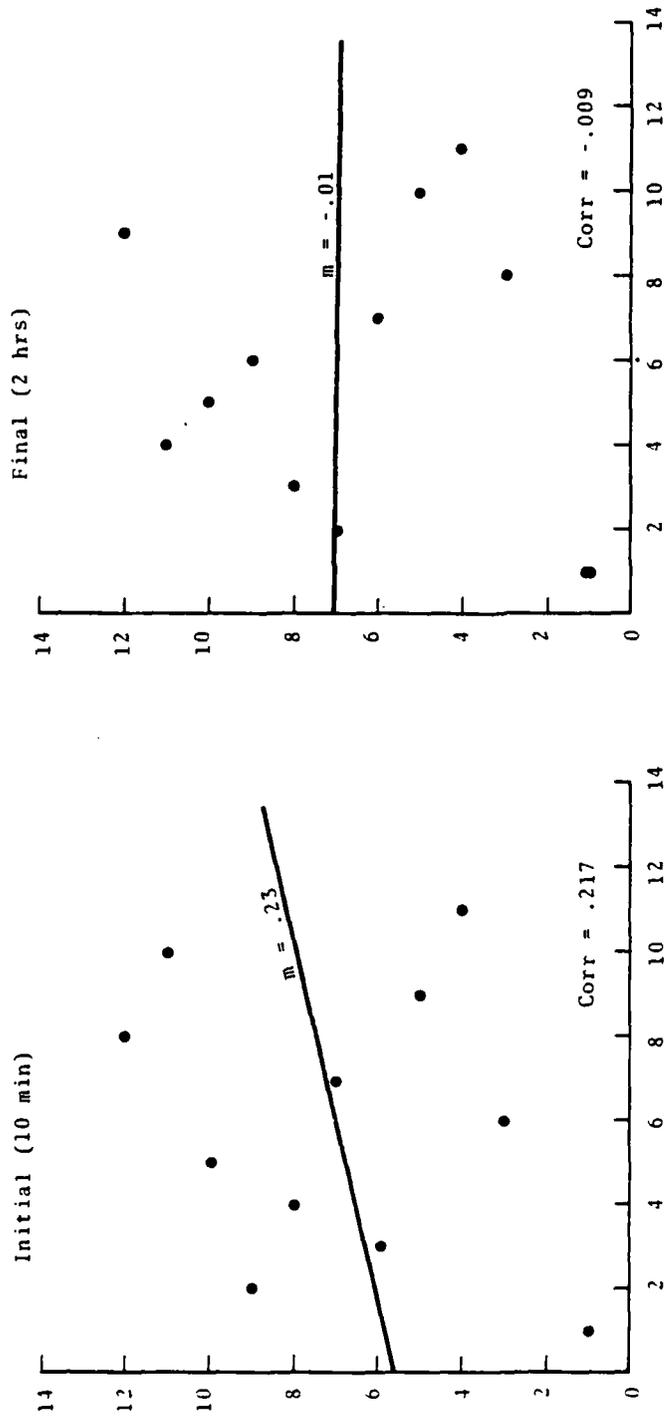


FIGURE A.2. STANDARD EFFECTIVENESS: MEAN DISPERSION PERCENTAGE RANKINGS WITH #2 FUEL OIL VS WITH #6 FUEL OIL (vertical scale) (horizontal scale)

$$\text{corr} = 1 - (6\sum d^2/n(n^2-1))$$

where n is the number of dispersants in the tests, and d is the difference between the assigned ranks. Table A.2 shows the results of significance testing at the 5 percent and 1 percent levels.

The results of these significance tests are clear: EPA test rankings of initial dispersion effectiveness are highly correlated with those of final dispersion; but the rankings for No. 6 oil have no significant correlation with those for No. 2 oil.

Difference of Means

Among the thirteen dispersants, eight may be classified as water-based, three as hydrocarbon based, and two as concentrates. The mean final percent dispersions for these three classes using No. 6 oil are

7 Water-based:	11.0%
2 Hydrocarbon-based:	4.9
2 Concentrate:	35.0
2 No data:	-

Although these data would seem to indicate that concentrates are, as a class, more effective than water-based dispersants, and hydrocarbon-based dispersants less effective, these impressions are not borne out by statistical tests. The t-statistic for water-based vs concentrates is .14 (d.f.=7) and for water-based vs hydrocarbon-based is .18 (d.f.=7). Neither statistic is significant.

The mean final percent dispersions for the three classes using No. 2 oil, instead of No. 6, are

7 Water-based:	21.7%
3 Hydrocarbon-based:	57.1
2 Concentrate:	58.0
1 No data:	-

TABLE A-2. SIGNIFICANCE OF RANKINGS BASED ON MEAN PERCENT DISPERSION AT 1:10 APPLICATION RATIO

	5% <u>corr >.553</u>	1% <u>corr >.684</u>
Initial vs. Final Dispersion		
--with No. 2 Oil	yes	yes
--with No. 6 Oil	yes	yes
No. 2 Fuel Oil vs No. 6 Fuel Oil		
--initial dispersion	no	no
--final dispersion	no	no

The t-statistic between the water-based and hydrocarbon-based dispersants is 3.5, which is significant at the 99% level, (d.f.=8). The t-statistic between the water-based and concentrate dispersants is 2.4, which is significant at the 95% level, (d.f.=7).

Thus the water-based dispersants are significantly less effective than the hydrocarbon or concentrate dispersants on No. 2 oil, but not on No. 6, based on EPA final dispersion data.

REFERENCES TO APPENDIX A

- A.1 McCarthy, L.T., I. Wilder, and J.S. Dorrlor, "Standard Dispersant Effectiveness and Toxicity Tests," Edison Water Quality Research Laboratory, U.S. Environmental Protection Agency, Report EPA-R2-73-201, May 1973.
- A.2 McCarthy, L.T., and G.P. Lindblom, "Chemical Dispersants for the Control of Oil Spills," ASTM Special Publication 659 (1977 Symposium, ASTM Committee F-20).

APPENDIX B

ANALYSIS OF VESSEL-MOUNTED DISPERSANT SPRAY SYSTEMS IN THE ABSENCE OF EXTERNALLY APPLIED AGITATION

Dispersant sprayed from a vessel-mounted boom depends for its effectiveness on the availability of adequate mixing energy. The total amount of energy required depends on the particular dispersant and oil involved. The sources of the energy are generally three: waves, externally applied mechanical agitation, and the spray itself. This last source of energy can be increased by increasing the spray volume and/or pressure. If spray energy and wave energy are inadequate, however, agitation must be added from breaker boards, ships' propellers, or other source.

Certain relationships must hold among the quantities that described a vessel-mounted spray system in the absence of externally applied mixing energy.

Definitions

- E_T = Total available mixing energy from waves and from the spray, per unit area of slick
- E_w = Wave mixing energy per unit area of slick
- E_s = Spray mixing energy, per unit area of slick
- V_O = Volume of dispersant sprayed on oil, per unit area of slick
- V_W = Volume of water sprayed on oil, per unit area of slick
- P = nozzle pressure, above atmospheric
- r = application ratio (dispersant/oil)
- δ = application density, dispersant volume per unit area of slick
- t = slick thickness

f = effectiveness
 = fraction of oil dispersed for given application ratio,
 total energy, and slick thickness
 = $f(\alpha, E_T, t)$

Analysis

If consistent units are employed (as will be assumed) it follows that

$$\begin{aligned}
 t &= V_O \\
 \delta &= V_D \\
 \alpha &= V_D/V_O = \delta/t
 \end{aligned}$$

A simple physical model for the spray energy is

$$E_S = \Delta P (\alpha_D V_D + \alpha_W V_W)$$

where α_D and α_W are dispersant and water densities, respectively. Further, since external agitation energy is not being considered, the total available mixing energy is

$$E_T = E_W + E_S$$

If water and dispersant densities are taken as unity, for simplicity,

$$\begin{aligned}
 E_T &= E_W + \Delta P (V_D + V_W) \\
 &= E_W + \Delta P V_S
 \end{aligned}$$

where V_S is the spray volume (water plus dispersant) per unit area of slick.

The above relationships are illustrated in Figure B-1 for a given slick thickness, t . The application ratio α is selected from considerations of oil type and slick thickness and the nozzle pressure drop ΔP from considerations of pump capability. The values of α and ΔP determine one curve from each of the two parametric families of curves shown.

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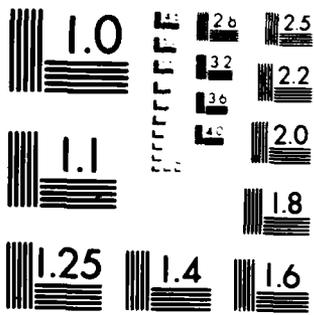
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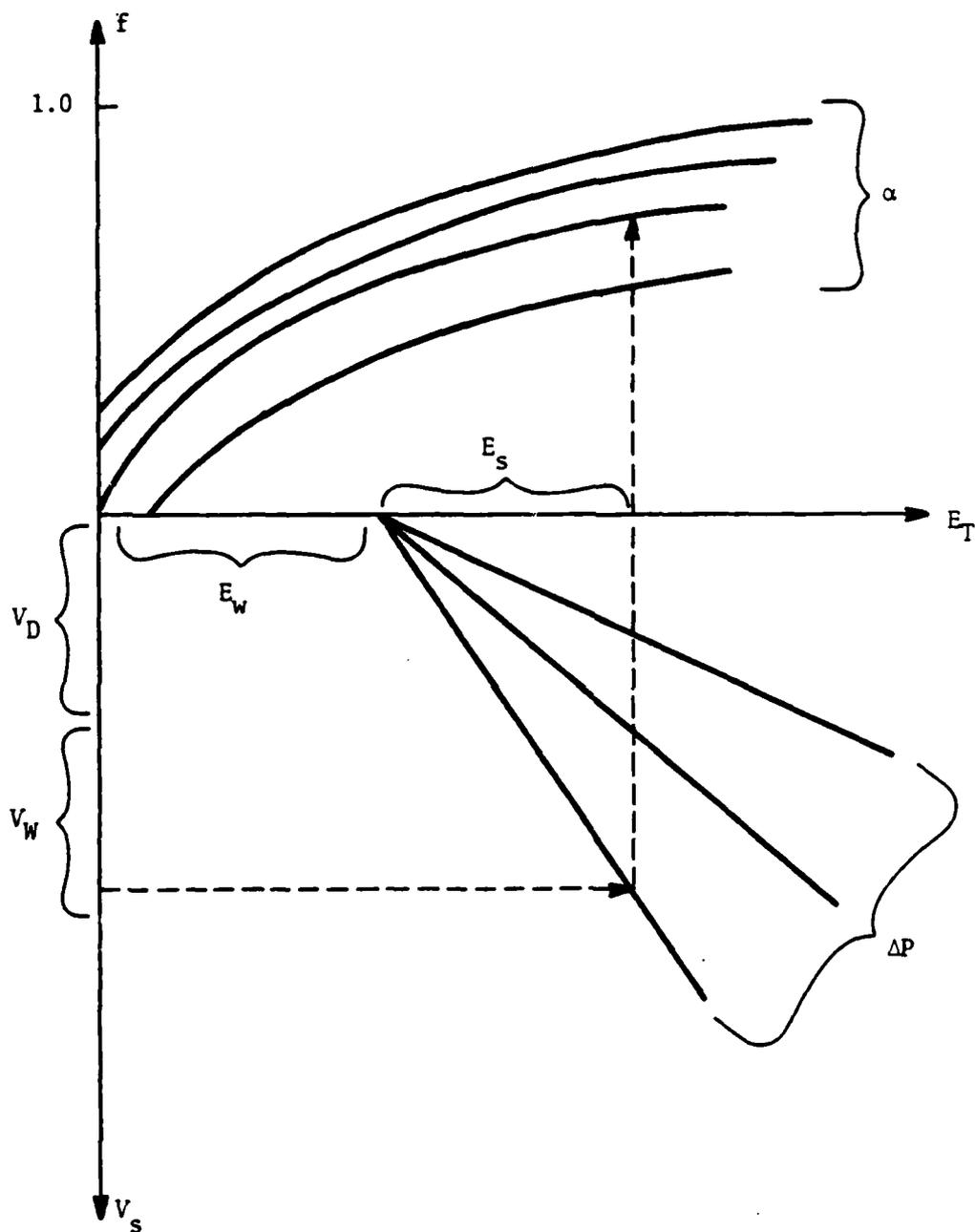


FIGURE B.1. RELATIONSHIPS AMONG PARAMETERS OF A VESSEL-MOUNTED SPRAY BOOM SYSTEM

The effectiveness curves shown for various values of α are purely hypothetical. Dispersants vary substantially in the shape of these curves. The more effective a dispersant the more rapidly these curves rise to $f=1.0$ as energy is increased.

This is the case for the "concentrates." The higher values of the effectiveness curves for concentrates, however, is partly offset by the reduced volume of concentrate employed, which has two effects:

- (1) a lower member of the family of α - curves is generally selected corresponding to a lower α ,
- (2) the total available mixing energy, E_T , is lower due to a lower value of V_D

The second of these effects can be counteracted, to an extent, by increasing the water volume, V_W , in the spray. Some concentrates, however, such as Corexit 9527 can be rendered less effective by too energetic a spray, which can break up the oil slick and thus reduce the time that the concentrate is in contact with the oil.

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