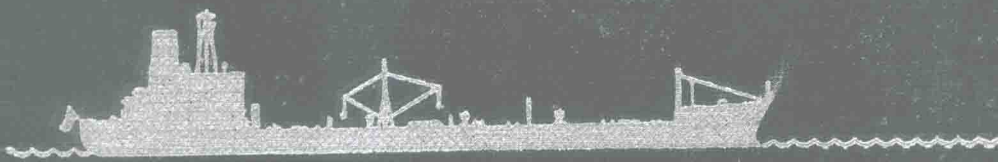

CHEMICAL DISPERSANTS FOR THE CONTROL OF OIL SPILLS

McCarthy/Lindblom/Walter

STP 659

AMERICAN SOCIETY FOR TESTING AND MATERIALS

CHEMICAL DISPERSANTS FOR THE CONTROL OF OIL SPILLS

A symposium
sponsored by ASTM
Committee F-20 on
Spill Control Systems
AMERICAN SOCIETY FOR
TESTING AND MATERIALS
Williamsburg, Va., 4–5 Oct. 1977

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L. T. McCarthy, Jr., Environmental Protection Agency,
G. P. Lindblom, Exxon Chemical Company, and
H. F. Walter, Department of Energy,
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Editorial Staff

A Note of Appreciation to Reviewers

This publication is made possible by the authors and, also, the unheralded efforts of the reviewers. This body of technical experts whose dedication, sacrifice of time and effort, and collective wisdom in reviewing the papers must be acknowledged. The quality level of ASTM publications is a direct function of their respected opinions. On behalf of ASTM we acknowledge with appreciation their contribution.

ASTM Committee on Publications

Related ASTM Publications

Oil Field Subsurface Injection of Water, STP 641 (1977), $10.75, 04-641000-16

Computerized Laboratory Systems, STP 578 (1975), $24.00, 04-578000-34

Manual on Presentation of Data and Control Chart Analysis, STP 15D (1976), $9.75, 04-015040-34

Foreword

The symposium on Chemical Dispersants for the Control of Oil Spills was held at Williamsburg, Va., 4–5 Oct. 1977. The symposium was sponsored by Committee F-20 on Spill Control Systems, American Society for Testing and Materials. L. T. McCarthy, Jr., presided as symposium chairman. The editors of this publication are L. T. McCarthy, Jr., G. P. Lindblom, Exxon Chemical Company, and H. F. Walter, Department of Energy.

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Introduction

Since 1975, industry and governmental officials charged with the responsibility for prevention, control, and cleanup of oil spills, particularly in the frontier areas such as North Slope, Beaufort Sea, Cook Inlet, and the Atlantic Outer Continental Shelf, became increasingly aware of the need for the inclusion of the dispersant options to mitigate environmental damage from potential oil spills. The adverse frigid environment in the Arctic and the severe wind, wave, and current forces manifested on the seas in frontier areas indicated to knowledgable parties that physical/mechanical control options such as booming and skimming were severely limited. The need for other oil spill control options in these areas led naturally to the reopening of the dispersant issue.

The Executive and Long Range Planning Committees of the ASTM F-20 Committee on Spill Control Systems recognized this need and decided to sponsor a symposium on dispersants. In February 1976, Dr. William Mott, director, Division of Environmental Control Technology, Energy Research and Development Administration (ERDA) (now Department of Energy (DOE)), accepted the chairmanship of the Dispersant Symposium. Originally scheduled for Dallas in January 1977, the symposium was postponed until October 1978 owing to a lack of interest, reflected in part by the numbers of abstracts submitted. This, of course, was an indication of the domestic hiatus on dispersants since the early 1970's and reflected also the limited amount of domestic research and development performed in recent years.

A complete turnaround, however, was triggered by the *Argo Merchant* incident. At the symposium, the statement was made that the *Argo Merchant* was to high-sea booms and skimmers what the *Torrey Canyon* was to oil spill dispersants. Somewhat overstated, perhaps, but there is an element of truth in the statement, and the point is well made. The lesson to be learned from the *Argo Merchant* is that the current state-of-the-art for containment and removal of oil spills from offshore waters has distinct limitations. Other available options such as burning, sinking, gelling, or the use of sorbents are even less desirable, being either environmentally unacceptable or technically unfeasible. Fortunately, the *Argo Merchant* oil was effectively dispersed by mother nature with minimal documented environmental impact. The significance of the ASTM Symposium on Dispersants is best understood in relation to the lessons learned from the *Argo Merchant* incident.

Another significant development subsequent to the *Argo Merchant* but preceding the symposium was the acceptance by the Environmental Protection Agency (EPA) of technical product data submitted by three dispersant manufacturers. The acceptance by EPA means that these products can be approved for use on a case-by-case basis according to Federal policy provisions promulgated in Annex X of the National Oil and Hazardous Substances Pollution Contingency Plan. Currently (June 1976), product data have been accepted by EPA for eight products with an additional five products under review. The exploration for oil and gas in frontier areas, the *Argo Merchant* incident, dispersant product data acceptance by EPA, and the inherent limitations of physical control options all contributed to the support and successful convening of the ASTM Symposium on Dispersants.

The control of open-ocean oil spills by the application of dispersant products, at controlled application rates, from systems demonstrated to be technically reliable for use in air or surface craft, is an environmentally acceptable control option. Based on the historical record of documented oil spill incidents, the major environmental impact is on, in, and around the shorelines and the shallow waters of the shoreline environment. Controlled application of dispersants to offshore oil spills can result in the least overall environmental damage to the shoreline. What remains to be demonstrated domestically is that oil spills can be dispersed in an environmentally acceptable manner, that is, in a manner that will result in the least overall environmental damage. Industry and government are cooperating in research programs to prove the technological feasibility of the techniques and products. It is essential for manufacturers and distributors of products together with oil industry representatives and state and Federal regulatory agency personnel to coordinate and cooperate in the research, development, and demonstration of products and applications systems that satisfy criteria for approval of dispersant use to mitigate the effects of oil spills.

In retrospect, the impetus triggered by the symposium continues. There is an improved relationship between industry and government officials on the dispersant issue, which only too recently was a very divisive subject. A greater understanding of the roles of government and industry, both of which are seriously concerned with environmental protection, is being manifested. Reasonable and objective parties polarized by "head-in-the-sand" attitudes can establish common grounds for compromise on divisive issues through adequate discussion, provided the proper forum for discussion is established. The ASTM F-20 Spill Control Systems Committee is such a forum, where industry and governmental interests are not only adequately represented but have an active role according to the scope of F-20 in

> . . . the formation of test methods, specifications, classifications, practices and definitions pertaining to performance, durability and strength of systems for the control of oil and other substances that float and the stimulation of research related thereto.

Many problems remain to be resolved, for differences of opinion will continue to exist not only on dispersants but also on other aspects of the broader environmental protection problem. Continued support of the ASTM F-20 Committee should be encouraged by the active participation of all interested parties.

For their foresight in originating the symposium, special recognition is given to LCDR George Brown, founding chairman of F-20, and Sam Bowman, ASTM Manager of F-20. The pioneering efforts of Dr. William Mott, DOE, are gratefully acknowledged. The momentum provided by his initiatives in the solicitation of papers and publicity of the symposium resulted in the successful meeting in Williamsburg. Behind-the-scenes support by the F-20 Executive and Long Range Planning Committees is appreciated.

Special thanks is also given to the following members of the Program Committee: Gerry Canevari of Exxon; Hans Crump of EPA; Tom Dalton of Coastal Services, Inc; Dan Fitzgerald of Atlantic Richfield Co.; Steve Kaufman of Sunshine Chemical Co.; Jack Sinclair of the United States Coast Guard, and Henry Walter of DOE. Without their support in attending meetings, organizing the program, soliciting of papers, reviewing papers, chairing sessions, and attending to many other details, the symposium would not have been so successful.

For chairing and organizing the excellent panel sessions, grateful thanks are offered to Gordon P. Lindblom of Exxon, who together with Henry Walter edited the topics from the panel session. The panel session was a significant contribution to the symposium's success in that it afforded a summary of current perspectives on dispersants from both industry and government viewpoints.

Additionally, grateful thanks are offered to the authors for their contributions, as well as for their patience and perseverance during the somewhat lengthy period from the submission of abstracts through their presentations at the symposium and subsequent publishing of the proceedings in this volume.

Finally, for those behind the scenes at ASTM, namely, Jane B. Wheeler, managing editor, and her staff, who by their diligent and meticulous attention to detail from the receipt of abstracts and papers to the review and editing for presentation and publication, made this volume possible, we deeply appreciate their excellent and competent support.

L. T. McCarthy, Jr.
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G. P. Canevari[1]

Some Observations on the Mechanism and Chemistry Aspects of Chemical Dispersion

REFERENCE: Canevari, G. P., "**Some Observations on the Mechanism and Chemistry Aspects of Chemical Dispersion,**" *Chemical Dispersants for the Control of Oil Spills, ASTM STP 659,* L. T. McCarthy, Jr., G. P. Lindblom, and H. F. Walter, Eds., American Society for Testing and Materials, 1978, pp. 5–17.

ABSTRACT: An overview of the mechanism of chemical dispersion is presented in order to put the subject in the proper perspective. The methodology and role of the surface active agent in the generation of finely dispersed oil droplets are reviewed.

This discussion of the dispersing mechanism will help resolve some of the misconceptions that have persisted for the past 10 years, such as the dispersant acting to either sink or solubilize the oil droplets into the water column, or both.

The incentives, concerns, and resultant present status of chemical dispersion are developed.

KEY WORDS: dispersants, oils, oil spill chemical, self-mix dispersant, mechanism, chemical treatment, incentives for dispersing

There has been a noticeable increasing awareness of the utility of chemical dispersants as a viable means to minimize damage from oil spills. Prior reluctance to consider chemical dispersion in a more positive perspective was basically due to two concerns—toxicity and effectiveness.

It should be emphasized that oil is dispersed to minimize damage from an unrecoverable oil spill that threatens shorelines. In order to assess the viability of this technique for handling oil spills, one must first appreciate the overall mechanism and related chemistry aspects. Accordingly, the following discussion encompasses:

1. mechanics of chemical dispersion and role of the surface active agent,
2. properties of chemically dispersed oil,

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3. misconceptions regarding chemical dispersion,
4. incentives for chemical dispersion,
5. limitations of chemical dispersion, and
6. development of self-mix dispersants.

Behavior of Spilled Oil at Sea

Before considering the mechanism and chemistry of chemical dispersion, a brief review of oil spill spreading behavior is relevant. When a volume of oil is spilled onto the surface of water, the oil has a driving force to film out or spread. In essence, a spreading pressure, sometimes expressed as a spreading coefficient, $S_{o/w}$, develops that is readily quantified by the oil-water interfacial relationship as

$$S_{o/w} = \gamma_w - \gamma_{o/w} - \gamma_o \tag{1}$$

where

$S_{o/w}$ = spreading coefficient for oil-on-water, ergs/cm^2 or dynes/cm,
γ_w = surface tension of water, dynes/cm,
γ_o = surface tension of oil, dynes/cm, and
$\gamma_{o/w}$ = interfacial tension of oil-and-water, dynes/cm.

By an examination of the force balance shown in Fig. 1, it can be seen that if $S_{o/w}$, the resultant spreading force, is positive, the oil will spread on the water; if negative, it will not spread but remain as a "lens" of liquid. For example, spreading coefficient values for Kuwait crude on seawater, reported by Canevari [*1*],[2] are positive and confirm that for this system the oil readily spreads on water phase.

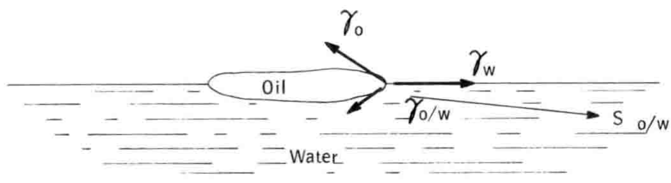
In recent years, several controlled oil spills conducted to define the manner, rate, and direction of spilled oil [*2,3*] have done a great deal to establish the ultimate fate of an oil spill.

Mechanism of Chemical Dispersion and Role of Surface-Active Agent

At the outset, it would be in order to consider terminology. The *Torrey Canyon*-era chemicals were basically cleaning agents and called detergents. Subsequently, formulations were prepared that were meant solely to disperse oil at sea and were called dispersants. The word emulsifier is also used.

The mechanism of chemical dispersion is quite straightforward. Let us first define a surface active agent (surfactant) as a compound that has an oil-compatible and a water-compatible group. Because of this amphi-

[2] The italic numbers in brackets refer to the list of references appended to this paper.



$$S_{o/w} = \gamma_w - \gamma_o - \gamma_{o/w}$$

For White Oil

$S_{o/w} = 72 - 33 - 52$
$= - 13$

White Oil Won't Spread

For Kuwait Crude

$S_{o/w} = 72 - 24 - 25$
$= + 23$

∴ Kuwait Crude Readily Spreads

FIG. 1—*Spreading coefficient* $S_{o/w}$ *for oil on water.*

phatic nature, it locates at an oil-water interface as depicted in Fig. 2. By its orientation at the interface, the surfactant reduces the interfacial tension. The generation of interfacial area in the nature of finely dispersed oil droplets is enhanced by the lowering of interfacial tension, since

$$W_K = \gamma_{o/w} A_{o/w} \quad (2)$$

where

W_K = mixing energy, ergs,
$A_{o/w}$ = interfacial area, cm^2, and
$\gamma_{o/w}$ = interfacial tension, dynes/cm.

It can now be appreciated that any surfactant (by definition), because of its molecular configuration, lowers interfacial tension. Hence, surfactants used as either wetting agents, foaming agents, detergents, or emulsifiers will act as a dispersant for oil-in-water to some degree. All surfactants exhibit the various surfactant-related characteristics. But, for instance, a particular surfactant will be known as a wetting agent if it possesses this characteristic to a greater degree than the others.

A detailed discussion of the chemistry of surface active agents is beyond the scope of this paper. It has been covered most completely in Refs *4–6*.

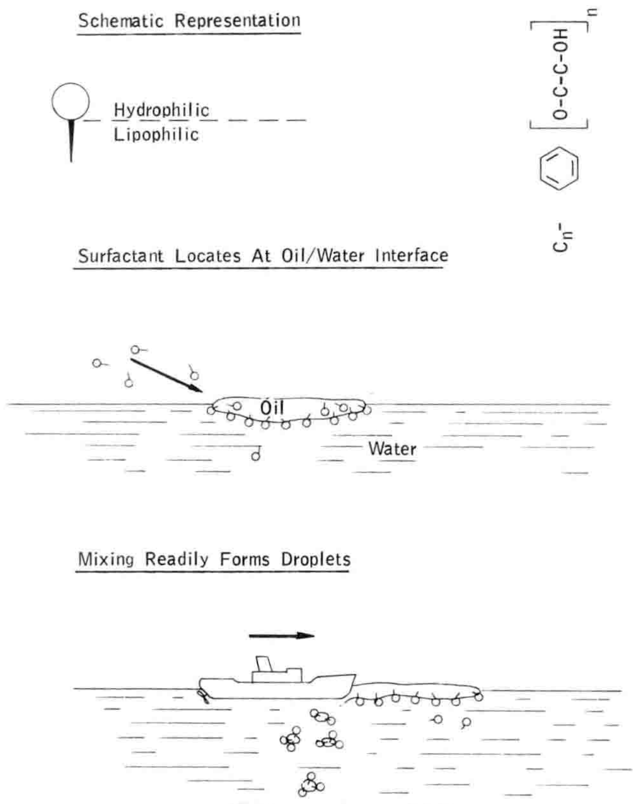


FIG. 2—*Mechanism of chemical dispersion of a typical surfactant* (*alkyl phenol-ethylene oxide*).

However, a brief review of surfactant types follows. The classification into the following three types is based upon the hydrophilic moiety of the surfactant molecule [5].

Anionic:

1. Oldest and best known are soaps such as salts of long-chain fatty acids, for example, sodium oleate,
2. sulfated oil,
3. sulfated alcohols such as the important sodium lauryl sulfate, and
4. petroleum sulfonates such as dodecyl benzene sulfonate.

Cationic:

1. Amines or quaternary ammonium salts such as cetyl trimethyl ammonium bromide,