PROJECT NO. 724110/001-2

COAST GUARD

OFFICE OF RESEARCH & DEVELOPMENT

AD 741247

INVESTIGATION OF SINKING METHODS FOR REMOVAL OF OIL POLLUTION FROM WATER SURFACES

PHASE II: METHODS OF TEST FOR LABORATORY EVALUATION OF OIL SINKING MATERIALS

by

E. C. Roshore

U. S. Army Engineer Waterways Experiment Station
Vicksburg, Mississippi 39180

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

February 1972

Report 2 of a Series

D D C
RECEIVED
MAY 10 1972
B

[redacted]

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

Prepared for: COMMANDANT (DAT)
U.S. COAST GUARD HEADQUARTERS
WASHINGTON, D.C., 20591

See AD 735 617

13

Destroy this report when no longer needed.
Do not return it to the originator.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
U. S. Army Engineer Waterways Experiment Station
Vicksburg, Mississippi

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
INVESTIGATION OF SINKING METHODS FOR REMOVAL OF OIL POLLUTION FROM WATER SURFACES; PHASE II: METHODS OF TEST FOR LABORATORY EVALUATION OF OIL SINKING MATERIALS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Report 2 of a series

5. AUTHOR(S) (First name, middle initial, last name)
E. C. Roshore

6. REPORT DATE
February 1972

7a. TOTAL NO. OF PAGES
68

7b. NO. OF REFS
1

8a. CONTRACT OR GRANT NO.
MIPR Z-70099-0-00583

b. PROJECT NO.
4110.1/1/1

c.
Formally project 4110/001

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT
This report is available from the National Technical Information Service, 5285 Port Royal Rd., Springfield, Va. 22151 Order No.______

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Commandant (DAT)
U. S. Coast Guard Headquarters
Washington, D. C. 20591

13. ABSTRACT

The objective of this program is to investigate materials that can be utilized in the cleanup of massive oil spills by sinking the oil. The program is divided into four phases as follows. Phase I: Survey of the State-of-the-Art. Phase II: Development of Standard Test Procedures. Phase III: Tests of Sinking Materials. Phase IV: Tests Analysis and Conclusions. This report covers Phase II. Laboratory tests were developed to evaluate the effectiveness of oil sinking materials under varying conditions. Tests were developed to determine: a. Optimum oil sinking material retention potential. This is an index of the maximum amount of oil a sinking agent or sorbent will retain when submerged. b. Sinking efficiency. This is an evaluation of the practical oil removal effectiveness of sinking agents. The value determined is the ratio of the weight of oil sunk to the weight of sinking agent used under a specific set of conditions. This test distinguishes between sinking agents and sorbents which do not effectively sink oil. c. Dynamic retention capability. An evaluation of the ability of a sinking agent to retain sorbed oil in a submerged state when subjected to the effects of current and different bottom conditions. d. Volatile loss-time characteristics of oil retained on glass wool. This is an evaluation of the actual weight of unweathered free oil left on the water surface in the dynamic retention capability test and is used, for calibration purposes, in connection with that test (see c. above). The tests developed are not applicable to Bunker C fuel oil due to its semisolid state at laboratory conditions. No significant difference was noted in results obtained due to water composition--fresh water or simulated sea water. Tables are presented evaluating the reproducibility of tests. It should be noted that screening tests indicate that very fine materials such as talcs, and materials such as chalks and asbestos, do not act as effective sinking agents without addition of surfactants which were not included.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT.	ROLE	WT	ROLE	WT.
Absorbers (materials)						
Oil pollution of rivers, harbors, etc.						
Sinking methods						

67725

Unclassified
Security Classification

29 March 1972

This report submitted in partial fulfillment of contract MIPR-Z-70099-0-00583 was prepared by the Concrete Division of the U. S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi, which is responsible for the facts and the accuracy of the data presented herein.

The contents of this report do not necessarily reflect the official views or policy of the Coast Guard. This report does not constitute a standard, specification or regulation.

This report, or the contents thereof, may not be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of such commercial products.

J. R. IVERSEN
Captain, U. S. Coast Guard
Chief, Applied Technology Division
Office of Research and Development
U. S. Coast Guard Headquarters
Washington, D. C. 20590

FOREWORD

This investigation, Phase II of an overall study authorized by DD Form 448, dated 25 June 1970, MIPR No. Z-70099-0-00583, from Commandant (FSP-1), U. S. Coast Guard, was oriented toward the development of laboratory test procedures for comparative evaluation of oil sinking materials to be used for removing oil films from water surfaces. In future phases, various sinking oil materials will be tested and evaluated in conjunction with each of several types of oil.

This study was conducted by personnel of the U. S. Army Engineer Waterways Experiment Station Concrete Division under the direction of Messrs. B. Mather, J. M. Polatty, V. D. Edgerton, R. W. Crisp, and B. J. Houston. Mr. Crisp was project leader for this phase of the program. This report was prepared by Mr. E. C. Roshore. Mr. Leo Tobias, Office, Chief of Engineers, served as liaison between the U. S. Coast Guard and the Waterways Experiment Station. Cdr William E. Lehr, Chief, Pollution Control Branch, Office of R&D, U. S. Coast Guard, was the project officer.

COL Ernest D. Peixotto, CE, was Director of the Waterways Experiment Station during the conduct of this study. Mr. F. R. Brown was Technical Director.

CONTENTS

Page

FOREWORD v

CONVERSION FACTORS, BRITISH TO METRIC UNITS OF MEASUREMENTS ix

SUMMARY. xi

GLOSSARY xiii

PART I: INTRODUCTION. 1

- Background 1
- Objective. 1
- Scope. 2

PART II: OPTIMUM SOM RETENTION POTENTIAL 14

- Water Composition. 15
- Reproducibility of Results 16

PART III: SINKING EFFICIENCY. 19

- Rate of Application of SOM 19
- System Temperature 20
- Initial Oil Film Thickness 22
- Nature of Oil Film, Fresh or Weathered 23
- Surface Condition, Calm or Agitated. 23
- Reproducibility of Results 25
- General Comments 25

PART IV: DYNAMIC RETENTION CAPABILITY. 37

- Flow Channel for Current Simulation. 37
- Factors Influencing Retention. 39

PART V: CONCLUSIONS 40

APPENDIX A: PROPOSED METHOD OF TEST FOR DETERMINATION OF OPTIMUM SOM RETENTION POTENTIAL OF SINKING AGENTS OR SORBENTS FOR OIL

APPENDIX B: PROPOSED METHOD OF TEST FOR EVALUATION OF THE SINKING EFFICIENCY OF SINKING AGENTS FOR OIL (DRY APPLICATION)

APPENDIX C: PROPOSED METHOD OF TEST FOR DETERMINATION OF DYNAMIC RETENTION CAPABILITY OF SINKING AGENTS FOR OILS

APPENDIX D: PROPOSED PROCEDURE FOR DETERMINATION OF VOLATILE LOSS-TIME CHARACTERISTICS OF OIL RETAINED ON GLASS WOOL

CONVERSION FACTORS, BRITISH TO METRIC UNITS OF MEASUREMENT

British units of measurement used in this report can be converted to metric units as follows:

Multiply	By	To Obtain
inches	2.54	centimeters
feet per second	0.3048	meters per second
Fahrenheit degrees	5/9	Celsius or Kelvin degrees*

---

* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: C = (5/9)(F - 32). To obtain Kelvin (K) readings, use: K = (5/9)(F - 32) + 273.15.

SUMMARY

The objective of this program is to investigate materials that can be utilized in the cleanup of massive oil spills by sinking the oil. The program is divided into four phases as follows.

Phase I: Survey of the State-of-the-Art.

Phase II: Development of Standard Test Procedures.

Phase III: Tests of Sinking Materials

Phase IV: Tests Analysis and Conclusions

This report covers Phase II. Laboratory tests were developed to evaluate the effectiveness of oil sinking materials under varying conditions. Tests were developed to determine:

a. Optimum oil sinking material retention potential. This is an index of the maximum amount of oil a sinking agent or sorbent will retain when submerged.

b. Sinking efficiency. This is an evaluation of the practical oil removal effectiveness of sinking agents. The value determined is the ratio of the weight of oil sunk to the weight of sinking agent used under a specific set of conditions. This test distinguishes between sinking agents and sorbents which do not effectively sink oil.

c. Dynamic retention capability. An evaluation of the ability of a sinking agent to retain sorbed oil in a submerged state when subjected to the effects of current and different bottom conditions.

d. Volatile loss-time characteristics of oil retained on glass wool. This is an evaluation of the actual weight of unweathered free oil left on the water surface in the dynamic retention capability test and is used, for calibration purposes, in connection with that test (see c above).

The tests developed are not applicable to Bunker C fuel oil due to its semisolid state at laboratory conditions. No significant difference was noted in results obtained due to water composition--fresh water or simulated sea water.

Tables are presented evaluating the reproducibility of tests.

It should be noted that screening tests indicate that very fine materials such as talcs, and materials such as chalks and asbestos, do not act as effective sinking agents without addition of surfactants which were not included.

GLOSSARY

Ambient temperature. The temperature of the surrounding air.

Laboratory test conditions. A temperature of 73.4 ± 3.6 F (23 ± 2 C) and a relative humidity of 50 ± 5 percent.

Sinking agent. A material that, when applied to floating oil, sorbs (adsorbs and/or absorbs) oil, creating a high-density mass which sinks, with or without agitation, thus removing oil from the surface.

Sorbent. A material that, when applied to floating oil, sorbs (adsorbs and/or absorbs) oil but does not effectively sink; oil and sorbent both remain on the surface.

SOM (Oil Sinking Material). Term used to identify materials submitted by manufacturers for evaluation as sinking agents. Twenty-three materials were identified in Phase I of this investigation.

Optimum SOM retention potential. An index of the optimum capability of a SOM to retain a given oil submerged. The index is determined by the retained oils:SOM ratio by weight at 18 hr, under static laboratory conditions. This index may be determined both for sinking agents and sorbents as presented in Appendix A.

Sinking efficiency. The ability of a SOM to act as a sinking agent for oil and sink an oil layer on water. Sinking efficiency is expressed by the oil:SOM ratio (by weight) required to sink at least 90 percent of the oil film. The test method is given as Appendix B.

Retention capability. Defined as the ability of the oil:sinking agent mass to retain its oil after sinking. The ratio of the weight of the oil retained to the weight of the sinking agent used is a measure of this retention capability.

Dynamic retention capability. The retention capability determined under dynamic conditions, i.e., the oil and sinking agent are placed on a moving water surface. Retention capability and dynamic retention capability are to be determined in accordance with the test methods presented as Appendixes C and D.

INVESTIGATION OF SINKING METHODS FOR REMOVAL OF OIL POLLUTION FROM WATER SURFACES

PHASE II: METHODS OF TEST FOR LABORATORY EVALUATION OF OIL SINKING MATERIALS

KEY

Oil Sinking Materials

Manufacturer	Identification No.	Trade Name
Phillips Scientific Corp. (a subsidiary of Phillips Petroleum Co.) Bartlesville, Okla. 74003	SOM-1	Latex coated barite
Pluess-Staufer (North American) Inc. 52 Beaver Street New York, N. Y. 10005	SOM-2	Omya Nautex H
Wyandotte Chemicals Corp. J. B. Ford Division Wyandotte, Mich. 48192	SOM-3	Zorb-All
United Sierra Division of Cyprus Mines Corp. Trenton, N. J. 08606	SOM-4	Mistron Vapor
United Sierra Division of Cyprus Mines Corp. Trenton, N. J. 08606	SOM-5	Mistron ZSC
Union Carbide Corp. Mining and Metals Division R&D Department Niagara Falls, N. Y. 14302	SOM-8	Calidria Asbestos K-G444
Waverly Minerals Products Co. 3018 Market Street Philadelphia, Pa. 19104	SOM-11	HI DRI

Oil Sinking Materials

Manufacturer	Identification No.	Trade Name
Dow Corning Corp. Midland, Mich. 48640	SOM-14	Silicone treated fly ash
Dow Corning Corp. Midland, Mich. 48640	SOM-16	Silicone treated silica
Destroyl Ltd. Goldlay, Burnt Mills Road Nevendon, Basildon Essex, United Kingdom	SOM-17	Cement by-product
Aqua Pura Inc. 1000 Country Club Lane NW Albuquerque, N. Mex. 87114	SOM-18	Hydrated potassium aluminum silicate
The Burns & Russell Co. P. O. Box 6063 Baltimore, Md. 21231	SOM-19	Treated silica BR Globulator 101
The Burns & Russell Co. P. O. Box 6063 Baltimore, Md. 21231	SOM-20	Treated silica BR Encapsulator 201
The Burns & Russell Co. P. O. Box 6063 Baltimore, Md. 21231	SOM-21	Treated silica BR Globulator 102
The Burns & Russell Co. P. O. Box 6063 Baltimore, Md. 21231	SOM-22	Treated silica BR Globulator 103
The Burns & Russell Co. P. O. Box 6063 Baltimore, Md. 21231	SOM-23	Treated silica BR Globulator 104

Oils

Identification No.	Description
1	North Louisiana paraffinic-based crude (low-viscosity crude oil)
2	South Louisiana naphthenic-based crude (low-viscosity crude oil)
4	Diesel oil
5	Bunker C (residual fuel oil)
6	Bachaguera, Argentina type asphaltic crude (high-viscosity crude oil)
7	SAE 30 wt. motor oil (lube oil)

INVESTIGATION OF SINKING METHODS FOR REMOVAL OF OIL POLLUTION FROM WATER SURFACES

PHASE II: METHODS OF TEST FOR LABORATORY EVALUATION OF OIL SINKING MATERIALS

PART I: INTRODUCTION

Background

1. The material presented and discussed in this report represents the second phase of a comprehensive program directed toward the evaluation of oil sinking materials (SOM's) which might be utilized in the cleanup of massive oil slicks on the open sea. The four phases which comprise this program are:

Phase I: Survey of the State-of-the-Art
Phase II: Development of Standard Test Procedures
Phase III: Tests of Oil Sinking Materials
Phase IV: Tests Analysis and Conclusions

Objective

2. The objective of Phase II was to develop a series of standard test procedures which might be used to evaluate the effectiveness of various sinking agents under a variety of laboratory conditions. In particular, methods were to be developed to evaluate the optimum SOM retention potential, sinking efficiency, and retention capability of each of a variety of oil sinking materials when these materials were applied to various oils.

3. A sinking agent is defined as a material that, when applied to floating oil, sorbs (adsorbs and/or absorbs) oil and sinks with the oil, thus removing oil from the surface. A material which sorbs (adsorbs and/or absorbs) oil but does not sink it is referred to as a sorbent. The definitions of these and other terms used in this report are given in the Glossary.

4. The effects of variation of the following parameters were to be investigated prior to and during the composition of the various methods of test.

- a. Oil film thickness
- b. Nature of oil film (fresh or weathered)
- c. System temperature
- d. Rate of application of sinking agent
- e. Nature of surface condition (calm or agitated)
- f. Type of bottom condition (sand, mud, gravel, etc.)
- g. Current flow (fluid velocity)
- h. Nature of water system (salt or fresh)

Naturally, all of these parameters would not influence each test procedure. Therefore, examination of the effects of those parameters deemed to have no appreciable influence on the results of a particular test would not be required in that particular test method.

Scope

5. The test procedures to be developed during the course of this investigation were to be broad enough in nature so as to allow for the evaluation of each of the various types of oil sinking materials obtained for evaluation (and described in the Phase I report) in conjunction with each of several types of petroleum products: residual fuel oil, diesel oil, lube oil, high-viscosity crude oil, low-viscosity crude oil, paraffinic-based crude oil, and naphthenic-based crude oil.

6. It should be noted at this point that at laboratory test conditions (see Glossary) the test methods developed during this phase of the investigation cannot be applied to residual fuel oil (Bunker C). This situation arises from the fact that at 73 F* residual fuel oil is semisolid in nature and cannot be appreciably penetrated or sorbed by any of the oil sinking materials (SOM's) subjected to evaluation in this investigation.

---

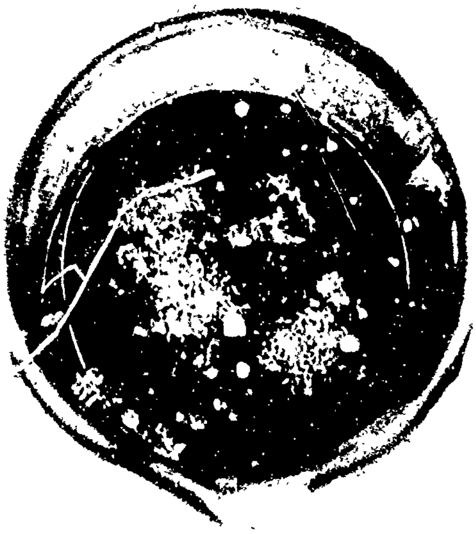
* A table of factors for converting British units of measurement to metric units is given on page ix.

This point is readily illustrated by the following photographs. These photographs (figs. 1 through 5) indicate visually the relative degrees of penetration and sorption exhibited at various time intervals by several of the SOM's placed on masses of residual fuel oil (tests conducted at 73 F). Each figure is made up of four photographs, one taken immediately after application of the SOM to the oil surface (oil on surface of oil-water mixture) and one each taken 2, 24, and 48 hr after application. The difficulty in differentiating between the SOM and the oil in fig. 4 is due to the dark natural coloration of the silicone treated fly ash rather then penetration into or sorption of the residual fuel oil; there was no actual penetration or sorption. The slight darkening of the sand particles in fig. 5 was due to the very slight penetration of the sand grains into the residual fuel oil. In no instances did the sand particles fully penetrate the oil.

a. Immediately after application

b. 2 hr after application

Fig. 1. Interaction of latex coated barite (SOM-1) with residual fuel oil (sheet 1 of 2)



c. 24 hr after application

d. 48 hr after application

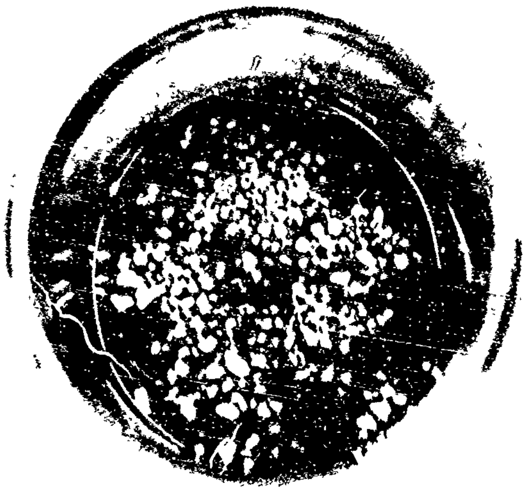
Fig. 1 (sheet 2 of 2)

a. Immediately after application

b. 2 hr after application

Fig. 2. Interaction of calcined clay (SOM-3) with residual fuel oil (sheet 1 of 2)

c. 24 hr after application



d. 48 hr after application

Fig. 2 (sheet 2 of 3)

a. Immediately after application

b. 2 hr after application

Fig. 3. Interaction of hydrophobic asbestos (SOM-8) with residual fuel oil (sheet 1 of 2)

c. 24 hr after application

d. 48 hr after application

Fig. 3 (sheet 2 of 2)

a. Immediately after application

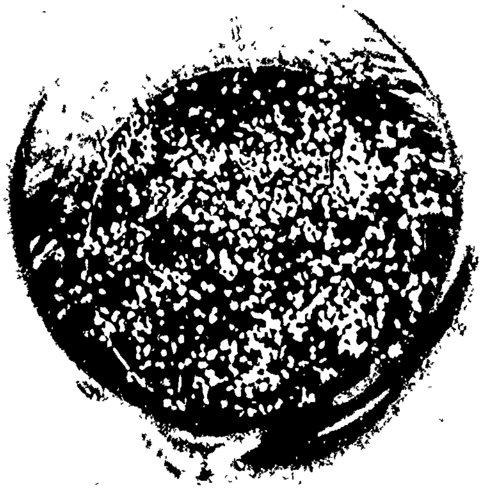
b. 2 hr after application

Fig. 4. Interaction of silicone treated fly ash (SOM-14) with residual fuel oil (sheet 1 of 2)

c. 24 hr after application

d. 48 hr after application

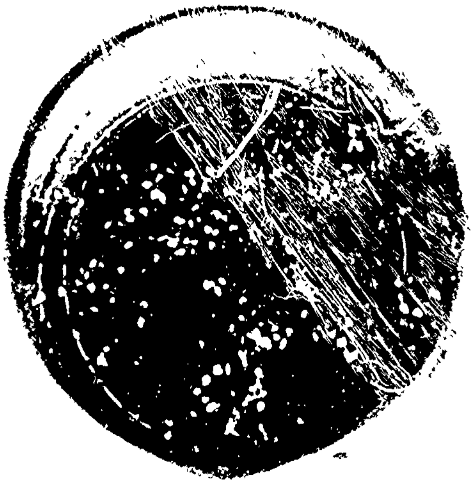
Fig. 4 (sheet 2 of 2)



a. Immediately after application

b. 2 hr after application

Fig. 5. Interaction of silicone treated sand (SOM-16) with residual fuel oil (sheet 1 of 2)



c. 24 hr after application

d. 48 hr after application

Fig. [illegible] (sheet [illegible] of [illegible])

PART II: OPTIMUM SOM RETENTION POTENTIAL

7. Optimum SOM retention potential is defined, for purposes of this investigation and the resulting methods of test, to be the ratio of the weight of oil effectively retained submerged for 18 hr to the weight of SOM effectively used. This index is not intended to indicate the potentials of the various SOM's as would exist under actual field conditions, but rather to indicate the absolute optimum retention capabilities of the individual materials under laboratory test conditions.

8. Initial investigations conducted during the formulation of these methods of test for determination of optimum SOM potential revealed that SOM's generally fall into two categories: (a) granular materials (sands, granulated clays, treated fly ashes), and (b) powdered materials (asbestos, talc, and chalk). These two categories of materials behave somewhat differently with regard to stability of the submerged oil-SOM mass.

9. In particular, it was found that in tests of granular sinking sorbents, the presence of an excess amount of oil above that amount which could be effectively sorbed by the SOM resulted merely in free oil floating on the water surface. In tests of powdered SOM's, the presence of an excess amount of oil (or insufficient amount of SOM) resulted in flotation of the majority of the oil-SOM mass. This appeared to indicate that the submerged physical behavior of the sinking agents was dependent more on the density and surface characteristics of the individual particles whereas the submerged physical behavior of the sorbents was dependent upon the density of the entire oil-sorbent mass.

10. A factor which probably magnified this difference in behavior was the pronounced tendency toward air entrapment by the oil-sorbent mass in cases where a sorbent was used. This was an even greater problem in tests involving the more viscous oils. To eliminate the effects of entrapped air, all tests were subjected to a vacuum pressure of 30 in. of mercury until such time as no drop in pressure was observed over a time interval of 5 min. Since it was determined that the volatile matter in the oils investigated at ambient conditions varied from 0.5 to 40 percent by weight, tests were conducted on each of the oils to determine if any significant

weight loss would be encountered during the vacuum process. With 30 grams of oil evacuated for 15 min at 30 in. of mercury, the volatile loss by weight varied from 0.53 percent for oil 1 to 0 percent loss for oil 7. For oils having large losses, blanks could be conducted along with test specimens.

11. These rather different modes of behavior of the oil-SOM masses necessitated the formulation of two slightly different methods of test for determination of optimum SOM retention potential, one for granular SOM's (Method A, Appendix A) and another for powdered sinking sorbents (Method B, Appendix A). The sample preparation procedures are identical, an absolute necessity if test results for all sinking sorbents are to be compared. The differences in these two methods, as will be noted, exist only in measurement technique.

12. Generally, asbestos, talc, and chalk should be tested in accordance with Method B for sorbents. The ultimate criteria for test method (A or B) should be determined in accordance with Appendix B for evaluation of sinking efficiency at standard conditions. If it is impossible to sink 90 percent of the oil film, the SOM is considered a sorbent and should be evaluated in this test procedure in accordance with Method B, Appendix A.

Water Composition

13. To examine the effects, if any, of variation in water composition on the optimum SOM retention potential of the various SOM's, 18 series of tests were conducted. In all series, the only variable was water composition, either ASTM simulated sea water* or distilled water. The 18 series of tests employed 15 different SOM's (either sinking agents or sorbents) and three representative oils.

14. In each test, known quantities of material and oil were mixed and allowed to stand for 1 hr. The oil:sinking agent or oil:sorbent mass was then submerged and the volume of free oil release was determined after a submergence period of 18 hr. This volume of release was converted

---

* Substitute ocean water meeting the specifications of ASTM Designation D-1141, Section 4.

to weight and then divided by the weight of sinking agent or sorbent used to obtain an oil release ratio. Since each series of two tests was conducted in the same manner, a one-to-one correspondence of this oil release ratio computed for the ASTM simulated sea water tests to their distilled water counterparts would indicate that this type of variation in water composition had no appreciable effect on the effectiveness of the sinking agents or sorbents used.

15. The data obtained from these tests are plotted in fig. 6, and as the least squares fit line visually indicates, there was no discernible variation in results for corresponding tests (a series), except the random experimental error. Thus, the conclusion that this type of variation in water composition results in no discernible variation in tests for optimum SOM retention potential appears justified.

16. The test method developed for the determination of the optimum SOM retention potential is given as Appendix A and is written in such a way as to allow for the testing of either a sinking agent or a sorbent for oil.

Reproducibility of Results

17. One of the criteria upon which a method of test is evaluated is reproducibility of test results. That is, if the test is repeated several times, will the results of all tests be similar in nature and magnitude? Test results for identical tests must not be so scattered that they cast significant doubt on the quality of the test procedure and accuracy of the resulting information.

18. To indicate the reproducibility characteristics of the method of test for determination of optimum SOM retention potential, several trial tests were performed using representative oils, sinking agents, and sorbents. Results of these tests, as indicated by the data and statistical evaluation given in table 1, indicate a substantial degree of reproducibility of results determined according to this test.

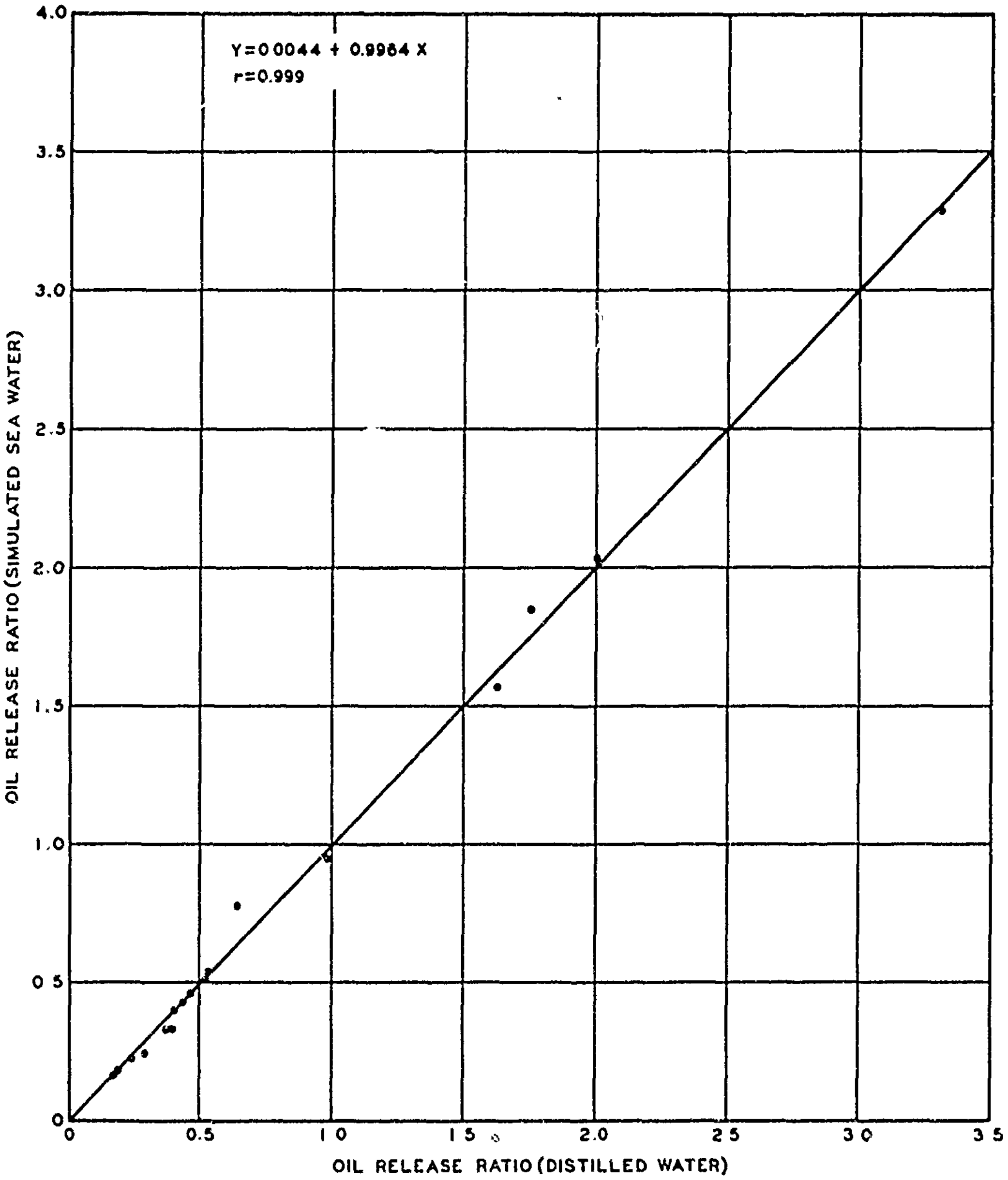


Fig. 6. Oil release in salt water versus oil release in fresh (distilled) water

Table 1

Reproducibility of Results of Optimum SOM Retention Potential Test

	Grams of Oil Retained after 18 hr of Submersion for Indicated Sinking Agents and Sorbents							
Test No.	SOM-1	SOM-3	SOM-8	SOM-14	SOM-2	SOM-5	SOM-11	SOM-16
1	23.2	22.8	27.0	24.0	24.1	24.5	25.8	24.1
2	24.5	22.4	28.3	22.4	25.0	24.5	25.0	23.3
3	23.6	22.4	28.3	23.2	24.5	23.7	23.3	23.3
4	23.2	21.9	26.6	21.5	24.1	25.8	25.0	23.7
5	22.8	23.2	29.2	24.0	26.2	22.9	21.6	24.1
6	23.2	22.8	28.7	23.2	26.2	23.7	23.3	23.7
7	23.6	21.9	28.7	23.2	24.5	23.3	22.9	23.7
8	23.2	21.9	28.7	23.2	24.5	23.3	24.5	23.7
Avg	23.4	22.4	28.2	23.1	24.9	24.0	23.9	23.7
Mean Standard Deviation	0.51	0.49	0.91	0.82	0.86	0.93	1.38	0.30
Amount of SOM Used, g	10	20	5	54	60	6	24	150
Type Oil Used	←Crude Oil→ (North Louisiana paraffinic-based crude oil)				←Diesel Oil→			

PART III: SINKING EFFICIENCY

19. The sinking efficiency of any SOM is, for purposes of this investigation and the resulting method of test, the ratio of the weight of oil sunk to the weight of sinking agent used. This ratio is intended to reflect the practical sinking efficiency of sinking agents under various laboratory conditions. It will not necessarily be a measure of the sinking effectiveness of SOM's under actual field conditions, but should, as laboratory tests in other areas of engineering endeavor to do, offer excellent opportunity for correlation with field performance capability.

20. Initially, it was felt that several factors would contribute significantly to the variation in interaction of the individual SOM with a particular oil: (a) rate of application of SOM, (b) system temperature, (c) initial oil film thickness, (d) nature of oil film, i.e. fresh or weathered, and (e) nature of fluid surface, i.e. calm or agitated. Influences of these factors are discussed in the following paragraphs.

Rate of Application of SOM

21. The investigation conducted to determine the effects, if any, of variation in rate of application of a SOM on sinking efficiency consisted merely of determining the sinking efficiency of several representative SOM's on various oils with each SOM being uniformly applied at rates ranging from 2.5 to 160 g/min. These sinking efficiency tests were conducted in accordance with the method of test presented in Appendix B.

22. As indicated graphically in fig. 7, variation in rate of application of sinking agents (within the ranges examined) appeared to have no appreciable effects upon sinking efficiency. The slight variations in test results for a particular oil and sinking agent were experimental errors. It should be noted that the slopes of all least squares fit lines are essentially zero.

23. Based on these pilot tests, the standard rate of application incorporated into the test method was suggested to be a rate such that the actual test operation, i.e. application, sorption, and sinking, be

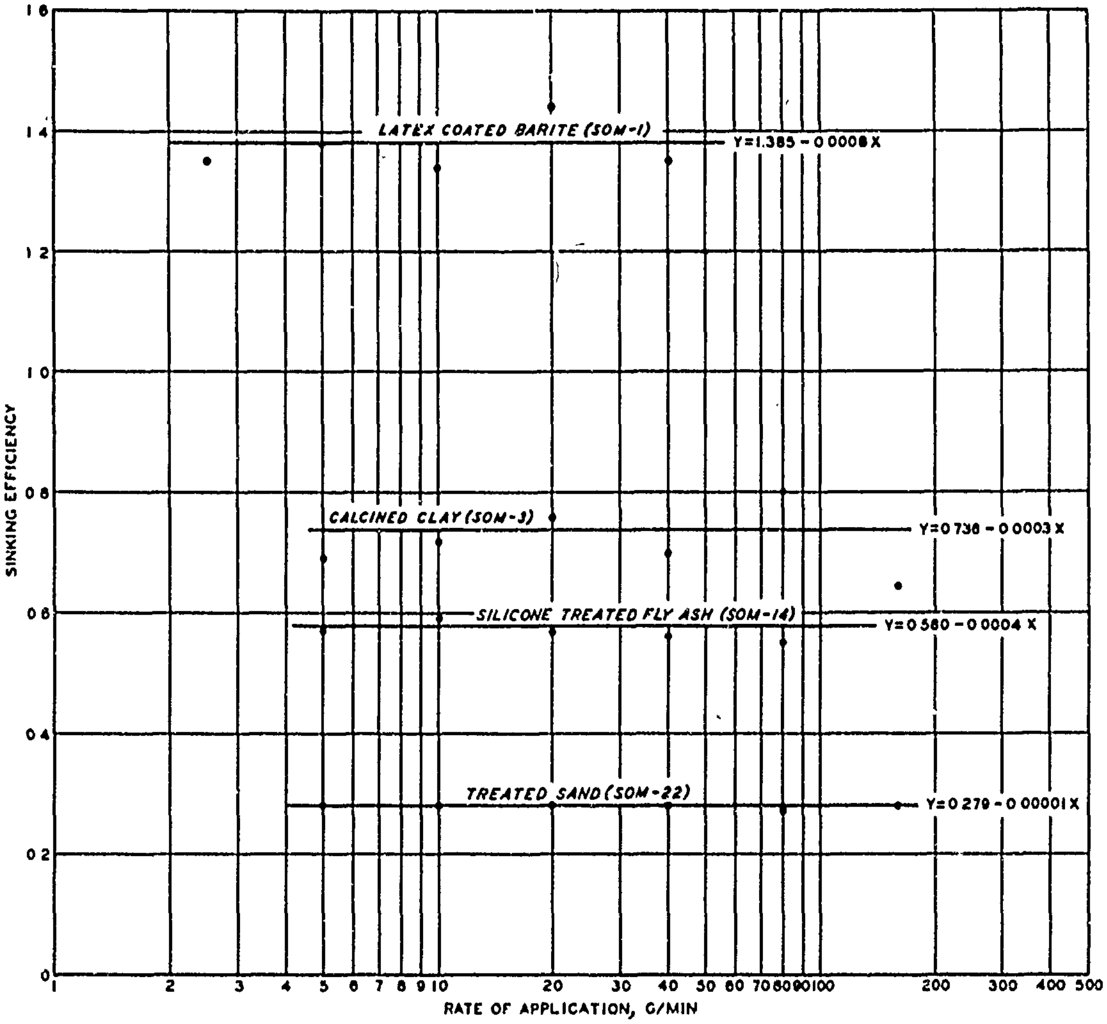


Fig. 7. Sinking efficiency versus rate of application

completed in a time interval of 5 to 10 min. This type of criterion provides for relatively uniform periods of time for sorption for all SOM's.

System Temperature

24. Variation in system temperature was found to have a significant effect, in most instances, upon the sinking efficiency of the various materials applied to various oils. Particular difficulties were encountered when attempting to conduct sinking efficiency tests in the lower temperature ranges with the more viscous oils. Pilot tests conducted at 60 F using a heavy crude oil (Venezuelan crude) indicated that the viscosity of this oil became so great at this temperature that the oil film acted as a semisolid

film, which very few SOM's could penetrate. Tests conducted at 40 F on this heavy crude revealed that none of the SOM's involved in this investigation were effective at such low temperatures.

25. The effects of variation in system (air, water, oil, SOM) temperature on the sinking efficiency of a particular material with a specific oil can be examined with the aid of a variable-temperature room. It should be noted that temperature of the oil defines precisely the viscosity and specific gravity of the particular oil in use, and, therefore, variation in system temperature will also reflect the effects of variation in viscosity and specific gravity of the oil in use.

26. A series of tests using temperatures of 40, 60, and 80 F should be adequate to reveal the effects of variation in system temperature on sinking efficiency for a specific oil and SOM. All materials involved in the testing should be brought to test temperature equilibrium prior to the actual test. The effect of variation in system temperature on the sinking efficiency-film thickness relations for calcined clay (SOM-3) is illustrated in fig. 8.

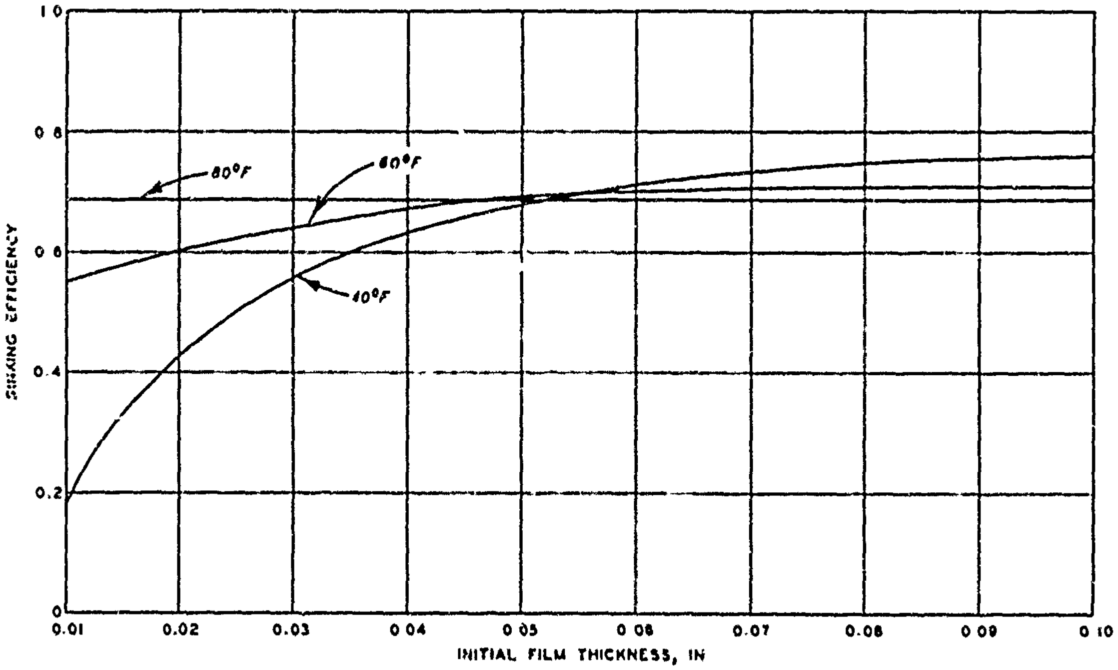


Fig. 8. Effects of variation in system temperature on sinking efficiency-film thickness relations; calcined clay (SOM-3) applied to light crude oil (South Louisiana naphthenic-based crude)

27. It should be kept in mind that the incorporation of system temperature as a variable is tantamount to varying the viscosity and density of the particular oil involved. For a defined temperature, the viscosity and density of a particular oil are established and to include these two parameters under the guise of "independent" variables would be a waste of time and effort. Should the relation between viscosity (or density) and sinking efficiency for a particular oil and sinking agent be desired, the temperature-viscosity relation can be determined for that oil and then used to convert the temperature-sinking efficiency relation.

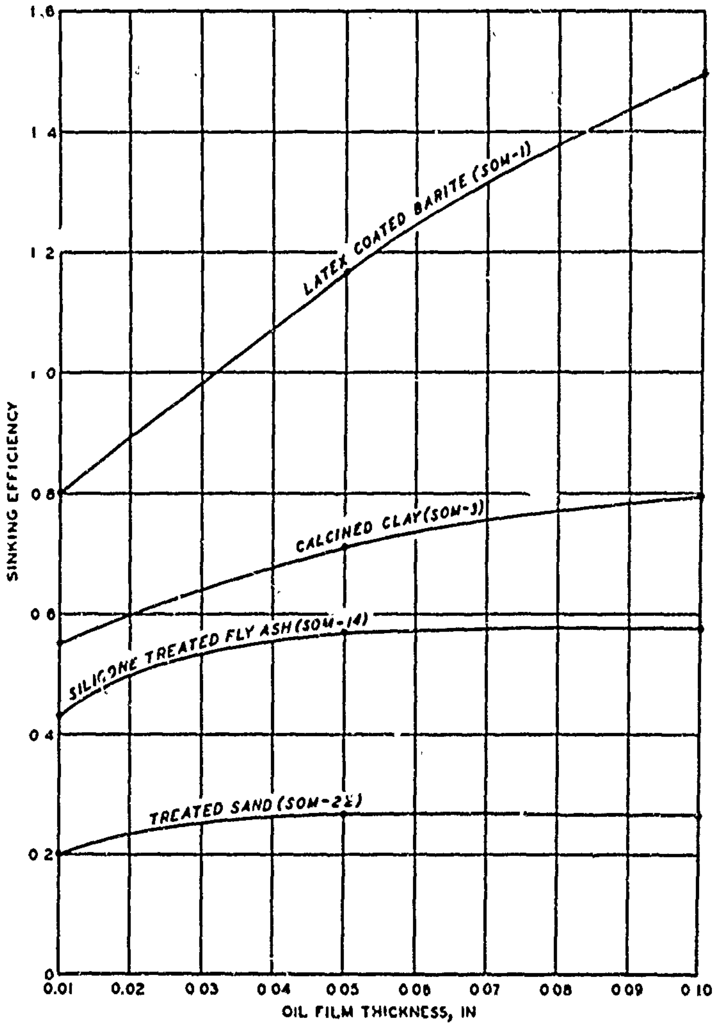


Fig. 9. Effects of variation in oil film thickness on sinking efficiency at 73 F

Initial Oil Film Thickness

28. Effects of variation in initial oil film thickness on sinking efficiency of a particular sinking agent can be evaluated by testing several beakers containing oil films of different thicknesses. System temperature, surface condition, rate of application, and nature of oil film (fresh or weathered) should be kept constant. A series of three tests using oil film thicknesses of 0.01, 0.05, and 0.10 in. should indicate the relation between initial film thickness and sinking efficiency. Results of such tests at laboratory test conditions are illustrated in fig. 9.

Nature of Oil Film, Fresh or Weathered

29. Tests can be conducted with both fresh and weathered oils to illustrate the changes in behavior of the oil and changes in oil-sinking agent interaction due to changes in viscosity and specific gravity brought about by the escape of volatile fractions. Relations between oil film thickness and sinking efficiency for tests conducted using fresh and weathered samples of the same oil are illustrated in fig. 10.

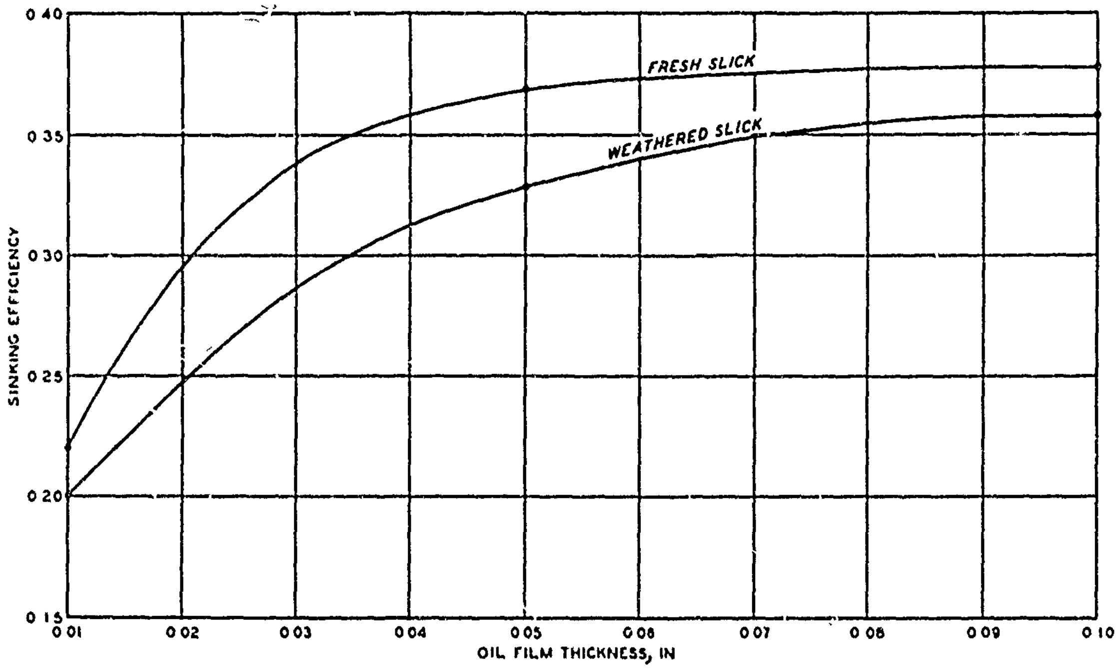


Fig. 10. Sinking efficiency versus oil film thickness; fresh and weathered versions of same light crude oil (oil 2 and SOM-22 at 73 F)

Surface Condition, Calm or Agitated

30. Investigation of the effects of surface agitation upon sinking efficiency was, of necessity, rather limited in this program. Due to the variety of types and intensities of agitation, a thorough investigation would require extensive financial support and considerably more time than was available to this investigation.

31. The nature of the surface agitation examined during the

Fig. 11. Oil film surface during agitation

formulation of the sinking efficiency test method is illustrated in fig. 11. This agitation was produced by a variable-frequency vibrating table which caused surface agitation without causing any significant degree of fluid circulation below the liquid-air interface. This characteristic was quite desirable since, if currents were produced along with the surface agitation, the resulting variation in sinking efficiency, if any, could not be attributed to surface agitation alone, but rather to a combination of surface agitation and fluid currents.

32. Another important aspect of the surface agitation produced was the absence of any physical discontinuities in the oil film itself. That is, the degree of agitation was not great enough to expose the underlying water at any point. While this degree of agitation naturally precludes the simulation of such violent surface conditions as would sometimes exist in the wake of a ship or where waves are actually breaking, it is necessary if the introduction of effects due to a second variable is to be avoided. In particular, since initial film thicknesses were computed from known oil densities and surface areas, any open breaks in the oil film would result in the introduction of unknown initial film thickness as another influencing factor, the effects of which could not be readily separated from those of the agitated surface condition.

33. Several pilot tests conducted with oils and sinking agents and sorbents representative of those to be investigated in this program

indicated that surface agitation of this nature resulted in no discernible change in the sinking characteristics of the systems examined. This conclusion is evidenced by the series of photographs shown in figs. 12 through 21. Each pair of photographs represents the results of two sinking efficiency tests, one (upper photograph) conducted under calm surface conditions, the other (lower photograph) conducted under agitated surface conditions.

Reproducibility of Results

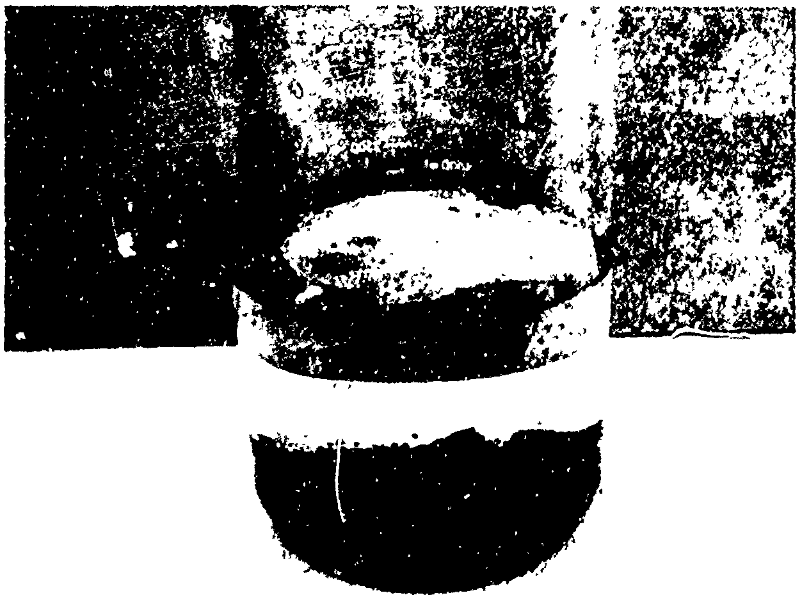
34. To indicate the reproducibility characteristics of the method of test for determination of sinking efficiency of sinking agents, three laboratory personnel conducted tests, individually, of identical materials under identical laboratory test conditions. The results of these tests are tabulated below and indicate rather good reproducibility, even when test personnel are rotated. In particular, for a series of three tests, the maximum deviation from the mean of the results of the three tests seldom exceeded 5 to 6%.

Material Used	Oil Film* Thickness in.	Weight of SOM Required, g Technicians A	B	C	Mean	Maximum Deviation from Mean, %
SOM-1	0.01	5.4	4.8	5.1	5.1	5.9
	0.05	17.4	18.1	16.4	17.3	5.2
	0.10	26.5	26.3	28.1	27.0	4.1
SOM-3	0.01	7.8	7.5	7.0	7.4	5.4
	0.05	30.1	27.8	28.2	28.7	4.9
	0.10	51.4	52.0	49.0	50.8	3.5
SOM-14	0.01	10.3	9.7	8.9	9.6	7.3
	0.05	34.4	35.4	37.8	35.9	5.3
	0.10	66.9	72.0	72.6	70.5	5.1
SOM-22	0.01	22.9	18.6	20.0	20.5	9.3
	0.05	80.5	74.4	72.6	75.8	6.2
	0.10	158.2	148.6	145.7	150.8	5.0

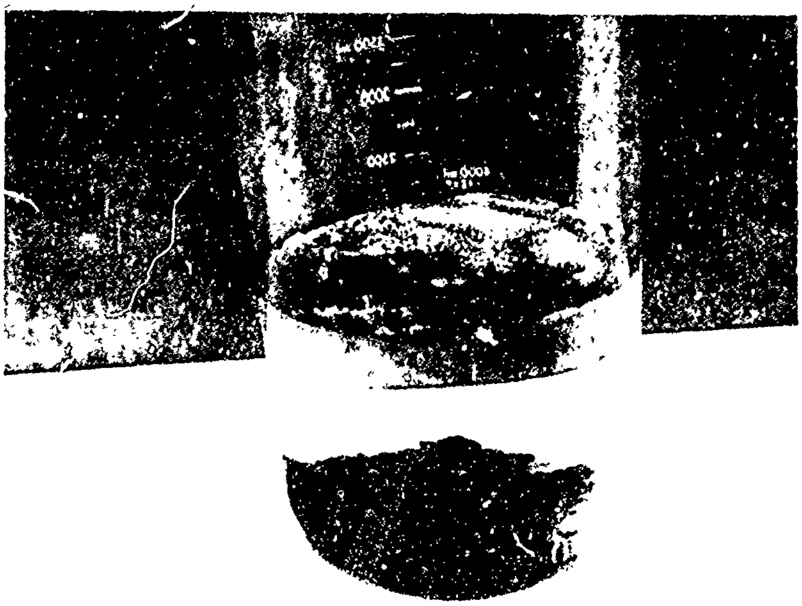
* Light crude oil (North Louisiana paraffin-based crude).

General Comments

35. The test procedure developed for sinking efficiency is given as



a. Calm surface



b. Agitated surface

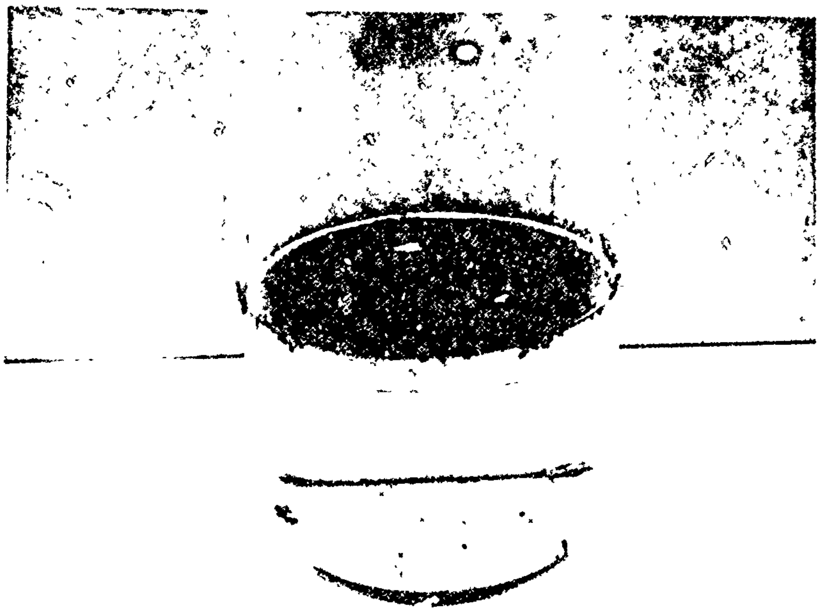
Fig. 12. Treated sand (COM-22) applied to light crude oil
(North Louisiana paraffin-based crude)

a. Calm surface

b. [illegible]

Fig. 13. Silicone treated fly ash ([illegible]) applied to light crude oil (North Louisiana paraffin-base [illegible])

a. Calm surface



b. Agitated surface

Fig. 14. Calcined clay (CM-3) applied to light crude oil (North Louisiana paraffin-based crude)

a. Calm surface

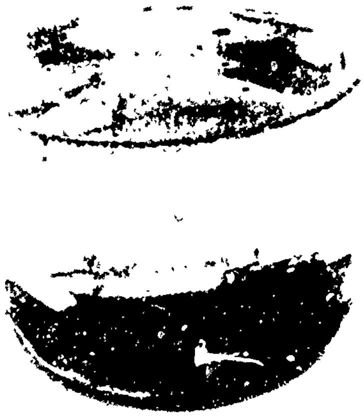
b. [illegible]

Fig. 15. Untreated [illegible] oil
([illegible])

a. Calm surface

b. Agitated surface

Fig. 1[illegible] . Hydrophobic [illegible] ([illegible] M-3) applied to light crude oil (North Louisiana paraffin-based crude)



a. Calm surface

b. [illegible]

Fig. 17. [illegible] applied to diesel oil

a. Calm surface

b. Agitated surface

Fig. 18. Calcined clay (SOM-3) applied to diesel oil

a. Calm surface

b. [illegible] surface

Fig. 19. Ground by-product ([illegible]) applied to diesel oil

a. Calm surface

b. Agitated surface

Fig. 20. Silicone treated fly ash (SCM-1[illegible]) applied to diesel oil

a. Calm surface

b. Agitated surface

Fig. 21. Latex coated barite ([illegible]M-1) applied to diesel oil

Appendix B. The actual conduct of a test to determine the sinking efficiency of a sinking agent is not unusually involved or complicated, but does require the undivided attention of the personnel performing the test. A tendency to apply more material than necessary to sink 90% of the floating oil has been observed, but with some experience and the exercising of good judgment this problem can easily be overcome.

36. It is particularly important to note that this test is directed toward the determination of the sinking efficiency of a particular sinking agent applied to a designated oil film and is not intended to reflect the retention characteristics of the material used. Also, materials such as sorbents, which do not sink oil, will not meet the minimum requirements of the test as they will not cause 90% of the oil to sink.

PART IV: DYNAMIC RETENTION CAPABILITY

37. Retention capability is defined as the ability of the oil-sinking agent mass to retain its oil after sinking. This is expressed as the ratio of the weight of oil retained to the weight of sinking agent used. Dynamic retention capability is the retention capability determined under dynamic conditions, i.e., the oil and sinking agent are placed on a moving water surface. The dynamic retention capability of a particular sinking agent is also expressed as the ratio of the weight of oil retained to the weight of sinking agent used. The tests which were developed (see Appendixes C and D) were directed toward the determination of the relations existing between the dynamic retention capability of a particular sinking agent and time elapsed since sorption. Both the actual testing and the physical sorption process undergone prior to conduct of the test are carried out under a defined set of standard laboratory conditions.

38. This test will not necessarily indicate the retention-time relations that would exist under actual field conditions. This is to be expected, however, since it would be virtually impossible to model the many extreme bottom conditions present on the ocean floor at depths over which the use of sinking agents is limited.* The test should, however, illustrate general behavior and possibly offer, as do many laboratory tests in other areas of engineering endeavor, opportunity for correlation with field performance characteristics.

Flow Channel for Current Simulation

39. The flow channel devised for simulation of fluid currents is shown in fig. 22. The circular channel itself was constructed of transparent plastic. Channel dimensions were: depth, 12 in.; width, 12 in.; and radius of tank, 24 in. Currents are produced by rotation of the circular channel (driven by variable-speed electric motor). The screen baffles

---

* National Oil and Hazardous Materials Pollution Contingency Plan, Annex X, June 1970.

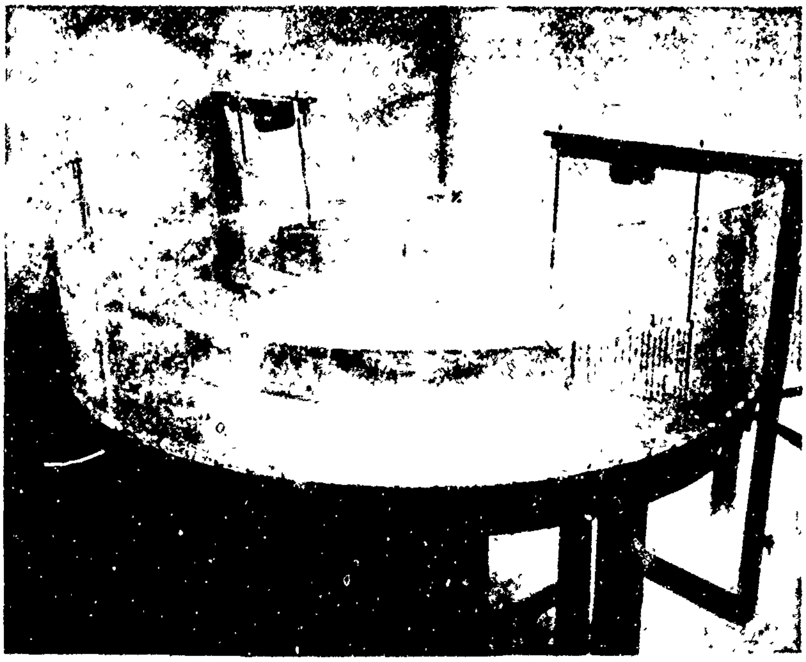


Fig. 22. Circular channel for simulating current flow

suspended in the tank impede the tendency of the fluid to flow with the tank, thus resulting in a relative channel flow in a direction opposite the direction of rotation of the channel.

40. The circular channel, as opposed to a common rectangular flume, offers several distinct advantages in this test. Most important is that of simplification of released oil recovery. Oil released from submerged oil-sinking agent masses may not, depending upon the density of the soil being examined, surface immediately. In these instances, the use of a rectangular flume would require a collection device capable of efficiently collecting submerged oil if this oil is not to be lost, prior to surfacing, in the baffled end of the flume. The circular tank eliminates the need for such an involved collection technique, since the channel is essentially "infinite" in length. Other advantages of the circular channel over the common rectangular flume are: size (requires less floor space) and economics of operation (requires less fluid, no danger of pump corrosion from salt water).

41. The major disadvantage of the circular channel stems from the centrifugal forces exerted on the fluid and floor materials due to rotation

of the tank. These forces result in nonuniform channel velocities. These current irregularities are not, however, felt to be very important at the velocities of interest, particularly since much more extreme irregularities would exist along the ocean floor. Moreover, various types of baffles can be used to reduce the degree of flow irregularity.

Factors Influencing Retention

42. Of the many factors which probably contribute to the degree of oil release from particular submerged oil-sinking agent masses, the most important are believed to be:

- a. Fluid velocity (including nature of currents, whether laminar or turbulent).
- b. Bottom topography.
- c. Nature and composition of floor material on which oil-sinking agent mass rests.
- d. Temperature.
- e. Quantity of oil sorbed with reference to the individual sinking agent's maximum efficiency.

43. The factors to be examined in this study, and thus expressly included in the method of test, are fluid velocity and nature and composition of floor material. This does not preclude evaluation of the effects of other parameters should this be desired.

PART V: CONCLUSIONS

44. The nature of this phase of this investigation is such that the bulk of the conclusions, i.e., the test methods formulated, have already been presented in Appendixes A through D. As with any other test procedures, it is imperative that the procedures developed in this investigation not be accepted as the best possible. They are felt to be the best possible in light of the limitations in time and financial support and the infancy of the area of investigation itself. Each of the methods developed should, however, be subjected to the continuous refinement and improvement which should become available through their use.

Recommendations

As mentioned previously, the methods of test developed during this investigation and presented herein do not encompass all of the many parameters which should be examined. Such an elaborate undertaking would have required time and financial support many times the magnitude of those available to this study. Further investigation is therefore recommended in the following areas:

a. Effects of variation in pressure on the behavior of submerged oil-sinking agent masses. This, it seems, would be imperative as the National Contingency Plan limits use of sinking agents to areas where depths are greater than or equal to 100 m.

b. Effects of variation in temperature, ocean floor topography, nature of fluid currents, and percentage of sorption capacity of sinking agent actually taxed during the sorption process upon retention characteristics of the submerged oil-sinking agent mass.

c. Effects of the many various types of agitation, above and beyond that examined in this study, upon sinking efficiency and retention.

d. The testing and sinking of highly viscous residual fuel oil (Bunker C).

e. Development of procedures to evaluate the retention characteristics of a submerged oil-sinking agent mass which is the product of realistic sinking agent application and sinking (material will not act at 100% efficiency) as opposed to the method of mixing and submerging (required to approach the 90% efficiency level specifically requested) used in the method of test presented in Appendix B of this report.

f. Refinement of the test methods developed in this investigation.

a. Test material (sinking agent or sorbent). (abbreviated SOM)

b. Oil (30 g).

c. ASTM substitute ocean water (ASTM designation: D-1141, Section [illegible]) or distilled water.

d. Surfactant-Isomal 265 (Johnson-March Corp., Philadelphia, Pennsylvania).

e. Petroleum jelly.

Procedure

4. Method A (for sinking agents):

a. The inside of each flask and graduated cylinder (fig. A1) to be used should be coated with a solution of one part Isomal 265 mixed with ten parts of water (by volume). After coating, the glassware should be oven dried at approximately 175 F for at least 2 hr. This treatment minimizes the tendency of the surfacing oil to adhere to the sides of the flask and cylinder and thus reduces the degree of inaccuracy of the test results. Allow glassware to cool to 73 F.

b. Weigh the flask to nearest 0.01 g (cylinder removed), add the SOM, and reweigh the flask. The final weight minus the initial weight will indicate the weight of SOM being used. The proportions of oil to SOM required to yield approximately 10 cc of free oil should be used. This volume of free oil is needed to allow for test variation within the range of volume of free oil released. Thirty grams of oil should be used in each test. A preliminary screening test to indicate the weight of a given SOM suitable for use with 30 g of a given oil can be made by placing 30 g of the oil in a 400-ml beaker, adding SOM to the oil from a preweighed container until the oil-SOM mass starts to thicken, lose gloss, or become viscous. At this point the mass should be stirred, water should be added, and the mass stirred an additional 30 sec. After the mixture stands for 10 to 15 min, the extent of surface oil will indicate whether too much or too little SOM has been used. The weight of SOM used can be determined by difference in the initial and final weighings of the container plus SOM. Additional screening tests with necessary adjustments should be conducted which will minimize work and time required to obtain the test results.

c. Add the 30 g of oil to the flask. This step may be simplified by use of the hypodermic syringe which will minimize the amount of oil brought into contact with the sides of the flask during this step of the operation. The balance may be used to indicate the point at which the required weight of oil has been added.

d. Use a rubber stopper to seal the flask and shake for 15 min with a Burrell shaker, adjusting the motion of the shaker as necessary to obtain good distribution of oil throughout the SOM. Several flasks may be shaken simultaneously, depending upon the

APPENDIX A

PROPOSED METHOD OF TEST FOR DETERMINATION OF OPTIMUM OIL RETENTION POTENTIAL OF SINKING AGENTS OR SORBENTS FOR OIL

Scope

1. This proposed method of test covers procedures for determining the optimum oil retention potential of a sinking agent or sorbent. This test measures the ability of a material to retain sorbed oil when submerged. A sinking agent for oil is defined as a material that, when applied to floating oil, sorbs (adsorbs and/or absorbs) oil and sinks with the oil, thus removing oil from the surface. A sorbent for oil is a material that, when applied to floating oil, sorbs (adsorbs and/or absorbs) oil but does not sink; oil and sorbent both remain on the surface. Optimum oil retention potential is the optimum capacity of an oil-sinking agent or oil-sorbent mixture to retain oil while submerged. It is expressed by the oil:SOM ratio (oil:sinking agent or oil:sorbent ratio) used.

Apparatus

2. The testing apparatus shall consist of the following:

a. 250-ml Erlenmeyer flask with ground joint.

b. 25-ml graduated cylinder with ground joint (units a and b to be used as indicated in fig. A1).

c. 400-ml beaker.

d. Variable-frequency vibrating table.

e. Balance sensitive to 0.01 g.

f. Burrell shaker.

g. 30-ml hypodermic syringe and needle (gage of needle should be determined so as to allow for easy but controlled flow of the particular grade of oil to be used).

h. Glass stirring rod.

i. Small-diameter plastic or rubber hose.

j. Funnel (small).

k. Vacuum apparatus (see fig. A2).

l. Rubber stopper for Erlenmeyer flask.

Materials

3. Materials used in this method are:

capacity of the individual shaker. In any event, if test results are to be comparable, each test (or set of tests) must be performed under the same conditions. If necessary, the contents of each flask may be stirred to ensure that all portions of the SOM have been brought into contact with the oil. This will be particularly necessary when the more viscous oils are being evaluated. Care should be taken, however, to prevent any unnecessary contact between the oil-SOM mass and the uppermost sides of the flask.

e. Apply 30-in. mercury vacuum (fig. A2) until such time as there is no loss in vacuum over a 5-min period of time.

f. Allow flask to stand for a period of time such that the total time elapsed in steps e and f is 1 hr.

g. Vibrate the stoppered flask for 30 min, adjusting the frequency of the vibrating table as necessary. Several flasks can be vibrated simultaneously; however, the vibratory motion of the table will have to be adjusted in order to accommodate the additional weight. It is emphasized, however, that if test results are to be comparable all tests must be performed under the same conditions. This step is particularly important in that it results in release of the free oil which is entrapped between solid particles and is not actually sorbed (absorbed and/or adsorbed). This consolidation process improves the reproducibility of test results, particularly for the coarser materials.

h. Remove stopper and affix the graduated cylinder in the top of the flask. The quality of the seal can be improved by coating the ground glass surfaces with petroleum jelly.

i. Add enough ASTM substitute ocean water to the flask-cylinder system to bring the free oil surface level to the 0.0-ml mark. The water should be added in such a manner as to minimize disturbance of the oil-SOM mass and minimize emulsification of the free oil. This can be facilitated by using a flexible rubber or plastic tube and funnel as illustrated in fig. A3. This will minimize the free-fall distance and disturbance. Care must be exercised to prevent the lower end of the tube from coming into contact with the rising liquid surface, since some of the oil would become attached to the tube.

j. Determine, by use of the cylinder graduations, the volume of free oil released. This measurement should be made to the nearest 0.5 ml and should include any sorbent which is suspended in the free oil column. Since test method A is designed to evaluate sinking agents, it is felt that this procedure would adequately penalize any materials which do not act fully as sinking agents. These readings should be made 2 hr after the addition of the water and 18 hr after the addition of the water. In most instances, volumetric differences between the 2- and

18-hr readings will be negligible. However, for certain materials, particularly the expansive clays and some oils, the differences will be substantial. In these cases, both readings should be reported and the 18-hr reading should be used to compute the optimum SOM retention potential.

k. Multiply the volumetric measurement of oil in cubic centimeters by the specific gravity of the oil used (determined at 73 F) to yield the weight in grams of free oil. Subtract this weight from the original weight of oil added to the flask to obtain, in grams, the weight of oil effectively sorbed and retained.

l. Divide the weight of oil adsorbed and/or absorbed by the weight of test material used to obtain the optimum retention potential expressed as an oil:SOM ratio. Any interesting or unusual items, such as volume of floating sorbents, should be noted in the test results. This test should be repeated at least three times for each individual oil and test material used and the results averaged.

5. Method B (for powdered materials):

a. Conduct test as described in method A, paragraphs a through g. The amount of sorbent used (see paragraph b, method A) should, in the end, be such that no free oil and/or oil-sinker mass floats to the surface upon addition of water to the flask. Several tests will probably be necessary to determine the optimum weight of sorbent required. (It should be kept in mind that while many different amounts of the same sorbent may be sufficient to retain the particular amount of oil used, there is a minimum amount of sorbent which adequately retains the oil. It is toward the determination of this minimum weight of sorbent that this test is directed.)

b. Allow the entire system to stand for 18 hr. Should, at any time during this 18-hr period, any appreciable volume (more than a trace) of free oil and/or oil-SOM mass rise to the water surface, repeat the test using slightly less sorbent than was previously used. Continue testing in this manner until the weight of sorbent which will yield only a trace of free oil and/or oil-SOM mass on the water surface is determined and verified by at least two additional tests.

c. Divide the weight of oil used by the minimum weight of sorbent used (the minimum weight which will satisfactorily retain the oil in the bottom of the flask) to obtain the optimum potential expressed as an oil:SOM ratio.

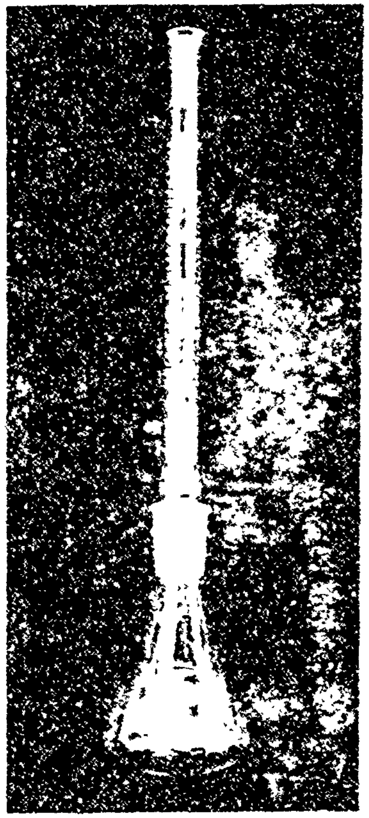


Fig. A1. 250-ml Erlenmeyer flask equipped with graduated cylinder

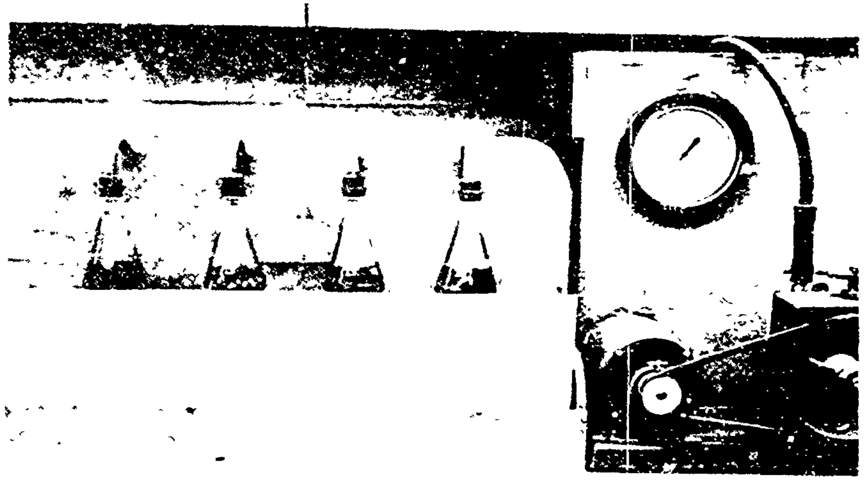


Fig. A2. Oil-SOM mixtures being subjected to entrapped air evacuation in vacuum apparatus

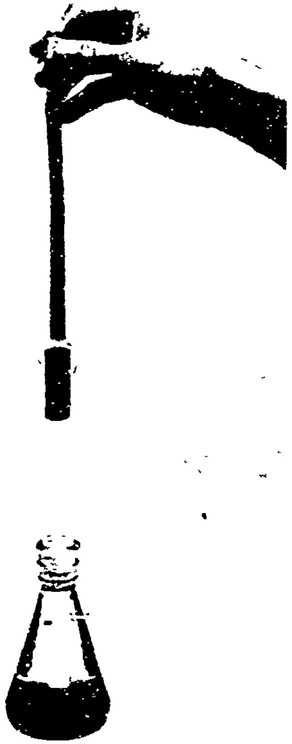


Fig. A3. Addition of water to 250-ml Erlenmeyer flask-graduated cylinder assembly

APPENDIX B

PROPOSED METHOD OF TEST FOR EVALUATION OF THE SINKING EFFICIENCY OF SINKING AGENTS FOR OIL (DRY APPLICATION)

Scope

1. This proposed method of test covers a procedure for evaluating the sinking efficiency of sinking agents for oil. A sinking agent for oil is a material that, when applied to floating oil, sorbs (adsorbs and/or absorbs) oil and sinks with the oil, thus removing oil from the surface. Sinking efficiency is the ability of a material to act as a sinking agent for an oil film on water. Sinking efficiency is expressed by the oil:sinking agent ratio (by weight) required to sink at least 90% of the oil film which is at the surface of an oil-water mixture. A material which does not sink oil, such as a sorbent, has no sinking efficiency and does not meet the minimum requirement for this test.

2. Of the many different factors which contribute to the interaction of an individual sinking agent with a particular oil, the most important are: (a) system temperature, (b) initial oil film thickness, and (c) nature of oil film (fresh or weathered). All of these factors should be examined in order to adequately evaluate the performance of various sinking agents when used with various types of oils.

Apparatus

3. The testing apparatus shall consist of the following:

   a. Stirring rod.

   b. 4000-ml beaker (Griffin low form, Pyrex).

   c. Balance sensitive to 0.01 g.

   d. 10-cc hypodermic syringe and needle (gage of needle should be determined so as to allow for easy but controlled flow of the particular grade of oil to be used).

   e. Device for controlling application of sinking agents (see fig. B1).

   f. Variable-temperature water bath or variable-temperature room.

   g. Timing device.

Materials

4. Materials used are:

   a. Test material (sinking agent or sorbent).

   b. Oil.

   c. ASTM substitute ocean water (ASTM designation: D-1141, Section 4).

   d. Oil-soluble dye (for use with nearly transparent oils).

Procedures

5. Test procedures are as follows:

   a. Bring components of the test apparatus and test materials to equilibrium at the designated test temperature. This will best be accomplished with a variable-temperature control room in which the entire testing operation can be performed. If desired, a water bath can be used in conjunction with a variable-temperature room to perform tests at air temperatures somewhat different from the fluid system temperature.

   b. Add 2000 ml of water to the 4000-ml beaker. At this level, the cross-sectional area of the water surface in the standard Griffin low form Pyrex beaker is 194.8 cm^2. Weigh the beaker and water to the nearest 0.01 g.

   c. Add oil to the water surface, the volume (weight) of which will be dictated by the particular oil film thickness desired, the type of oil used, and the system temperature at which the test is to be performed. The weight of oil required can be computed from the known surface area and the known density of the oil at the particular temperature of interest. If necessary, an oil-soluble dye can be used in conjunction with the oil to help eliminate problems of visually determining when the oil slick has been effectively sunk. Place the beaker in position for application of the sinking agent through the application device (see fig. B1).

   d. Sprinkle the sinking agent through the top of the sorbent application funnel. This apparatus is designed simply to ensure that (1) all tests are conducted using the same free-fall distance (30 in.) for each SOM, and (2) all SOM's applied actually fall on the fluid surface.

      The SOM should be applied uniformly and at a constant rate until barely enough material has been applied to effectively sink 90 to 100% of the oil. The time elapsed during the actual application-sorption-sinking operation should not exceed 10 min and should not be less than 5 min.

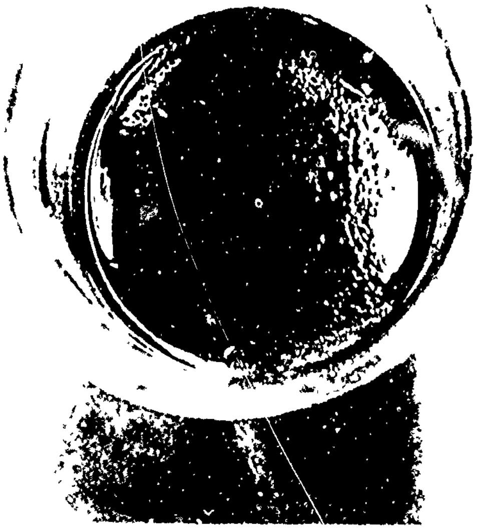
      In all instances, some if not all of the oil-sinking agent mass will float until significant agitation is applied. This can be accomplished by stirring the system vigorously after the sinking agent has been applied. The stirring should not be so violent as to emulsify any free oil.

This phase of the test procedure requires some experience and good judgment on the part of the test personnel in that, with most materials not sinking until after vigorous agitation is applied, a decision must be made as to when barely enough material has been applied to effectively sink 90 to 100% of the oil. In the majority of cases, it can be safely assumed that this point has been reached when the fluid surface is no longer glossy as it is when appreciable free oil is present. Fig. B2 illustrates these conditions.

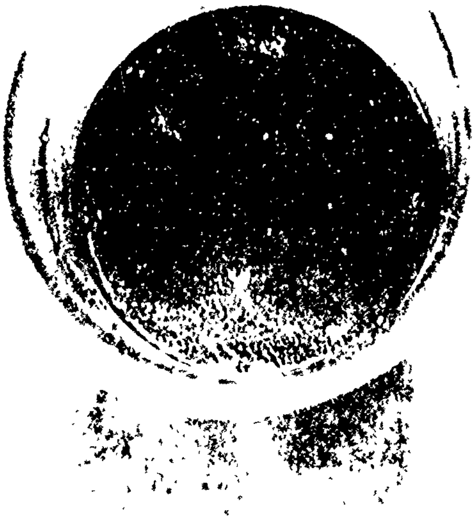
e. Sinking efficiency of the sinking agent used is, in each case, computed by dividing the weight of oil sunk by the weight of the sinking agent required to sink the oil. The test should be conducted three times and the results of the three tests averaged. Any pertinent observations such as oil release (see note) with time should be noted with the test results.

Note: If long-term oil release measurements are desired, a glass funnel with a graduated stem may be placed over the sunken oil-sinking agent mass and the volume of oil release may be measured for as long as desired.

Fig. B1. Device to aid in controlling application of sinking agents



a. Amount of sinking agent insufficient for total sinking



b. Amount of sinking agent [illegible] sufficient for [illegible]

Fig. B2. Typical appearance [illegible] slick surface after application [illegible] agent.

APPENDIX C

PROPOSED METHOD OF TEST FOR DETERMINATION OF DYNAMIC RETENTION CAPABILITY OF SINKING AGENTS FOR OILS

Scope

1. This proposed method of test covers a procedure for determining the dynamic retention capability of a sinking agent for oil. Retention capability is defined as the ability of the oil:sinking agent mass to retain its oil after sinking. This is expressed as the ratio of the weight of the oil retained to the weight of sinking agent used. Dynamic retention capability is the retention capability determined under dynamic conditions, i.e., the oil and sinking agent are placed on a moving water surface. A sinking agent for oil is defined as a material that, when applied to floating oil, sorbs (adsorbs and/or absorbs) oil and sinks with the oil.

2. Factors which will affect the retention capabilities of the various sinking agents and the effects of which should be examined are: (a) fluid velocity and (b) bottom conditions (sand, mud, rock, etc.).

Apparatus

3. The testing apparatus shall consist of the following:

a. Circular flow channel for simulation of current flow (see fig. C1).

b. Current meter (see fig. C2).

c. Variable-frequency vibrating table.

d. Balance sensitive to 0.01 g.

e. 400-ml beaker.

f. 10-cc hypodermic syringe and needle (gage of needle should be determined so as to allow for easy but controlled flow of the particular grade of oil to be used).

g. Weighing pan (aluminum pie plate).

Materials

4. Materials to be used are:

a. Sinking agent.

b. Oil.

c. ASTM substitute ocean water (ASTM designation: D-1141, tion 4).

d. Fine glass wool.

e. Bed material for bottom of channel (sand, mud, rock, etc).

Procedures

5\. Test procedures are as follows:

a. Place the bed material desired (sand, mud, or rock) in the circular flow channel. This bed material should be clean enough to prevent contamination of the water as such will result in collection of impurities along with the released oil. This in turn will cause the calculated weight of oil released (based on volatile loss-time relationships) to be too great.

b. Add ASTM substitute ocean water to the flow channel and allow the system to reach standard laboratory temperature (i.e., 73 ± 2 F).

c. Begin actual fluid flow (mechanical rotation of the circular channel in this case) and allow the currents to reach equilibrium. This step will require different periods of time for different fluid velocities and different types of channels. The point at which stabilization of velocity is reached can be determined with a current meter similar to the one pictured in fig. C2. After stabilization has been achieved, the velocity profile of the channel cross section should also be determined.

d. Place known amounts of sinking agent and oil (at standard temperature) in the 400-ml beaker, using the hypodermic syringe for the addition of the oil. The total amount of sinking agent and oil is determined by the cross section of the particular flow channel used, and the ratio (by weight) of the two components is determined by the amount of oil that the particular sinking agent will adsorb and/or absorb. This ratio should have been previously obtained in the determination of the optimum sorption retention potential of the sinking agent.

e. Place the beaker containing the sinking agent and oil on the vibrating table and vibrate for 45 min. The beaker should be covered appropriately during this operation.

f. Allow covered beaker to stand at standard laboratory temperature (73 ± 2 F) until all components are in temperature equilibrium. This standing time should not exceed 75 min.

g. Add the known weight of sinking agent-oil mass to the moving channel. Any residue left in the beaker should be weighed, this weight to be proportioned according to the original weights of sinking agent and oil mixed, and then subtracted from these original weights to yield the actual weights of materials subjected to test. (Example: Assume that 700 g of sinking agent was mixed with 300 g of oil and that 10 g of oil-sinking agent mass remained in the mixing container after the majority of the mass was added to the channel. Then by proportion of weights originally mixed, 7 g of sinking agent and 3 g of oil remained as residue in the container. Therefore, 693 g of sinking agent and 297 g of oil were added to the channel.)

h. Weights of oil released should be determined (according to step i) at points in time (with reference to initial immersion, i.e., addition of the oil-sinking agent mass to the channel) of t = 0, 1, 2, 3, 12, and 24 hr, and t = 3, 7, 14, and 21 days. Some of the later release measurements may be eliminated, obviously, if at some point it is observed that release is no longer occurring.

i. Determination of the weight of free unweathered oil floating on the surface at any time should be accomplished by removing this free oil, using the fine glass wool, driving off volatile fractions at a temperature and for a period of time determined by the type of oil being examined and by the volatile loss characteristics determined according to the "Proposed Procedure for Determination of Volatile Loss-Time Characteristics of Oil Retained on Glass Wool," and determining the weight of oil residue remaining after volatile evaporation.

j. This weight of oil residue should then be divided by a conversion factor previously determined according to the "Proposed Procedure for Determination of Volatile Loss-Time Characteristics of Oil Retained on Glass Wool," this computation yielding the weight of free unweathered oil released since the time of the previous collection of surface oil.

k. This weight of free unweathered oil collected should then be added to the weights of oil collected at the preceding times of removal. This total weight multiplied by 100 and then divided by the weight of oil placed in the channel as determined in step g of this test method will represent the weight of free unweathered oil released over the period of time, t , expressed as a percentage of the weight of free unweathered oil originally adsorbed and/or absorbed. Such time-release characteristics for a specific sinking agent, oil, and fluid velocity can be represented in graphical form as indicated in fig. C3.

l. The weight of oil retained is determined by subtracting the total weight of oil collected (see paragraph k above) from the weight of oil placed in the channel.

m. The dynamic retention capability is then computed by dividing the weight of oil retained by the weight of sinking agent used.

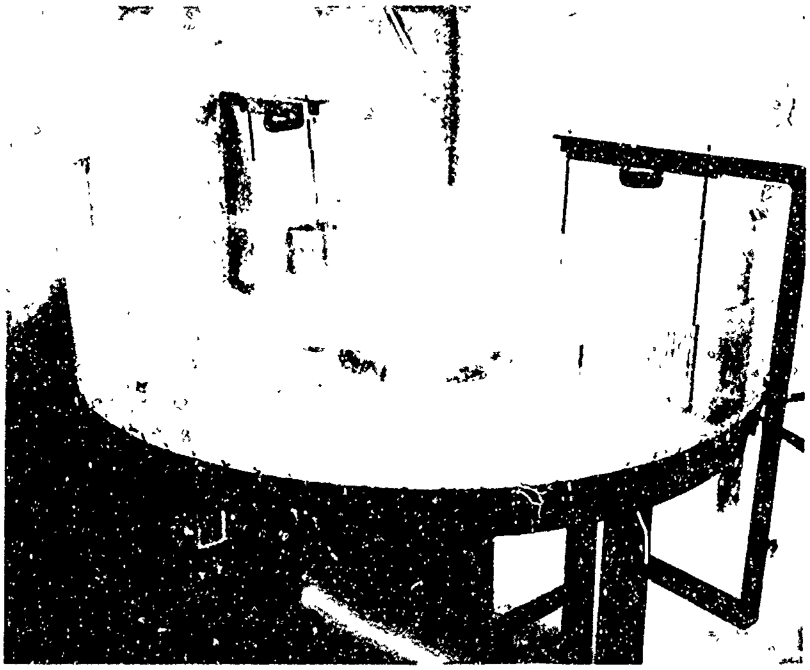


Fig. C1. Circular channel for simulating current flo

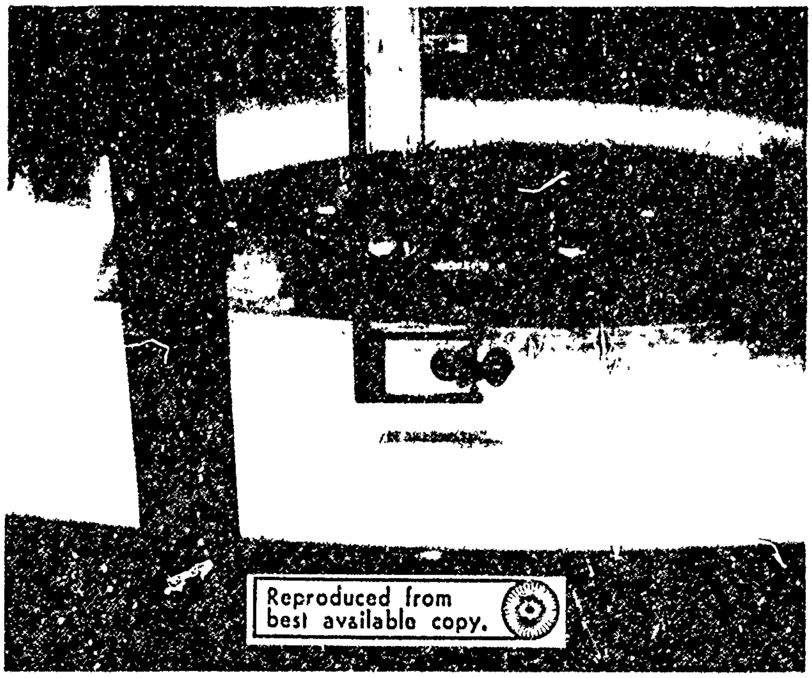


Fig. C2. Current meter

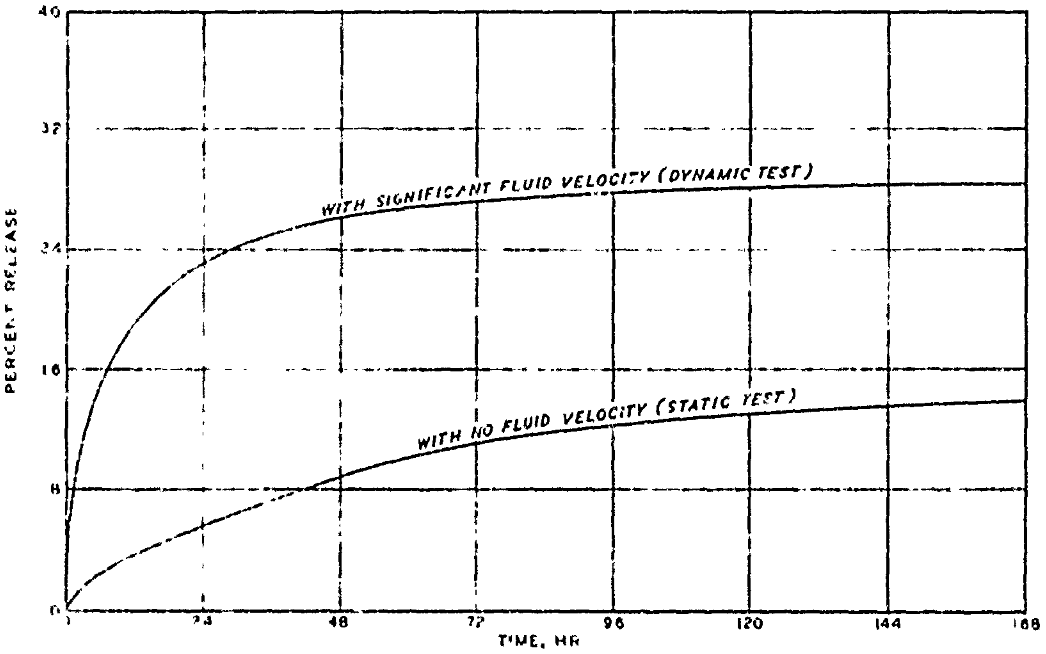


Fig. C3. Effects of fluid velocity on retention characteristics; percent release as a function of time

APPENDIX D

PROPOSED PROCEDURE FOR DETERMINATION OF VOLATILE LOSS-TIME CHARACTERISTICS OF OIL RETAINED ON GLASS WOOL

Scope

1. This test is intended to be used for calibration purposes, the resulting volatile loss-time relations to be used in the computation of the actual weights of unweathered free oil floating on a water surface.

2. The basic premise underlying this procedure is: if one determines, for a particular weight oil-water-glass wool combination and evaporation temperature, the volatile loss-time relation after total evaporation of the water component at low relative humidity, one can then use this relation to compute the weight of unweathered free oil removed from a system by evaporating the volatiles from this removed oil (at the same temperature and for the same evaporation period), determining the weight of the oil residue, and multiplying this weight by an appropriate factor based on the "calibration" test.

3. The accuracy of this operation is highly dependent upon using an evaporation period the length of which is great enough to ensure complete evaporation of the water component (usually less than 24 hr) and that the mathematical computations are based on the relatively flat portion of the residual oil volatile loss-time curve. It is also important that the evaporation temperature used, for a particular oil, be high enough so that equilibrium (no appreciable loss) is reached in a realistic period of time, and at the same time low enough so that enough residue is left to make reasonably accurate computations. In particular, diesel fuel must be treated at somewhat lower temperatures than those used for crude oils since total evaporation of diesel fuel will occur at the higher temperatures. Total evaporation would yield no useful data. Low humidity environment appreciably decreases the time required for water evaporation, and thus system equilibrium.

Apparatus

4. The apparatus used for this test are:

   a. Oven.

b. Weighing pan (aluminum pie plate).

c. Fine glass wool.

d. Large pan for containing water and oil film.

e. Balance sensitive to 0.01 g.

f. Desiccator.

Materials

5. Materials used in the test are:

a. Oil.

b. ASTM substitute ocean water.*

c. Oil-soluble dye.

Procedures

6. Test procedures are as follows:

a. Allow all materials to stabilize at standard laboratory temperature (73 ± 2 F).

b. Add ASTM substitute ocean water* to large pan.

c. Determine tare weight of aluminum pie plate and glass wool to nearest 0.01 g.

d. Place 10 g of fresh oil on the water surface and allow significant dispersion to occur.

e. Remove the free oil from the water surface by dragging the fine glass wool over the surface as illustrated in fig. D1.

f. Place all glass wool (contaminated and uncontaminated) in the weighing pan, weigh the system to the nearest 0.01 g, and place this unit in an oven or room (less than 30% relative humidity desirable).

g. Continue evaporation of volatiles at 100 F until equilibrium is essentially reached. The unit should be weighed at 24, 48, and 72 hr so that any appreciable decrease in rate of evaporation will be obvious. Experience has indicated that evaporation periods of 24, 48, and 72 hr are normally adequate to obtain a calibration curve.

h. Allow the unit to cool to 73 F at 50% relative humidity.

i. Weigh the unit to the nearest 0.01 g.

j. Subtract the tare weight (step c) from the total weight (step i) to yield the weight of residual.

k. Divide this weight by 10 to obtain the number of grams of residual yielded per gram of unweathered free oil.

---

* ASTM Designation: D1141, Section 4

7. This test should be conducted three times recording residual weights at 24, 48, and 72 hr. The values determined in step k should be averaged to yield the conversion factor for each time increment which, when divided into the weight of residual determined in any future test, will yield the weight of unweathered free oil collected in that test. The three time intervals should be plotted so that a conversion factor can be obtained for the convenient time used. Values less than 24 hr are meaningless, since the procedure is based on the complete evaporation of the water which will normally require 12 to 20 hr. It is also important to note that the conversion factor should be obtained on the same approximate amount of oil, as the oil-water relation will affect the rate of volatile evaporation from the oil during the first 24 hr.

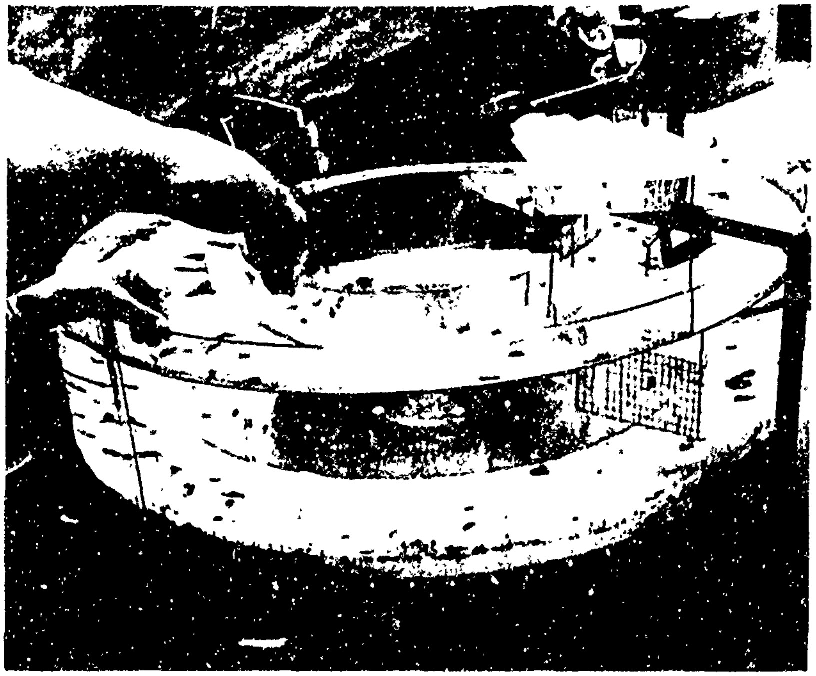


Fig. D1. Removal of released oil from fluid surface by using glass wool