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Efficiency and Retentivity Testing and Performance of Sinking Agents in the Removal of Oil Spills

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EFFICIENCY AND RETENTIVITY TESTING AND PERFORMANCE OF
SINKING AGENTS IN THE REMOVAL OF OIL SPILLS

by

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for the

Centre of Spill Technology
Environmental Protection Service

Condensation of the 300-page full Report

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ABSTRACT

A method for the removal of oil spills on water involves the application of a sinking agent to the surface of the oil spill and the subsequent sinking of the spill. This condensed report contains techniques for the testing of sinking agents to determine their efficiency in the removal of oil, and their ability to retain oil once removed by the action of sinking. The report also provides information concerning the effects of oil layer thickness initially, free fall distance for the sinking agent, temperature and oil type on the efficiency of removal and on the retentivity.

RESUME

Une méthode pour l'enlèvement des nappes d'huile sur l'eau consiste à incorporer un agent de sédimentation à la nappe d'huile qui, par la suite, tombe au fond de l'eau. Ce rapport condensé expose des techniques permettant la détermination de l'efficacité d'agents de sédimentation pour nappes d'huile. En plus, la capacité de lier en permanence l'huile aux agents de sédimentation est étudiée. De plus, la présente étude fournit une série d'information sur les effets de l'épaisseur de la nappe d'huile, de la vitesse de chute libre de l'agent de sédimentation, de la température et du type d'huile en regard de l'efficacité du procédé. La retentivité de l'huile par les agents de sédimentation a aussi été prise en considération.

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CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations associated with this study can be grouped as follows:-

1. Sinking agents, of the same general type as Oil-Lok 501, are capable of absorbing or adsorbing oil and spontaneously sinking the resultant mass. These materials, sinking agents in the best interpretation of the term, usually show very little difference between the true and apparent specific gravities, with the values involved lying well in excess of 2.0. The similarity of the true and apparent specific gravities, and normally a relatively high bulk density value, imply little in the way of internal porosity, so that entrapped and/or entrained air release and slow penetration by oil into the internal pores are not factors delaying or preventing the sinking of agent/oil masses. Such agents will even sink spontaneously, at 21°C, oils as viscous as bunker oil.
2. On the other hand, agents of the same general type as Zorb-All and Hi-Dri, which display significant differences between their true and apparent specific gravities, and show relatively low values for the bulk or loose densities, indicating a distinctly porous structure, do not sink oil spontaneously. Such materials require some form of agitation of the agent/oil mass before sinking can be accomplished and, with highly viscous oil conditions such as those pertaining in the case of bunker oil, the mass can not be sunk, even after prolonged agitation, in any simple manner or convenient time interval.
3. In general, agents with spontaneous sinking characteristics tend to be less efficient in the removal

of oil than agents where some form of agitation is required to induce sinking. This can be noted from the higher ratio by weight of agent to oil required for the spontaneous sinking agent where test conditions are comparable. The longer time-in-contact of the agent with the oil which is afforded the nonspontaneous sinking material underlies, to a considerable extent, this apparently superior efficiency. The higher efficiency for materials similar in physical nature to Zorb-All and Hi-Dri is, however, an advantage offset by the necessity of agitating to sink. Exposure without sinking for any prolonged period of an agent/oil mass can not but fail to accomplish the desired feature of rapid oil removal.

4. The effect of initial oil layer thickness treated is to decrease the efficiency of the agent as the oil layer treated decreases in thickness. This effect is most pronounced with agents which sink oil spontaneously, since the decrease of time-in-contact with decreasing layer thickness reduces the efficiency. The effect is very much diminished with nonspontaneous action agents, since the time-in-contact is only very slightly affected by layer thickness variation.
5. The effect of increasing the free fall distance for the sinking agent is to decrease the efficiency of the agent, and this effect is most pronounced with agents of the spontaneous sinking type. Again, this devolves from the reduced time-in-contact resulting from the increased velocity of fall brought about by the increased free fall distance. Agents which do not sink oil spontaneously, but require agitation to attain this end, are as might be expected only

very slightly decreased in efficiency by increasing free fall distance.

6. The effect of decreasing temperature is to increase the efficiency of the sinking agent, the extent of the increase in efficiency being associated directly with the extent to which the oil viscosity is increased by temperature decrease. Quantitatively, the effect is somewhat greater with spontaneous sinking agents than with those which are nonspontaneous, since the increase in oil viscosity in extending the time-in-contact is more effective relative to those agents displaying spontaneous sinking.
7. The effect of oil type must, for this study, be restricted to the effect of viscosity in this connection. It would appear that, for spontaneous sinking agents, the efficiency increases quite strongly with increasing oil viscosity, so that agents of this type are more efficient in the treatment of viscous oils. When the nonspontaneous agent types are considered, here again efficiency increases with increasing oil viscosity but, because of the lesser effect in increasing the time-in-contact, such efficiency increases are of a minor nature. Agents which do not sink oil spontaneously do not sink highly viscous oils at all.
8. In general, disregarding any disadvantage which might be associated with the necessity for agitation when nonspontaneous agents are involved, this type of sinking agent appears to be more efficient in oil removal.
9. Oil retentivity after sinking appears to be quite variable, but no agent tested retained, after 150 hours, more than about 80 percent of the oil originally sunk and, in some cases, the retention factor was as low as 30 percent. The importance of this situation can not

be overemphasized. For example, an agent may sink oil quite efficiently, but 70 percent of the oil sunk may rise to the surface again within 150 hours of the time of sinking. It is apparent that the initial efficiency in sinking oil has been of little value in the overall picture, and the use of the sinking agent has certainly not brought about the oil removal conditions desired.

10. While experimental work relative to the toxicity situations surrounding the use of sinking agents was not a part of the study directive, literature surveys force certain observations.
 - (a) The application of finely-divided sinking agents of a silica-base or asbestos-base requires that the working personnel involved be protected by the use of masks of the proper design.
 - (b) The toxicity of oils relative to bottom life decreases with the degree of aging of the oil at the surface prior to sinking. For sinking actions carried out relative to fresh oil spills, the consensus is that bottom life would be adversely affected.
 - (c) On this basis the use of sinking agents in the removal of oil spills could only be justified when the possible consequences to shore life as the result of oil deposition would be more hazardous than the effect on bottom life as the result of sinking. It is not felt that this situation is liable to arise with any significant frequency. The use of sinking agents in the removal of oil spills located far from the shore and over deep waters is, to some extent, feasible but rarely likely to be practical.

1. INTRODUCTION

1.1 General

The steadily increasing demand for petroleum products and by-products, and the corresponding increase in the quantities of crude and other petroleum oils shipped by water, has multiplied the possibilities of oil spill occurrences. In spite of operative and technological advances aimed at preventing such spills they will occur and, on this account, the need for improved methods applicable to the containment, treatment and removal of oil spills becomes daily more urgent.

The containment of oil spills implies the use of techniques of treatment intended to minimize the extension or spreading of the oil spill on the water from its point of origin. Mechanical and chemical methods of containment may be applied. Where the first category is concerned, references (3)(14)(21)(23)(31)(36)(37) and (39) provide a general picture of the state of the art. Several chemical methods of containment are covered by references (12)(18)(19)(34) and (39).

Containment, while of fundamental importance, usually represents only a preliminary step in the total treatment of oil spills. A subsequent step must involve the removal of the spill. This may be accomplished by means of two general procedures, one involving the collection of the oil spill by one means or another and its eventual disposal; the other involving its disposal without any preliminary collection process.

Where oil spills are collected, and the oil subsequently dis-

posed of, the procedures applied include either mechanical collection techniques or methods involving the application of surface absorbents followed by collection of the oil-soaked absorbent. Mechanical collection methods, which include the use of skimmers, suction devices, free vortex and vortex axial separation equipment, continuous absorbent belt devices and ultra-filtration techniques are described in, for example, such references as (1)(3)(20)(21)(23)(28)(29)(31)(34)(35)(40)(41) and (42). Descriptions of those processes which involve the application to the spill of surface absorbents, with the collection and disposal of the floating oil-soaked absorbent, may be found in references (7)(15)(18)(27)(31)(33)(34)(40)(42)(54)(60)(61)(62) and (65).

It is possible to dispose of oil spills without any preliminary collection procedures. Several methods of approach have been applied here, and these include the application of dispersants, the use of combustion techniques with or without the aid of burning agents, and the use of sinking agents which adsorb oil and sink it to the sea bottom. Dispersant techniques are, in general, described in references (2)(4)(5)(6)(7)(10)(22)(26)(31)(38)(40)(46)(50)(52)(57)(58)(63)(64)(65) and (69). An idea of combustion procedures is given by references (17)(31)(32)(40)(47) and (59), while a picture of those methods involving sinking agents can be gained from references (9)(24)(25)(31)(40)(43)(48)(54) and (65).

The eventual fate of untreated oil spilled on the sea has attracted the attention of several writers, prominent among whom is ZoBell (70) and (71), while the effects of such oil spillage on the environment and on the ecology can be gleaned from references (8)(11)(49) and (53).

A general view of the toxicity of various petroleum oils, and of that of many of the chemicals used as dispersants, absorbents, etc., relative to marine life, as well as of the methods of testing to determine the toxicities of such substances, is given by references (16)(30)(44)(55)(57)(67) and (68).

1.2 The Use of Sinking Agents in Oil Spill Treatment

The apparent ease with which oil spills may be treated by sinking agents has frequently given rise to a considerable optimism with respect to this method of treatment. The technique presents both advantages and disadvantages, at least on the surface. In general, the purpose of this study is to explore such purported advantages and disadvantages. In particular, its purpose is to outline methods and results relative to the determination of the efficiency of sinking agents under variable conditions of free fall, ambient temperature, etc., and to the measurement of the oil retention ability of sinking agents.

1.2.1 Sinking Agent Materials. When added to an oil spill, the function of a sinking agent is to provide, by absorption and/or adsorption, an oil/agent mass of a specific gravity high enough, relative to the maximum specific gravity of the water at the spill location, to permit the mass to sink to the sea, lake or river bed. To this end, any material intended for use as a sinking agent should display certain fairly well-defined characteristics. Such a material should be oleophilic and hydrophobic, and should continue to be oleophilic in the presence of a large excess of water. It should be a granular or fine particulate solid of large specific surface,

and with a specific gravity in the approximate range of 2.4 to 3.0. For economic reasons, cheapness and abundant availability are important criteria. Any sinking agent, to be suitable in a general sense, should be capable of treating an extensive variety of oil types.

Naturally occurring materials, naturally occurring materials treated with various chemical substances, and synthetic materials have all been employed as sinking agents. Some of these materials include sands, fly ash, clays, cementitious products and byproducts, and minerals. Many substances such as silicones, stearates, waxes and long-chain aliphatic amines have been used to coat such materials in order to render them more oleophilic and/or hydrophobic.

1.2.2 Particle Size Effects. The quantity of oil absorbed by a sinking agent appears generally to increase with decreasing particle size, although the rate of increase is not particularly significant for particle sizes less than about 300 micron. Again, the ability to retain oil, once sunk, improves with increasing agent fineness. On the other hand, the use of fine material requires the application of some form of mechanical action, agitation, stirring, etc., in order to produce and sink an oil/agent mass. Where such mechanical action is not applied, the length of time to sink oil may be very much prolonged. Under such circumstances, the fine sinking agent resting on the oil spill may yield a saucer-like configuration which can be inverted by wave action, with corresponding sinking of the agent with very much less than its optimum oil-removing capability.

Fine sinking agent material has the further disadvantage of being difficult to disperse dry even in light winds; this difficulty mounting to

impossible proportions with higher wind velocities. To a certain extent, this difficulty can be overcome by agent dispersion in the form of a slurry.

1.2.3 Retention of Sunken Oil. The fineness of the sinking agent as a factor having a bearing on the ability to retain sunken oil has been mentioned. Other factors have effects in this direction. When oil has been sunk in relatively shallow water, the action of tides, storms, currents and passing vessels may markedly increase the rate at which sunken oil is released by the agent. Again, the quantity of oil sunk per weight unit of sinking agent will very strongly affect retentivity and, when oil is sunk under high oil-to-agent ratios, an early release of significant amounts of oil can be anticipated. Such high oil-to-agent ratios can be obtained by, among other conditions, the treatment of thick oil layers, the treatment of viscous oils and prolonged oil-agent contact times.

1.2.4 Effects of Oil Viscosity and Layer Thickness. Oil spills may involve oils of high viscosity, such as bunker type oils. On the other hand, oil spills involving lower viscosity oils, such as crude oils or fuel oils, may require treatment. Furthermore spills of this latter type may, in time, show substantial increases in viscosity as the result of volatilization and weathering effects. Nor can the fact be ignored that the viscosity of any oil is influenced by temperature, increasing with decreasing temperature, so that water and air temperatures at the spill location have a definite bearing on oil viscosity.

When viscosity alone is concerned, most sinking agents operate most efficiently when the oil spill to be treated is reasonably viscous.

Where lower viscosity oils are involved, similar levels of efficiency can be obtained where the spill layer thickness treated is proportionately greater. What is implied here is that time-in-contact with respect to agent and oil is of prime importance, and some adequate time-in-contact is necessary in order to allow a given sinking agent to perform in an optimum manner.

1.2.5 Conditions Under Which Sinking Agents Have Been Used. The appeal of the sinking agent treatment technique is largely based on the rapidity and apparent simplicity of the operation. Neglecting any complications, the oil spill is treated with a sinking agent which sinks the oil without the effort and expense of collection and subsequent recovery or disposal. There are, of course, those complications which have to do with the problem of dry dispersal, the need for mechanical action or agitation with certain types of sinking agent and/or oil, retention ability, etc.

There is, further than these complications, the question of the danger to bottom life, and to marine life in general, implied by the carrying to the sea bottom of large oil/agent masses. Oil untreated at the sea surface gradually evaporates to some extent, with the residue degrading by weathering to a further extent. Only a relatively small proportion of the original spill finds its way to the sea bed, and this strongly weathered portion is much less toxic than the oil from the original spill. Almost 100 percent of the oil in an oil spill treated immediately by sinking agent reaches the sea bed in its more toxic form and, once on the bottom, degrades at an extremely slow rate. It is on the basis of this question of the danger to marine life that several suggestions as to severe limitations concerning the use of sinking agents have been put forward.

It has been suggested that sinking agents be used only where other methods have been tried without success and, even then, only where there is immediate danger of serious harbour or shoreline pollution. This must obviously be a matter for a most experienced judgement; the result of weighing possible bottom life damage against harbour or shoreline damage. It should be noted, however, that even where the damage to the shoreline appears to be the more important factor, oil sinking in shoal waters may result in later shoreline pollution by deposition of sunken oil through tidal action. An additional point in reference to this and similar suggestions is that, if sinking agents are not to be applied until after many other approaches have failed, the time delay factor may result for uncontained spills in oil layers thin enough to reduce very significantly the efficiency of any sinking agent tried.

Suggestions have also been made to the effect that the use of sinking agents should be confined to spills in areas further offshore than the respective continental shelves, away from shellfish beds and from areas where the currents are predominantly shoreward.

The use of chemical dispersants, prior to the application of a sinking agent, has been suggested as a means of preventing heavy oil deposits over small sea bed areas. The problem of obtaining, from the use of dispersants, oil layers of critical thinness, with corresponding reduction in sinking agent efficiency, arises in any such treatment procedure, as does that of the possible added toxicity of the dispersant substances carried down with the agent/oil masses.

1.2.6 Testing of Sinking Agents. Sinking agents may be tested to determine the critical but very general characteristics of efficiency of removal of oil and ability to retain sunken oil. While such test goals are representative of the general areas of exploration, each test group can be divided into subgroups, each subgroup reflecting the effects of some specific factor of influence. The following variables, each capable of exerting a profound influence on sinking agent efficiency, might be given test consideration:-

- | | |
|---------------------------|----------------------------|
| (a) Sinking agent factors | (c) Ambient temperature |
| 1. composition | (d) Seawater density |
| 2. specific gravity | (e) Dispersion factors |
| 3. bulk or loose density | 1. dispersion technique |
| 4. applied coating | 2. wind velocity influence |
| 5. particle size | 3. wave action influence |
| (b) Oil factors | 4. free fall height |
| 1. oil type | |
| 2. oil layer thickness | |

The determination of the ability of a sinking agent to retain sunken oil might require that the following variables be given test consideration:-

- | | |
|---------------------------|-------------------------------------|
| (a) Sinking agent factors | (b) Oil factors |
| 1. composition | 1. oil type |
| 2. applied coating | 2. oil-to-agent ratio |
| 3. particle size | (c) Below-surface factors |
| | 1. static conditions |
| | 2. dynamic conditions (tides, etc.) |

Many of the conditions encountered in the field are extremely difficult to duplicate in the laboratory, or even in a large-scale test area. For example, the influence of sinking agent dispersion technique, the effect of wind and wave actions on dispersion, and the retention of oil under dynamic below-surface conditions are among the field conditions most difficult to simulate in the laboratory. As a result, most approaches to testing aim at obtaining a comparison of results between sinking agent types under laboratory conditions relatively easily reproduced, rather than under conditions closely duplicating those encountered in the field.

1.2.6.1 Testing to determine efficiency. Techniques which have been applied to explore sinking agent efficiency vary considerably in methodology, some being quite simple and others relatively complex. Generally the degree of complexity increases with attempts to reproduce more faithfully conditions in the field. Representative testing techniques can be found in references (25)(43)(56) and (65).

1.2.6.2 Testing to determine oil retention. Oil retention under static conditions can be determined in the laboratory with relative ease, and several methods have been devised to explore this property. Determining the retentivity under dynamic conditions requires much more complicated testing methods in the laboratory environment, and it is virtually impossible to arrange for laboratory testing procedures which can duplicate with any exactitude the flow characteristics of ocean and shore currents and tidal actions.

One of the factors which should be given consideration in all retentivity tests carried out in other than a sealed environment is that

of volatilization losses associated with oil released to the test vessel surface. When such losses are not accounted for, particularly in the testing of oils with significant fractions of relatively volatile components, retentivity values erring on the high side are common if the final step depends on the measurement of the amount of released oil.

Static testing procedures are outlined in references (25)(43) and (65), with a dynamic testing technique being outlined in reference (25).

2. TESTING PROCEDURES USED IN THIS STUDY

2.1 General

The primary aims of this study can be briefly outlined as:-

- (a) The development and application of a method of testing to determine the efficiency of a limited number of sinking agents under variable conditions of oil type tested, oil layer thickness treated, free fall distance for the sinking agent, and temperature.
- (b) The development and application of a method of testing to ascertain the retentivity of the selected sinking agents under static conditions and with respect to various oil types.
- (c) The exploration of any factors of interest arising out of (a) and (b) of the foregoing.

2.2 Determination of Sinking Agent Characteristics

The sinking agents involved in this study, together with pertinent data as to general type and a source of supply, are given in the fol-

lowing:-

- (a) Oil-Lok 501 - a carbonized, chemically-coated, basalt-base material of a granular nature. The supplier was International Oil-Lok Control Ltd., 1250-505 Burrard Street, Vancouver, British Columbia.
- (b) Zorb-All - a calcinated clay material of a semigranular nature. Supplied by Wyandotte Chemicals Limited, 1253 McGill College Avenue, Montreal, Quebec.
- (c) Hi-Dri - a hydrated magnesium aluminum silicate of a semigranular nature. Supplied by Tenenier Absorbent Products Limited, 185 Young Street, Hamilton, Ontario.

The particular characteristics of interest with respect to the sinking agents investigated were, apart from those of efficiency and retentivity in oil treatment, the true specific gravity, the apparent specific gravity and the bulk or loose density.

2.2.1 True Specific Gravity. The true specific gravity is the specific gravity of the sinking agent unaffected by any particulate porosity. Air pycnometric methods were applied in the determination of the true specific gravity, with the results shown in Table 1.

2.2.2 Apparent Specific Gravity. The apparent specific gravity is the specific gravity of the sinking agent as affected by particulate porosity. This characteristic is important with respect to the ability of a sinking agent to sink oil rapidly and, in many cases, without some form of

agitation. When the apparent specific gravity is appreciably less than the true specific gravity, the indication is that the particles may be porous to a significant degree. Such porosity is most frequently not penetrated rapidly by liquids such as water and oil, and this is particularly the case when an oil of relatively high viscosity, either natural or temperature induced, is involved. In such cases the agent/oil mass tends to resist sinking until time and/or agitation brings this action about.

The apparent specific gravity was explored by rapid measurement, using both water and oil pycnometric methods, with the results shown in Table 1.

2.2.3 Bulk or Loose Density. The bulk or loose density is representative of the density of the sinking agent relative to large masses and, to a certain extent, reflects both the capacity for packing and the particulate porosity. Lower loose density values would suggest storage, handling and treatment difficulties. The bulk density was measured using large graduated containers, and provided the results given in Table 1.

TABLE 1

CHARACTERISTICS OF SINKING AGENTS

Sinking Agent	Specific Gravity		Bulk or Loose Density, lb/ft ³
	True	Apparent	
Oil-Lok 501	2.79 ± 0.02	2.57 ± 0.03	93.3 ± 0.5
Zorb-All	2.71 ± 0.02	2.05 ± 0.03	35.4 ± 0.5
Hi-Dri	2.98 ± 0.02	2.10 ± 0.03	33.4 ± 0.5

2.2.4 Interpretation of Results. There was a considerable difference between the true and apparent specific gravities where Zorb-All and Hi-Dri were concerned, these differences reflecting, in our opinion, porosity with respect to the granules involved. This situation is also indicated by the values representing the bulk or loose densities for these agents.

Such differences relative to true and apparent specific gravity, where significant enough, can lead to resistance to immediate sinking of oil. Under such circumstances, delay periods after application and/or agitation procedures are often required to bring about sinking action. With high viscosity oils, or with environmental conditions leading to high viscosities, there is always the possibility that sinking may be indefinitely or intolerably prolonged, even under conditions of agitation.

2.3 Determination of Oil Characteristics

The oils involved in this study, together with pertinent data as to supplier, are given in the following:-

- (a) Western Crude Oil - a crude oil of origin in western Canada, supplied by Petrofina Canada Limited from the Montreal refinery, and carrying their designation 'Western Crude Oil'.
- (b) No. 2 Fuel Oil - a furnace fuel oil of the light type supplied by Petrofina Canada Limited from the Montreal refinery, and carrying their designation 'Blue No. 2 Fuel Oil'.
- (c) Bunker Oil - a heavy fuel oil supplied by Petrofina Canada Limited from the Montreal refinery, and carrying their designation 'No. 6 Bunker Oil'.

These test oils were investigated to determine certain characteristics which were felt to be capable of exerting some influence with respect to the efficiency and retentivity properties of the sinking agents. These characteristics were the specific gravity, the viscosity and the volatile loss property. The volatile loss testing situation is outlined in Section 2.5.1; only the testing procedures for specific gravity and viscosity are outlined in this section.

2.3.1 Specific Gravity. The specific gravity of the oils of relatively low viscosity was measured pycnometrically. Large volumetric containers were used to determine the specific gravity of oils of high viscosity. Specific gravity tests were carried out at $21 \pm 1^{\circ}\text{C}$ and at $2 \pm 1^{\circ}\text{C}$. The test results are shown in Table 2.

TABLE 2

SPECIFIC GRAVITY OF TEST OILS

Oil	Specific Gravity	
	$21 \pm 1^{\circ}\text{C}$	$2 \pm 1^{\circ}\text{C}$
Western Crude	0.830 ± 0.001	0.839 ± 0.001
No. 2 Fuel	0.840 ± 0.001	0.850 ± 0.001
No. 6 Bunker	0.964 ± 0.001	0.971 ± 0.001

2.3.2 Viscosity. The viscosity for oils of low or medium viscosity was measured using a Cannon-Fenske Viscosimeter. High viscosity oils were tested using a Concentric Cylinder Viscosity Apparatus. The viscosity tests were carried out at $21 \pm 1^{\circ}\text{C}$ and at $2 \pm 1^{\circ}\text{C}$. The test results are shown in

Table 3. The difficulties surrounding the determination of bunker oil viscosity at 2°C render the final average value doubtful. It is nevertheless apparent that, because of the high viscosity values involved, the sinking of this oil by sinking agents can be expected to present a problem.

TABLE 3

VISCOSITY OF TEST OILS

Oil	Viscosity at $21 \pm 1^\circ\text{C}$ (cSt)		Viscosity at $2 \pm 1^\circ\text{C}$ (cSt)	
	Average	Std. Devn.	Average	Std. Devn.
Western Crude	6.85	± 0.05	55	± 1
No. 2 Fuel	4.23	± 0.04	7.5	± 0.1
No. 6 Bunker	4.2×10^3	$\pm 0.1 \times 10^3$	1.5×10^5	$\pm 0.2 \times 10^5$

2.4 Testing of Sinking Agent Efficiency

Since the experimental work in this area was to include the effects of free fall distance, oil layer thickness, temperature, etc., it was felt that a test apparatus capable of accomodating changes in these factors, while maintaining an adequate dispersion technique with respect to the application of the sinking agent, would have to be developed. Since the test procedure projected could not be carried out in a sealed environment without the addition of apparatus features of a complicating nature, volatility loss corrections would be avoidable only when each test series was carried out over a time interval short enough to minimize such losses. The final apparatus design took this factor into consideration, and each test series was carried out over an interval short enough to allow the omission

of volatility loss corrections without the introduction of significant error.

2.4.1 The Test Apparatus. In general the testing procedure involved the floating of a layer of test oil on a saline solution simulating sea water, the saline solution having been prepared in accordance with specification ASTM D-1141. The saline solution and the oil layer were contained in a rectangular test cell of a height sufficient to permit significant variation in the free fall distance for the sinking agent. The agent, as a measured weight for each individual treatment, was then spread evenly on a slide plate incorporated at the top of the test cell. Release of the sinking agent to fall evenly on the oil layer was accomplished by a spring-actuated device which very rapidly retracted the slide plate. The test cell is shown in Figure 1.

The thickness of the oil layer at the start of each test, and after each treatment with sinking agent, was determined by lowering a pair of pointed stainless steel probes through the oil layer. These probes were charged, connected to a resistance measuring device and, in the last stages of the measurement operation, were lowered using a micrometer. When a sudden decrease in the indicated resistance was observed, the oil layer thickness was obtained from the micrometer readings. Each layer thickness determined represented the averaging of readings at three and often four locations. The oil layer thickness measuring device is shown in Figure 2.

For each test series the addition of sinking agent, and the measurement of the resultant oil layer thickness, was continued until the oil layer showed significant patches exposing the underlying saline solution. While the totality of oil removal, using this criterion, varied

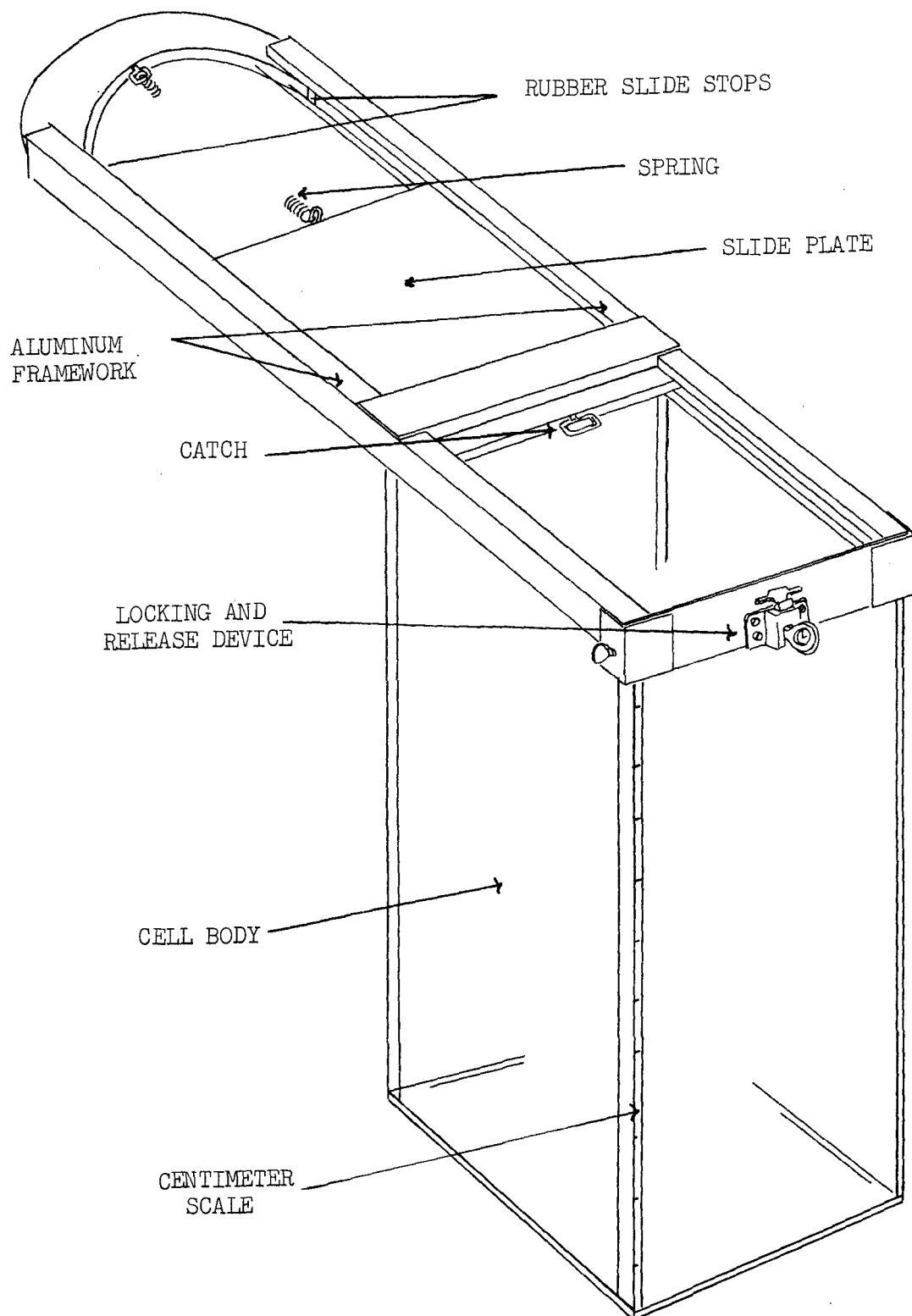


FIGURE 1 THE TEST CELL

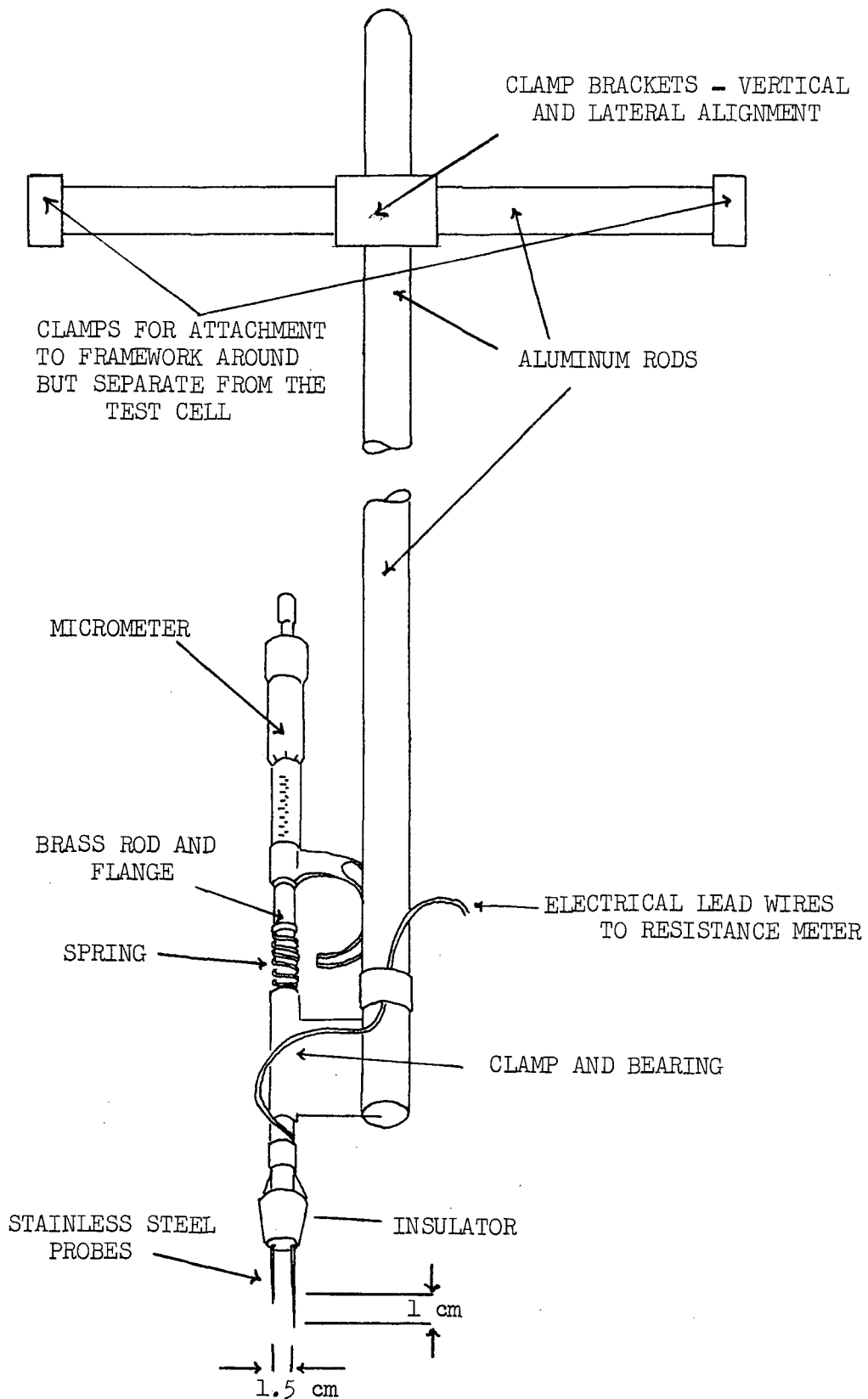


FIGURE 2 OIL LAYER THICKNESS MEASUREMENT DEVICE

somewhat with the oil type under test, approximately 90 percent of the initial oil quantity was sunk at this point. The very considerable and disproportionate decrease in sinking agent efficiency which occurs once water patches are exposed obviates any further continuation of the test series. With nondiscontinuous oil layers, repetitive measurement values of thickness gave averages with standard deviations approximating ± 0.1 mm.

The raw data relative to accumulated weight of sinking agent added and successive oil layer thickness were treated, in each test series, using the proper oil density value, so as to obtain:-

- (a) A plot of accumulated layer thickness and weight of oil removed by sinking versus accumulated weight of sinking agent added.
- (b) A tabulation of sinking agent efficiency in terms of the weight of sinking agent required to remove a unit weight of oil, for a variety of initial oil layer thicknesses each removed to about a 1 mm to 1.5 mm residual thickness.
- (c) A plot of sinking agent weight required to remove oil, for test cell conditions, to 1 mm to 1.5 mm residual thickness versus starting or initial oil layer thickness.
- (d) A plot of sinking agent weight/unit oil weight required to remove oil, for projected field conditions, to 1 mm to 1.5 mm residual thickness versus starting or initial oil layer thickness.

From the data for the accumulated test series, tabulations and plots providing comparative information relative to sinking agent efficiency

under variable conditions of free fall distance, temperature, etc., were prepared.

2.5 Testing of the Oil Retention Ability Under Static Conditions

When a sinking agent is dispersed onto an oil layer the ratio of agent/oil for the sunken mass depends, for a given agent, a given oil, a fixed free fall distance and a fixed testing temperature, on the time-in-contact of the sinking agent with the oil. This time-in-contact is, for the conditions described, very largely a function of the oil layer thickness, the quantity of agent applied and its rate of addition. For example, when a relatively thin layer of oil is treated by a specific sinking agent, the agent/oil ratio for the sunken mass will be very much higher than in the case where a significantly thicker oil layer was so treated. Similarly, the use of increasing quantities of a sinking agent and/or increased rates of addition in the treatment of a specific oil layer thickness results in increasing agent/oil ratios.

It is apparent that one of the factors influencing the retention ability of a sinking agent will be this agent/oil ratio, and it can be expected that the lower the ratio, beyond some approximate limiting value, the greater will be the extent to which oil will be released, particularly in those intervals immediately following on the sinking process. A relatively heavy oil release might continue, under such circumstances, until the agent/oil ratio for the sunken mass was increased to some value characteristic of the particular sinking agent involved. Beyond this value, some continued release at a much diminished rate might be anticipated.

It was intended to use the oil layer thickness measuring device described in Section 2.4.1 for the retentivity studies. The application required the determination of the increasing surface oil layer thickness as dictated by oil release from the sunken agent/oil mass. This form of measurement can not be carried out when the oil released yields a discontinuous oil layer at the surface. To avoid such a situation, a float of oil at the surface was provided for after each sinking process. To accomplish this, an initial oil layer of sufficient thickness was floated on the saline solution to leave, after the addition of the quantity of sinking agent required for a given retention test, a surface oil layer without discontinuities. Released oil could now be determined by measuring the increasing thickness of this float.

Since retention testing under static conditions was by necessity carried out in an unsealed environment, the testing of an oil with a significant fraction of relatively volatile components required that volatility loss corrections be applied in order to compensate for volatility losses with respect to the surface exposure of the released oil and the initial oil float. Such corrections were made when required, and the volatility data necessary to such corrections were obtained by the technique outlined in Section 2.5.1.

It should be apparent, from several facets of the foregoing, that decisions as to the quantity of sinking agent required to be added initially to a given oil float must be based to a degree on a knowledge of the efficiency of the sinking agent. For this reason, retention tests were not carried out until after the efficiency tests had been completed.

2.5.1 Volatility Loss Testing. Each oil type to be explored in the test series was examined to determine, at $21 \pm 1^{\circ}\text{C}$, time-based volatility losses. For each oil, saline solution was used to fill a 1 liter beaker to approximately the halfway point. Using the exact surface area exposed in each case, in combination with the appropriate oil density value, a weight of oil capable of providing a layer thickness of 15 mm to 20 mm was calculated. The beaker and saline solution was retained on a scale, and the oil was carefully floated onto the solution until the calculated weight had been transferred. The oil layer thickness was measured immediately, using the thickness measuring device.

At varying time intervals the oil layer thickness was measured and, for each oil, the raw data obtained was used to develop tables and plots showing the volatile weight loss versus the time interval. Figures 3 and 4 show respectively the 150 hour and 24 hour characteristics of western crude oil, Figure 5 shows both situations for No. 2 fuel oil and Figure 6 shows both aspects for No. 6 bunker oil.

The volatility loss curve shows, in each case, the same general contour, indicating high early losses decreasing in time to low loss values. As might be expected, western crude oil displays the highest volatility loss factor, this being based on the relatively high proportion of volatile components in crude oil.

No 2 fuel oil and No. 6 bunker oil show generally similar loss curves, although the bunker oil curve indicates a somewhat higher early loss rate.

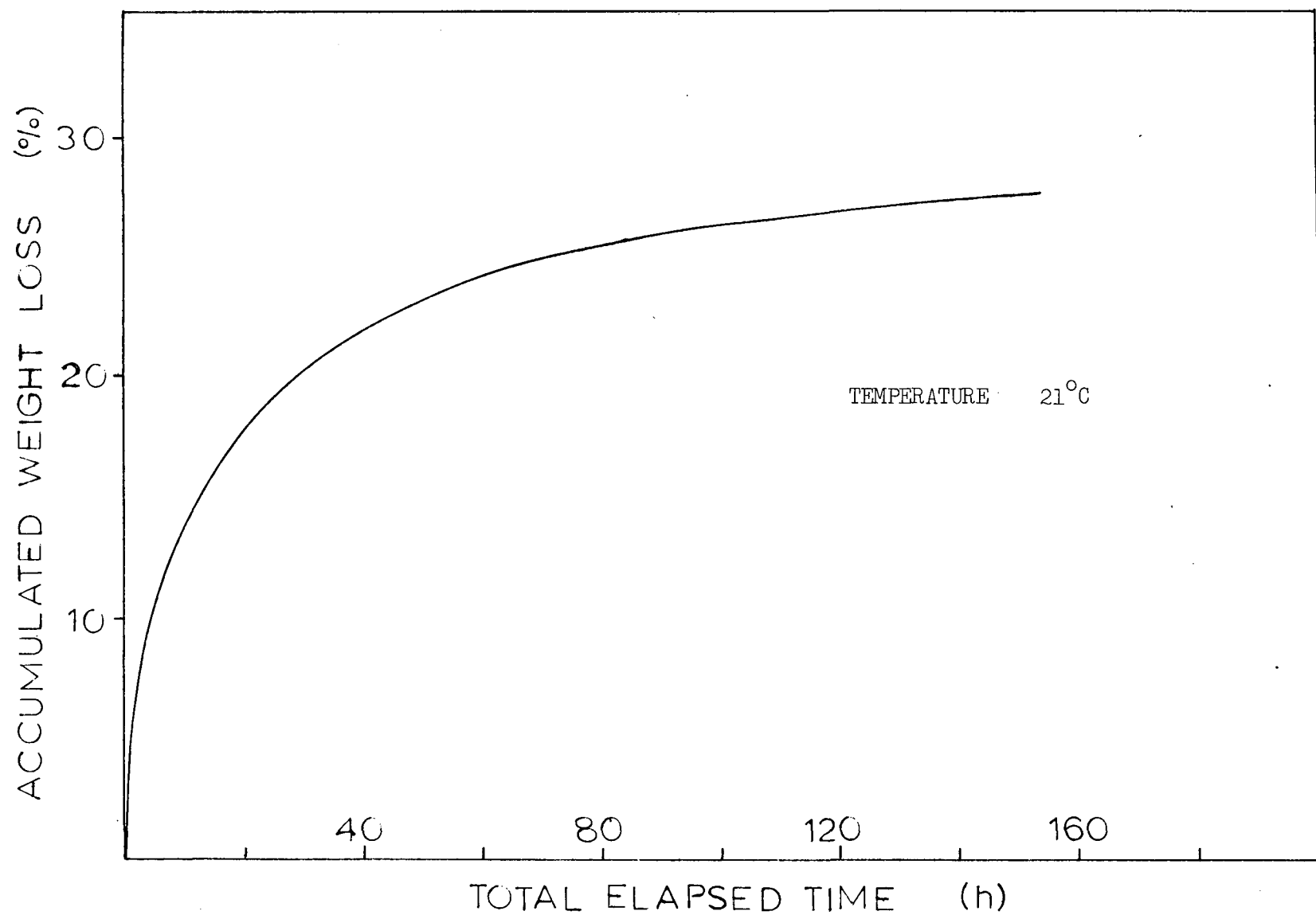


FIGURE 3 VOLATILITY LOSS - WESTERN CRUDE OIL - TOTAL ELAPSED TIME VS ACCUMULATED WEIGHT LOSS
(0-150 h)

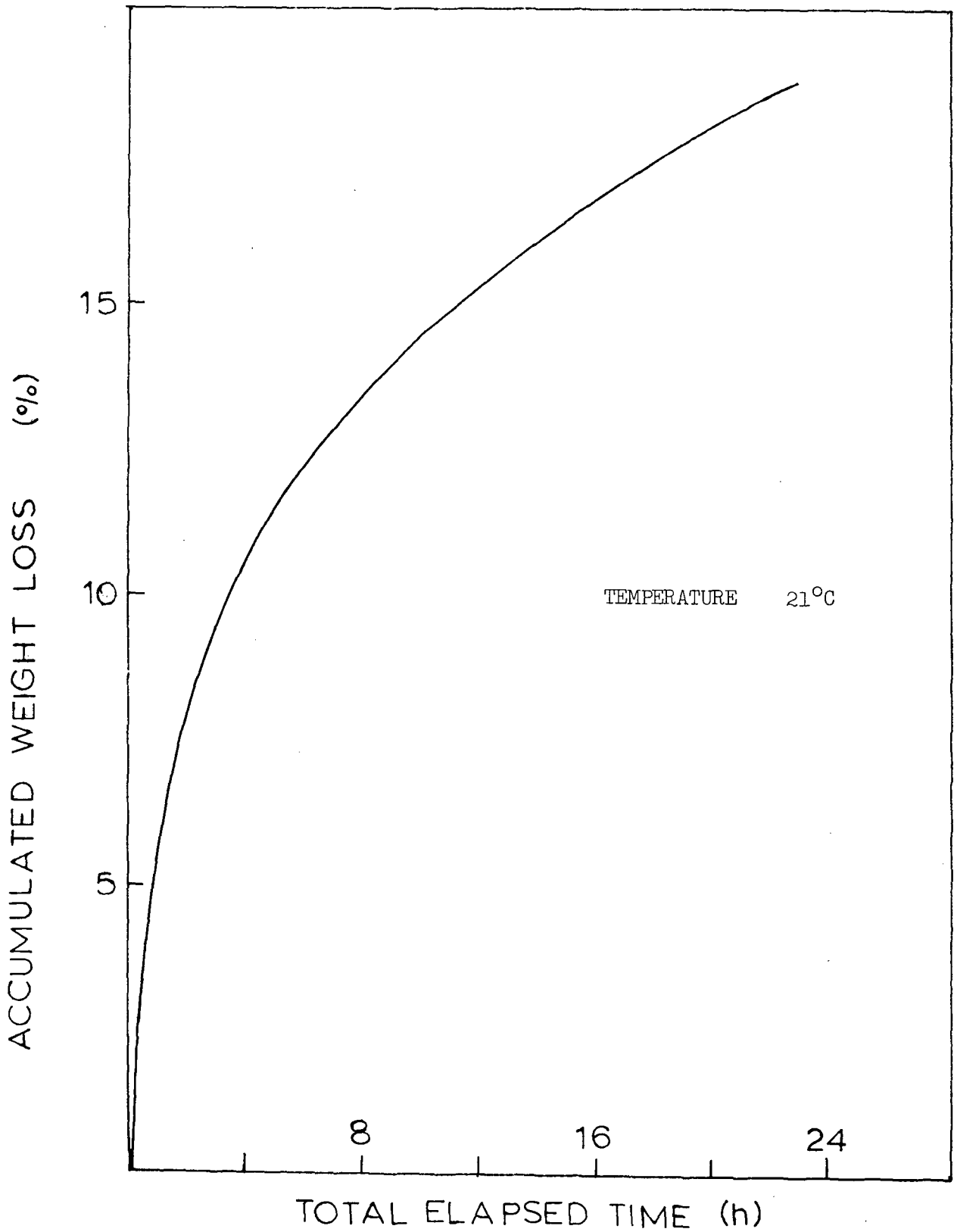


FIGURE 4 VOLATILITY LOSS - WESTERN CRUDE OIL - TOTAL ELAPSED TIME
VS ACCUMULATED WEIGHT LOSS (0-24 h)

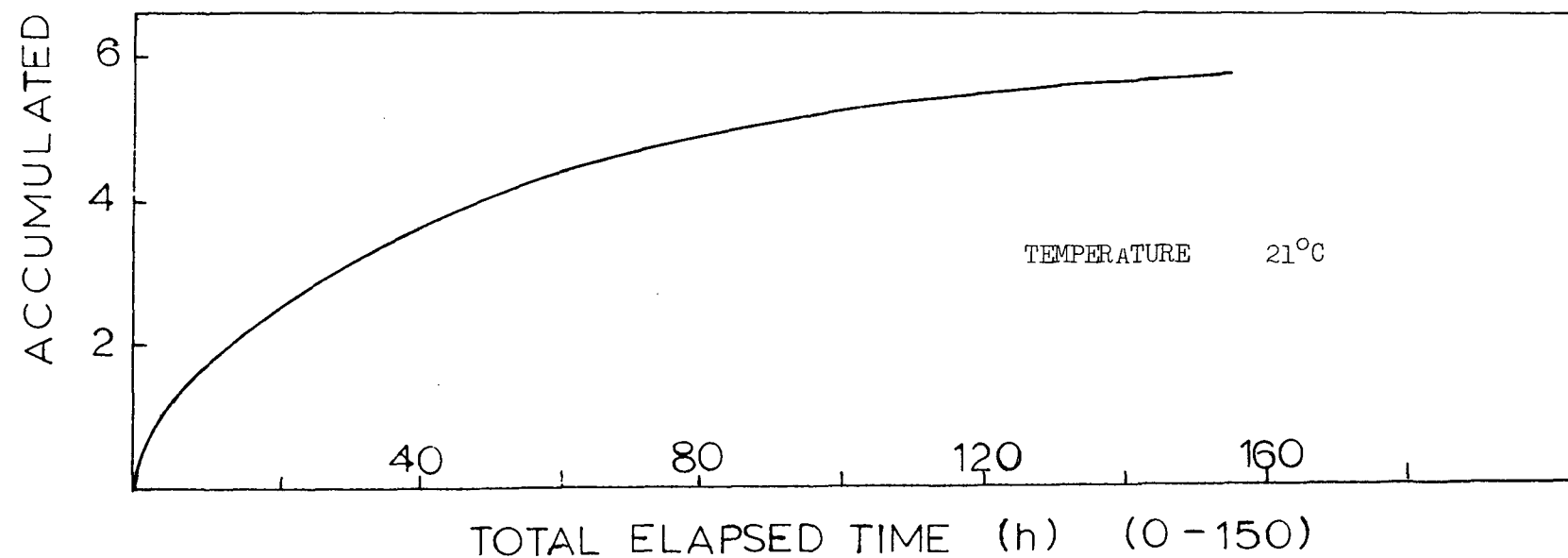
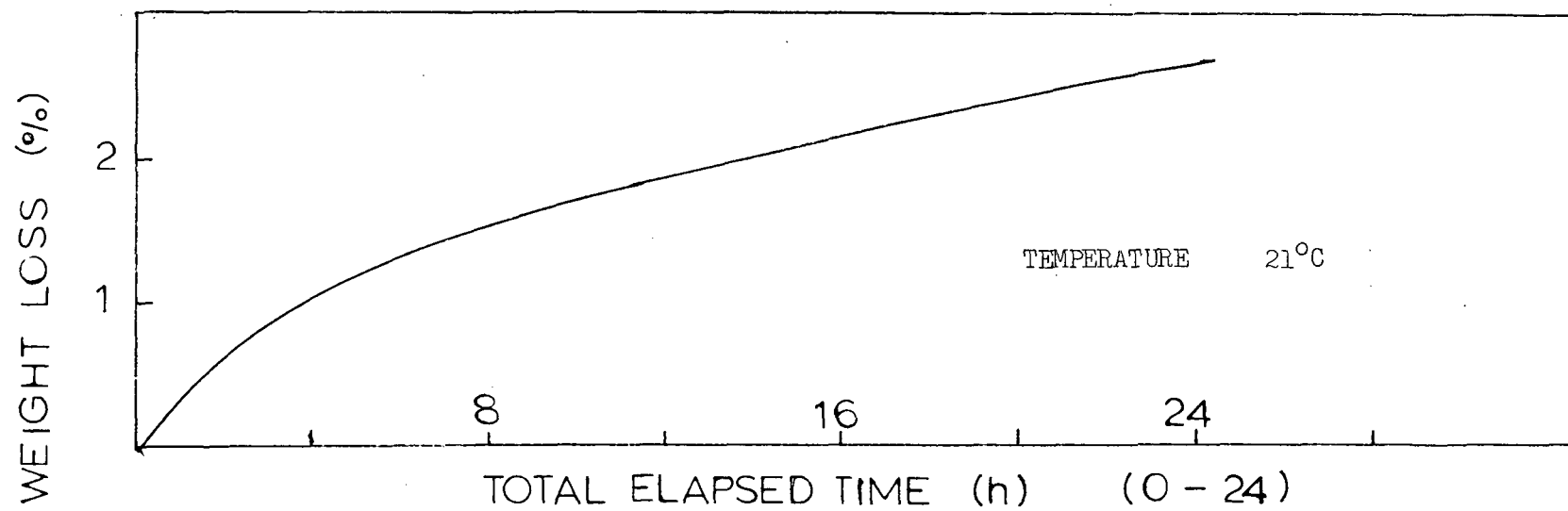


FIGURE 5 VOLATILITY LOSS - NO. 2 FUEL OIL - TOTAL ELAPSED TIME VS ACCUMULATED WEIGHT LOSS

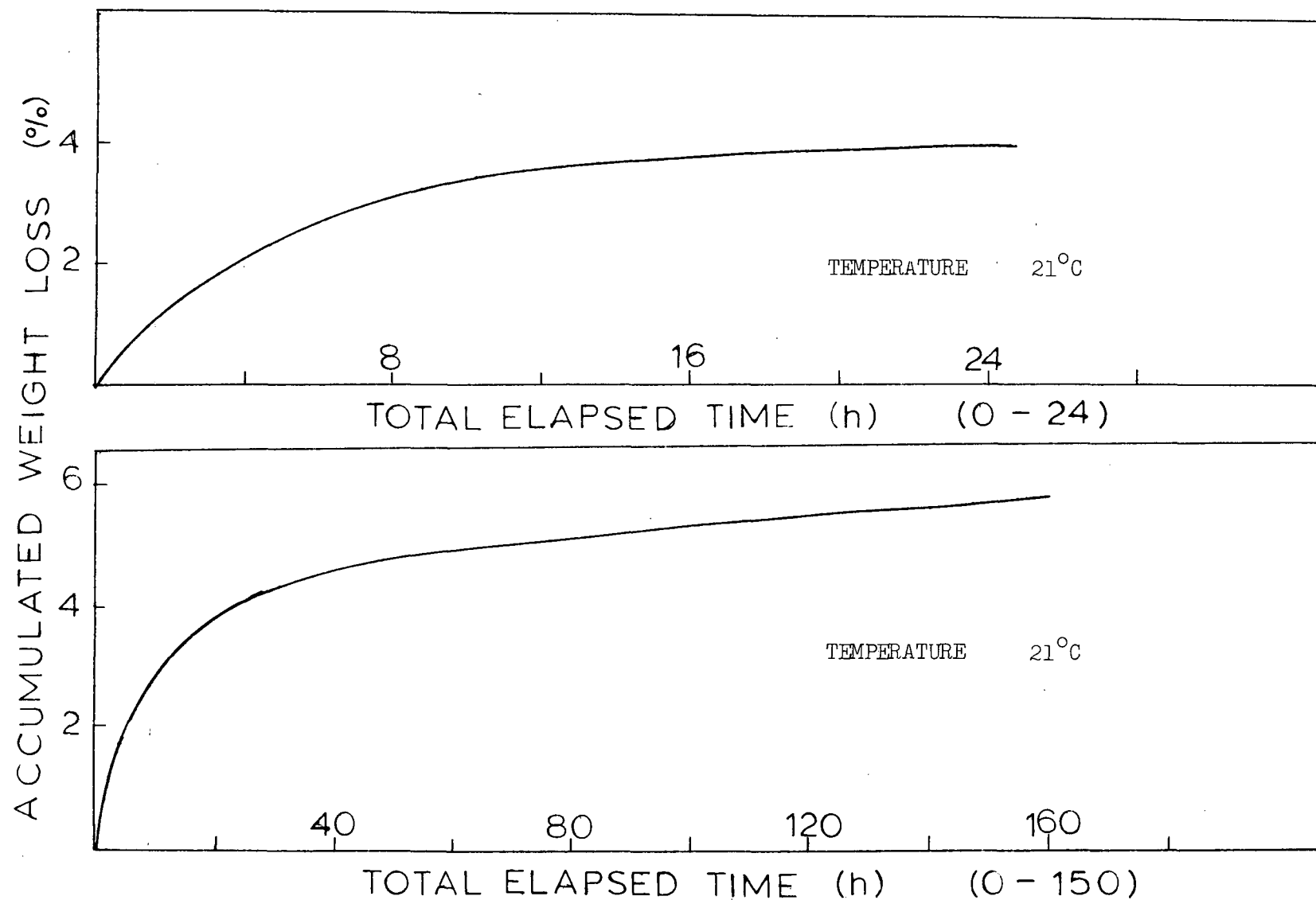


FIGURE 6 VOLATILITY LOSS - NO. 6 BUNKER OIL - TOTAL ELAPSED TIME VS ACCUMULATED WEIGHT LOSS

2.5.2 Retention Testing Procedure. Each sinking agent and oil type combination was tested under static conditions and at $21 \pm 1^{\circ}\text{C}$. For each combination, saline solution was used to fill a 1 liter beaker to about the halfway point. Using the exact surface area in each case, together with the appropriate oil density, a weight of oil capable of yielding a layer thickness of 15 to 20 mm was calculated. While retaining the beaker and saline solution on a scale, oil was carefully floated onto the solution surface until the calculated weight was attained. The oil layer thickness resulting was determined immediately.

Using efficiency data for the sinking agent/oil combination under test, and for a 15 cm free fall parameter, a quantity of sinking agent was weighed out which, in consideration of the weight of floated oil involved, gave an agent/oil ratio appreciably lower than the minimum value obtained in the efficiency investigation. This quantity of sinking agent was dispersed evenly and slowly onto the oil surface from the 15 cm height. When penetration and sinking was not spontaneous, agitation by stirring was applied. The agitation technique was identical to that adopted in the efficiency tests when nonspontaneous sinking situations occurred. Immediately the agent/oil mass was sunk, the residual oil layer at the surface was measured as to thickness with the measurement device.

At various recorded time intervals the layer thickness was recorded for each test system. The raw data indicated that for each test, and with the passage of time, there was a decreasing augmentation of the surface layer thickness by released oil. Indeed, as the more extended time intervals were explored, the increments of thickness change shifted from

positive to negative values. This effect represented the ongoing influence of volatilization losses over the test interval for both the initial residual oil float and the accumulating released oil.

The correction for volatility losses for the initial oil float is simple and involves, for each time interval, a consideration of the initial float weight and the volatility loss as percent weight loss for the time interval and oil type involved. This latter information was available from the tests outlined under Section 2.5.1, and from the associated test results.

The correction for volatility losses as applicable in the case of the accumulation of released oil in the float is less easily accomplished. In order to simplify the procedure, the assumption was made that, over any specified period or time interval, the volatilization losses would be adequately accounted for by taking the oil weight in the float at the time interval involved, correcting it for the initial oil float and its losses, and dividing the result by a factor incorporating one-half of the volatility loss for the time interval under consideration. The following equations were thus developed:-

$$R_t = \frac{M_t - \left[\frac{I}{(1 - V_{dp}/100)} \cdot \left(1 - \frac{V(dp + t)}{100} \right) \right]}{(1 - V_t/200)} \quad (1)$$

$$S_o = T_o - I \quad (2)$$

$$\%OR_t = \frac{(S_o - R_t) \times 100}{S_o} \quad (3)$$

$$SA/O_t = \frac{SA}{S_o - R_t} \quad (4)$$

$$O_t = S_o - R_t \quad (5)$$

where:-

- R_t = oil released in time t (g)
- % OR_t = retained oil/initially sunken oil by weight (%)
- M_t = oil in float at time t (g)
- t = time interval from sinking (h)
- dp = delay period after floating oil and before adding sinking agent (h)
- I = initial oil in float after delay period and after adding sinking agent (g)
- V_t = volatility loss by weight in time t (%)
- V_{dp} = volatility loss by weight during delay period (%)
- S_o = oil in initially sunken agent/oil mass (g)
- T_o = total oil in float after delay period (g)
- SA = total weight sinking agent added (g)
- O_t = oil in sunken mass at time t (g)
- SA/O_t = agent/oil ratio by weight in sunken mass at time t

The values of V_t and V_{dp} are, of course, obtained from the appropriate volatility loss plots or tabulations, as is the value of $V_{(dp + t)}$.

We were appreciative of the fact that this technique of calculation provided for the most significant error relative to the oil with the highest volatility loss, that is for western crude oil. We were also aware of the fact that no compensation was included to offset specific gravity changes in the oils with volatility losses. This situation is, again, really important only in the case of western crude oil, where the change in specific

gravity with volatility losses is appreciable (the value changes in about 144 hours at 21°C from 0.83 to 0.89). We felt, however, that in the volatility and retentivity tests, the results were good enough for comparative purposes without the complication of additional correction factors.

3. TEST RESULTS FOR EFFICIENCY AND RETENTIVITY TESTING

3.1 General

In the interests of brevity, the very considerable accumulation of raw data, the tabulations and the multiplicity of plots can not all be shown in this condensed Report. Only such data or data derivatives as are concise and of immediate moment are included herein.

It should be noted, however, that multiple measurements and tests involved obtaining the associated averages and standard deviations after rejection of data, where required, by appropriate techniques of statistical analysis.

3.2 Efficiency of Oil-Lok 501 in Removing the Three Oil Types

The condensation of all test data relative to the effects of variation of initial oil layer thickness treated, of free fall distance, of oil type and of ambient temperature is given by Figures 7 and 8. Figure 7 shows, on the basis of weight of sinking agent required per unit weight of oil removed, the effects of variation in initial oil layer thickness treated, free fall distance and oil type under 21°C test conditions; with Figure 8 showing the same effects for the 2°C testing temperature. Table 4 shows, in particular, the effect of temperature on Oil-Lok 501 efficiency in the removal of two of the oil types tested.

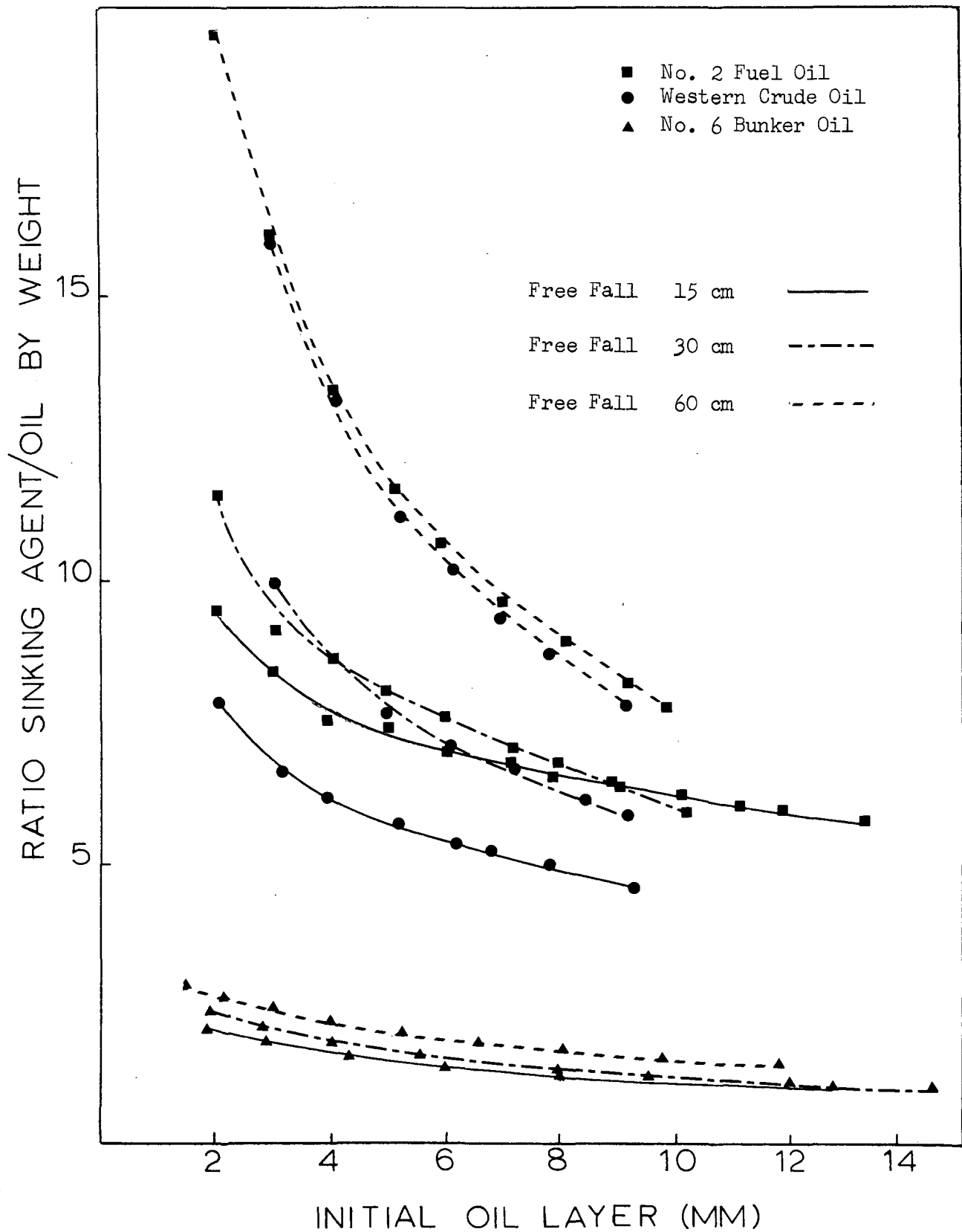


FIGURE 7 EFFECT OF INITIAL OIL LAYER THICKNESS, OIL TYPE AND FREE FALL DISTANCE ON OIL-LOK 501 EFFICIENCY (21°C)

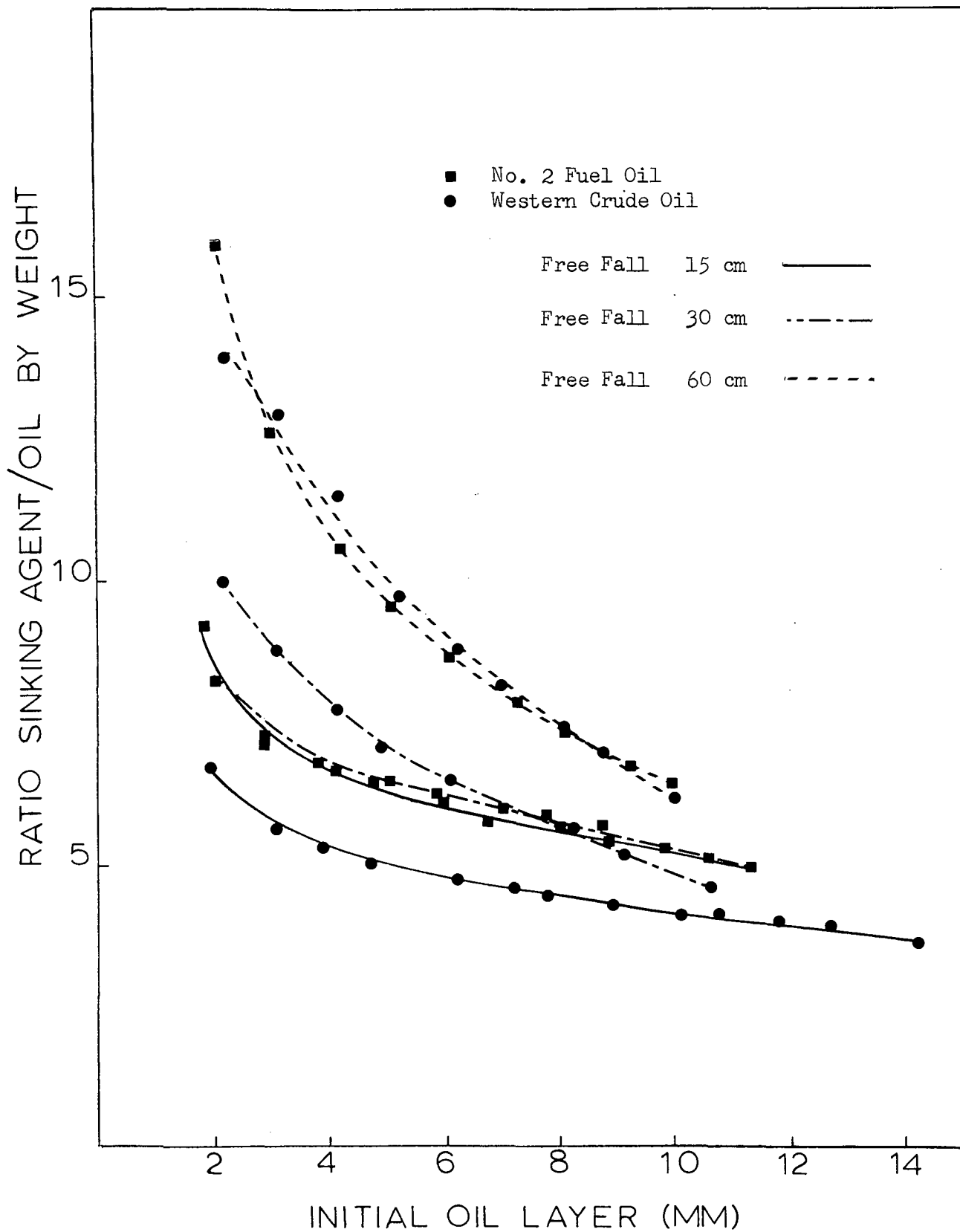


FIGURE 8 EFFECT OF INITIAL OIL LAYER THICKNESS, OIL TYPE AND FREE FALL DISTANCE ON OIL-LOK 501 EFFICIENCY (20°C)

TABLE 4

OIL-LOK 501 AND TWO TEST OILS - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Ratio Sinking Agent/Oil By Weight		
Western Crude	21°C	2°C	% Less Sinking Agent
Initial Oil Layer about 9 mm			
15	4.49	4.32	4
30	5.83	5.18	11
60	7.75	6.99	10
Initial Oil Layer about 7 mm			
15	5.15	4.64	10
30	6.69	6.06	9
60	9.29	8.19	12
Initial Oil Layer about 4 mm			
15	6.07	5.31	12
30	8.56	7.72	10
60	13.0 ¹	11.4 ⁴	12
No. 2 Fuel Oil	21°C	2°C	% Less Sinking Agent
Initial Oil Layer about 10 mm			
15	6.15	5.29	14
30	5.88	5.28	10
60	7.75	6.45	18
Initial Oil Layer about 7 mm			
15	6.67	5.77	13
30	6.96	5.98	14
60	9.60	7.90	18
Initial Oil Layer about 4 mm			
15	7.45	6.69	10
30	8.62	6.78	21
60	13.3 ⁴	10.6 ¹	20

Because of the high viscosity of No. 6 bunker oil, the testing of this oil at 21°C required the application of delay and stirring modifications, after the addition of sinking agent, in order to sink the agent/oil mass. Tests on this oil at 20°C could not be carried out, since the extreme viscosity at this temperature rendered impossible, even with delay and stirring modifications, the sinking of the agent/oil mass with any ease or in any practical time period.

3.2.1 The Effect of Oil Layer Thickness Treated. Regardless of the free fall distance, the testing temperature or the oil type, the efficiency of the sinking agent decreases with decreasing oil layer thickness treated. The decrease in efficiency is always nonlinear, showing a distinct acceleration with decreasing layer thickness treated. The decrease in efficiency is generally due to the decreased time-in-contact of the sinking agent with the oil as the layer thickness treated is diminished.

3.2.2 The Effect of Free Fall Distance. The efficiency of the sinking agent decreases with increasing free fall distance, irrespective of the oil type or the testing temperature. The effect of free fall distance in decreasing the efficiency increases with decreasing oil layer thickness under treatment. The decrease in efficiency results from the decreased time-in-contact of the sinking agent with the oil, itself the result of the increased velocity of fall implied by the increased free fall distance. Note that, with increasing oil layer thickness treated, the effect of increasing free fall distance is diminished, particularly where the lower viscosity oils are involved.

3.2.3 The Effect of Temperature. For specific values of initial oil

layer treated, free fall distance and oil type, the efficiency of the sinking agent is higher at 2°C than it is at 21°C. Thus, in general, the effect of decreasing temperature is to increase sinking agent efficiency. This increase in efficiency is due mainly to the increased time-in-contact afforded by the viscosity increases associated with temperature decreases. Table 4 demonstrates the effect clearly.

3.2.4 The Effect of Oil Type. The efficiency of Oil-Lok 501 at 21°C is generally similar for western crude oil and No. 2 fuel oil, but is much higher for No. 6 bunker oil. Table 5 shows this situation clearly for an initial oil layer treated of 9 mm. It is apparent that this tendency results from the similar viscosities of the western crude and No. 2 fuel oils, and the much higher viscosity of the No. 6 bunker oil. The lower initial oil layer thicknesses treated result in a sinking agent efficiency decrease much greater for western crude and No. 2 fuel oils than for No. 6 bunker oil and, again, this is based on the much higher viscosity for the bunker oil. Table 5 indicates this situation for an initial oil layer thickness of 4 mm.

Although test results at 2°C were not obtained relative to the No. 6 bunker oil, western crude oil and No. 2 fuel oil show, at this temperature, generally similar sinking agent efficiencies. Table 6 clearly illustrates the point for 9 mm and 4 mm oil layer thicknesses treated.

3.3 Efficiency of Zorb-All in Removing the Three Oil Types

This sinking agent had shown a significant difference between the true and apparent specific gravity values, as well as a generally low value for the bulk or loose density (see Table 1). The indications here were the presence of internal porosity not immediately penetrable by water and even

TABLE 5

EFFECT OF OIL TYPE ON OIL-LOK 501 EFFICIENCY (21°C)

Free Fall (cm)	Ratio Sinking Agent/Oil By Weight		
	15	30	60
Initial Oil Layer 9 mm			
Western Crude Oil	4.49	5.83	7.75
No. 2 Fuel Oil	6.29	6.39	8.19
No. 6 Bunker Oil	1.10	1.19	1.50
Initial Oil Layer 4 mm			
Western Crude Oil	6.07	8.56	13.0 ¹
No. 2 Fuel Oil	7.45	8.62	13.3 ⁴
No. 6 Bunker Oil	1.52	1.75	2.16

TABLE 6

EFFECT OF OIL TYPE ON OIL-LOK 501 EFFICIENCY (2°C)

Free Fall (cm)	Ratio Sinking Agent/Oil By Weight		
	15	30	60
Initial Oil Layer 9 mm			
Western Crude Oil	4.32	5.18	6.99
No. 2 Fuel Oil	5.41	5.62	6.79
Initial Oil Layer 4 mm			
Western Crude Oil	5.31	7.72	11.4 ⁴
No. 2 Fuel Oil	6.69	6.78	10.6 ¹

less so by oil, the rapidity of penetration being dependent to a degree on the viscosity of the oil.

Preliminary testing indicated that Zorb-All, upon application to a western crude or No. 2 fuel oil float on a saline solution, sank through the oil layer to the oil/saline solution interface. At this interface, air bubbles emitted (and possibly partially entrained) by the porous sinking agent prevented the agent/oil mass from sinking through the interface to the bottom of the saline solution in the test vessel. Agitation by rapid stirring was required to dislodge the air bubbles entrapped in the mass, and to sink the agent/oil conglomerate. On this basis, all tests involving Zorb-All were subjected to delay and stirring procedures.

It was apparent that, because of this tendency for Zorb-All to be arrested in its descent at the oil/saline solution interface, the effect of free fall distance would very likely be minimal, even in the case of relatively thin initial oil layers treated. It was, therefore, decided to carry out only the 15 and 60 cm free fall distances with respect to the testing of Zorb-All.

Again, during the exploratory testing work, it was noted that Zorb-All could not sink No. 6 bunker oil at all, at least under normal conditions of testing. The agent adsorbed the oil, but the agent/oil mass stayed at the interface of the oil and saline solution layers and could not be sunk in any free manner, even after prolonged agitation. Pushing the agitated agent/oil mass to the bottom of the saline solution merely resulted in its slow rise to the interface when released. It was assumed that emitted and entrapped air, among other factors, was responsible for this persistency

in floating. Tests involving No. 6 bunker oil were, on this basis, omitted from the test series.

The data from the experimental runs are condensed in the forms of Figures 9 and 10. Figure 9 shows the effects of initial oil layer thickness treated, free fall distance and ambient temperature on the efficiency of Zorb-All in the removal of western crude oil, while Figure 10 provides the same information relative to the removal of No. 2 fuel oil. Table 7 shows, in particular, the effect of temperature on Zorb-All efficiency in the removal of the two oil types tested.

3.3.1 The Effect of Oil Layer Thickness Treated. The efficiency of Zorb-All decreases only very slightly with decreasing initial oil layer thickness, and only a very slight acceleration in the efficiency decrease occurs with decreasing oil layer. Sinking action was found to take place spontaneously to a slight extent only, and this occurred exclusively in relation to initial oil layer thicknesses treated of 2 mm or less. The properties described in Section 3.3 formed the general basis for these characteristics.

3.3.2 The Effect of Free Fall Distance. Within the limits of experimental error, there was no effect of free fall distance in decreasing the efficiency of the agent, and this can be attributed to the properties as outlined in Section 3.3.

3.3.3 The Effect of Temperature. A minor increase in efficiency results from temperature decrease, and this is exemplified by the data of Table 7. Although the relative increase appears significant in some instances, these are minimal on a quantitative basis.

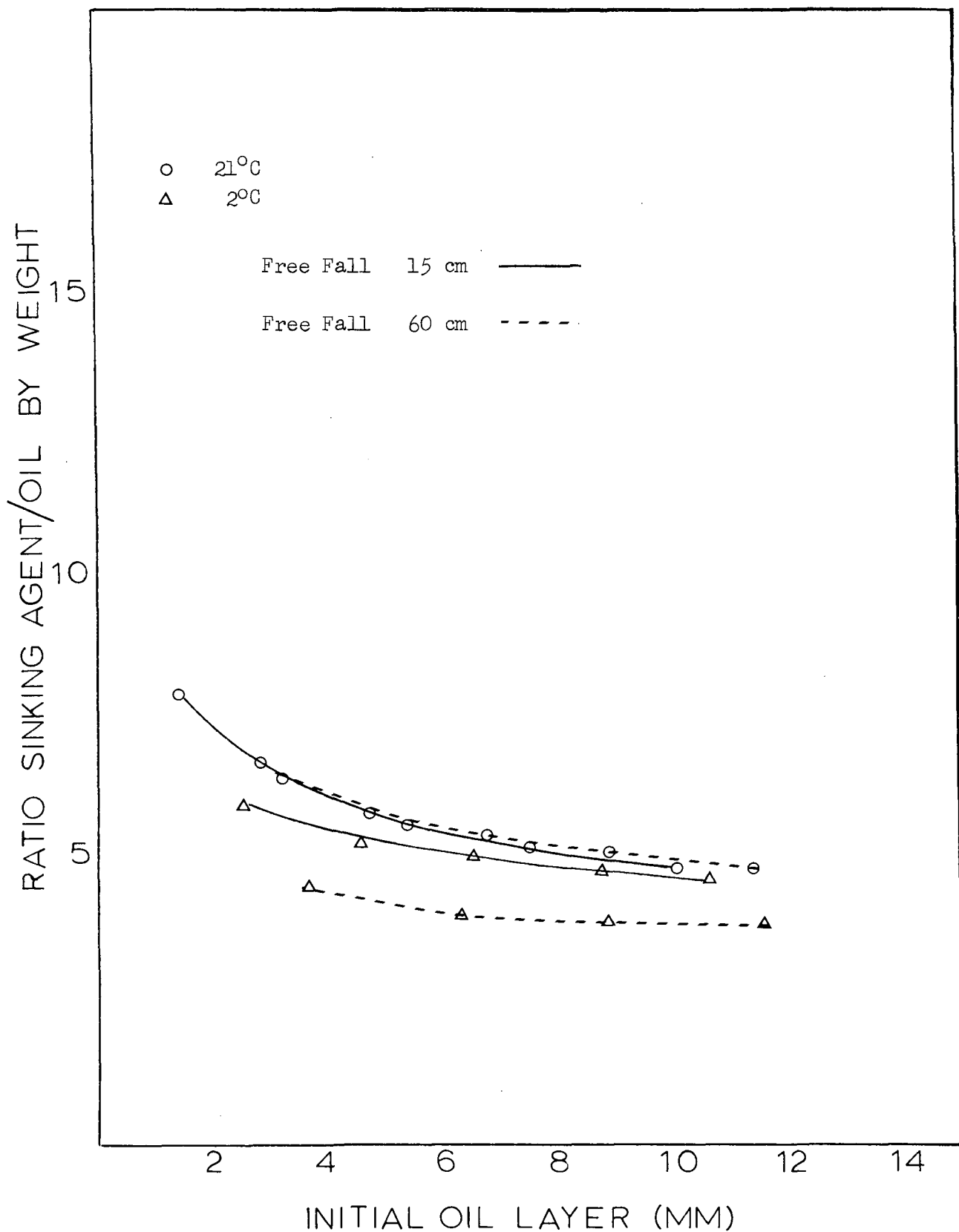


FIGURE 9 ZORB-ALL AND WESTERN CRUDE OIL - EFFECT OF INITIAL OIL LAYER THICKNESS, FREE FALL DISTANCE AND TEMPERATURE ON SINKING AGENT EFFICIENCY

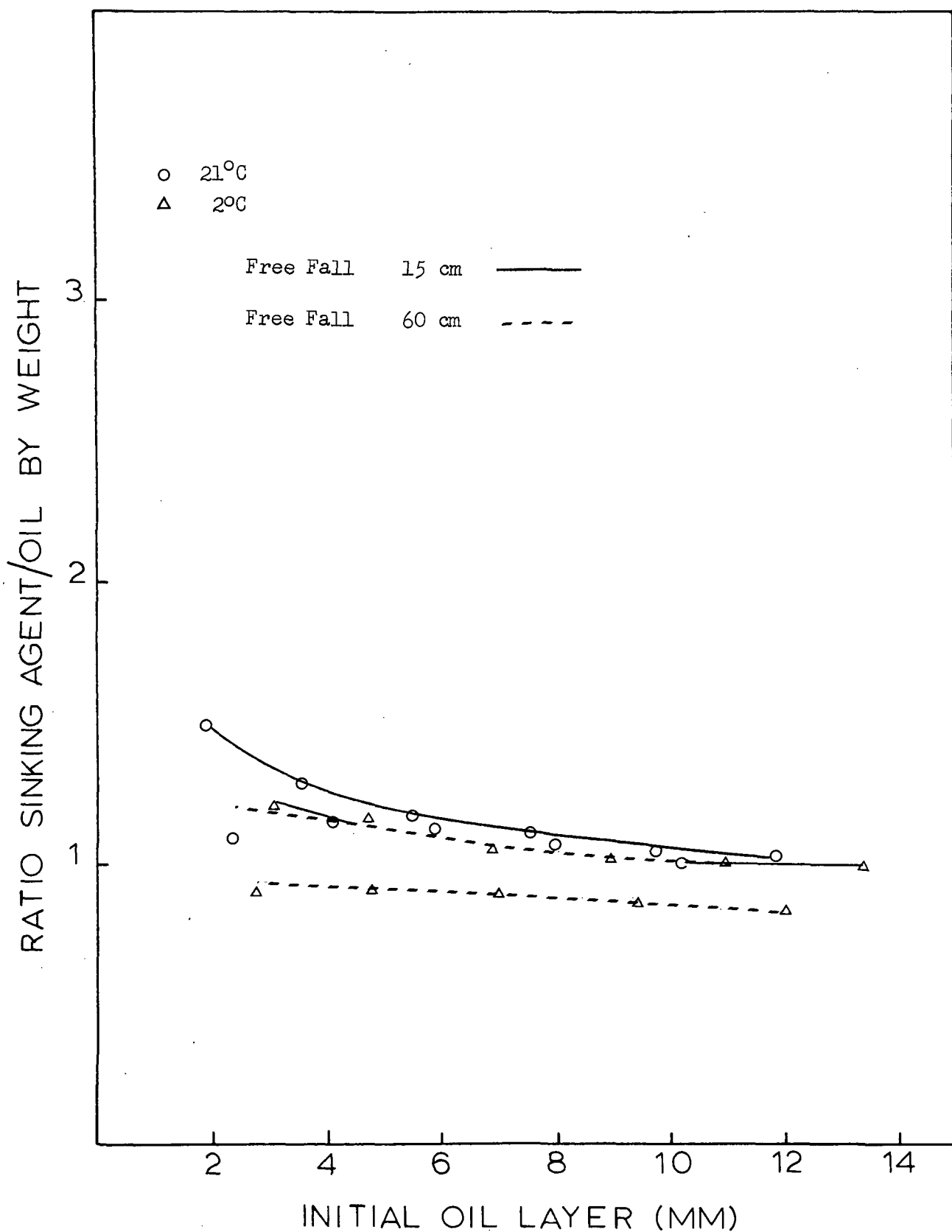


FIGURE 10 ZORB-ALL AND NO. 2 FUEL OIL - EFFECT OF INITIAL OIL LAYER THICKNESS, FREE FALL DISTANCE AND TEMPERATURE ON SINKING AGENT EFFICIENCY

TABLE 7

ZORB-ALL AND TWO TEST OILS - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Ratio Sinking Agent/Oil By Weight		
Western Crude	21°C	2°C	% Less Sinking Agent
Initial Oil Layer about 10 mm			
15	0.98	0.92	6
60	0.97	0.77	21
Initial Oil Layer about 7 mm			
15	1.06	1.03	3
60	1.10	0.81	26
Initial Oil Layer about 4 mm			
15	1.29	1.07	17
60	1.18	0.91	23
No. 2 Fuel Oil	21°C	2°C	% Less Sinking Agent
Initial Oil Layer about 10 mm			
15	1.04	1.00	4
60	1.00	0.86	14
Initial Oil Layer about 7 mm			
15	1.09	1.05	4
60	1.12	0.89	20
Initial Oil Layer about 4 mm			
15	1.28	1.16	9
60	1.14	0.91	20

3.3.4 The Effect of Oil Type. Little of a definitive nature can be stated in this connection, since tests were not carried out on the No. 6 bunker oil. A comparison of the appropriate test results for western crude and No. 2 fuel oils shows, possibly, some bias towards a somewhat higher efficiency relative to the western crude. This is, however, generally within the limits of experimental error, so that the tendency can only be described as "vague".

3.4 Efficiency of Hi-Dri in Removing the Three Oil Types

The comments to be made with respect to Hi-Dri parallel closely those made relative to Zorb-All, which latter were made in Section 3.3, and the findings of the preliminary testing work were, in general, identical. Certain somewhat significant differences were, however, noted in the comparison of the two agents. The two most important of these were:-

- (a) The Hi-Dri material contained a larger proportion of finely-divided material.
- (b) The agent/oil masses emitted or entrained more air and, after agitation, sank somewhat less readily than the Zorb-All/oil masses. This may reflect the greater degree of porosity suggested by the comparable true and apparent specific gravity values.

All of the tests involving Hi-Dri were subjected to delay and stirring procedures, and only the 15 and 60 cm free fall distances were tested. Because of a lack of sinking capability where No. 6 bunker oil was concerned, similar to that described in Section 3.3 covering Zorb-All, no tests involving this oil were carried out.

The data from the Hi-Dri investigations are condensed as Figures 11 and 12. Figure 11 shows the effects of initial oil layer thickness treated, free fall distance and ambient temperature on the efficiency of Hi-Dri in the removal of western crude oil, with Figure 12 showing the same information with respect to the removal of No. 2 fuel oil. Table 8 shows the effect of temperature, in particular, on Hi-Dri efficiency in the removal of the two oil types tested.

3.4.1 The Effect of Oil Layer Thickness Treated. The efficiency of the agent falls off very slightly with decreasing oil layer thickness, and the acceleration of this decrease in efficiency with decreasing oil layer thickness is extremely slight. These effects are somewhat more exaggerated relative to the results obtained in the testing of No. 2 fuel oil. Spontaneous sinking action was achieved in all cases to a very partial degree only, and even this was limited to instances involving initial oil layer thicknesses of 2 mm or less. These characteristics reflect the porous nature of Hi-Dri and its associated effects, all as described in Sections 3.4 and 3.3.

3.4.2 The Effect of Free Fall Distance. Increases in the free fall distance, as anticipated generally, showed no significant effect on the efficiency of Hi-Dri, any tendencies in this direction being normally within the limits of experimental error. A minor exception here occurred relative to the testing of No. 2 fuel oil, and here the decrease in agent efficiency with increasing free fall distance was somewhat more obvious.

3.4.3 The Effect of Temperature. Where the western crude oil tests are concerned, some increase in efficiency of the agent results from a de-

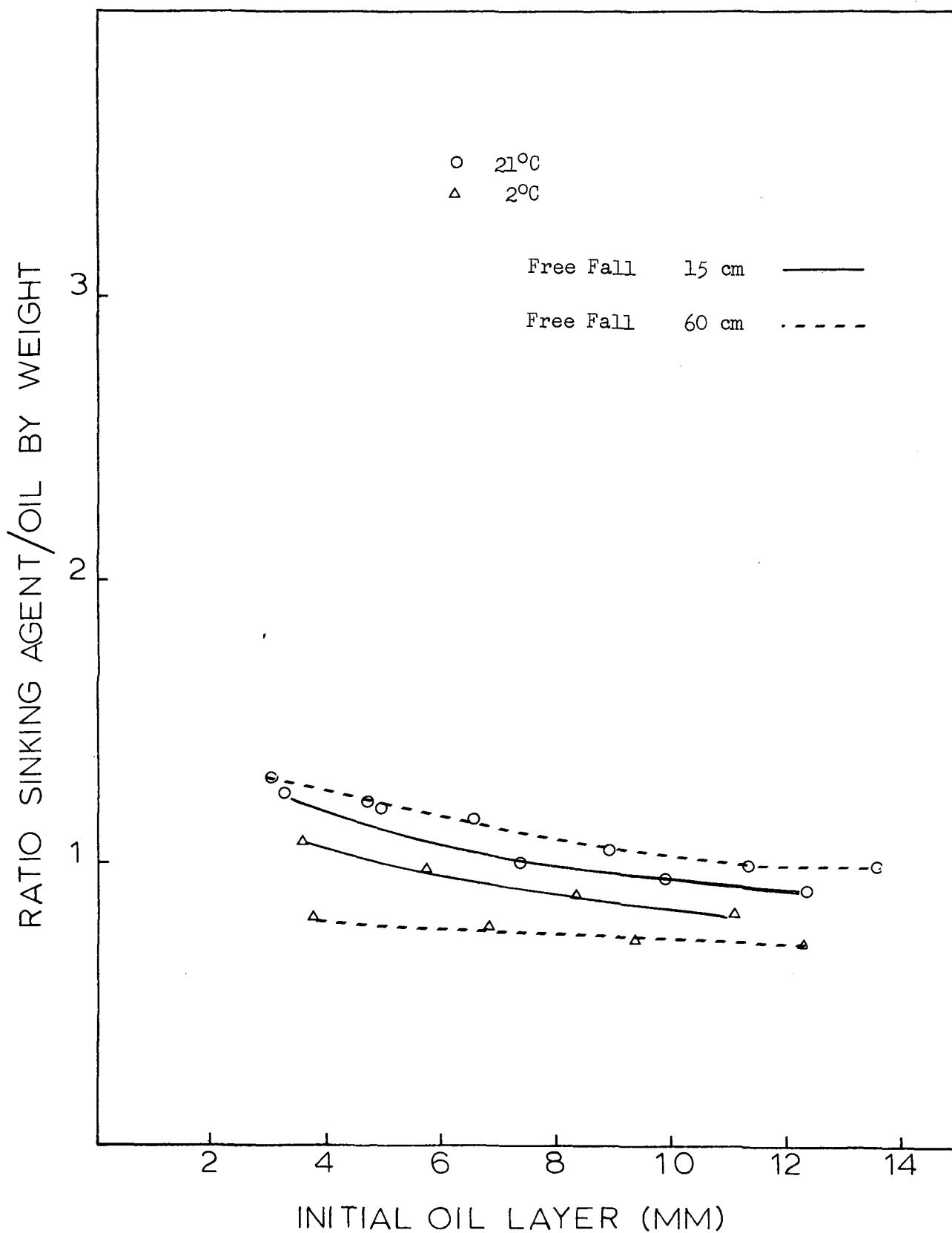


FIGURE 11 HI-DRI AND WESTERN CRUDE OIL - EFFECT OF INITIAL OIL LAYER THICKNESS, FREE FALL DISTANCE AND TEMPERATURE ON SINKING AGENT EFFICIENCY

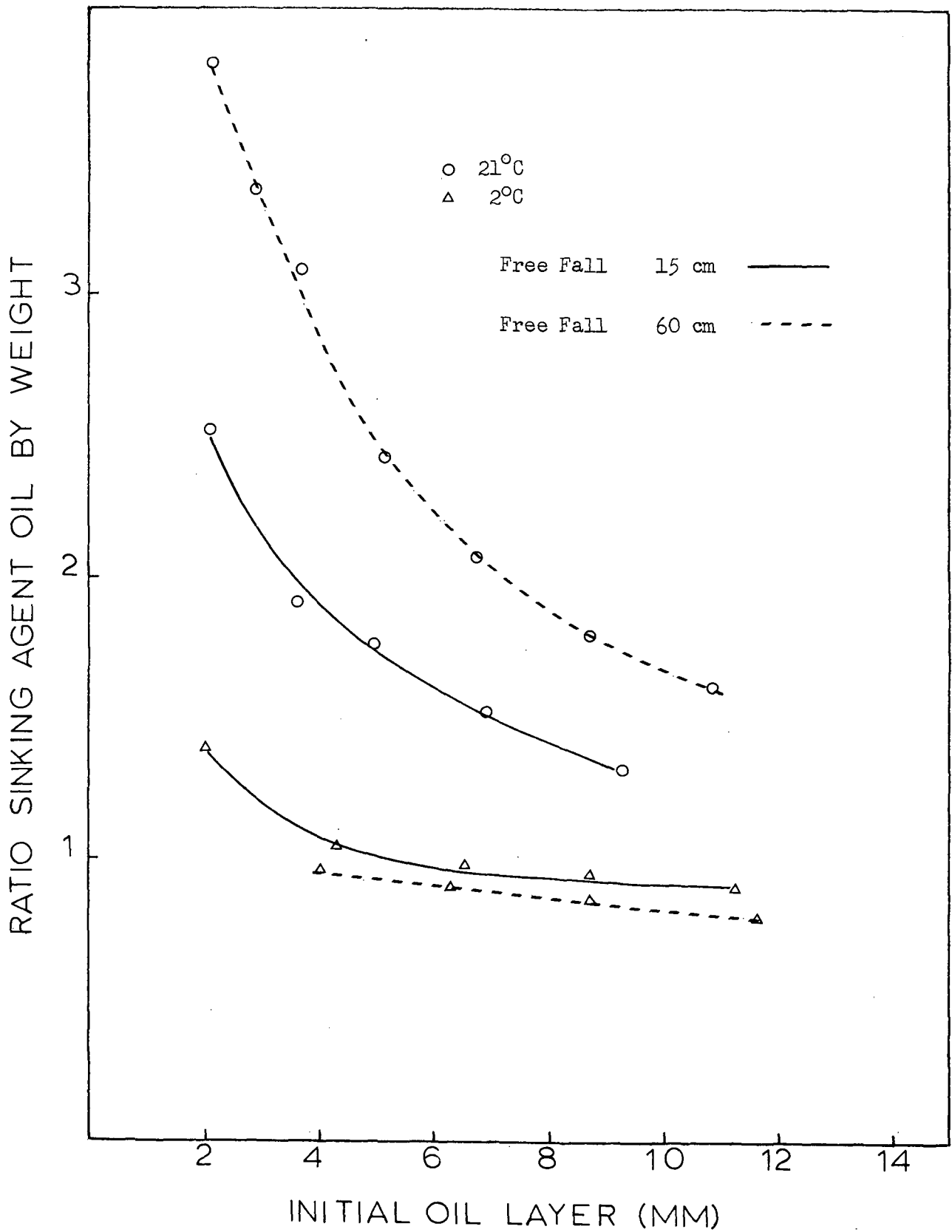


FIGURE 12 HI-DRI AND NO. 2 FUEL OIL - EFFECT OF INITIAL OIL LAYER THICKNESS, FREE FALL DISTANCE AND TEMPERATURE ON SINKING AGENT EFFICIENCY

TABLE 8

HI-DRI AND TWO TEST OILS - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Ratio Sinking Agent/Oil By Weight		
Western Crude	21°C	2°C	% Less Sinking Agent
Initial Oil Layer about 10 mm			
15	0.95	0.87	14
60	0.99	0.72	27
Initial Oil Layer about 7 mm			
15	1.03	0.97	6
60	1.16	0.77	34
Initial Oil Layer about 4 mm			
15	1.26	1.06	16
60	1.31	0.80	39
No. 2 Fuel Oil	21°C	2°C	% Less Sinking Agent
Initial Oil Layer about 10 mm			
15	1.31	0.88	33
60	1.59	0.78	50
Initial Oil Layer about 7 mm			
15	1.51	0.96	36
60	2.07	0.88	57
Initial Oil Layer about 4 mm			
15	1.90	1.03	46
60	3.08	0.95	69

crease in temperature, the effect being most noticeable with the thinner initial oil layers treated, and being most likely due to oil viscosity increases associated with decreasing temperature. In no case is the actual quantitative increase in this direction of more than an insignificant nature. The situation differs somewhat with respect to the tests on No. 2 fuel oil, and the effect of decreasing temperature in increasing the agent efficiency is distinctly more marked. Table 8 illustrates the two aspects.

3.4.4 The Effect of Oil Type. Again we can compare only the western crude oil and the No. 2 fuel oil in this connection, since the No. 6 bunker oil was not tested for reasons previously outlined. A comparison of the appropriate figures indicates that there is a definite bias towards a higher efficiency in the removal of western crude oil, particularly when the 21°C testing temperature is considered. This may be attributed to a variation in oil viscosity, with western crude oil showing the higher viscosity. The fact that the viscosity difference is significantly greater at 2°C than at 21°C is not, however, quite supported by the experimental evidence, since the difference in efficiency at 2°C does not reflect this greater viscosity difference.

3.5 The Effect of Sinking Agent Type on Oil Removal Efficiency

The data provided in the foregoing, together with additional plotted data from the full Report, permits the following conclusions relative to the removal of western crude oil:-

- (a) Oil-Lok 501 removes oil less efficiently than Zorb-All or Hi-Dri.
- (b) Oil-Lok 501 is more sensitive to initial oil layer thickness treated, decreasing in efficiency more

rapidly with decreasing layer thickness

- (c) The lower sensitivity of Zorb-All and Hi-Dri relative to (b) is largely due to the role played by internal porosity in arresting the fall of the agent at the oil/saline solution interface. This arrest factor carries with it, however, the disadvantage that these agents will not sink western crude oil without agitation. Oil-Lok 501, on the other hand, will sink this oil spontaneously.
- (d) The efficiency of Zorb-All and Hi-Dri is relatively unaffected by free fall distance, while that of Oil-Lok 501 is seriously decreased by increased free fall distance.
- (e) The efficiency of Zorb-All and Hi-Dri is improved by temperature decrease, but the magnitude of the improvement is not as high as that enjoyed by Oil-Lok 501 in this connection. The higher order of improvement here reflects the fact that, since there is no arrest factor with Oil-Lok, time-in-contact is increased significantly by the increased oil viscosity accompanying decreased temperature. This improvement does not, however, allow an order of efficiency for Oil-Lok matching those of the other two agents.
- (f) The efficiencies of Zorb-All and Hi-Dri in the removal of western crude oil are almost identical.
- (g) If a substance is to be judged a sinking agent on the basis of its ability to sink oil spontaneously, then neither Zorb-All nor Hi-Dri can be classed as true sinking agents.

The effects of sinking agent type relative to the removal of No. 2 fuel oil are almost identical, and in general the same comments apply here as made in the case of western crude oil removal. It should be noted, however, that in the removal of No. 2 fuel oil the efficiency of Zorb-All is somewhat higher than that of Hi-Dri, and this is particularly so at the 21°C

testing temperature.

The No. 6 bunker oil was tested at 21°C only, and with Oil-Lok 501 only. Zorb-All and Hi-Dri were unable to sink this oil, neither at 21°C nor at 2°C. Oil-Lok 501 could not sink this oil in a practical manner at 2°C.

3.6 Ability of Sinking Agents to Retain Sunken Oil

The experimental data in this connection involved only the 21°C testing temperature and the 15 cm free fall distance. Equations (1) to (5) were employed for all calculations required to retrieve the final results from the data analyses, and expanded charts for Figures 3 to 6 were used to obtain the volatility loss values needed in the form of percent by weight.

3.6.1 Oil-Retentivity - Oil-Lok 501. In the testing of this sinking agent the following final data was obtained:-

Oil	Agent/Oil Ratio By Weight For Sunken Mass		
	Initial	Stability Period	Test Finished
Western Crude Oil	3.58	4.8 (24 h)	4.9 (140 h)
No. 2 Fuel Oil	3.41	4.5 (24 h)	4.6 (140 h)
No. 6 Bunker Oil	1.67	2.2 (24 h)	2.4 (140 h)

In general it can be assumed that, for a given oil, any initial ratio of agent/oil for a sunken mass lower than the stability period value will result in rapid oil release to the level indicated in the last column.

3.6.2 Oil Retentivity - Zorb-All. The following final data was obtained relative to the testing of Zorb-All:-

Oil	Agent/Oil Ratio by Weight for Sunken Mass		
	Initial	Stability Period	Test Finished
Western Crude Oil	1.48	1.6 (24 h)	1.7 (120 h)
No. 2 Fuel Oil	1.10	3.3 (48 h)	3.7 (140 h)

No. 6 bunker oil could not be tested for the reasons outlined in Sections 3.4 and 3.3. It can be assumed that, in general, for a given oil, any initial ratio of agent/oil for a sunken mass lower than the stability period value involved will result in rapid oil release to the level indicated in the last column.

3.6.3 Oil Retentivity - Hi-Dri. The best results for this sinking agent showed:-

Oil	Agent/Oil Ratio by Weight for Sunken Mass		
	Initial	Stability Period	Test Finished
Western Crude Oil	1.09	1.2 (24 h)	1.2 (120 h)
No. 2 Fuel Oil	1.06	2.5 (48 h)	2.9 (140 h)

Again, No. 6 bunker oil could not be tested. Again it can be assumed that, for a given oil, any initial ratio of agent/oil for a sunken mass lower than the stability period value involved will result in rapid oil release to the level indicated in the final column.

3.6.4 Oil Retentivity Comparisons. Table 9 shows comparable oil retention data for 21°C and a 15 cm free fall distance for the agent applied. All of the values have been rounded-off to less than the proper number of significant figures for simple comparisons. Table 10 shows, for the same conditions, the sinking efficiency and the oil retentivity values with respect to, in each case, grams of oil per 100 grams of sinking agent applied.

TABLE 9

OIL RETENTIVITY CHARACTERISTICS *

Sinking Agent	Ratio Sinking Agent/Oil By Weight						% Oil Retained		
	Initial			Final					
	Western	No. 2	No. 6	Western	No. 2	No. 6	Western	No. 2	No. 6
Oil-Lok 501	3.6	3.4	1.7	4.9	4.6	2.4	73	75	70
Zorb-All	1.5	1.1	-	1.7	3.7	-	85	30	-
Hi-Dri	1.1	1.1	-	1.2	3.0	-	88	35	-

* Temperature 21°C Free Fall Distance 15 cm

TABLE 10

OIL EFFICIENCIES AND RETENTIVITIES PER 100 GRAMS OF SINKING AGENT USED *

Sinking Agent	Initial Oil Sunk (g)			Final Oil Sunk (g)		
	Western	No. 2	No. 6	Western	No. 2	No. 6
Oil-Lok 501	28	29	60	20	22	42
Zorb-All	67	91	--	59	27	--
Hi-Dri	91	91	--	83	33	--

* Temperature 21°C Free Fall Distance 15 cm

The following points may be emphasized:-

- (a) The ability of Oil-Lok 501 to sink oil improves according to the order:- western crude oil, No. 2 fuel oil, No. 6 bunker oil. The ability to retain sunken oil is approximately similar for each oil type.
- (b) The ability of Zorb-All to sink oil is distinctly superior to that of Oil-Lok 501, and this ability is somewhat better for No. 2 fuel oil than it is for western crude oil. Western crude is, however, retained to a better extent than No. 2 fuel oil.
- (c) The ability of Hi-Dri to sink oil is distinctly superior to that of Oil-Lok 501. It sinks No. 2 fuel oil equally as well as Zorb-All, and western crude somewhat better than Zorb-All. The western crude oil is retained to an extent significantly better than that for No. 2 fuel oil and, in general, for both oils, somewhat better than the retentive ability of Zorb-All.
- (d) Zorb-All and Hi-Dri sink and retain western crude oil to a better degree than Oil-Lok 501, and they sink and retain No. 2 fuel oil to an extent slightly better than Oil-Lok in each case. Both agents require agitation to sink the agent/oil mass, however, as opposed to the spontaneous sinking action of the Oil-Lok material.

In the foregoing there is no intention to imply that a further reduction in the oil retained would not occur with a more extended test interval. It is anticipated, however, that the agent/oil ratio for the sunken mass would not be significantly increased in such an extended interval.

Again, there is no intention to imply, in any of the instances considered, that a sunken mass carrying initially an agent/oil ratio higher

than the stability value will not lose oil. On the contrary, oil may be lost at any initial ratio, such loss being based not on the attainment of a specific ratio value but on the adjustment of the interparticle distribution of oil and agent. The experimental approach for the retentivity tests was purposely from initial ratios lower than the critical, this in order to locate the critical ratio as it arose out of oil loss. The extent to which oil might be lost from initially sunken masses of ratio greater than the critical might, however, be expected to be relatively low, but further experimental work would have to be carried out in order to explore this situation properly.

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