STUDIES IN CHEMISTRY

PART I: INVESTIGATION INTO THE PERFORMANCE OF SEVERAL SINKING AGENTS IN THE REMOVAL OF OIL SPILLS

PART II: THE APPLICATION OF LAOCN 3 TO THE ANALYSIS OF THE PROTON MAGNETIC RESONANCE SPECTRA OF SEVERAL OLEFINIC ACETYLENES

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DEDICATION

With thanks to my children who endured my long absences and short temper, and to my parents, and most of all to my wife who suffered and worked along with me.

ABSTRACT

PART I: INVESTIGATION INTO THE PERFORMANCE OF SEVERAL SINKING AGENTS IN THE REMOVAL OF OIL SPILLS

Anatol Feldman

This thesis describes techniques for the testing of several sinking agents to determine their efficiency in the removal of oil, and their ability to retain oil once removed by the action of sinking. It also provides information concerning the effects of oil layer thickness treated initially, free fall distance for the sinking agent, temperature, and oil type on the efficiency of removal and on the retentivity of sinking agents.

In general the heavy sinking agent Oil-Lok 501 was the most effective for the removal of viscous oils such as No. 6 Bunker. Lighter oils such as No. 2 Fuel oil and Western Crude were best removed by the non-spontaneous sinking agents Zorb-All and Hi-Dri, which had to be stirred before they would sink. For these sinking agents, the free fall distance and initial oil layer treated had little effect on their efficiency. Lower temperature produced more coherent oil/agent masses and increased the amount of oil carried to the bottom of the test cell. The retentivity of the sinking agents for the oils after sinking proceeded in decreasing order of Hi-Dri, Zorb-All, and Oil-Lok.

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1 INTRODUCTION

The main sources of oil pollution are not the spectacular accidents, but the incremental amounts that are lost from oil wells and pipe line leaks, from refinery and petrochemical effluents, from tankers cleaning their holds, and from sewers releasing industrial and automobile wastes. Chronic man-made pollution far exceeds the natural seepage rates and is straining the ecological balance. Oil spills in the arctic regions are particularly hazardous to the environment because their effects can be preserved for half a century or more.

The need for improved methods applicable to the containment, treatment, and removal of oil spills becomes daily more urgent. The growth of oil tanker size may turn a single incident into a major catastrophy. Oil spreading on water acquires the uncontrollable strength of the natural forces of tides and currents. Present day technology is incapable of dealing with these forces.

When the Tampico Maru in 1957 ran aground off a forlorn part of the Mexican coast, the only ones to suffer were the seaweeds and shell life. Recovery was fairly rapid and within two years the natural balance had been restored.

During the Torrey Canyon incident in the English Channel in 1967, the English and French governments attacked the spilled oil with booms, bombs, dispersants, and sinking agents. Booms and bombs failed to halt the onslaught of the black tide. The haphazard application of dispersants caused so much injury that their use is now strictly regulated. Sinking methods, the last to be tried, were also the most useful.

The Santa Barbara coast in 1969 was simultaneously hit by a leaking oil well that could not be plugged and a storm that hampered the new mechanical oil removal devices, such as endless belts and drum skimmers. The storm ruined booms and made ineffective the use of sorbents. But the silt that was carried down the rivers sunk an incalculable amount of oil and greatly reduced coastal pollution.

A host of oil curtailment methods now exist: a new generation of super-surfactants that are claimed to be non-toxic; monomolecular piston films that herd the oil into a fraction of their spreadable area; waxed or siliconized sorbents with increased affinity for oil; magnetic liquids which are miscible with the oil and magnetize it so that, in theory, all that is necessary is to pass a giant electromagnet over the site of the spill. New booms have been developed which are less prone to fall apart with the first wave.

Despite advances in oil pollution handling methods, sinking agents have a serviceable role to play, although their use is still a controversial subject. There is something inherently distasteful in dumping tons of dusty ores in the ocean. The main advantage of sinking agents is that their recovery is not necessary and, when swiftly applied, serve to localize the spill.

The general aims of this study involving sinking agents can be briefly outlined as follows.

1. To review, develop, and apply a method of testing to determine the efficiency of a limited number of sinking agents.

2. To review, develop, and apply a method of testing to ascertain the oil retentivity of the selected agents under laboratory conditions.

3. To explore any factors arising out of 1 and 2.

4. To review methods other than sinking agents that have been used to restrain major or minor oil spills.

5. To look at the problem of oil pollution in general and its effect on the environment today.

Figure 1 is an outline of the experimental testing procedures.

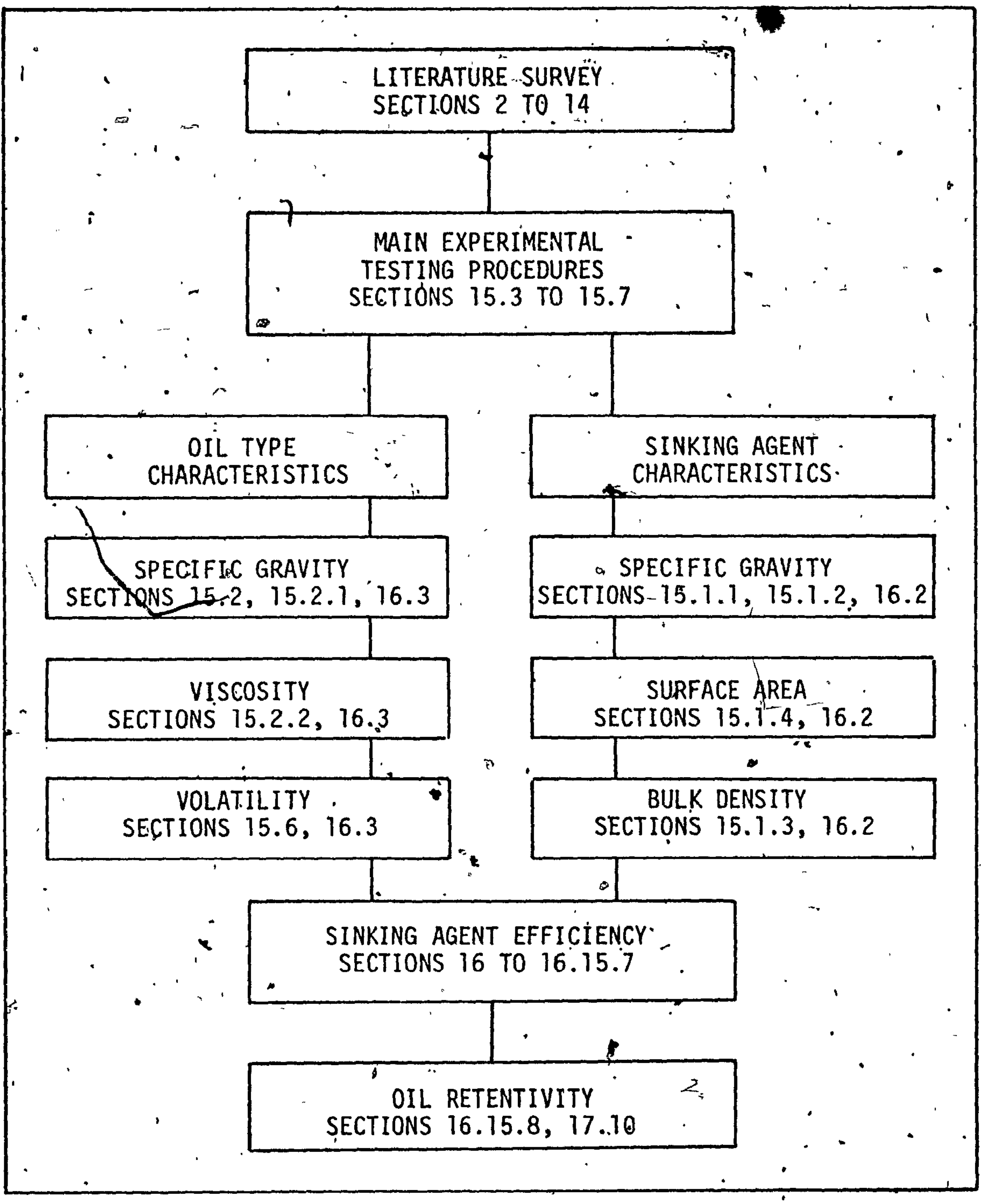


FIGURE 1 PLAN OF EXPERIMENTAL ORGANIZATION

2 ORIGIN OF OIL

The earliest theories on the origin of oil were inorganic in nature. It was thought that carbon dioxide in ground water was reduced by alkali metals in the earth to yield acetylene and other hydrocarbons. Another hypothesis was that acidic waters reacted with metal carbides to form petroleum hydrocarbons (1).

Although the chemical composition of crude oil yields few clues as to the nature of the source material, the presence in petroleum of optically active material, and the detection of porphyrins in 1934, indicated that at least part of the source material must have been organic in nature. Porphyrins are the degraded products of both chlorophyll, the photosynthetic pigment of plants, and the hematins, the respiratory pigments of animals.

The exact mechanisms of transformation are still not known, but present day thinking on the formation of oil agrees on several factors (1,2,3).

1. Petroleum is always associated with the formation of marine sediments. Most of the source material was probably accumulated fatty acids and hydrocarbons of marine organisms. The carbohydrate, lignin, and proteineous portions of living organisms played a far smaller part in oil formation.

2. The ocean was probably not the only source of hydrocarbons. A total of about 2×10^{8} tons of

volatile hydrocarbons is released into the atmosphere each year. Most of this material is ultimately broken down into carbon dioxide and water, but part of it condenses and is returned to the earth with the natural precipitation of rain and snow.

3. The natural radioactivity found in sediments did not supply sufficient heat and radiation to be counted as a factor in the formation of oil.

4. Anaerobic bacteria degraded and altered the source material.

5. Temperatures above 80 to 90°C were also not required.

6. Very high pressures were probably not necessary to the formation of oil.

7. Clays and other fine grained minerals which are always present in the sedimentary oozes may have acted as slow catalysts for the further alteration and degradation of source material into oil.

3 OIL IN THE ENVIRONMENT

3.1 Sources of Pollution

The earth manufactures enormous quantities of oil and releases on occasion some of it herself. Natural seepages have been known throughout history: mentioned in the Bible, in the works of Herodotus, and in the writings of Marco Polo. The Athabasca tar sands are the remains of a giant seep.

Best estimates for world wide seepage is about 0.6×10^6 tons per year, concentrated mainly around the Pacific area (4). Present day world wide production of crude oil is estimated to be between 3×10^9 and 4×10^9 tons a year, and about 0.01% of the amount handled is accidently spilled from tankers, pipelines, and oil wells (5). This means that 0.3×10^6 to 0.4×10^6 tons of oil, some authors say a million tons, are released into the environment each year.

A large quantity of oil is also released "unavoidably" from sewers carrying industrial and automobile waste oils, estimated to be 0.6×10^6 tons. Effluents from refineries, petrochemical plants, and tankers at sea flushing their tanks are estimated to add another 0.4×10^6 tons. During the six years of World War II 4×10^6 tons of oil were lost by destroyed tankers. On a yearly basis the total amounts to nearly four times the natural seepage rate.

3.2 Tanker Size

Tankers are growing larger (5,6). Technical innovations have continually extended the limits to their growth. During the years of World War II the average tanker measured 16 000 tons. Fifteen years later there were tankers that could carry 20 000 tons and by 1965 carrying capacity was 27 000 tons. The Torrey Canyon held in 1967 approximately 117 000 tons of crude oil. Today 500 000 ton tankers are under construction and 800 000 ton tankers are expected to be built in the next few years.

Although the existence of larger ships means fewer ships and less traffic, it also means that when accidents do occur the monster ships have so much draft and inertia, a stranding or collision is more likely to result in total destruction and to create an oil spill of major proportion.

3.3 The Stagnant Seas

The Caspian Sea has suffered intense and continuous oil pollution from natural sources, offshore drilling, and the petroleum industry in the area (7). The production of phytoplankton on which all marine life depends has fallen dramatically and the formerly abundant fishing industry has been decimated.

The Baltic Sea through natural causes is a stagnant basin, oxygen deficient due to insufficient water exchange with the Atlantic (7). The situation in the Baltic is similar to that in Lake Erie, but the Baltic is 15 times as big. The Baltic serves as a major shipping highway that caters to the industrial centres of Northern Europe.

Spent liquors from the paper industry, arsenic, cyanide, detergents, and mercury are tainting the fish. Fibres from cellulose industries discharged in great quantities are suffocating bottom life. The Baltic Sea is threatened today with becoming a vast hydrogen sulphide desert with no life but anaerobic bacteria (7). A major oil spill disaster may well tip the balance beyond the sea's recuperative powers.

3.4 Sub-lethal Amounts of Oil and Cancer

The marine ecology of the world is changing rapidly. In the Sargasso Sea, the bane of sailing vessels, tar balls and oil globules are more abundant than the Sargassum Weed (5). From accidental oil spills in the ocean we have some idea of the effects of gross pollution on the environment (8,9,10,11,12). Far less is known about the insidious effects of chronic sub-lethal amounts.

1. Oil in water has the capacity to partition and concentrate various pesticides such as DDT (13).

2. Lobster fishermen have found that baiting lobster traps with kerosene soaked bricks is as effective as using live bait (14).

3. The low boiling saturated hydrocarbon fractions found most abundantly in crude oil can seriously interfere with marine biological processes (14, 15,16,17).

4. Chemical senses of marine life are involved at extremely low concentrations in escape from predators, in sexual stimulation, in the schooling

of fish, and in the location of home streams. Innocuous levels can produce drastic chemotaxical alteration in behaviour (18).

Weathered crude oil residues, like the floating tar balls in the Sargasso Sea, contain the higher boiling polynuclear aromatic hydrocarbons, some of which have been found to be carcinogenic in nature (11). Crude oils have caused skin cancer in refinery workers (5). Carcinomas have been found on the lips of a Pacific food fish in an area chronically polluted by an oil refinery. It has been estimated that crude oil contains carcinogens such as 3,4-benzpyrene at a concentration of 1 ppm (19). This means that the Torrey Canyon which lost about 100 000 tons of oil also distributed 200 pounds of carcinogenic material into the environment.

3.5 The Fragile Ocean

The oceans are a great regulator of the planet's weather, not only because 70% of the solar energy falls on their surface, but also because they contain most of the supply of fresh water and are involved in the production of a large fraction of the earth's oxygen. In certain tropical regions the salt nuclei sprayed out by waves plays an important role in the spawning and growth of hurricanes.

If a cross-section of the ocean's depths were plotted on a logarithmic scale, to a depth of ten kilometers, the top millimeter of the ocean would cover half the page. This is the part that is responsible for gas diffusion, in particular the absorption of excess carbon dioxide produced in recent decades. The effect of gross pollution on this fragile microlayer of the ocean is not known (20).

4 THE ACCIDENTS

4.1 1957: The Wreck of the Tampico Maru

In March on a deserted portion of the Mexican coastline, an oil tanker, the Tampico Maru, carrying 8000 tons of diesel fuel ran aground (21). A long gash across her hull was ripped open, her forward section filled and settled. She was swung around by the surf until she lay broadwise across the entrance to a small cove.

The leaking oil formed a turbid emulsion with the sand and shell particles in the surf and began to cover the bottom of the cove with a suffocating sludge. Because of the inaccessible location news of the destruction of life in this cove spread slowly.

When scientists from the Scripps Institute of Oceanography visited the area about a month after the accident, they found the beach littered with dead clams, lobsters, abalones, sea urchins, star fish, mussels, and a host of smaller forms. Very few animals survived the destruction.

A tiny snail that lived above the high water mark and so escaped the worst effect of the oil, and a large anemone, were the only surviving species. The anemone is an animal very resistant to oil pollution. It has been found in the effluent of oil refineries that use sea water as a coolant.

Indications of heavy pollution lasted for three months (22).

But by the end of the summer the beach was beginning to recover. The destruction of grazing animals which fed on seaweed produced subsequently an exceptionally luxuriant growth of algae.

Two years after the incident, the cove had almost returned to normal. Most lost species had been able to re-establish themselves. But some had not. New species had moved in that were previously absent, and some animals previously abundant had disappeared. It will take a very long time for the ecological balance to return to its original state (23).

4.2 1967: The Torrey Canyon Disaster

On Saturday March 18th the tanker Torrey Canyon (24) loaded with about 117,000 tons of crude oil from Kuwait ran aground on the high part of some submerged reefs in the English Channel. Several of her 18 cargo tanks were holed and oil immediately began to pour out. Within a few hours a Dutch salvage tug reached the stranded tanker, but failed to pull her free. In addition to the leak, oil was being pumped into the sea in an attempt to lighten the boat. A Royal Navy boat soon arrived and sprayed the spreading oil with detergent.

During the next few days rising high winds further damaged the Torrey Canyon. Salvage attempts by several tugs only managed to rip her in two. A flotilla of 20 ships attempted to curtail and disperse the oil by spraying with detergents. An estimated one million gallons of various detergents were poured on the oil slicks (24).

The Royal Navy and Air Force tried to bomb the vessel with high explosives, aviation kerosene, and napalm to obliterate the wreck. But fires failed to last. One week after grounding the first oil came ashore at Sennen Cove on the Cornish coast (25). By April 11th a 50-kilometer stretch of Cotés du Nord in France became polluted (25,26).

In England, notwithstanding the failure of detergents at sea, the battle of the beaches was fought with more detergents. At Sennen Cove, the first to be hit, oil lay in some places more than a foot thick. On rocky coasts detergents were sprayed under high pressure. On sandy beaches bulldozers ploughed and scraped the sand together, and the mounds were sprayed with detergent. It was hoped that the incoming and outgoing tides would scrub the beaches clean.

Detergents were not used with wisdom (24,27). Buckets and drums of undiluted detergent were tossed from cliff tops. The emulsion of oil, water, and detergent was far more destructive than the oil itself. The emulsified oil penetrated deeper and turned some beaches into areas of oil/detergent quicksand. Snails that were seen crawling on top of oil covered seaweed fronds, disappeared when pounded by waves of dispersants.

The dispersant used against the oil from the Torrey Canyon was mostly BP1002 which is toxic at 5-25 ppm to a variety of crustaceans, molluscs, and delicate seaweeds. At 0.5 ppm BP1002 can affect the growth and development of the larvae of barnacles (28). Besides the one million gallons of detergent sprayed at sea, another two million gallons were dispersed on shore. And yet it had been known well before the Torrey Canyon incident, the havoc that detergents can produce (29).

Along the Cornish coast, as in the case of the Tampico Maru wreck, the annual green algae received an initial setback. But the virtual elimination of various species of grazing molluscs produced in a few months such an algae spurt that even previously bare rocks became covered with a thick slippery growth of green weeds (28,31).

In the beginning of May the French discovered another 50 000 tons of oil in mid-channel, drifting slowly into the Bay of Biscay. However coastal pollution, when this oil finally hit the shore, was low. Instead of spraying with detergent, the French treated the weathered oil patches with blackboard chalk to which had been added 1% sodium stearate to render it more oleophilic in nature. About 3000 tons of chalk sunk about 20 000 tons of oil in 390 feet of water.

The oil~~, having been~~ at sea much longer, had lost most of its volatile and short term toxic components. This thicker and denser oil probably required much less sinking agent than would otherwise have been required. There has so far been no report of oil refloating (26,30).

Britain and Ireland (32) provide a breeding station or winter quarters for a large proportion of the Atlantic sea birds. The birds were the worst sufferers in the Torrey Canyon oil spill. An estimated 10 000 to 30 000 sea birds were killed; about 6000 birds were treated at special rehabilitation centres; 150 were returned to health and released; and 40 died within a month after release (24,33). Of the birds worst affected were the auks, a species of water birds the size of ducks, well adapted to feeding on the wing (34,35). Their natural response to danger is diving, and so they received a larger coating than necessary when trying to escape the hazard of oil by diving into it (36). The oil caused their feathers to stick together, and their plumage lost the capacity to protect from cold. Their metabolic rate went up and their fat stores became exhausted.

The birds that were rescued were washed with trichloroethylene solution, which not only removed the oil but also removed their natural wax cover (34,35). Rehabilitation was thus overly prolonged. Some newer cleaning agents with which waxing takes place during cleaning are now being used. But the variety of 300 different wax molecules that can be found in the secretions of some preen glands is hard to replicate with an artificial replacement (37).

The majority of the initial cadavers were badly oil stained with feathers falling out of swollen tissues. The dead and dying birds were emaciated, suffering from great atrophy of their pectoral muscles, the main flight muscles. They weighed about one third their normal weight. Those birds that did not succumb immediately to an overdose of oil suffered from internal haemorrhage, inflamed intestines, congested lungs, and discoloured kidneys. The birds that survived the oil and survived the de-oiling procedures, developed after several weeks in captivity due to their enforced flightless state and unnaturally long grounding, arthritis in their legs, and cracked webs and skin which eventually became infected. In general, the longer a bird was kept, the less were its chances for survival (34,35).

4.3 1969: The Santa Barbara Blow-out

On January 28th during normal operation on a drilling platform off the Santa Barbara coast, it became necessary to replace a worn drill bit in Well A-21. Sections of drill pipe were removed and drilling mud pumped in. Drilling mud is a special lubricant used to cool and lubricate drill bits, and maintain hydrostatic counter pressure. When the eighth section of drill pipe was removed, drilling mud began to flow back out of the well and formed a 20-foot geyser above the platform. About 200 yards off the northeast corner of the platform large boils of explosive poisonous natural gas began to bubble on the surface (38).

The next day helicopter surveillance revealed an oil slick about 25 square miles around the platform. Long wind-driven windrows were beginning to reach the shores of Santa Barbara (39).

The Federal Water Pollution Control Administration permitted dispersants to be used in combatting the spreading oil slicks; but perhaps mindful of the damage caused by these agents, changed its mind for and against their use several times during the initial days of the blow-out; and finally allowed only limited spraying around the platform to reduce the fire hazards (39).

To protect coastal areas plastic booms in 500-foot long sections were made ready, but it soon became apparent that the booms under construction could not meet their requirements. Fittings broke even under low stress, sections jack-knifed and construction of these plastic booms was abandoned. Booms made of telephone poles strung together by steel cables proved unmanageable and were finally beached by the Coast Guard attempting to use them (39).

A two day storm hampered all oil containment efforts. A ship rammed other oil barriers set in front of the Santa Barbara harbour, and oil came ashore. The storm deposited on the shores a tremendous amount of driftwood and debris and seaweed, all of which later became covered with oil, making cleanup more difficult (38,39).

When the storm subsided work was continued to plug the leak of Well A-21. Finally ten days after the blow-out the well was plugged with drilling mud and cement. The leak was over.

The battle for the beaches was a failure. Booms, floating skimmers, bubble carriers, and polyurethane drum and wringers did not find conditions suitable for operation in Santa Barbara. Burning was tried for oil, and oil and straw, but was unsuccessful.

Straw mulchers capable of broadcasting 8-10 tons of straw per hour were used, but recovery was difficult and legal disposal sites were limited. Santa Barbara city officials did not permit the use of the city dump, and other disposal sites were inaccessible because the roads had been washed out during the rains.

On February 24th Well A-41 on the same platform blew out.

In two days the river of oil measured 8.5 miles long and 1000 feet wide. Huge underwater rubber tent funnels were installed on the ocean floor to siphon off the upwelling oil. But the leak was uncontrollable. It increased and decreased without apparent cause. It was finally plugged with mud and cement on March 1st.

On December 1st there was still another leak. A pipeline on the same platform broke and released 17 000 gallons of oil (38).

The amount of oil that coated Santa Barbara varied with the observer. An agreed upon estimate was that during the worst days the leakage rate was 20 000 to 200 000 gallons per day (39).

Santa Barbara was lucky for it probably suffered more from the early storms than from the oil. The rivers carried down excess silt which mixed with the tide of incoming oil and acted as natural sinking agents, and reduced the possible contamination of the shore. Santa Barbara was used to oil spills (40). Oil leaks have been recorded in this area since Vancouver's visit in 1792. Perhaps life here had become adjusted to chronic pollution. In this area lives an insect called the Petroleum Fly that spends its larval stage feeding in pools of oil (41).

The bird toll was only 3000 to 4000, mostly cormorants, another species of diving birds (38). Seals and sea lions were seen to romp in the oil covered waters. There were no large fish kills during the oil spill. Larvae of the common fish and macroplankton remained or quickly returned to their former abundance. The oil created a mess but no lasting damage (42).

5 CHEMISTRY AND PHYSICS OF PETROLEUM

5.1 General Characteristics

The physical characteristics of crude oil can vary from light volatile liquids of reddish-brown colour to viscous semi-solid black tars. They can smell pleasantly or emit an overwhelming odour of rotten eggs and garlic. The boiling point of some of its constituents can vary from -161.5^{0}C for methane to 354^{0}C for anthracene. Solubility in water can vary from 150 ml/l for butane to 3 ppm for decane. In the ash from crudes almost half the elements of the periodic table have been identified.

Oil varies from oilfield to oilfield and even from well to well in the same oilfield. The oil can contain, besides dissolved gases, dissolved solids and colloidal suspensions (43).

5.2 Hydrocarbon Constituents

The hydrocarbons present in crude oil range from methane to molecules of 60 or more carbon atoms (43,44,45).

5.2.1 Normal or Straight Chain Paraffins. N-alkanes are important constituents of crude oil, particularly in low boiling fractions. Their concentration decreases progressively with increasing molecular weight of the fractions.

5.2.2 Branched Chain Paraffins. Because of isomerism in branched alkanes, the number of individual compounds which can be present in a particular fraction increases as the molecular weight increases. But the predominating members in the lower boiling fractions are those with only a slight degree of branching.

5.2.3 Naphthenes. This is a petrochemical term for cycloalkanes with or without alkyl side chains. Crude oil contains many substituted monocyclic naphthenes such as cyclopentane and cyclohexane with side chains one to three carbon atoms long. But crystalline monocyclic naphthenes with side chains of 20 to 30 carbon atoms have been isolated.

Other common constituents of crude oil are monocyclic ring fragments strung together by alkyl chains, or condensed into various branched decalins. Tetracyclic and pentacyclic naphthenes have been identified. In certain lubricating oils graphitic plates containing ten condensed rings have been identified.

5.2.4 Aromatics. Benzene, toluene, xylene, ethyl benzene, and others are important constituents in crude oil. As in the case of the naphthenes, the rings may be condensed or connected by alkyl chains into various combinations. Saturated and unsaturated ring hybrids also exist. These mixed naphthene-aromatic compounds appear in the higher boiling fractions and residues (44).

5.3 Non-hydrocarbon Components

Crude oils also have many sulphur, nitrogen, and oxygen containing compounds and, in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. Although non-hydrocarbon components are present throughout the entire boiling range of crude oils, they are more concentrated in the heavier residues. During the refining process the non-hydrocarbons are the most intractable. Inorganic salts cause breakdowns, liberate free HCl, and corrode distillation equipment. Trace metals such as vanadium and nickel poison catalysts (43,44).

5.3.1 Sulphur Compounds. Organic sulphur compounds are present in all crudes, but their concentrations can vary from 0.05% to 5%. The distribution of sulphur is not uniform but increases with increasing molecular weight of the fractions. Sulphur is also present as hydrogen sulphide gas or elemental sulphur dissolved in the oil.

In the lower boiling fractions the main sulphur compounds are the highly objectionable mercaptans or thiols. Prevalent in the higher boiling ranges are cyclic mercaptans and cyclic sulphides.

5.3.2 Nitrogen Compounds. Compounds containing nitrogen are present in highest concentration in asphaltic distillation residues. Several nitrogen compounds that have been isolated are alkyl substituted quinolines and pyridines, as have derivatives of indoles, pyrroles, and carbazoles.

Trace amounts of a class of compounds called porphyrins whose basic structure consists of four pyrrole rings joined by methyne groups have been identified by optical spectroscopy and electron spin resonance. Porphyrins form very stable complexes with vanadium and nickel. They are powerful interfacial agents promoting the formation of emulsions of oil and water. Their presence pointed to the biological origin of petroleum due to their similarity to chlorophyll and hematins (1,46).

5.3.3 Oxygen Compounds. The oxygen compounds that have been identified are almost all acidic in nature. Very few alcohols, ketones, and other neutral oxygen compounds have been found. Their presence is probably responsible for the formation of oil-water emulsions. The molecular weights encountered have been as high as 1400.

6 THE NATURAL FATE OF OIL

6.1 Evaporation

The two to four years required to remove the gross effects of most oil spills, when put on a time scale of 500 million years during which the oil was born in the bowels of the earth, means almost instant disintegration and dispersion upon exposure to the sea and air.

The sea provides a very large table on which the oil can spread. A gallon of oil can cover many acres. Over this large surface area, evaporation can remove a good part of the oil spilled. Chromatographic experiments have shown that within a few weeks at the most, depending on the size and type of oil spilled and the state of the ocean, the oil will have lost most of its volatile and also more toxic components. Twenty to thirty per cent of an oil spill can be lost through evaporation; this is very effective for removal of fractions C_1 to C_{16}, most of whose boiling points range up to 225°C.

The rougher the state of the sea, in terms of evaporation, the better (48,49).

The massive evaporation occurring during the first few hours of an oil spill can leave the oil cooler, increasing its viscosity and damping its rate of spread. The density of the residual oil also increases with time as would be expected as the more volatile components are lost. The rapid and selective removal of the lower boiling fractions leaves a part of the oil that is far more intractable and which is still after all the main portion of the spill. It contains in abundance long term toxic material in the form of substituted tricyclic and higher ring aromatics (50,51).

6.2 Dissolution

Simultaneous with evaporation from above, dissolution occurs from below, and the effects on the oil are much the same. Distinction between them is not easy.

Remembering the large volume of seawater available, solution and oil-in-water emulsification can also be considerable. It has been estimated that five tons of oil might pass into a layer of water five meters deep beneath a typical 100-ton slick during the first day (52). The oil in the water column is readily adsorbed by any available detritus: clay and silt and skeletal remains of organisms in the ocean. The weighted oil can be distributed by subsurface currents or can sink even further, sometimes for weeks and months before it reaches the bottom.

Oil in the water column, besides sinking or dispersal by currents, is further dispersed by the microorganisms of the sea. Microplankton swimming through are coated inside and out. Copepods and barnacle larvae, an important group of zooplankton which form the main food of many fish, feed by filtering out microplankton. The oily copepods and barnacle larvae become part of the food chain in the ocean. Ingested hydrocarbons can be passed on from animal to animal virtually unchanged except perhaps in concentration, which increases on the food ladder.

6.3 Chocolate Mousse

Concurrently with dissolution and evaporation the action of the sea and natural surfactants in the oil lead to another kind of emulsion, water in oil. This emulsion is a gel-like substance of light brown colour containing 70-80% water and is called "chocolate mousse". This gel can be produced quite rapidly even in mild sea conditions. Once formed, chocolate mousse is stable; chemical and biological reactions are slowed; the available exposed surface is less. Its buoyancy approaching that of water may make it sink eventually.

If it is washed on shore, the chocolate mousse picks up sand and debris and, when the water evaporates, leaves tarry compact lumps which degrade very slowly. But stranded chocolate mousse due to breaking waves, and abrasive movements of sand and rock, and the indiscriminate eating habits of several variety of limpets, is weathered faster than chocolate mousse at sea (49,52).

6.4 Chemical and Biological Degradation

The chemical goulash that is found in crude oil precludes definite answers, products, mechanisms, or pathways that can be followed with certainty. Although there are differences, chemical and biological degradation, like evaporation and dissolution, are very much intertwined.

Oxidation may be initiated by UV light from the sun; propagated through the formation of free radicals; it may be encouraged by certain mineral salts in the ocean; or catalyzed by enzymes; or inhibited by the presence of sulphur compounds in the oil (53).

Although most of the constituents of oil will oxidize, oxidation will affect primarily the medium and higher molecular weight hydrocarbons. It may lead to carboxylic acids of lower molecular weight which are weathered more easily, degraded and dissolved; or it may lead to the formation of higher molecular weight products by radical-radical combinations, by condensation of aldehydes and ketones, or by esterification between alcohols and carboxylic acid. Much is known about the degradation of the individual components of crude oil, but little is known about their fate in more complex mixtures (52).

Oil oxidizing yeasts, bacteria, and fungi are all capable of consuming a great variety of hydrocarbons. But on the open ocean yeast and fungi are very scarce. Degradation can be further hampered because each species of microbe will attack known enemies and strictly leave others alone. For instance, a microbe called Nocardia oxidizes even numbered alkanes attached to cyclic compounds if and only if n-alkanes are also present (53). There are no super-bacteria that can dispose of all the possible constituents found in crude oil. Complete degradation is possible but only by numerous mixed cultures. Sometimes the presence of bacteria that can utilize the primary oxidation products including complex acids, alcohols, and ketones are as important as those that can breach the original hydrocarbon.

Under favourable circumstances an oil spill increases bacterial growth and increases the level of protozoa which in turn increases the level of higher animals. Nevertheless oil is not a very good ocean fertilizer because of its high oxygen demand. It has been estimated that complete oxidation of one liter of oil would require 400 000 liters of oxygen from the sea water, neglecting replenishment from the atmosphere or photosynthetic activity (54,55).

From methane to ethane to propane to snaky chains of 30 carbons or more, n-alkanes are the easiest for microbes to digest; longer chains are degraded slower, due perhaps to their lower solubility. Biodegradability is further affected by the molecular architecture: unbranched chains are degraded faster than branched chains. The order of microbial preference in decreasing order is n-alkanes, isoalkanes, and cycloalkanes. The place of easiest entry is usually a terminal methyl group to give an alcohol or aldehyde. The final products are carboxylic acids (54).

Certain strains of Pseudomonas have no trouble subsisting on an aromatic diet of benzene and toluene. Alkyl groups on the ring seem to make the aromatic compounds more palatable (55).

Figure 2 indicates some of the possible mechanisms for the dispersal and degradation of spilled oil on the ocean. The final fate of oil that has been spilled and has not evaporated, has not been dissolved or sunk, or beached, is to float as black-brown indestructible tarry lumps, hard on the outside, soft and toxic on the inside. They may be covered with slime mold, and goose barnacles, and provide a niche for a species of isopods. These lumps now chronically pollute the ocean surface (56,57,58).

7 DYNAMICS OF AN OIL SLICK

7.1 Assumptions

When an oil spill occurs there is an immediate need to determine how rapidly the oil will spread and where it will go in a given time. A knowledge of these factors provides a basis for effective confinement, control, and clean-up of the spill. The spreading behaviour of an oil spill like the behaviour of a puff of smoke can be intuitively understood. The mathematics however to describe the phenomena can be quite complex.

Because even the best of theories gives results that only occasionally correspond to reality only a simplified picture on the nature of the forces involved is presented.

Initially the assumptions are made that the properties of the

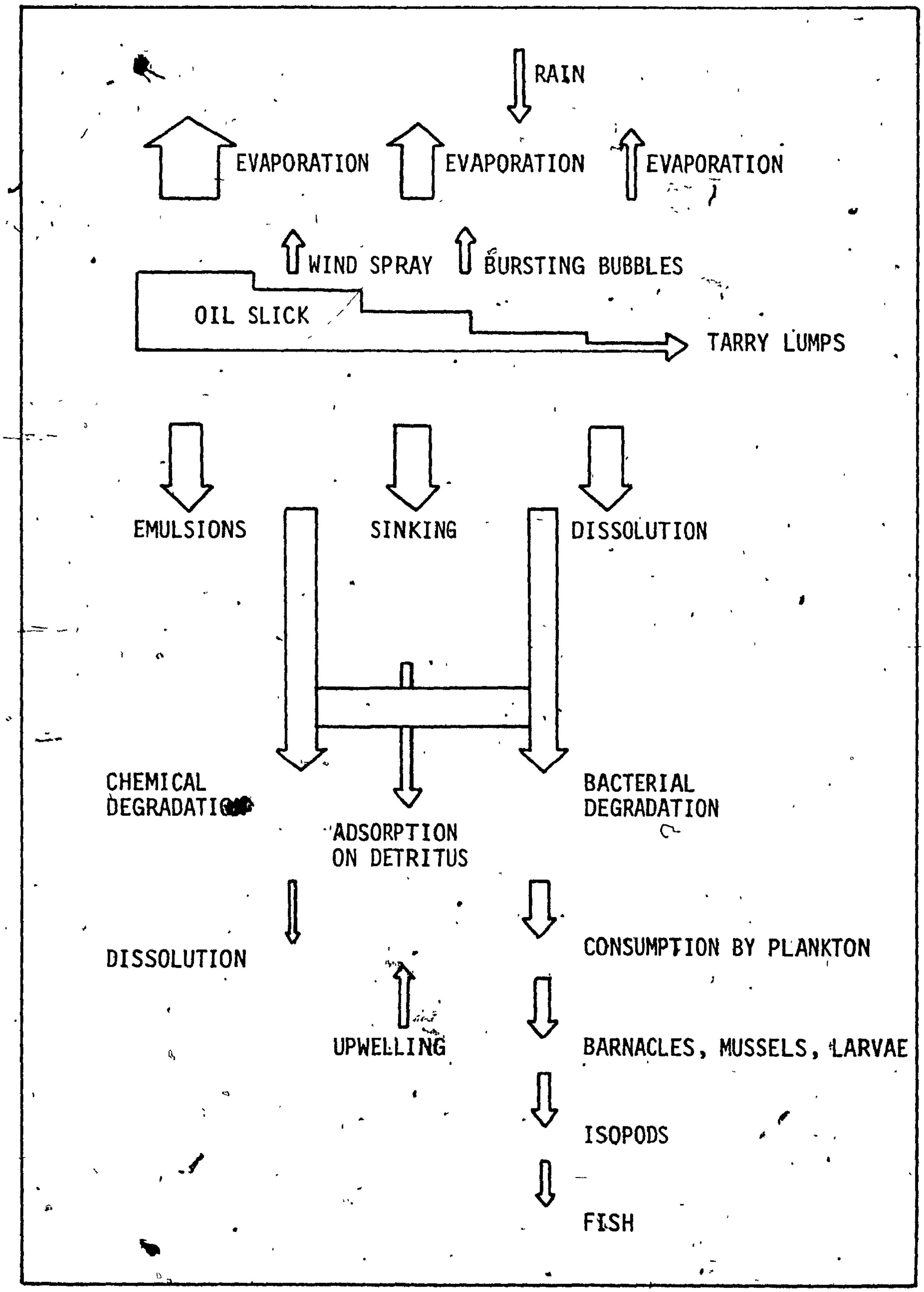


FIGURE 2 POSSIBLE MECHANISMS RESPONSIBLE FOR THE DEGRADATION OF OIL IN THE SEA

spilled oil remain invariant with time; that it does not age; that selective evaporation of the lighter components which changes density, viscosity, and surface tension does not occur; and that despite its varied composition, the oil is treated as a single component fluid of constant properties (59,60,61,62).

7.2 Spreading Forces

The behaviour of spreading oil can be described in terms of gravity, inertia, viscosity, and surface tension forces. The following arguments were developed by Fay in 1969 (62).

The volume of oil spilled is given by

$$V = l^2 h \tag{1}$$

where l = diameter of the slick

h = thickness

Constants like π are unnecessary to the argument. As the oil spreads outward, the moving layer of oil drags with it a thin layer of water. Some water therefore moves upward and outward to replace the spreading oil. Figure 3 indicates the leading edge of the spreading oil. The thickness δ of the uppermost layer of water set into motion by the viscous forces has the magnitude

$$\delta = \sqrt{\nu t} \tag{2}$$

where ν = kinetic viscosity of the water

t = time

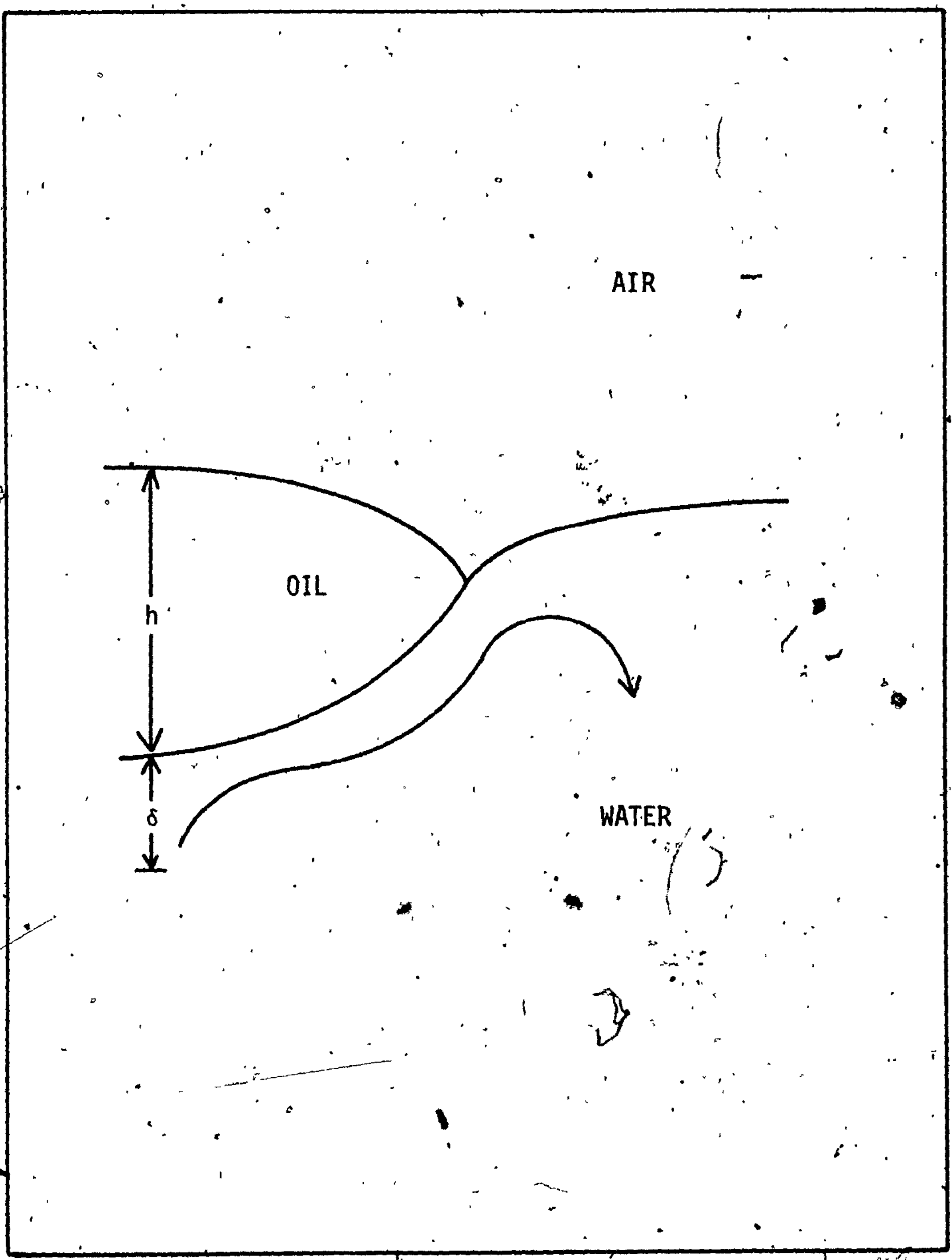


FIGURE 3 THE LEADING EDGE OF AN OIL SLICK. h IS THE THICKNESS, AND δ REPRESENTS THE THICKNESS OF WATER SET IN MOTION (61)

7.2.1 Surface Tension. The ultimate film thickness and amount of spreading will depend on a balance of surface tension forces as shown in Figure 4. The oil film has an upper surface tension of σ_o, and a lower interfacial tension σ_{ow}. The surface tension of the water is σ_w. The net surface tension, also called the spreading coefficient is

$$s = \sigma_w - (\sigma_o + \sigma_{ow}) \qquad (3)$$

The net surface tension acting on the oil divided by the cross-sectional area of the slick is given by

$$F_{st} = \frac{s}{lh} = \frac{sl}{l^2 h} = \frac{sl}{V} \qquad (4)$$

7.2.2 Gravity. The other spreading force, gravity, produces a horizontal force per unit volume.

$$F_g = \frac{PA}{V} \qquad (5)$$

and Pressure = P = $\Delta\rho gh$

Area = A = lh

where $\Delta\rho$ = difference in mass density between water and oil

g = gravitational acceleration

l = diameter of the slick

h = thickness

Upon substitution we obtain

$$F_g = \frac{\Delta\rho gh^2 l}{V} = \frac{\Delta\rho gh^2 l}{l^2 h} = \frac{\Delta\rho gh}{l} \times \frac{l^2}{l^2} = \frac{\Delta\rho gV}{l^3} \qquad (6)$$

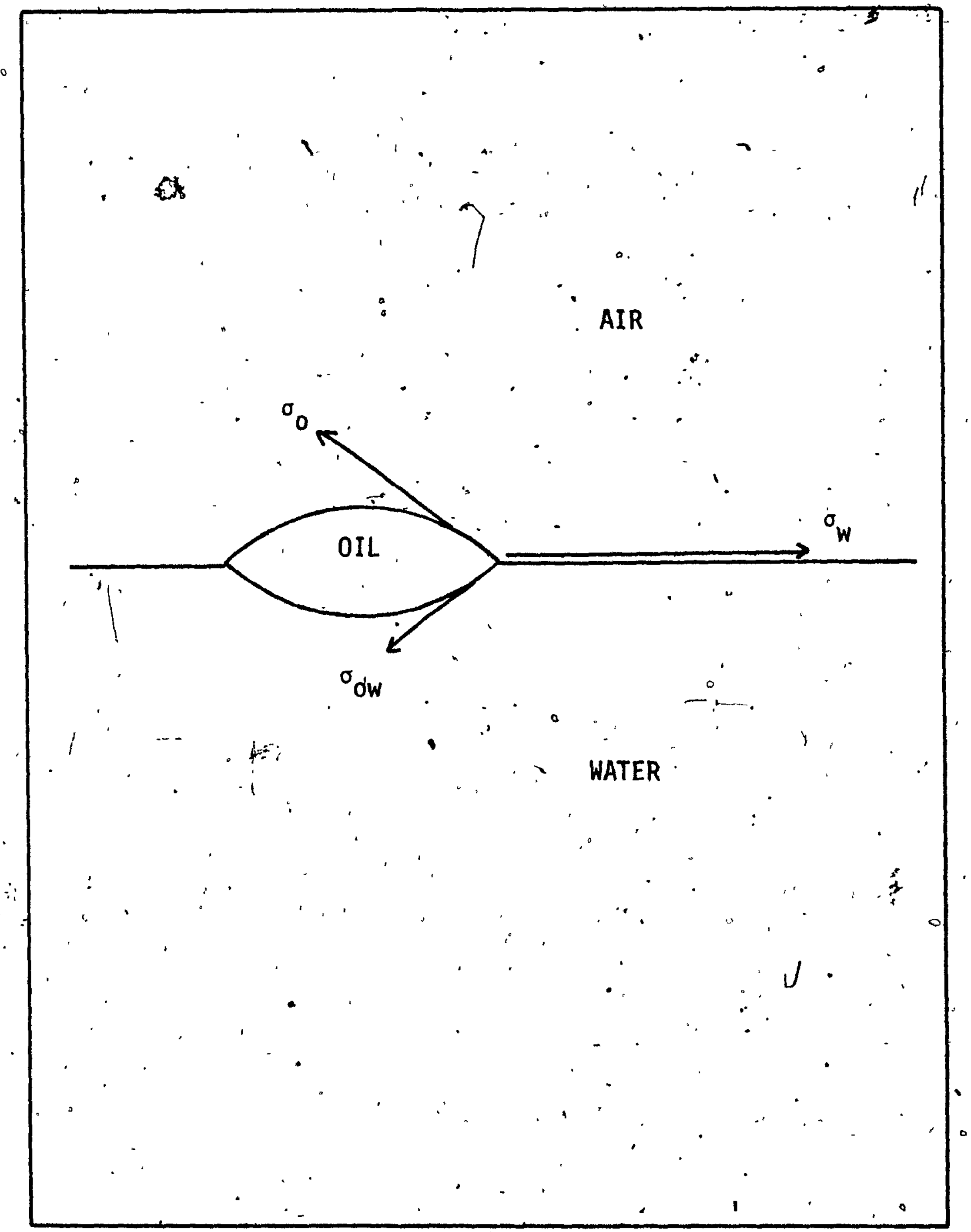


FIGURE 4 SURFACE TENSION FORCES ACTING ON AN OIL DROPLET ON WATER. σ_o IS THE SURFACE TENSION OF THE OIL, σ_w IS THE SURFACE TENSION OF THE WATER, AND σ_{ow} IS THE INTERFACIAL TENSION (79).

7.2.3 Gravity and Surface Tension Spreading Forces. By comparing the two spreading forces, gravity and surface tension, we see that since 1 increases with time, gravity will be the dominating spreading force at the beginning of the oil spill. Surface tension, however, will ultimately dominate at longer times.

By setting the two forces equal and using equations (4) and (6), we can find the critical thickness of oil where the dominating force of gravity gives way to surface tension forces.

$$F_{st} = F_g \tag{7}$$

$$\frac{s}{lh} = \frac{\Delta\rho gh}{l} \tag{8}$$

$$\Delta\rho gh^2 = s \tag{9}$$

Therefore,

$$h_c = \sqrt{\frac{s}{\Delta\rho g}} \tag{10}$$

For typical values of $s = 30$ dynes/cm and $\Delta\rho = 0.05$ gm/cm^3, we obtain $h_c \approx 8$ mm. According to these calculations, gravity ceases to play a role in the spreading of oil when the thickness of the spill reaches about 8 mm.

7.3 Retarding Forces

7.3.1 Inertia. The retarding inertial force acting on the oil is the product of the mass density ρ and acceleration l/t^2.

$$F_i = \frac{\rho l}{t^2} \tag{11}$$

7.3.2 Viscosity. The viscous force per unit volume is the product of the absolute viscosity $\rho\nu$, and the velocity gradient $l/t\delta$, divided by the oil thickness h.

$$F_\nu = \frac{\rho\nu l}{t\delta h} = \frac{\rho\nu l}{th\sqrt{\nu t}} = \frac{\rho\nu^{1/2} l}{t^{3/2} h} \times \frac{l^2}{l^2} = \frac{\rho\nu^{1/2} l^3}{t^{3/2} V} \tag{12}$$

7.3.3 Inertial and Viscous Retarding Forces. The ratio of viscous to inertial forces is very small at the beginning of the spread.

$$\frac{F_\nu}{F_i} = \frac{\rho\nu^{1/2} l^3}{t^{3/2}\ V} \times \frac{t^2}{\rho l} = \left[\frac{\nu^{1/2}}{V}\right] l^2 t^{1/2} \tag{13}$$

Inertia is the dominating retarding force at the start. The two forces become equal when the oil film thickness h equals the water thickness δ. This transition from inertial to viscous retarded spread does not occur for a fixed thickness, nor at a given time, but varies on the size of the spill.

7.4 The Three Spreading Domains

Oil spreading on water passes through three phases.

1. Beginning: Gravity-Inertia

   Gravity is the dominating spreading force and inertia is the dominating retarding force.

   Using equations (6) and (11) we obtain

$$F_g = F_i \qquad (14)$$

$$\frac{\Delta\rho g V}{l^3} = \frac{\rho l}{t^2} \qquad (15)$$

$$\rho l^4 = \Delta\rho g t^2 V \qquad (16)$$

$$l^4 = \frac{\Delta\rho}{\rho} g t^2 V, \qquad (17)$$

$$l^4 = \Delta g t^2 V \qquad (18)$$

where Δ = ratio of density difference between water and oil to density of oil.

$$l = \left[\Delta g t^2 V\right]^{1/4} \qquad (19)$$

2. Intermediate: Gravity-Viscosity

Gravity is still the dominating spreading force but now viscosity of the oil begins to exert a retarding force.

Using equations (6) and (12) we obtain.

$$F_g = F_\nu \qquad (20)$$

$$\frac{\Delta\rho g V}{l^3} = \frac{\rho \nu^{1/2} l^3}{t^{3/2} V} \qquad (21)$$

$$\rho \nu^{1/2} l^6 = \Delta\rho g t^{3/2} V^2 \qquad (22)$$

$$l^6 = \frac{\Delta\rho g t^{3/2} V^2}{\rho \nu^{1/2}} \qquad (23)$$

$$l = \left[\frac{\Delta\rho g t^{3/2} V^2}{\nu^{1/2}}\right]^{1/6} \tag{24}$$

3. Final: Surface Tension-Velocity

The oil slick is now so thin that gravity has lost its power to spread the oil. It is surface tension that continues to spread the oil and viscosity that tends to retard it.

Using equations (4) and (12) we obtain

$$F_{st} = F_{\nu} \tag{25}$$

$$\frac{\sigma l}{V} = \frac{\rho \nu^{1/2} l^3}{t^{3/2} V} \tag{26}$$

$$\rho \nu^{1/2} l^2 = s t^{3/2} \tag{27}$$

$$l = \left[\frac{s^2 t^3}{\rho^2 \nu}\right]^{1/4} \tag{28}$$

The spreading of the oil once it has entered the surface tension regime is seen to be independent of the volume spilled.

7.5 Spreading Behaviour in a Moving Stream

With only slight modification it is possible to estimate the width l of a slick located in a stream of uniform speed u.

$$\text{Volume Flow Rate of Oil} = V = hlu \tag{29}$$

$$\text{Flow Time} = t = \frac{x}{u} \qquad (30)$$

where x = down stream distance

With these changes the three spreading regimes become

Beginning, $$l = \left[\frac{\Delta g \dot{V} l x^2}{u^3}\right]^{1/3} \qquad (31)$$

Intermediate, $$l = \left[\frac{\Delta \rho\, l^2 \dot{V}^2 x^{3/2}}{\nu^{1/2}\ u^{1/2}}\right]^{1/6} \qquad (32)$$

Final, $$l = \left[\frac{s^2 x^3}{\rho^2 \nu u^3}\right]^{1/4} \qquad (33)$$

The final expression indicates that the slick expands down stream as $x^{3/4}$, and decreases with an increase of current speed. The oil will spread less rapidly in a strong current.

It seems however to be independent of the oil discharge rate. A further disadvantage is that this equation predicts that the slick will grow without bound until the slick is of monomolecular thickness (63). Yet it is known that after initial rapid spreading, the slick ceases to spread before it reaches monomolecular thickness. The oil stops spreading when the spreading coefficient σ changes from positive to negative values. The strength of σ depends on the very small concentration of surfactants in the oil, which may after a time evaporate or dissolve (64).

7.6 Actual Behaviour by Remote Sensing

Remote sensing of oil slicks by infrared or microwave techniques indicates that during an oil spill the oil fractionates into a thick, slow spreading region, surrounded by a very much larger, thinner and faster spreading region. The thicker region of the oil contains more than 90% of the oil in less than 10% of the visible slick (65,66).

8 OIL IN THE ARCTIC

8.1 Oil Behaviour

Because of the slow natural degradation in the Arctic, an oil spill might persist for fifty years. There are no acceptable theories for the behaviour of oil in the arctic regions. There is some speculation that due to ice roughness, an oil spill would not become so thin as to enter the surface tension spreading regime. The slick would remain sufficiently thick so that the oil could not even enter the intermediate stage where it is spread by gravity and retarded by viscosity. The only forces acting on the spill would be the spreading force of gravity and the retarding force of inertia. A spill of crude oil might have its temperature sufficiently lowered by evaporation to freeze, in which case very little spreading of any kind will occur (68,69).

Biological degradation of oil in the Arctic Ocean is very slow. The microbial population is small and its activity is depressed during the six dark winter months. It is further suppressed because the ice above inhibits oxygen replenishment. Evaporation under the ice cover is not possible. Chemical degradation is also reduced by the insulating ice. For oil on top of the ice a snowfall may effectively block evaporation.

Dissolution into the water and migration into the ice become important factors for the dissipation of oil. The waters between the ice floes are much less turbulent than the open seas of temperate climes, and dissolution and emulsification into the water is reduced (70).

8.2 Modes of Spreading

Depending on the season and location, oil may spread on the ice, under the ice, on the water, or in several ways at one and the same time.

The oil, depending on its temperature at the time of the spill, may or may not penetrate into the ice; penetration would depend on the nature of the ice. The density of sea ice is about 0.91 gm/cc, but multiyear ice has a density of 0.85 gm/cc. Due to brine migration that produces a porous structure, oil will tend to migrate into this ice (70).

A layer of snow on top of an oil spill can produce a crystalline mulch, 80% water, dry to the touch. This saturated snow mulch can form in a matter of hours (69).

Oil cleanup in the Arctic Ocean is immensely more difficult because of the continuously changing ice pack matrix (68,71). The alternate closing and opening of the ice pack disperses the oil both under and over the ice. The oil on top of the ice could have a significant effect on its albedo, causing it to melt at a greater rate than the surrounding ice. The melt water flowing out into the rest of the ice or the ocean disperses more oil. Under the ice, deep ridges which project through the oil layer can randomly churn the oil in a net lateral diffusion of oil away from the direction of the drift. Because of the alternate melting on top and freezing on the bottom, oil underneath the ice pack in about four to five years could find itself on top (67).

Although pressure ridges in the ice pack may extend 100 to 200 feet deep, the average thickness is only 9 to 13 feet. During the two month summer period, the Arctic receives more radiation than any other comparable part of the world. This veneer of ice plays a very important part in the heat exchange between the oceans and the atmosphere, and would be very sensitive to any changes of albedo caused by an oil spill.

9 SURFACE ACTIVE AGENTS

The spreading of oil on water is a complex affair. Two petroleum compounds of the same viscosity, density, and molecular weight range can behave quite differently.

As an oil slick spreads, its rate of evaporation of the lighter components increases because of the increase in surface area.

The resulting increase in oil viscosity reduces in turn the spreading rate. The evaporation may cool and further increase the oil viscosity. Spreading is in essence self-retarding. The final film thickness after the oil has passed through the gravity-inertia and the gravity-viscosity regimes is predicated on a balance of surface tension forces between the oil and the water (72).

9.1 The Hydrophilic-Lipophilic Balance

A surface active agent, or surfactant, is a compound that contains both water compatible, hydrophilic, and oil compatible, lipophilic, groups. Due to this amphiphatic nature, a surfactant locates and arranges itself at the oil-water interface. The ratio of hydrophilic to lipophilic portions is called the hydrophilic-lipophilic balance (HLB) and it determines the type of dispersion produced. Figure 5 is a schematic representation of the two types of dispersions that can form.

A surfactant that is principally water soluble disperses oil in water. The water-in-oil emulsion called "chocolate mousse" is due to the natural oil soluble surfactants present in the oil (72).

There are anionic, cationic, and non-ionic surfactants. An effective surfactant must not only disperse the oil, but also prevent the oil from recoalescing and reforming the oil slick by physically repelling droplet collisions. When properly dispersed, the oil will not cling or wet a solid surface, but will maintain itself as a discrete droplet (72).

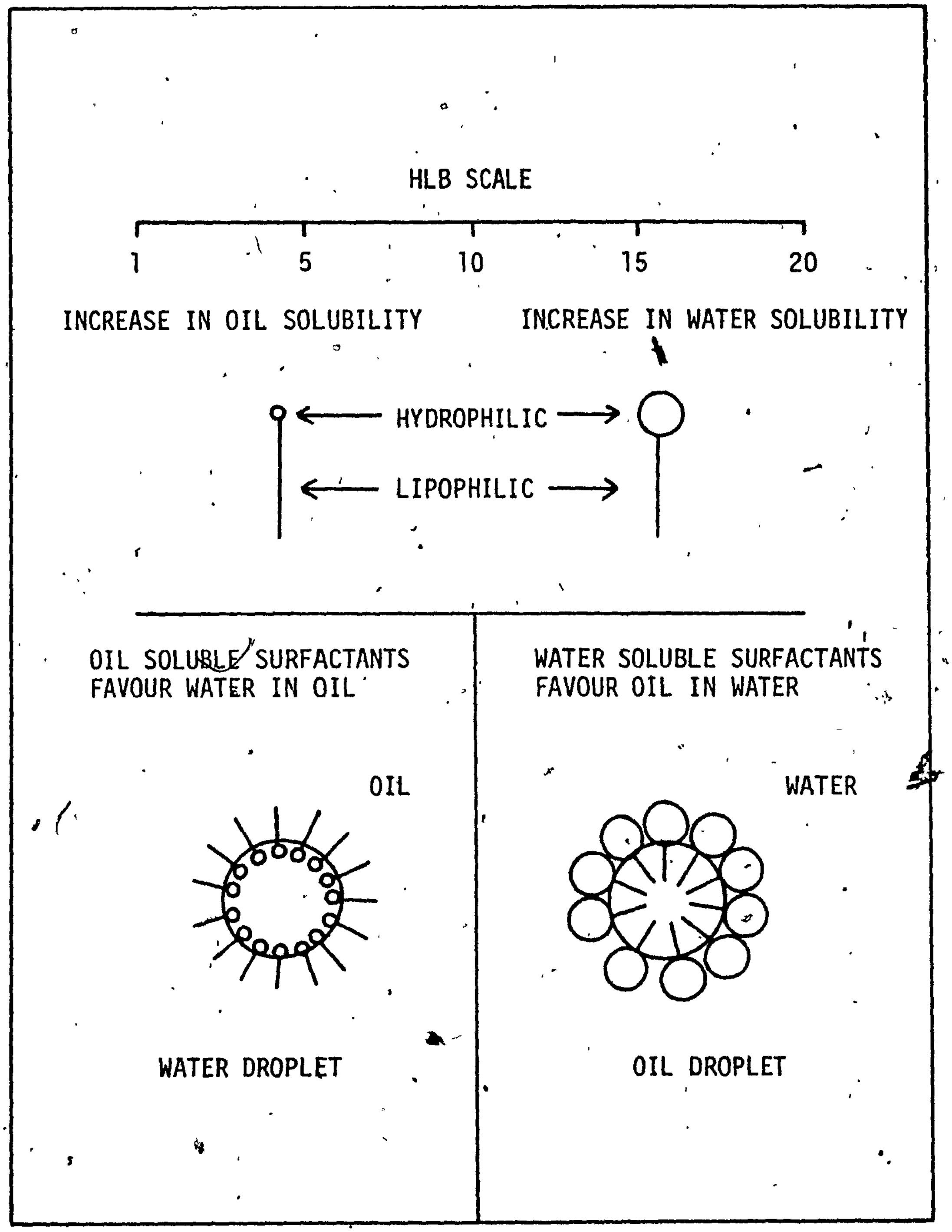


FIGURE 5 THE HYDROPHILIC-LIPOPHILIC BALANCE AND OIL-WATER EMULSIONS (72).

9.2 Disadvantages

If the oil slick can be detected from the air, application of dispersants by spraying presents little problem. The mixing of the dispersant is the limiting step. Methods employing boat propellers, fire hoses, and spray booms fitted to ships are labourious and time consuming. A small oil spill of 1000 tons can spread over 10 square miles in one day. A fleet of 20 boats would require about nine hours to completely mix and disperse the oil. But suitable work boats are usually not immediately available at the site of the oil spill (73).

9.3 Super Surfactants

A new generation of dispersants have been developed which require little or no mixing. This greatly diminishes the labour of agitating and stirring miles of ocean.

The chemical surfactant is predominantly oil soluble so that it lies to the left on the HLB scale. When the oil phase comes in contact with a water boundary, part of the surfactant has a strong driving force to diffuse into the water phase. During this transportation, a small amount of oil "associated" with the surfactant is carried into the water phase. For this system to work as an oil slick dispersant, the surfactant must initially be brought into contact with the oil phase.

A three component system of oil-water-surfactant is formed at the interface. The size of droplet formed by these no-mix dispersants is determined by a diffusion mechanism and not by mechanical mixing or stirring. Droplets of uniform size are produced (75).

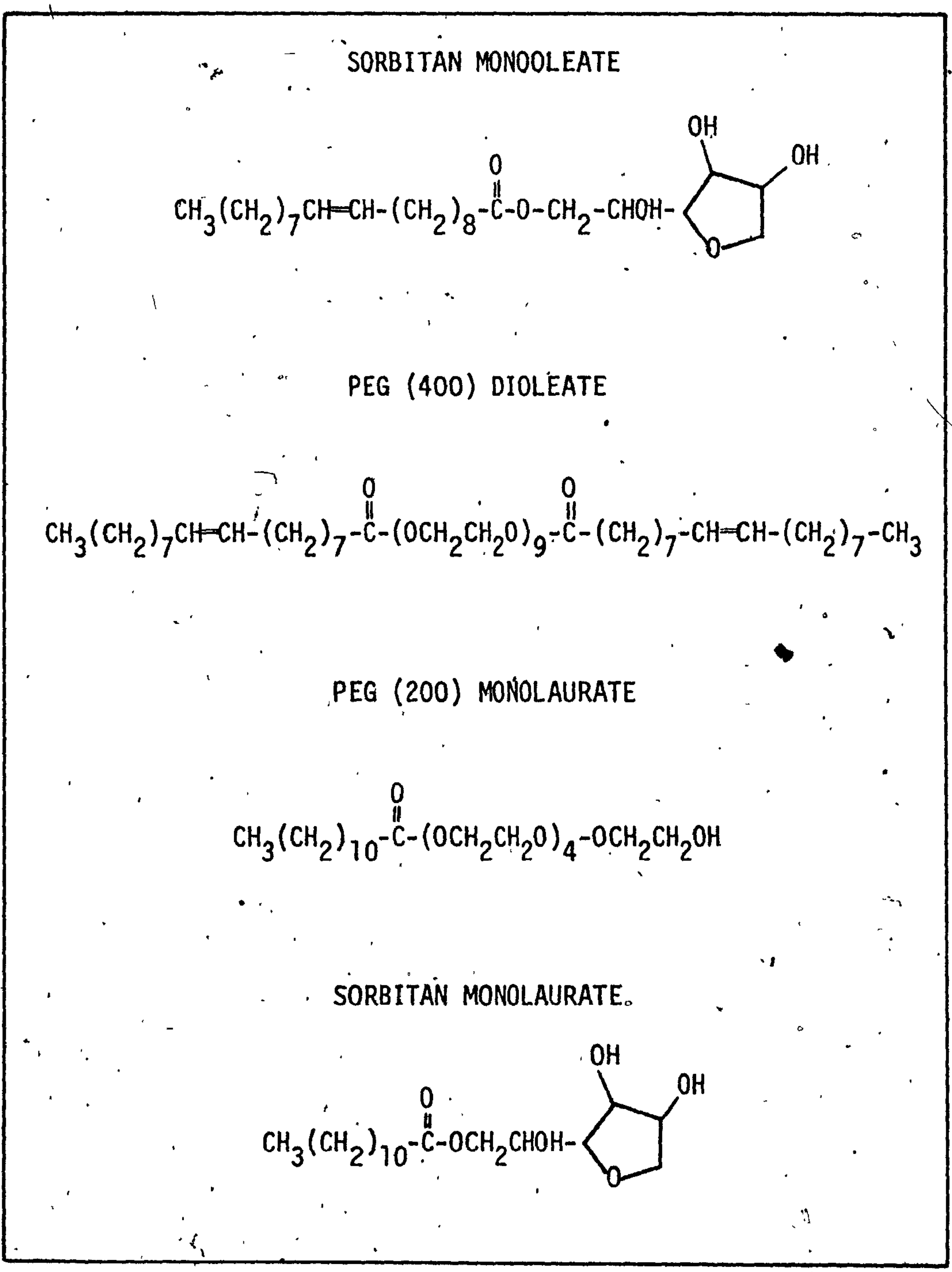
9.4 Piston Films

Besides the dispersants which require mixing and the dispersants which require no mixing, some surfactants have been produced which are insoluble in both oil and water. They alter the balance of interfacial tension forces at the air-oil-water junction, and drive back and reduce the area of small oil slicks. This allows oil recovery devices to operate more efficiently on thicker oil layers.

Piston films consist of two parts: a long hydrocarbon chain which is insoluble in water, and an oxygen containing slightly water soluble segment that reduces their oil solubility (79,80,81,82). Some typical structures are shown in Figure 6.

9.4.1 Mode of Operation. The effectiveness of these piston films is measured by the monomolecular pressure they produce. This is the difference between the surface tension of the water and the surface tension of the water covered by the film. The higher the film pressure of the piston, the faster it will spread and the thicker the oil layer that it can contain (82).

The balance of forces between the spreading force of the oil and the counter pressure of the monomolecular film layer is represented diagramatically in Figure 7.



$$CH_3(CH_2)_7CH{=}CH{-}(CH_2)_7{-}\overset{O}{\overset{\|}{C}}{-}(OCH_2CH_2O)_9{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}CH_3$$

$$CH_3(CH_2)_{10}{-}\overset{O}{\overset{\|}{C}}{-}(OCH_2CH_2O)_4{-}OCH_2CH_2OH$$

FIGURE 6 THE CHEMICAL STRUCTURES OF SEVERAL PISTON FILMS (82).

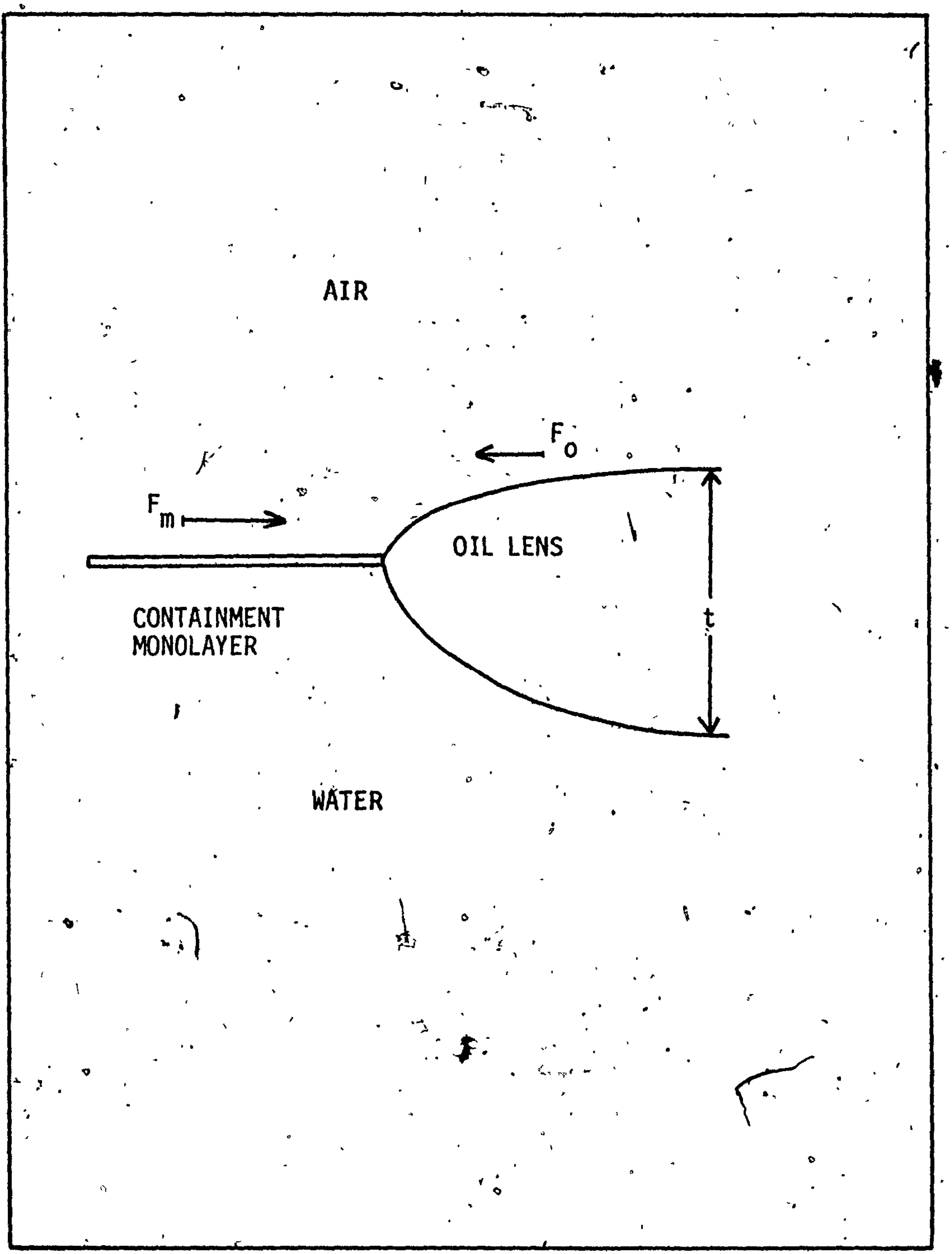


FIGURE 7 SCHEMATIC OF AN OIL LENS IN EQUILIBRIUM WITH A MONOLAYER SURFACE FILM. t IS THE THICKNESS OF THE OIL LENS, F_o IS THE SPREADING PRESSURE OF THE OIL, AND F_m IS THE SPREADING PRESSURE OF THE SURFACE FILM (84).

The oil-lens thickness may be calculated from an equation first derived by Langmuir (83).

$$t^2 = \frac{-2(F_o - F_m)\rho w}{g\,\rho_o(\rho_w - \rho_o)} \qquad (34)$$

where t = oil lens thickness

ρ_o = oil density

ρ_w = water density

g = gravitational constant

F_o = spreading pressure of the oil

F_m = spreading pressure of the piston film

Sorbitan monooleate has a spreading pressure of 40.8 dynes/cm and an initial spreading velocity of 39.2 cm/sec (81). This is sufficient to operate on crude oil slicks characterized by a spreading pressure of about 30 dynes/cm. The lenses produced have thicknesses of 0.5 to 1 cm (80).

Piston films in calm weather can be useful in driving out oil from inaccessible locations between ships, under docks, in harbours, and in quiet rivers (80).

9.5 Toxicity

Surfactants vary widely in their toxological properties. At the time of the Torrey Canyon disaster, the dispersant PB1002 was unfortunately dissolved in an aromatic solvent which acted as a "carrier" for the surfactant to enable it to penetrate the oil. The combination was toxic to marine organisms in concentrations of a few parts per million (28,76,77,78). Dispersants have since been developed which are claimed to be far less toxic to life.

The efficiency of any particular surfactant depends on the method of application, the amount of mixing, and the type of oil. When the oil has a viscosity of about 1000 centistokes, most dispersants lose a good part of their effectiveness. In the tropics the surface temperature of the water is likely to reduce the interfacial tension and permit more rapid dispersion (72,74).

Experience has shown that despite the laboratory efficiency of most detergents, they are often applied in excessive amounts at an oil spill (24). These oil dispersing agents may provide preferred sources of carbon for bacteria thereby delaying the already slow microbial degradation of an oil spill (19). By their very nature dispersants, even of the new non-toxic variety, alter the surface tension of the aqueous media at the site of application. The surface tension of normal sea water is about 74 dynes/cm at 20°C. Dispersants can lower surface tension to a lethal 35 dynes/cm. The net effect is again to reduce biodegradation (53).

Certain other dispersants are toxic because they damage cell membranes and disturb the passage of material in and out of the cell. Even the term non-toxic is misleading because they most probably have never been tested on the full spectrum of organisms that can be affected. Non-toxic dispersants may have quite toxic breakdown products (11).

All dispersants to fulfill their function drive the short and long term poisons into the environment. The more effective the dispersant, the finer the oil droplet produced, and the more marine life is damaged (11,53). Dispersants are now for the most part strictly controlled products or forbidden (39).

10 SORBENTS

10.1 Variety of Sorbents

The variety of materials that have been dumped onto spilled oil range from straw to polyurethane foam, and from wool to pine bark to poultry feathers. This may be taken as a testament perhaps to the general ineffectiveness of sorbents. A partial list of sorbents is shown in Table 1.

10.2 The Contact Angle

The phenomenon of wetting and spreading of liquids on solids has been little investigated to determine the most appropriate sorbent for a particular oil. Oil and water compete for the surface of the sorbent. The spreading of a liquid on a solid depends on the contact angle that a drop of liquid makes on that solid (87). Figure 8 illustrates the forces acting on a drop.

The spreading coefficient s of a liquid is

$$s = \sigma_s - \sigma_l - \sigma_{sl} \qquad (35)$$

where σ_s = surface tension of the solid

σ_l = surface tension of the liquid

TABLE 1

VARIETY OF SORBENTS USED IN OIL SPILLS *

Plant Materials	Minerals	Polymers	Miscellaneous
straw	various clays	synthetic rubber	leather shavings
hay	asbestos	polystyrene	wool
reeds	volcanic ash	polypropylene	paper waste
seagrass	mineral wool	viscose rayon	charcoal
gorse		cellulose acetate	poultry feathers
sawdust		acrylic	
pine bark		nylon 6,6	
peat		polyethylene terphalate	
bagasse			
sisal fibres			
cotton waste			
cork granules			
ground corn cobs			
natural rubber			

* (References 85,86,87,88)

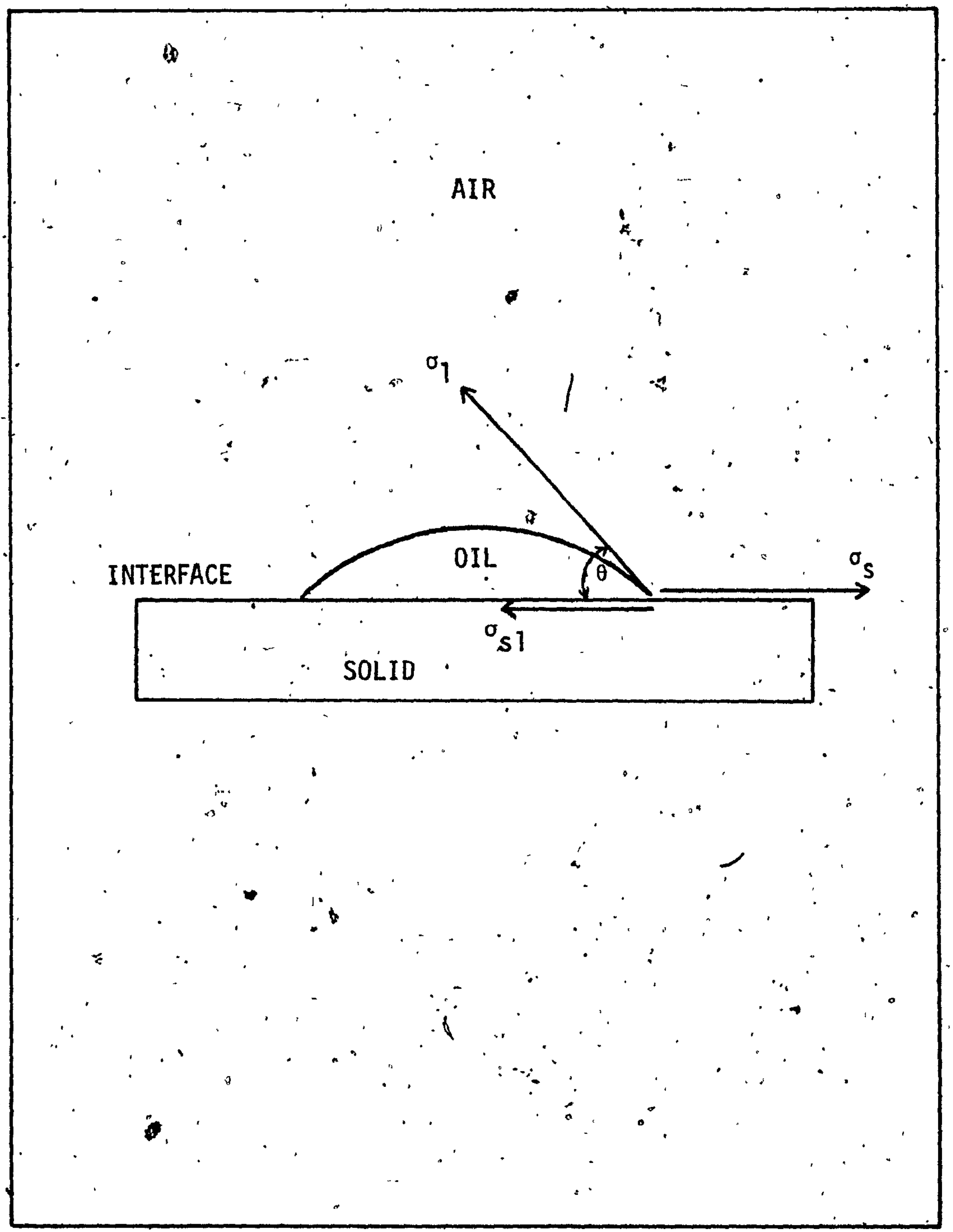


FIGURE 8 THE CONTACT ANGLE θ OF A DROP. σ_1 IS THE SURFACE TENSION OF THE LIQUID, σ_s IS THE SURFACE TENSION OF THE SOLID, AND σ_{s1} IS THE INTERFACIAL TENSION. (COMPARE WITH FIGURE 4)

σ_{sl} = interfacial tension

Compare with equation (3).

We can resolve σ_s, which is difficult to measure, into σ_{sl} and $\sigma_l \cos\theta$.

$$\sigma_s = \sigma_{sl} + \sigma_l \cos\theta \tag{36}$$

Therefore,
$$s = \sigma_l(\cos\theta - 1) \tag{37}$$

For oil to spread on the sorbent s must be positive. A good sorbent would be one producing a very small contact angle with the oil. To increase the adhesive properties of the sorbents and reduce the contact angle, many of them are coated with wax or silicone.

10.3 Porosity

In some cases absorbtion does not only involve the contact angle, but is also dependent on the porosity of the surface (87). The behaviour is essentially that of capillary rise. The driving force is that of the pressure difference across the curved surface of the meniscus. Figure 9 shows an idealized capillary.

The force which causes the liquid to rise is

$$F = 2\pi r\sigma_l \cos\theta \tag{38}$$

where r = radius of the capillary

At equilibrium the downward force due to gravity prevents the liquid from rising.

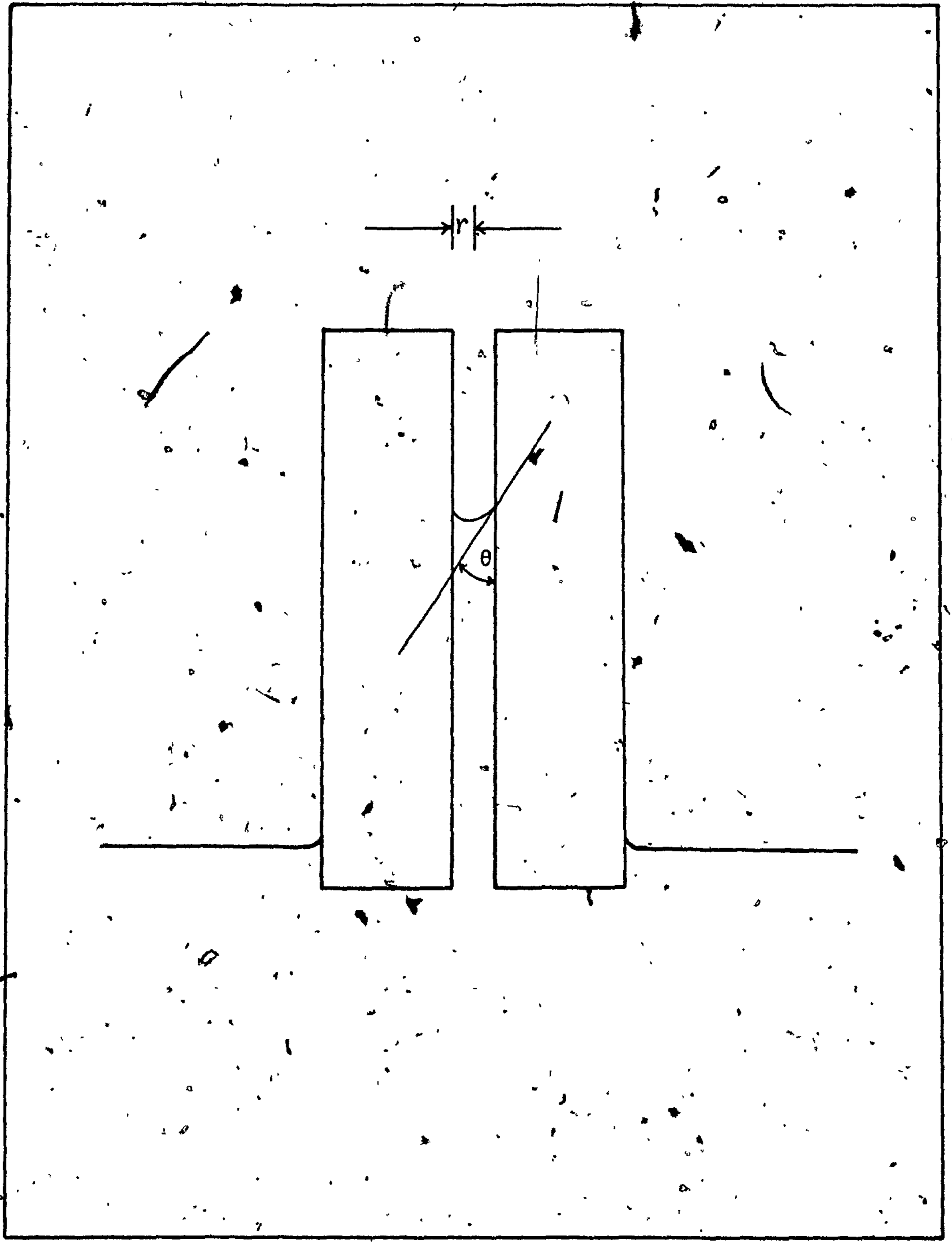


FIGURE 9 CAPILLARY RISE: r IS THE RADIUS OF THE CAPILLARY AND θ IS THE CONTACT ANGLE.

$$F = PA = P\pi r^2 \tag{39}$$

Equating (38) and (39) we obtain

$$P\pi r^2 = 2\pi r\sigma_1\cos\theta \tag{40}$$

$$P = \frac{2\sigma_1\cos\theta}{r} \tag{41}$$

For small contact angles

$$P \approx \frac{2\sigma_1}{r} \tag{42}$$

The pressure is directly proportional to σ_1, so that liquids with large surface tension will wet a porous solid more readily.

In addition to large pressure difference, the rate of entry of the liquid into the capillary should also be large (87). The quantity in equation (43) has the dimensions of velocity.

$$\frac{\sigma_1\cos\theta}{\eta_1} = \frac{\text{surface tension}}{\text{viscosity}} \tag{43}$$

This gives a measure of the penetrating power of a liquid.

10.4 Sorbent Qualities

The qualities of a good sorbent are that it must preferentially be wetted by oil; that it require little pretreatment and minimal protection from the elements; and that it be readily available in large quantities at short notice. It should have reasonable mechanical strength for handling and a large surface area on application, yet be of low volume for ease of transportation (85,86,87).

A sorbent of fair reputation, especially for the thicker oils, is straw. It has often been used to line beaches to prevent an incoming tide from depositing its oil. But straw is expensive in terms of labour and manpower (85).

The modern plastics and synthetics such as polyurethane foam have good pick-up capabilities but are relatively uneconomical (89,90). Even those sorbent systems that can manufacture foam on site and can simultaneously mulch and broadcast the sorbent require elaborate harvesting systems. It has been estimated that using polyurethane foam chips on a calm sea about 3000 gallons of oil-covered water can be treated per hour. The cost of running such an operation would be in the neighbourhood of $200-300 per hour (89).

Leather shavings, like poultry feathers, are specialist materials with potential for the thinner oils, but have been rarely applied in practice (85).

10.5 Magnetic Sorbents

Some sorbents have been magnetized to make harvesting and collecting easier. Polystyrene beads approximately 3-5 mm in diameter, with a density of about one pound per cubic foot, are treated with an adhesive and 40 mesh powdered iron in a forced air tumbler. This produces a coated ferromagnetic sorbent with a density of about four pounds per cubic foot.

The magnetic pellets are spread on the oil in a ratio of two pounds of sorbent to a gallon of oil. A rotating magnetic drum picks up the oil and water-soaked sorbent. The adhering oil is scraped into a slanted hopper.

Magnetic sorbents have been found to be two to ten times as effective as non-magnetic sorbents. The more viscous the oil, the less advantage there is in magnetizing the sorbent (91).

10.6 Disadvantages of Sorbents

There is no single universal sorbent capable of sponging up efficiently Bunker C and No. 2 Fuel oil. It is in the nature of most major oil spills to release vast quantities of the wrong type of oil for the most readily available sorbent. Oil spills tend to occur unexpectedly, at awkward hours, in inaccessible locations, in foggy or stormy weather that can whip oil and water into chocolate mousse, for which no sorbent exists at all (85).

All sorbents after dispersal over many square miles of ocean present the problem of harvesting and disposal. Burning the recovered wet sorbent-oil mixture may not always be possible, and it changes a problem of water pollution to air pollution. Dumping in quarries may result in contaminated ground water. Reclamation and separation of oil and sorbent for the possible reuse of both would be ideal, but it is also the most expensive method (85).

11 BOOMS

11.1 Boom Requirements

Booms are used as floating walls for oil containment to facilitate cleanup. Booms must be exceedingly strong, yet flexible to defy tidal, ocean, or river currents. They must be capable of containing vast quantities of oil without excessive leakage. They must be manoeuverable on towing, and resistant to sun, oil, and fire (92).

Most present day booms were developed on a hit or miss basis, and fail to contain oil when carried by currents in excess of 1 mph. On the open sea booms are inadequate because mooring boats are unmanoeuverable at the very low speeds required. On rivers booms may be swept under and submerged when pulled tight against moorings by waves and currents (93). Figure 10 illustrates several common boom types.

These booms fail in frontal assaults against the oil except in the calmest rivers or sheltered harbours. On swifter bodies of water they may on occasion be used when angled into the current to direct the flow of oil to collection points. Frequent mooring is essential, for the skirt or fence will lift under water between mooring points, reducing their effective under-water depth. Multiple moorings will also prevent the formation of angled cusps which leak oil more readily (93,94).

11.2 Individual Booms

Other types of booms have been developed, some of which come closer to the requirements mentioned. Figure 11 illustrates three types of moderately successful booms.

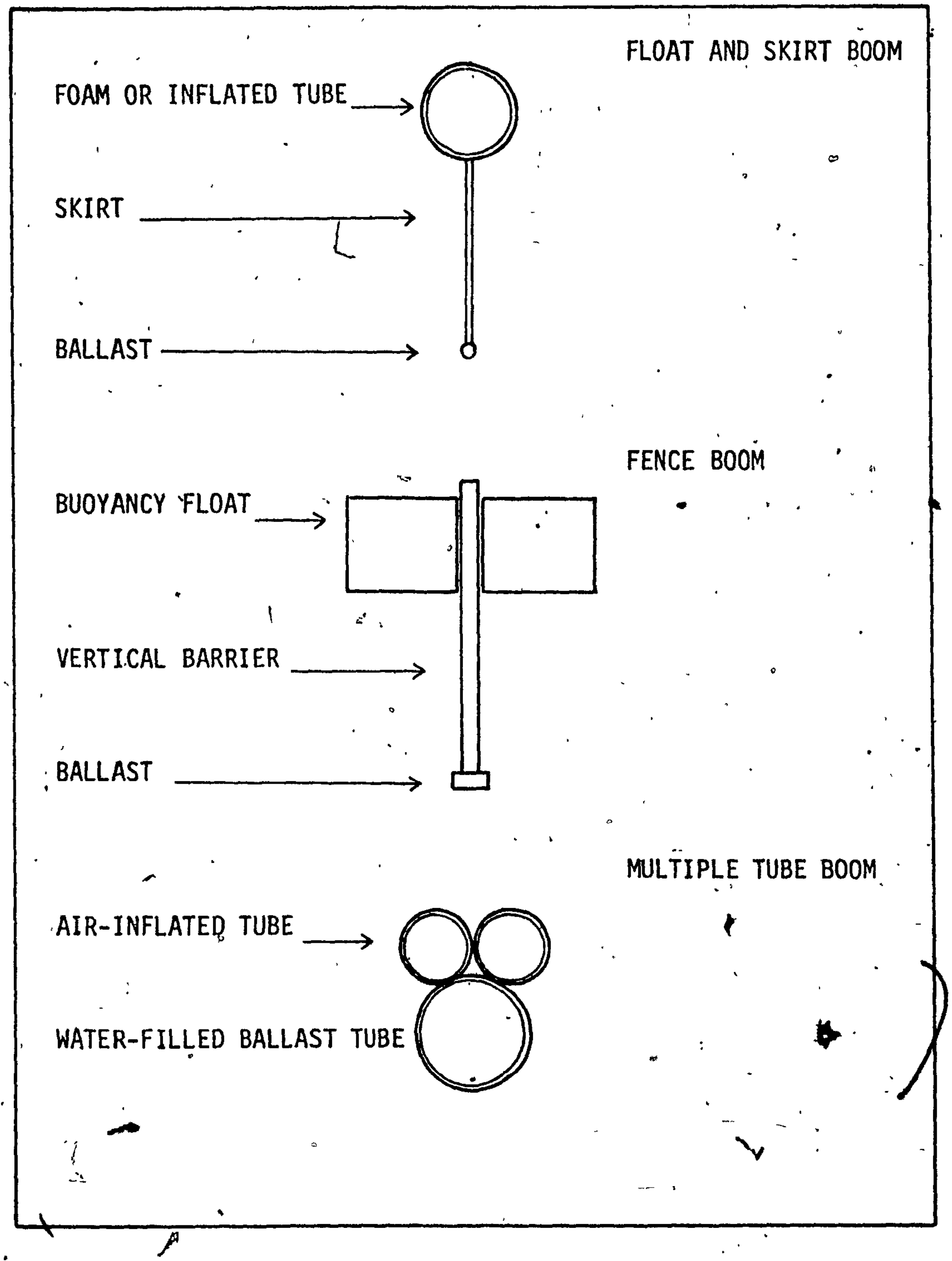


FIGURE 10 SIMPLE BOOMS (93).

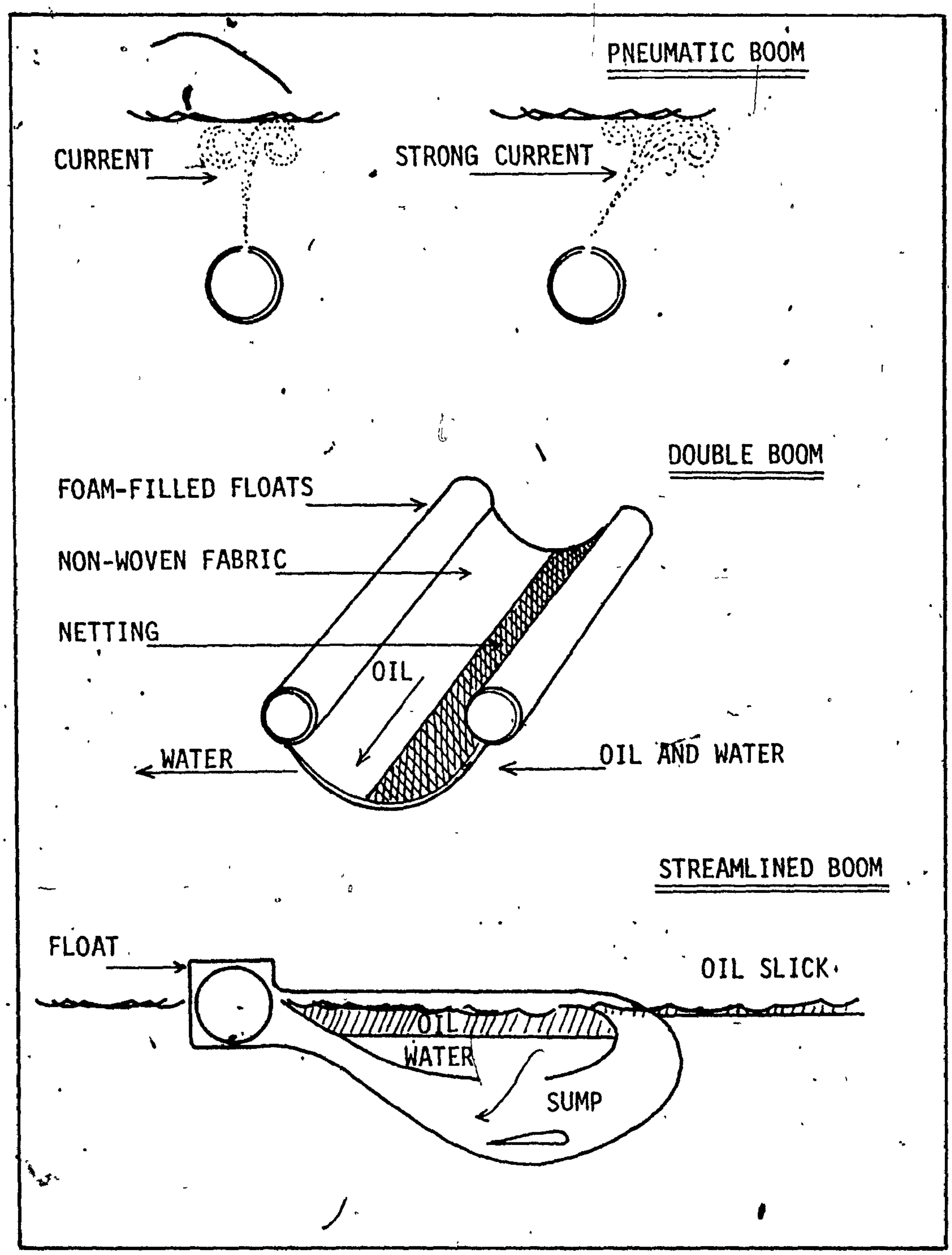


FIGURE 11 COMPLEX BOOMS (95,96,97).

11.2.1 The Pneumatic Boom. Pneumatic booms consist of perforated underwater pipes through which forced air is blown. The rising air-water mixture creates counter currents to restrict the spread of oil. The advantages of a pneumatic boom are that it allows the unrestricted passage of ships, it is less susceptible to environmental factors, and it is safe from fire. The disadvantages are that: it requires extensive installation and maintenance, it is ineffective in case of a power or pipe failure, and it fails to contain oil in currents greater than 1/2 mph (92,95).

11.2.2 The Double Boom. The double boom consists of two parallel floats linked their full length in 50-foot segments. Netting fastened to a nonwoven material permits water to float through but retains the oil which floats to a collection point. This boom when placed across the current at an angle is claimed to be effective in separating and collecting the oil in currents of greater than 2.6 mph (96).

11.2.3 The Streamlined Boom. In the streamlined boom the waves sweeping over the top of the leading edge of the boom deposit the oil into the sump. This boom manages to collect oil with an efficiency of 80-90% in currents in excess of 2 mph. In towing, this boom requires only one third the effort of conventional booms (97).

12 BURNING

12.1 Disadvantages to Burning

Burning spilled oil presents in theory an advantage of economy, equipment, and manpower. As the Torrey Canyon incident demonstrated, it is not as easy to burn a tanker or its spilled cargo as it might appear (24,98). Unburnable oil emulsions can form on contact with water.

To ignite a weathered oil slick is very difficult. To maintain substantial combustion is even more difficult: an oil layer less than 2 mm thick will not burn. A burning patch of oil decreases its own viscosity until spreading reduces its thickness to the extent that wind and waves separate the burning slick into small pools. Heat exchange with the water then extinguishes the fires quite rapidly. Once the volatile fractions have been burned off, the resulting viscous tar-like residue is almost unignitable (99).

12.2 Burning Agents

To assist combustion, several burning agents have been developed. Hydro-igniters are agents that ignite on contact with water; they contain sodium or magnesium. Auto-igniters are substances which react with the carbon or hydrogen of the spilled oil; they contain chlorates of sodium or potassium. Wicking agents consist of a light powdery material made from silicates. Due to their large surface area and porous structure, they act like millions of candle wicks to maintain combustion (98).

Some specific burning agents are described below.

1. Cab-O-Sil is composed of extremely fine particles of sand whose surface is treated with a silane coating to make it hydrophobic. Applied as a water slurry, the water sinks through the oil and the light buoyant cab-o-sil powder rises to the top of the oil. The treated area can then be ignited by rags soaked in lighter fluid (100).

2. Oilex Fire is a combination sorbent and hydro-igniting chemical. It ignites on application and then acts as a wicking agent to maintain combustion (98).

3. Straw, a good sorbent, is also a good wicking agent. Burned straw forms filamentous carbon threads that behave as wicks (98).

On freshly spilled oil, burning agents promote combustion. Under actual field testing they are a disappointment offering problems of application, ignition, containment, and maintenance of sufficient burning thickness (101).

13 MECHANICAL REMOVAL

13.1 General

One advantage of mechanical removal methods is that the recovered oil can be separated from water and reused. To be effective the machines must be available at the spill site very quickly. In very large spills, mechanical devices do not prove useful, as was the case in the Santa Barbara blowout. Their main capability lies in controlling oil pollution in sheltered harbours and dockyards (102). Figure 12 shows several mechanical oil removers.

13.2 The Variable Pitch Screw

In the variable pitch screw, oil and water enter the system and are trapped between the threads. As the pitch of the threads progressively diminishes, the oil layer thickens sufficiently to be removed by a pump from a chamber situated at the end of the screw. Water is removed from the sump through an opening below the screw casing.

Erratic motion of the waves is absorbed by the last stages of the variable pitch screw and the whole device follows the movement of the swell. Several variable pitch screws can be attached catamaran fashion and the collected oil pumped into accompanying small tankers. Such system would be expected to pick up oil at 10 000 gallons per hour (103).

13.3 The Free Vortex

This method is useful for small oil spills in inaccessible locations around piers or ships in harbours. The large impeller creates a powerful vortex that can draw in oil from appreciable distances. Upon

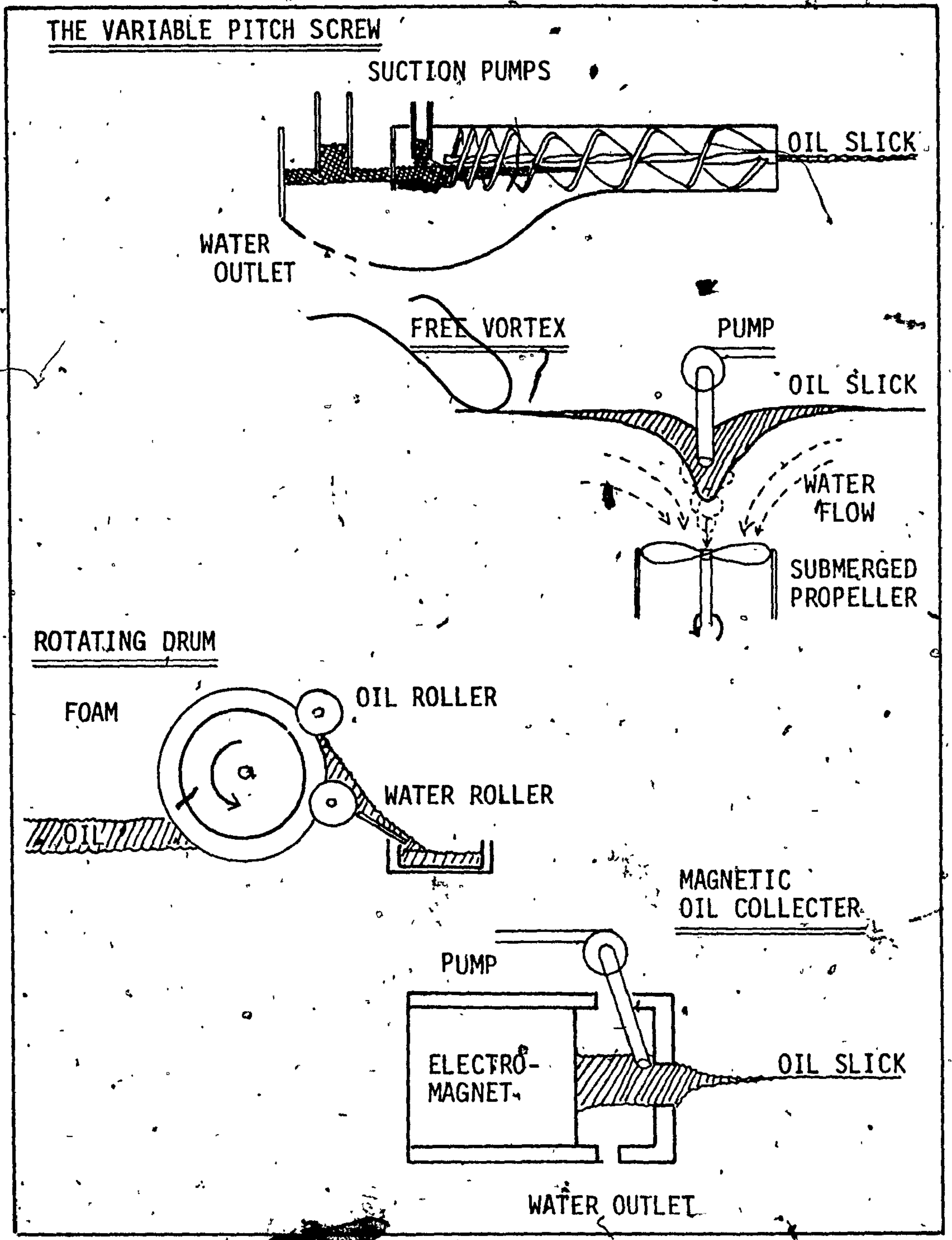


FIGURE 12 SEVERAL MECHANICAL OIL REMOVERS (103,104,106,107).

approaching the vortex the oil collects in the central pocket and can be removed by pumping. This device is claimed to be effective for oil slicks of 0.001 inches to over 5 inches. The vortex device could also be used in conjunction with polyurethane sorbents. In development is a prototype capable of removing 2000 gallons of oil per minute (104).

13.4 Endless Belts

A continuously cycled, buoyant oleophilic polypropylene felt belt is used to recover the oil in calm water. One belt 20 inches wide and 800 feet long can lick 7000 gallons of oil per hour from a slick 6 mm thick. A set of wringers remove the sorbed oil from the belt material (105).

13.5 Rotating Drums

A polyurethane-covered drum rotating in the water absorbs oil and water. A low pressure metal roller removes water from the foam drum, while a second high pressure roller removes the oil. Such a drum skimming over the oil in a catamaran works well in sheltered water (106).

13.6 Magnetic Liquids

Magnetic liquids called ferrofluids are capable of magnetizing the oil. Ferrofluids consist of a colloidal dispersion of magnetic iron oxide Fe_3O_4 or αFe_2O_3 in a light saturated hydrocarbon. Ferrofluids do not settle on standing or in the presence of a strong magnetic field. The particles in suspension do not flocculate in a magnetic field because their size is small enough, about 100 Å, that Brownian movement disperses the particles. Phase separation is thus prevented. Ferrofluids behave like a flock of non-interacting magnets capable of being magnetized to 200-300 gauss. In principle 12 500 gallons of oil per hour can be recovered (107).

The process of magnetic oil/water separation consists of:

1. The oil phase is magnetized by adding, mixing, or spraying the ferrofluid. The ratio of ferrofluid to oil is 1:20. The amount of mixing depends on the state of the sea.

2. The magnetized oil-water mixture is passed through the poles of an electromagnet 20 000 gauss strong.

3. The magnetized oil is pumped off the magnetic collector.

14 THE USE OF SINKING AGENTS

14.1 Function of Sinking Agents

The primary function of sinking agents is to localize the effects of an oil spill. A spill as big as in the Torrey Canyon incident has the potential of polluting 1500 km of shoreline. The same 100 000 tons of oil could be sunk in an area 25 square km if the slick was 4 mm thick (26). Most sinking agents in themselves are non-toxic to pelagic marine life. Albeit personnel may require some protection during handling of fine powders. Near estuaries and rivers, water-carried mud and silt often act as natural sinking agents (38). The appeal of sinking agents is based on the rapidity and relative simplicity of the operation, without the subsequent effort and expense of collection and disposal.

14.2 Variety of Sinking Agents

Sinking agents, although not as numerous as sorbents, still encompass a surprising variety. They may consist of sand dredged up from the ocean bottom and used dry or in slurry form. Sand has also been used coated by wax or silicone; sand-coated wax is reputed to have good retentive properties. Sand particles have been rendered oleophilic by injection of long chain amine salts into water/sand slurries. The sand may be given a coating of oil and then heated to produce a film of carbon on the sand grains (108).

Other oil-sinking agents may be brick dust, crushed stone, gravel, various clays, powdered coke, volcanic ash, slaked lime, Portland cement, and gypsum which sets into hard cakes. Fuel ash is produced by the ton in power stations and may be used untreated or coated with silicone. Chalk coated with 1% sodium stearate was used by the French in the Torrey Canyon incident (26,108,109,110).

14.3 Requirements of Sinking Agents

The qualities of a good sinking agent are similar to those for good sorbents, the main difference lying in the densities of the materials.

Sinking agents should be oleophilic and hydrophobic and, for the retention of oil, should continue to be oleophilic in the presence of a large excess of water. Ideally, for sinking an oil of specific gravity of 0.90 only 20% by weight of a sinking agent such as sand is required. In actual field conditions, it has been necessary to use two to three times the weight of oil. From an economic view, cheapness and abundant availability of sinking agents are important criteria (108).

Granular material should have a specific gravity of 2.4 to 3.0 and as large a surface area as possible. This is for oil adsorption purposes and also so that hydraulic pressure reduces air-filled pore spaces and increases the specific gravity to maintain the sinking process (108).

Fine powders have larger surface areas and a corresponding potential for sinking and retaining greater quantities of oil. But fine powders suffer from the difficulty of application even in moderate winds. They may clog machinery and pose health hazards. Fine powders on application may produce saucer-like pods on the oil; these pods may be inverted by wave action and so spill the bulk of the sinking agent. The use of powders necessitates mixing large areas of water. In slurry form they can be applied with high impact velocity to penetrate the oil, but their oleophilic character may in some cases be impaired by long contact with water (108,109).

14.4 Effect of Oil Viscosity

Oil spills may involve oils of high viscosity, such as Bunker type oils, or the very low viscosity crude and fuel oils. Weathering may change in a relatively short period of time the characteristics of any spilled oil by increasing the viscosity and turning portions of it into emulsions. Sinking agents operate most efficiently with oils of reasonable viscosity. For freshly spilled crudes similar levels of efficiency can be obtained when the oil layer thickness is greater.

Very viscous oils may be difficult to sink because they require agitation, even when agents of high specific gravity are used.

14.5 Testing of Sinking Agents

Sinking agents may be tested to determine their general characteristics to remove and retain the oil. The efficiency of a sinking agent depends on a number of variables.

1. Sinking Agent Factors
   a) composition
   b) specific gravity
   c) bulk density
   d) particle coating
   e) particle size
   f) method of application
2. Oil Factors
   a) oil type
   b) oil layer thickness
3. Dispersion Factors
   a) ambient temperature
   b) influence of wind velocity
   c) wave action, currents, and tides

Due to the difficulty of producing dynamic field conditions in the laboratory, or even in a large scale test area, most testing does not take into account dispersion factors.

Testing in the laboratory usually involves only the addition of a sufficient quantity of sinking agent to dispose of a known quantity of oil. The following testing procedures can be compared to the testing procedures used in this study in Section 15.5.

In one test 50 ml of oil floating on seawater was sunk by manual sprinkling of sinking agent. Only visual observation served to determine the point at which the 50 ml of oil were deemed to be sunk. The efficiency of the sinking agent was expressed as the weight of agent required to sink 50 ml of oil (111).

Another test consisted of the addition of 150 gm of sinking agent in slurry form to a 3-ml slick of oil whose weight was known. Floating oil/agent masses were stirred to induce maximum sinking. Visual estimates of the amount of floating oil were made immediately after application and at timed intervals after (112). No effort was made to take into account loss of oil through evaporation.

A similar test involved the addition of sinking agent to a known volume of oil. The weight of oil was calculated from the specific gravity. The agent was sprinkled through a specially designed funnel for easier application. A fixed free fall of 30 inches was used. Again only a visual estimate was used to determine when 90% to 100% of the oil had sunk. The efficiency was measured as the ratio of the weight of oil sunk to the weight of sinking agent required (113).

A titration method used for sorbents but transferable to sinking agents was the dropwise addition of oil to a previously weighed agent. The end point was reached when the individual oil/agent lumps coalesced into a single mass. The sorption capacity was the ratio of the volume of oil used to the amount of sinking agent treated (86).

14.6 Oil Retentivity of Sinking Agents

Most oil retentivity tests consist of "dry mixing" the oil and agent, and observing the amount of oil released after the addition of water. Few tests take into account volatility losses. The testing procedures used in this laboratory (see Section 15.7) can be compared with the following retentivity tests.

In one test 50 gm of sand were mixed with water and treated with a surfactant. This slurry was mixed with 30 gm of oil and transferred to a 250-ml flask fitted with a calibrated tube. The amount of oil released at the end of 24 hours was measured. The amount of oil retained was then 30 minus the amount of floating oil. The efficiency of sinking agent was the ratio of the amount of oil sunk to the weight of sand used (112).

In another test 10 gm of sand were thoroughly mixed with 10 gm of crude oil. Seawater was added and the whole allowed to stand for 24 hours. The seawater and any floating oil were then decanted. Oil adhering to the walls of the beaker was wiped off and discarded. Only the retained oil was dissolved out of the sinking agent, and the amount of oil was determined absorptiometrically (112).

In one method the sinking agent was mixed with oil in an evacuated flask to ensure the release of oil which was only trapped between the solid particles and was not actually absorbed. A graduated cylinder was then fitted to the top of the flask and seawater added to a calibrated mark. The volume of released oil was determined from the cylinder graduations, 2 hours and 18 hours after the first addition of water. From the specific gravity, the weight of released oil could be determined and subtracted from the initial weight to give the weight of adsorbed oil. No corrections however were made for the disappearance of volatile components (113).

One form of dynamic testing made use of a circular flow channel that was provided with a means of producing and measuring different flow rates. To simulate natural conditions the bottom of the channel could be covered by sand, mud, or rocks. Known weights of sinking agent/oil were put into the moving water. Refloated oil was obtained by catching on fine glass wool. The total weight released was subtracted from the amount added to give the weight retained. The dynamic retention capability was given by the ratio of oil retained to the weight of sinking agent used (113).

14.7 Ecology and Sinking Agents

Untreated oil evaporates and loses its excessive toxicity quite rapidly. Oil that has reached bottom by the sedimenting action of silt and floating detritus has done its worst damage to the surface community. Sinking agents carry to the bottom relatively fresh toxic oil and therefore degradation in the absence of oxygen is slower. Potential slow release of sunken oil can force the entry of oil into the water column. Fishing and destruction of bottom life must be weighed against damage to coastal communities. The use of sinking agents to treat an oil spill requires a balance between several evils, and experienced judgment is necessary to choose the lesser.

15 TESTING PROCEDURES USED IN THIS STUDY

15.1 Determination of Sinking Agent Characteristics

The variables of interest affecting the efficiency of sinking agents depend on the true specific gravity, the apparent specific gravity, the surface area, and the bulk or loose density.

15.1.1 True Specific Gravity. The true specific gravity is the specific gravity of the sinking agent, unaffected by any particulate porosity.

15.1.2 Apparent Specific Gravity. The apparent specific gravity is the specific gravity of the sinking agent affected by the particulate porosity. When the apparent specific gravity is appreciably less than the true specific gravity, the indication is that the particles are porous, with large surface areas. This characteristic will affect its spontaneous sinking ability. The pores are frequently not penetrated rapidly by liquids such as oil, especially where oils of relatively high viscosity are encountered. In such cases the agent/oil mass will resist sinking without some form of agitation.

The apparent specific gravity was determined using water pycnometers.

15.1.3 Bulk or Loose Density. The bulk density of the sinking agents reflects to a certain extent both the capacity for packing and the particulate porosity. Low bulk density values suggest problems of storage, handling, and treatment. The bulk density was measured using large graduated containers.

15.1.4 Surface Area. The surface area of the sinking agents was determined according to the method of Brunauer, Emmet, and Teller in the normal BET gas adsorption apparatus. The samples were tested as "received" to give a realistic picture of the surface areas involved (114,115).

15.2 Determination of Oil Characteristics

The properties of the various oils capable of exerting influence on the efficiency and retentive properties of the sinking agents were investigated. The properties of importance were the specific gravity, the viscosity, and the volatility of the oil.

15.2.1 Specific Gravity. Pycnometers were used to determine the specific gravity of low or medium viscosity oils. But they proved impractical for a high viscosity oil like No. 6 Bunker. For this oil a large graduated cylinder was used. Specific gravity tests were carried out at room temperature and at 2 ± 1°C.

15.2.2 Viscosity. A Cannon-Fenske Viscometer was used to test the viscosity of the low and medium viscosity oils. No. 6 Bunker oil was measured at room temperature using a Concentric Cylinder Viscosity Apparatus. At 2 ± 1°C, due to its asphalt-like consistency, the viscosity of No. 6 Bunker oil was estimated by extrapolation from literature values.

15.3 The Oil Layer Thickness Measurement Device

The device is shown in Figure 13. An aluminum rod carried the measuring apparatus proper. This consisted of a micrometer with a traverse of 250 mm and a reading uncertainty of ±0.01 mm per single reading. The micrometer body was firmly clamped to the aluminum rod. The traversing head of the micrometer contacted the flanged end of a brass rod, itself carried by a bushing firmly attached to the aluminum rod. Between the top of the bushing housing and the underside of the brass rod flange, a spring ensured that, with any upward or downward movement of the micrometer head, the brass rod would follow these motions exactly.

The opposite end of the brass rod carried two finely-pointed stainless steel probes about 1/16 inch diameter. These probes were firmly attached to, but insulated from, the brass rod. Insulated lead-off wires were attached to these probes. These wires led to a charging and resistance measuring device. The pointed ends of the probes were separated laterally by a distance of about 1.5 cm, and the points of the probes were displaced in the vertical plane by a distance of very close to 1 cm. One probe thus hung 1 cm lower than the other.

The main vertical aluminum rod was capable of being connected to a horizontal aluminum rod by a universal clamp which permitted the vertical rod and associated testing equipment to be positioned laterally and vertically in the test cell. The horizontal rod was equipped with clamps which allowed it to be attached to a rigid framework surrounding, but separate from, the test cell.

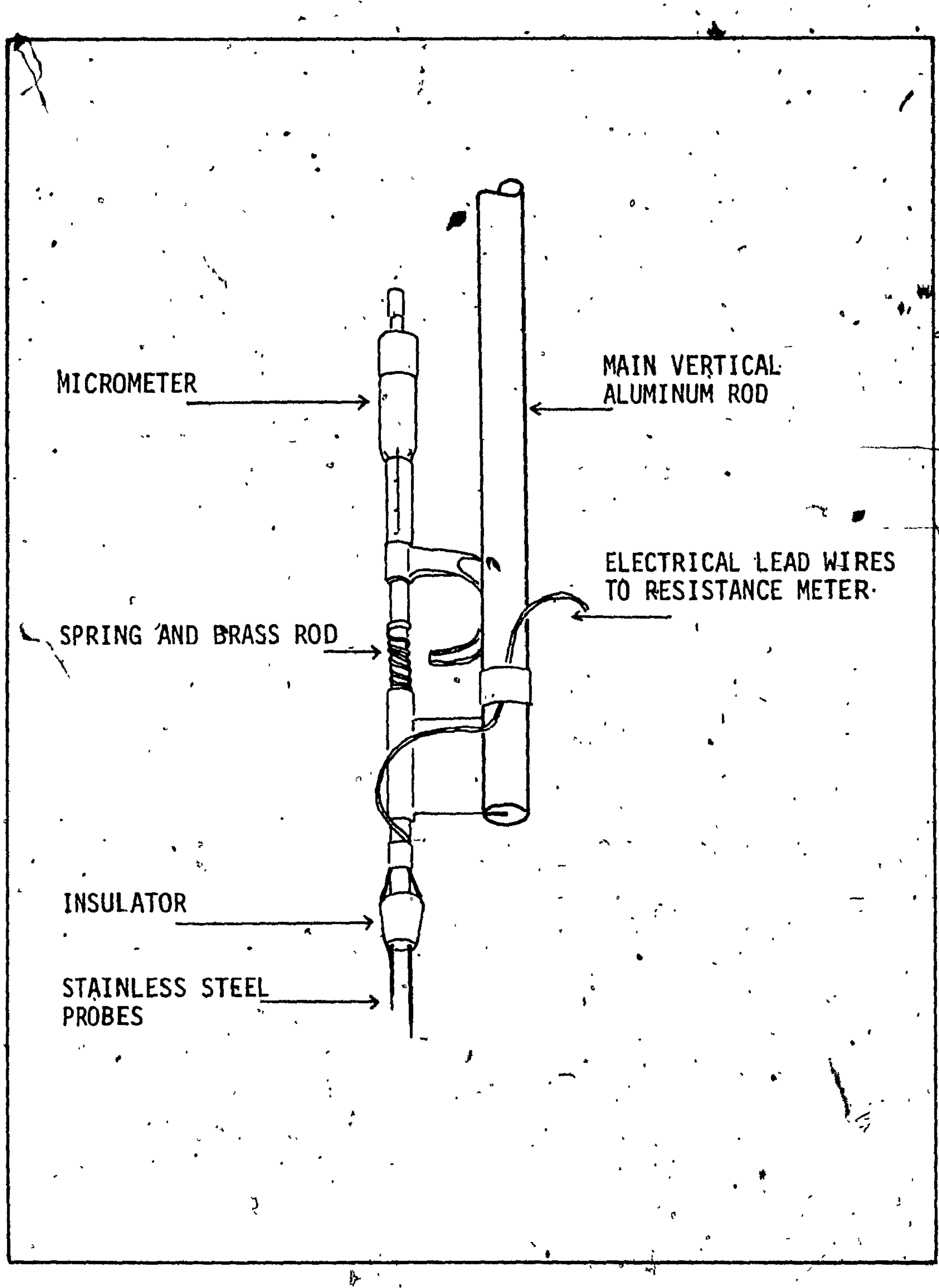


FIGURE 13 OIL LAYER THICKNESS MEASUREMENT DEVICE

In practice, the device was attached to the rigid framework when an oil layer thickness was to be determined. The vertical rod was then located at the centre of the test cell and perpendicular to the oil surface. The micrometer was adjusted to full retraction of the probes. The vertical rod was then positioned so that the longer of the two probes entered the oil layer and the shorter was just above the oil surface. The micrometer was then adjusted to lower the probes until the shorter probe just touched the oil surface. The micrometer reading was taken at this point. The micrometer was now adjusted, lowering both probes simultaneously, until the shorter probe just penetrated below the lower surface of the oil layer, as evidenced by a significant decrease in the resistance as read by the resistance measuring device. The micrometer reading at this point was taken. The difference between the first and second micrometer readings yielded the oil layer thickness. Two additional, and sometimes three additional, oil thickness values were determined for points equidistant from the sides of the cell and its centre. All readings were averaged to provide the final oil layer thickness.

15.3.1 Calibration of the Oil Layer Thickness Testing Device. A 500-ml beaker was examined to determine its inside diameter. The measurements were made with a Starrett No. 579E telescoping gauge. The values obtained are given in Table 1-1 of Appendix I, and represent the various beaker levels in volume values.

Since it was planned to carry out the testing procedure for calibration with the oil layer, for each test, contained between the

300-ml and 400-ml level markings, the diameter was taken as

$$83.6 \pm 0.1 \text{ mm}$$

with the associated surface area for the oil layer projected as

$$5489 \pm 6 \text{ mm}^2$$

The specific gravity of the No. 2 Fuel oil used for calibration purposes was determined at 21 ± 1^{o}C, by the method described in Section 15.2.1 and reported in Section 16.3 as being

$$0.840 \pm 0.001$$

with the density at 21^{o}C accepted as being

$$(8.40 \pm 0.01) \times 10^{-4} \text{ gm/mm}^3$$

Varying weights of No. 2 Fuel oil were accurately weighed out and floated successively onto saline solutions contained in beakers, the saline solution layer being in each case such as to permit the oil layer to lie between the 300-ml and 400-ml level marks of the beaker. The thickness of each oil layer was calculated from the relationship

$$L = \frac{W}{d \times A} \qquad (44)$$

where L = oil layer thickness (mm)

W = oil weight (gm)

d = oil density (gm/mm^3)

A = oil layer surface area (mm^2)

Table 1-2 of Appendix I indicates the calculated oil layer thickness values as associated with the oil weights taken.

For each test, the oil layer thickness was determined by application of the testing device at four general locations on the oil surface. These are shown in Figure 1-1, Appendix I. The values obtained for these tests, along with the associated average values, standard deviations, and calculated values, are given in Table 2. Also shown in this table are the percent relative errors with respect to the calculated values.

Test 5 can be presumed to be of dubious value, since the oil surface was discontinuous. This situation provides some indication that, at least where No. 2 Fuel oil is concerned, the examination of oil layer thicknesses less than approximately 1 mm may not lead to data of practical significance.

Table 2 data indicated somewhat greater differences between the calculated and measured values than might have been anticipated from the measurement device uncertainty of about ±0.01 mm per single measurement. Since two readings are required for a final thickness measurement at each location, a final uncertainty of ±0.02 mm is implied. It was noted that the four measurements taken per test showed differences greater than this implied level of uncertainty.

A careful investigation disclosed three source contributions to these differences, there being two major and one minor source. The two major sources were, first, a lack of smoothness at the location of

TABLE 2

CALIBRATION MEASURED AND CALCULATED OIL LAYER THICKNESSES

Test	Thickness at Location (mm)				Average (mm)	Standard Deviation (±mm)	Calculated Value (mm)	Relative Error (%)
	1	2	3	4				
1	7.41	7.05	7.43	7.26	7.2^8	0.1^7	7.25	+ 0.41
2	6.80	6.83	6.80	6.44	6.7^1	0.1^8	6.58	+ 2.0
3	2.94	2.79	2.97	2.79	2.78^2	0.09^6	2.933	- 2.1
4	1.46	1.40	1.44	1.55	1.45^7	0.06^4	1.524	- 4.6
5	0.45	0.81	0.86	0.93	0.7^6	0.2^1	0.548	+39

the saline solution/oil interface and, second, residual vibrational effects transmitted from the environment to the test beaker. The minor source involved the relatively small surface explored. Little could be done with respect to the lack-of-smoothness phenomenon, but reduction of the vibrational effect and the use of a larger surface area in the test cell resulted in a considerable improvement in the reproducibility of the measurements, as evidenced by the agreement of measured values generally found during the course of the regular testing procedures.

Figure 14 provides a plot of the calculated and measured thicknesses reported in Table 2. On the basis of this plot, the fact that the differences generally approximated a 0.1 mm level and the fact that a significantly improved situation was obtained under actual test conditions using the test cell, the measurement device for oil layer thickness determination was considered adequate for the purposes of this study.

15.4 The Test Cell

The test cell and its upper aluminum framework are shown in Figure 15. The rectangular plexiglas cell body, constructed using 1/4 inch sheet, measured 249.50 ± 0.04 mm by 249.45 ± 0.04 mm with respect to its interior dimensions, yielding a surface area for any oil layer of $(6.224 \pm 0.002) \times 10^4$ mm^2. The internal length of the cell body was 90.09 ± 0.05 cm, allowing free fall values of up to approximately 60 cm.

The top of the cell was equipped with a detachable aluminum framework constructed from extruded forms, and having plastic-lined

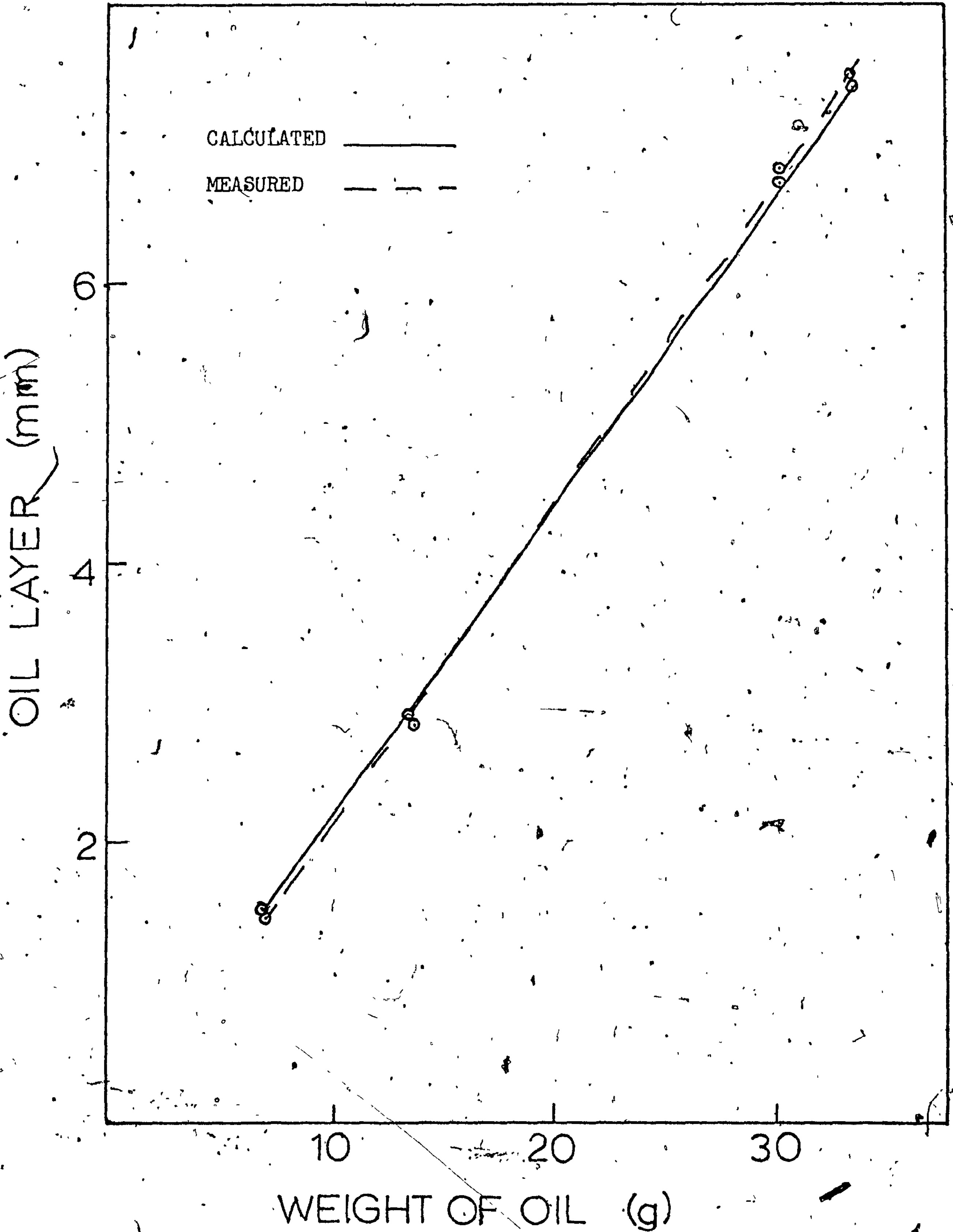


FIGURE 14, CALIBRATION CURVE FOR OIL LAYER THICKNESS MEASUREMENT DEVICE

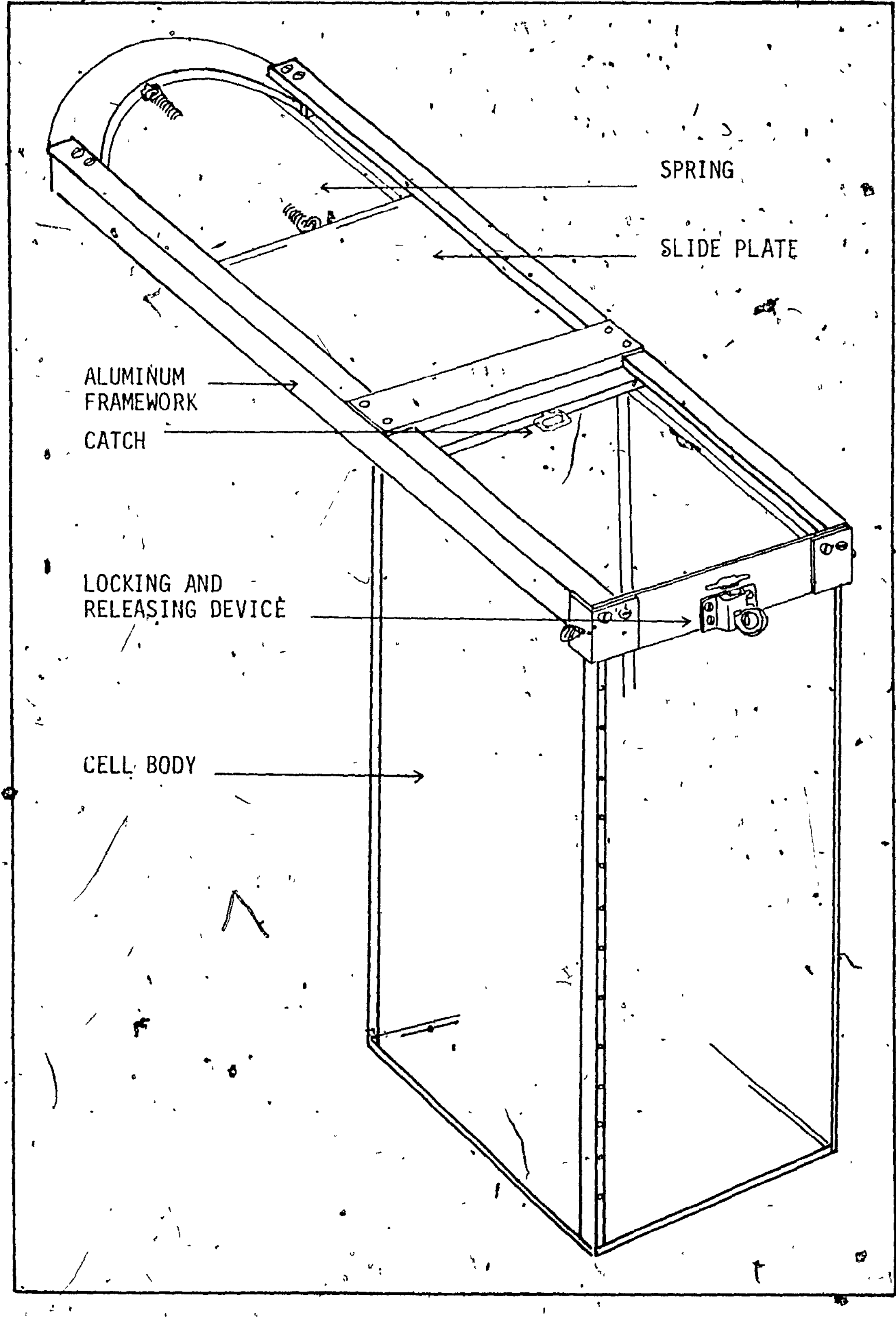


FIGURE 15   THE TEST CELL

slide grooves to carry the plexiglas slide plate. The detachable frame carried a locking and release catch which engaged a pin set into the underside of the slide plate. It also carried, at the opposite end, a securing pin for the spring. Rubber stops were provided in the frame slide grooves to take up the shock of stopping the rapidly-retracted slide plate.

A centimeter scale was attached to an outside corner of the test cell, which permitted measurement of the distance from the top of the slide plate to the top of the oil layer under test.

In practice, simulated ocean water prepared according to ASTM D-1141 specification was poured into the cell to the mark. A weighed quantity of oil calculated to produce the required starting oil layer thickness was carefully floated on the saline solution. A measured amount of sinking agent was dispersed on the oil by spreading it evenly on the spring activated plate. Upon release of the locking pin, the plate retracted rapidly, spilling the sinking agent on the oil in a reproducible manner.

The oil layer thickness at the start of each test and after each treatment with sinking agent was determined as described in Section 15.3.

With the highly viscous No. 6 Bunker oil some difficulty was experienced due to the fact that some oil was dragged down by the tip of the shorter probe. To minimize this problem two sharp stainless steel sewing needles were attached to the probes. The oil layer thickness was recorded as the average of the two values obtained when the probe moved into the saline solution and the probe moved back into the oil layer. A difference of about 0.3 mm between these values was generally found.

In each test series, sinking agent was added and the decrease in oil layer measured, until the oil layer became discontinuous. At this point about 95% of the oil had been sunk and the test was terminated. The appearance of water patches produced a disproportionate decrease in sinking agent efficiency.

15.5 Efficiency Testing Procedure

Each test series was conducted for a particular sinking agent, a particular oil, a temperature, and free fall distances of 15 cm, 30 cm, and 60 cm. Using the test cell area and the density of the test oil, a quantity of oil calculated to yield a layer of between 10 mm and 15 mm was weighed out and floated carefully on the water.

Sinking agent in 100-gm quantities was spread evenly over the retractable slide of the cell and dispersed on the oil by release of the locking pin. Those sinking agents that did not sink to the bottom were given three 15-second hand stirring periods with a glass rod. The oil layer thickness was determined after each sinking agent dispersal. The 100-gm treatment procedure was repeated until the appearance of exposed water patches.

The large volume of experimental data was organized in the following form.

1. <u>Group A Tables</u>. These contain the raw experimental data, and carry information on accumulated sinking agent, oil layer thickness, and weight of oil removed after each treatment. These will be found in the appropriate Appendix.

2. <u>Group A Figures</u>. These contain the plots of the raw experimental details. They involve the accumulated weight of sinking agent added versus both the accumulated weight and layer of oil removed. These will be found in the appropriate Appendix.

3. <u>Group B Tables</u>. These contain the analyzed raw data to provide information concerning the weight of sinking agent and the agent/oil ratio required to remove oil to a set layer thickness, starting from specific initial thicknesses. These will be found in the appropriate Appendix.

4. <u>Group B Figures</u>. These contain plots of the analyzed data concerning weight of sinking agent required for various starting oil thicknesses, and the projected field conditions showing the agent/oil ratio required for various starting oil

thicknesses. These will be found in the appropriate Appendix.

5. Combination Figures Group A and B. These contain the comparison plots of raw and analyzed data showing the effects of free fall distance, temperature, etc., on the various oils. Carried in the body of the text, they form the basis of any commentary.

15.6 Volatility Loss Testing

Each oil type to be explored in the test series was examined to determine, at 21 ± 1^{0}C, time-based volatility losses. For each oil, saline solution was used to fill a 1-liter beaker to approximately the halfway point. The average surface area at this general location was 81 cm^2. Using the exact surface area 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 oil layer thickness was measured immediately after oil addition, using the thickness measuring device.

At varying time intervals the oil layer thickness was measured again, and for each oil the raw data obtained was used to develop tables and plots showing the volatile weight loss versus the time interval.

15.7 Retention Testing Procedure

The oil layer thickness measuring device previously described was used also to test agent/oil retentive capacities by determination of the increasing surface oil released from the sunken agent/oil mass. These measurements could best be carried out when the oil released was sufficient to produce a continuous surface, with no water patches visible. To accomplish this, a sufficiently thick layer of oil was floated to leave, after the initial addition of the sinking agent, a measurable residue.

Each sinking agent and oil type combination was tested at room temperature under static conditions. For each combination, saline solution was used to fill a 1-liter beaker to approximately the halfway point. The average surface area at this general location was 81 cm^2. 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 mm to 20 mm was calculated.

Oil was carefully floated onto the solution surface until the calculated weight was attained. The oil layer thickness resulting was determined immediately. Then a quantity of sinking agent was weighed out which, in consideration of the weight of floated oil involved, generally 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 a 15-cm height. Where penetration and sinking was not spontaneous, the agent/oil mass was stirred, as previously mentioned. Immediately the agent/oil mass was sunk, the residual oil layer at the surface was measured.

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, for Western Crude oil, at the end of one day, more oil had evaporated than was released. The increments of thickness change shifted from positive to negative values.

To correct for these volatility losses the assumption was made that for any specified period or time interval, volatility losses would be adequately accounted for by taking the oil weight in the 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.

$$R_t = \frac{M_t - \dfrac{I\left[1 - \dfrac{V_{(dp + t)}}{100}\right]}{\left[1 - \dfrac{V_{dp}}{100}\right]}}{\left[1 - \dfrac{V_t}{200}\right]} \qquad (45)$$

where R_t = amount of released oil in time t (gm)

M_t = oil in float at time t (gm)

I = initial oil in float after delay period and after adding sinking agent (gm)

t = time interval from sinking (hr)

dp = delay period after floating oil and before adding sinking agent (hr)

V_t = volatility loss by weight in time t (%)

V_{dp} = volatility loss by weight in delay period (%)

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

The amount of oil in the initial sunken mass S_o is given by

$$S_o = T_o - I \qquad (46)$$

where T_o = total oil in float after delay period (gm)

The amount of oil in the sunken mass O_t, at any time, is given by

$$O_t = S_o - R_t \qquad (47)$$

The amount of oil retained, OR_t, as a ratio of the amount of oil initially sunk is given by

$$OR_t = \frac{(S_o - R_t)}{S_o} \qquad (48)$$

The efficiency of the sinking agent is given by the ratio

$$SA/O_t = \frac{SA}{S_o - R_t} \qquad (49)$$

where SA = weight of sinking agent used (gm)

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. No compensation was included to offset specific gravity changes in the oils with volatility losses. This situation is, again, really important in the case of Western Crude oil, where the change in specific gravity with volatility losses was appreciable: the value changed in approximately 144 hours at 21°C from 0.83 to 0.89. In the volatility and retentivity tests, the results were good enough for comparative purposes without the complication of additional corrections.

16 TEST RESULTS

16.1 General

Raw test data have been accumulated in the Appendices. Only such data or data derivatives of immediate moment are included in the body of the report.

For multiple measurements or tests, only the average value and the standard deviation are shown. A bracketed figure to the immediate right of the average value represents, where it occurs, the number of contributing values.

The circles in the graphs serve only as point loci and do not indicate uncertainty parameters. The latter can usually be obtained directly from the corresponding tabulated data. Some comparison plots of individual test results do not carry circled point loci.

16.2 Sinking Agent Characteristics

The sinking agents involved in this study, together with pertinent data as to general type and sources of supply, are given in the following.

1. <u>Oil-Lok 501</u> is 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.

2. <u>Zorb-All</u> is a calcinated clay material of a semi-granular nature. It was supplied by Wyandotte Chemicals Ltd., 1253 McGill College Avenue, Montreal, Quebec.

3. <u>Hi-Dri</u> is a clay material, a hydrated magnesium aluminum silicate of a semigranular nature. It was supplied by Tenenier Absorbent Products Ltd., 185 Young Street, Hamilton, Ontario.

The test results obtained with repect to true and apparent specific gravities, bulk or loose densities, and ~~the~~ surface areas are shown in Table 3.

There was a considerable difference between the true and the apparent specific gravities where Zorb-All and Hi-Dri were concerned, as reflected by the high surface area values of these materials. The situation is also indicated by the representative values in the bulk densities.

The surface area values corroborate the visual impression that Hi-Dri was a dustier sinking agent than Zorb-All, clouding the

TABLE 3

CHARACTERISTICS OF SINKING AGENTS

Sinking Agent	Specific Gravity		Bulk or Loose Density (lb/ft)	Surface Area (m^2/gm)
	True	Apparent		
Oil-Lok 501	2.79 ± 0.02	2.67 ± 0.03	93.3 ± 0.5	4.6
Zorb-All	2.71 ± 0.02	2.05 ± 0.03	35.4 ± 0.5	75.1
Hi-Dri	2.98 ± 0.02	2.10 ± 0.03	33.4 ± 0.5	83.8

water in the test tank. Oil-Lok did not release entrapped pore air on contact with oil or water and should therefore have had the least surface area.

It is the difference between the true and apparent specific gravities that produces the characteristics of a spontaneous sinking agent or one that requires agitation before sinking. For high viscosity oils this brings about the possibility that the time required to sink such oils is intolerably prolonged.

16.3 Oil Type Characteristics

Three oil types were selected for the study.

1. Western Crude Oil is a crude oil of origin in western Canada, supplied by Petrofina Canada Ltd. from the Montreal refinery and carrying their designation 'Western Crude Oil'.

2. No. 2 Fuel Oil is a furnace fuel oil supplied by Petrofina Canada Ltd. from the Montreal refinery and carrying their designation 'Blue No. 2 Fuel Oil'.

3. Bunker Oil is a heavy fuel oil supplied by Petrofina Canada Ltd. from the Montreal refinery and carrying their designation 'No. 6 Bunker Oil'.

The test results relative to specific gravity at the temperatures tested are shown in Table 4, together with the measurement

TABLE 4

SPECIFIC GRAVITY OF TEST OILS

Oil	Specific Gravity	
	21 ± 1°C	2 ± 1°C
Western Crude	0.830 ± 0.0001	0.839 ± 0.0001
No. 2 Fuel	0.840 ± 0.0001	0.850 ± 0.0001
No. 6 Bunker	0.964 ± 0.0001	0.971 ± 0.0001

uncertainties.

The test results with respect to the viscosity values at the temperatures tested are shown in Table 5, together with the appropriate averages and standard deviations.

It can be seen that, while at room temperature No. 2 Fuel oil and Western Crude oil have somewhat similar viscosities, at 2°C this is no longer the case. Western Crude oil at the lower temperature is far more viscous and this will have some bearing on the subsequent sinking agent efficiency tests. At 2°C No. 6 Bunker oil acquires the properties of asphalt, and the viscosity value in the table is only an estimate from the literature (103). It is apparent that the sinking of the oil can be expected to present a problem.

16.4 Efficiency of Oil-Lok 501 in Removing Western Crude Oil

The pertinent appendix is Appendix II. The experimental data and the data treatment results are given as

Group A Tables	Tables 2-1 to 2-6
Group A Figures	Figures 2-1 to 2-6
Group B Tables	Tables 2-7 to 2-12
Group B Figures	Figures 2-7 to 2-18

16.4.1 Effect of Oil Layer Thickness Treated. For Oil-Lok 501 Figures 16 and 17 are the raw data comparison plots at 21°C and 2°C for the three free fall distances of 15 cm, 30 cm, and 60 cm.

The decrease in layer thickness treated is implied by the

TABLE 5

VISCOSITY OF TEST OILS

Oil	Viscosity at 21 ± 1^{o}C (cSt)		Viscosity at 2 ± 1^{o}C (cSt)	
	Average	Standard Deviation	Average	Standard Deviation
Western Crude	6.85 (4)	± 0.05	55 (4)	± 1
No. 2 Fuel	4.23 (4)	± 0.04	7.5 (4)	± 0.1
No. 6 Bunker	4.2×10^3 (4)	± 0.1×10^3	1.5×10^5	

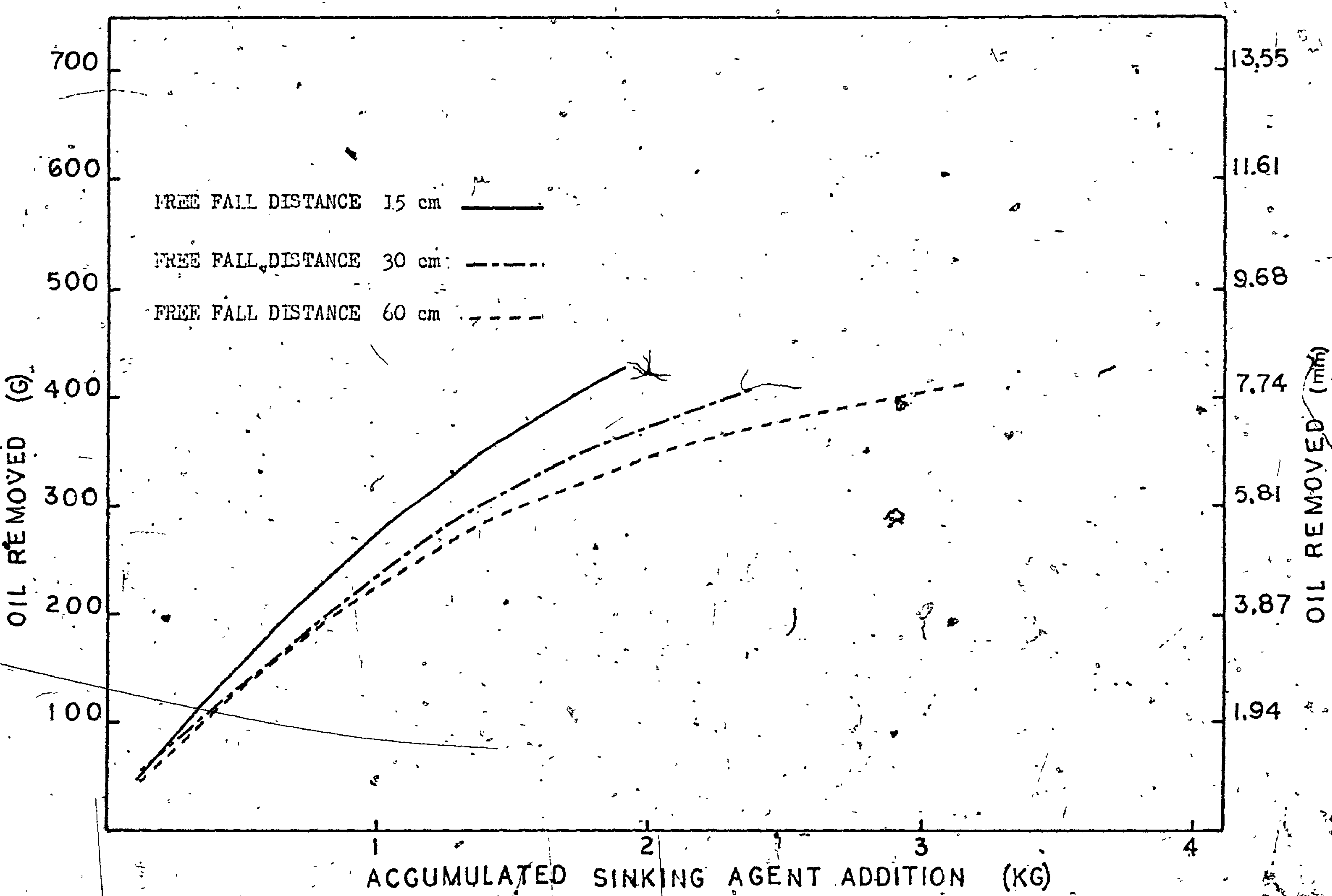


FIGURE 16 OIL-LOK 501 AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE AT 21°C

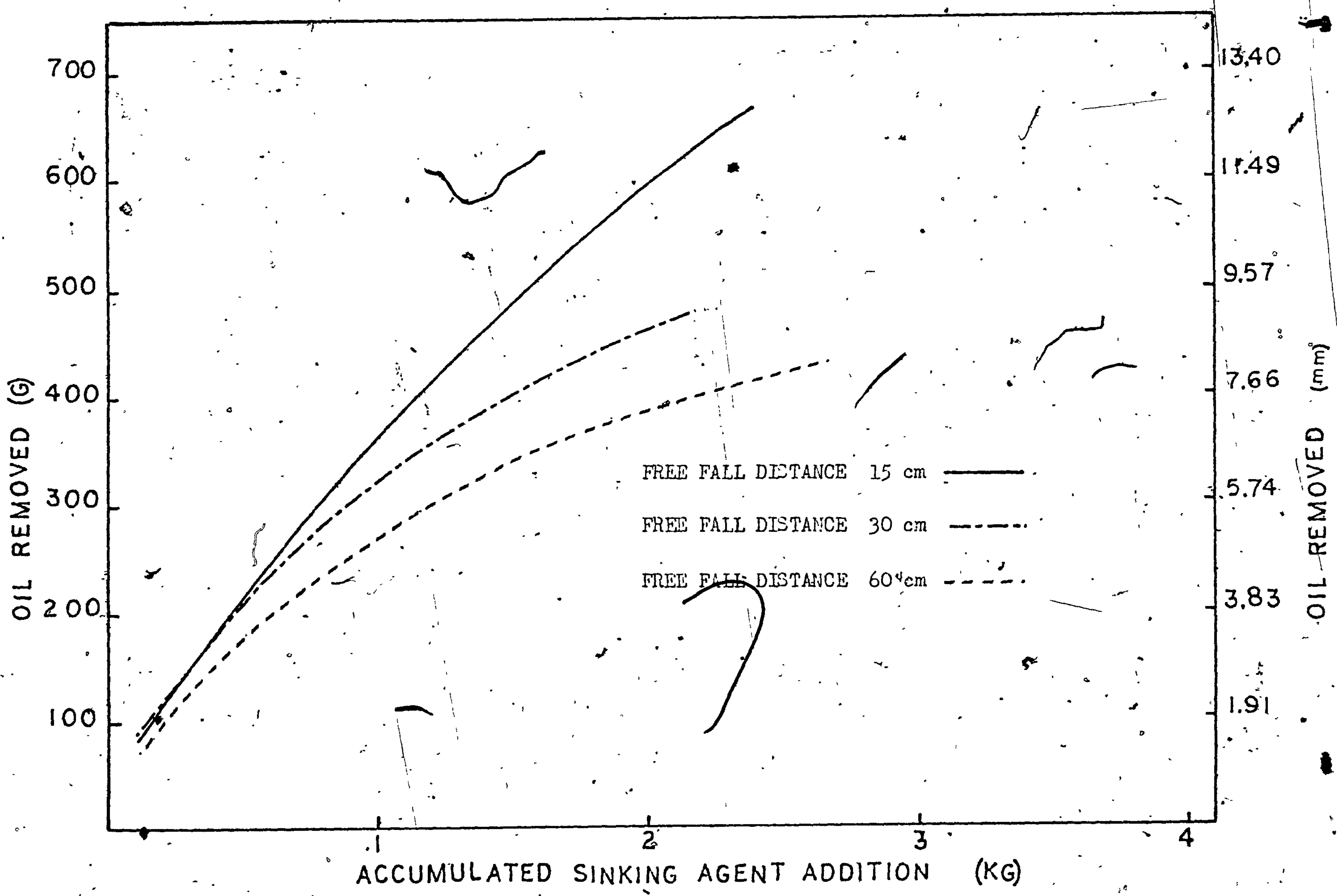


FIGURE 17 OIL-LOK 501 AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE AT 2°C

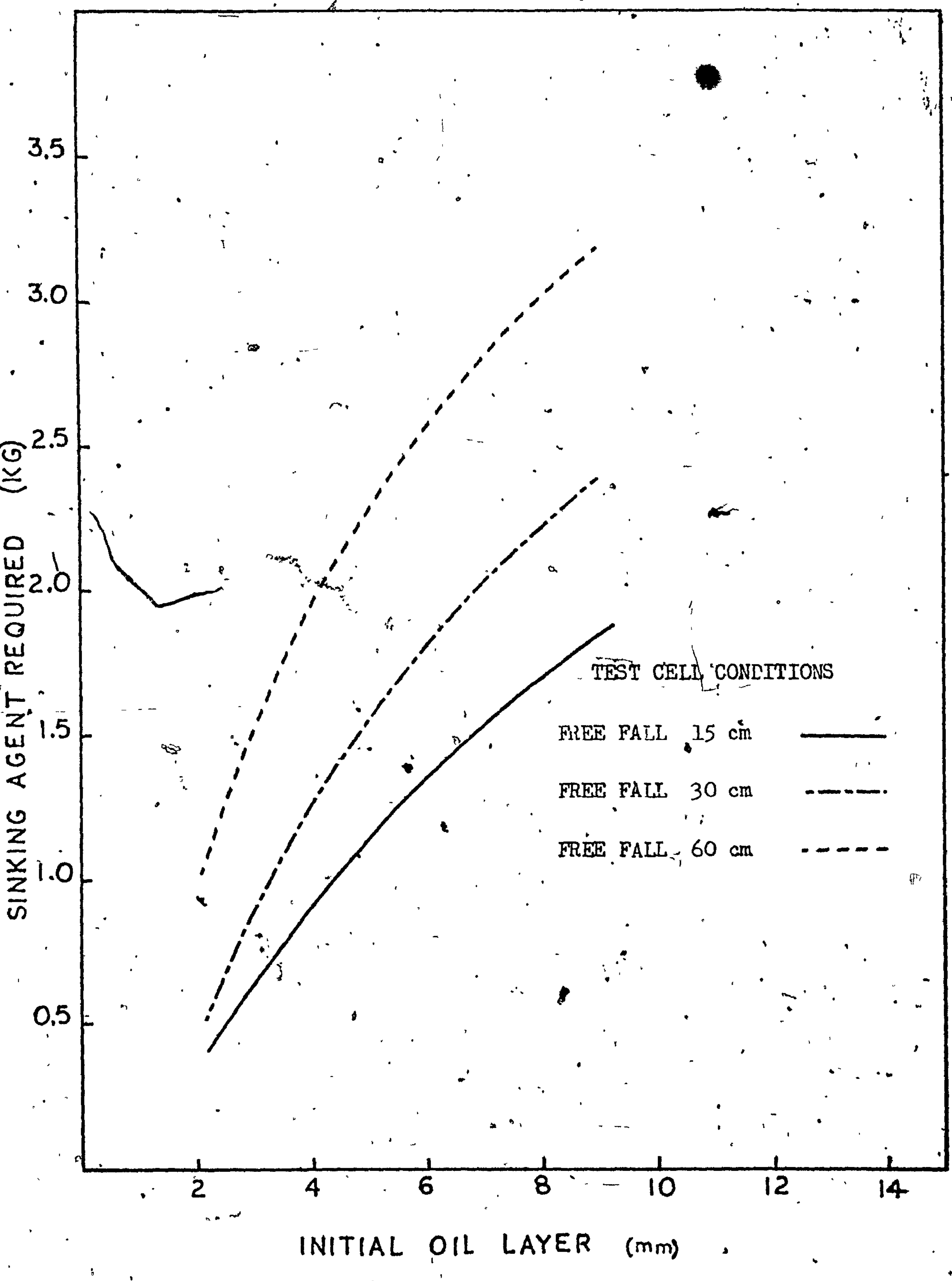


FIGURE 18 OIL-LOK 501 AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER (21°C)

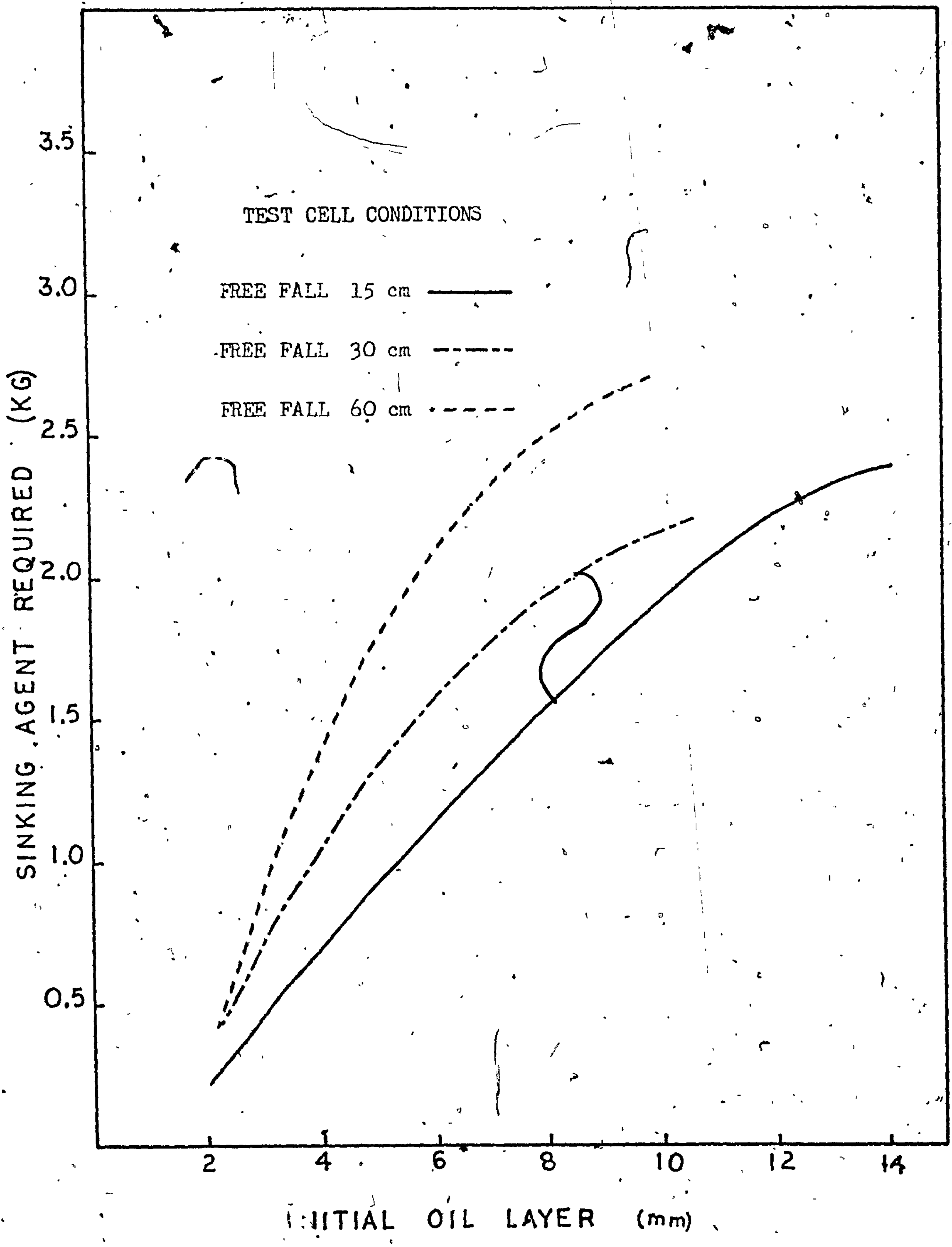


FIGURE 19 OIL-LOK 501 AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER (2°C)

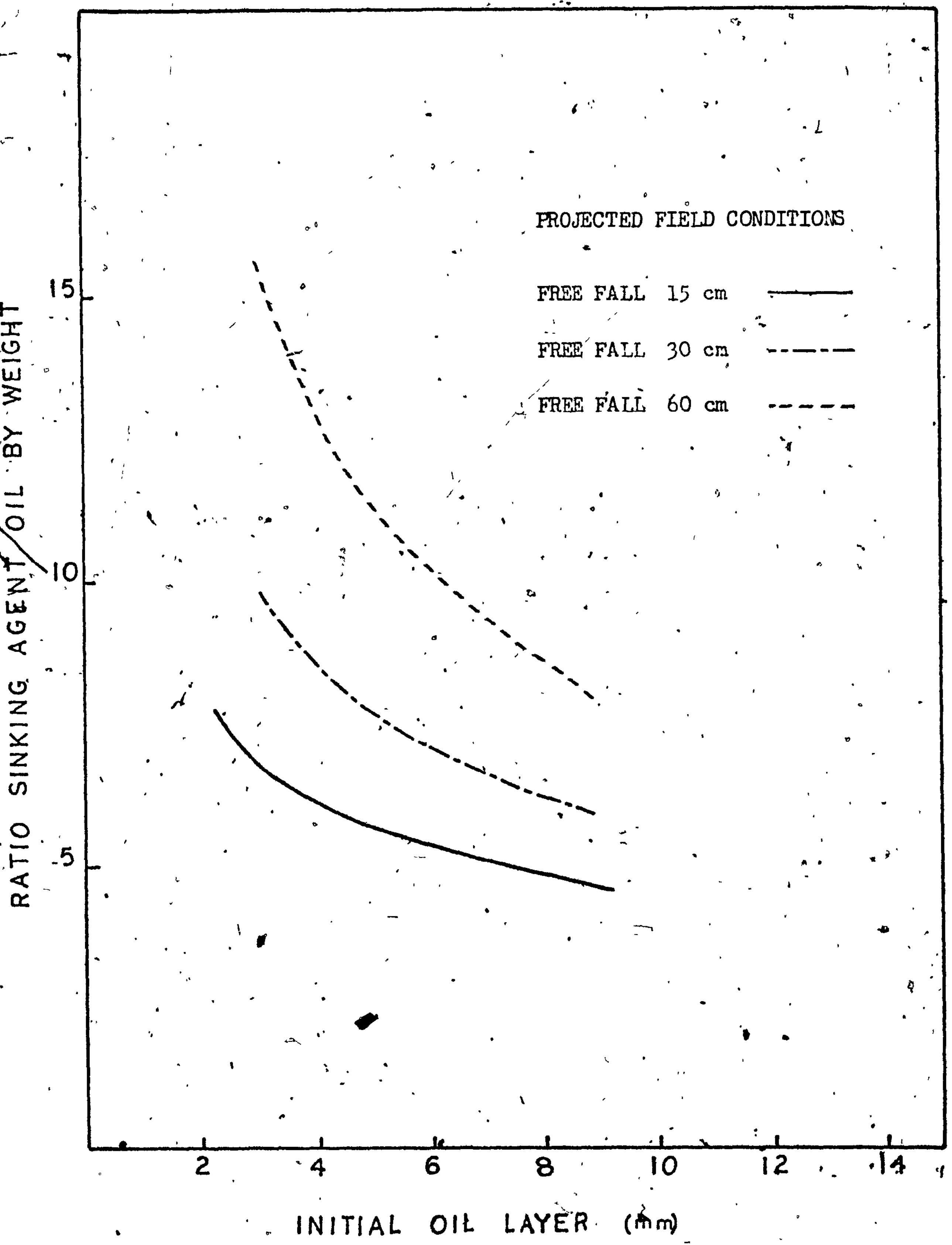


FIGURE 20 OIL-LOK 501 AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER (21°C)

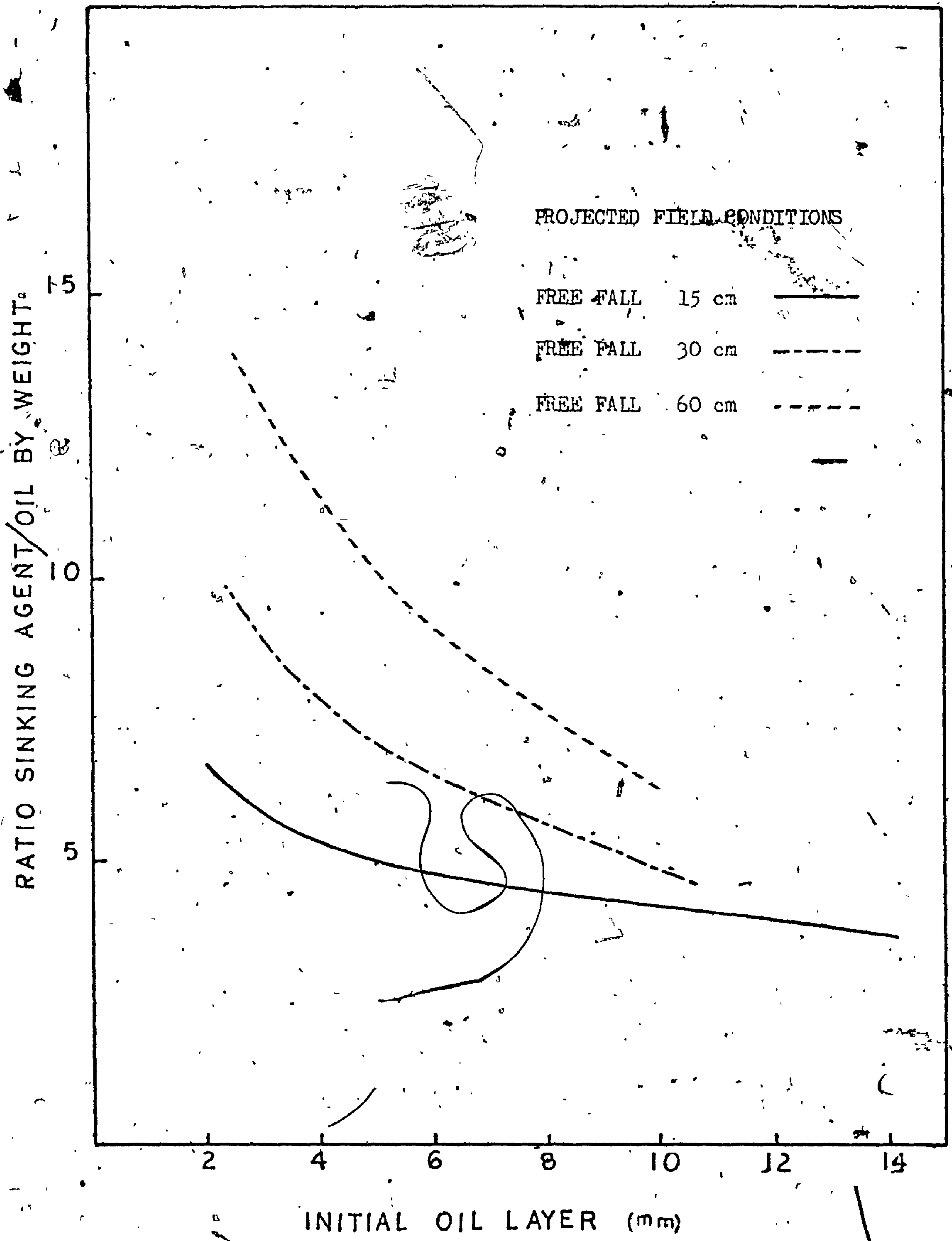


FIGURE 21 OIL-LOK 501 AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER (2°C)

16.4.2 **Effect of Free Fall Distance.** Figures 16, 18, and 20 at 21^{0}C all show the influence of free fall distance on sinking agent efficiency. It is apparent from the test cell and the projected field conditions that the efficiency of the sinking agent decreases with increasing free fall distance.

Figures 17, 19, and 21 at 2^{0}C show an identical situation. The decrease in efficiency results from the increased velocity with increased free fall distance, lessening the time-in-contact between the sinking agent and the oil. This effect diminishes as the initial oil layer thickness increases.

16.4.3 **Effect of Temperature.** The pairs of graphs, 16 and 17, 18 and 19, and 20 and 21, all indicate that for any specific initial oil layer and any specific free fall distance, the efficiency of the sinking agent is better at the lower temperature. This is due simply to the increased viscosity of the oil at the lower temperature, which increases the time-in-contact between the sinking agent and the oil.

Table 6 demonstrates this effect quite clearly.

16.5 Efficiency of Oil-Lok 501 in Removing No. 2 Fuel Oil

The pertinent appendix is Appendix III. The experimental data and the data treatment results are given as

Group A Tables	Tables 3-1 to 3-6
Group A Figures	Figures 3-1 to 3-6
Group B Tables	Tables 3-7 to 3-12
Group B Figures	Figures 3-7 to 3-18

TABLE 6

OIL-LOK 501 AND WESTERN CRUDE OIL - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Initial Oil Layer Thickness (mm)	Ratio: Sinking Agent/Oil - By Weight		
		Temperature		Decrease in Sinking Agent Required (%)
		21°C	2°C	
15		4.49	4.32	4
30	9	5.83	5.18	11
60		7.75	6.99	10
15		5.15	4.64	10
30	7	6.69	6.06	9
60		9.29	8.19	12
15		6.07	5.31	12
30	4	8.56	7.72	10
60		13.01	11.44	12

16.5.1 Effect of Oil Layer Thickness Treated. For Oil-Lok 501 Figures 22 and 23 are the raw data comparison plots at 21°C and 2°C for the three free fall distances. Both plots show again that, in general, the efficiency of Oil-Lok 501 decreases with decreasing oil layer thickness.

Figures 24 and 25 represent the test cell conditions at 21°C and 2°C, plotted as the amount of Oil-Lok 501 required [illegible] sink No. 2 Fuel oil to a floating layer of 1-1.5 mm, starting from variable oil layer values. These plots show the decrease in Oil-Lok 501 efficiency as the initial oil layer decreases.

Figures 26 and 27 are the projected field conditions at 21°C and 2°C, plotted as the ratio of Oil-Lok 501 to amount of No. 2 Fuel oil sunk versus variable initial oil layers. This shows, as before, the decrease in Oil-Lok 501 efficiency as the oil layers get thinner.

16.5.2 Effect of Free Fall Distance. Figures 22, 24, and 26 at 21°C show that the efficiency of the sinking agent, Oil-Lok 501, decreases with increasing free fall distance, although the difference between the 15-cm and 30-cm conditions is small.

Figures 23, 25, and 27 at 2°C show a similar situation with even less difference between the 15-cm and 30-cm conditions.

Again the fact that a free fall of 60 cm is the least efficient is due to the decrease in time-of-contact between the sinking agent and No. 2 Fuel oil at the greater free fall distance.

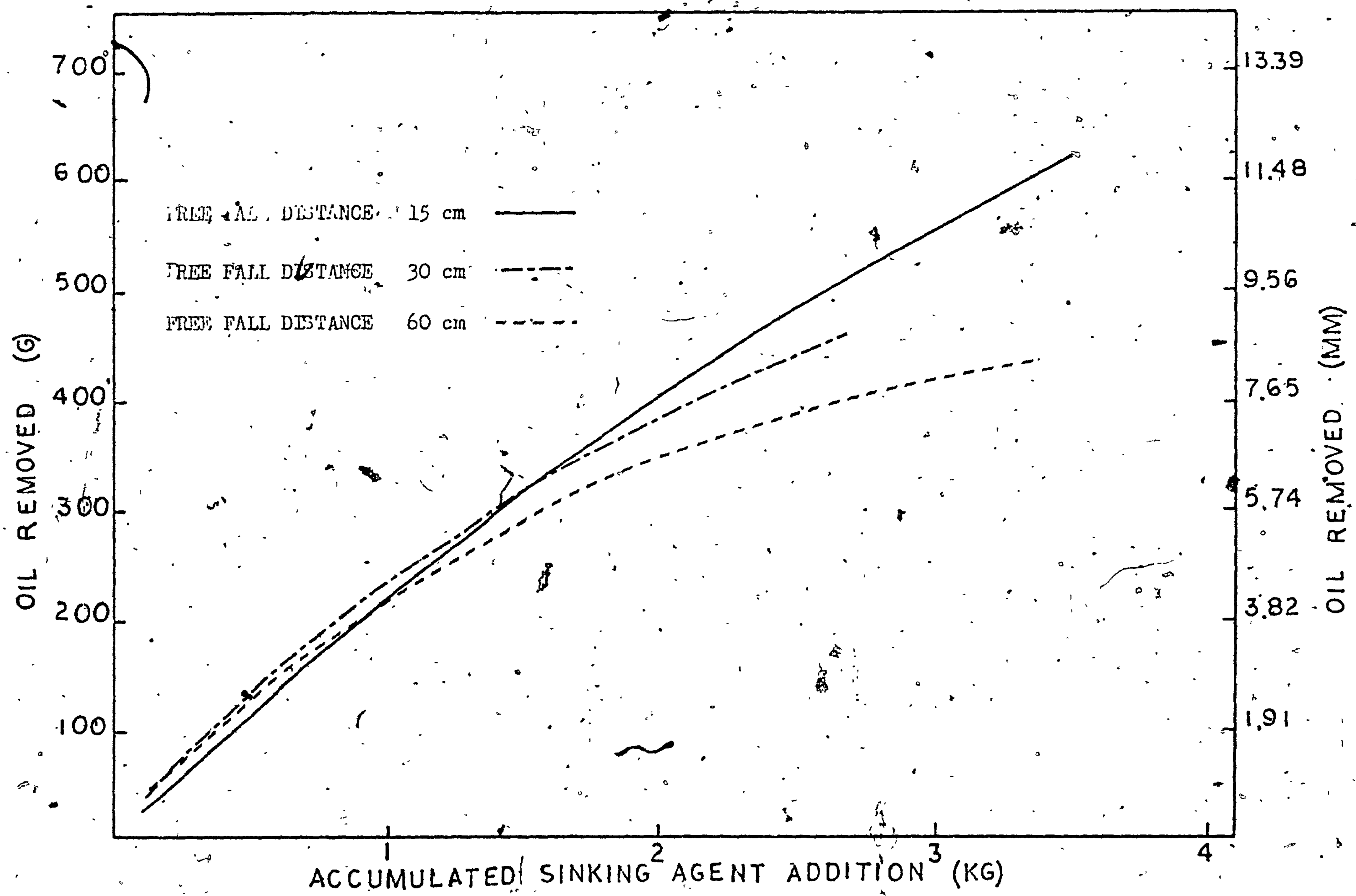


FIGURE 22 OIL-LOK 501 AND NO. 2 FUEL OIL - EFFECT OF FREE FALL DISTANCE AT 21°C

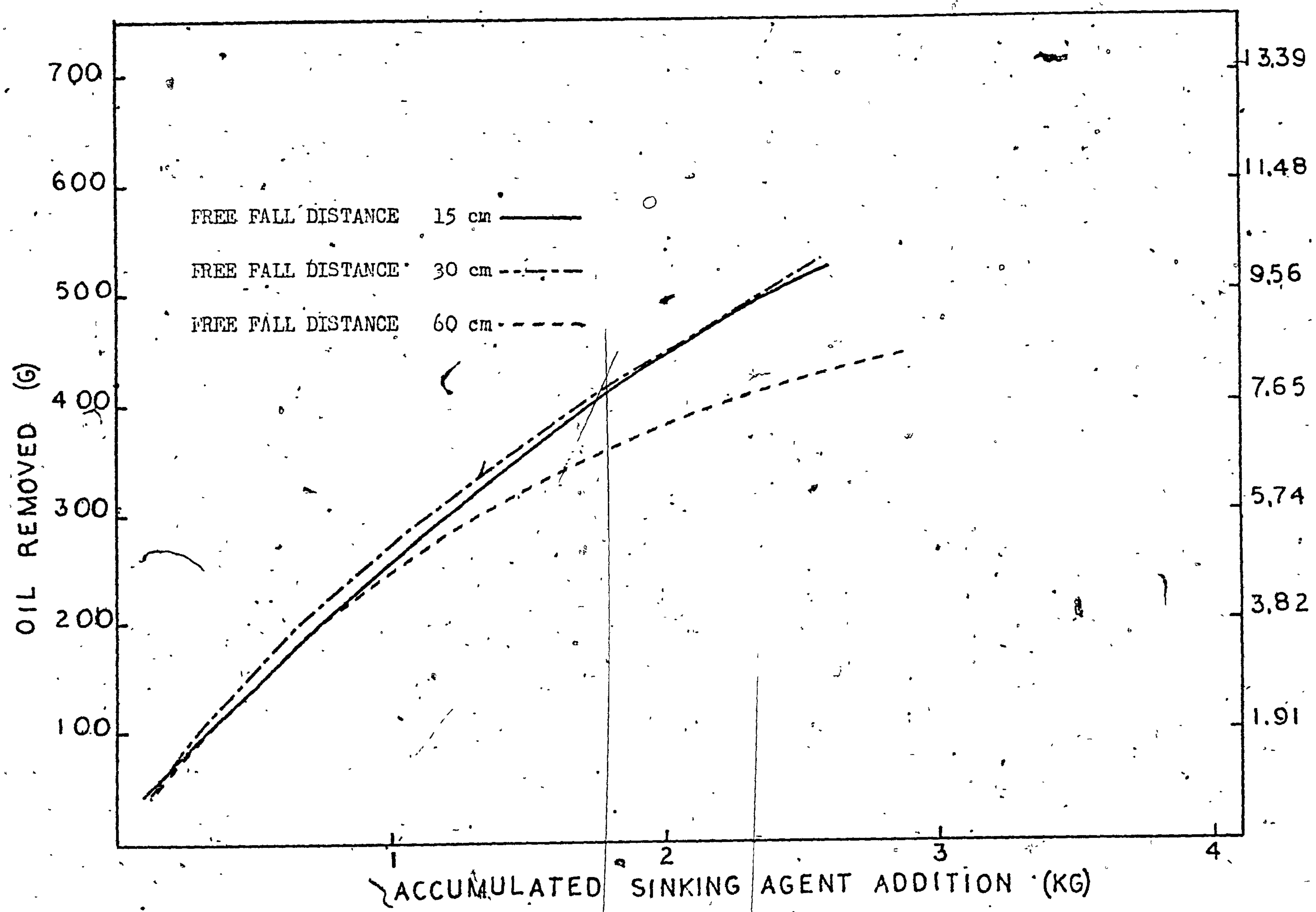


FIGURE 23 OIL-LOK 501 AND NO. 2 FUEL OIL - EFFECT OF FREE FALL DISTANCE AT 2°C

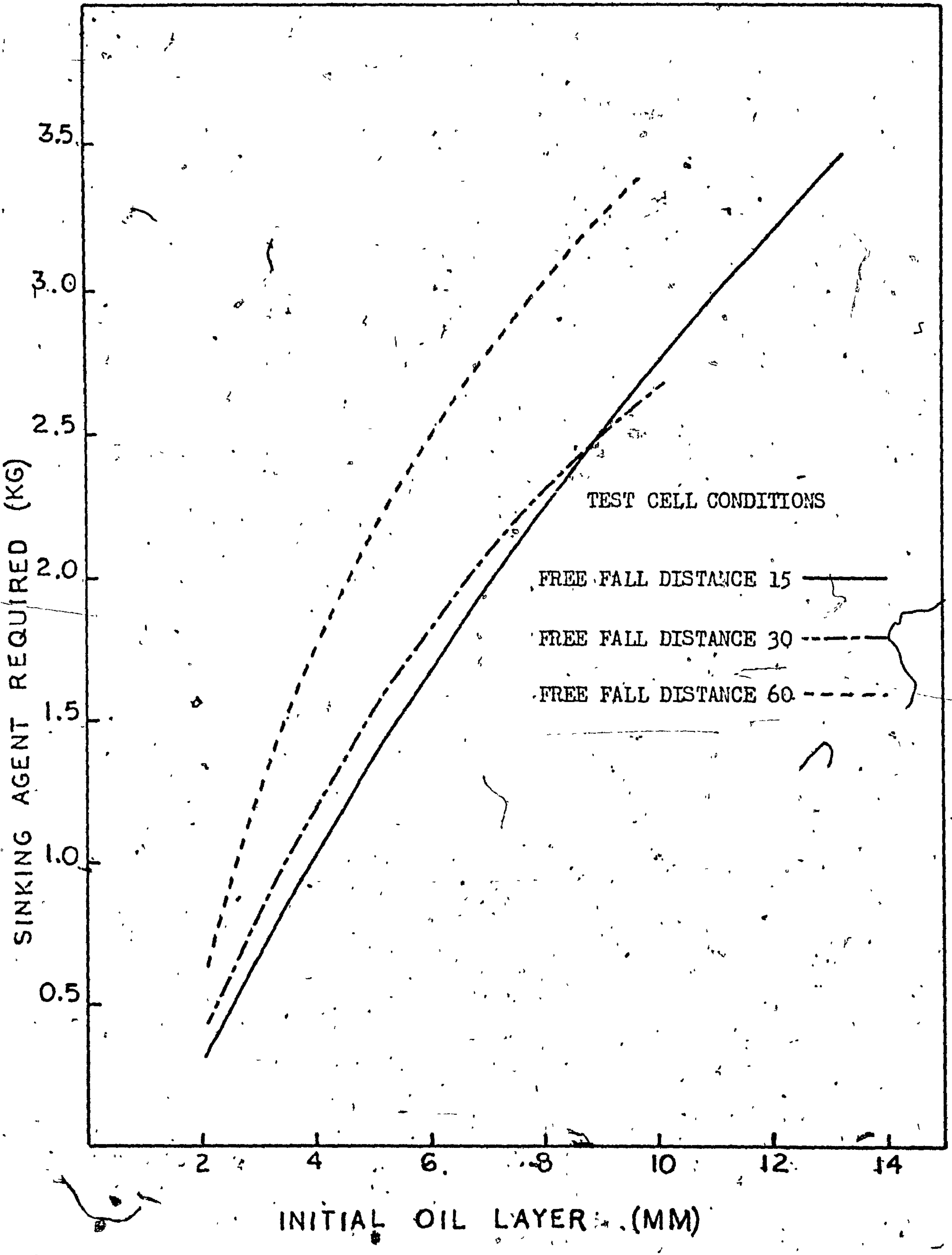


FIGURE 24 OIL-LOK 501 AND NO. 2 FUEL OIL - EFFECT OF FREE FALL DISTANCE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER (21°C)

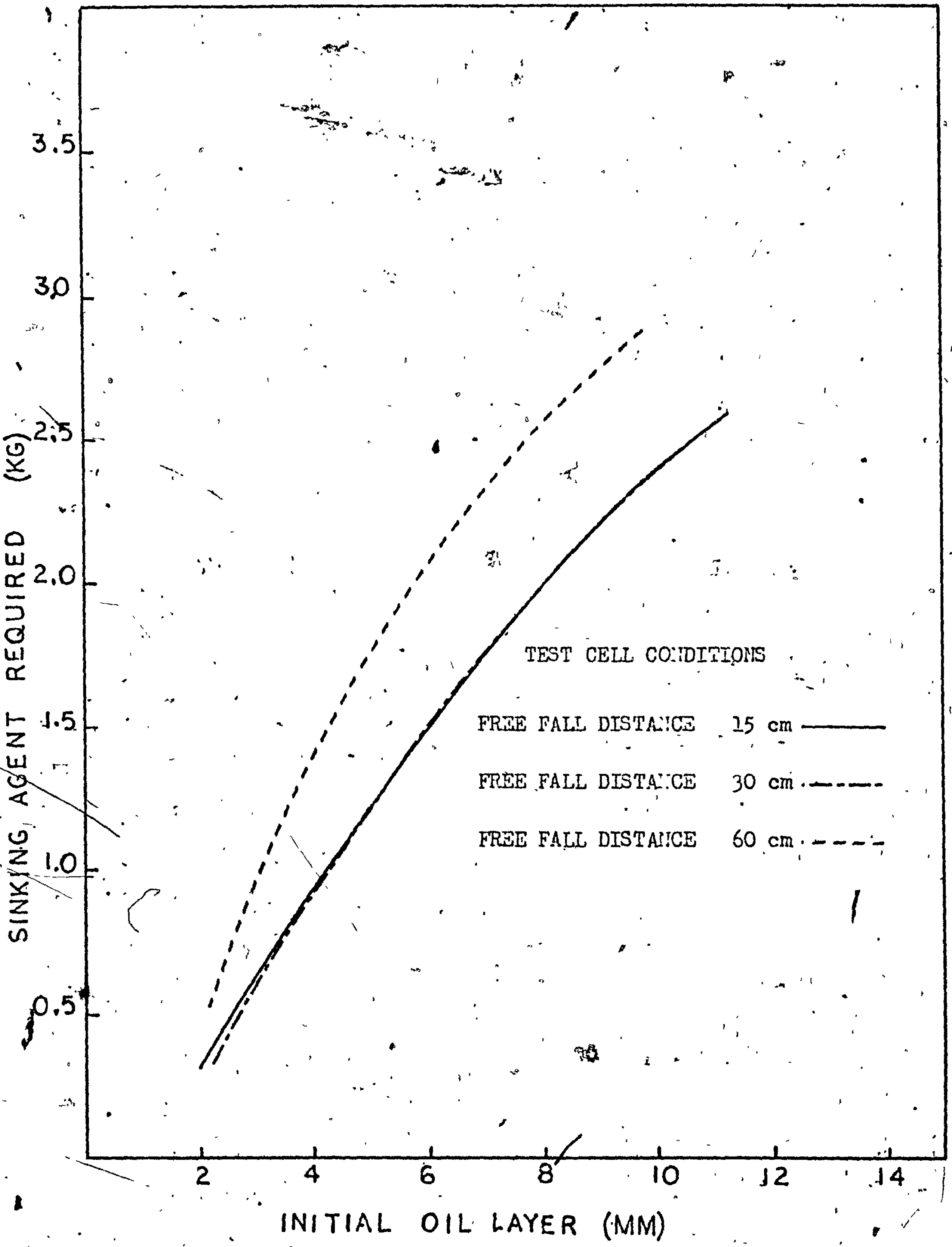


FIGURE 25 OIL-LOK 501 AND NO. 2 FUEL OIL - EFFECT OF FREE FALL DISTANCE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER (2°C)

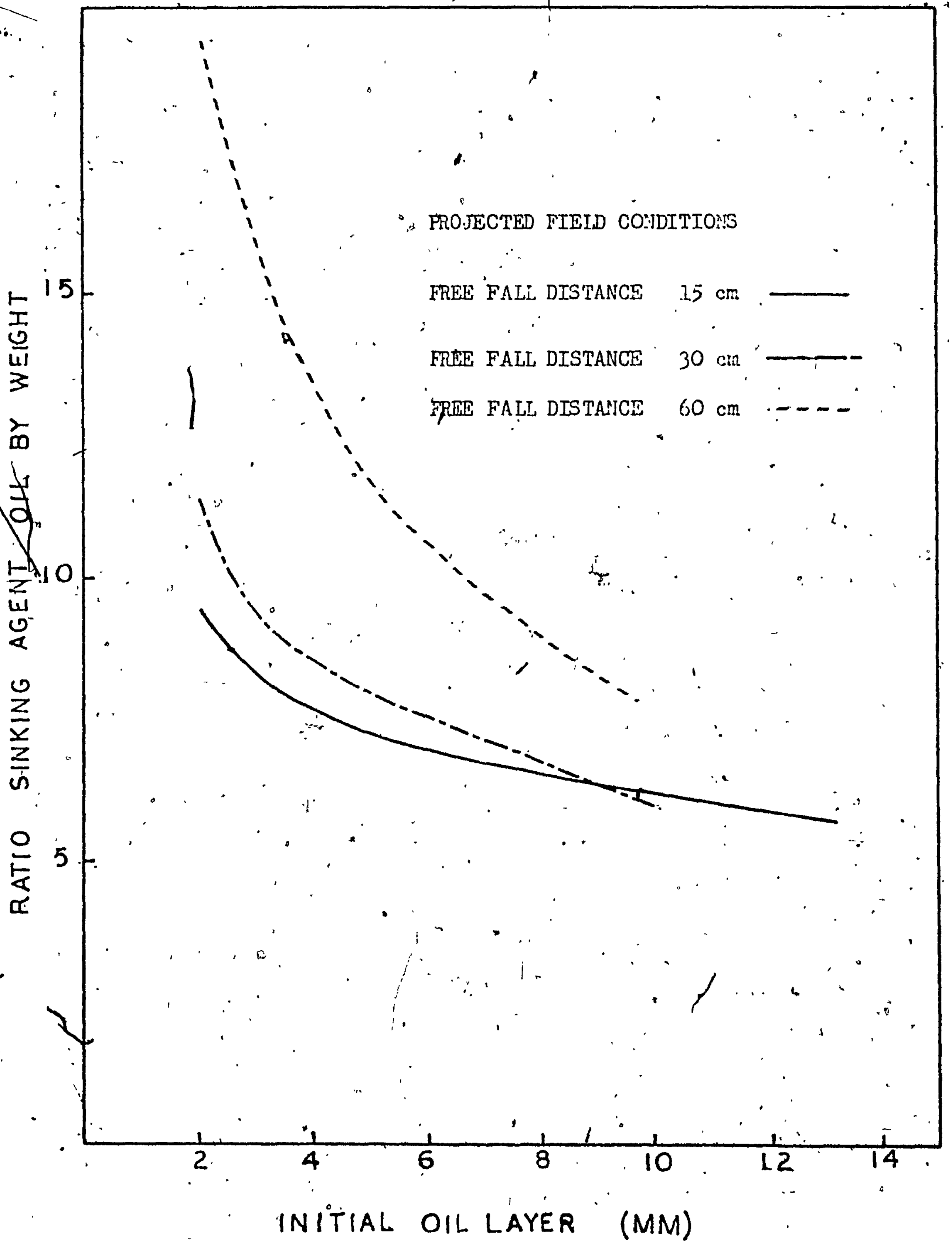


FIGURE 26. OIL-LOK 501 AND NO. 2 FUEL OIL - EFFECT OF FREE FALL DISTANCE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER (21°C)

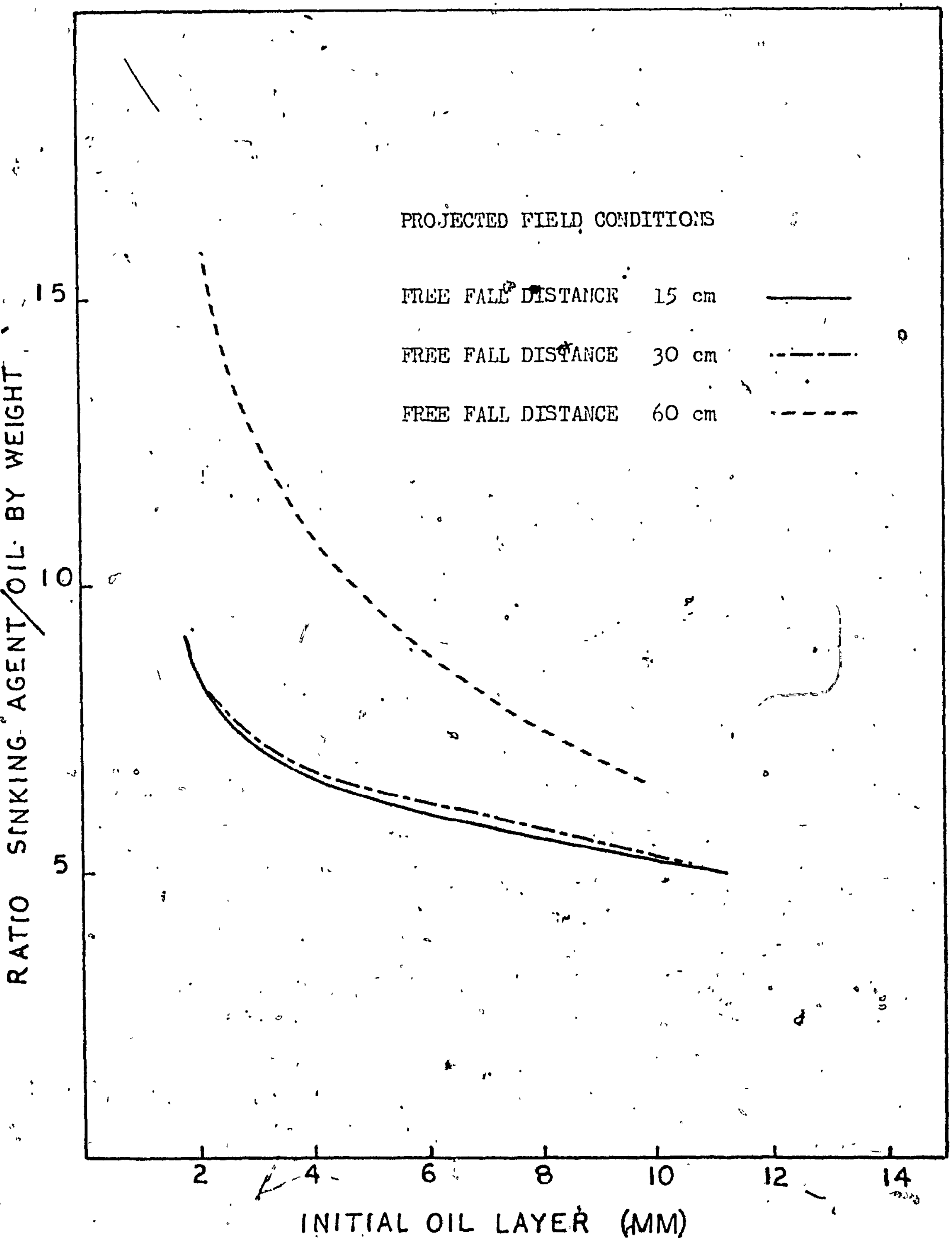


FIGURE 27 OIL-LOK 501 AND NO. 2 FUEL OIL - EFFECT OF FREE FALL DISTANCE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER (2°C)

16.5.3 Effect of Temperature. Comparison of the appropriate pairs of figures, from Figure 22 to 27, indicate that the efficiency of Oil-Lok 501 increased as the temperature was lowered. The increase in efficiency is due to the increased viscosity of No. 2 Fuel oil at 2°C. Table 7 indicates the situation.

16.6 Efficiency of Oil-Lok 501 in Removing No. 6 Bunker Oil.

The pertinent appendix is Appendix IV. The experimental data and the data treatment results are given as

Group A Tables	Tables 4-1 to 4-3
Group A Figures	Figures 4-1 to 4-3
Group B Tables	Tables 4-4 to 4-9
Group B Figures	Figures 4-3 to 4-9

The high viscosity of No. 6 Bunker oil, even at room temperature, required the modification of the oil layer thickness measuring device as outlined in Section 15.4 and, in addition, required the stirring procedure mentioned in Section 15.5.

A considerable amount of oil and sinking agent were carried down the sides of the test tank after each application, and time had to be allowed for the oil to refloat. This additional time was not critical in respect to volatility losses.

Due to the difficulties encountered in testing No. 6 Bunker, the data obtained was somewhat less reliable, but not of sufficient significance to obviate the testing technique.

TABLE 7

OIL-LOK 501 AND NO. 2 FUEL OIL - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Initial Oil Layer Thickness (mm)	Ratio: Sinking Agent/Oil - By Weight		
		Temperature		Decrease in Sinking Agent Required (%)
		21°C	2°C	
15		6.15	5.29	14
30	10	5.88	5.28	10
60		7.75	6.45	18
15		6.67	5.77	13
30	7	6.96	5.98	14
60		9.60	7.90	18
15		7.45	6.69	10
30	4	8.62	6.78	21
60		13.34	10.61	20

At 2°C attempts to test Oil-Lok 501 in removing No. 6 Bunker oil were not successful. The sinking agent remained on the surface of the oil, even after three days. Stirring and agitation were of no avail. In no instance could the sinking agent/oil mass be sunk with ease in any practical time period.

On the basis of these difficulties, further testing of Oil-Lok 501 on No. 6 Bunker oil at 2°C was abandoned.

16.6.1 Effect of Oil Layer Thickness Treated. Figure 28 contains the raw data comparison plots for Oil-Lok 501 on No. 6 Bunker oil at 21°C. The evidence here again shows that regardless of the free fall distance, as the oil layer thickness treated decreases, the efficiency of Oil-Lok 501 decreases.

Figures 29 and 30, which are the test cell conditions and projected field conditions of Oil-Lok 501 on No. 6 Bunker at 21°C, indicate again the same general trend.

16.6.2 Effect of Free Fall Distance. The three Figures 28, 29, and 30 all show that a slight decrease in efficiency of Oil-Lok 501 occurs with increasing free fall distance.

16.7 Effect of Oil Type on Oil-Lok 501

Figures 31 and 32 are the total comparison plots of the efficiency of Oil-Lok 501 in dealing with the three oil types, and brings in perspective the behaviour of Oil-Lok 501. The efficiency of this sinking agent is generally similar for Western Crude and No. 2 Fuel oil, but is much greater for No. 6 Bunker oil.

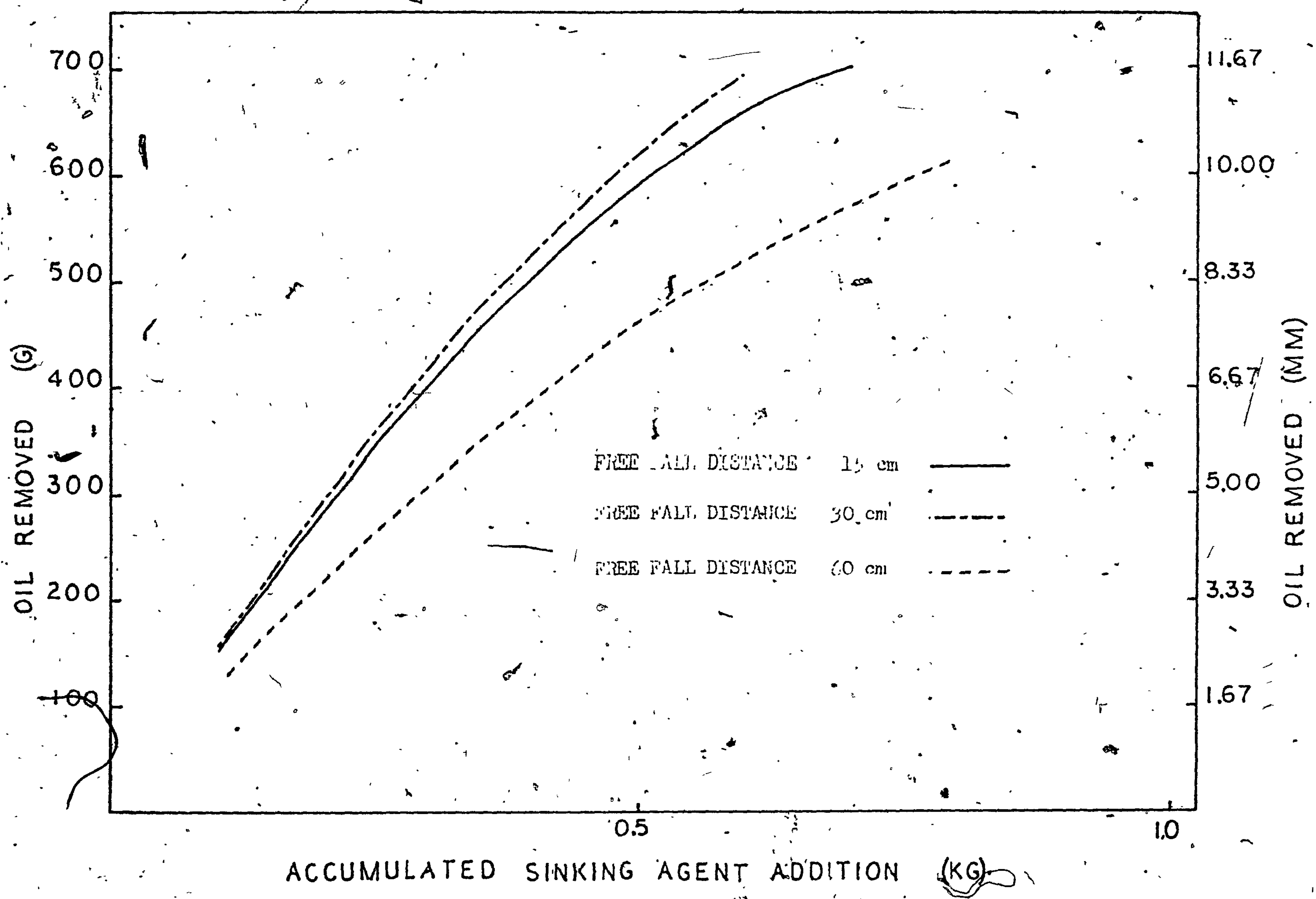


FIGURE 28 OIL-LOK 501 AND NO. 6 BUNKER OIL - EFFECT OF FREE FALL DISTANCE AT 21°C

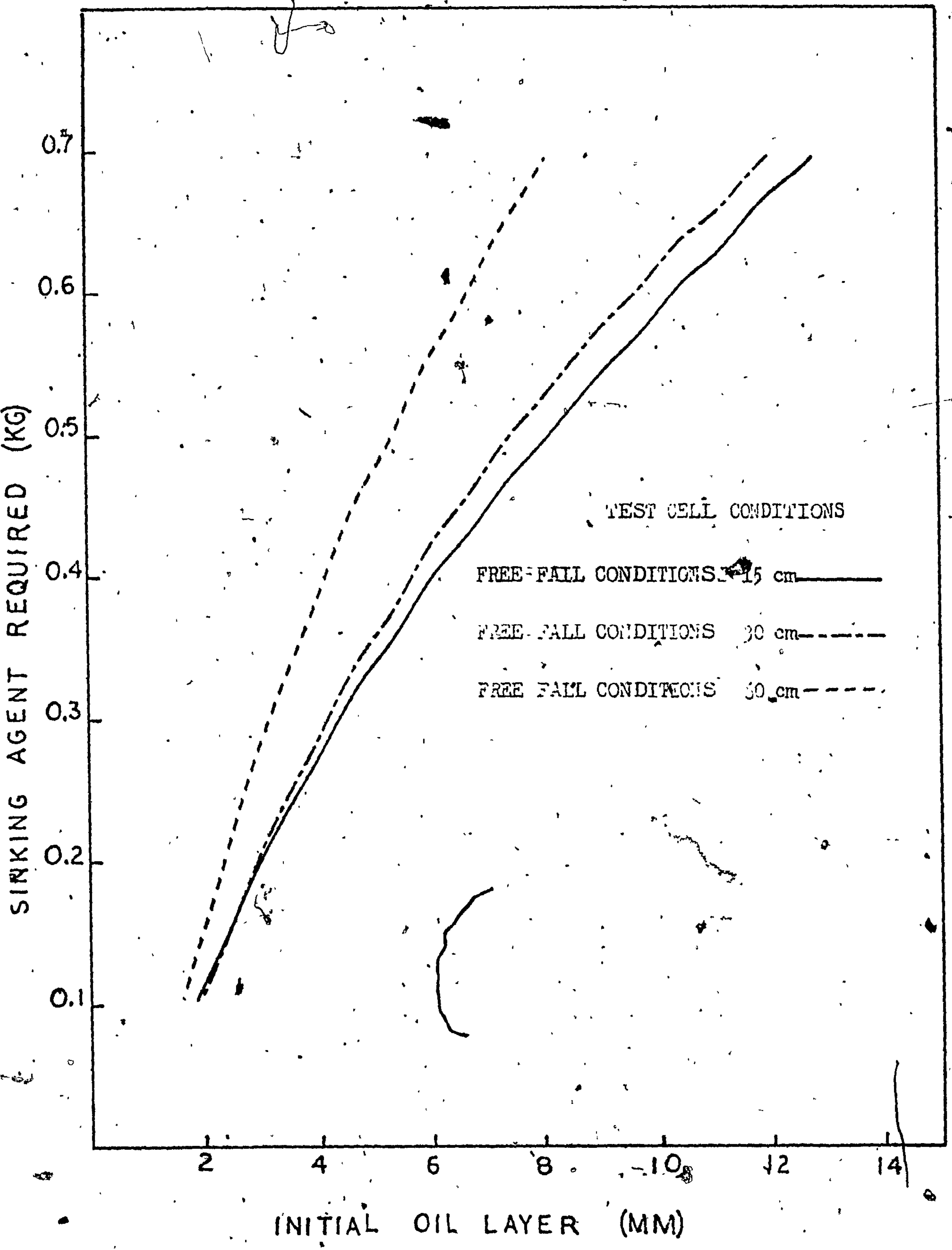


FIGURE 29 OIL-DOT 501 AND NO. 6 BUNKER OIL - EFFECT OF FREE FALL DISTANCE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER (21°C)

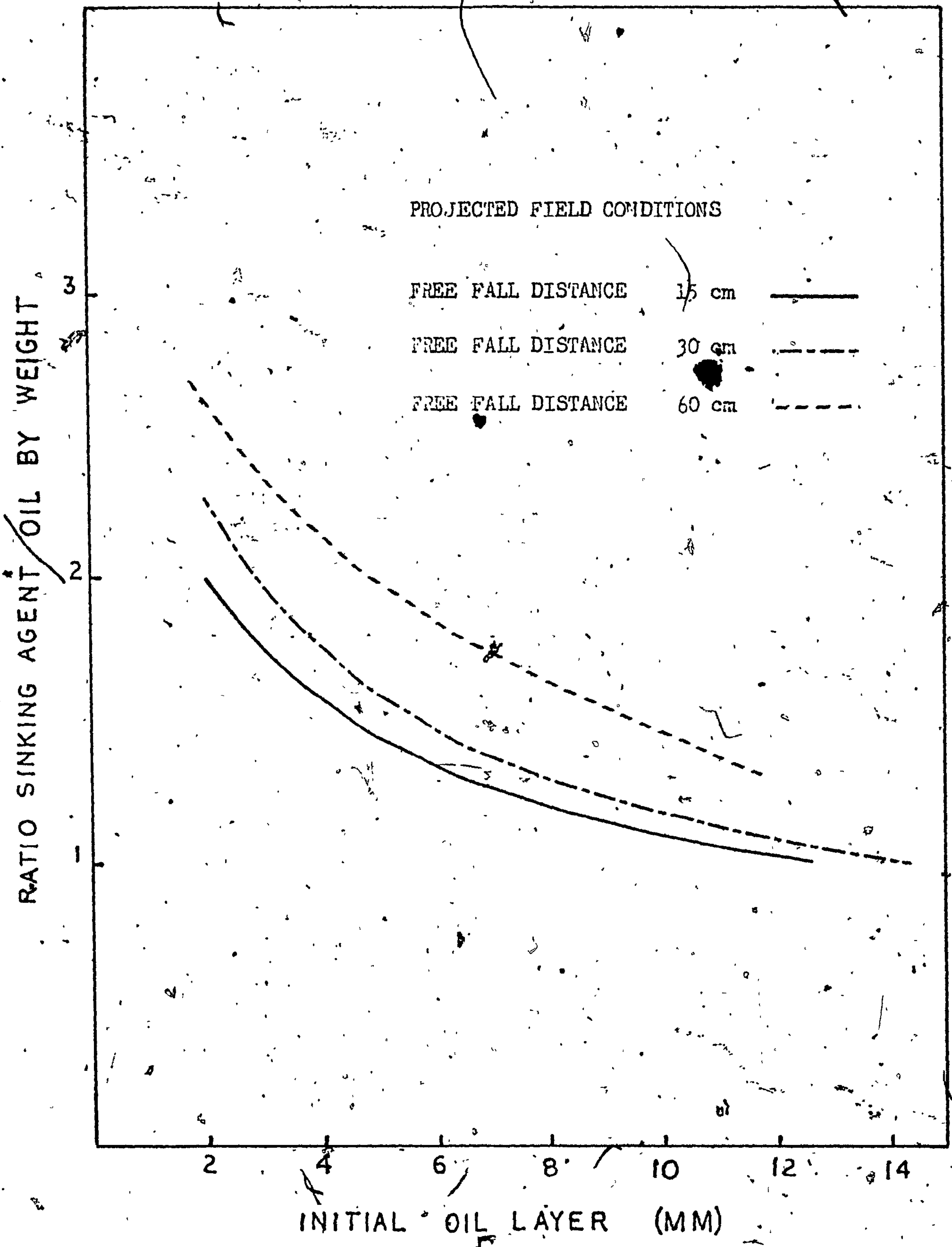


FIGURE 30 OIL-LOK 501 AND NO. 6 BUNKER OIL - EFFECT OF FREE FALL DISTANCE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER (21°C)

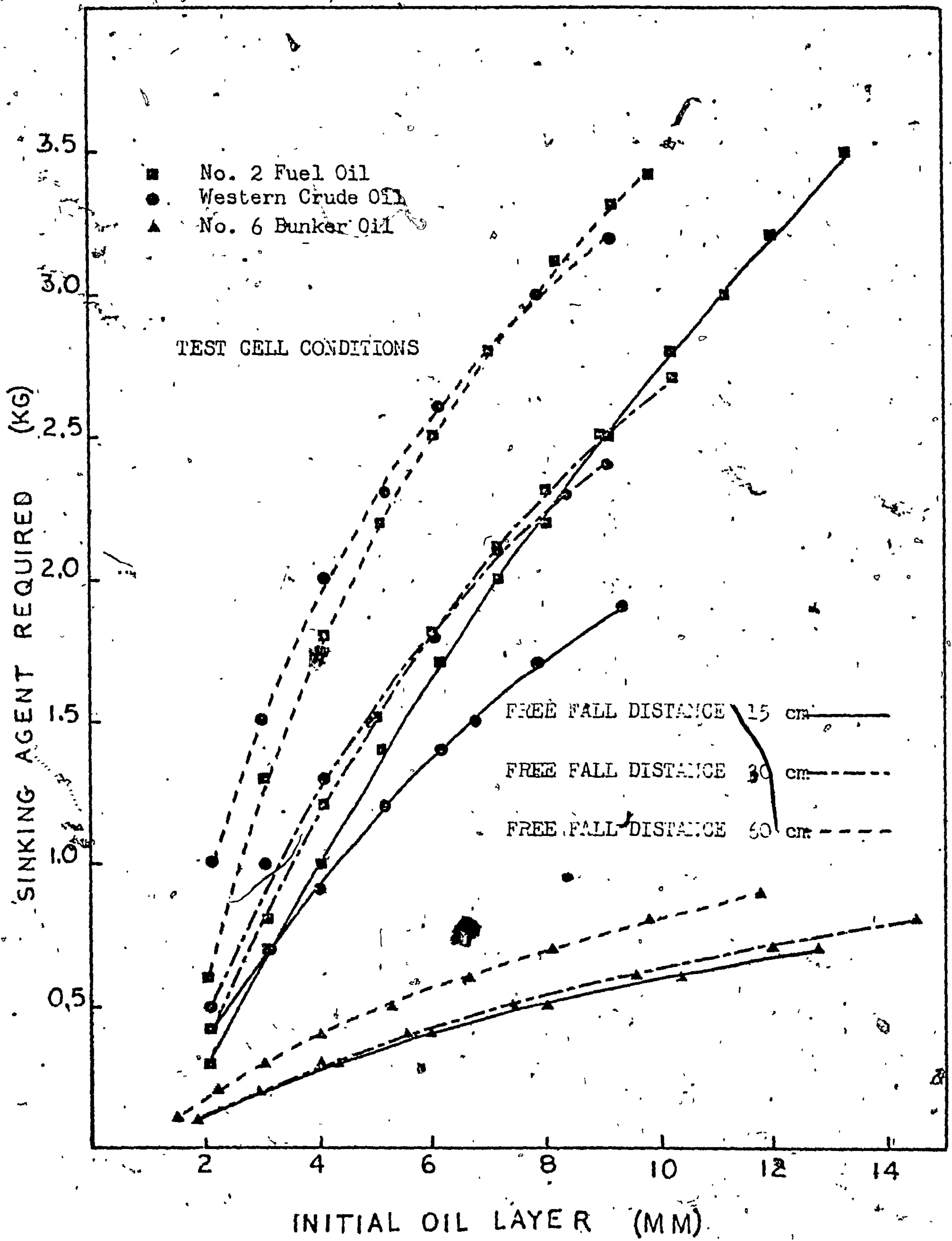


FIGURE 31 EFFECT OF OIL TYPE AND FREE FALL DISTANCE ON EFFICIENCY OF OIL-LOK 501 (21°C)

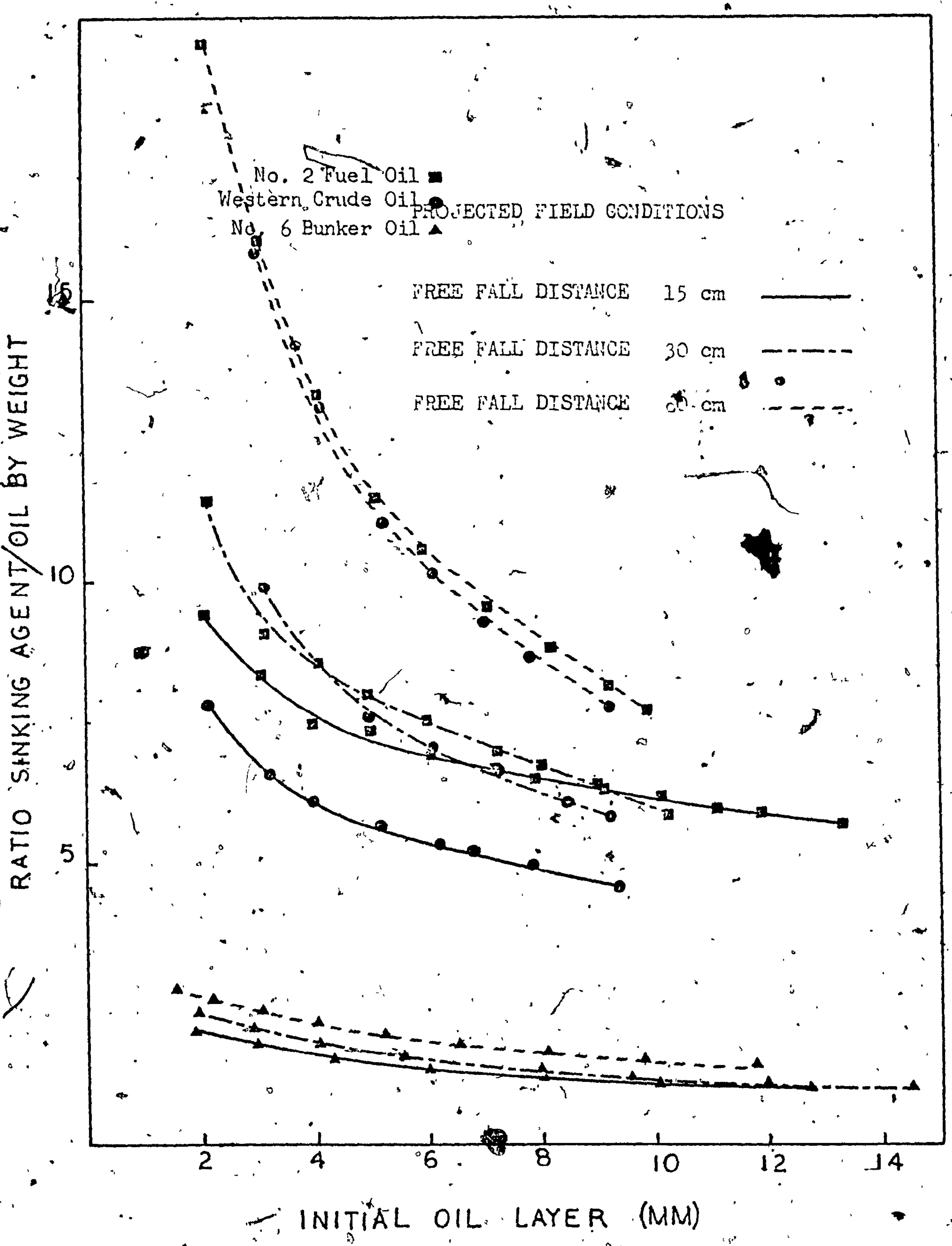


FIGURE 32 EFFECT OF OIL TYPE AND FREE FALL DISTANCE ON EFFICIENCY OF OIL-LOK 501 (21°C)

The graphs indicate that, due to the far greater viscosity of No. 6 Bunker, the changes in efficiency due to free fall distance on initial oil layer thickness are not as drastic as for the other oils.

Table 8 brings these situations out in tabular form in terms of the ratio of sinking agent to oil by weight, for initial oil layer thicknesses of 9 mm and 4 mm.

Figures 33 and 34 show a similar situation for the 2°C testing temperature, although No. 6 Bunker oil is not included here because it was unsinkable at this low temperature.

The sinking agent efficiency is generally of the same order for Western Crude and No. 2 Fuel oils; this similarity is exemplified in Table 9.

In general, even in the comparison of Western Crude oil and No. 2 Fuel oil where the viscosity of the former is slightly higher than that of the latter, it is apparent that the efficiency of Oil-Lok 501 increases to a degree with increasing viscosity of the oil treated, up to some limiting viscosity beyond which oil cannot be sunk conveniently.

16.8 Preliminary Testing of Zorb-All

This sinking agent had shown a significant difference between the true and apparent specific gravities. It had, as well, a large surface area, a generally low value for the loose or bulk density, and the presence of internal pores not immediately penetrable by water or oil.

TABLE 8

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

Oil	Initial Oil Layer - 9 mm			Initial Oil Layer - 4 mm		
	Ratio: Sinking Agent/Oil					
	Free Fall (cm)			Free Fall (cm)		
	15	30	60	15	30	60
Western Crude	4.49	5.83	7.75	6.07	8.56	13.01
No. 2 Fuel	6.29	6.39	8.19	7.45	8.62	13.34
No. 6 Bunker	1.10	1.19	1.50	1.52	1.75	2.16

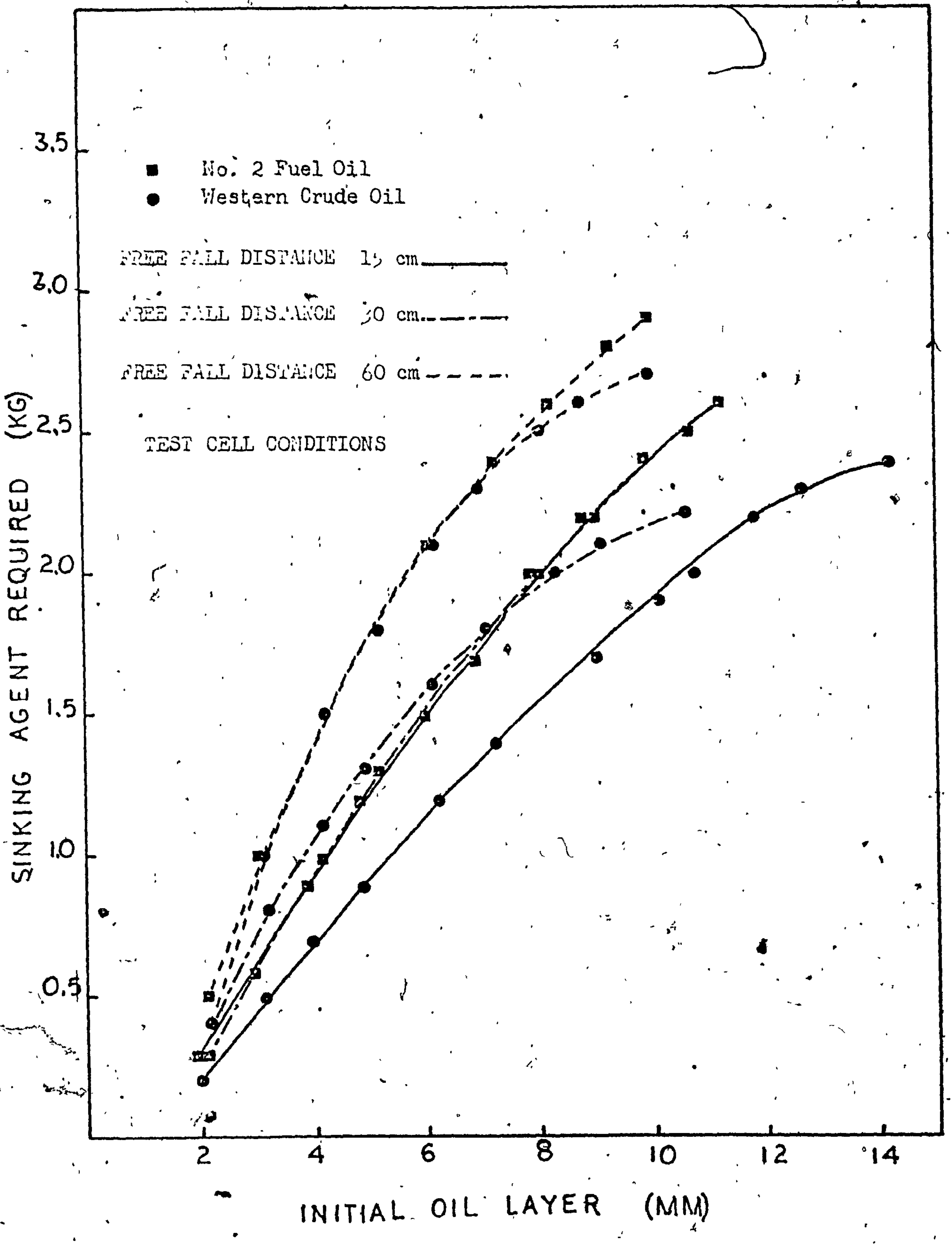


FIGURE 33 EFFECT OF OIL TYPE AND FREE FALL DISTANCE ON EFFICIENCY OF OIL-LOK 501 (2°C)

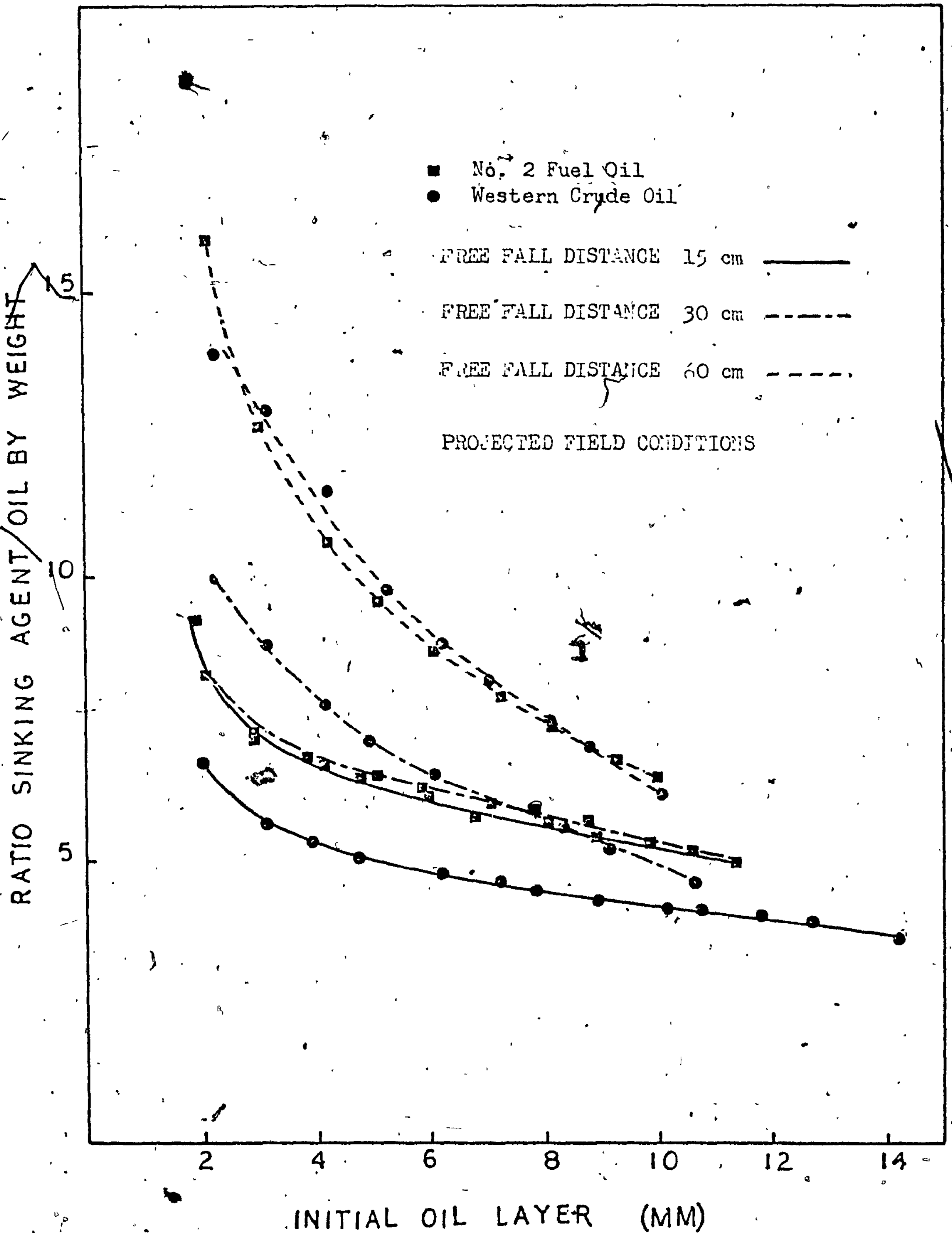


FIGURE 34 EFFECT OF OIL TYPE AND FREE FALL DISTANCE ON EFFICIENCY OF OIL-LOK 501 (2°C)

TABLE 9

EFFECT OF OIL TYPE ON OIL-LOK 501 (2^{o}C)

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

Early testing of Zorb-All indicated that the release of emitted air bubbles by the porous sinking agent prevented the resultant agent/oil mass from sinking. To dislodge entrapped air bubbles, stirring was required. The effect of free fall distance would, in such a situation, be minimal and it was therefore decided to carry out only the ~~15-cm~~ and 60-cm free fall distances.

Again, during the exploratory testing work, it was noted that Zorb-All could not sink No. 6 Bunker oil at all, even after prolonged agitation. When pushed to the bottom, the combined agent/oil mass rose slowly to the surface again. Tests involving Bunker oil were therefore omitted from this test series.

16.8.1 Efficiency of Zorb-All in Removing Western Crude Oil. The pertinent appendix is Appendix V. The experimental data and data analyses are given as

Group A Tables	Tables 5-1 to 5-4
Group A Figures	Figures 5-1 to 5-2
Group B Tables	Tables 5-5 to 5-8
Group B Figures	Figures 5-3 to 5-6

16.8.2 Effect of Oil Layer Thickness Treated. Figures 35 and 36, presenting the test cell and projected field conditions combined for 21°C and 2°C, indicate that the efficiency of Zorb-All falls off only slightly as the oil layers treated get thinner. Spontaneous sinking action of Zorb-All begins only near the end when the oil layers are about 2 mm thin.

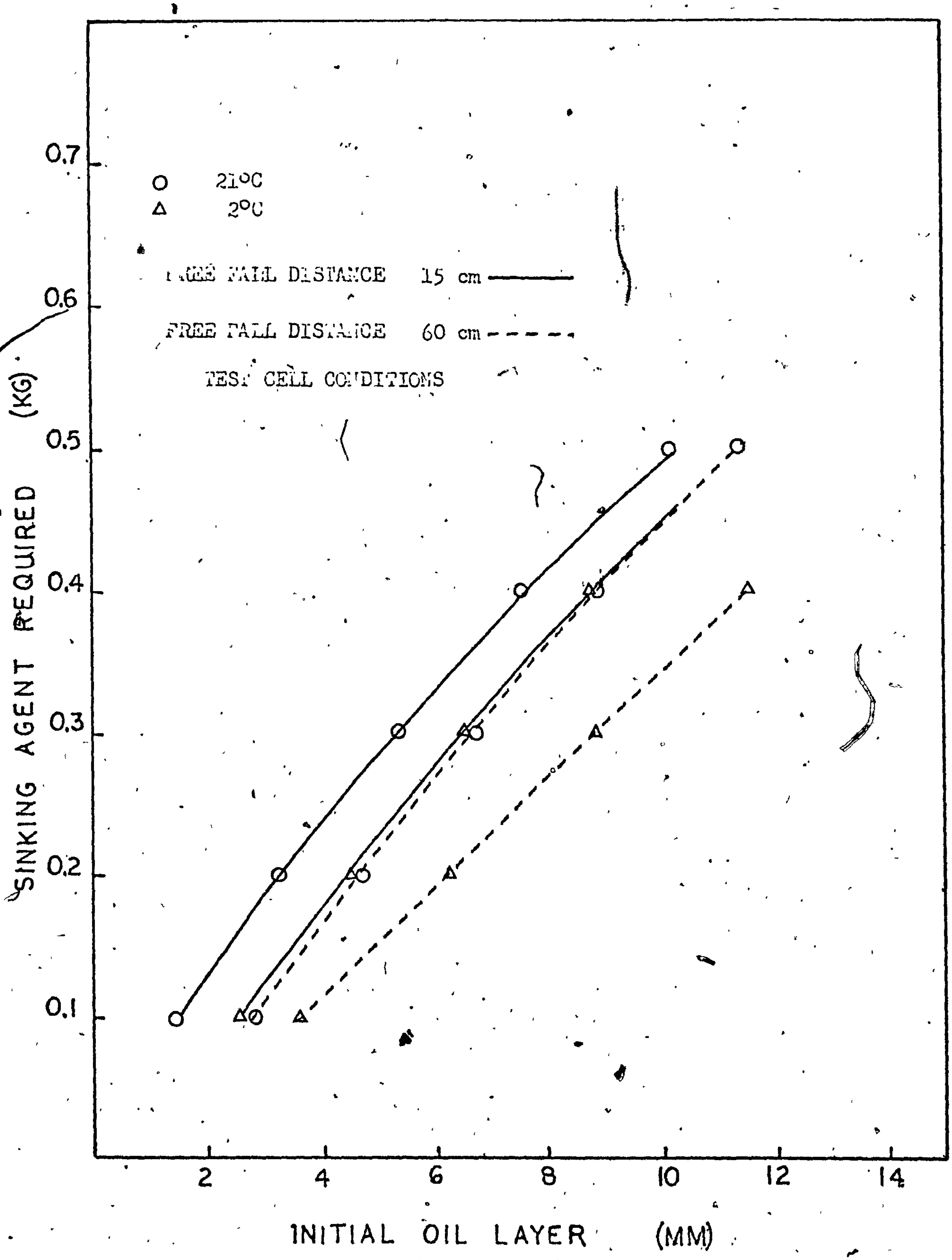


FIGURE 35 ZORB-ALL AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER

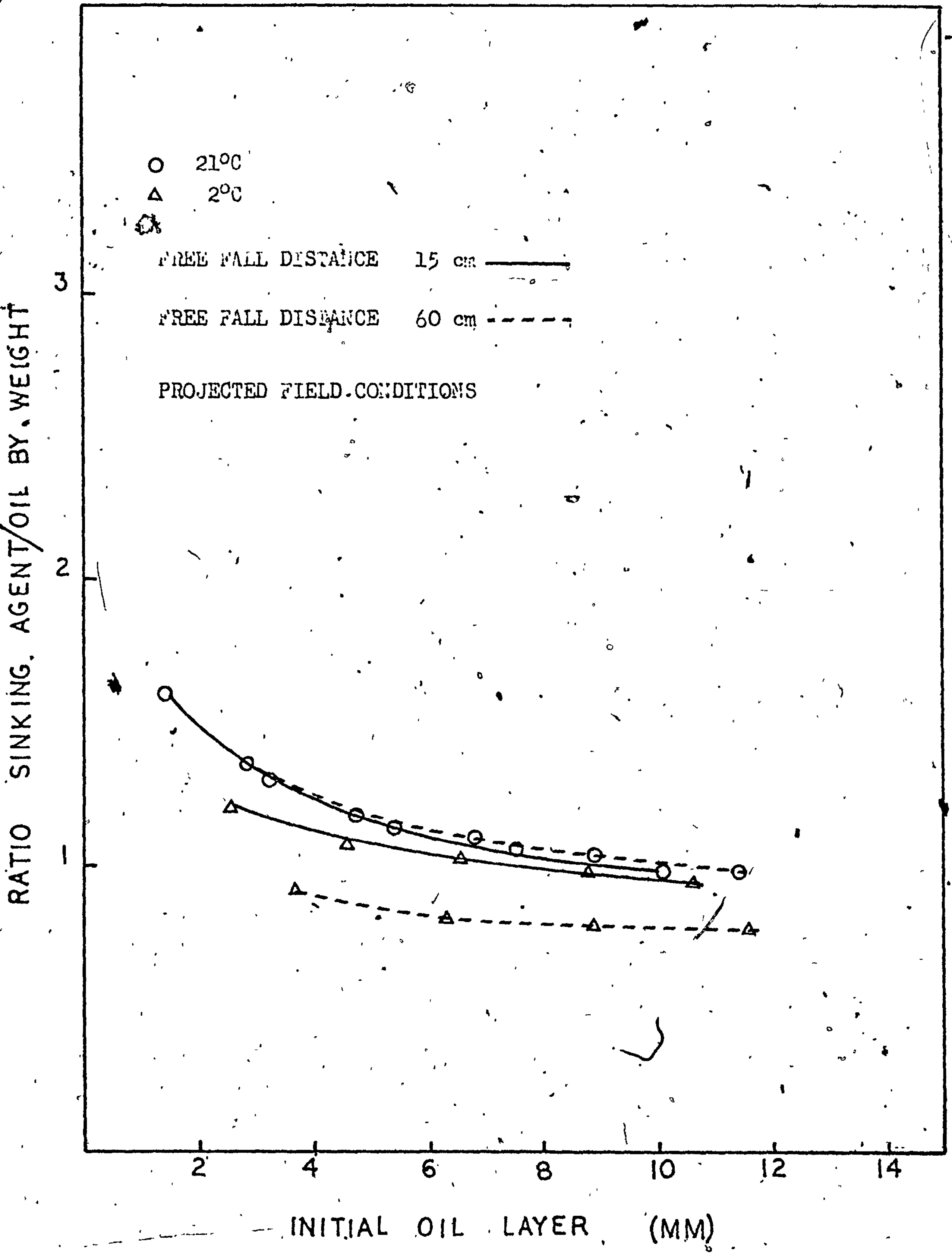


FIGURE 36 ZORB-ALL AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER

16.8.3 Effect of Free Fall Distance. As expected, since the time-in-contact of agent and oil was independent of the free fall velocity, the free fall distance had little significant effect on the efficiency of Zorb-All.

16.8.4 Effect of Temperature. Figures 35 and 36 indicate only the nominal increases in efficiency of Zorb-All at the lower temperature. This can also be seen in Table 10. Note that, in all instances, the actual quantitative effects are small.

16.9 Efficiency of Zorb-All in Removing No. 2 Fuel Oil

The pertinent appendix is Appendix VI. The experimental data and data analyses are given as

Group A Tables	Tables 6-1 to 6-4
Group A Figures	Figures 6-1 to 6-2
Group B Tables	Tables 6-5 to 6-8
Group B Figures	Figures 6-3 to 6-6

16.9.1 Effect of Oil Layer Thickness Treated. Figures 37 and 38, presenting the test cell and projected field conditions combined for 21°C and 2°C, show that the efficiency of Zorb-All on No. 2 Fuel oil decreases only very slightly with decreasing initial oil layer thickness. The spontaneous sinking action of Zorb-All emerges only with very thin oil layers.

16.9.2 Effect of Free Fall Distance. Within limits of experimental error, the free fall distance had, again, little significant effect on the efficiency of Zorb-All.

TABLE 10

ZORB-ALL AND WESTERN CRUDE OIL - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Initial Oil Layer Thickness (mm)	Ratio: Sinking Agent/Oil - By Weight		
		Temperature		Decrease in Sinking Agent Required (%)
		21°C	2°C	
15	10	0.98	0.92	6
60		0.97	0.77	21
15	7	1.06	1.03	3
60		1.10	0.81	26
15	4	1.29	1.07	17
60		1.18	0.91	23

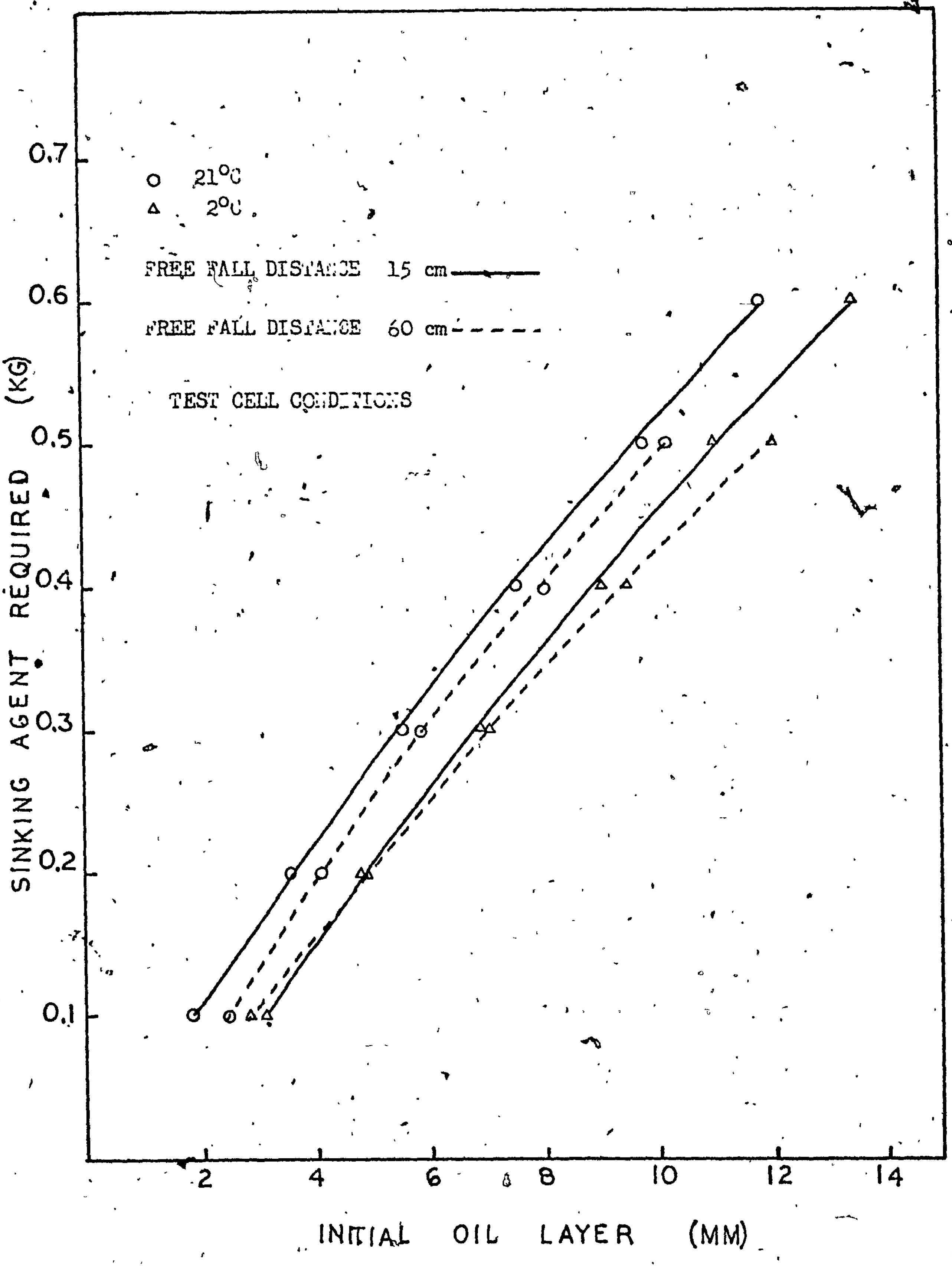


FIGURE 37 ZORB-ALL AND NO. 2 FUEL OIL – EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER

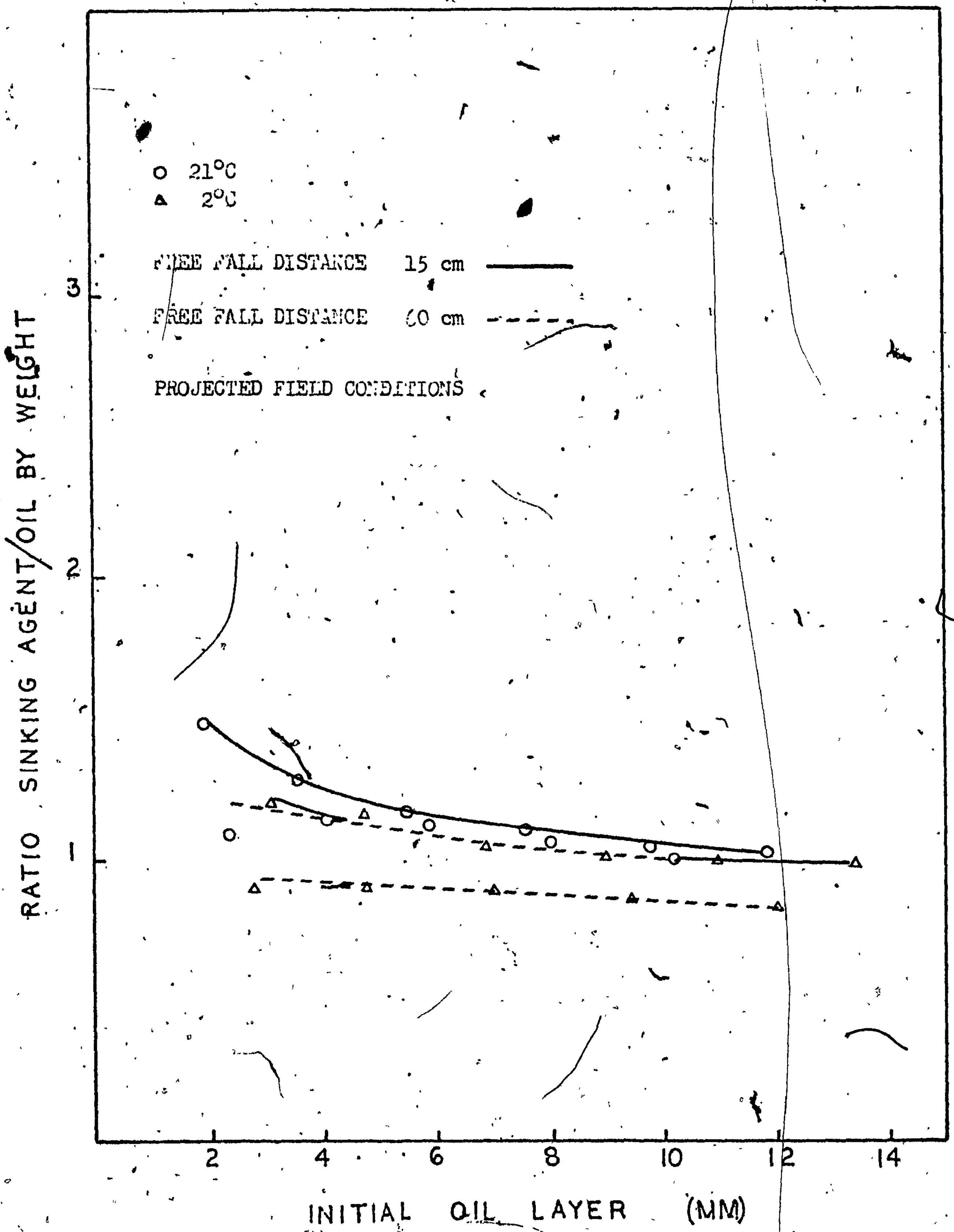


FIGURE 38 ZORB-ALL AND NO. 2 FUEL OIL - EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER

16.9.3 Effect of Temperature. Figures 37 and 38 indicate, again, the only nominal increase in efficiency of Zorb-All on No. 2 Fuel oil at the lower temperature. Table 11 shows the general effect of temperature.

16.10 Effect of Oil Type on Zorb-All Efficiency

Comparison of the appropriate tables and figures brings the weight of evidence to indicate a somewhat higher efficiency of Zorb-All relative to Western Crude oil at both room temperature and 2°C. See Table 12 for the comparisons. The large increase in viscosity of Western Crude at the lower temperature did not seem to result in an expected large increase of efficiency of Zorb-All. No. 6 Bunker oil could not be tested for further comparison.

16.11 Preliminary Testing of Hi-Dri

Zorb-All and Hi-Dri are both clay-like materials of similar specific gravity and surface area. Their behaviour regarding No. 2 Fuel oil and Western Crude oil were expected to be similar.

Except for the fact that Hi-Dri contained a larger proportion of finely-divided material, it was tested exactly as Zorb-All. The agent/oil mass was subjected to a delay and a stirring period, and only the 15-cm and 60-cm free fall distances were used. The testing of No. 6 Bunker oil had to be foregone.

TABLE 11

ZORB-ALL AND NO. 2 FUEL OIL - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Initial Oil Layer Thickness (mm)	Ratio: Sinking Agent/Oil - By Weight		
		Temperature		Decrease in Sinking Agent Required (%)
		21°C	2°C	
15	10	1.04	1.00	4
60		1.00	0.86	14
15	7	1.09	1.05	4
60		1.12	0.89	20
15	4	1.28	1.16	9
60		1.14	0.91	20

TABLE 12

EFFECT OF OIL TYPE ON ZORB-ALL EFFICIENCY *

Oil	Temperature - 21°C		Temperature - 2°C	
	Ratio: Sinking Agent/Oil			
	Free Fall (cm)		Free Fall (cm)	
	15	60	15	60
Western Crude	0.98	0.97	0.92	0.77
No. 2 Fuel	1.04	1.00	1.00	0.86

* Initial Oil Layer - 10 mm

16.11.1 Efficiency of Hi-Dri in Removing Western Crude Oil. The pertinent appendix is Appendix VII. The experimental data and the data analyses are given as

Group A Tables	Tables 7-1 to 7-4
Group A Figures	Figures 7-1 to 7-2
Group B Tables	Tables 7-5 to 7-8
Group B Figures	Figures 7-3 to 7-6

16.11.2 Effect of Oil Layer Thickness Treated. Figures 39 and 40, presenting the test cell and projected field conditions combined for the two temperatures, as in the previous figures for the Zorb-All cases, are used to indicate the effect of initial layer treated on Hi-Dri efficiency.

It is seen that the efficiency of Hi-Dri falls off very slightly as the initial oil layers get thinner. The acceleration of this effect is extremely slight.

Spontaneous sinking action is achieved only at the end of a test run, where the final oil layers are 2 mm and less.

16.11.3 Effect of Free Fall Distance. Within limits of experimental error, the free fall distance had little significant effect on the efficiency of Hi-Dri.

16.11.4 Effect of Temperature. Figures 39 and 40 show a slight increase in efficiency of Hi-Dri at the lower temperature. The difference is most noticeable with the thinner oil layers; however, the actual increase is small. Table 13 indicates the general effect.

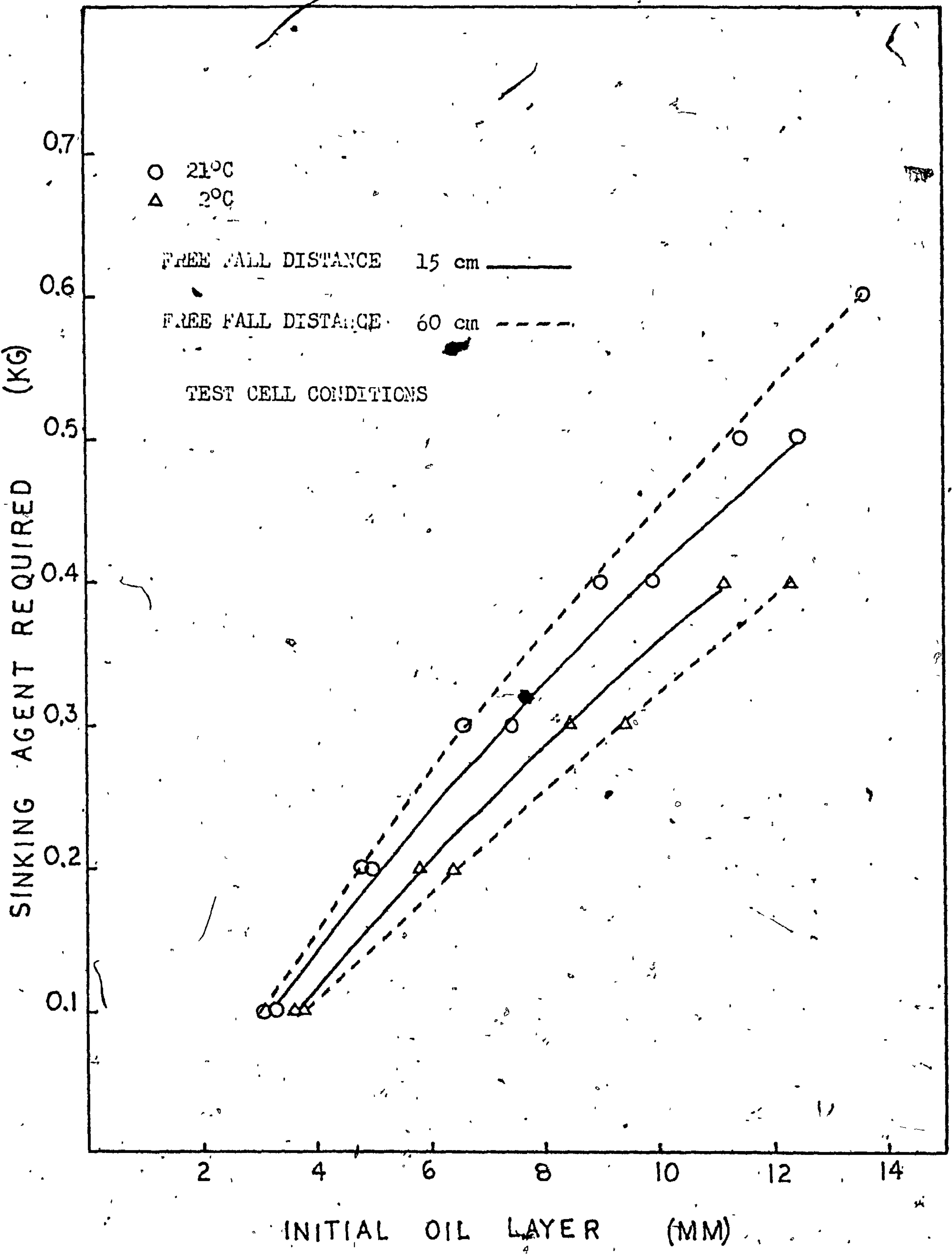


FIGURE 39 HI-DRI AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER

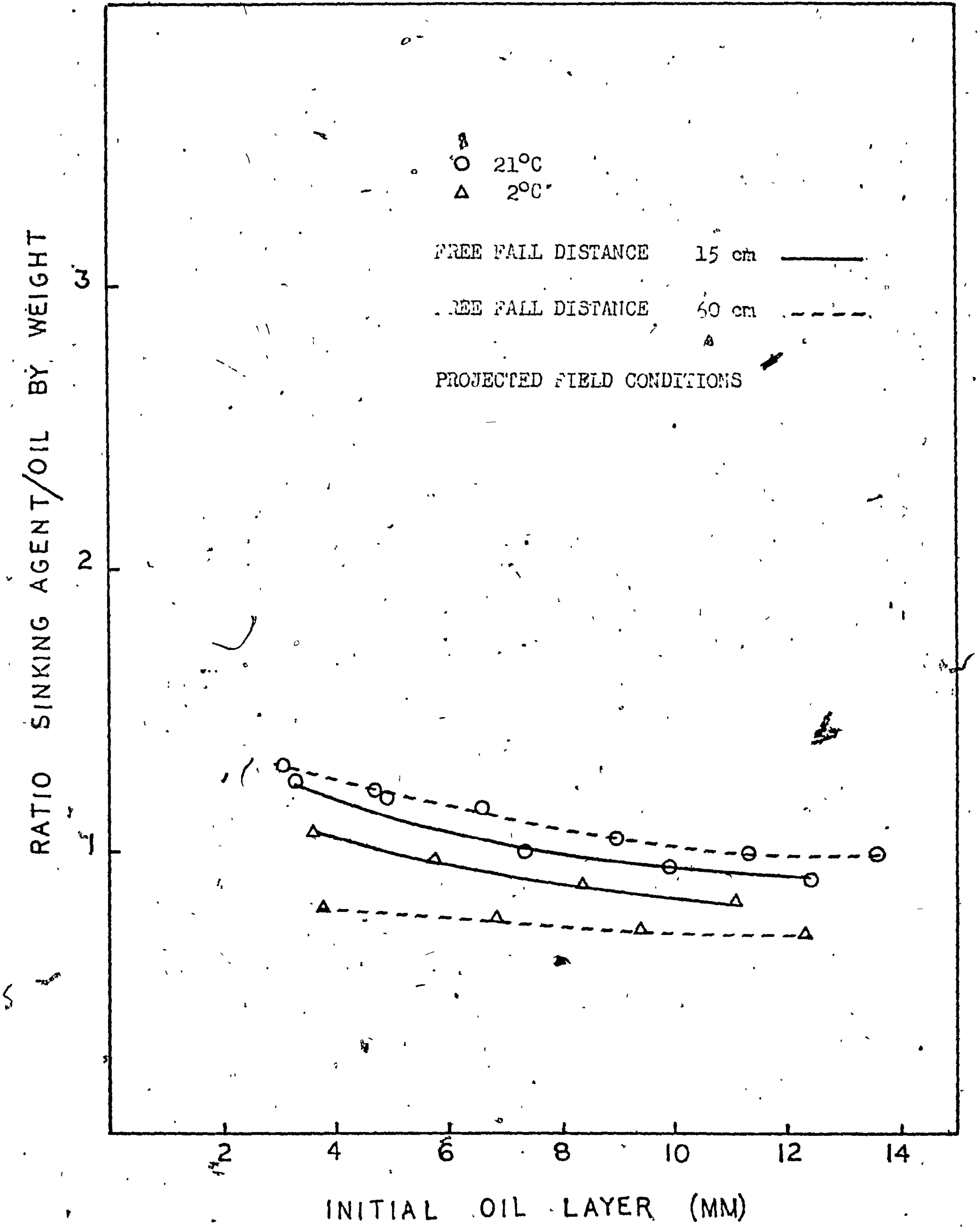


FIGURE 40 HI-DRI AND WESTERN CRUDE OIL - EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER

TABLE 13

HI-DRI AND WESTERN CRUDE OIL - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Initial Oil Layer Thickness (mm)	Ratio: Sinking Agent/Oil - By Weight		
		Temperature		Decrease in Sinking Agent Required (%)
		21°C	2°C	
15	10	0.95	0.87	14
60		0.99	0.72	27
15	7	1.03	0.97	6
60		1.16	0.77	34
15	4	1.26	1.06	16
60		1.31	0.80	39

16.12 Efficiency of Hi-Dri in Removing No. 2 Fuel Oil

The pertinent appendix is Appendix VIII. The experimental data and the data analyses are given as

Group A Tables	Tables 8-1 to 8-4
Group A Figures	Figures 8-1 to 8-2
Group B Tables	Tables 8-5 to 8-8
Group B Figures	Figures 8-3 to 8-6

16.12.1 Effect of Oil Layer Thickness Treated. Figures 41 and 42, representing the test cell and projected field conditions, indicate the change of efficiency of Hi-Dri with initial oil layer thickness. Except for the 21°C testing temperature, the change is still minimal.

16.12.2 Effect of Free Fall Distance. The free fall distance shows little effect on the efficiency of Hi-Dri, except at the thinner initial oil layers. This effect is most noticeable at 21°C.

16.12.3 Effect of Temperature. Figures 41 and 42 indicate that, at room temperature, the combination of low viscosity and incipient spontaneous sinking of Hi-Dri tends to decrease its efficiency, especially at lower initial oil thickness layers. Table 14 indicates the general effect.

At 2°C the increased viscosity of No. 2 Fuel oil, although improving the performance of Hi-Dri, seems to mute any change in efficiency due to free fall distance or initial oil layer.

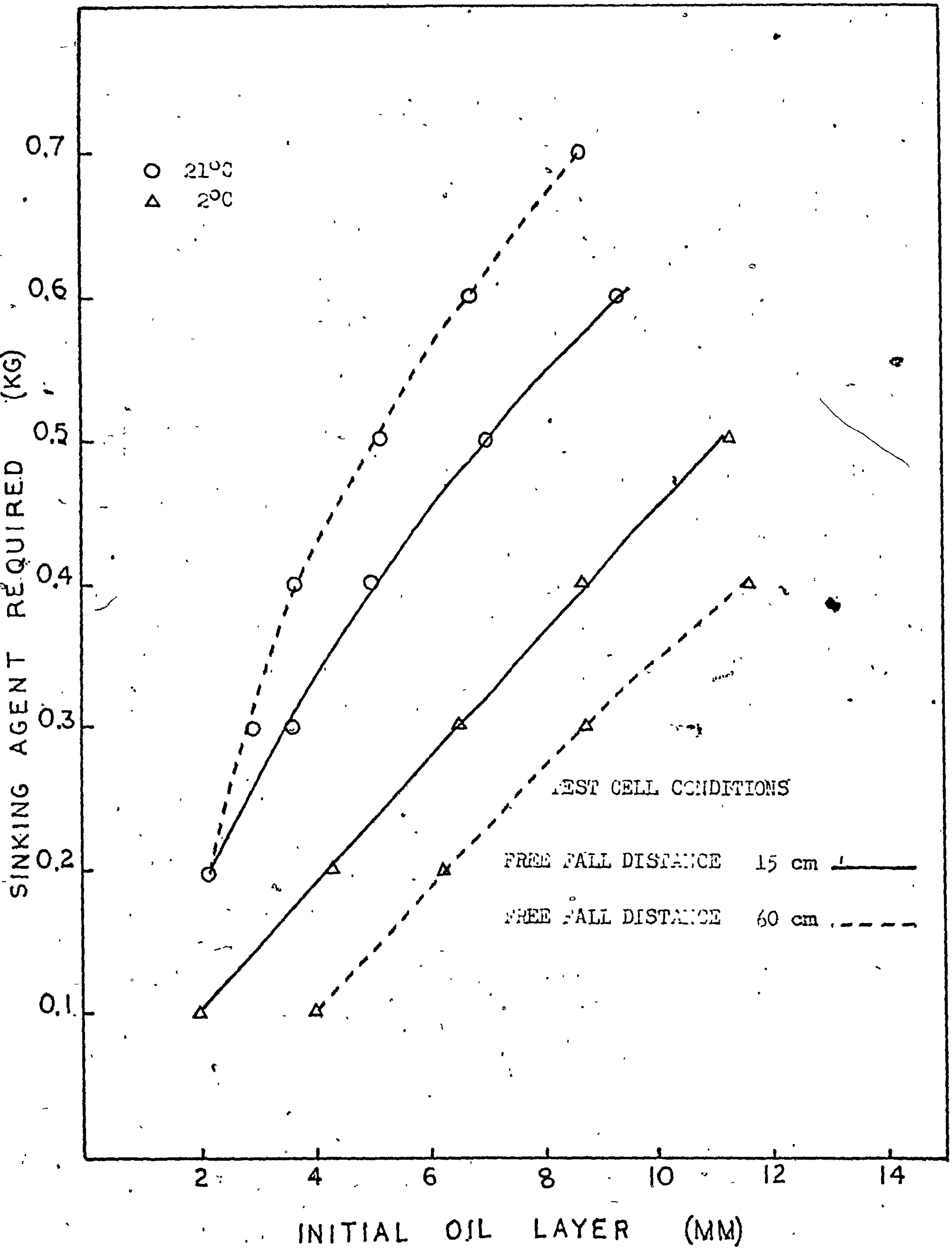


FIGURE 41 HI-DRI AND NO. 2 FUEL OIL – EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER

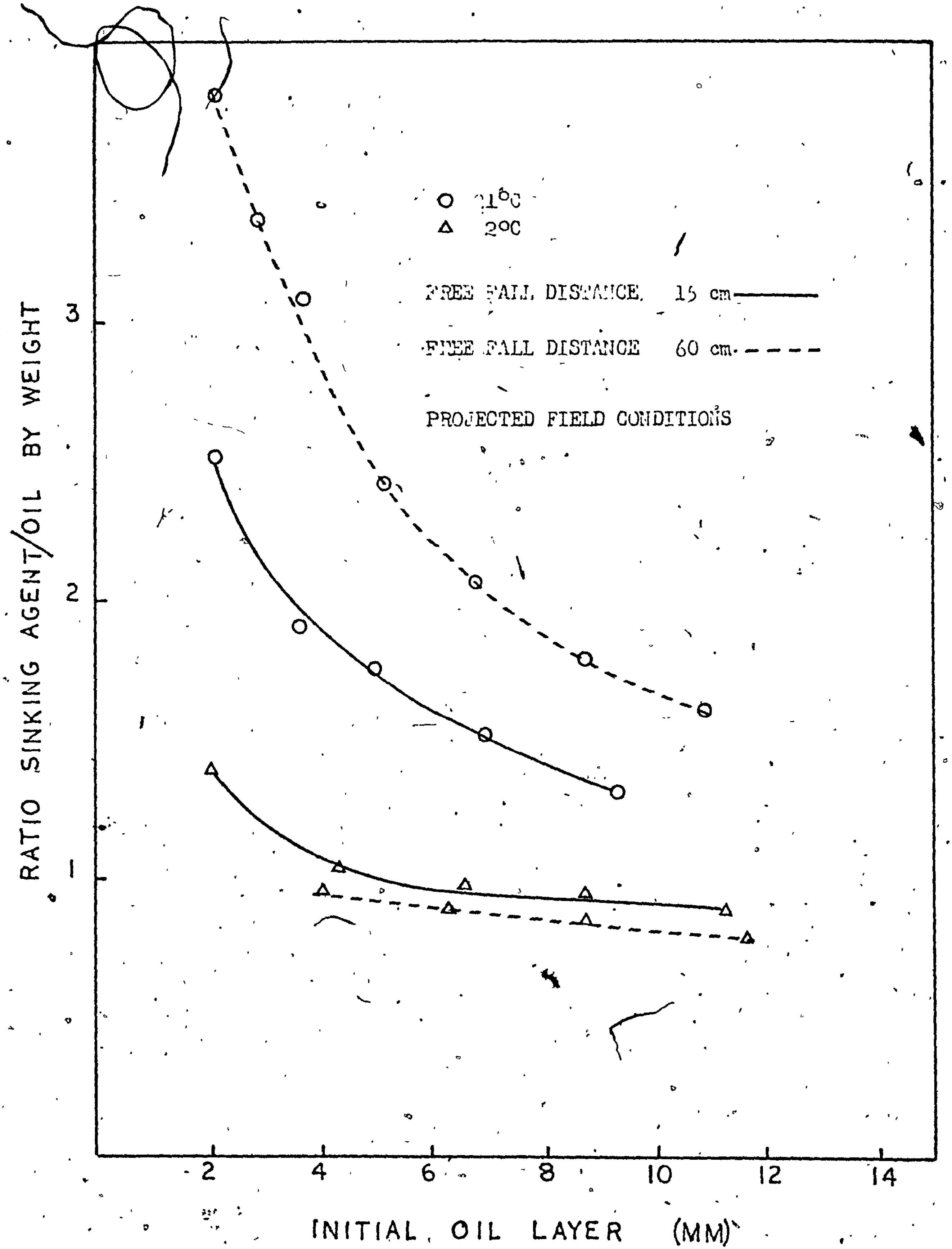


FIGURE 42 HI-DRI AND NO. 2 FUEL OIL – EFFECT OF FREE FALL DISTANCE AND TEMPERATURE ON RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER

TABLE 14

HI-DRI AND NO. 2 FUEL OIL - EFFECT OF TEMPERATURE ON EFFICIENCY

Free Fall (cm)	Initial Oil Layer Thickness (mm)	Ratio: Sinking Agent/Oil - By Weight		
		Temperature		Decrease in Sinking Agent Required (%)
		21°C	2°C	
15	10	1.31	0.88	33
60		1.59	0.78	50
15	7	1.51	0.96	36
60		2.07	0.88	57
15	4	1.90	1.03	46
60		3.08	0.95	69

16.13 Effect of Oil Type on Hi-Dri Efficiency

Comparison of the appropriate tables and figures indicates that the efficiency of Hi-Dri in removing No. 2 Fuel oil at 2^{0}C is similar to the efficiency of Hi-Dri in removing Western Crude at room temperature. See Table 5 for the oil viscosity values.

Table 15, which compares room temperature values, indicates the general result that Hi-Dri is slightly more efficient in removing Western Crude than No. 2 Fuel oil.

Hi-Dri at 2^{0}C shows no drastic increase in removing Western Crude oil, even though its viscosity has jumped to 55 centistokes at this low temperature. Compare Figures 40 and 42.

16.14 Oil Volatility Losses

The pertinent appendix is Appendix IX, encompassing Tables 9-1 to 9-3. These tables contain the experimental data for volatility losses of Western Crude, No. 2 Fuel, and No. 6 Bunker oils. No attempt was made to carry these tests beyond 150 hours, as the losses appeared to stabilize fairly well around this interval.

Figures 43 and 44 indicate the volatility characteristics of Western Crude oil for the overall 150 hours, and for 24-hour volatility tests. Figures 45 and 46 cover the same situation for No. 2 Fuel oil and No. 6 Bunker oil.

The volatility loss curves for all oils contain the same general exponential contours, indicating high early losses that decrease

TABLE 15

EFFECT OF OIL TYPE ON HI-DRI EFFICIENCY (21^oC)

Oil	Initial Oil Layer - 10 mm		Initial Oil Layer - 4 mm	
	Ratio: Sinking-Agent/Oil			
	Free Fall (cm)		Free Fall (cm)	
	15	60	15	60
Western Crude	0.95	0.99	1.26	1.31
No. 2 Fuel	1.31	1.59	1.90	3.08

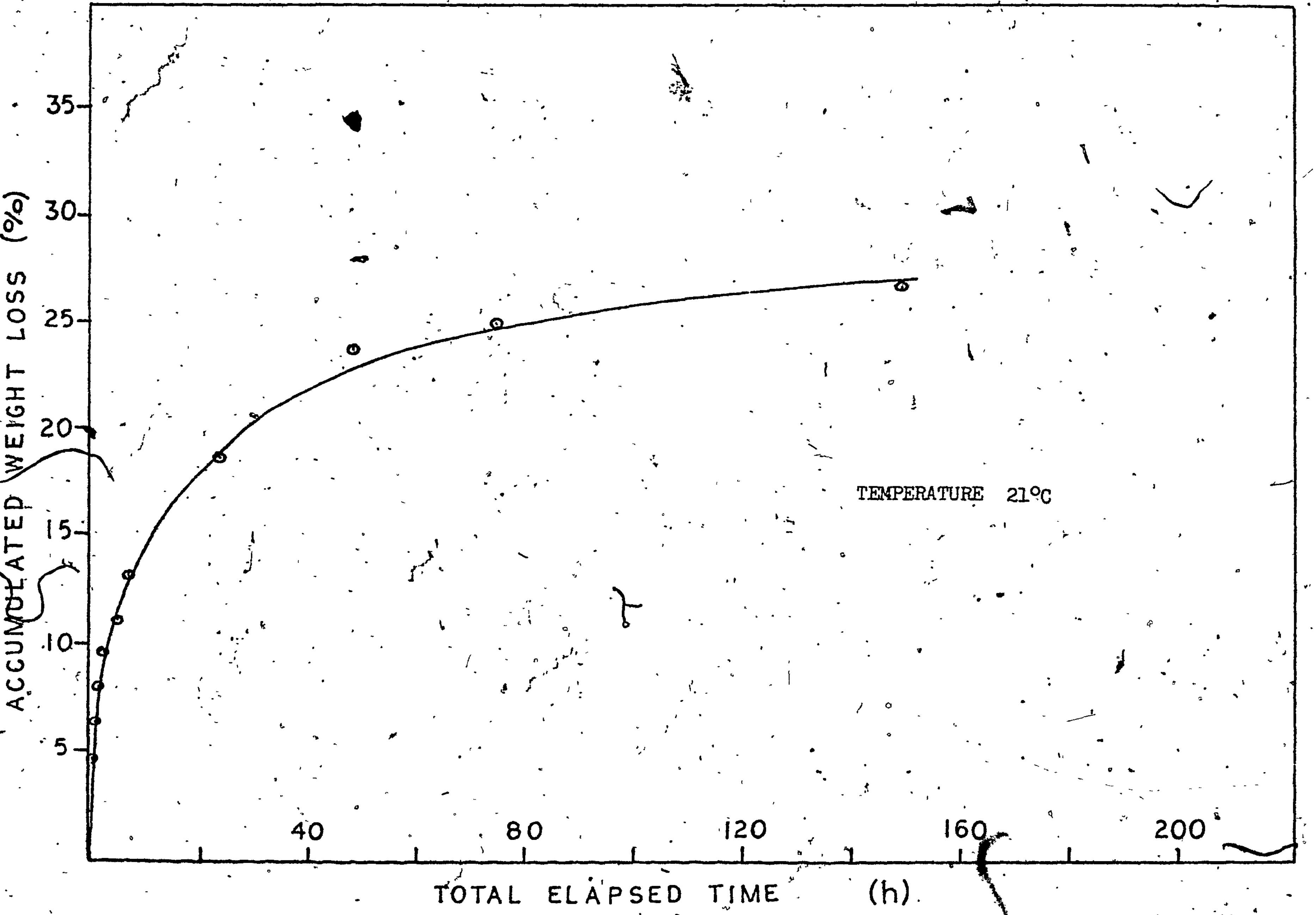


FIGURE 43 VOLATILITY LOSS FOR WESTERN CRUDE OIL – TOTAL ELAPSED TIME VS ACCUMULATED WEIGHT LOSS (0–150 h)

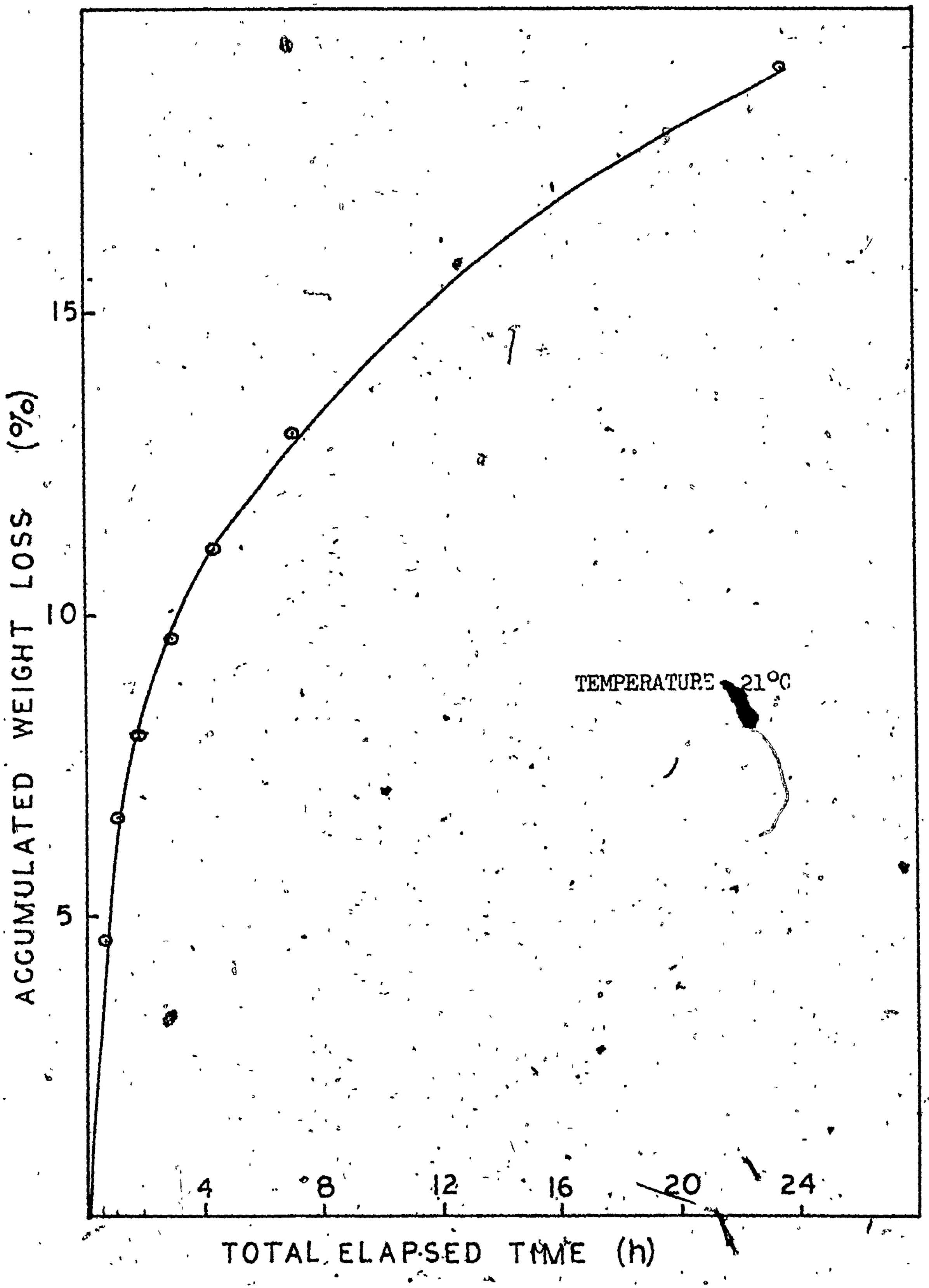


FIGURE 44 VOLATILITY LOSS FOR WESTERN CRUDE OIL - TOTAL ELAPSED TIME VS ACCUMULATED WEIGHT LOSS (0-24 h)

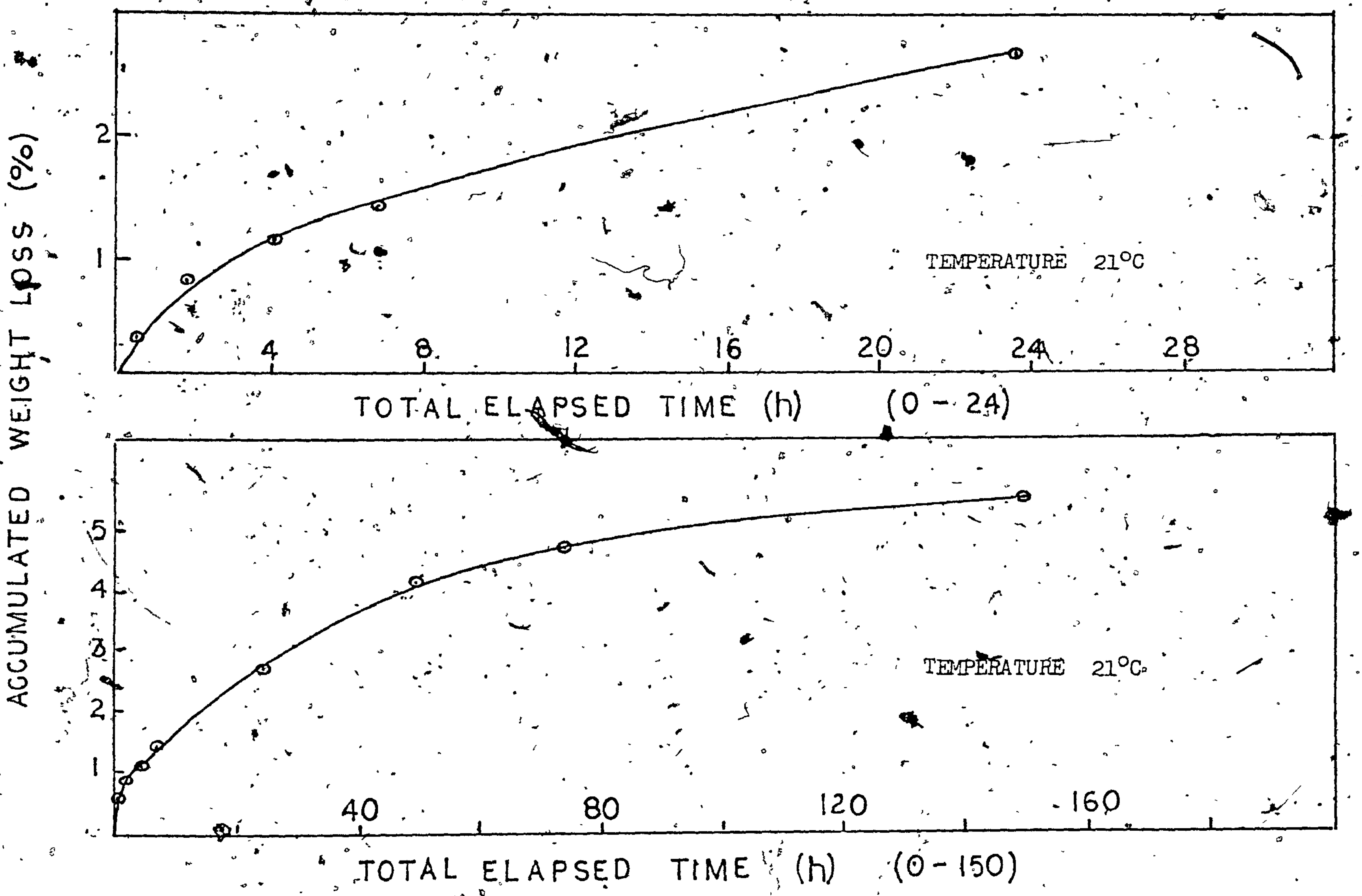


FIGURE 45 VOLATILITY LOSS FOR NO. 2 FUEL OIL - TOTAL ELAPSED TIME VS ACCUMULATED WEIGHT LOSS

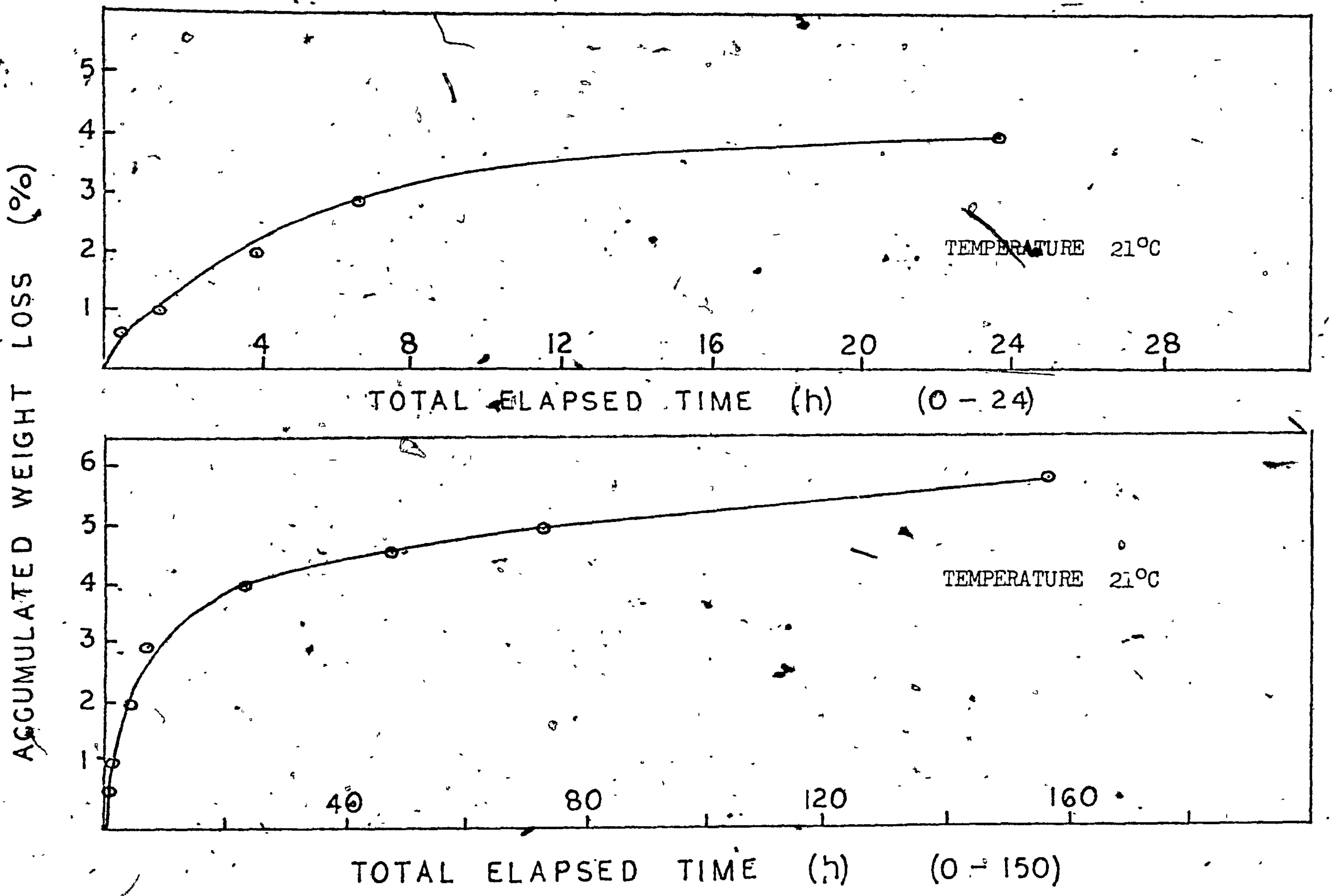


FIGURE 46 VOLATILITY LOSS FOR NO. 6 BUNKER OIL - TOTAL ELAPSED TIME VS ACCUMULATED WEIGHT LOSS

with time. Within 40 hours the exponential oil losses are stabilized.

Western Crude oil displays the highest initial losses due to the relatively high proportion of volatiles in this oil. No. 2 Fuel oil and No. 6 Bunker oil show generally similar loss curves, with the more complex Bunker oil having a higher initial loss, but also earlier stabilization.

16.15 Ability of Sinking Agents to Retain Oil

The experimental data in this connection are reported in Tables 10-1 to 10-7 of Appendix X. Only the 21^{o}C testing temperature and the 15-cm free fall distance were applied. Equations 45 to 49 were employed for all calculations required to retrieve some of the results of the data analyses, and expanded charts for Figures 43 to 46 were used to obtain the volatility loss values required as per cent by weight.

16.15.1 Oil-Lok 501 and Western Crude Oil. Table 10-1 covers the situation relative to Western Crude oil. It will be noted that, with an initial oil layer of 14.90 mm and a charge of 175.9 gm of Oil-Lok, the initial ratio by weight of agent/oil for the sunken mass was 3.58. This ratio stabilized in time at about 4.9, representing a retained oil level of approximately 73%. It will be noted that the sinking agent/oil ratios listed in Table 2-7 (21^{o}C and 15 cm) range from 4.5 to 7.8, and it can be assumed that any initial ratio of agent/oil for the sunken mass lower than 4.9 can be expected to stabilize, after oil loss, at the 4.9 value. Thus, while agent/oil masses may be sunk with lower agent/oil ratios than 4.9, such sinkings will result in rapid oil release to the stability level ratio of 4.9 approximately.

16.15.2 Oil-Lok 501 and No. 2 Fuel Oil. Table 10-2 covers the situation for No. 2 Fuel oil. Here the initial oil layer was 17.69 mm, and a charge of 212.2 gm of Oil-Lok resulted in an initially sunken mass with a ratio of agent/oil of 3.41. The stability value of the ratio was about 4.5, and this represented a retained oil level of approximately 75%. Table 3-7 (21°C and 15 cm) showed sinking agent ratios ranging from 6.29 to 9.42, and it can be assumed that any sunken mass with an initial value of the ratio lower than 4.5 will result in stabilization at this value after rapid release of oil.

16.15.3 Oil-Lok 501 and No. 6 Bunker Oil. Table 10-3 indicates the data relative to the retentivity for No. 6 Bunker oil. The initial oil layer here was 17.22 mm, and the addition of 102.8 gm of Oil-Lok resulted in a sunken mass with an agent/oil ratio of 1.67. The stabilization ratio was about 2.4, and this represented an oil retained value of around 70%. Table 4-4 (21°C and 15 cm) shows agent/oil ratios ranging from 1.07 to 2.01, and it can be anticipated that sinkings with initial ratios lower than 2.4 will lose oil rapidly until a stable ratio of about 2.4 is established.

16.15.4 Zorb-All and Western Crude Oil. Table 10-4 provides the data for the testing of Western Crude oil. Here the initial oil layer was 14.87 mm, and 97.4 gm of the agent resulted in a sunken mass with an agent/oil ratio initially at a value of 1.48. The ratio stabilized at approximately 1.7, at which point a retained oil value of about 85% applied. Table 5-5 (21^{0}C and 15 cm) shows agent/oil ratios with values from 0.98 to 1.60, and the assumption may be made that initial ratio values lower than about 1.7 for a sunken agent/oil mass will result in rapid oil loss until the stability zone of 1.7 approximately is attained.

16.15.5 Zorb-All and No. 2 Fuel Oil. Table 10-5 indicates the situation for No. 2 Fuel oil. Here the initial oil layer is 17.00 mm, the agent addition is 79.7 gm, and the initial agent/oil ratio for the sunken mass is 1.10. Stability is then attained at a ratio value of about 3.7, and the retained oil level at this point was approximately 29.5%. Table 6-5 (21^{0}C and 15 cm) showed agent/oil ratios varying from 1.04 to 1.48, and it is expected that sunken masses with ratios lower than 3.7 will lose oil rapidly, stabilizing at a ratio of around 3.7.

16.15.6 Hi-Dri and Western Crude Oil. The oil retentivity data for Western Crude oil are given in Table 10-6. With an initial oil layer of 15.59 mm and 82.4 gm of agent applied, an initial ratio by weight of agent to oil of 1.09 was obtained. A ratio of about 1.2 was achieved when the situation stabilized, with the retained oil level at this point being around 88%. Table 7-5 (21^{0}C and 15 cm) shows a range of agent/oil ratios of 0.95 to 1.26, and it may be assumed that, for any value of the ratio less than 1.2, oil will be released rapidly by the sunken mass until a 1.2 ratio is achieved.

16.15.7 Hi-Dri and No. 2 Fuel Oil. Table 10-7 represents the findings for No. 2 Fuel oil. The initial oil layer of 17.22 mm, with 49.8 gm of agent added, resulted in a sunken mass with a starting agent/oil ratio of 1.06. The ratio at the stabilization point was about 3.0, and the retained oil level at this point approximated 35%. Sunken masses with ratios lower than this, as exemplified by the range of 1.31 to 2.55 shown by Table 8-5 (21°C and 15 cm), can be expected to lose oil rapidly until a ratio of around 3.0 is reached.

16.15.8 Oil Retentivity Comparisons. Table 16 shows comparable oil retention data for 21°C and for a 15-cm free fall distance of the agent applied. All of the values given here have been rounded off to less than the proper number of significant figures for simple comparisons.

Table 17 shows, for the conditions outlined in Tables 10-1 to 10-7, the sinking efficiency and the oil retentivity values with respect to, in each case, grams of oil per 100 grams of sinking agent applied.

An examination of the data involved permits the following points to be emphasized.

1. 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.

TABLE 16

OIL RETENTIVITY CHARACTERISTICS *

Sinking Agent	Ratio: Sinking Agent/Oil - By Weight						Amount of Oil Retained (%)		
	Initial Ratio			Final Ratio					
	Western Crude	No. 2 Fuel	No. 6 Bunker	Western Crude	No. 2 Fuel	No. 6 Bunker	Western Crude	No. 2 Fuel	No. 6 Bunker
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 17

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

Sinking Agent	Initial Oil Sunk (gm)			Final Oil Sunk (gm)		
	Western Crude	No. 2 Fuel	No. 6 Bunker	Western Crude	No. 2 Fuel	No. 6 Bunker
Oil-Lok 501	28	29	60	19	22	42
Zorb-All	67	91	-	59	27	-
Hi-Dri	91	91	-	83	33	-

* Temperature - 21°C

Free Fall Distance - 15 cm

2. 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 oil is, however, retained to a significantly better extent than is No. 2 Fuel oil.

3. The ability of Hi-Dri to sink oil is distinctly superior to that of Oil-Lok 501, and about the same as that of Zorb-All. 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.

4. 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 501 in each case. Both agents require agitation to sink the agent/oil mass, as opposed to the spontaneous sinking action of the Oil-Lok material.

Although a further reduction in the oil retained might occur with a more extended test interval, it is anticipated that the agent/oil ratio for the sunken mass would not be significantly increases in such an extended interval. The experimental approach of the retentivity tests was purposely from initial ratios lower than the critical ratio, in order to locate the critical ratio as it arose out of oil loss.

17 CONCLUSIONS

17.1 Western Crude Oil and Effect of Sinking Agent Type

Figures 47, 48, and 49, together with previous discussions, indicate that the higher density of Oil-Lok 501, which enables it to act as a spontaneous sinking agent even with viscous oils, is also responsible for its greater sensitivity to initial oil layer thickness, oil viscosity, and free fall distance.

The performance of Oil-Lok 501 in the removal of Western Crude decreases rapidly with decreasing oil layer thickness and decreases again with increasing free fall distance. The efficiency of Oil-Lok 501 in the removal of Western Crude oil, although improved at low temperatures, does not match the levels of Hi-Dri and Zorb-All.

Oil-Lok 501 is the least efficient sinking agent, as can be seen from Tables 6, 10, and 13. At an initial oil layer thickness of about 4 mm, the Oil-Lok/Western Crude oil ratio stands at 6.07, while for Zorb-All and Hi-Dri the ratios are 1.29 and 1.26, respectively.

The lower sensitivity of Zorb-All and Hi-Dri to initial oil layer thickness is solely due to their large surface area, internal porosity, and consequent lower density, which increases the time-of-contact between agent and oil to optimum oil adsorption. This may be the reason why the large increase in viscosity at $2^{\circ}C$ of Western Crude did not drastically improve the performance of these two agents.

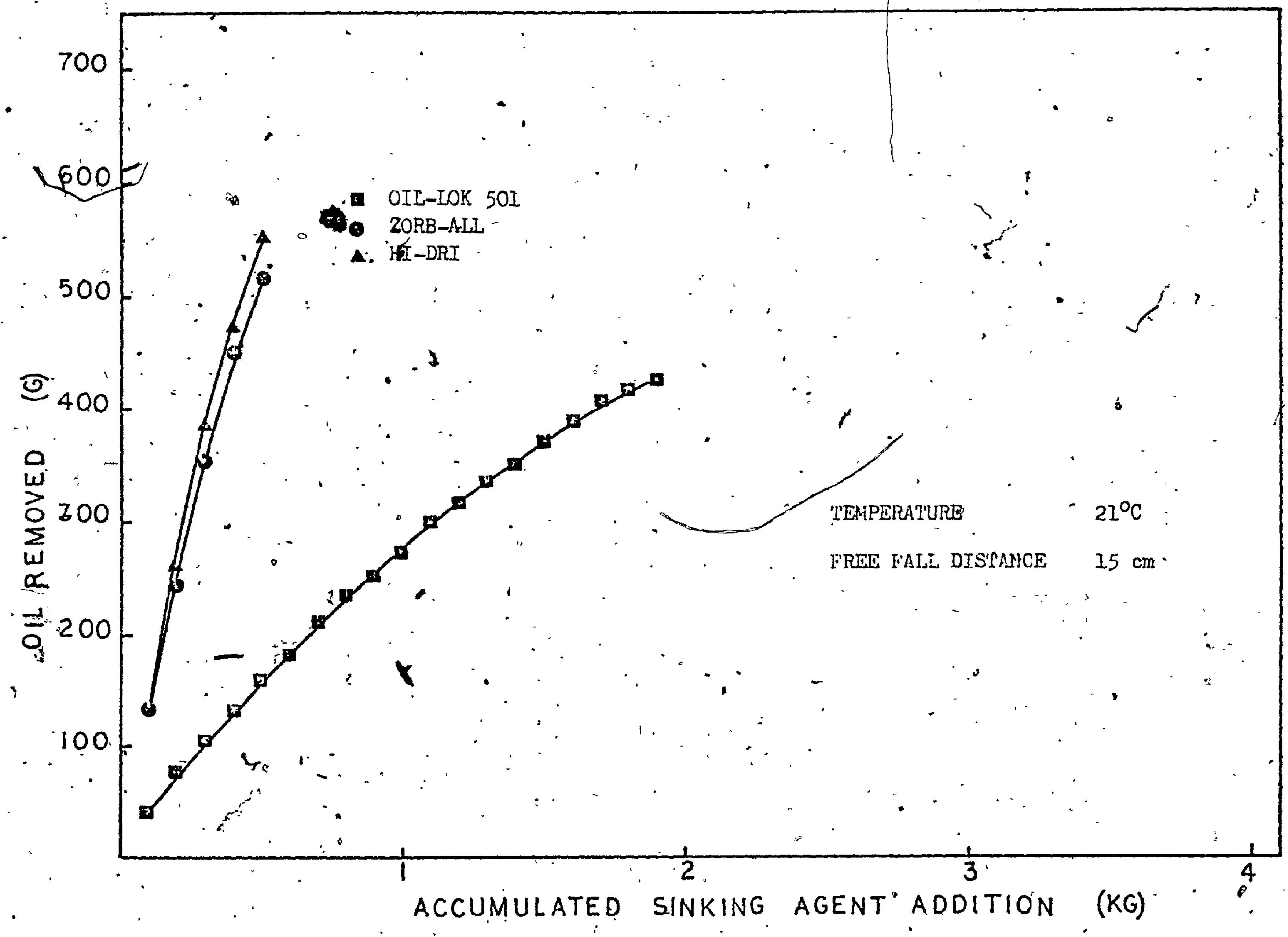


FIGURE 47 EFFICIENCY OF SINKING AGENTS IN REMOVAL OF WESTERN CRUDE OIL – WEIGHT SINKING AGENT ADDED VS OIL REMOVED

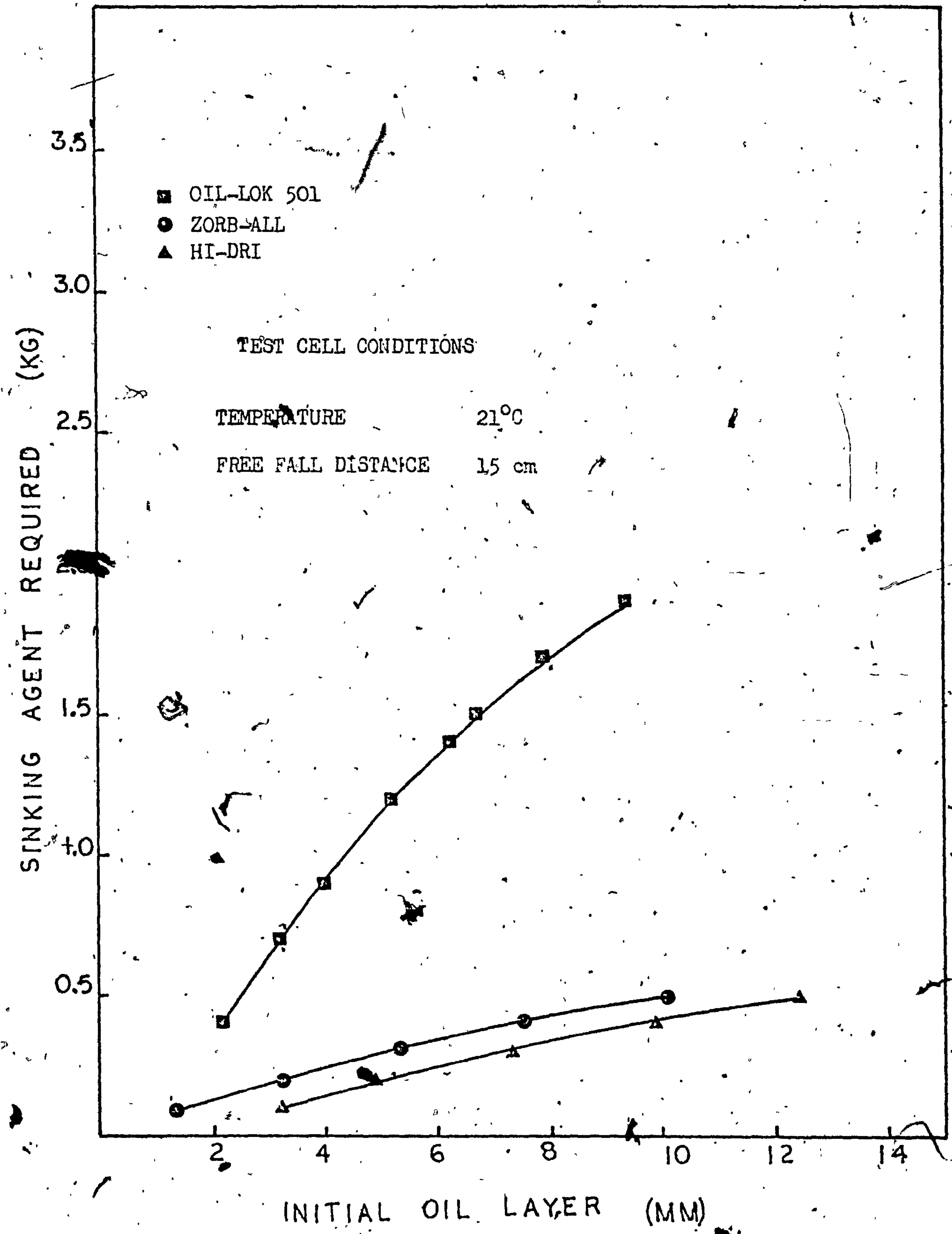


FIGURE 48 EFFICIENCY OF SINKING AGENTS IN REMOVAL OF WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

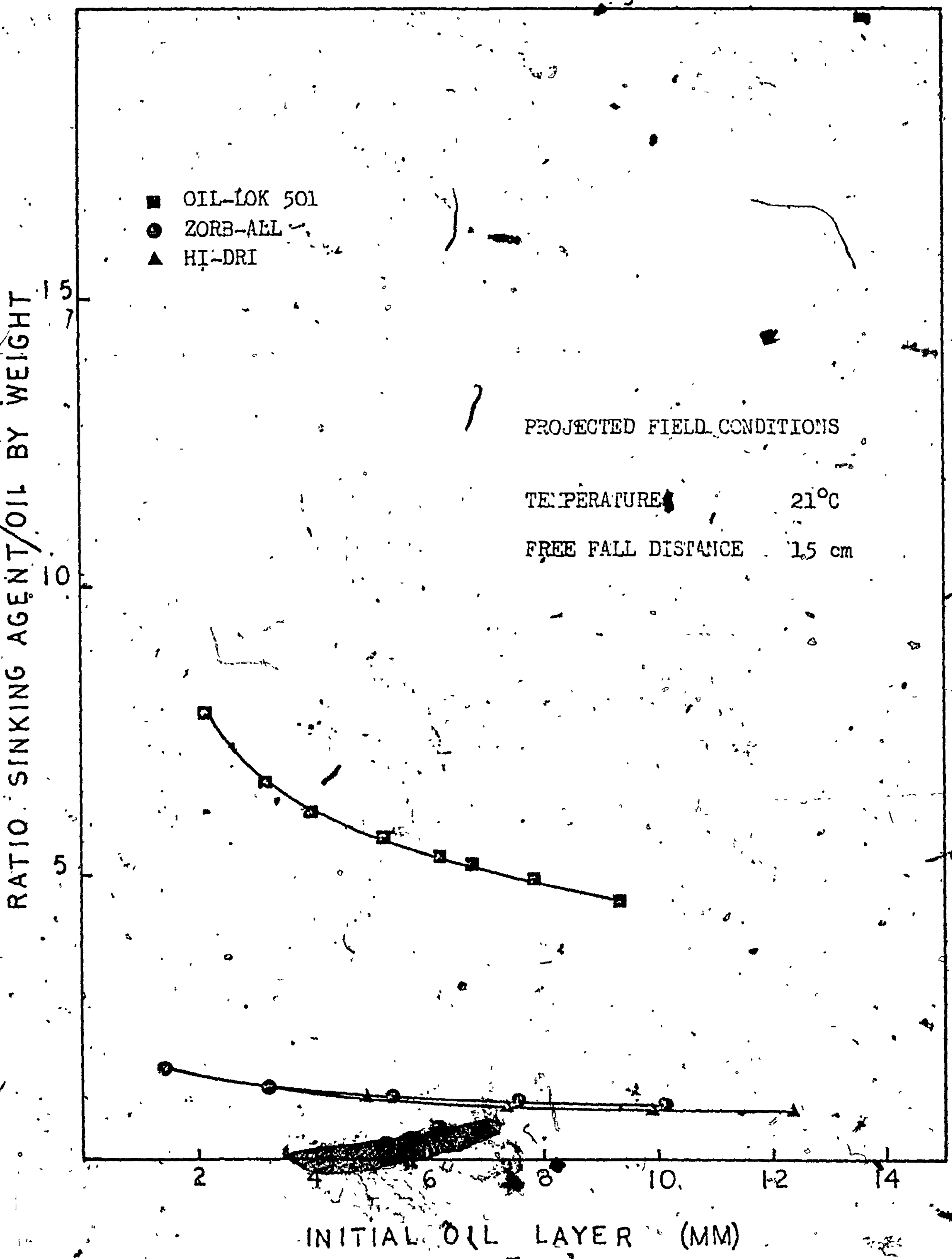


FIGURE 49 EFFICIENCY OF SINKING AGENTS IN REMOVAL OF WESTERN CRUDE OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

Zorb-All and Hi-Dri behave almost identically in the removal of Western Crude oil. Both these agents require agitation and stirring to dispose of the agent/oil mass; they cannot be classified, therefore, as true sinking agents.

17.2 No. 2 Fuel Oil and Effect of Sinking Agent Type

Figures 50, 51, and 52, together with previous discussions, indicate that the effect of sinking agent type for No. 2 Fuel oil is almost identical to that for the removal of Western Crude oil. It should be noted that, in the removal of No. 2 Fuel oil, the efficiency of Zorb-All is somewhat higher than that of Hi-Dri, particularly at the 21°C testing temperature.

The combination of a large free fall distance, namely 60 cm, and a low viscosity makes the removal of No. 2 Fuel oil at room temperature by Oil-Lok 501 a very inefficient process.

17.3 No. 6 Bunker Oil and Effect of Sinking Agent Type

The Bunker oil test series were, of necessity, restricted to Oil-Lok 501 at 21°C. Comparison of Figures 32, 49, and 52 indicate that Oil-Lok 501 on No. 6 Bunker oil is in the same range of efficiency as both Zorb-All and Hi-Dri on Western Crude and No. 2 Fuel oil. The 2°C testing series could not be carried out with No. 6 Bunker oil.

17.4 Spontaneous Sinking Agents

Oil-Lok 501 belongs to the class of sinking agents capable of adsorbing oils of wide-ranging viscosity and sinking the resultant mass. It is best described as a spontaneous sinking agent. These

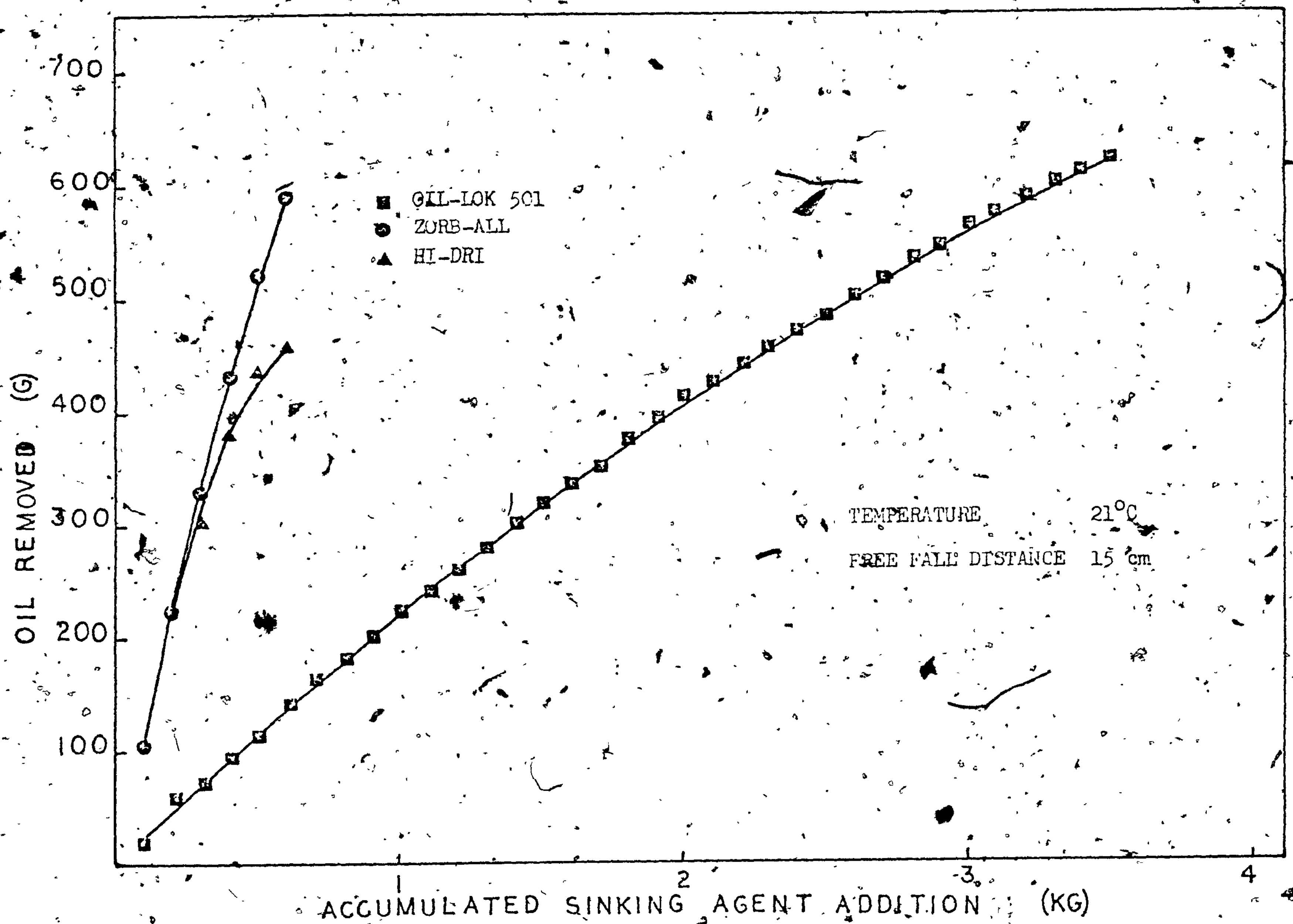


FIGURE 50 EFFICIENCY OF SINKING AGENTS IN REMOVAL OF NO. 2 FUEL OIL - WEIGHT SINKING AGENT ADDED VS OIL REMOVED

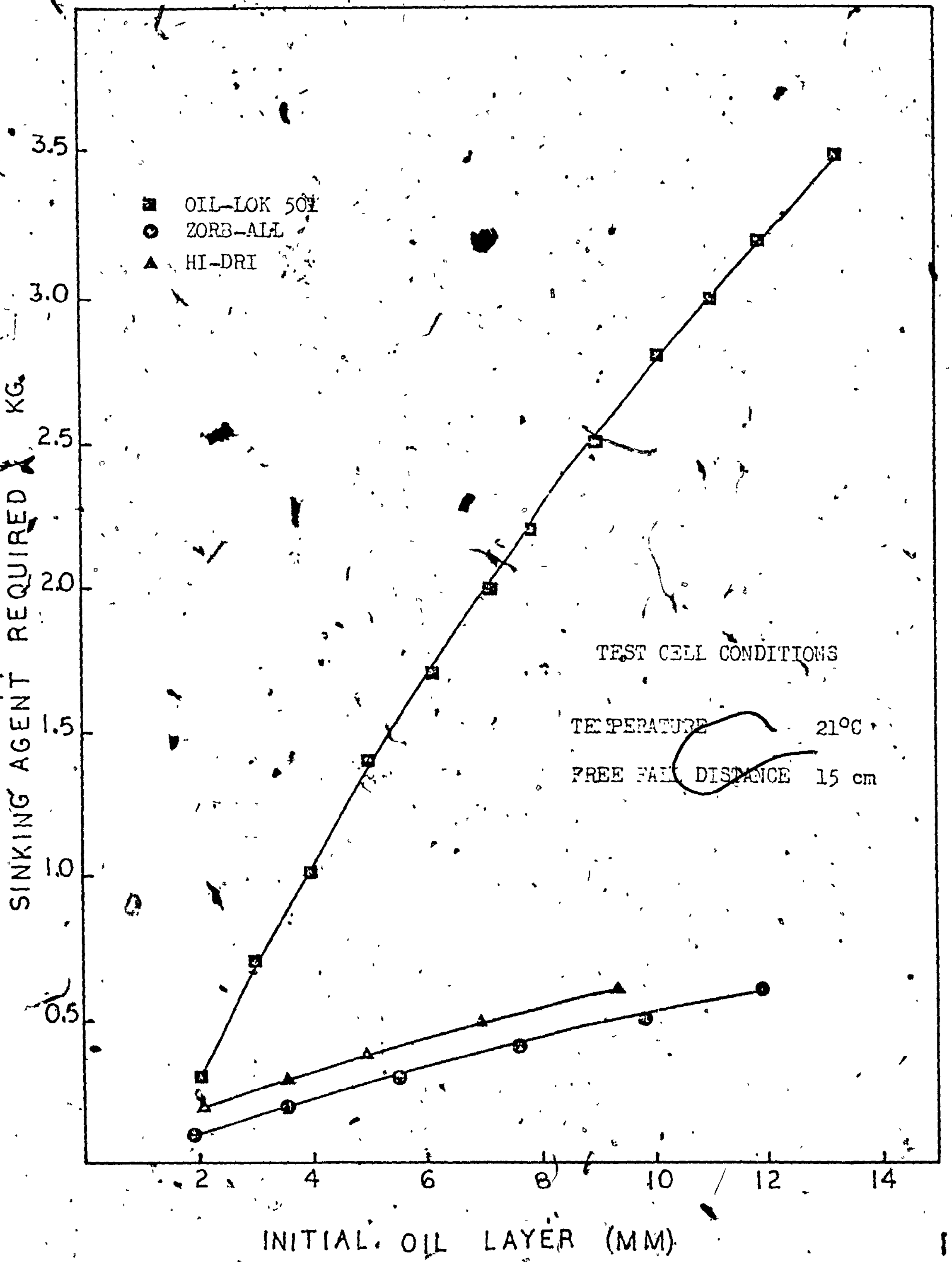


FIGURE 51 EFFICIENCY OF SINKING AGENTS IN REMOVAL OF NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

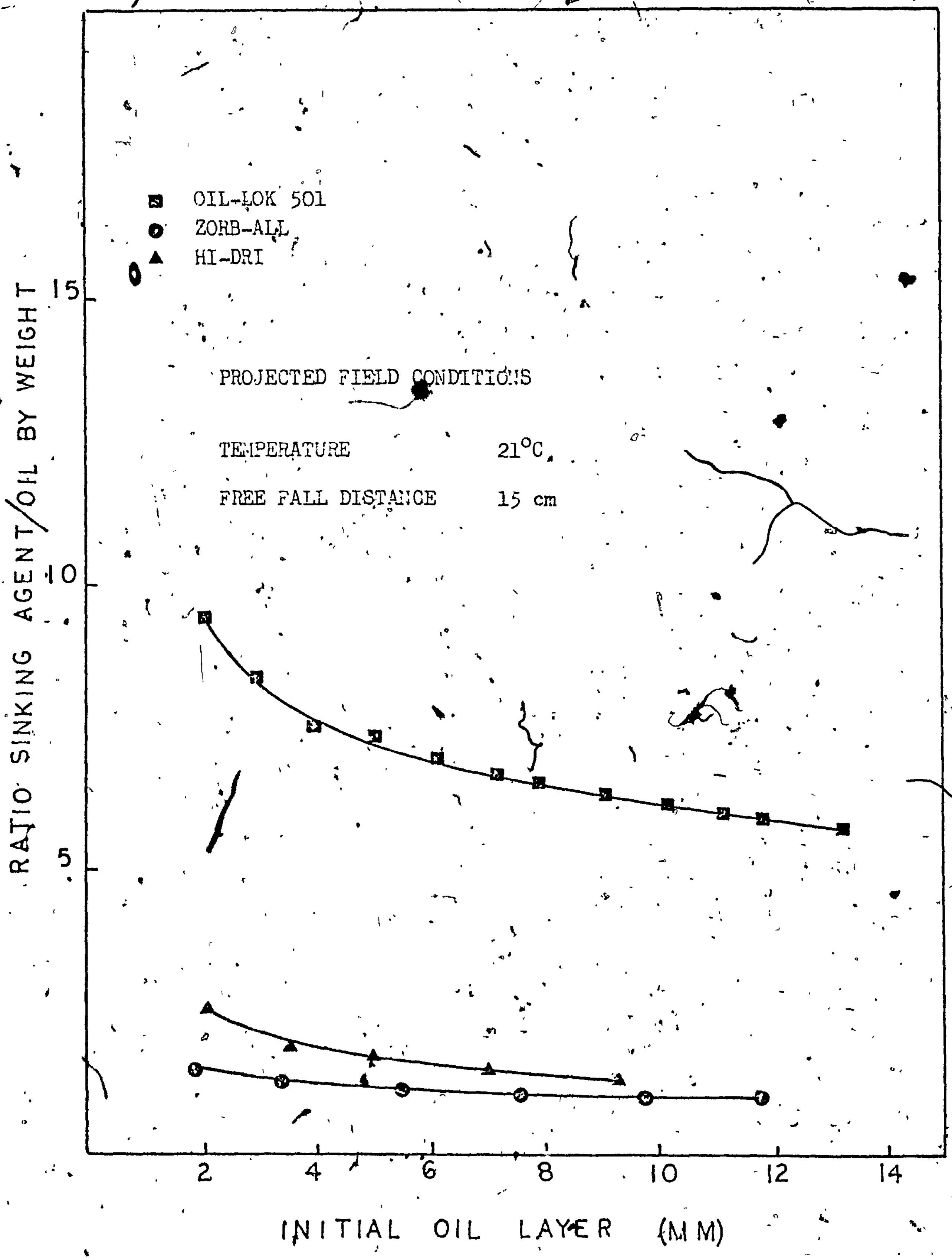


FIGURE 52 EFFICIENCY OF SINKING AGENTS IN REMOVAL OF NO. 2 FUEL OIL – RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

agents are characterized by relatively high specific gravity, with values involved lying well in excess of 2.0.

The similarity between the true and apparent specific gravity, the small surface area, and the normally high bulk densities imply little internal porosity, so that entrapped air and slow penetration by oil into the pores are not factors delaying or preventing the sinking of the agent/oil mass.

In general, spontaneous sinking agents tend to be less efficient in the removal of light oils. The time-of-contact with the oil is small; the agent and oil do not form cohesive masses; and sinking occurs before the optimum adsorption of oil has occurred. At an initial oil layer thickness of 4 mm, and free fall distance of about 60 cm, the agent to oil ratio for sinking Western Crude oil and No. 2 Fuel oil are both about 13. With No. 6 Bunker oil the viscosity is sufficient to retain the sinking agent so that more adsorption can occur and the agent to oil ratio required drops to 2. Consult Table 8.

17.5 Non-spontaneous Sinking Agents

Zorb-All and Hi-Dri are non-spontaneous sinking agent types. They display significant differences between the true and apparent specific gravity; they have relatively low bulk density values; and are characterized by fairly large surface areas. They possess a distinct porous structure and, although they adsorb the thinner oils well, the entrapped air acts to prevent the spontaneous sinking of the agent/oil mass. The advantage in the amount of oil these agents are capable of adsorbing is, in part, offset by the fact that require agitation to be fully effective.

For oils of higher viscosity, such as No. 6 Bunker oil, Zorb-All and Hi-Dri do not act as sinking agents at all, but must be classified as sorbents only.

17.6 Effect of Initial Oil Layer Thickness

For spontaneous sinking agents such as Oil-Lok 501, the effect of decreasing the initial oil layer thickness treated is to decrease the efficiency of the agent. For non-spontaneous sinking agents, because their arrest at the oil/water interface allows sufficient time for optimum oil adsorbtion to occur, oil layer thickness has little effect on efficiency. On the other hand, very thin initial oil layers of 2 mm and less produce incipient sinking of all agents and decrease to some extent the efficiency of the non-spontaneous sinking agents such as Zorb-All and Hi-Dri as well.

17.7 Effect of Free Fall Distance

Free fall velocity affects the efficiency of spontaneous sinking agents such as Oil-Lok 501 to a far greater extent than the non-spontaneous sinking agents such as Zorb-All and Hi-Dri. But the effect of increasing the free fall distance tends to decrease, to a certain extent, ~~the efficiency~~ of most agents.

17.8 Effect of Temperature

The effect of decreasing temperature is to increase the efficiency of the sinking agent by increasing oil viscosity. Again, the effect is quantitatively greater for spontaneous sinking agents. For the non-spontaneous sinking agent, optimum adsorption is quickly reached during the arrest period at the oil/water interface and an increase in viscosity beyond a certain point does not improve sinking efficiency.

17.9 Oil Retentivity

Oil retentivity after sinking appears to be quite variable, but no agent retains, after 150 hours, more than about 80% of the oil originally sunk and; in some cases, the retention factor is as low as 30%.

For example, Zorb-All is quite efficient in sinking No. 2 Fuel oil. The ratio of agent to oil is 1.1 for a free fall distance of 15 cm and an initial oil layer thickness of 17.05 mm. But it is apparent that its initial efficiency in sinking oil is of little value in the overall picture since as much as 70% of the sunken oil was released. Practical considerations would require, perhaps, excessive amounts of Zorb-All to ensure minimum oil release.

17.10 Effect of Oil Type

Oil viscosity is the main parameter to be considered. 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 non-spontaneous 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.

17.11 Recommendations for Further Studies

Several areas in which more research would be valuable have come to light in the course of this study.

1. No systematic studies have been reported on the effect of various coatings on sinking agents.
2. Theoretical treatment on the mechanisms of a liquid spreading on a solid is still in its infancy.
3. Some thought ought to be given to the preparation of sulphate-enriched compacted waste and compost to aid in the anaerobic decomposition of sunken oil.
4. Extensive in-field studies instead of laboratory simulations are required for the adequate testing of sinking agents.

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APPENDIX I

OIL LAYER THICKNESS MEASUREMENT DEVICE

CALIBRATION DATA

TABLE 1-1

MEASUREMENT OF INTERNAL DIAMETER OF BEAKER

Level (ml)	Diameter (mm)
200	83.3 ± 0.1
250	83.5 ± 0.1
300	83.6 ± 0.1
350	83.6 ± 0.1
400	83.7 ± 0.1
500	83.9 ± 0.1

TABLE 1-2

CALCULATION OF LAYER THICKNESS FROM WEIGHT OF OIL

Test	Weight of Oil (g)	Oil Layer Thickness (mm)
1	33.4489 ± 0.0002	7.25 ± 0.02
2	30.3652 ± 0.0002	6.58 ± 0.02
3	13.5239 ± 0.0002	2.933 ± 0.007
4	7.0271 ± 0.0002	1.524 ± 0.003
* 5	2.5261 ± 0.0002	0.548 ± 0.001

* Water patches showed through the oil layer

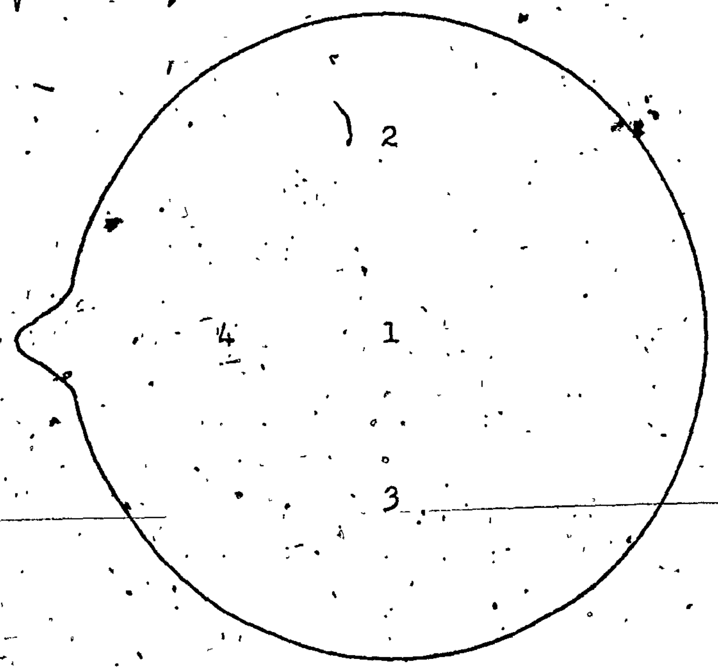

FIGURE 1-1 LOCATION OF CALIBRATION TESTS

APPENDIX II

OIL-LOK 501 AND WESTERN CRUDE OIL

EXPERIMENTAL DATA AND DATA ANALYSES

TABLE 2-1

RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	9.31 (3)	± 0.03	-	-	-	-
1	8.46 (3)	± 0.05	100	0.85	44.0	44.0
2	7.82 (3)	± 0.03	200	0.64	33.0	77.0
3	7.2^{5} (3)	± 0.1^{0}	300	0.5^{7}	$29.^{5}$	$106.^{5}$
4	6.76 (2)	± 0.02	400	0.4^{9}	$25.^{3}$	$131.^{8}$
5	6.17 (3)	± 0.03	500	0.59	30.5	$162.^{3}$
6	5.75 (3)	± 0.05	600	0.42	21.7	$184.^{0}$
7	5.20 (3)	± 0.07	700	0.55	28.4	$212.^{4}$
8	4.74 (3)	± 0.06	800	0.46	23.8	$236.^{2}$
9	4.40 (2)	± 0.01	900	0.34	17.5	$253.^{7}$
10	3.99 (3)	± 0.07	1000	0.41	21.2	$274.^{9}$
11	3.49 (3)	± 0.05	1100	0.50	25.8	$300.^{7}$
12	3.17 (3)	± 0.07	1200	0.52	16.6	$317.^{3}$
13	2.80 (3)	± 0.06	1300	0.37	19.1	$336.^{4}$
14	2.51 (3)	± 0.02	1400	0.29	15.0	$351.^{4}$
15	2.11 (3)	± 0.05	1500	0.40	20.6	$372.^{0}$
16	1.7^{7} (3)	± 0.1^{0}	1600	0.3^{4}	$17.^{6}$	$389.^{6}$
17	1.43 (3)	± 0.07	1700	0.3^{4}	$17.^{6}$	$407.^{2}$
18	1.27 (3)	± 0.05	1800	0.16	8.3	$415.^{5}$
19	1.12 (3)	± 0.04	1900	0.15	7.7	$423.^{2}$
			WATER PATCH DISCONTINUITIES			
20	0.98 (3)	± 0.09	2000	0.14	7.2	$430.^{4}$

*

Starting Oil Weight	485 g
Free Fall Distance	15 cm
Temperature	21°C

TABLE 2-2

RAW DATA – OIL-LOK 501 AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	9.07 (3)	± 0.02	–	–	–	–
1	8.33 (3)	± 0.06	100	0.74	38.3	58.3
2	7.6^{4} (3)	± 0.2^{9}	200	0.6^{9}	$35.^{6}$	$73.^{9}$
3	7.17 (3)	± 0.02	300	0.4^{7}	$24.^{3}$	$98.^{2}$
4	6.7^{7} (3)	± 0.1^{4}	400	0.4^{0}	$20.^{7}$	$118.^{9}$
5	6.5^{5} (3)	± 0.1^{5}	500	0.3^{2}	$16.^{5}$	$135.^{4}$
6	6.02 (3)	± 0.06	600	0.4^{3}	$22.^{2}$	$157.^{6}$
7	5.6^{5} (3)	± 0.1^{0}	700	0.3^{7}	$19.^{1}$	$176.^{7}$
8	5.2^{9} (3)	± 0.1^{3}	800	0.3^{6}	$18.^{6}$	$195.^{3}$
9	4.84 (3)	± 0.02	900	0.4^{5}	$23.^{3}$	$218.^{6}$
10	4.44 (3)	± 0.06	1000	0.40	20.6	$239.^{2}$
11	4.04 (3)	± 0.03	1100	0.40	20.6	$259.^{8}$
12	3.65 (3)	± 0.07	1200	0.39	20.1	$279.^{9}$
13	3.29 (3)	± 0.03	1300	0.36	18.6	$298.^{5}$
14	3.04 (3)	± 0.08	1400	0.25	12.9	$311.^{4}$
15	2.84 (3)	± 0.04	1500	0.20	10.3	$321.^{7}$
16	2.62 (3)	± 0.02	1600	0.22	11.4	$331.^{1}$
17	2.46 (3)	± 0.08	1700	0.16	8.3	$341.^{4}$
18	2.24 (3)	± 0.03	1800	0.22	11.4	$352.^{8}$
19	2.06 (3)	± 0.05	1900	0.18	9.3	$363.^{1}$
20	1.85 (3)	± 0.07	2000	0.21	10.8	$372.^{9}$
21	1.6^{3} (3)	± 0.1^{3}	2100	0.2^{2}	$11.^{4}$	$384.^{3}$
22	1.40 (3)	± 0.03	2200	0.2^{3}	$11,^{9}$	$396.^{2}$
23	1.24 (3)	± 0.02	2300	0.16	8.3	$404.^{5}$
24	1.10 (3)	± 0.09	2400	0.14	7.2	$411.^{7}$
		WATER PATCH DISCONTINUITIES				
25	1.02 (3)	± 0.05	2500	0.08	4.1	$415.^{8}$

* Starting Oil Weight 467 g   Free Fall Distance 30 cm
Temperature 21°C

TABLE 2-3

RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	9.10 (3)	± 0.07	-	-	-	-
1	8.30 (3)	± 0.05	100	0.80	41.3	41.3
2	7.77 (3)	± 0.04	200	0.53	27.4	68.7
3	7.40 (3)	± 0.06	300	0.37	19.1	87.8
4	6.94 (3)	± 0.05	400	0.46	23.8	111.6
5	6.52 (3)	± 0.05	500	0.42	21.7	133.3
6	6.12 (3)	± 0.04	600	0.40	20.6	153.9
7	5.75 (3)	± 0.08	700	0.37	19.2	173.1
8	5.4^{7} (3)	± 0.1^{2}	800	0.2^{8}	14.^{4}	187.^{5}
9	5.13 (3)	± 0.02	900	0.3^{4}	17.^{6}	205.^{1}
10	4.75 (3)	± 0.06	1000	0.38	19.6	224.^{7}
11	4.4^{5} (3)	± 0.1^{2}	1100	0.3^{0}	15.^{5}	240.^{2}
12	4.08 (3)	± 0.05	1200	0.3^{7}	19.^{1}	259.^{3}
13	3.8^{0} (3)	± 0.1^{1}	1300	0.2^{8}	14.^{5}	273.^{8}
14	3.55 (3)	± 0.09	1400	0.2^{5}	12.^{9}	286.^{7}
15	3.34 (3)	± 0.04	1500	0.21	10.8	297.^{5}
16	3.14 (3)	± 0.07	1600	0.20	10.3	307.^{8}
17	2.94 (3)	± 0.09	1700	0.20	10.3	318.^{1}
18	2.75 (3)	± 0.09	1800	0.19	9.8	327.^{9}
19	2.57 (3)	± 0.02	1900	0.18	9.3	337.^{2}
20	2.42 (3)	± 0.01	2000	0.15	7.7	344.^{9}
21	2.22 (3)	± 0.03	2100	0.20	10.3	355.^{2}
22	2.06 (3)	± 0.04	2200	0.16	8.3	363.^{5}
23	1.94 (3)	± 0.04	2300	0.12	6.2	369.^{7}
24	1.85 (3)	± 0.05	2400	0.09	4.6	374.^{3}
25	1.7^{5} (3)	± 0.1^{3}	2500	0.1^{0}	5.^{2}	379.^{5}
26	1.64 (3)	± 0.01	2600	0.1^{1}	5.^{7}	385.^{2}
27	1.55 (3)	± 0.05	2700	0.09	4.6	389.^{8}
28	1.47 (3)	± 0.06	2800	0.08	4.1	393.^{9}
29	1.37 (3)	± 0.08	2900	0.10	5.2	399.^{1}
30	1.2^{7} (3)	± 0.1^{0}	3000	0.1^{0}	5.^{2}	404.^{3}
31	1.1^{8} (3)	± 0.1^{1}	3100	0.0^{9}	4.^{6}	408.^{9}
32	1.10 (3)	± 0.01	3200	0.0^{8}	4.^{1}	413.^{0}
			WATER PATCH DISCONTINUITIES			
33	1.0^{3} (3)	± 0.1^{8}	3300	0.0^{7}	3.^{6}	416.^{6}

* Starting Oil Weight 467 g Free Fall Distance 60 cm

Temperature 21°C

TABLE 2-4

RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	14.2^{2} (3)	± 0.3^{7}	-	-	- -	-
1	12.6^{5} (3)	± 0.2^{0}	100	1.5^{7}	$82.^{0}$	$82.^{0}$
2	11.83 (3)	± 0.03	200	0.8^{2}	$42.^{8}$	$124.^{8}$
3	11.2^{8} (3)	± 0.1^{2}	300	0.5^{5}	$28.^{7}$	$153.^{5}$
4	10.73 (3)	± 0.04	400	0.5^{5}	$28.^{7}$	$182.^{2}$
5	10.14 (3)	± 0.04	500	0.59	30.9	$213.^{1}$
6	9.56 (4)	± 0.02	600	0.58	30.2	$243.^{3}$
7	8.97 (4)	± 0.03	700	0.59	30.9	$274.^{2}$
8	8.3^{8} (4)	± 0.1^{1}	800	0.5^{9}	$30.^{8}$	$305.^{0}$
9	7.84 (4)	± 0.04	900	0.5^{3}	$28.^{2}$	$333.^{2}$
10	7.21 (4)	± 0.05	1000	0.63	32.9	$366.^{1}$
11	6.7^{3} (4)	± 0.1^{2}	1100	0.4^{8}	$25.^{0}$	$391.^{1}$
12	6.2^{3} (3)	± 0.1^{1}	1200	0.5^{0}	$26.^{2}$	$417.^{3}$
13	5.7^{3} (4)	± 0.1^{6}	1300	0.5^{0}	$26.^{1}$	$443.^{4}$
14	5.2^{6} (4)	± 0.1^{3}	1400	0.4^{7}	$24.^{5}$	$467.^{9}$
15	4.8^{3} (3)	± 0.1^{0}	1500	0.4^{3}	$22.^{5}$	$490.^{4}$
16	4.38 (4)	± 0.06	1600	0.4^{5}	$23.^{5}$	$513.^{9}$
17	3.9^{5} (3)	± 0.1^{2}	1700	0.4^{3}	$22.^{5}$	$536.^{4}$
18	3.5^{5} (3)	± 0.1^{7}	1800	0.4^{0}	$20.^{9}$	$557.^{3}$
19	3.1^{4} (4)	± 0.1^{1}	1900	0.4^{1}	$21.^{4}$	$578.^{7}$
20	2.7^{6} (3)	± 0.1^{7}	2000	0.3^{8}	$19.^{9}$	$598.^{5}$
21	2.39 (3)	± 0.01	2100	0.3^{7}	$19.^{3}$	$617.^{8}$
22	2.00 (3)	± 0.04	2200	0.39	20.4	$638.^{2}$
23	1.63 (3)	± 0.07	2300	0.37	19.3	$657.^{5}$
24	1.43 (3)	± 0.03	2400	0.20	10.6	$668.^{1}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 743 g Free Fall Distance 15 cm

Temperature 2°C

TABLE 2-5

RAW DATA – OIL-LOK 501 AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	10.67 (4)	± 0.07	- -	–	–	–
1	9.1^8 (4)	± 0.1^0	100	1.4^9	77.^{8}	77.^{8}
2	8.3^3 (4)	± 0.1^3	200	0.8^5	44.^{4}	122.^{2}
3	7.69 (4)	± 0.06	300	0.6^4	33.^{4}	155.^{6}
4	7.1^1 (4)	± 0.1^1	400	0.5^8	30.^{3}	185.^{9}
5	6.61 (4)	± 0.07	500	0.5^0	26.^{1}	212.^{0}
6	6.1^6 (4)	± 0.3^8	600	0.4^5	23.^{5}	235.^{5}
7	5.73 (4)	± 0.08	700	0.4^3	22.^{4}	257.^{9}
8	5.32 (4)	± 0.07	800	0.41	21.4	279.^{3}
9	4.9^5 (4)	± 0.2^4	900	0.[illegible]^7	19.^{3}	298.^{6}
10	4.54 (4)	± 0.09	1000	0.4^1	21.^{4}	320.^{0}
11	4.1^5 (4)	± 0.1^2	1100	0.3^9	20.^{4}	340.^{4}
12	3.7^7 (4)	± 0.1^5	1200	0.3^8	19.^{8}	360.^{2}
13	3.44 (4)	± 0.03	1300	0.3^3	17.^{2}	377.^{4}
14	3.1^5 (4)	± 0.3^1	1400	0.2^9	15.^{1}	392.^{5}
15	2.9^0 (4)	± 0.1^5	1500	0.2^5	13.^{0}	405.^{5}
16	2.6^4 (4)	± 0.1^4	1600	0.2^6	13.^{6}	419.^{1}
17	2.4^0 (4)	± 0.1^7	1700	0.2^4	12.^{5}	431.^{6}
18	2.1^9 (4)	± 0.1^7	1800	0.2^1	11.^{0}	442.^{6}
19	1.9^7 (4)	± 0.1^4	1900	0.2^2	11.^{5}	454.^{1}
20	1.7^8 (4)	± 0.1^2	2000	0.1^9	9.^{9}	464.^{0}
21	1.5^9 (4)	± 0.1^1	2100	0.1^9	9.^{9}	473.^{9}
22	1.4^2 (3)	± 0.1^6	2200	0.1^7	8.^{9}	482.^{8}
			WATER PATCH DISCONTINUITIES			

* Starting Oil Weight 557 g Free Fall Distance 30 cm

Temperature 2°C

TABLE 2-6

RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	10.0^{2} (4)	± 0.1^{2}	-	-	-	-
1	8.7^{3} (4)	± 0.5^{2}	100	1.2^{9}	$67.^{4}$	$67.^{4}$
2	8.02 (4)	± 0.09	200	0.7^{1}	$37.^{1}$	$104.^{5}$
3	7.44 (4)	± 0.09	300	0.58	30.3	$134.^{8}$
4	6.9^{8} (4)	± 0.1^{6}	400	0.4^{6}	$24.^{0}$	$158.^{8}$
5	6.5^{6} (4)	± 0.1^{0}	500	0.4^{2}	$21.^{9}$	$180.^{7}$
6	6.1^{8} (4)	± 0.2^{0}	600	0.3^{8}	$19.^{8}$	$200.^{5}$
7	5.84 (4)	± 0.07	700	0.3^{4}	$17.^{8}$	$218.^{2}$
8	5.4^{7} (4)	± 0.1^{3}	800	0.3^{7}	$19.^{3}$	$237.^{5}$
9	5.1^{5} (4)	± 0.1^{8}	900	0.3^{2}	$16.^{7}$	$254.^{3}$
10	4.8^{1} (4)	± 0.1^{1}	1000	0.3^{4}	$17.^{8}$	$272.^{0}$
11	4.4^{8} (4)	± 0.1^{4}	1100	0.3^{3}	$17.^{2}$	$289.^{2}$
12	4.1^{7} (4)	± 0.1^{3}	1200	0.3^{1}	$16.^{2}$	$305.^{4}$
13	3.90 (4)	± 0.03	1300	0.2^{7}	$14.^{1}$	$319.^{5}$
14	3.6^{6} (4)	± 0.1^{7}	1400	0.2^{4}	$12.^{5}$	$332.^{0}$
15	3.4^{6} (4)	± 0.1^{0}	1500	0.2^{0}	$10.^{4}$	$342.^{4}$
16	3.2^{6} (4)	± 0.1^{0}	1600	0.2^{0}	$10.^{4}$	$352.^{8}$
17	3.0^{8} (4)	± 0.1^{0}	1700	0.1^{8}	$9.^{4}$	$362.^{2}$
18	2.91 (4)	± 0.04	1800	0.1^{7}	$8.^{9}$	$371.^{1}$
19	2.75 (4)	± 0.03	1900	0.16	8.4	$379.^{5}$
20	2.59 (4)	± 0.07	2000	0.16	8.4	$387.^{9}$
21	2.44 (4)	± 0.08	2100	0.15	7.8	$395.^{7}$
22	2.2^{9} (4)	± 0.1^{0}	2200	0.1^{5}	$7.^{8}$	$403.^{5}$
23	2.15 (4)	± 0.09	2300	0.1^{4}	$7.^{3}$	$410.^{8}$
24	2.0^{1} (4)	± 0.1^{3}	2400	0.1^{4}	$7.^{3}$	$418.^{1}$
25	1.8^{8} (4)	± 0.1^{4}	2500	0.1^{3}	$6.^{8}$	$424.^{9}$
26	1.7^{5} (4)	± 0.1^{2}	2600	0.1^{3}	$6.^{8}$	$431.^{7}$
27	1.6^{0} (4)	± 0.1^{3}	2700	0.1^{5}	$7.^{8}$	$439.^{5}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 524. g Free Fall Distance 60 cm
Temperature 2°C

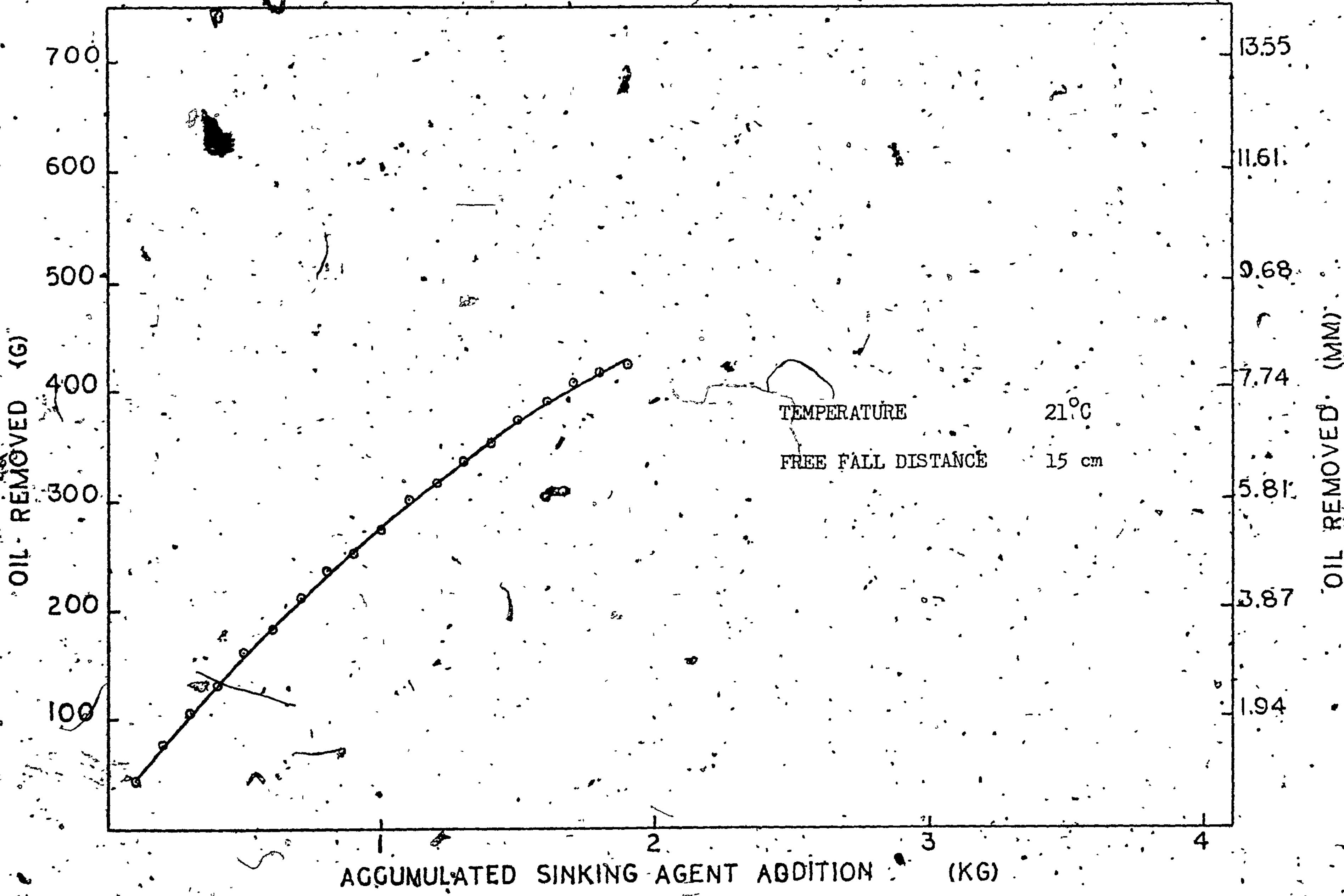

FIGURE 2-1 OIL-LOK 501 AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

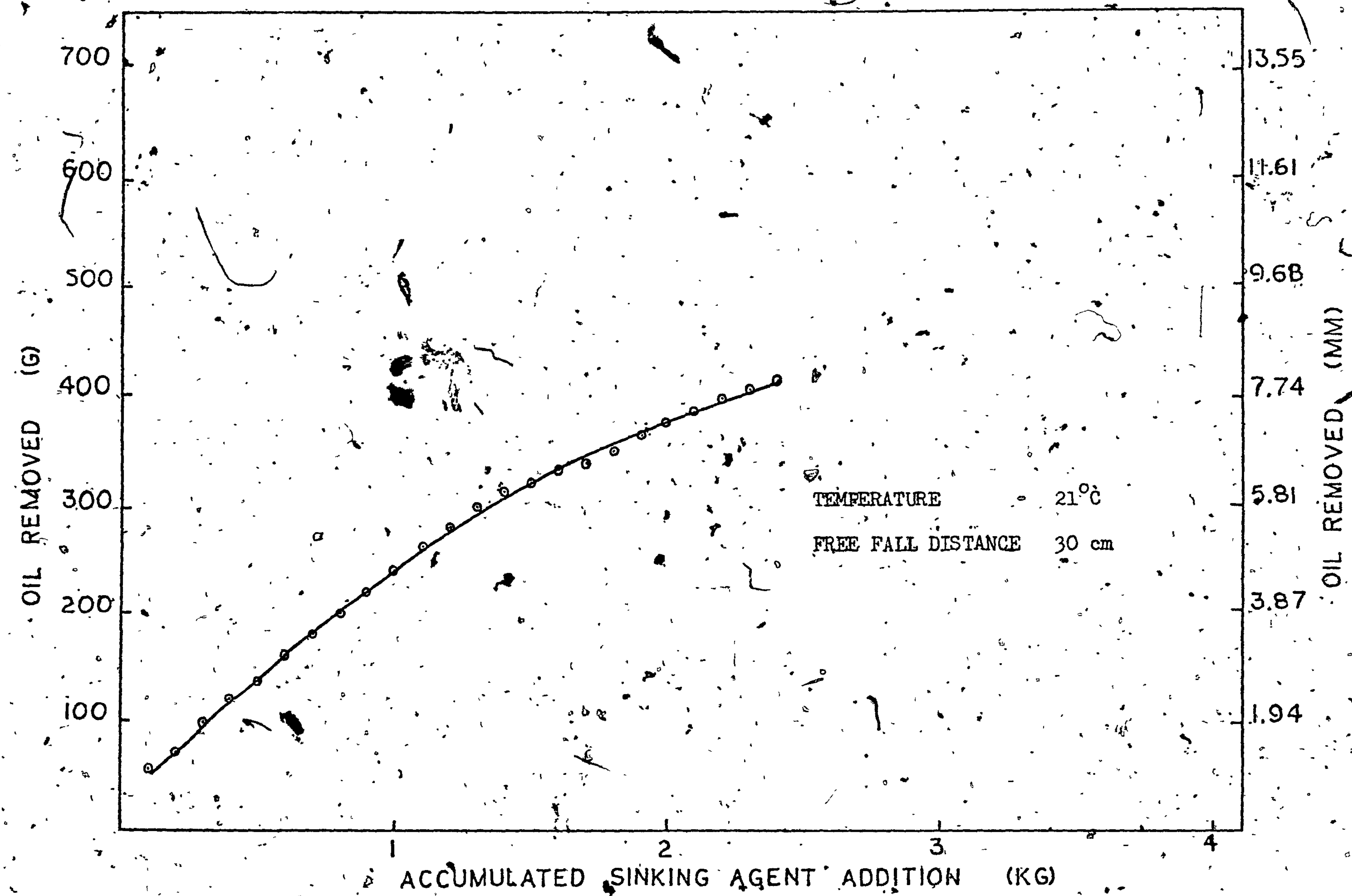

FIGURE 2-2 . OIL-LOK 501 AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

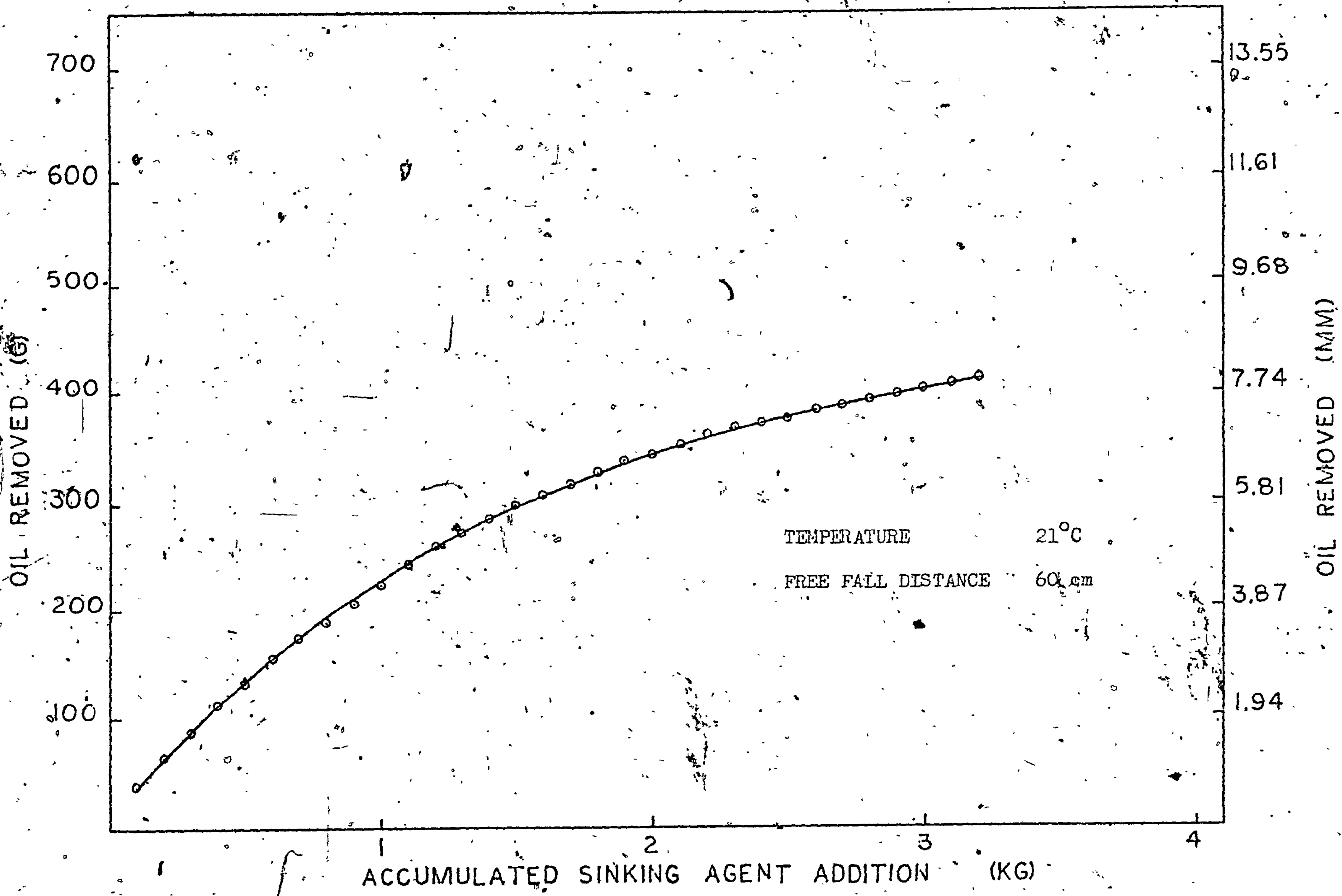

FIGURE 2-3 OIL-LOK 501 AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

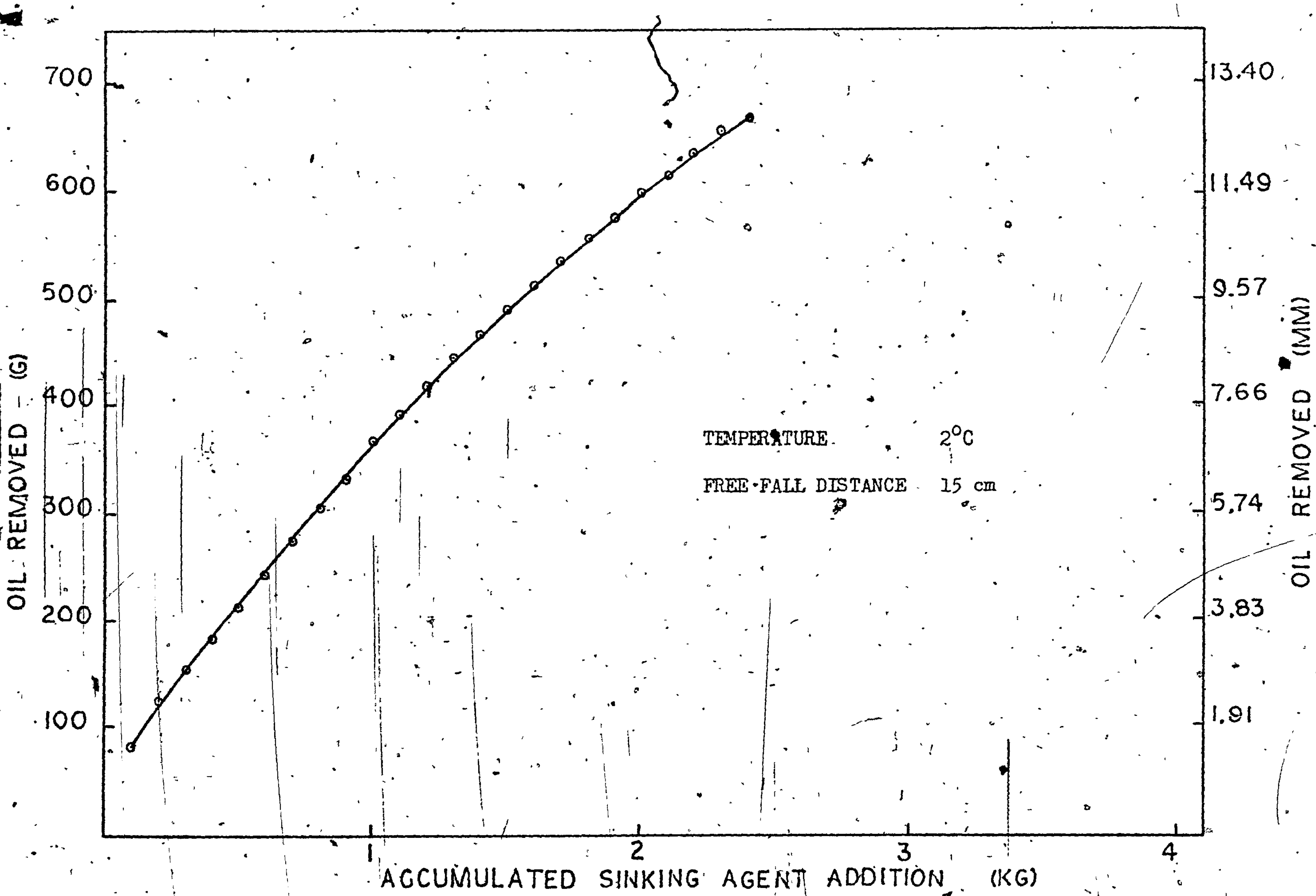

FIGURE 2-4 OIL-LOK 501 AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

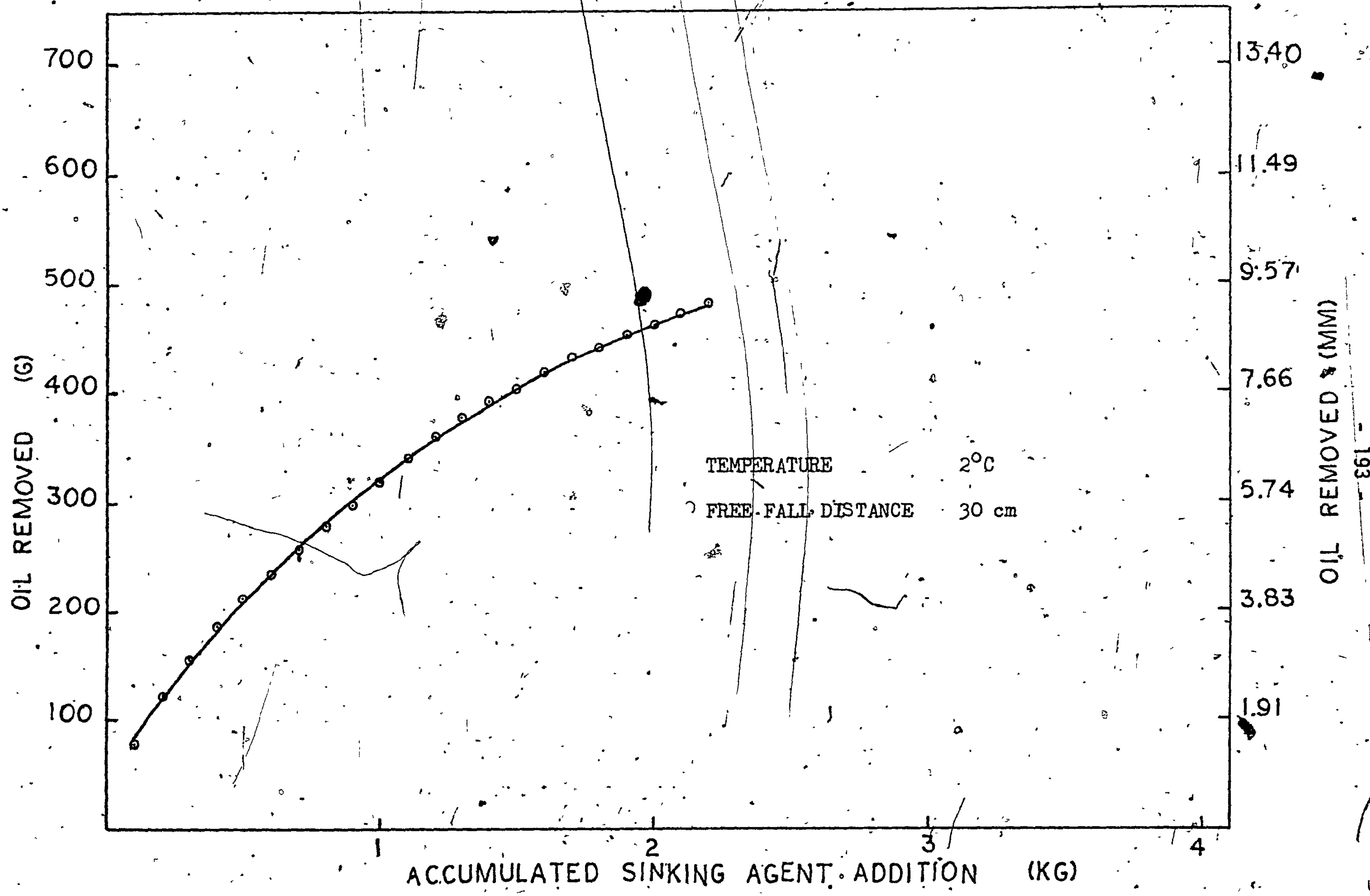

FIGURE 2-5 OIL-LOK 501 AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

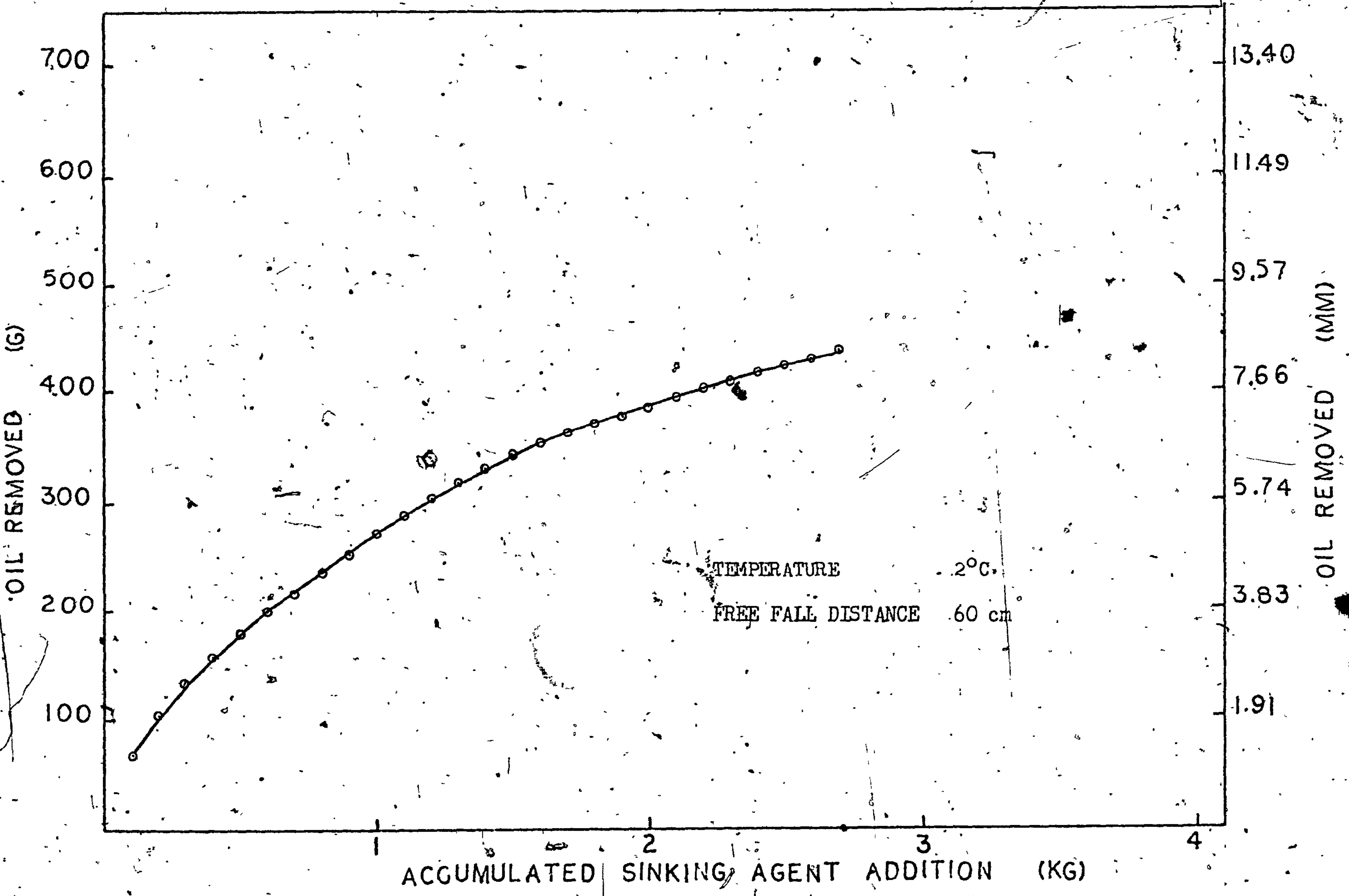

FIGURE 2-6 OIL-LOK 501 AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

TABLE 2-7

ANALYSIS OF RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.12 mm (g)	Sinking Agent/Oil Ratio by Weight
9.31	1900	423.2	4.49
7.82	1700	346.2	4.91
6.76	1500	291.4	5.15
6.17	1400	260.9	5.37
5.20	1200	210.8	5.69
3.99	900	148.3	6.07
3.17	700	105.9	6.61
2.11	400	51.2	7.81

* Free Fall Distance 15 cm Temperature 21°C

TABLE 2-8

ANALYSIS OF RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.10 mm (g)	Sinking Agent/Oil Ratio by Weight
9.07	2400	411.7	5.83
8.33	2300	373.4	6.16
7.17	2100	313.5	6.69
6.02	1800	254.1	7.08
4.84	1500	193.1	7.76
4.04	1300	151.9	8.56
3.04	1000	100.3	9.97
2.06	500	49.6	10.08

* Free Fall Distance 30 cm Temperature 21°C

TABLE 2-9

ANALYSIS OF RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.10 mm (g)	Sinking Agent/Oil Ratio by Weight
9.10	3200	$413.^{0}$	7.75
7.77	3000	$345.^{3}$	8.69
6.94	2800	$301.^{4}$	9.29
6.12	2600	$257.^{1}$	10.1^{1}
5.13	2300	$207.^{9}$	11.0^{6}
4.08	2000	$153.^{7}$	13.0^{1}
2.94	1500	$94.^{5}$	15.8^{7}
2.06	1000	$49.^{5}$	20.2^{0}

* Free Fall Distance 60 cm Temperature 21°C

TABLE 2-10

ANALYSIS OF RAW DATA - OIL-LOK 501 AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.43 mm (g)	Sinking Agent/Oil Ratio by Weight
14.22	2400	$668.^{1}$	3.59
12.65	2300	$586.^{1}$	3.92
11.83	2200	$543.^{3}$	4.05
10.73	2000	$485.^{9}$	4.12
10.14	1900	$455.^{0}$	4.18
8.97	1700	$393.^{9}$	4.32
7.84	1500	$334.^{9}$	4.48
7.21	1400	$302.^{0}$	4.64
6.23	1200	$250.^{8}$	4.78
4.83	900	$177.^{7}$	5.06
3.95	700	$131.^{8}$	5.31
3.14	500	$89.^{5}$	5.59
2.00	200	$29.^{9}$	6.69

* Free Fall Distance 15 cm Temperature 2°C

TABLE 2-11

ANALYSIS OF RAW DATA – OIL-LOK 501 AND WESTERN CRUDE OIL*

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.42 mm (g)	Sinking Agent/Oil Ratio by Weight
10.67	2200	482.8	4.56
9.18	2100	405.0	5.18
8.33	2000	360.6	5.55
7.11	1800	296.9	6.06
6.16	1600	247.3	6.47
4.95	1300	184.2	7.06
4.15	1100	142.4	7.72
3.15	800	90.3	8.85
2.19	400	40.2	9.95

* Free Fall Distance 30 cm Temperature 2°C.

Table 2-12

ANALYSIS OF RAW DATA – OIL-LOK 501 AND WESTERN CRUDE OIL*

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.60 mm (g)	Sinking Agent/Oil Ratio by Weight
10.02	2700	439.5	6.14
8.73	2600	372.1	6.99
8.02	2500	335.0	7.48
6.98	2300	280.7	8.19
6.18	2100	239.0	8.78
5.15	1800	185.2	9.71
4.17	1500	129.9	11.44
3.08	1000	77.3	12.94
2.15	400	28.7	13.94

* Free Fall Distance 60 cm Temperature 2°C

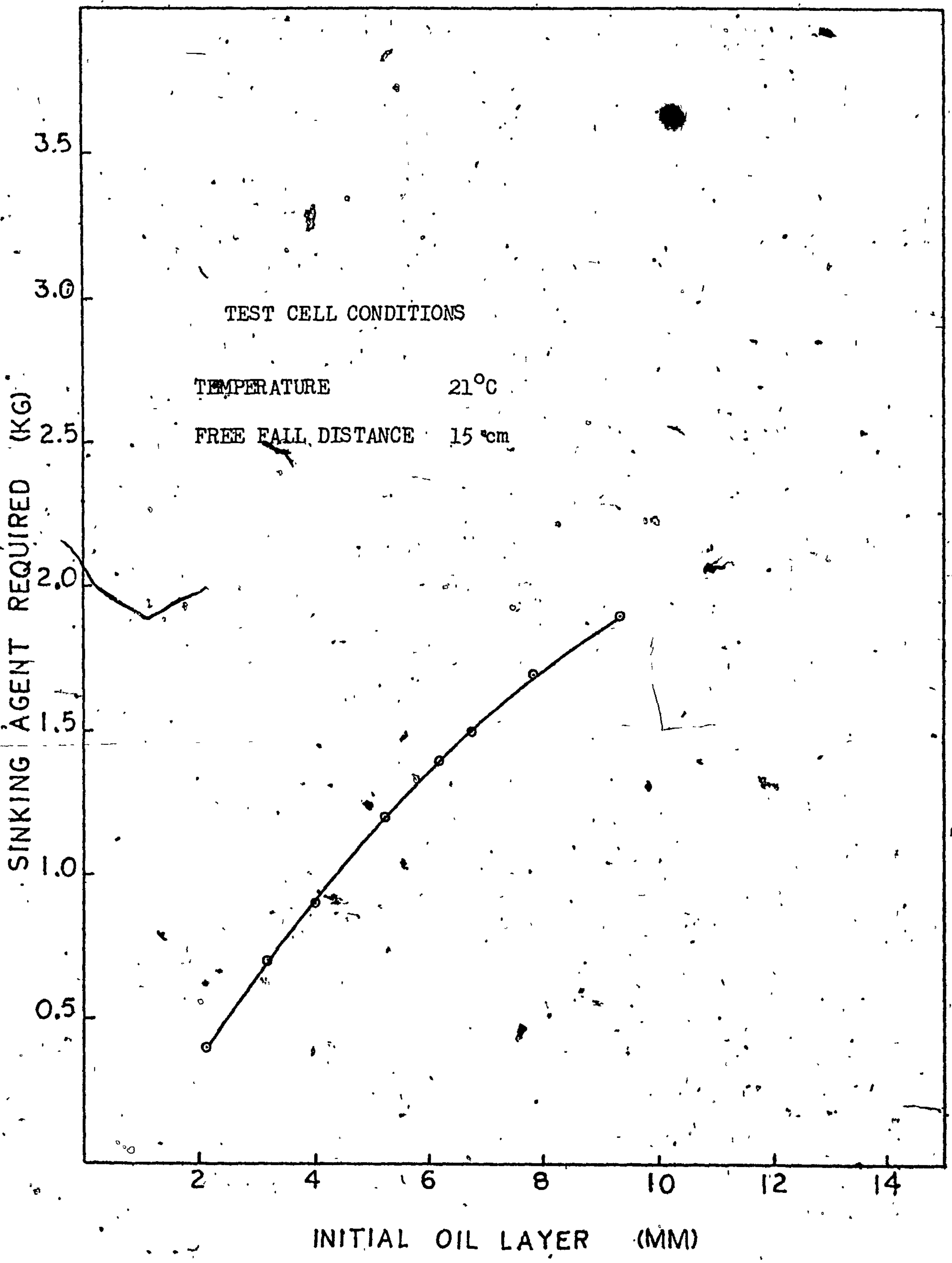

FIGURE 2-7 OIL-LOK 501 AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

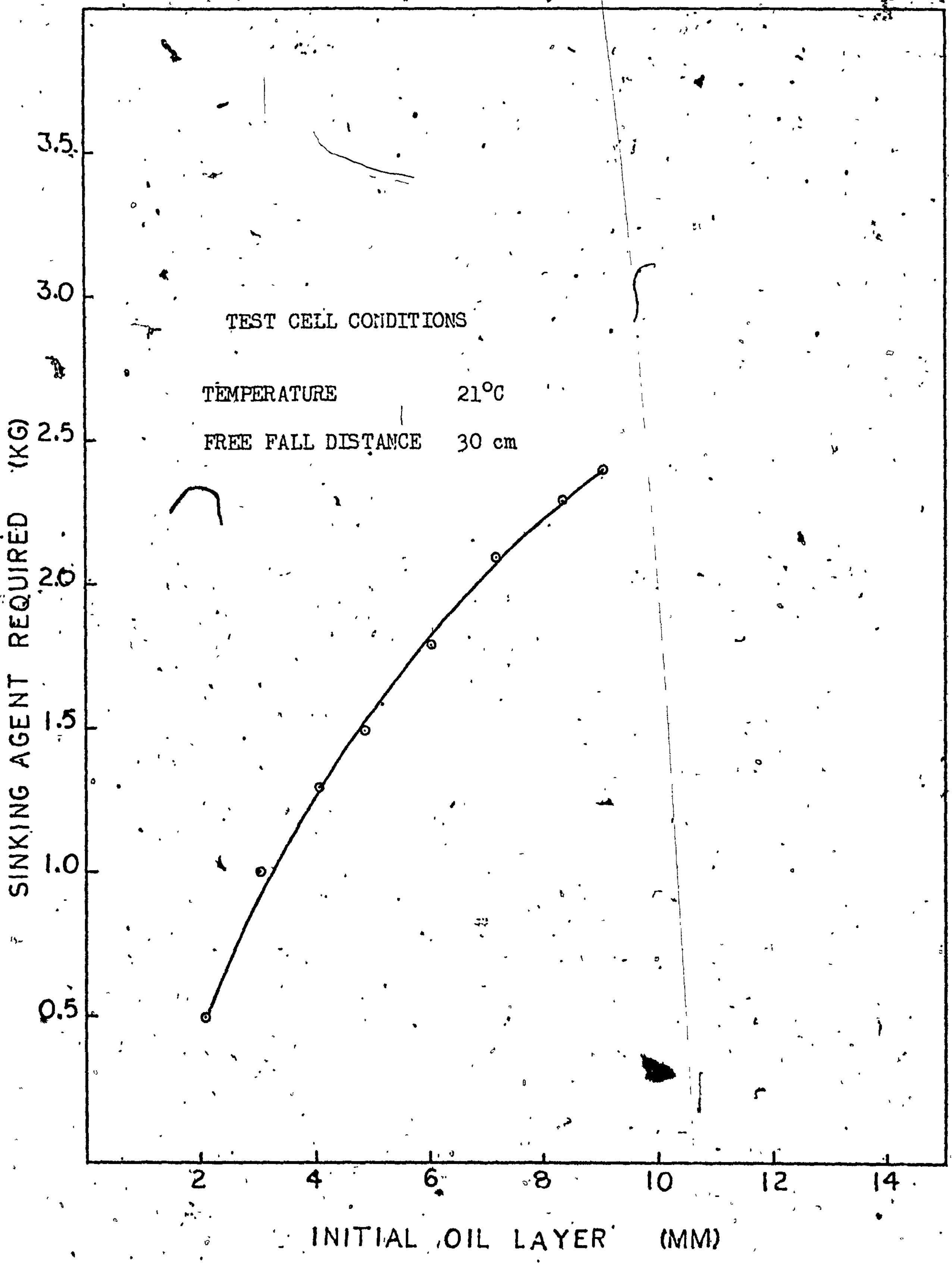

FIGURE 2-8 OIL-LOK 501 AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

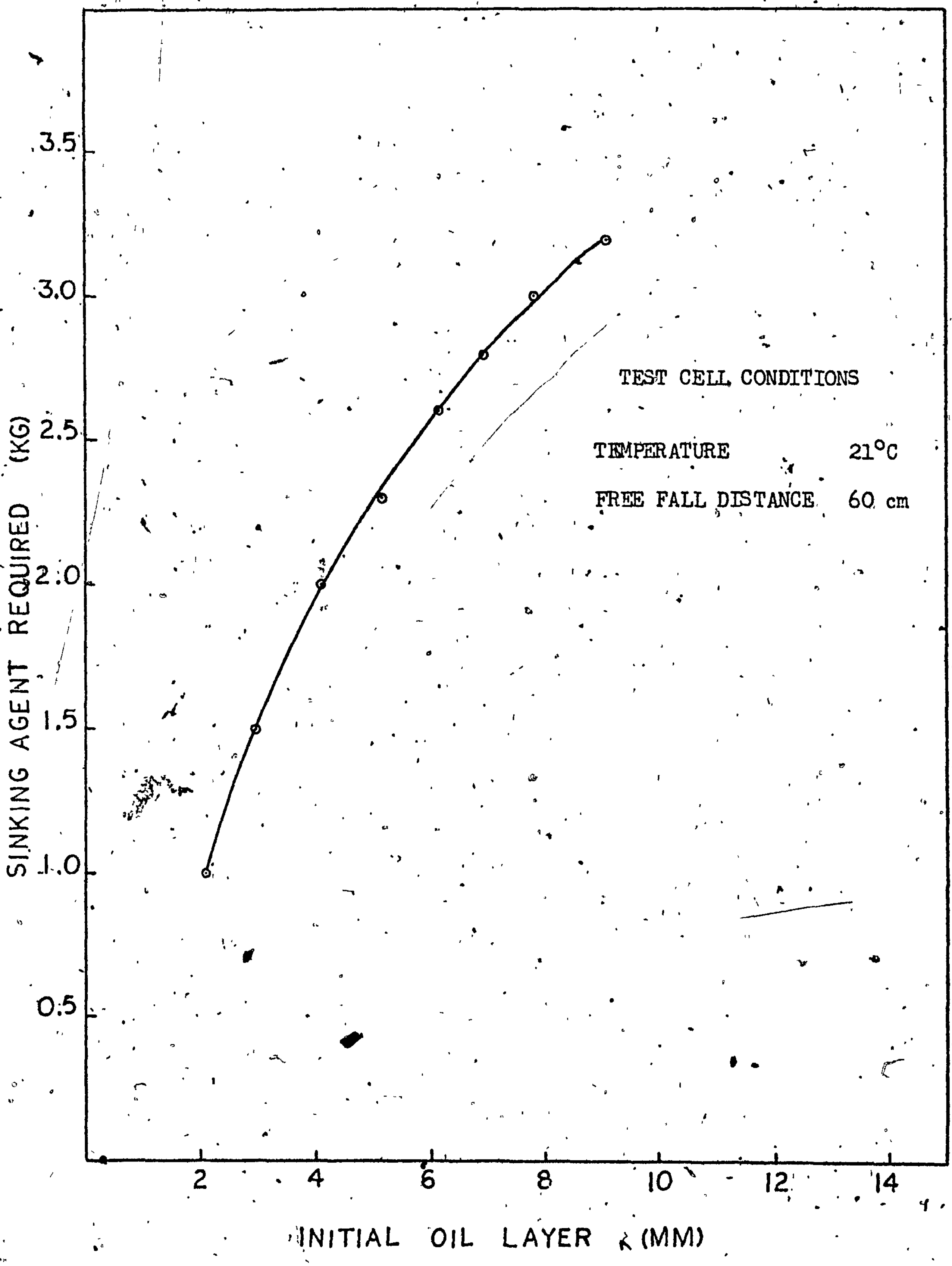

FIGURE 2-9 OI -LOK 501 AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

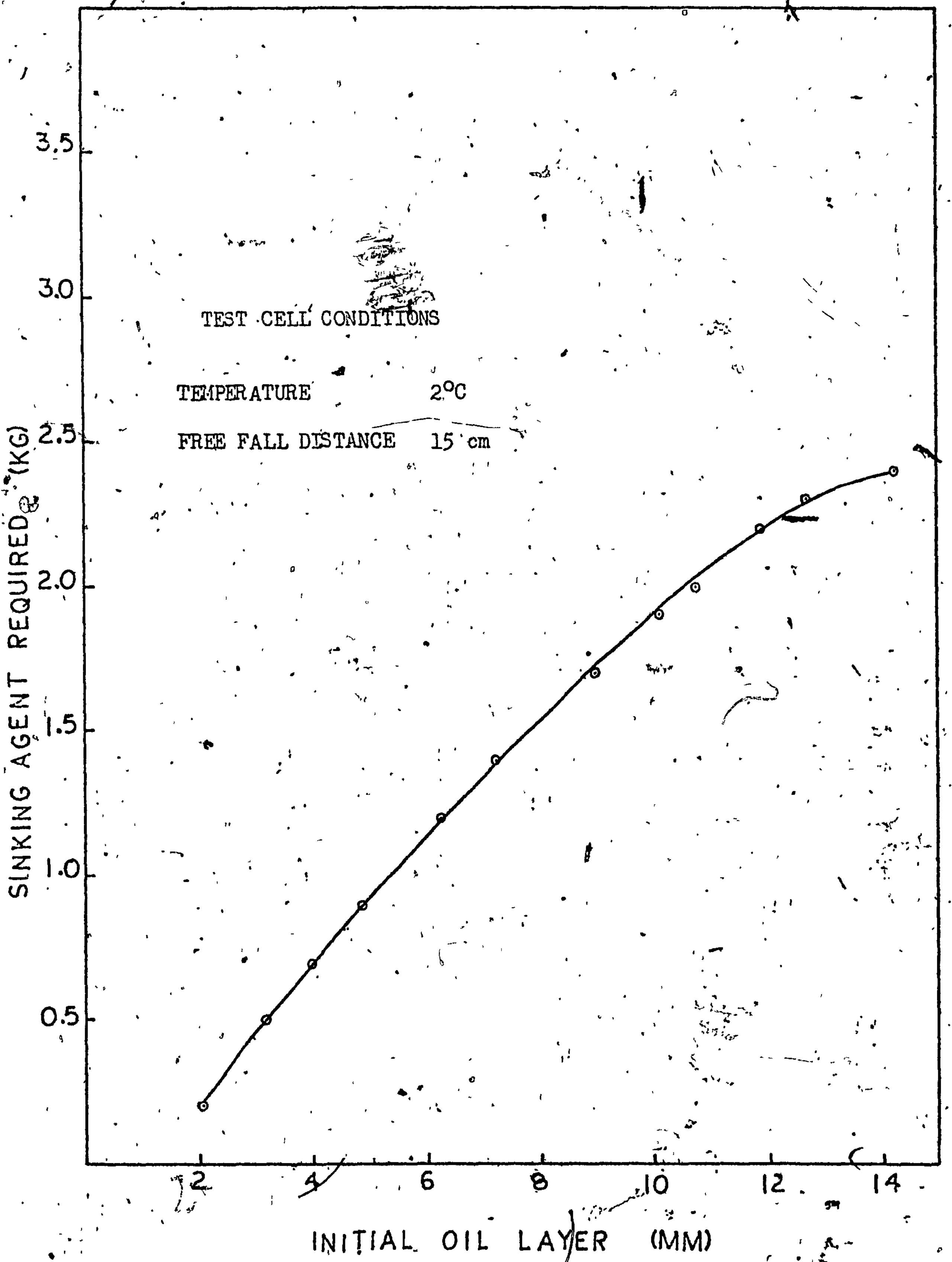

FIGURE 2-10 OIL-LOK 501 AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

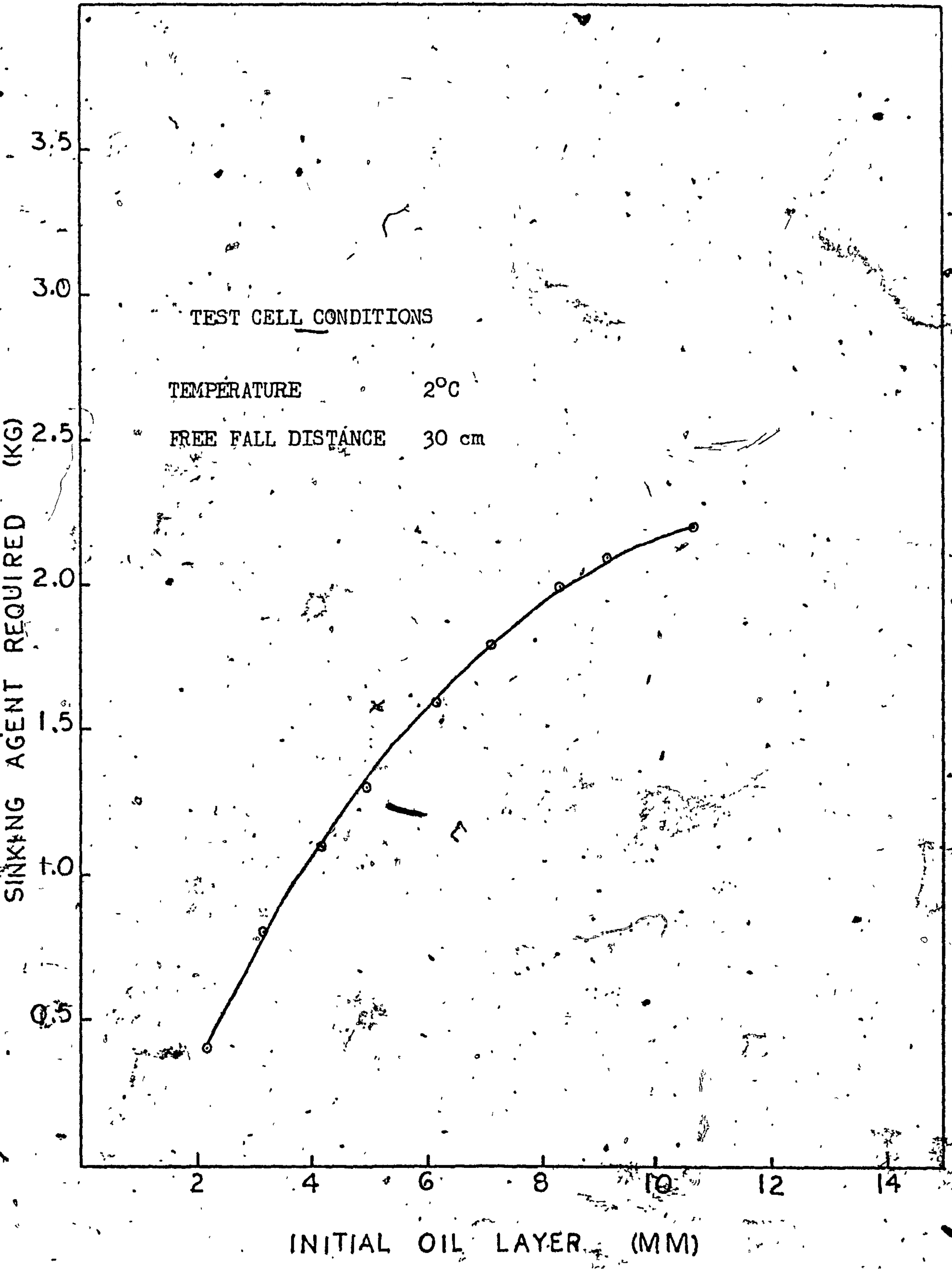

FIGURE 2-11 OIL-LOK 501 AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

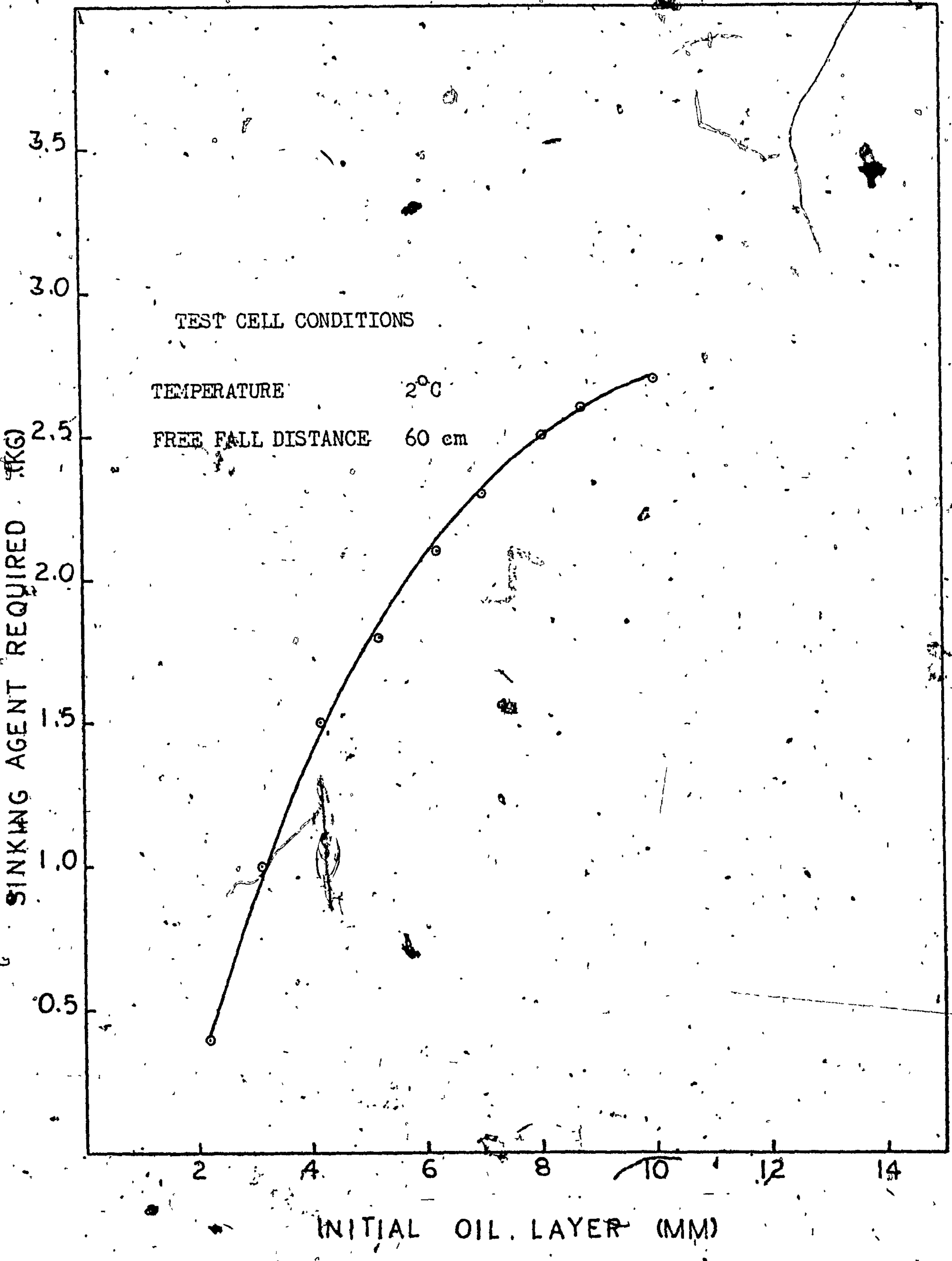

FIGURE 2-12 OIL-MOK 501 AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

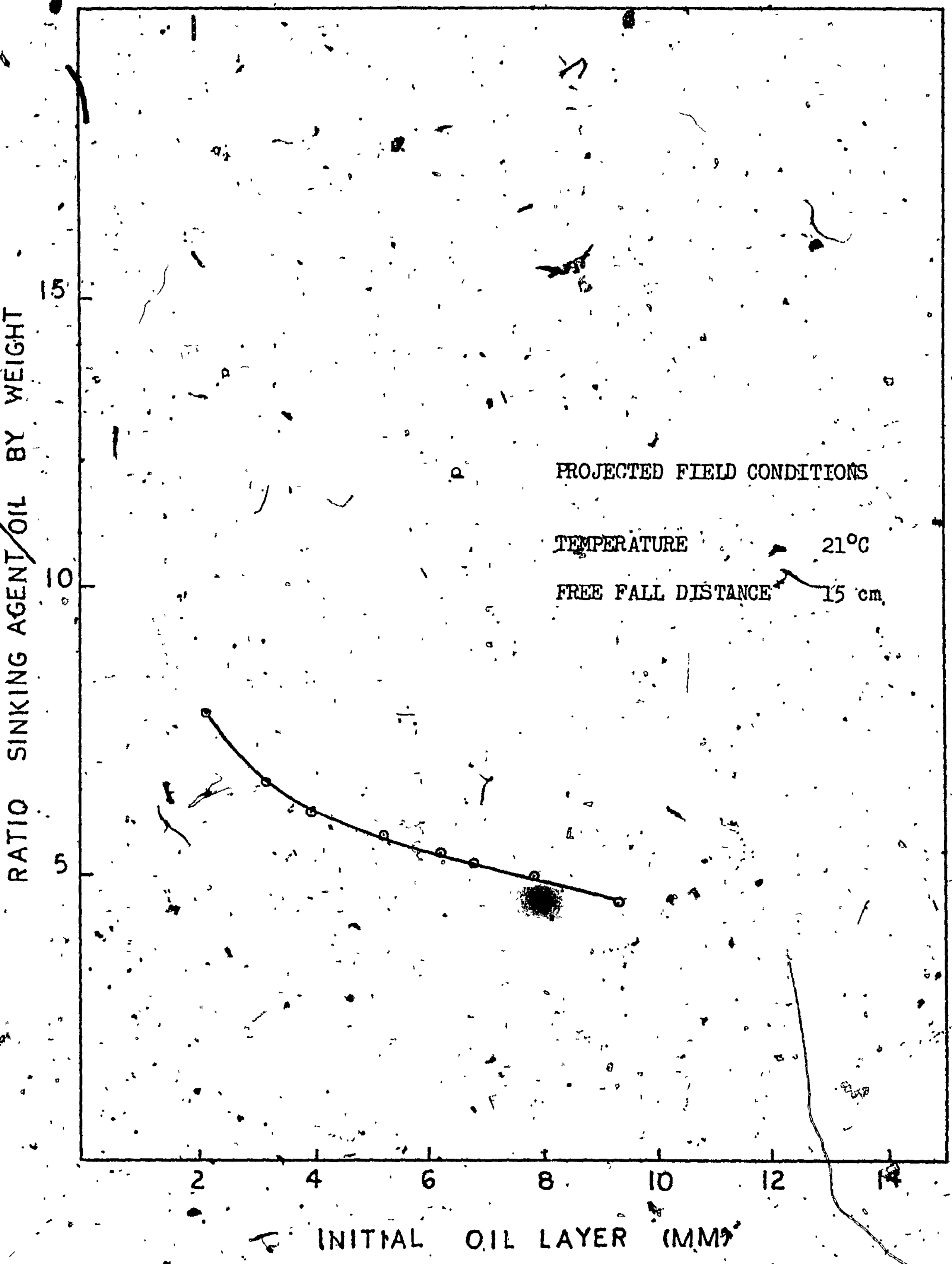

FIGURE 2-13 OIL-LOK 501 AND WESTERN CRUDE OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

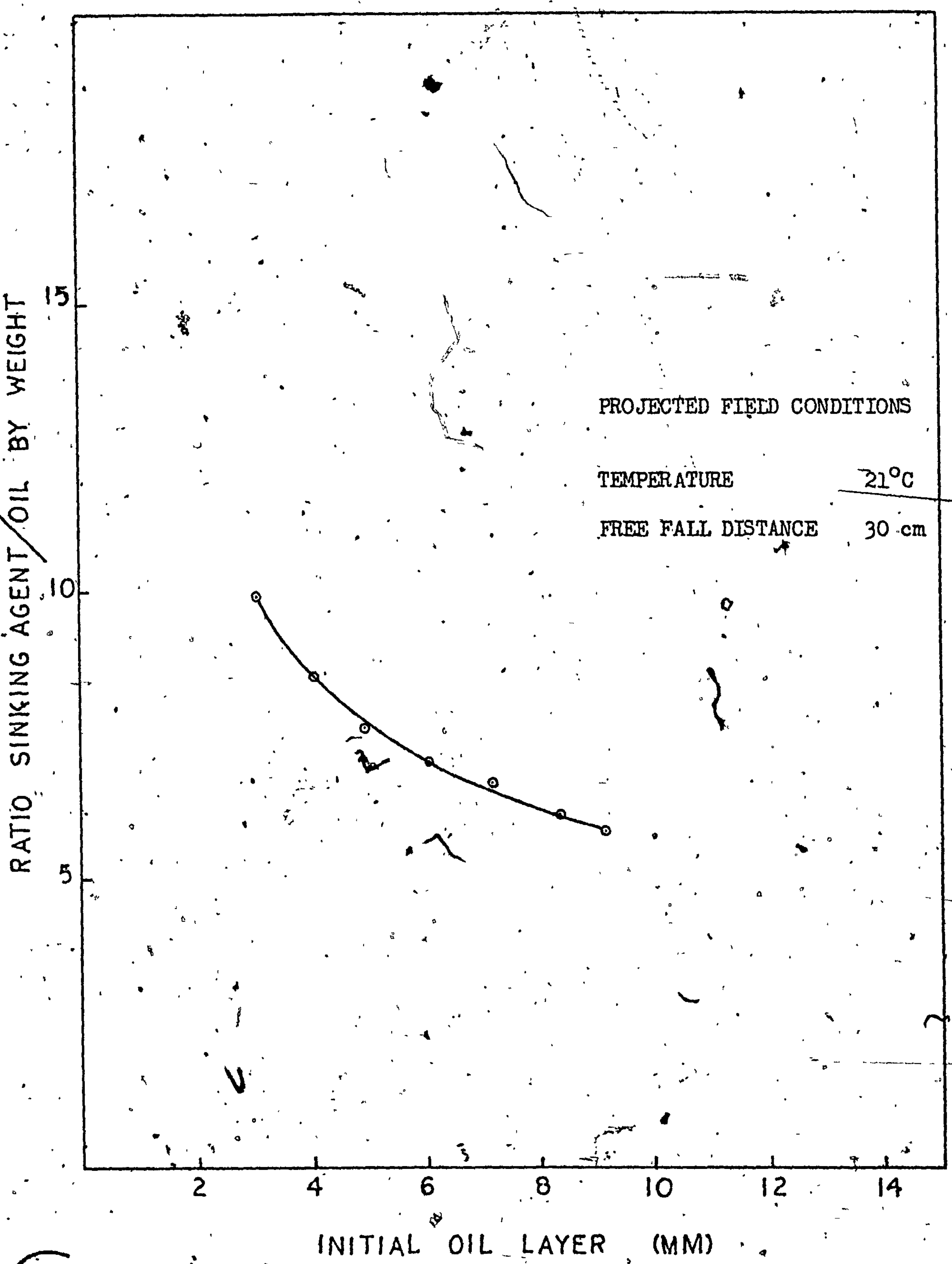

FIGURE 2-11 OIL-LOK 501 AND WESTERN CRUDE OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

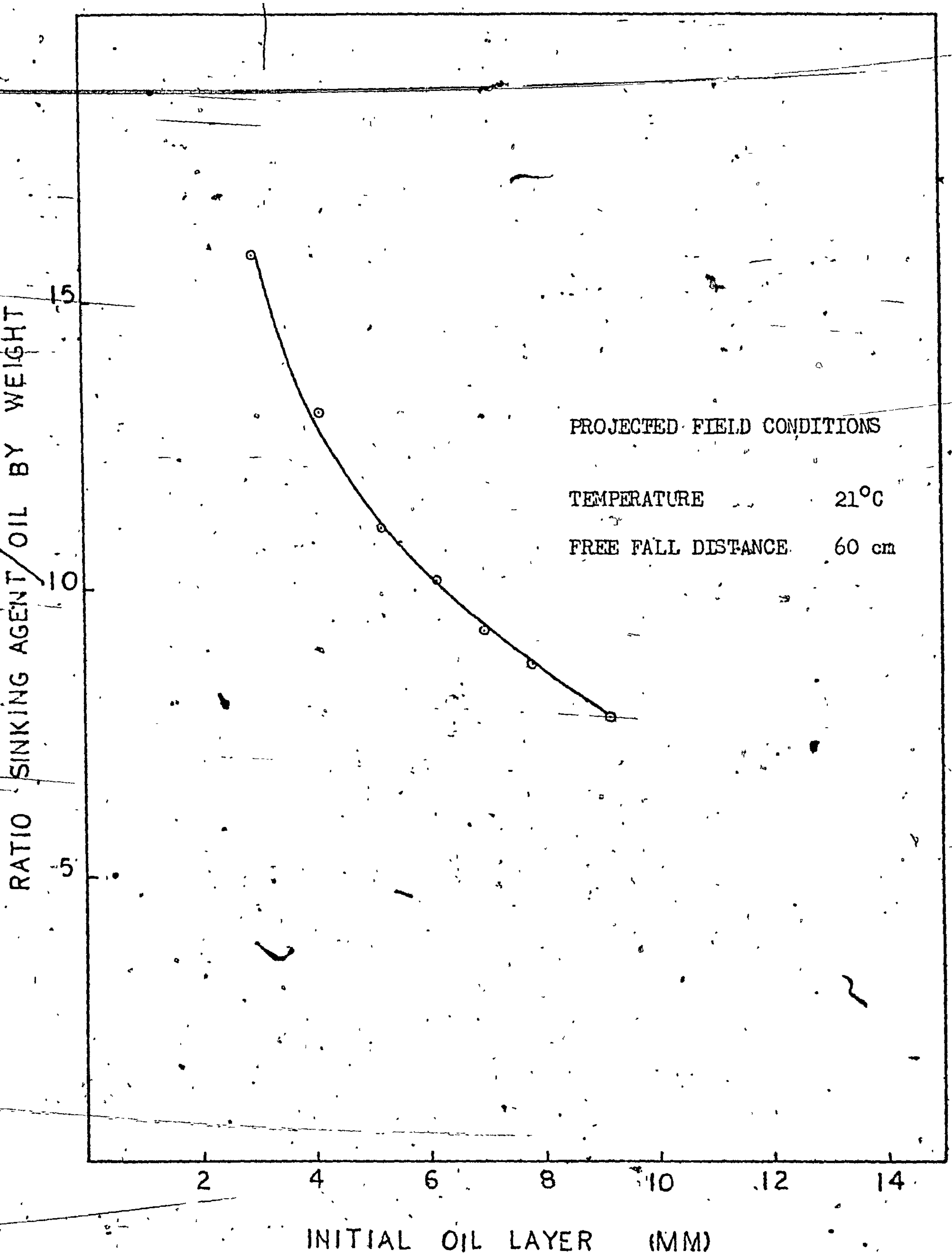

FIGURE 2-15 OIL-LOK 501 AND WESTERN CRUDE OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS.

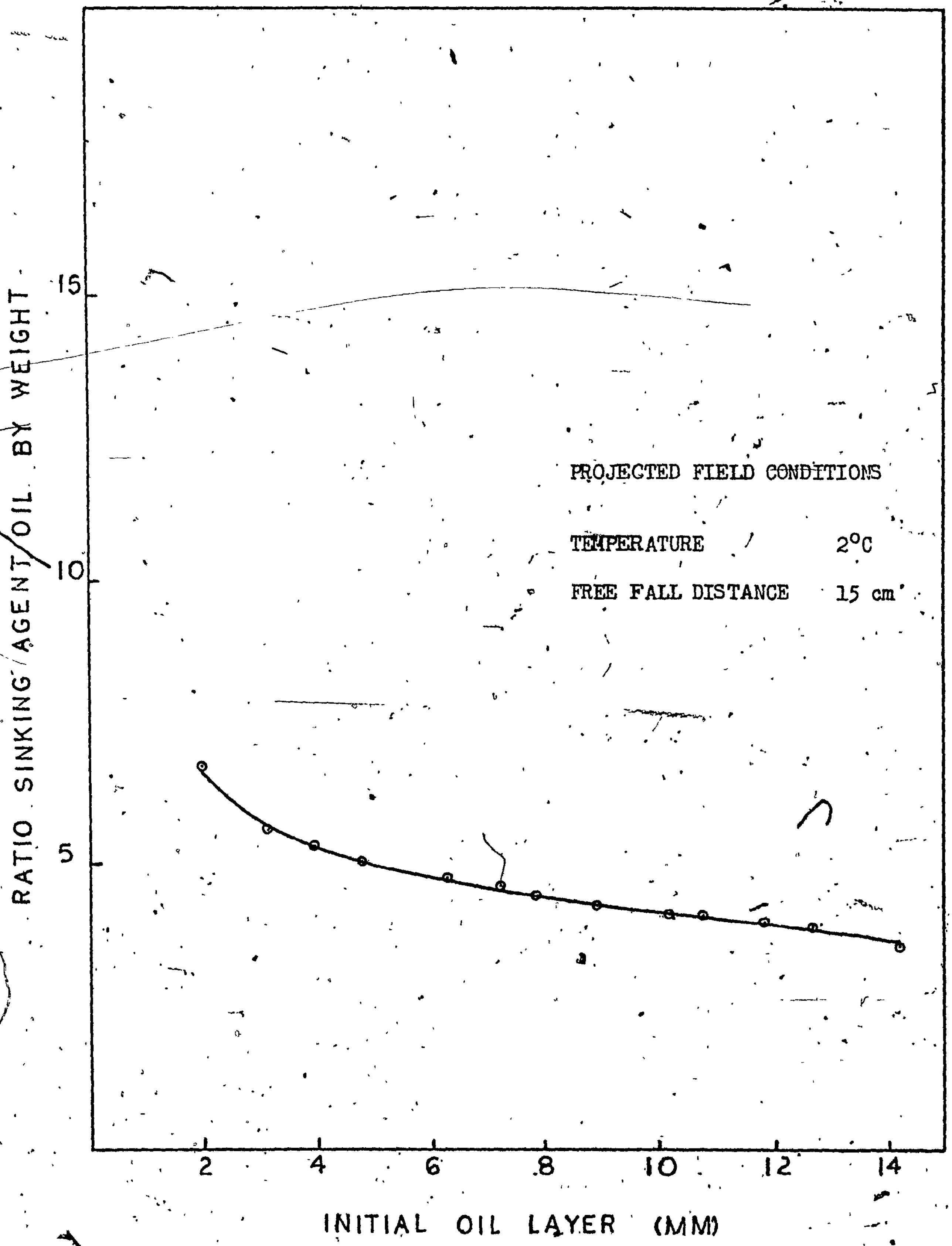

FIGURE 2-16 OIL-LOK 501 AND WESTERN CRUDE OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

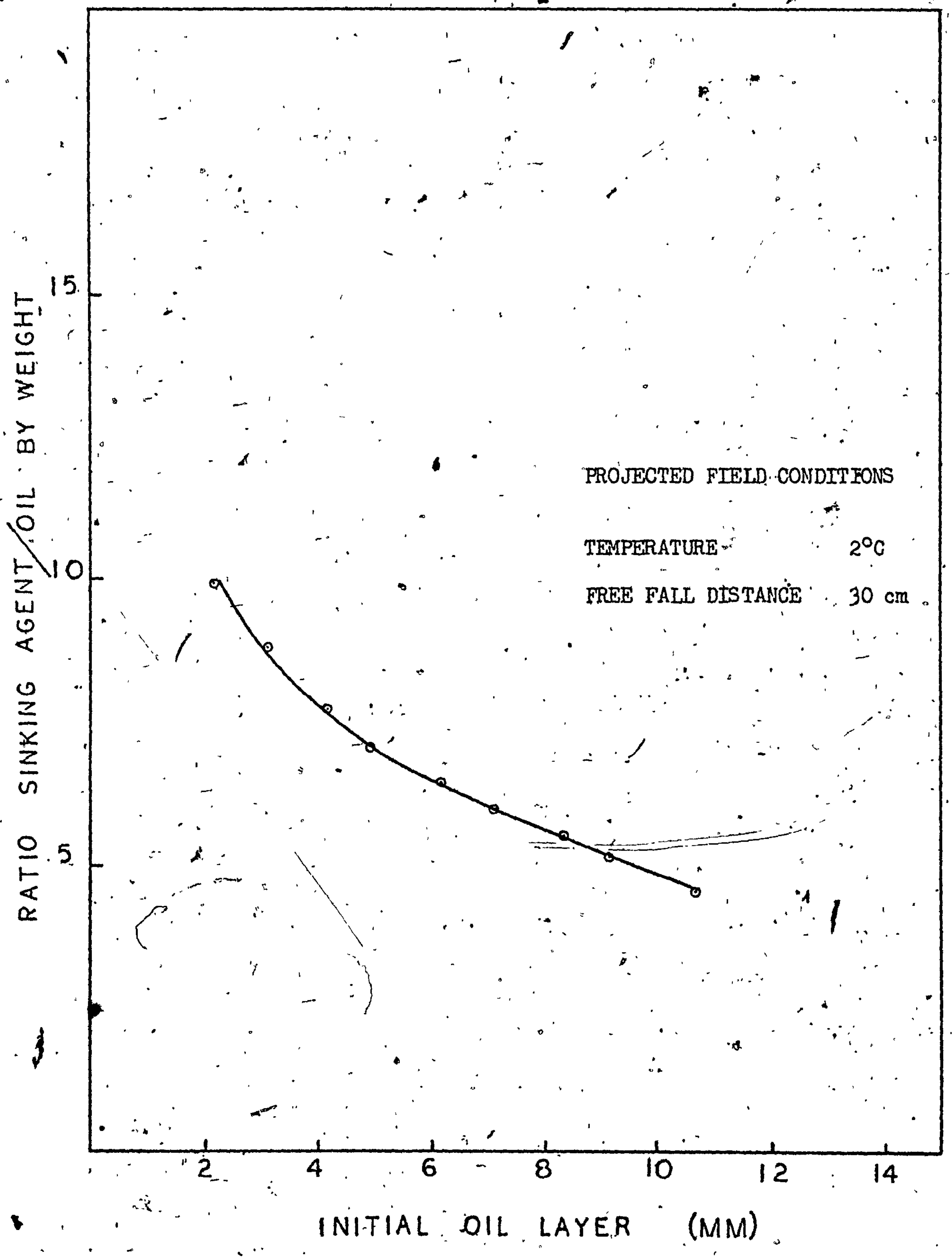

FIGURE 2-17 OIL-LOK 501 AND WESTERN CRUDE OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

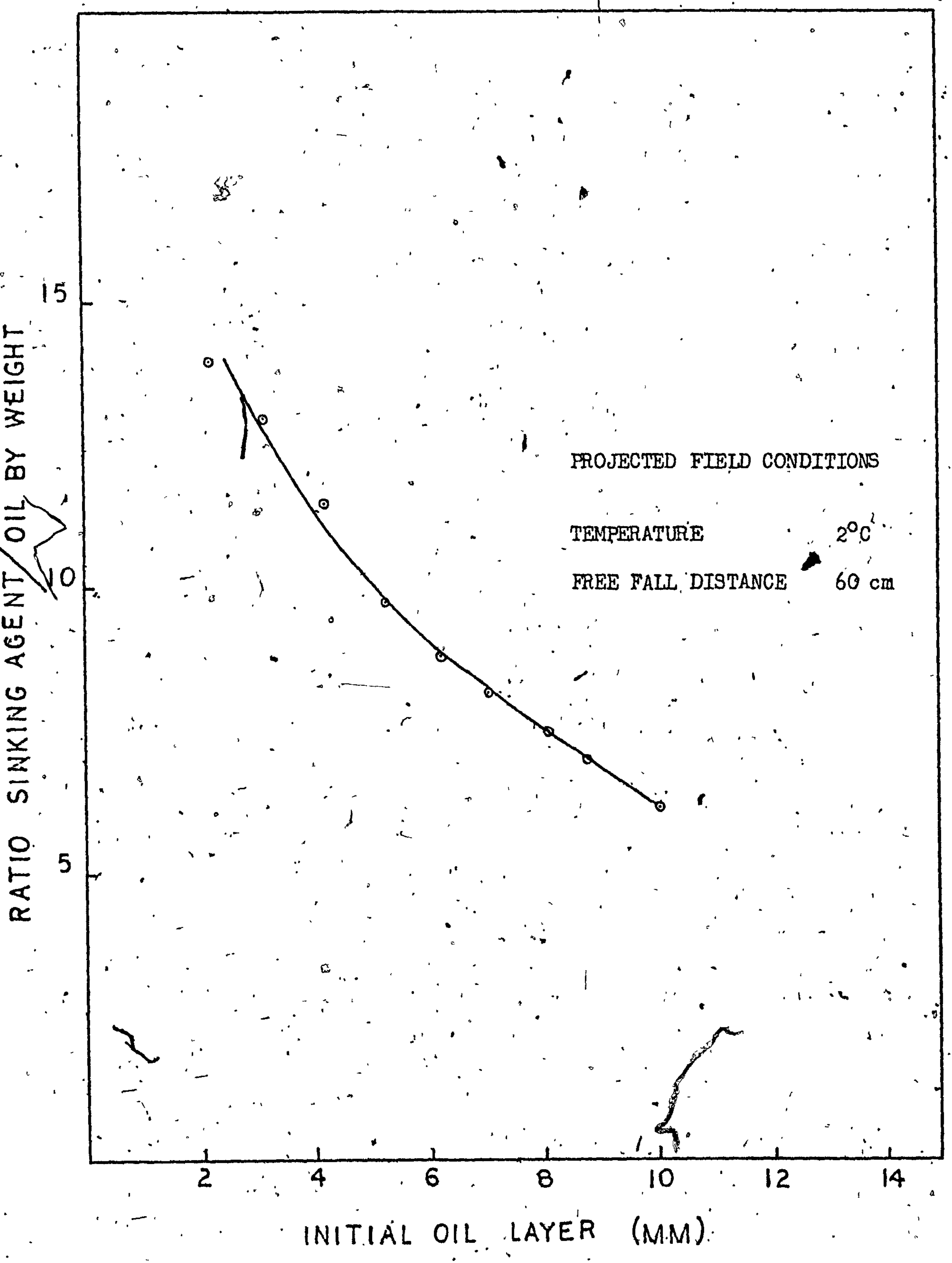

FIGURE 2-18 OIL-LOK 501 AND WESTERN CRUDE OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

APPENDIX III

OIL-LOK 501 AND NO. 2 FUEL OIL

EXPERIMENTAL DATA AND DATA ANALYSES

TABLE 3-1

RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL*

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	13.27 (3)	± 0.08	-	-	-	-
1	12.94 (3)	± 0.17	100	0.33	17.2	17.2
2	12.20 (3)	± 0.02	200	0.74	38.7	55.9
3	11.89 (3)	± 0.18	300	0.31	16.2	72.1
4	11.50 (3)	± 0.09	400	0.39	20.4	92.5
5	11.11 (3)	± 0.02	500	0.39	20.4	112.9
6	10.53 (3)	± 0.06	600	0.58	30.3	143.2
7	10.13 (3)	± 0.11	700	0.40	20.9	164.1
8	9.78 (3)	± 0.08	800	0.35	18.3	182.4
9	9.42 (3)	± 0.03	900	0.36	18.8	201.2
10	9.03 (3)	± 0.01	1000	0.39	20.4	221.6
11	8.65 (3)	± 0.02	1100	0.38	19.9	241.5
12	8.33 (3)	± 0.04	1200	0.32	16.7	258.2
13	7.90 (3)	± 0.02	1300	0.43	22.5	280.7
14	7.51 (3)	± 0.02	1400	0.39	20.4	301.1
15	7.16 (3)	± 0.03	1500	0.35	18.3	319.4
16	6.81 (3)	± 0.02	1600	0.35	18.3	337.7
17	6.50 (3)	± 0.08	1700	0.31	16.2	353.9
18	6.09 (3)	± 0.03	1800	0.41	21.4	375.3
19	5.71 (3)	± 0.06	1900	0.38	19.9	395.2
20	5.30 (3)	± 0.06	2000	0.41	21.4	416.6
21	5.05 (3)	± 0.06	2100	0.25	13.1	429.7
22	4.82 (3)	± 0.01	2200	0.23	12.0	441.7
23	4.51 (3)	± 0.03	2300	0.31	16.2	457.9
24	4.23 (3)	± 0.03	2400	0.28	14.6	472.5
25	3.99 (3)	± 0.01	2500	0.24	12.5	485.0
26	3.67 (3)	± 0.04	2600	0.32	16.7	501.7
27	3.34 (3)	± 0.03	2700	0.33	17.2	518.9
28	3.02 (3)	± 0.03	2800	0.32	16.7	535.6
29	2.81 (3)	± 0.06	2900	0.21	11.0	546.6
30	2.51 (3)	± 0.04	3000	0.30	15.7	562.3
31	2.30 (3)	± 0.04	3100	0.21	11.0	573.3
32	2.03 (3)	± 0.03	3200	0.27	14.1	587.4
33	1.81 (3)	± 0.05	3300	0.22	11.5	598.9
34	1.56 (3)	± 0.05	3400	0.25	13.1	612.0
35	1.42 (3)	± 0.03	3500	0.14	7.3	619.3
			WATER PATCH DISCONTINUITIES			
36	1.33 (3)	± 0.05	3600	0.09	4.7	624.0
37	1.21 (3)	± 0.02	3700	0.11	5.8	629.8

* Starting Oil Weight 693 g Free Fall Distance 15 cm

Temperature 21°C

TABLE 3-2

RAW DATA – OIL-LOK 501 AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	10.19 (3)	± 0.02	–	–	–	–
1	9.46 (3)	± 0.02	100	0.73	38.2	38.2
2	8.89 (3)	± 0.02	200	0.57	29.6	67.8
3	8.39 (3)	± 0.02	300	0.50	26.0	93.8
4	7.94 (3)	± 0.02	400	0.45	23.5	117.3
5	7.58 (3)	± 0.02	500	0.36	18.6	135.9
6	7.17 (3)	± 0.03	600	0.41	21.3	157.2
7	6.74 (3)	± 0.05	700	0.43	22.7	179.9
8	6.32 (3)	± 0.02	800	0.42	21.8	201.7
9	5.97 (3)	± 0.04	900	0.35	18.3	220.0
10	5.58 (3)	± 0.03	1000	0.39	20.6	240.6
11	5.21 (3)	± 0.04	1100	0.37	19.3	259.9
12	4.96 (3)	± 0.04	1200	0.25	13.1	273.0
13	4.62 (3)	± 0.02	1300	0.34	17.9	290.9
14	4.36 (3)	± 0.03	1400	0.26	13.4	304.3
15	4.06 (3)	± 0.03	1500	0.30	15.5	319.8
16	3.83 (3)	± 0.04	1600	0.23	12.2	332.0
17	3.61 (3)	± 0.02	1700	0.22	11.5	343.5
18	3.30 (3)	± 0.03	1800	0.31	16.2	359.7
19	3.08 (3)	± 0.01	1900	0.22	11.7	371.4
20	2.79 (3)	± 0.06	2000	0.29	15.0	386.4
21	2.54 (3)	± 0.04	2100	0.25	13.2	399.6
22	2.32 (3)	± 0.04	2200	0.22	11.7	411.3
23	2.07 (3)	± 0.06	2300	0.25	12.9	424.2
24	1.91 (3)	± 0.06	2400	0.16	8.4	432.6
25	1.71 (3)	± 0.04	2500	0.20	10.6	443.2
26	1.49 (3)	± 0.14	2600	0.22	11.3	454.5
27	1.40 (3)	± 0.06	2700	0.09	4.5	459.0
		WATER PATCH DISCONTINUITIES				
28	1.29 (3)	± 0.04	2800	0.11	5.8	464.8
29	1.11 (3)	± 0.08	2900	0.18	9.4	474.2

* Starting Oil Weight 533 g   Free Fall Distance 30 cm

Temperature 21°C

TABLE 3-3

RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	9.85 (3)	± 0.03	–	–	–	–
1	9.17 (3)	± 0.01	100	0.68	35.6	35.6
2	8.64 (2)	± 0.01	200	0.53	27.7	63.3
3	8.16 (3)	± 0.04	300	0.48	25.1	88.4
4	7.78 (3)	± 0.02	400	0.38	19.9	108.3
5	7.45 (3)	± 0.04	500	0.33	17.2	125.5
6	7.04 (3)	± 0.04	600	0.41	21.4	146.9
7	6.67 (3)	± 0.02	700	0.37	19.3	166.2
8	6.28 (3)	± 0.02	800	0.39	20.4	186.6
9	5.98 (3)	± 0.02	900	0.30	15.7	202.3
10	5.70 (2)	± 0.01	1000	0.28	14.6	216.9
11	5.38 (2)	± 0.00	1100	0.32	16.7	233.6
12	5.11 (3)	± 0.05	1200	0.27	14.1	247.7
13	4.82 (3)	± 0.06	1300	0.29	15.2	262.9
14	4.56 (3)	± 0.10	1400	0.26	13.6	276.5
15	4.24 (3)	± 0.03	1500	0.32	16.7	293.2
16	4.04 (3)	± 0.01	1600	0.20	10.5	303.7
17	3.80 (3)	± 0.03	1700	0.24	12.6	316.3
18	3.53 (3)	± 0.01	1800	0.27	14.1	330.4
19	3.35 (3)	± 0.06	1900	0.18	9.4	339.8
20	3.18 (3)	± 0.09	2000	0.17	8.9	348.7
21	3.00 (2)	± 0.04	2100	0.18	9.4	358.1
22	2.79 (3)	± 0.03	2200	0.21	11.0	369.1
23	2.63 (3)	± 0.02	2300	0.16	8.4	377.5
24	2.46 (3)	± 0.03	2400	0.17	8.9	386.4
25	2.35 (3)	± 0.10	2500	0.11	5.7	392.1
26	2.22 (3)	± 0.05	2600	0.13	6.8	398.9
27	2.13 (3)	± 0.04	2700	0.09	4.7	403.6
28	2.05 (3)	± 0.06	2800	0.08	4.2	407.8
29	1.92 (3)	± 0.02	2900	0.13	6.8	414.6
30	1.84 (3)	± 0.07	3000	0.08	4.2	418.8
31	1.74 (3)	± 0.04	3100	0.10	5.2	424.0
32	1.65 (3)	± 0.03	3200	0.09	4.7	428.7
33	1.55 (3)	± 0.05	3300	0.10	5.2	433.9
34	1.46 (3)	± 0.06	3400	0.09	4.7	438.6
			WATER PATCH DISCONTINUITIES			
35	1.43 (3)	± 0.04	3500	0.03	1.6	440.2

* Starting Oil Weight 515 g Free Fall Distance 60 cm

Temperature 21°C

TABLE 3-4

RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	11.2^{9} (3)	± 0.1^{0}	-	-	-	-
1	10.53 (3)	± 0.09	100	0.7^{6}	$40.^{2}$	$40.^{2}$
2	9.89 (3)	± 0.05	200	0.64	33.9	$74.^{1}$
3	9.41 (3)	± 0.08	300	0.48	25.4	$99.^{5}$
4	8.99 (3)	± 0.06	400	0.42	22.2	$121.^{7}$
5	8.50 (3)	± 0.03	500	0.49	25.9	$147.^{6}$
6	8.06 (3)	± 0.09	600	0.44	23.3	$170.^{9}$
7	7.69 (3)	± 0.03	700	0.37	19.6	$190.^{5}$
8	7.3^{0} (3)	± 0.1^{1}	800	0.3^{9}	$20.^{6}$	$211.^{1}$
9	6.8^{8} (3)	± 0.1^{3}	900	0.4^{2}	$22.^{2}$	$233.^{3}$
10	6.40 (3)	± 0.06	1000	0.4^{3}	$25.^{4}$	$258.^{7}$
11	6.00 (3)	± 0.07	1100	0.40	21.2	$279.^{9}$
12	5.60 (3)	± 0.04	1200	0.40	21.2	$301.^{1}$
13	5.2^{1} (3)	± 0.2^{4}	1300	0.3^{9}	$20.^{3}$	$321.^{4}$
14	4.83 (3)	± 0.08	1400	0.3^{5}	$20.^{1}$	$341.^{5}$
15	4.47 (3)	± 0.05	1500	0.36	19.0	$360.^{5}$
16	4.13 (3)	± 0.06	1600	0.34	18.0	$378.^{5}$
17	3.8^{1} (3)	± 0.2^{9}	1700	0.3^{2}	$16.^{9}$	$395.^{4}$
18	3.51 (3)	± 0.07	1800	0.3^{0}	$15.^{9}$	$411.^{3}$
19	3.21 (3)	± 0.09	1900	0.30	15.9	$427.^{2}$
20	2.9^{1} (3)	± 0.4^{6}	2000	0.3^{0}	$15.^{9}$	$443.^{1}$
21	2.62 (3)	± 0.07	2100	0.2^{9}	$15.^{3}$	$458.^{4}$
22	2.2^{6} (3)	± 0.2^{6}	2200	0.3^{5}	$19.^{0}$	$477.^{4}$
23	1.9^{2} (3)	± 0.1^{6}	2300	0.3^{4}	$18.^{0}$	$495.^{4}$
24	1.7^{0} (3)	± 0.1^{6}	2400	0.2^{2}	$11.^{7}$	$507.^{1}$
25	1.5^{0} (3)	± 0.3^{4}	2500	0.2^{0}	$11.^{5}$	$518.^{6}$
26	1.32 (3)	± 0.07	2600	0.1^{8}	$9.^{4}$	$528.^{0}$
		WATER PATCH DISCONTINUITIES				
27	1.1^{9} (3)	± 0.2^{6}	2700	9.1^{3}	$6.^{9}$	$534.^{9}$

* Starting Oil Weight 597 g   Free Fall Distance 15 cm

Temperature 2°C

TABLE 3-5

RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	11.4^{2} (3)	± 0.1^{9}	-	-	-	-
1	10.66 (3)	± 0.05	100	0.7^{6}	$40.^{3}$	$40.^{3}$
2	9.9^{6} (3)	± 0.1^{1}	200	0.7^{0}	$37.^{0}$	$77.^{3}$
3	9.3^{1} (3)	± 0.1^{0}	300	0.6^{5}	$34.^{4}$	$111.^{7}$
4	8.7^{6} (3)	± 0.1^{6}	400	0.5^{5}	$29.^{0}$	$140.^{7}$
5	8.26 (3)	± 0.04	500	0.5^{0}	$26.^{5}$	$167.^{2}$
6	7.85 (3)	± 0.06	600	0.41	21.7	$188.^{9}$
7	7.45 (3)	± 0.09	700	0.40	21.2	$210.^{1}$
8	7.06 (3)	± 0.02	800	0.39	20.6	$230.^{7}$
9	6.71 (3)	± 0.02	900	0.35	18.5	$249.^{2}$
10	6.3^{1} (3)	± 0.1^{4}	1000	0.4^{0}	$21.^{2}$	$270.^{4}$
11	5.91 (3)	± 0.08	1100	0.4^{0}	$21.^{1}$	$291.^{5}$
12	5.5^{2} (3)	± 0.2^{6}	1200	0.3^{9}	$20.^{7}$	$312.^{2}$
13	5.16 (3)	± 0.08	1300	0.3^{6}	$19.^{0}$	$331.^{2}$
14	4.83 (3)	± 0.03	1400	0.33	17.5	$348.^{7}$
15	4.5^{1} (3)	± 0.1^{5}	1500	0.3^{2}	$16.^{9}$	$365.^{6}$
16	4.23 (3)	± 0.05	1600	0.2^{8}	$14.^{8}$	$380.^{4}$
17	3.8^{8} (3)	± 0.1^{3}	1700	0.3^{5}	$18.^{5}$	$398.^{9}$
18	3.55 (3)	± 0.09	1800	0.3^{3}	$17.^{5}$	$416.^{4}$
19	3.24 (3)	± 0.08	1900	0.31	16.4	$432.^{8}$
20	2.92 (3)	± 0.08	2000	0.32	16.9	$449.^{7}$
21	2.62 (3)	± 0.09	2100	0.30	15.9	$465.^{6}$
22	2.32 (3)	± 0.03	2200	0.30	15.9	$481.^{5}$
23	2.0^{6} (3)	± 0.2^{1}	2300	0.2^{6}	$13.^{8}$	$495.^{3}$
24	1.82 (3)	± 0.03	2400	0.2^{4}	$12.^{6}$	$507.^{9}$
25	1.58 (3)	± 0.06	2500	0.24	12.7	$520.^{6}$
26	1.37 (3)	± 0.05	2600	0.21	11.1	$531.^{7}$
			WATER PATCH DISCONTINUITIES			
27	1.21 (3)	± 0.01	2700	0.16	8.5	$540.^{2}$

* Starting Oil Weight 604 g Free Fall Distance 30 cm

Temperature 2°C

TABLE 3-6

RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	9.95 (3)	± 0.07	–	–	–	–
1	9.25 (3)	± 0.07	100	0.70	37.0	37.0
2	8.68 (3)	± 0.09	200	[illegible]	30.2	67.2
3	8.13 (3)	± 0.17	300	0.55	29.1	96.3
4	7.65 (3)	± 0.31	400	0.48	25.4	121.7
5	7.20 (3)	± 0.14	500	0.45	23.8	145.5
6	6.78 (3)	± 0.06	600	0.42	22.2	167.7
7	6.40 (3)	± 0.01	700	0.38	20.1	187.8
8	6.03 (3)	± 0.08	800	0.37	19.6	207.4
9	5.67 (3)	± 0.19	900	0.35	19.0	226.4
10	5.33 (3)	± 0.09	1000	0.34	18.0	244.4
11	5.03 (3)	± 0.04	1100	0.30	15.9	260.3
12	4.71 (3)	± 0.02	1200	0.32	16.9	277.2
13	4.41 (3)	± 0.07	1300	0.30	15.9	293.1
14	4.13 (3)	± 0.03	1400	0.28	14.8	307.9
15	3.87 (3)	± 0.07	1500	0.26	13.7	321.6
16	3.61 (3)	± 0.15	1600	0.25	13.8	335.4
17	3.37 (3)	± 0.01	1700	0.24	12.7	348.1
18	3.15 (3)	± 0.17	1800	0.22	11.7	359.8
19	2.95 (3)	± 0.10	1900	0.20	10.5	370.3
20	2.75 (3)	± 0.13	2000	0.20	10.6	380.9
21	2.57 (3)	± 0.09	2100	0.18	9.5	390.4
22	2.39 (3)	± 0.02	2200	0.18	9.6	400.0
23	2.22 (3)	± 0.11	2300	0.17	8.9	408.9
24	2.07 (3)	± 0.07	2400	0.15	8.0	416.9
25	1.92 (3)	± 0.19	2500	0.15	7.9	424.8
26	1.79 (3)	± 0.03	2600	0.13	6.9	431.7
27	1.66 (3)	± 0.08	2700	0.13	6.9	438.6
28	1.56 (3)	± 0.08	2800	0.10	5.3	449.9
29	1.46 (3)	± 0.10	2900	0.10	5.3	449.2
			WATER PATCH DISCONTINUITIES			

* Starting Oil Weight 526 g   Free Fall Distance 60 cm

Temperature 2°C

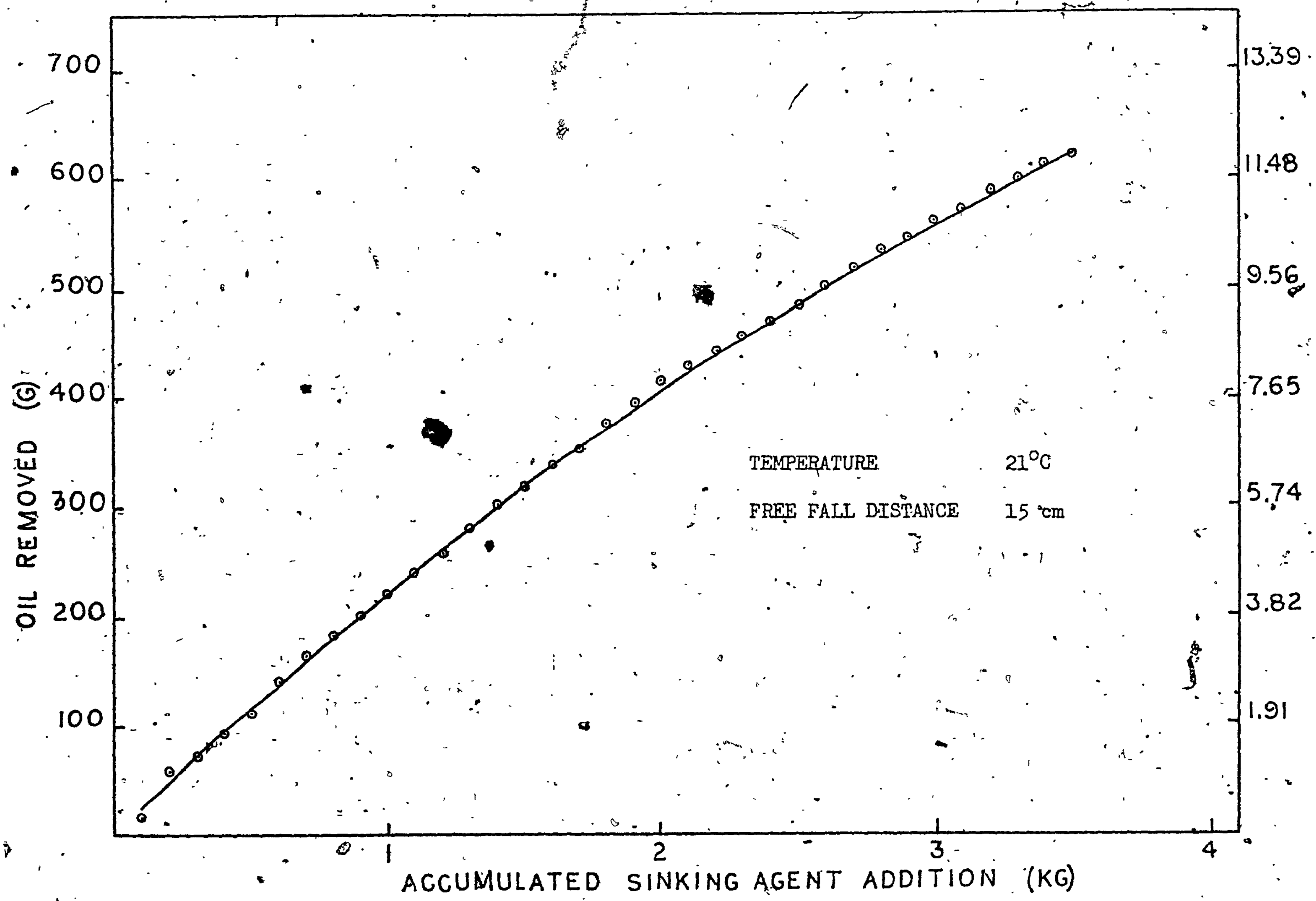

FIGURE 3-1 OIL-LOK 501 AND NO. 2 FUEL OIL - SINKING AGENT ADDED VS OIL REMOVED

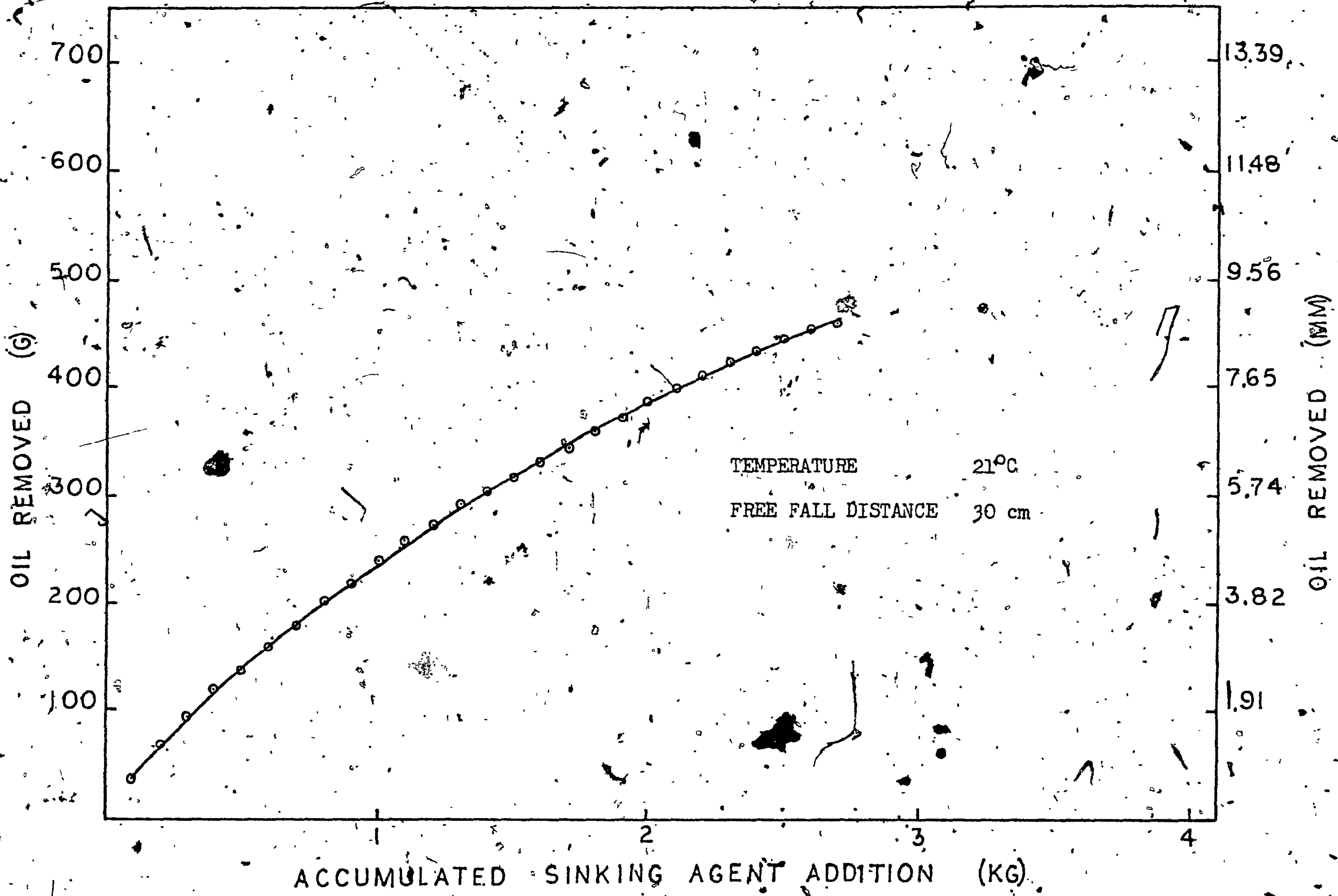

FIGURE 3-2 OIL-LOK 501 AND NO. 2 FUEL OIL - SINKING AGENT ADDED VS OIL REMOVED

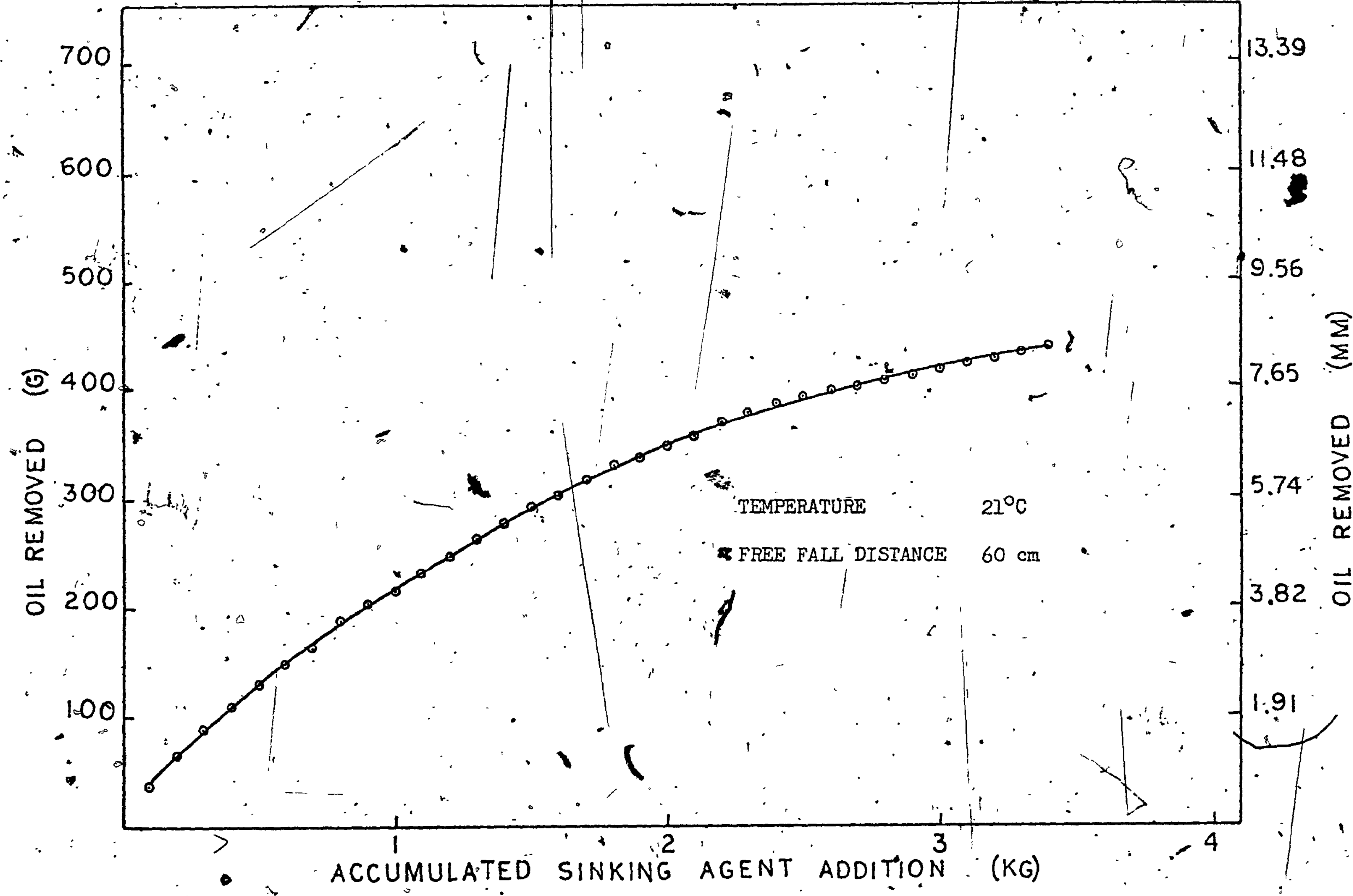

FIGURE 3-3 OIL-LOK 501 AND NO. 2 FUEL OIL - SINKING AGENT ADDED VS OIL REMOVED

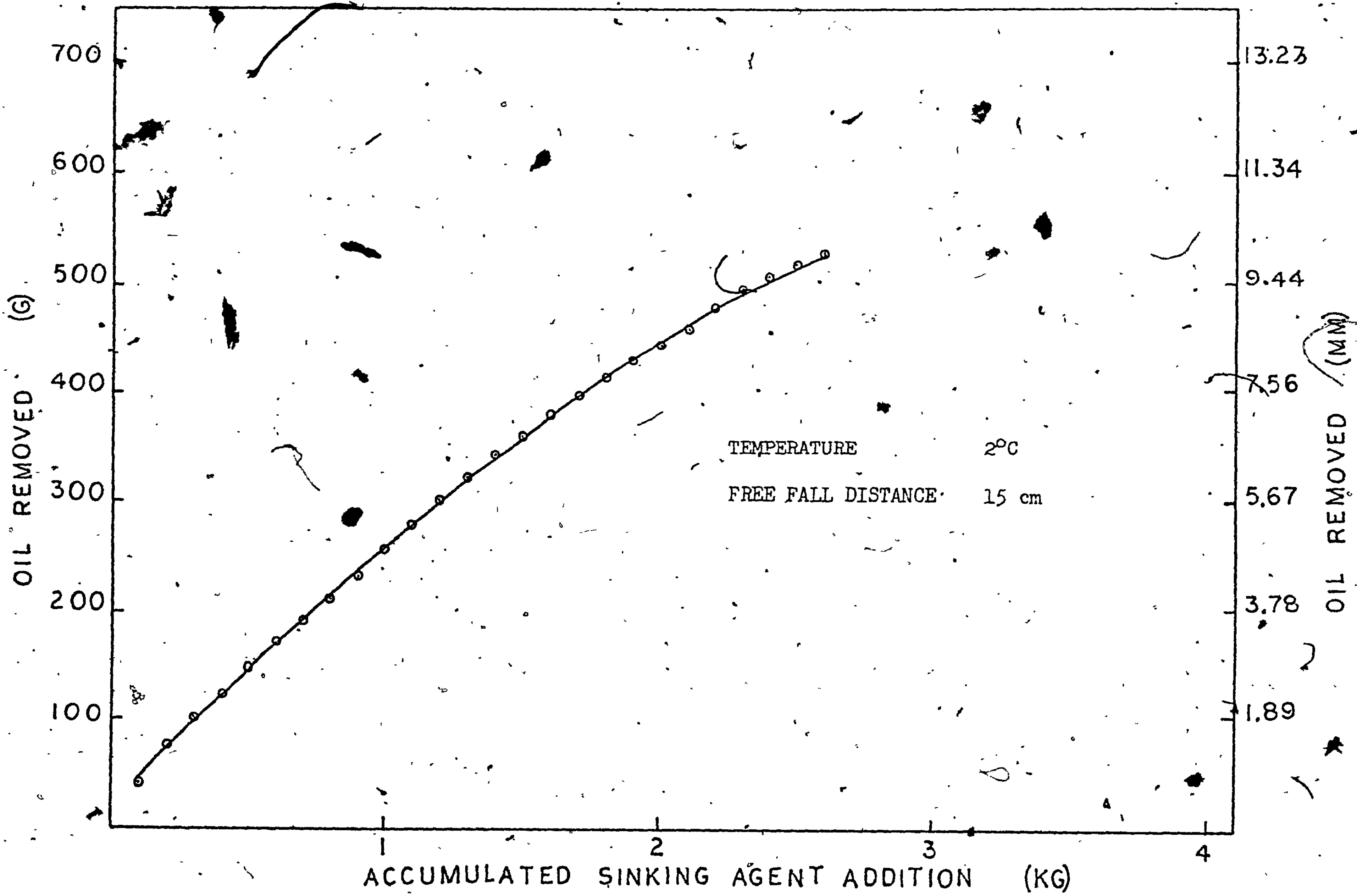

FIGURE 3-4 OIL-LOK 501 AND NO. 2 FUEL OIL - SINKING AGENT ADDED VS OIL REMOVED

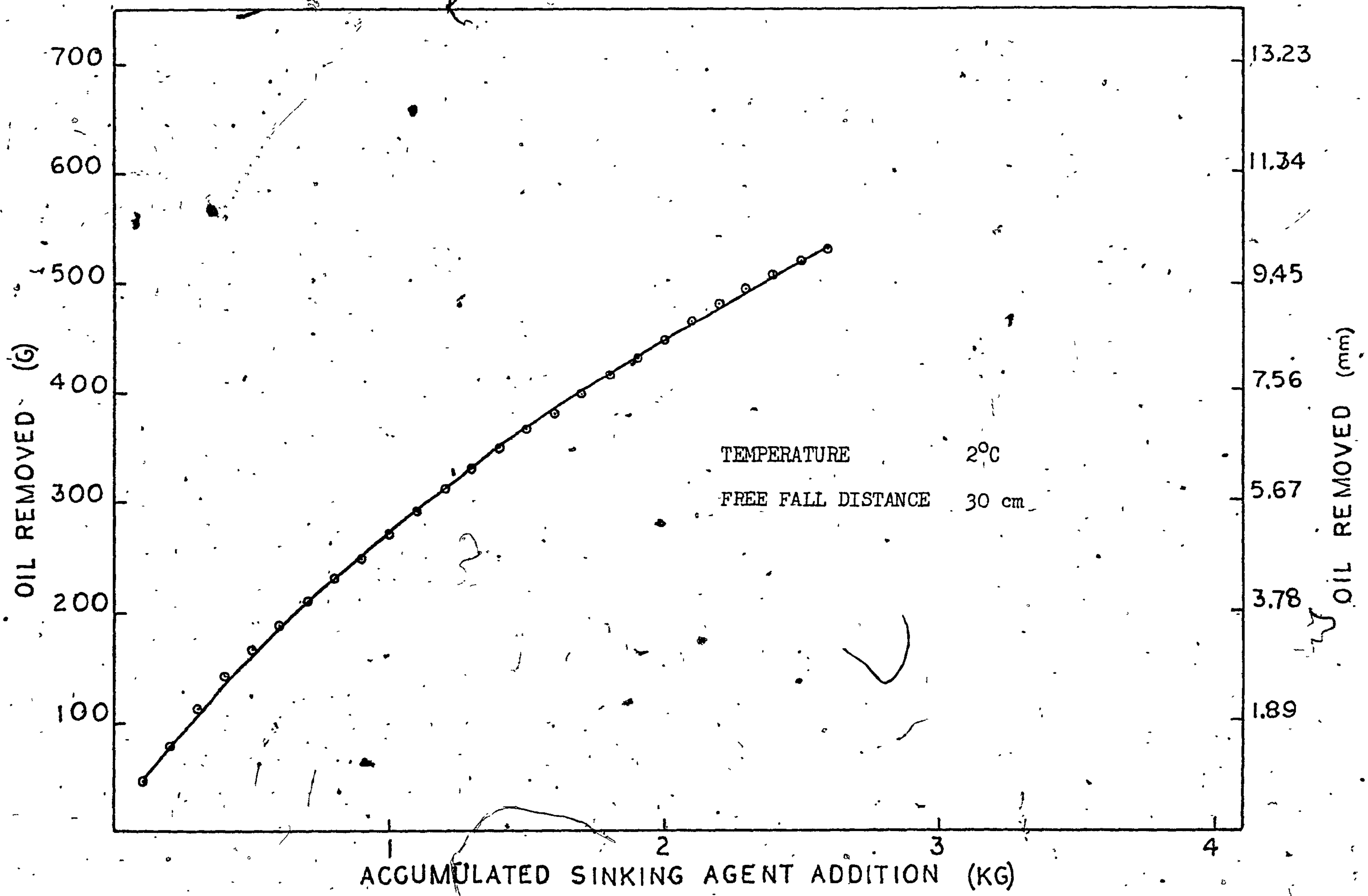

FIGURE 3-5 OIL-LOK 501 AND NO. 2 FUEL OIL-- SINKING AGENT ADDED VS OIL REMOVED

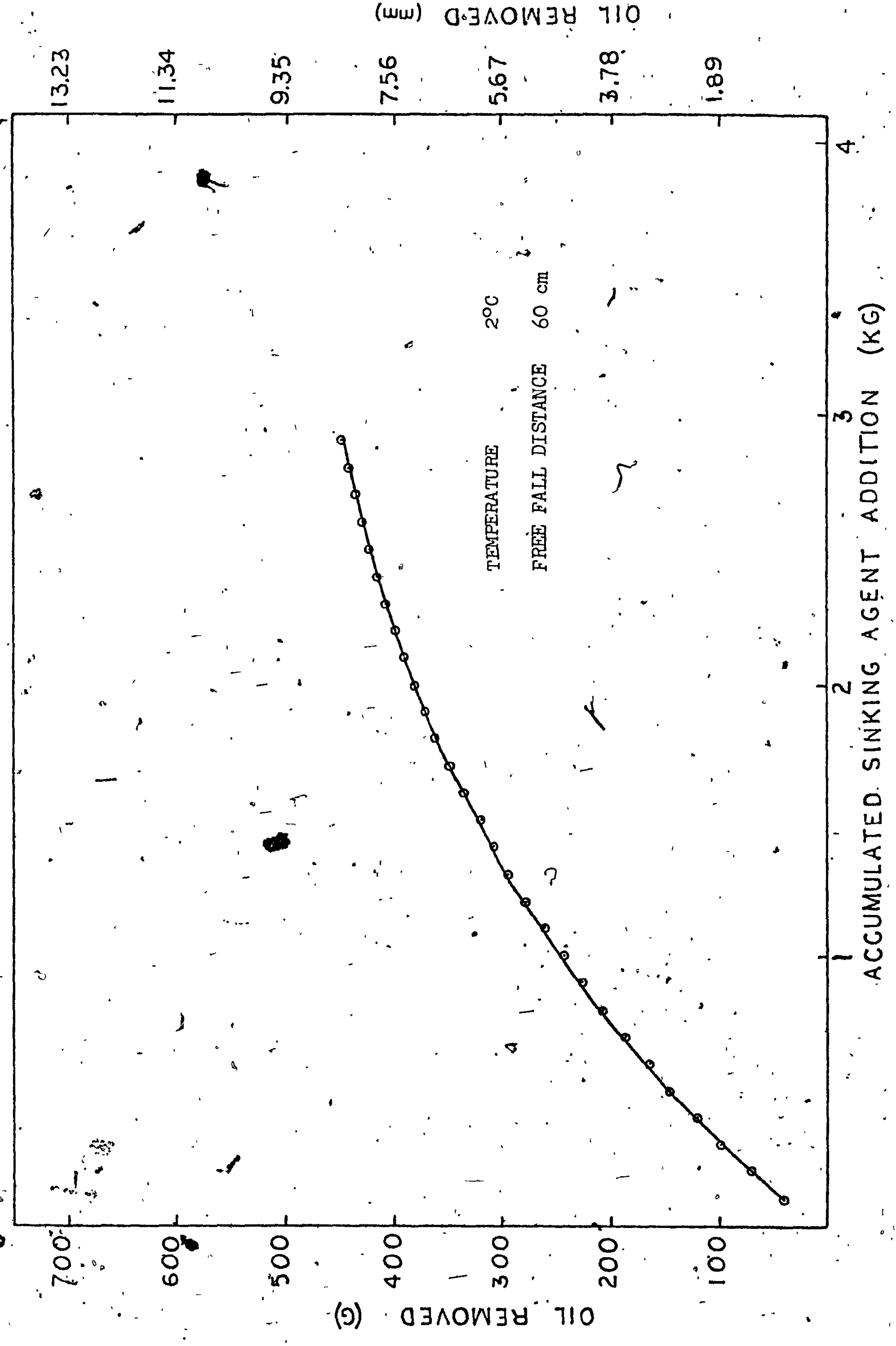

FIGURE 3-6. OIL-LOK 501 AND NO. 2 FUEL OIL - SINKING AGENT ADDED VS OIL REMOVED

TABLE 3-7

ANALYSIS OF RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.42 mm (g)	Sinking Agent/Oil Ratio by Weight
13.27	3500	619.3	5.65
11.89	3200	547.2	5.85
11.11	3000	506.4	5.92
10.13	2800	455.2	6.15
9.03	2500	397.7	6.29
7.90	2200	338.6	6.50
7.16	2000	299.9	6.67
6.09	1700	244.0	6.97
5.05	1400	189.6	7.38
3.99	1000	134.3	7.45
3.02	700	83.7	8.36
2.03	300	31.9	9.42

* Free Fall Distance 15 cm Temperatur[illegible]21°C

TABLE 3-8

ANALYSIS OF RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.40 mm (g)	Sinking Agent/Oil Ratio by Weight
10.19	2700	459.0	5.88
8.89	2500	391.2	6.39
7.94	2300	341.7	6.73
7.17	2100	301.8	6.96
5.97	1800	239.0	7.53
4.96	1500	186.0	8.06
4.06	1200	139.2	8.62
3.08	800	87.6	9.13
2.07	400	34.8	11.48

* Free Fall Distance 30 cm Temperature 21°C

TABLE 3-9

ANALYSIS OF RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.46 mm (g)	Sinking Agent/Oil Ratio by Weight
9.85	3400	438.6	7.75
9.17	3300	403.0	8.19
8.16	3100	350.2	8.85
7.04	2800	291.7	9.60
5.98	2500	236.3	10.58
5.11	2200	190.9	11.52
4.04	1800	134.9	13.34
3.00	1300	80.5	16.13
2.05	600	30.8	19.49

* Free Fall Distance 60 cm Temperature 21°C

TABLE 3-10

ANALYSIS OF RAW DATA - OIL-LOK 501 AND N). 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.32 mm (g)	Sinking Agent/Oil Ratio by Weight
11.29	2600	528.0	4.92
9.89	2400	453.9	5.29
8.99	2200	406.3	5.41
8.06	2000	357.1	5.60
6.88	1700	294.7	5.77
6.00	1500	248.1	6.04
4.83	1200	186.5	6.43
4.13	1000	149.5	6.69
2.91	600	84.9	7.07
1.92	300	32.6	9.20

* Free Fall Distance 15 cm Temperature 2°C

TABLE 3-11

ANALYSIS OF RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.57 mm (g)	Sinking Agent/Oil Ratio by Weight
10.66	2500	491.4	5.08
9.96	2400	454.4	5.28
8.76	2200	391.0	5.62
7.85	2000	342.8	5.83
7.06	1800	301.0	5.98
5.91	1500	240.2	6.24
5.16	1300	200.5	6.48
3.88	900	132.8	6.78
2.92	600	82.0	7.32
2.06	300	36.4	8.24

* Free Fall Distance 30 cm Temperature 2°C

TABLE 3-12

ANALYSIS OF RAW DATA - OIL-LOK 501 AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.46 mm (g)	Sinking Agent/Oil Ratio by Weight
9.95	2900	449.2	6.45
9.25	2800	412.2	6.79
8.13	2600	352.9	7.37
7.20	2400	303.7	7.90
6.03	2100	241.8	8.68
5.03	1800	188.9	9.53
4.13	1500	141.3	10.61
2.95	1000	78.9	12.67
2.07	500	31.3	15.97

* Free Fall Distance 60 cm Temperature 2°C

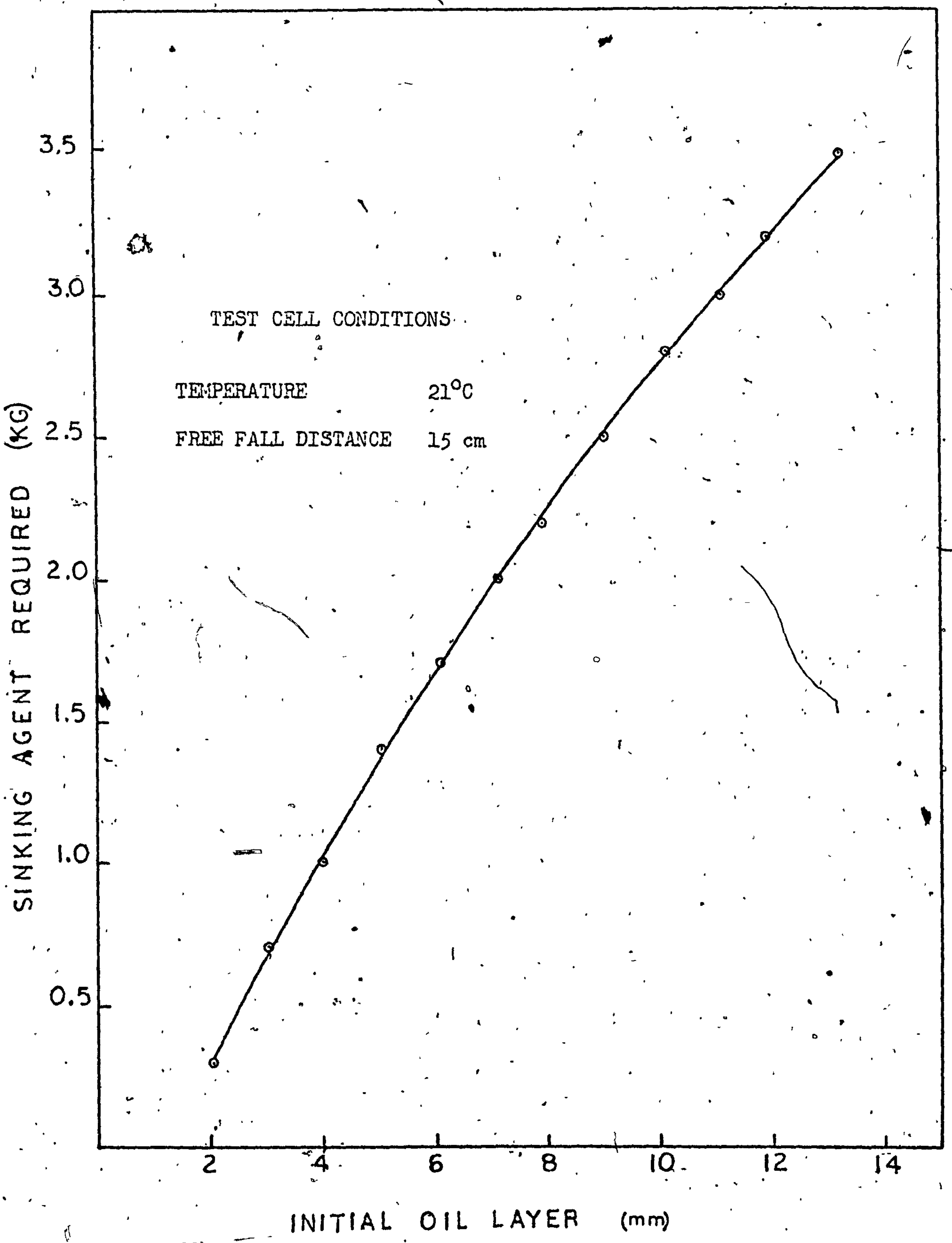

FIGURE 3-7 OIL-LOK 501 AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

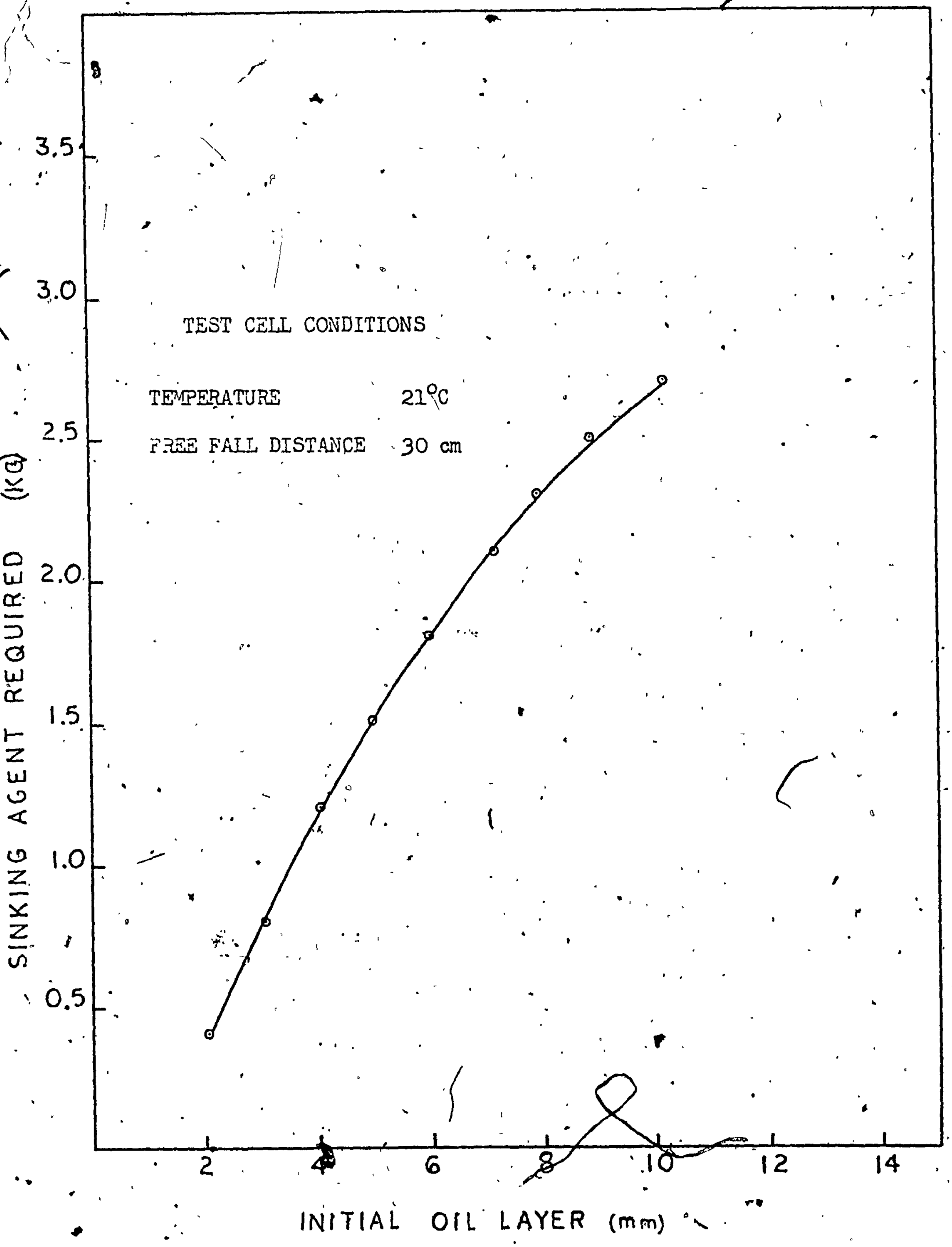

FIGURE 3-8 OIL-LOK 501 AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

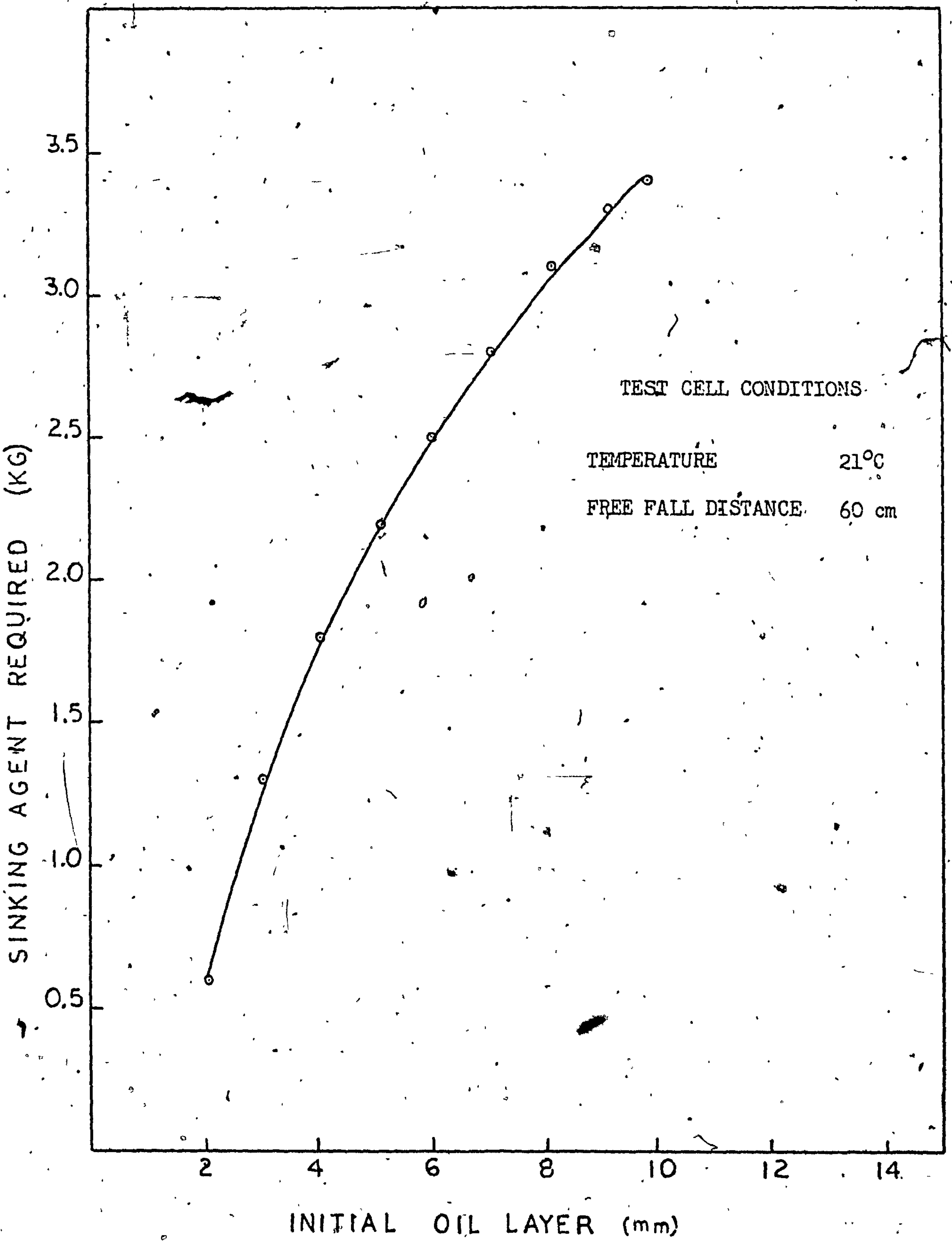

FIGURE 3-9 OIL-LOK 501 AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

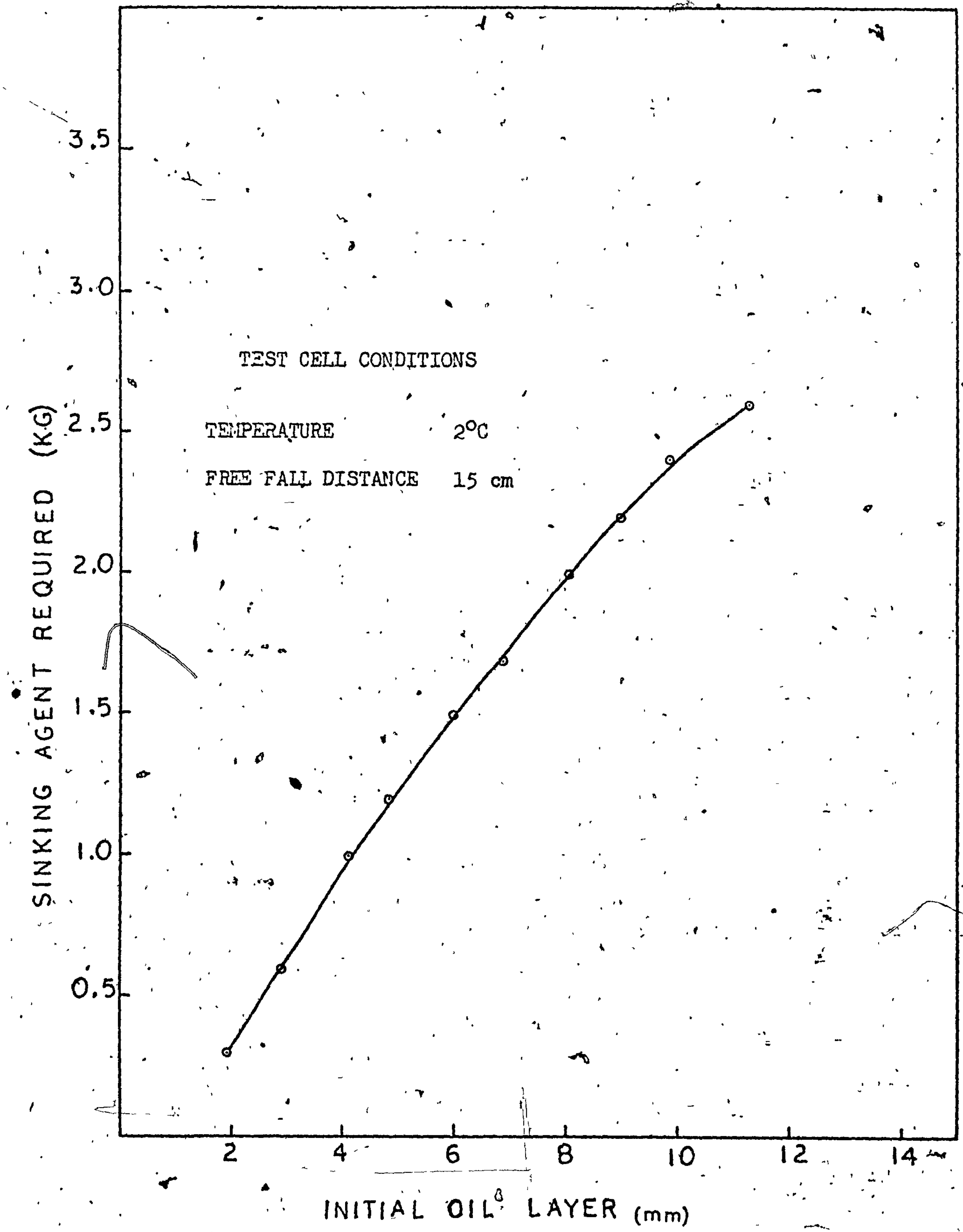

FIGURE 3-10 OIL-LOK 501 AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

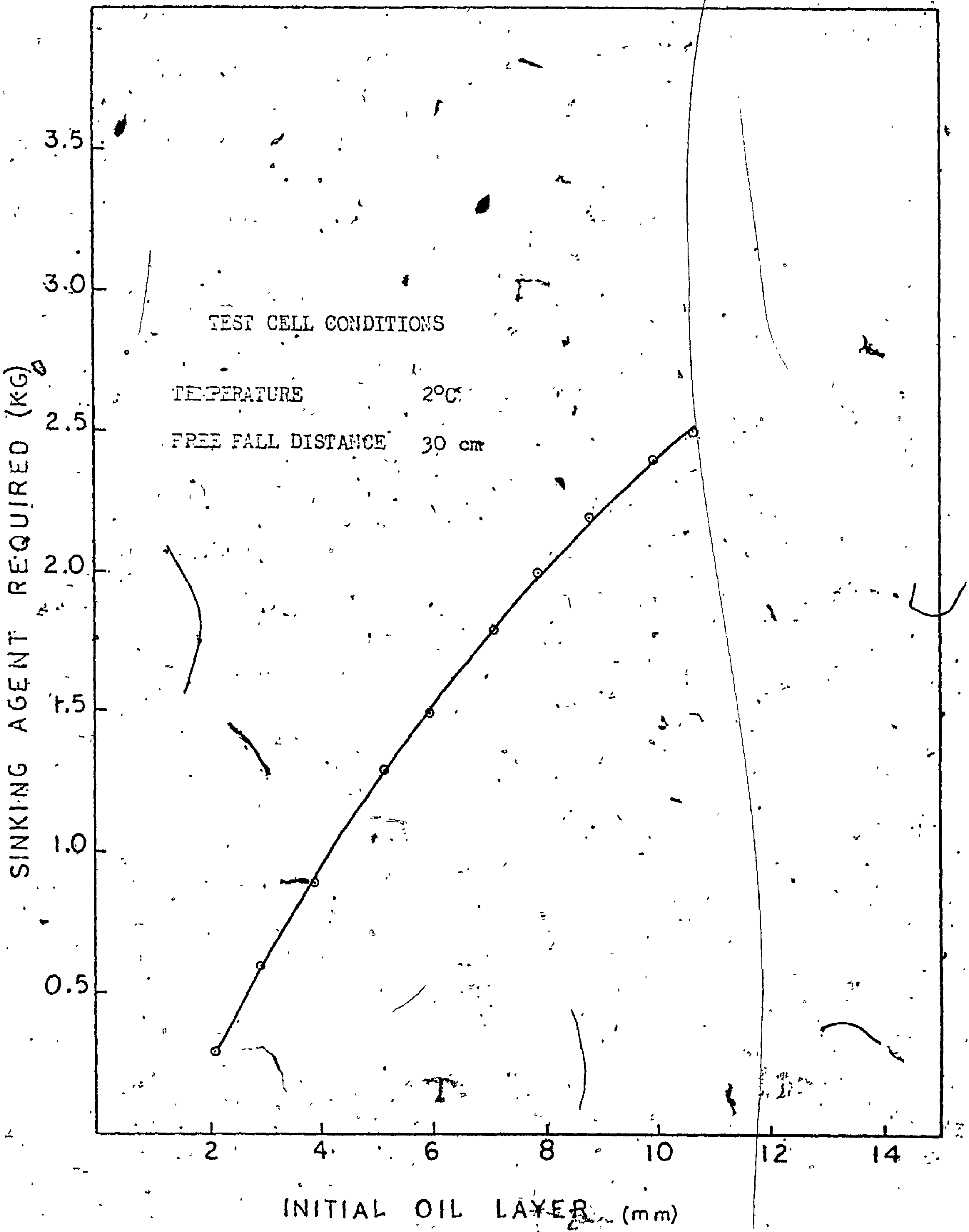

FIGURE 3-11 : OIL-LOK 501 AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

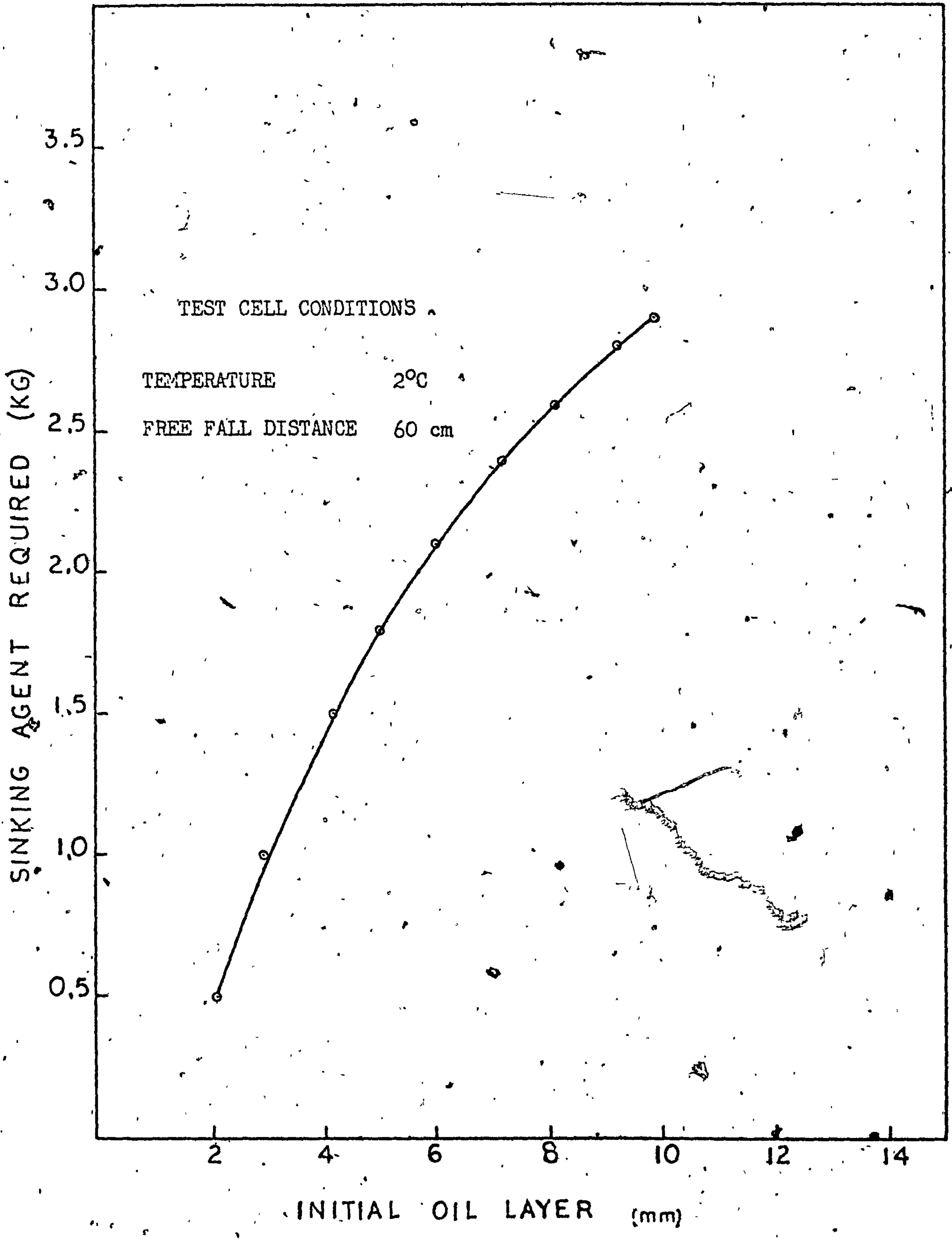

FIGURE 3-12 OIL-LOK 501 AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

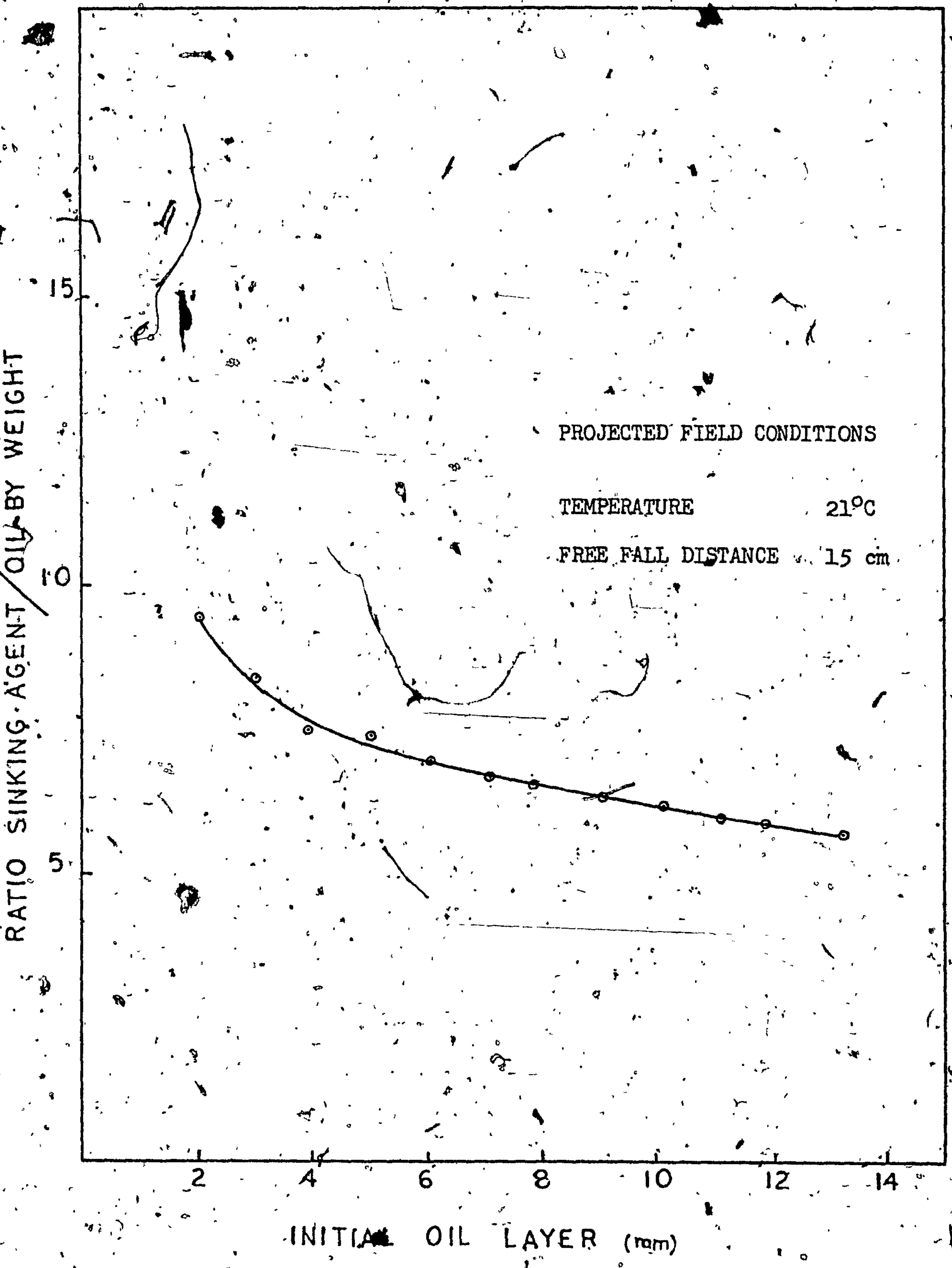

FIGURE 3-13 OIL-LOK 501 AND NO. 2 FUEL OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

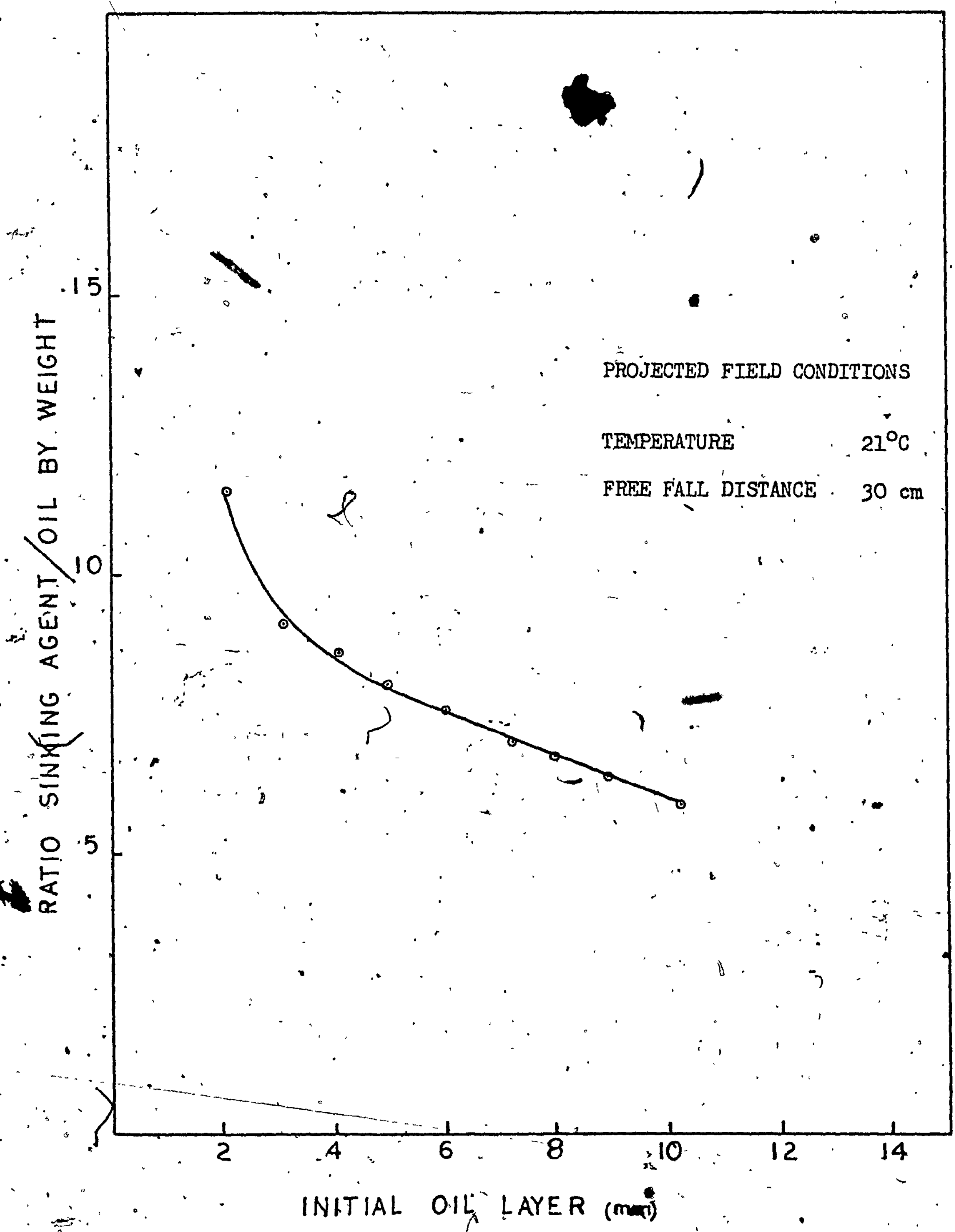

FIGURE 3-14 OIL-LOK 501 AND NO. 2 FUEL OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

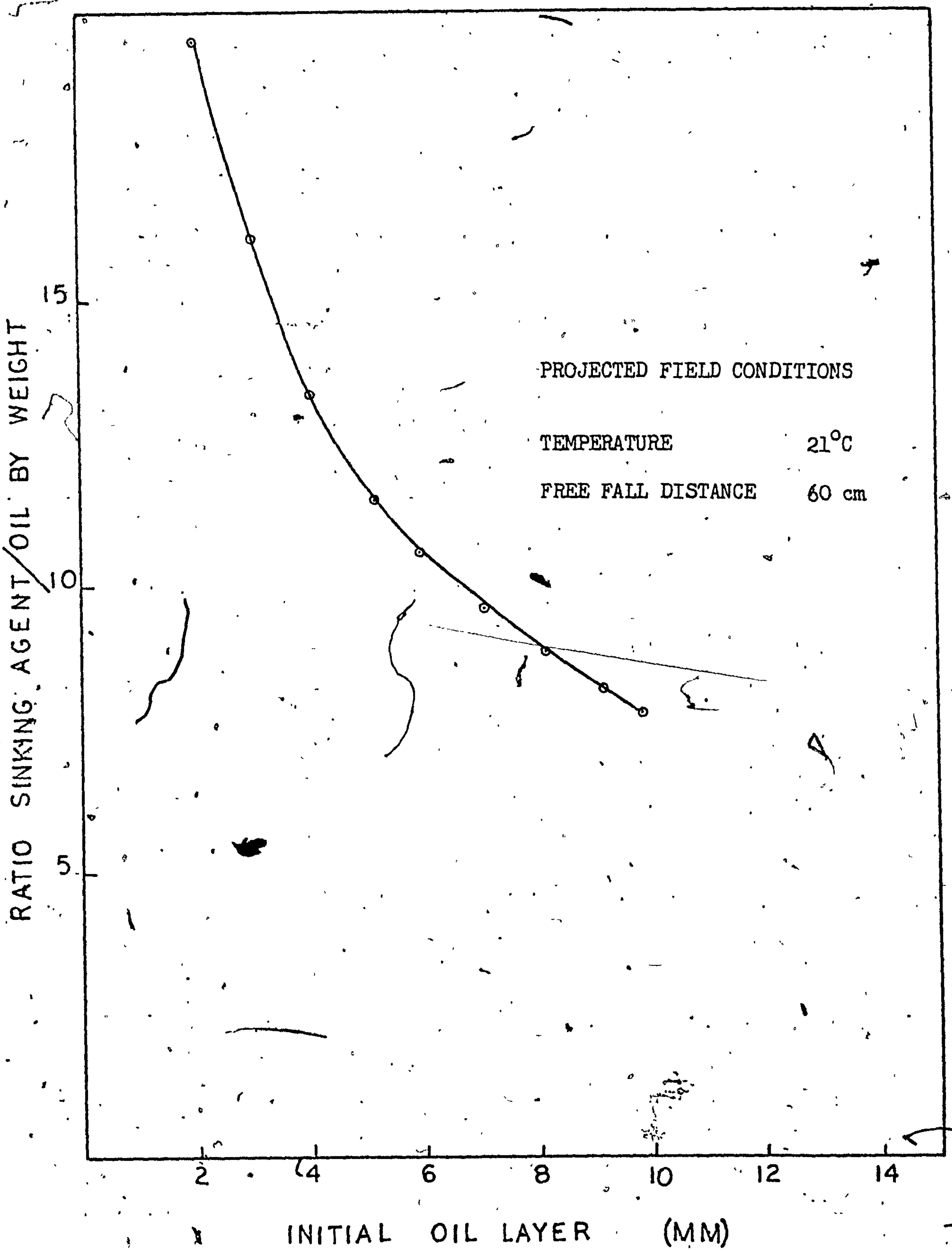

FIGURE 3-15 OIL-LOK 501 AND NO. 2 FUEL OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

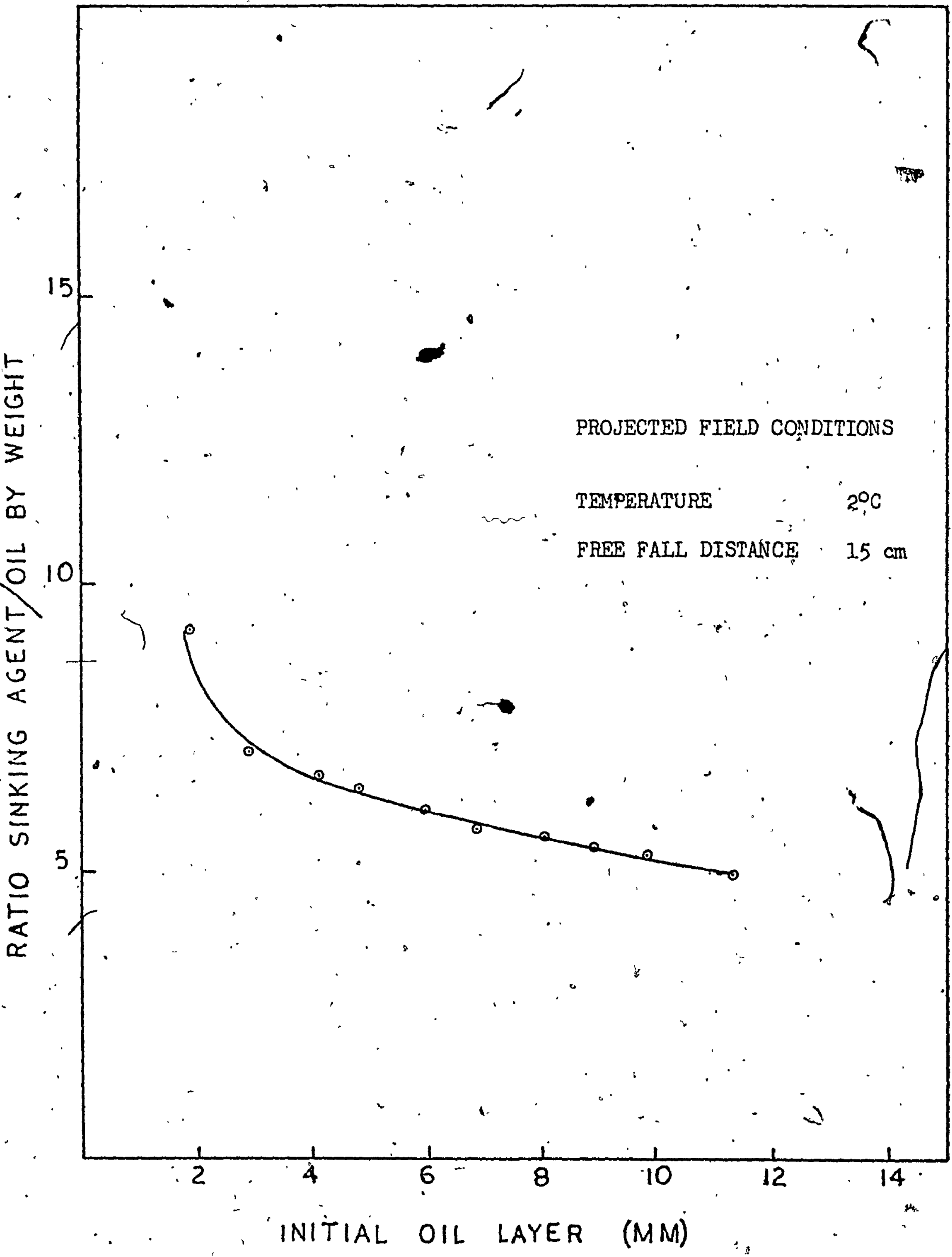

FIGURE 3-16 OIL-LOK 501 AND NO. 2 FUEL OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

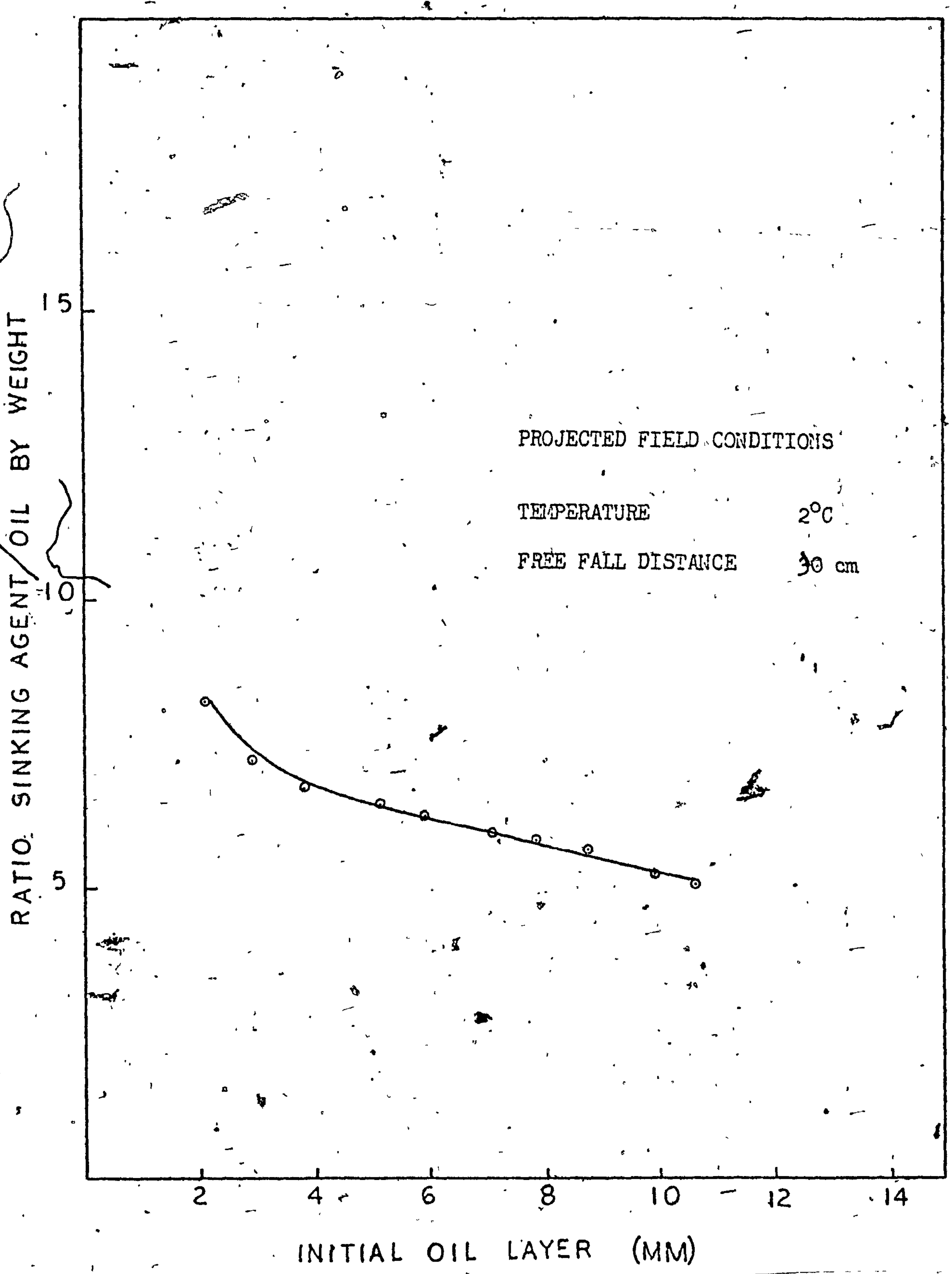

FIGURE 3-17 OIL-LOK 501 AND NO. 2 FUEL OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

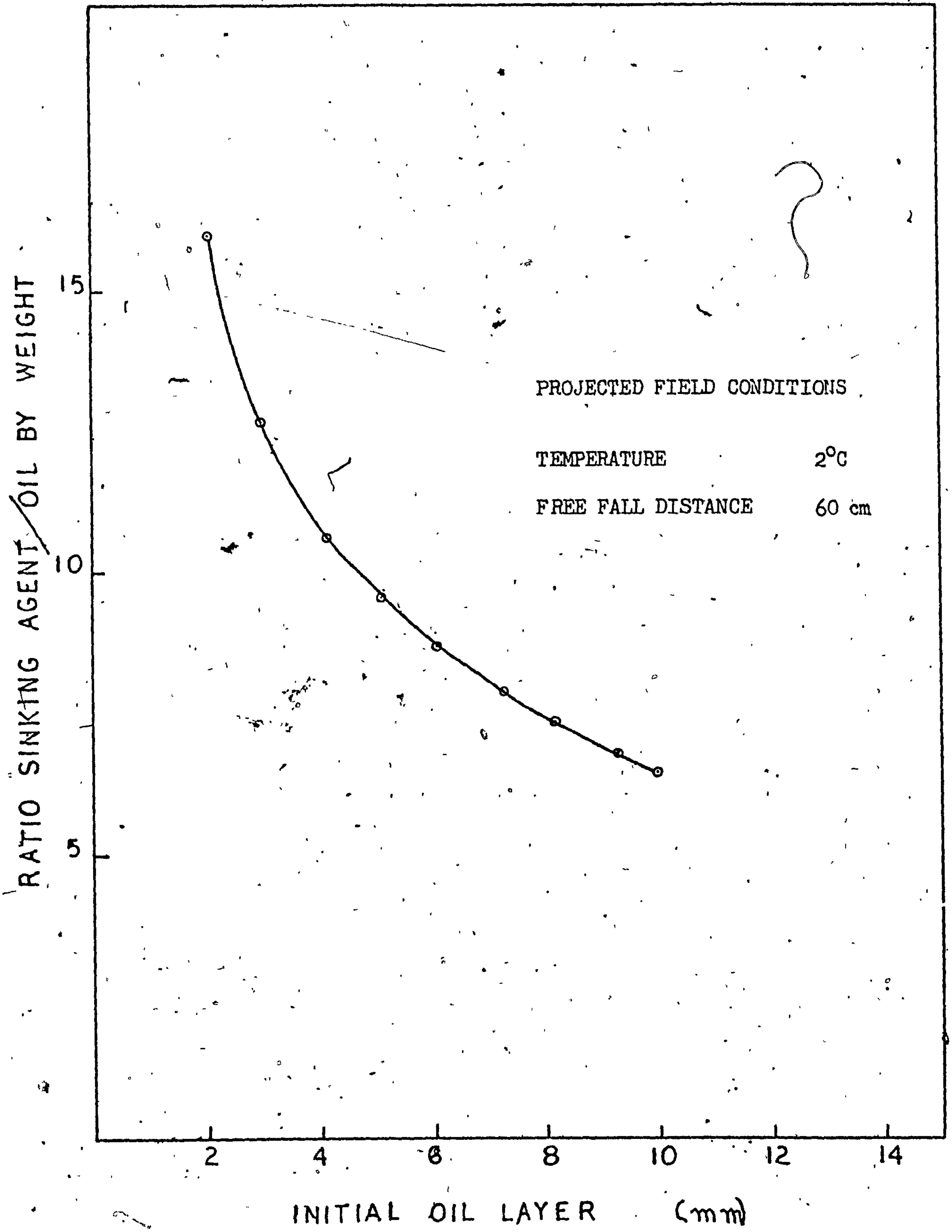

FIGURE 3-18 OIL-LOK 501 AND NO. 2 FUEL OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

APPENDIX IV

OIL-LOK 501 AND NO. 6 BUNKER OIL

EXPERIMENTAL DATA AND DATA ANALYSES

TABLE 4-1

RAW DATA – OIL-LOK 501 AND NO. 6 BUNKER OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	12.73 (3)	± 0.06	-	-	-	-
1	10.33 (3)	± 0.01	100	2.40	144.0	144.0
2	8.0^{2} (3)	± 0.1^{0}	200	2.3^{1}	138.^{6}	282.^{6}
3	5.9^{9} (3)	± 0.1^{1}	300	2.0^{3}	121.^{8}	404.^{4}
4	4.3^{0} (3)	± 0.1^{0}	400	1.6^{9}	101.^{4}	505.^{8}
5	2.89 (3)	± 0.08	500	1.4^{1}	84.^{6}	590.^{4}
6	1.84 (3)	± 0.04	600	1.05	63.0	653.^{4}
7	1.01 (3)	± 0.06	700	0.83	49.8	703.^{2}
		WATER PATCH DISCONTINUITIES				
8	0.20 (3)	± 0.04	800	0.81	48.6	751.^{8}

* Starting Oil Weight	764 g	Free Fall Distance	15 cm
Temperature	21°C		

TABLE 4-2

RAW DATA - OIL-LOK 501 AND NO. 6 BUNKER OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	14.48 (3)	± 0.04	-	-	-	-
1	11.98 (3)	± 0.05	100	2.50	150.0	150.0
2	9.5^6 (3)	± 0.1^3	200	2.4^2	145.^{2}	295.^{2}
3	7.3^9 (3)	± 0.1^2	300	2.1^7	130.^{2}	425.^{4}
4	5.5^3 (3)	± 0.2^5	400	1.8^4	110.^{4}	535.^{8}
5	4.0^4 (3)	± 0.2^1	500	1.5^1	90.^{6}	626.^{4}
6	2.8^2 (3)	± 0.1^2	600	1.2^2	73.^{2}	699.^{6}
7	1.9^1 (3)	± 0.1^4	700	0.9^1	54.^{6}	754.^{2}
8	1.1^9 (3)	± 0.1^1	800	0.7^2	43.^{2}	797.^{4}
			WATER PATCH DISCONTINUITIES			
9	0.51 (3)	± 0.09	900	0.6^8	40.^{8}	838.^{2}

* Starting Oil Weight	868 g	Free Fall Distance	30 cm
Temperature	21°C		

TABLE 4-3

RAW DATA - OIL-LOK 501 AND NO. 6 BUNKER OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	11.77 (3)	± 0.07	-	-	-	-
1	9.7^8 (3)	± 0.2^2	100	1.9^9	$119.^4$	$119.^4$
2	8.1^0 (3)	± 0.1^7	200	1.6^8	$100.^8$	$220.^2$
3	6.6^0 (3)	± 0.1^2	300	1.5^0	$90.^0$	$310.^2$
4	5.2^4 (3)	± 0.2^9	400	1.3^6	$81.^6$	$391.^8$
5	4.00 (3)	± 0.05	500	1.2^4	$74.^4$	$466.^2$
6	3.02 (3)	± 0.09	600	0.98	58.8	$525.^0$
7	2.2^1 (3)	± 0.2^4	700	0.8^1	$48.^6$	$573.^6$
8	1.52 (3)	± 0.08	800	0.6^9	$41.^4$	$615.^0$
			SLIGHT WATER PATCH DISCONTINUITIES			
9	0.91 (3)	± 0.08	900	0.61	36.6	$651.^6$
			WATER PATCH DISCONTINUITIES			
10	0.3^5 (3)	± 0.1^6	1000	0.5^6	$33.^6$	$685.^2$

* Starting Oil Weight 706 g Free Fall Distance 60 cm

Temperature 21°C

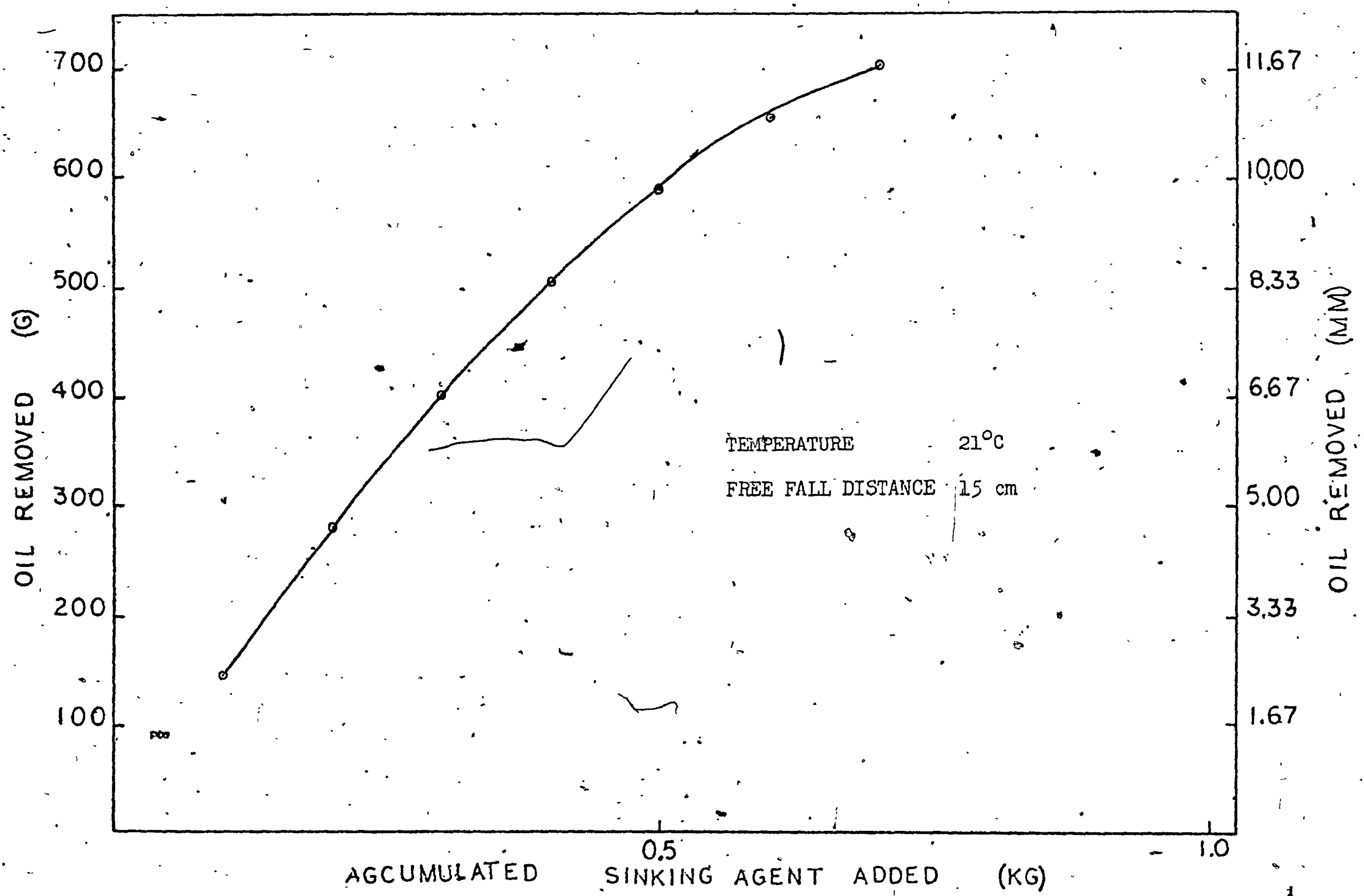

FIGURE 4-1 OIL-LOK 501 AND NO. 6 BUNKER OIL - SINKING AGENT ADDED VS OIL REMOVED

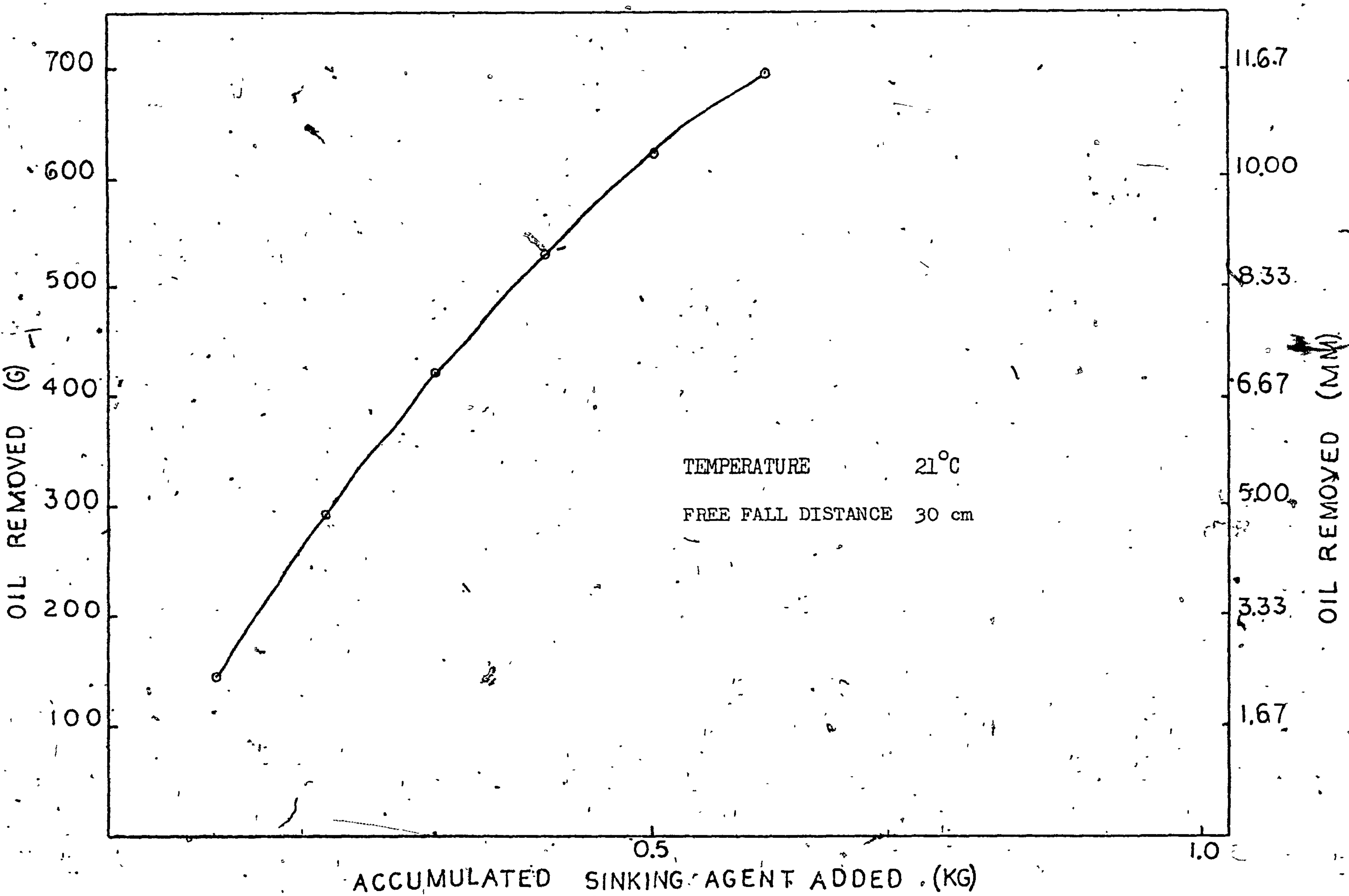

FIGURE 4-2 OIL-LOK 501 AND NO. 6 BUNKER OIL - SINKING AGENT ADDED VS OIL REMOVED

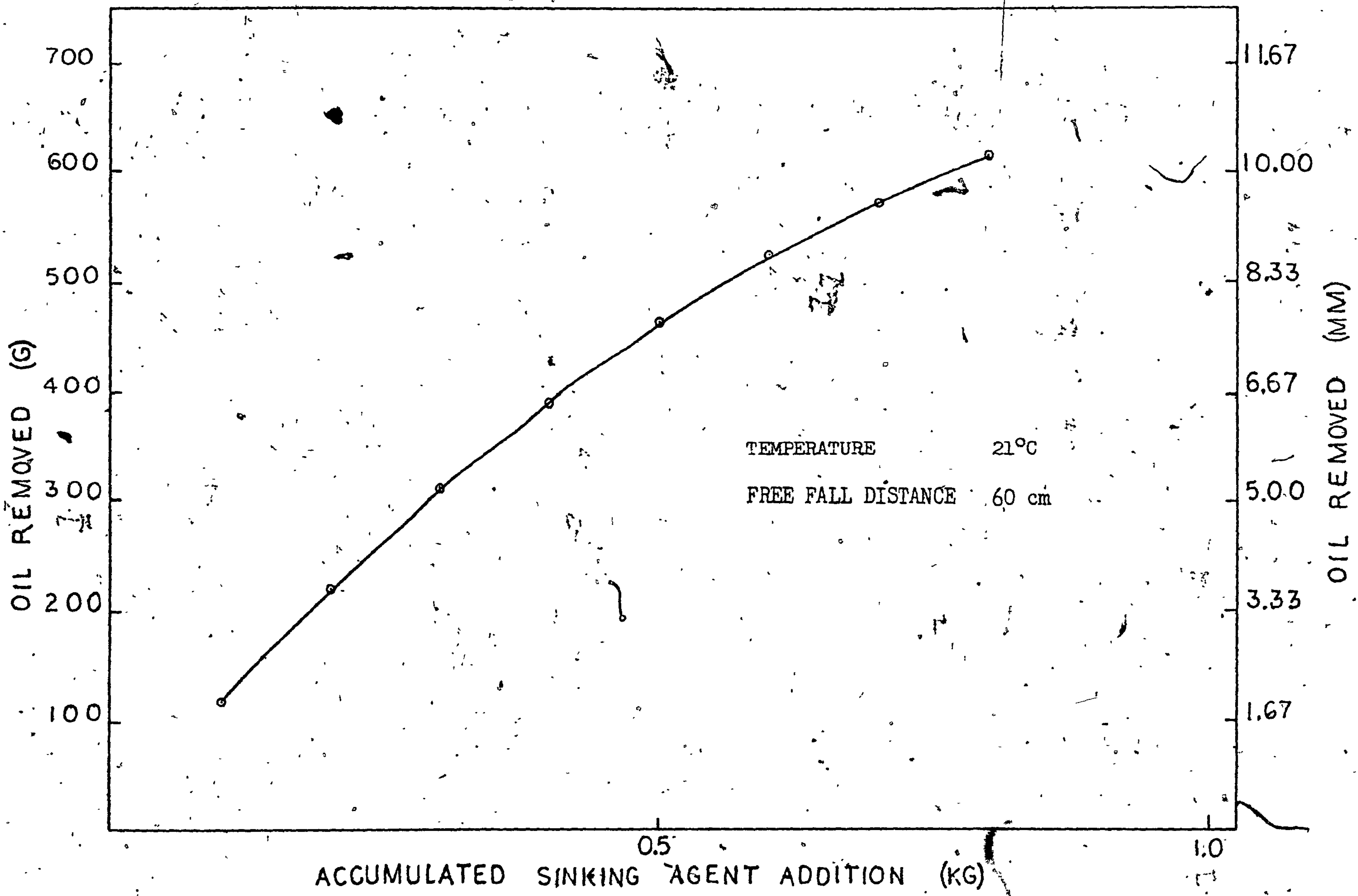

FIGURE 4-3 OIL-LOK 501 AND NO. 6 BUNKER OIL - SINKING AGENT ADDED VS OIL REMOVED

TABLE 4-4

ANALYSIS OF RAW DATA - OIL-LOK 501 AND NO. 6 BUNKER OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.01 mm (g)	Sinking Agent/Oil Ratio by Weight
12.73	700	703.2	1.00
10.33	600	559.2	1.07
8.02	500	420.6	1.19
5.99	400	298.8	1.34
4.30	300	197.4	1.52
2.89	200	112.8	1.77
1.84	100	49.8	2.01

* Free Fall Distance 15 cm Temperature 21°C

TABLE 4-5

ANALYSIS OF RAW DATA - OIL-LOK 501 AND NO. 6 BUNKER OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.19 mm. (g)	Sinking Agent/Oil Ratio by Weight
14.48	800	797.4	1.00
11.98	700	647.4	1.08
9.56	600	502.2	1.19
7.39	500	372.0	1.34
5.55	400	261.6	1.53
4.04	300	171.0	1.75
2.82	200	97.8	2.04
1.91	100	43.2	2.31

* Free Fall Distance 30 cm Temperature 21°C

TABLE 4-6

ANALYSIS OF RAW DATA - OIL-LOK 501 AND No. 6 BUNKER OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 0.91 mm (g)	Sinking Agent/Oil Ratio by Weight
11.77	900	651.6	1.38
9.76	800	532.2	1.50
8.10	700	431.4	1.62
6.60	600	341.4	1.76
5.24	500	259.8	1.92
4.00	400	185.4	2.16
3.02	300	126.6	2.37
2.21	200	78.0	2.56
1.52	100	36.6	2.73

Free Fall Distance 60 cm Temperature 21°C

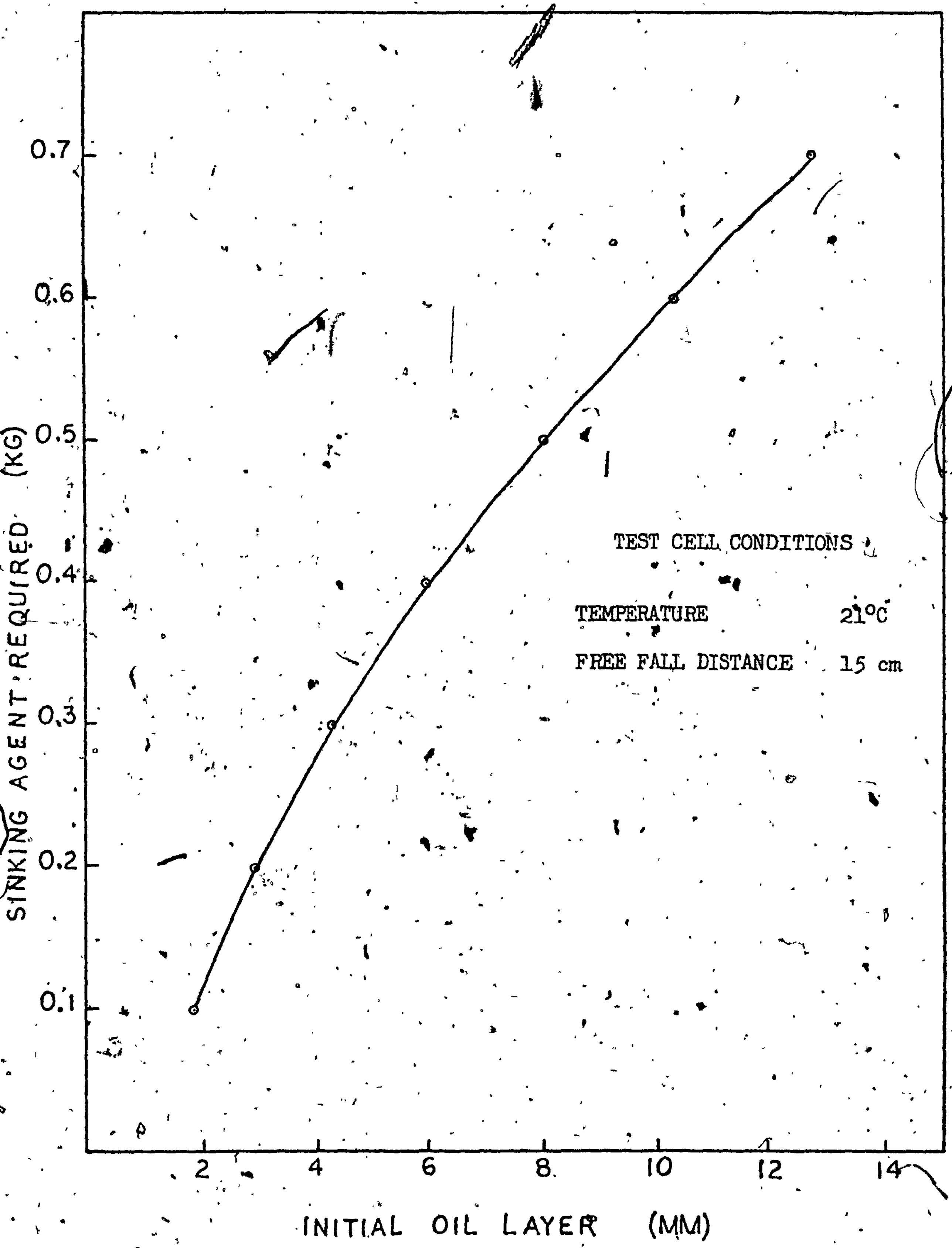

FIGURE 4-4 OIL-LOK 501 AND NO. 6 BUNKER OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

APPENDIX V

ZORB-ALL AND WESTERN CRUDE OIL

EXPERIMENTAL DATA AND DATA ANALYSES

TABLE 5-1

RAW DATA - ZORB-ALL AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	10.10 (3)	± 0.09	-	-	-	-
1	7.53 (3)	± 0.05	100	2.57	132.8	132.8
2	5.3^{7} (3)	± 0.1^{2}	200	2.1^{6}	$111.^{6}$	$244.^{4}$
3	3.22 (3)	± 0.07	300	2.1^{5}	$111.^{1}$	$355.^{5}$
4	1.42 (3)	± 0.05	400	1.80	92.9	$448.^{4}$
5	0.21 (3)	± 0.07	500	1.21	62.5	$510.^{9}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 534 g Free Fall Distance 15 cm

Temperature 21°C

TABLE 5-2

RAW DATA - ZORB-ALL AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	11.38 (3)	± 0.03	-	-	-	-
1	8.89 (3)	± 0.04	100	2.49	129.6	129.6
2	6.72 (3)	± 0.09	200	2.17	112.1	240.7
3	4.72 (3)	± 0.26	300	2.00	103.3	344.0
4	2.86 (3)	± 0.36	400	1.86	96.1	440.1
5	1.44 (2)	± 0.06	500	1.42	73.4	513.6
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight - 577 g Free Fall Distance 60 cm

Temperature 21°C

TABLE 5-3

RAW DATA - ZORB-ALL AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	11.3^{0} (3)	± 0.2^{9}	-	-	-	-
1	8.7^{2} (3)	± 0.2^{8}	100	2.5^{8}	$134.^{7}$	$134.^{7}$
2	6.5^{1} (3)	± 0.2^{4}	200	2.2^{1}	$115.^{4}$	$250.^{1}$
3	4.5^{1} (3)	± 0.2^{1}	300	2.0^{0}	$104.^{4}$	$354.^{5}$
4	2.5^{4} (3)	± 0.1^{1}	400	1.9^{7}	$102.^{9}$	$457.^{4}$
5	0.93 (3)	± 0.06	500	1.6^{1}	$84.^{1}$	$541.^{5}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 599 g   Free Fall Distance 15 cm

Temperature 2°C

TABLE 5-4

RAW DATA – ZORB-ALL AND WESTERN CRUDE OIL*

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	11.5^4 (3)	$\pm 0.1^0$	–	–	–	–
1	8.8^4 (3)	$\pm 0.2^4$	100	2.7^0	$141.^0$	$141.^0$
2	6.2^7 (3)	$\pm 0.1^0$	200	2.5^7	$134.^2$	$275.^2$
3	3.6^3 (3)	$\pm 0.1^1$	300	2.6^4	$137.^8$	$412.^0$
4	1.5^3 (3)	$\pm 0.2^3$	400	2.1^0	$110.^0$	$522.^0$
			WATER PATCH DISCONTINUITIES			

* Starting Oil Weight 603 g   Free Fall Distance 60 cm

Temperature 2°C

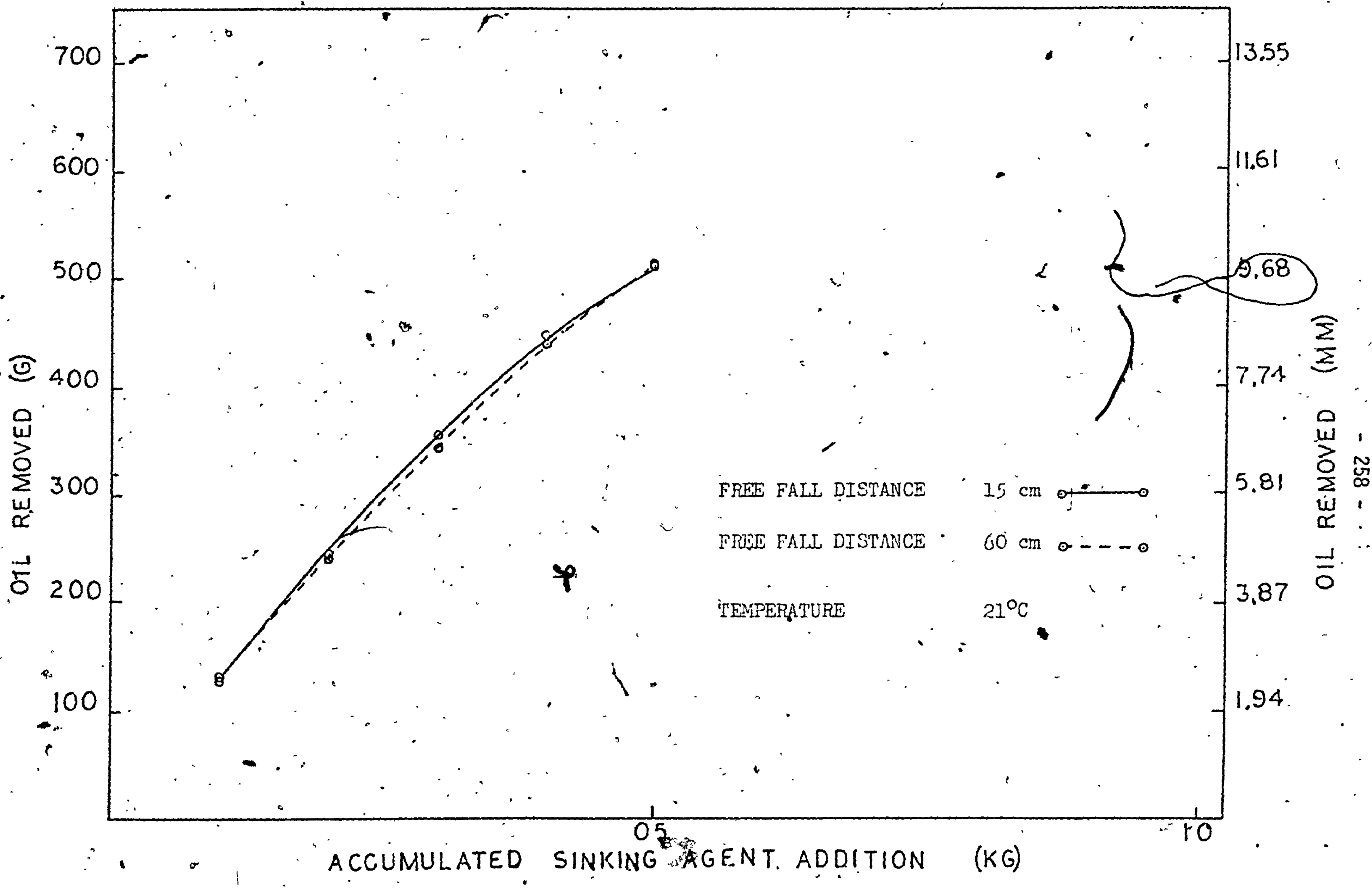

FIGURE 5-1 ZORB-ALL AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

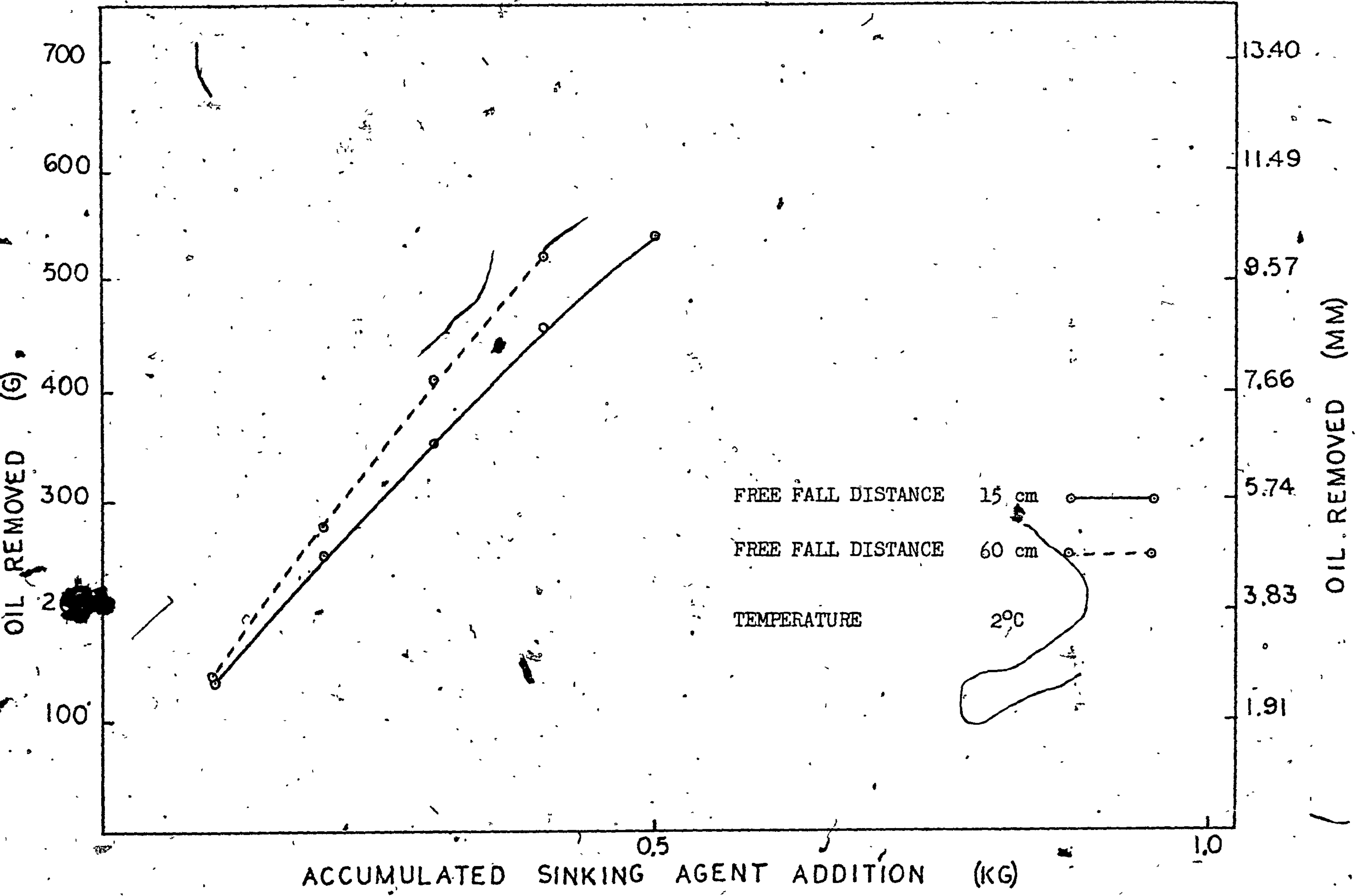

FIGURE 5-2 ZORB-ALL AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

TABLE 5-5

ANALYSIS OF RAW DATA - ZORB-ALL AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 0.21 mm (g)	Sinking Agent/Oil Ratio by Weight
10.10	500	510.9	0.98
7.53	400	378.1	1.06
5.37	300	266.5	1.13
3.22	200	155.4	1.29
1.42	100	62.5	1.60

* Free Fall Distance 15 cm Temperature 21°C

TABLE 5-6

ANALYSIS OF RAW DATA - ZORB-ALL AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.44 mm (g)	Sinking Agent/Oil Ratio by Weight
11.38	500	513.5	0.97
8.89	400	384.9	1.04
6.72	300	272.8	1.10
4.72	200	169.5	1.18
2.86	100	73.4	1.36

* Free Fall Distance 60 cm Temperature 21°C

TABLE 5-7

ANALYSIS OF RAW DATA - ZORB-ALL AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 0.93 mm (g)	Sinking Agent/Oil Ratio by Weight
11.30	500	541.5	0.92
8.72	400	406.8	0.98
6.51	300	291.4	1.03
4.51	200	187.0	1.07
2.54	100	84.1	1.19

* Free Fall Distance 15 cm Temperature 2°C

TABLE 5-8

ANALYSIS OF RAW DATA - ZORB-ALL AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.53 mm (g)	Sinking Agent/Oil Ratio by Weight
11.54	400	522.0	0.77
8.84	300	381.0	0.79
6.27	200	246.8	0.81
3.63	100	110.0	0.91

* Free Fall Distance 60 cm Temperature 2°C

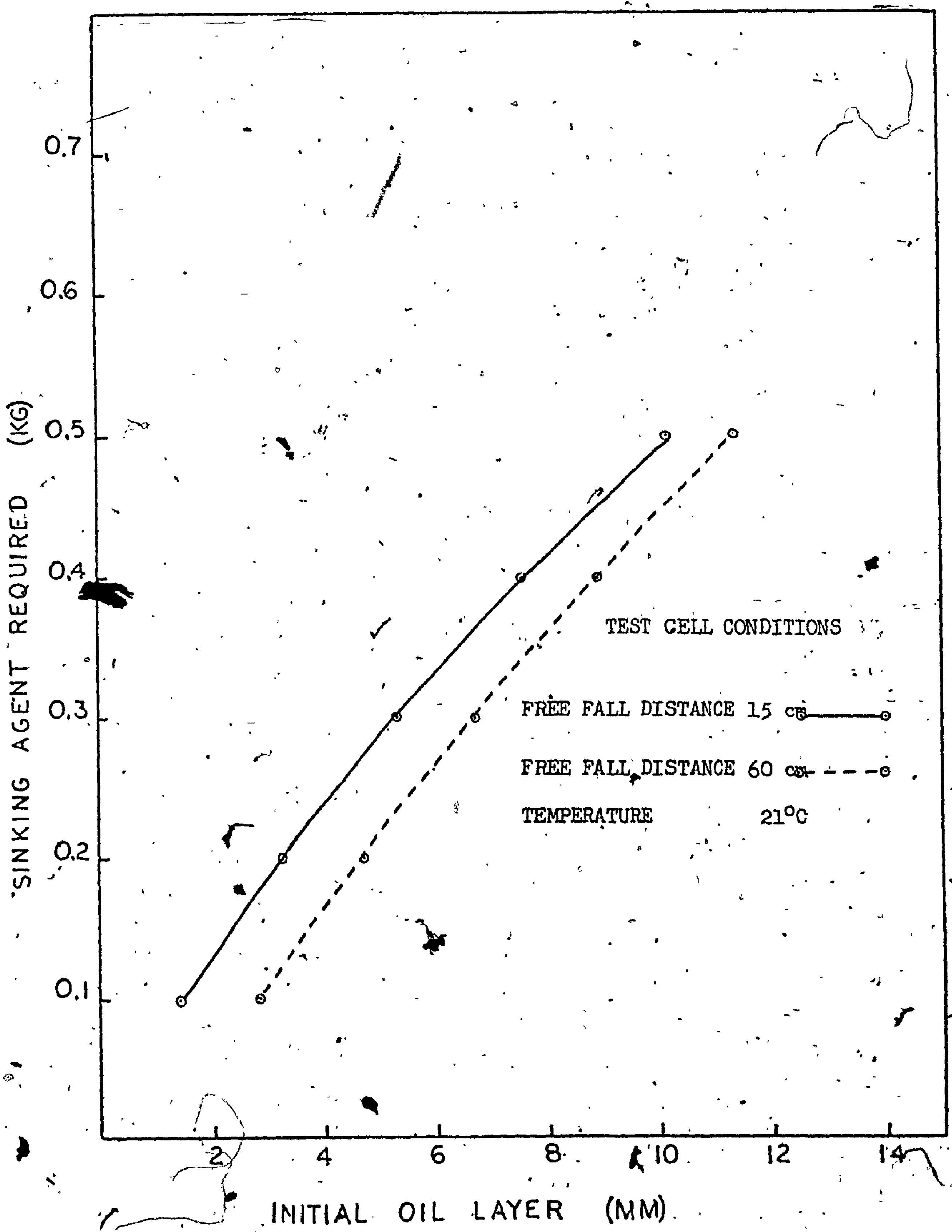

FIGURE 5-3 ZORB-ALL AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

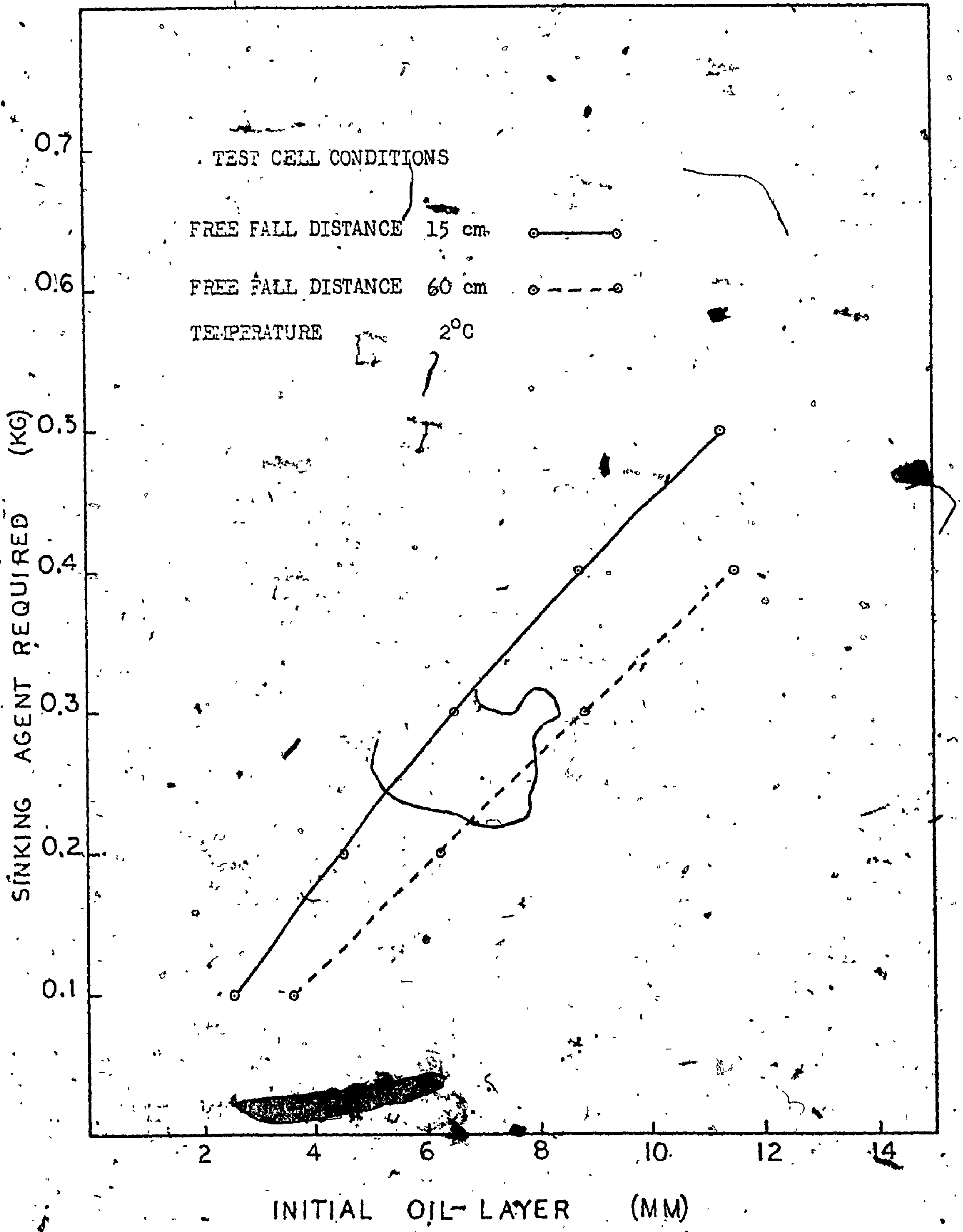

FIGURE 5-4 ZORB-ALL AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

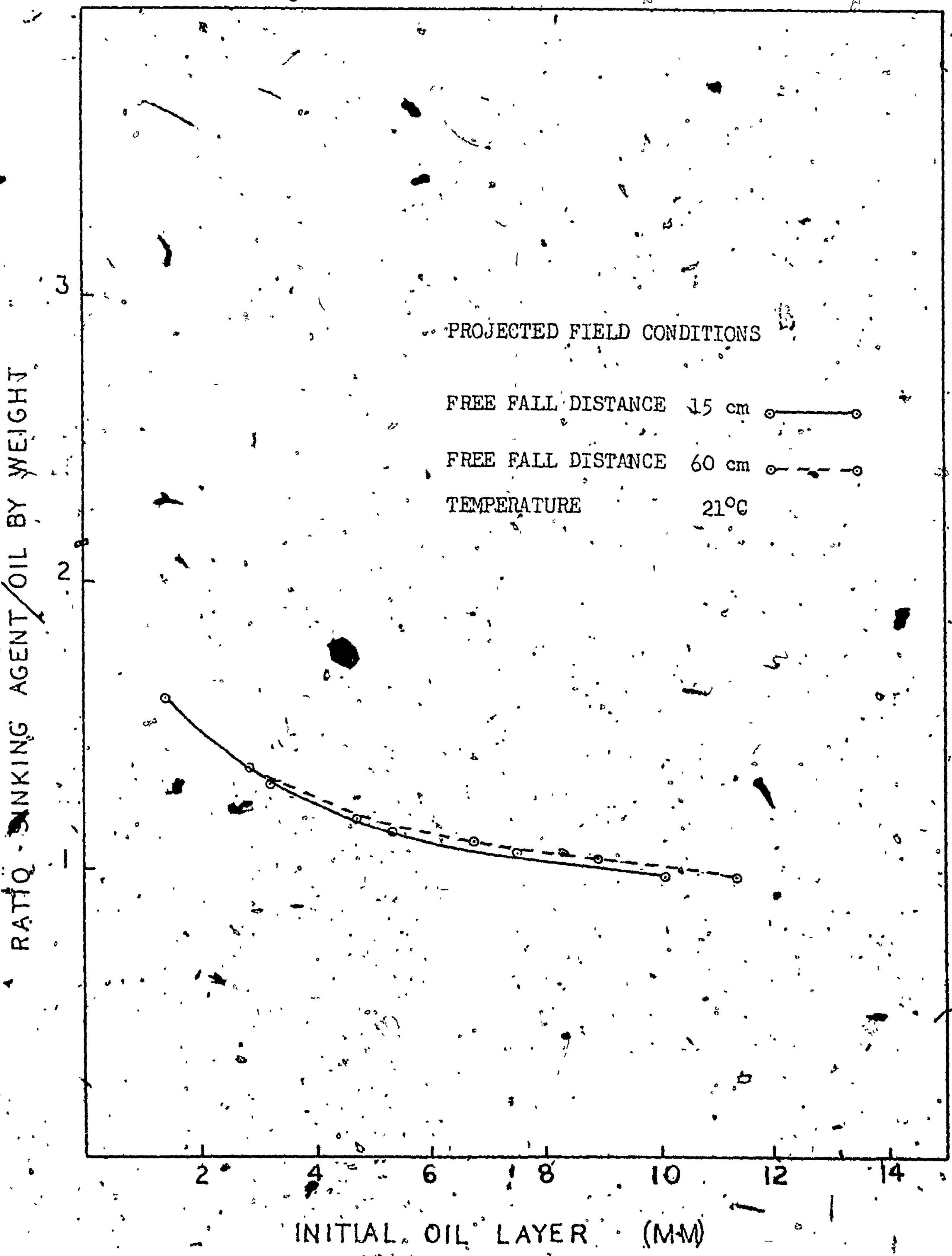

FIGURE 5-5 ZORB-ALL AND WESTERN CRUDE OIL – RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

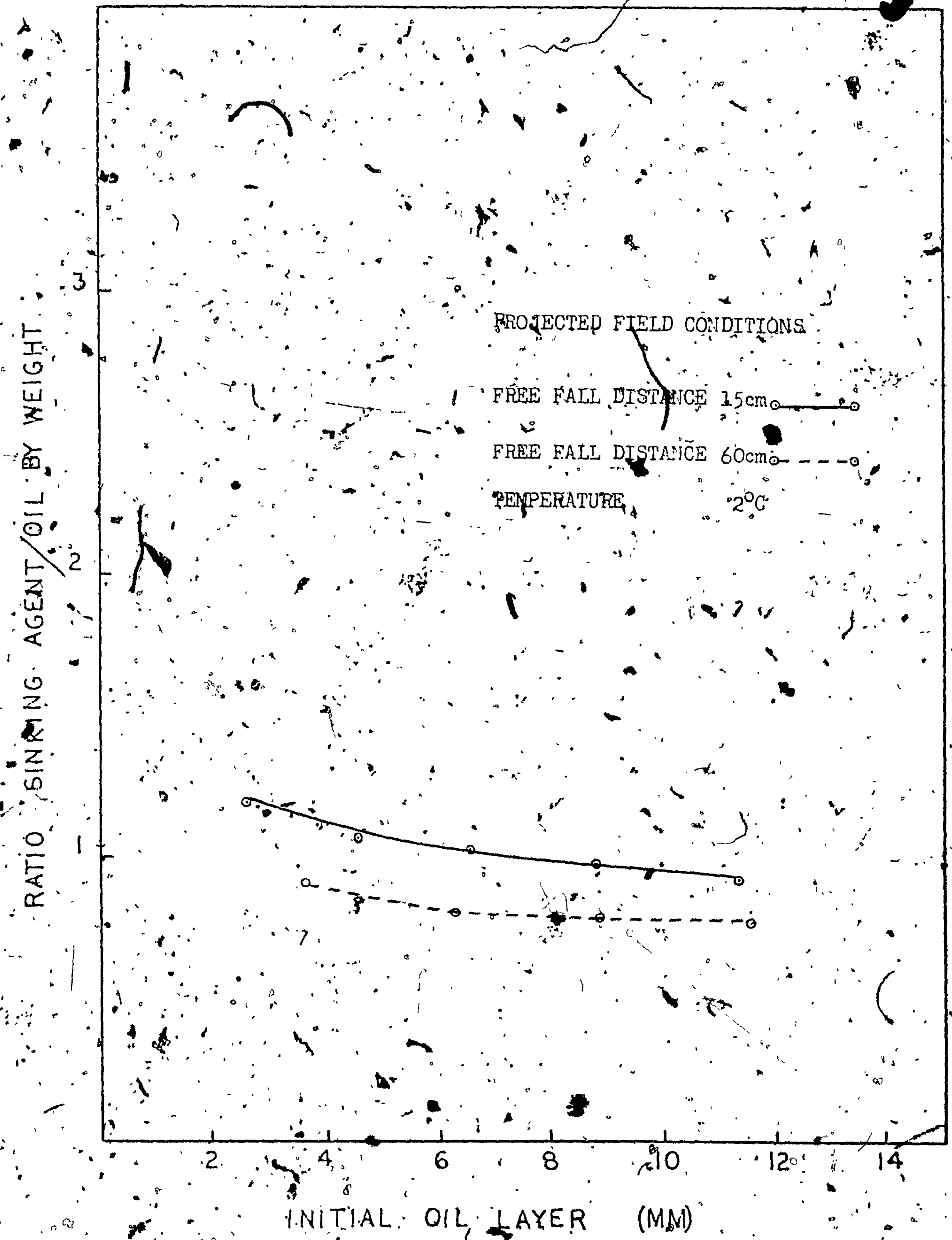

FIGURE 5-6, ZORB-ALL AND WESTERN CRUDE OIL - RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER THICKNESS

APPENDIX VI

ZORB-ALL AND NO. 2 FUEL OIL

EXPERIMENTAL DATA AND DATA ANALYSES

TABLE 6-1

RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	11.86 (3)	± 0.02	-		-	-
1	9.79 (3)	± 0.02	100	2.07	108.2	108.2
2	7.58 (3)	± 0.02	200	2.21	115.5	223.7
3	5.51 (3)	± 0.06	300	2.07	108.2	331.9
4	3.58 (3)	± 0.02	400	1.93	100.9	432.8
5	1.87 (3)	± 0.36	500	1.71	89.4	522.2
6	0.58 (3)	± 0.06	600	1.29	67.4	589.6
			WATER PATCH DISCONTINUITIES			

* Starting Oil Weight 620 g Free Fall Distance 15 cm

Temperature 21°C

TABLE 6-2

RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	10.23 (3)	± 0.01	-	-	-	-
1	8.0^{1} (3)	± 0.4^{5}	100	2.2^{2}	$116.^{0}$	$116.^{0}$
2	5.84 (3)	± 0.01	200	2.1^{7}	$113.^{4}$	$229.^{4}$
3	4.0^{9} (3)	± 0.1^{7}	300	1.7^{5}	$91.^{5}$	$320.^{9}$
4	2.4^{7} (3)	± 0.2^{8}	400	1.6^{2}	$84.^{7}$	$405.^{6}$
5	0.72 (3)	± 0.03	500	1.7^{5}	$91.^{5}$	$497.^{1}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 534 g Free Fall Distance 60 cm

Temperature 21°C

TABLE 6-3

RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	13.45 (3)	± 0.09	-	-	-	-
1	11.03 (3)	± 0.08	100	2.42	128.0	128.0
2	8.99 (3)	± 0.09	200	2.04	107.9	235.9
3	6.91 (3)	± 0.08	300	2.08	110.0	345.9
4	4.76 (3)	± 0.03	400	2.15	113.7	459.6
5	3.07 (3)	± 0.09	500	1.69	89.4	549.0
6	1.4^{9} (3)	± 0.1^{3}	600	1.5^{8}	$83.^{6}$	$632.^{5}$
		WATER PATCH DISCONTINUITIES				

Starting Oil Weight 710 g Free Fall Distance 15 cm

Temperature 2°C

TABLE 6-4

RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL*

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	12.07 (3)	± 0.03	-	-	-	-
1	9.45 (3)	± 0.04	100	2.62	138.6	138.6
2	7.05 (3)	± 0.09	200	2.40	127.0	265.6
3	4.8^{0} (3)	± 0.1^{0}	300	2.2^{5}	$119.^{0}$	$384.^{6}$
4	2.7^{9} (3)	± 0.1^{1}	400	2.0^{1}	$106.^{3}$	$490.^{9}$
5	0.66 (3)	± 0.08	500	2.1^{3}	$112.^{7}$	$603.^{6}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 662 g Free Fall Distance 60 cm

Temperature $2^{\circ}C$

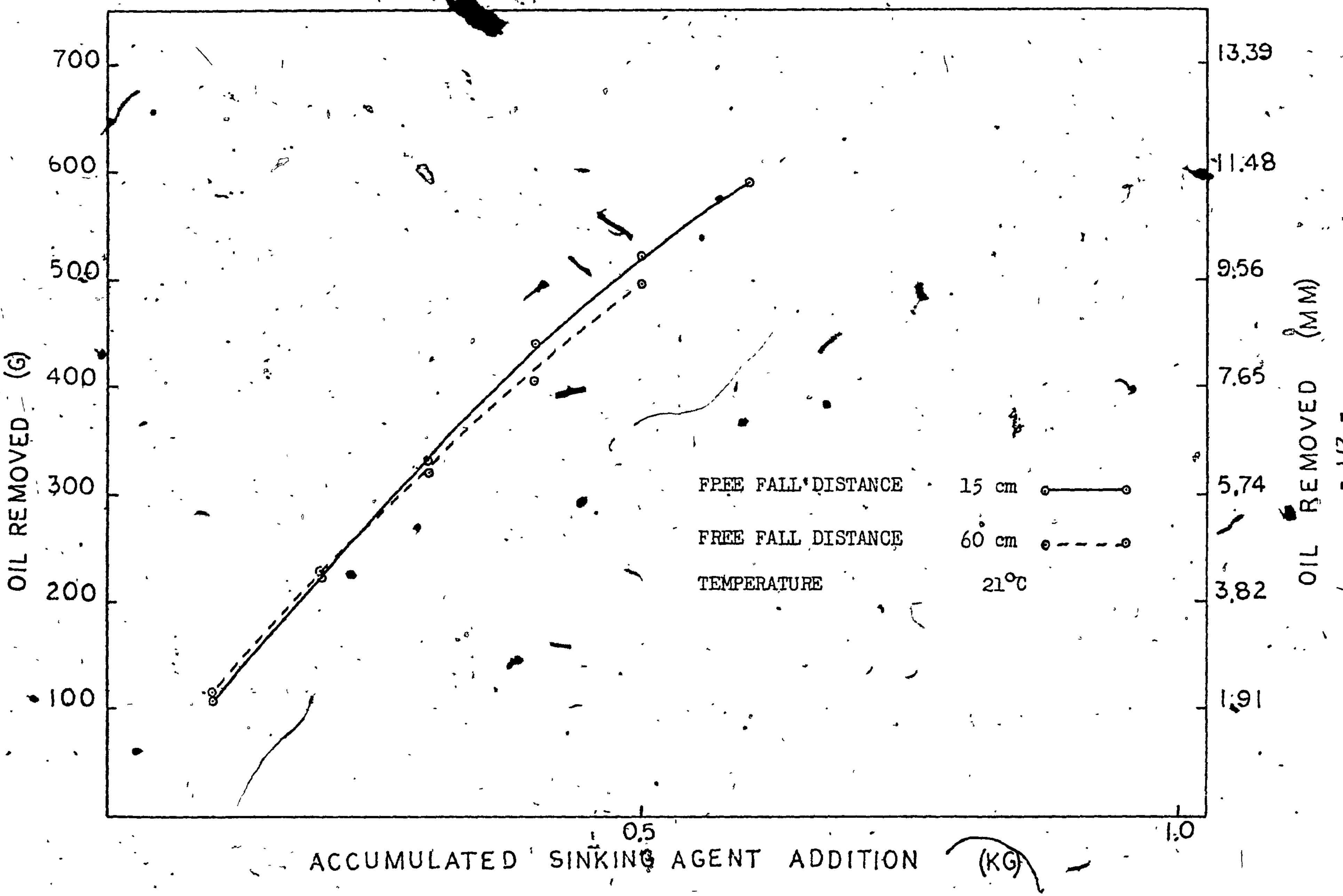

FIGURE 6-1 ZORB-ALL AND NO. 2 FUEL OIL - SINKING AGE~~NT ADDED~~ VS OIL REMOVED

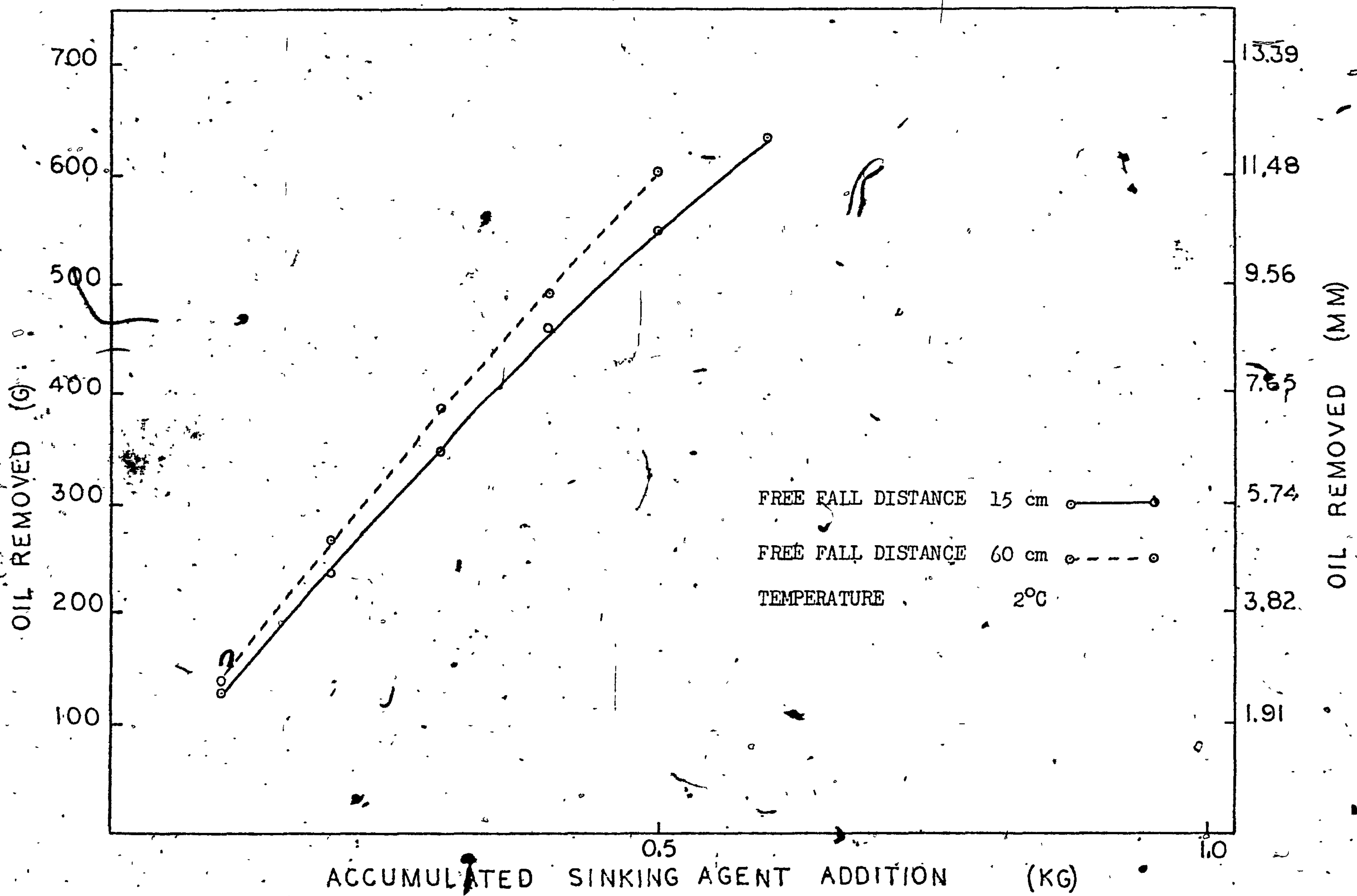

FIGURE 6-2 ZORB-ALL AND NO. 2 FUEL OIL - SINKING AGENT ADDED VS OIL REMOVED

TABLE 6-5

ANALYSIS OF RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 0.58 mm (g)	Sinking Agent/Oil Ratio by Weight
11.86	600	589.6	1.02
9.79	500	481.4	1.04
7.58	400	365.9	1.09
5.51	300	257.7	1.16
3.58	200	156.8	1.28
1.87	100	67.4	1.48

* Free Fall Distance 15 cm Temperature 21°C

TABLE 6-6

ANALYSIS OF RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 0.72 mm (g)	Sinking Agent/Oil Ratio by Weight
10.23	500	497.1	1.00
8.01	400	381.1	1.05
5.84	300	267.7	1.12
4.09	200	176.2	1.14
2.47	100	91.5	1.09

* Free Fall Distance 60 cm Temperature 21°C

TABLE 6-7

ANALYSIS OF RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.49 mm (g)	Sinking Agent/Oil Ratio by Weight
13.45	600	632.5	0.95
11.03	500	504.5	0.99
8.99	400	396.6	1.01
6.91	300	286.6	1.05
4.76	200	172.9	1.16
3.07	100	83.5	1.20

* Free Fall Distance 15 cm Temperature 2°C

TABLE 6-8

ANALYSIS OF RAW DATA - ZORB-ALL AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 0.66 mm (g)	Sinking Agent/Oil Ratio by Weight
12.07	500	603.6	0.83
9.45	400	465.0	0.86
7.05	300	338.0	0.89
4.80	200	219.0	0.91
2.79	100	112.7	0.89

* Free Fall Distance 60 cm Temperature 2°C

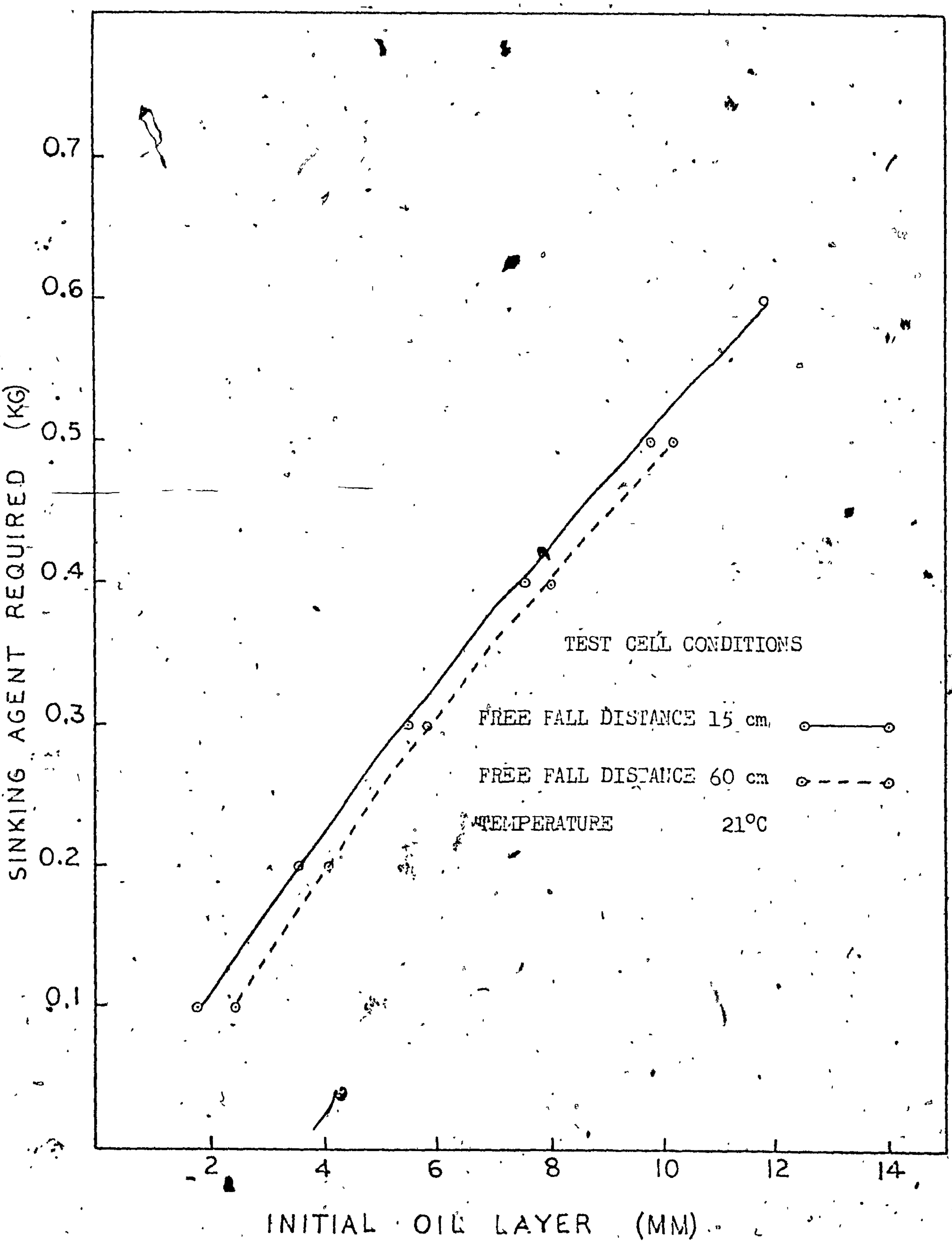

FIGURE 6-3 ZORB-ALL AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

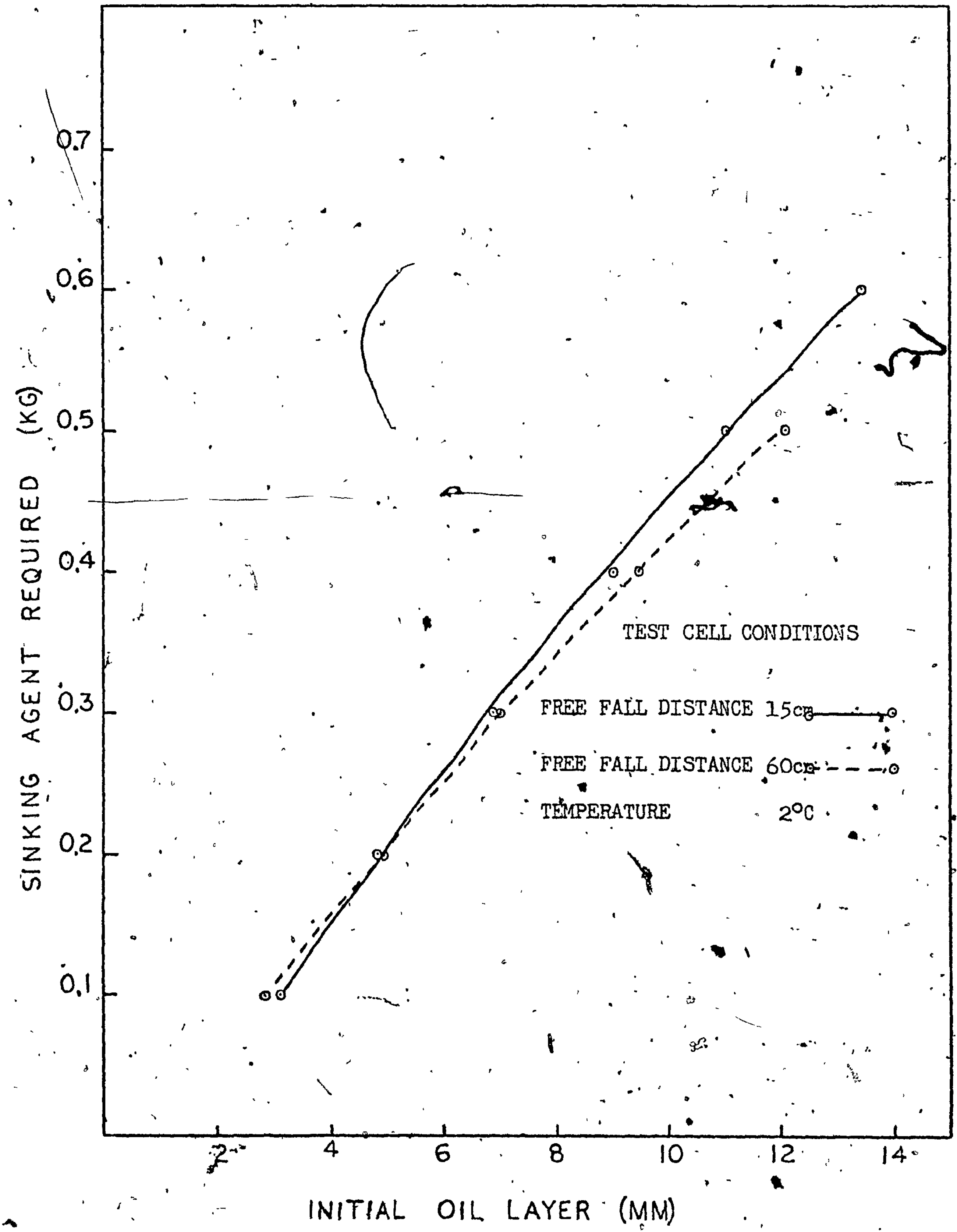

FIGURE 6-4 ZORB-ALL AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

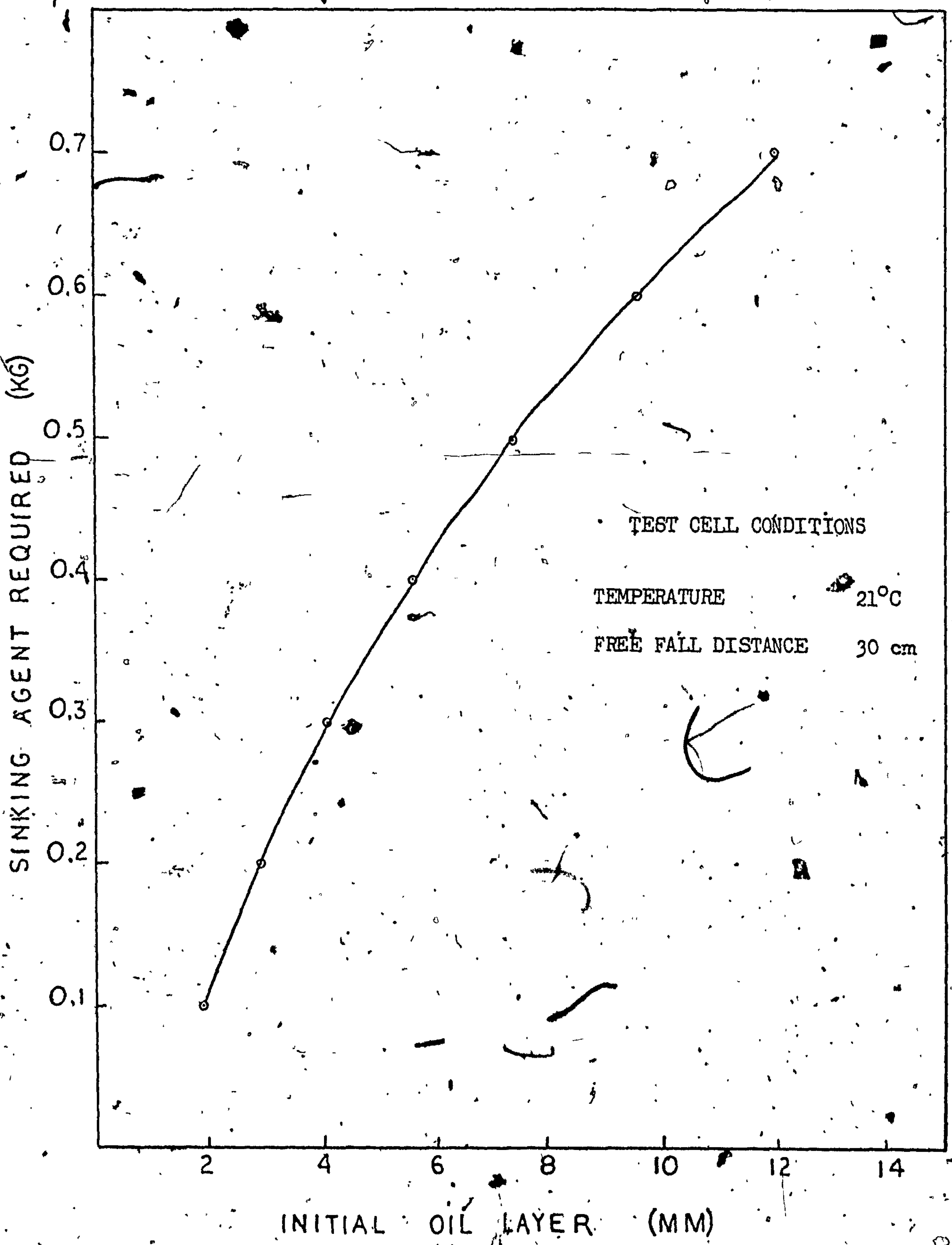

FIGURE 4-5 OIL-LOK 501 AND NO. 6 BUNKER OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

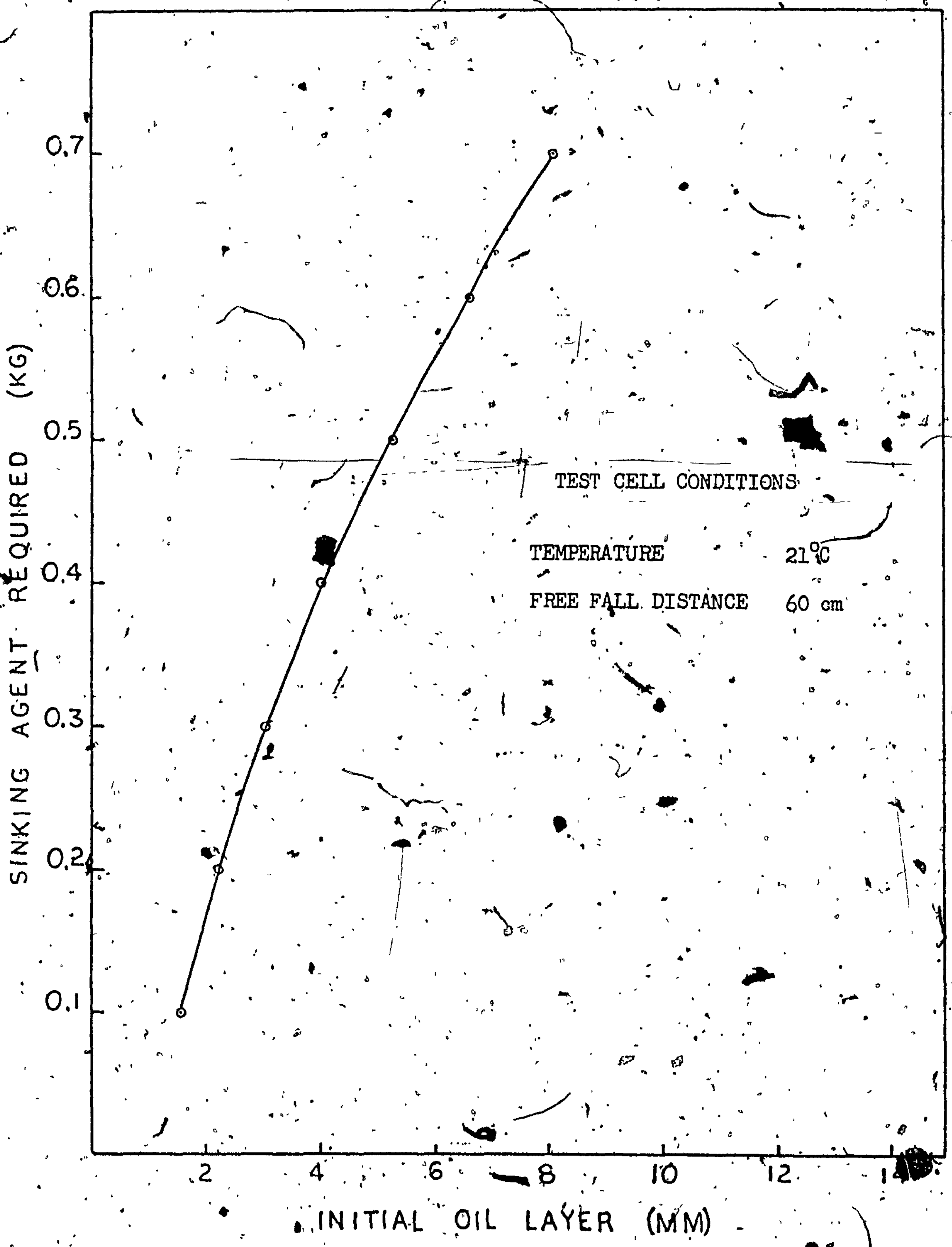

FIGURE 4-6 OIL-LOK 501 AND NO. 6 BUNKER OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

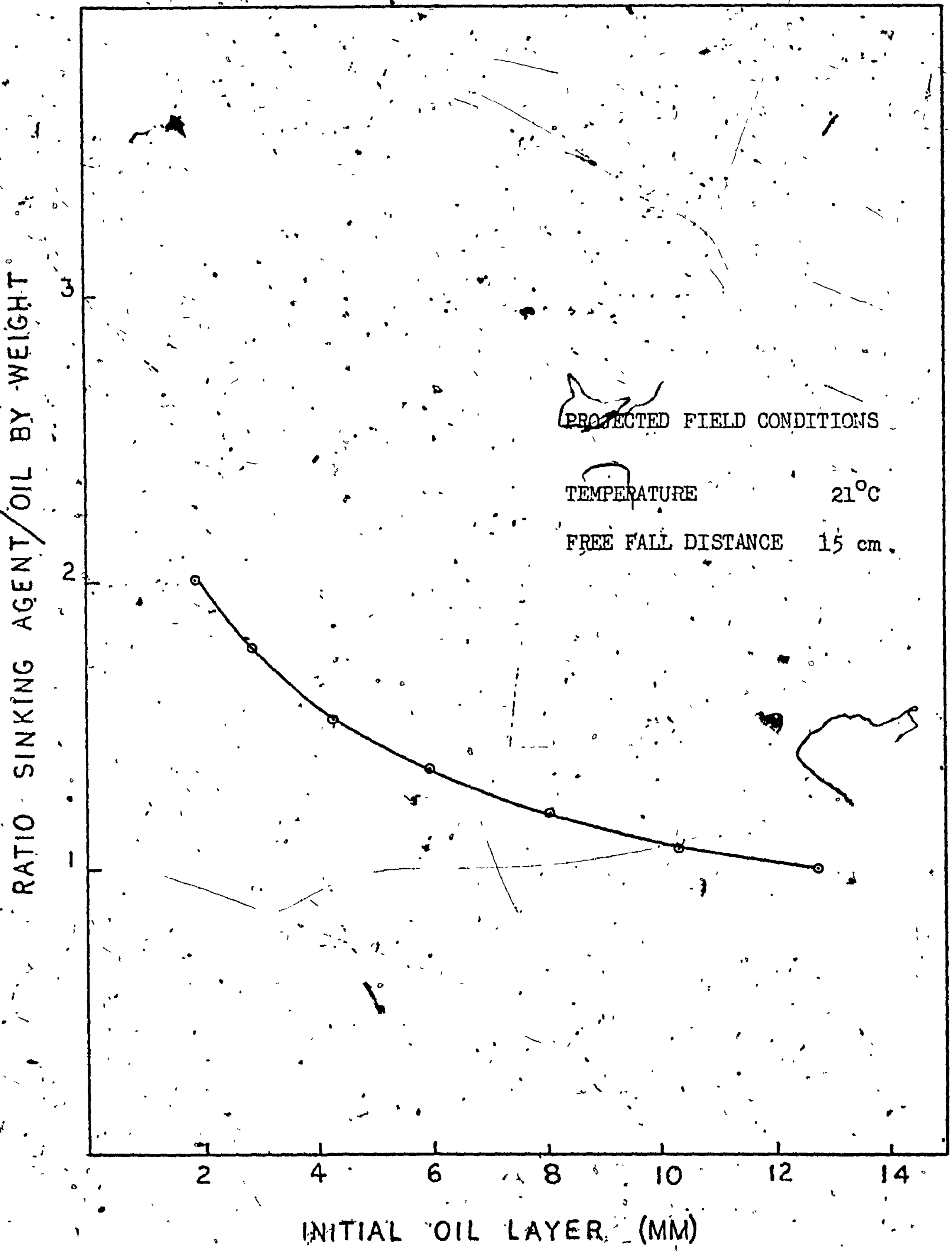

FIGURE 4-7 OIL-LOK 501 AND NO. 6 BUNKER OIL - RATIO SINKING AGENT/ OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

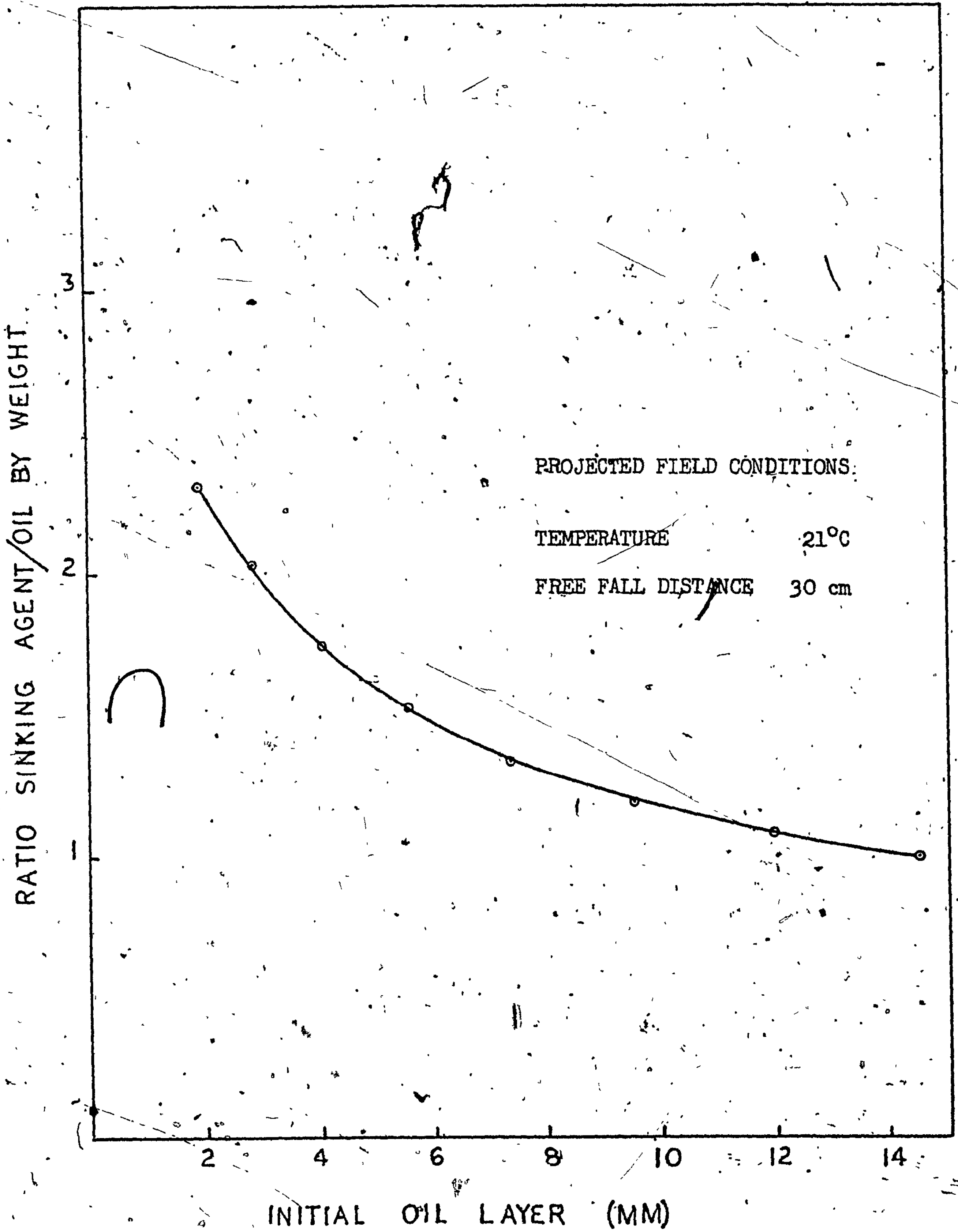

FIGURE 4-8 OIL-LOK 501 AND NO. 6 BUNKER OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

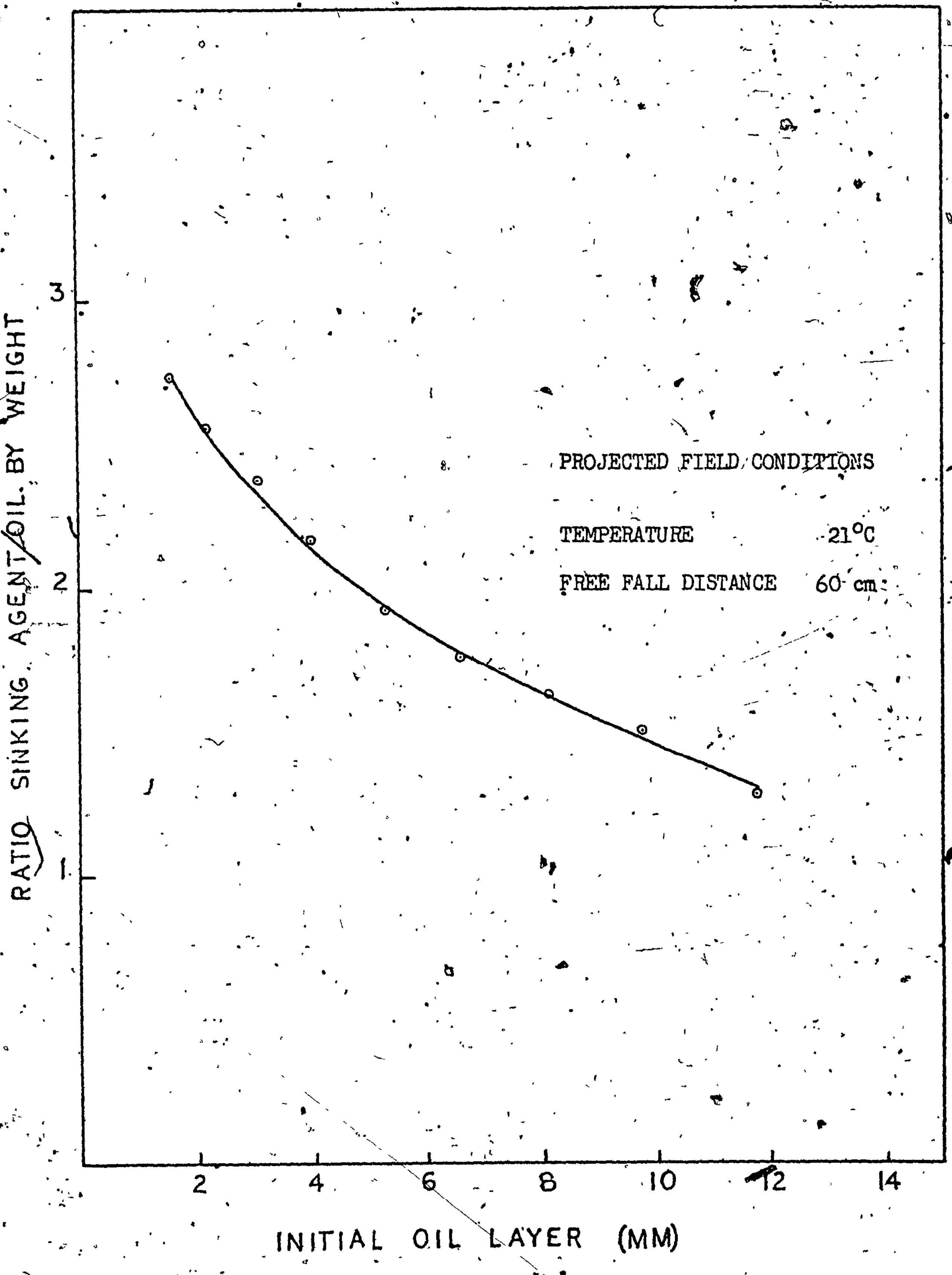

FIGURE 4-9 OIL-LOK 501 AND NO. 6 BUNKER OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

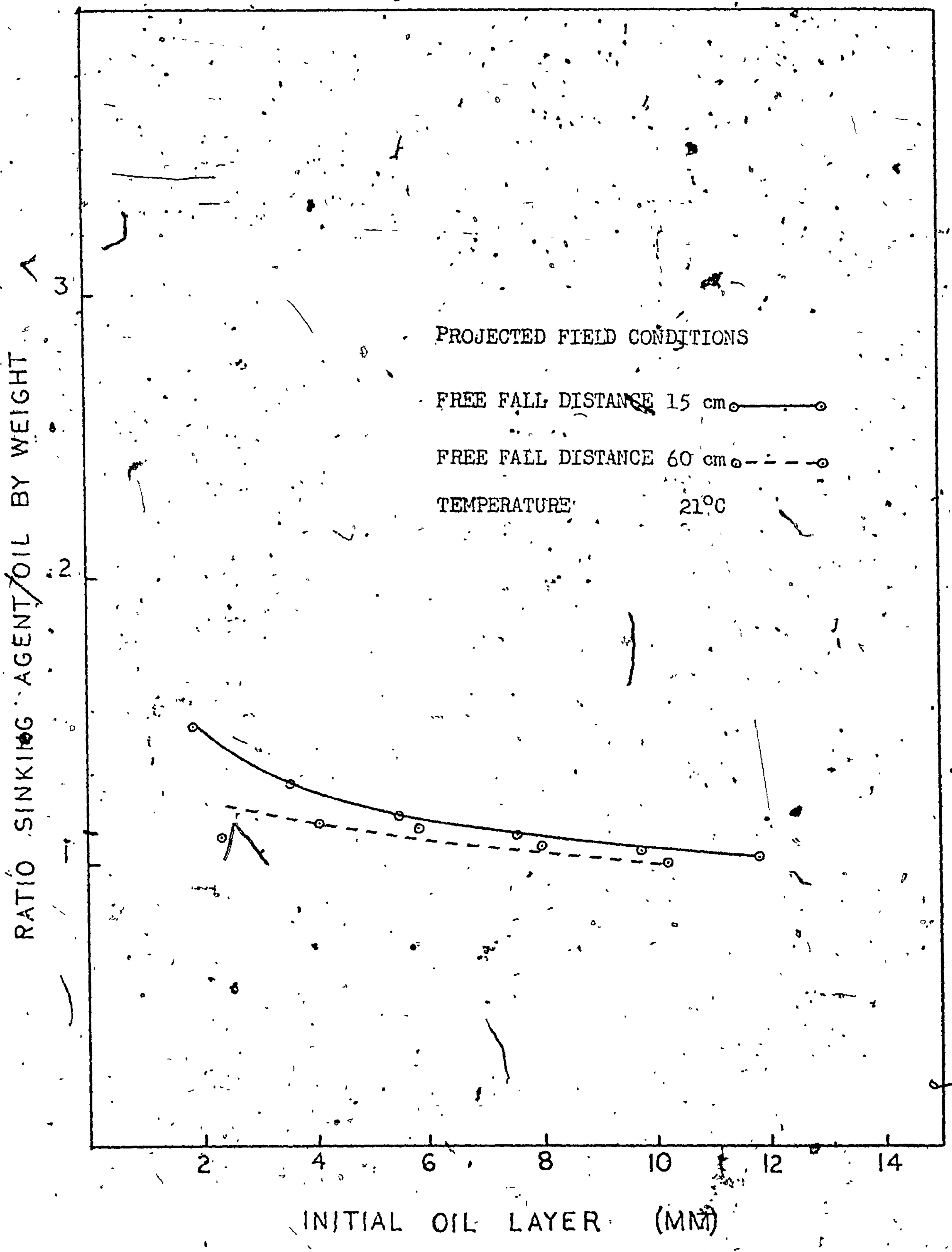

FIGURE 6-5 ZORB-ALL AND NO. 2 FUEL OIL - RATIO SINKING AGENT/OIL VS INITIAL OIL LAYER THICKNESS

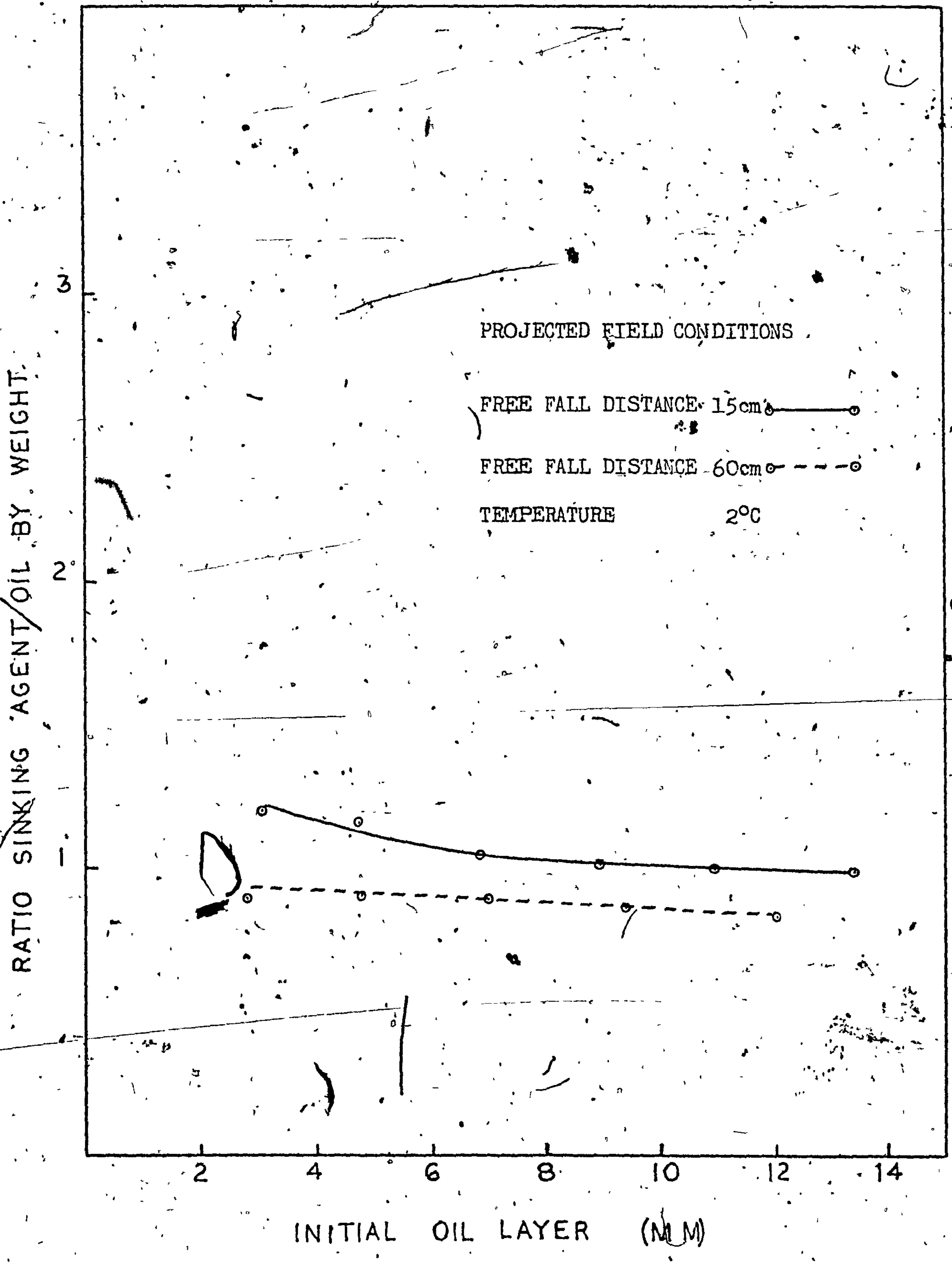

FIGURE 6-6 ZORB-ALL AND NO. 2-FUEL OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS.

APPENDIX VII

HI-DRI AND WESTERN CRUDE OIL

EXPERIMENTAL DATA AND DATA ANALYSES

TABLE 7-1

RAW DATA - HI-DRI AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	12.39 (3)	± 0.07	-	-	-	-
1	9.9^{1} (3)	± 0.2^{8}	100	2.4^{8}	$128.^{1}$	$128.^{1}$
2	7.35 (3)	± 0.02	200	2.5^{6}	$132.^{2}$	$260.^{3}$
3	4.9^{3} (3)	± 0.1^{4}	300	2.4^{2}	$125.^{0}$	$385.^{3}$
4	3.26 (3)	± 0.06	400	1.6^{7}	$86.^{3}$	$471.^{6}$
5	1.72 (3)	± 0.09	500	1.54	79.6	$551.^{2}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 637 g Free Fall Distance 15 cm

Temperature 21°C

TABLE 7-2

RAW DATA - HI-DRI AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	13.56 (3)	± 0.01	-	-	-	-
1	11.3^{6} (3)	± 0.2^{1}	100	2.2^{0}	$113.^{6}$	$113.^{6}$
2	8.96 (3)	± 0.05	200	2.4^{0}	$124.^{0}$	$237.^{6}$
3	6.5^{5} (3)	± 0.2^{1}	300	2.4^{1}	$124.^{5}$	$362.^{1}$
4	4.7^{5} (3)	± 0.2^{6}	400	1.8^{0}	$93.^{0}$	$455.^{1}$
5	3.0^{5} (3)	± 0.1^{1}	500	1.7^{0}	$87.^{8}$	$542.^{9}$
6	1.57 (3)	± 0.09	600	1.4^{8}	$76.^{4}$	$619.^{3}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 700 g Free Fall Distance 60 cm

Temperature 21°C

TABLE 7-3

RAW DATA – HI-DRI AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	11.1^{2} (3)	± 0.1^{0}	–	–	–	–
1	8.36 (3)	± 0.05	100	2.7^{6}	$144.^{1}$	$144.^{1}$
2	5.7^{7} (3)	± 0.1^{1}	200	2.5^{9}	$135.^{2}$	$279.^{3}$
3	3.6^{2} (3)	± 0.1^{6}	300	2.1^{5}	$112.^{3}$	$391.^{6}$
4	1.8^{2} (3)	± 0.2^{3}	400	1.8^{0}	$94.^{0}$	$485.^{6}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 590 g   Free Fall Distance 15 cm

Temperature 2°C

TABLE 7-4

RAW DATA - HI-DRI AND WESTERN CRUDE OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	12.29 (3)	± 0.11	-	-	-	-
1	9.42 (3)	± 0.05	100	2.87	149.8	149.8
2	6.38 (3)	± 0.07	200	3.04	158.7	308.5
3	3.79 (3)	± 0.09	300	2.59	135.2	443.7
4	1.40 (3)	± 0.10	400	2.39	124.8	568.5
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 607 g Free Fall Distance 60 cm

Temperature 2°C

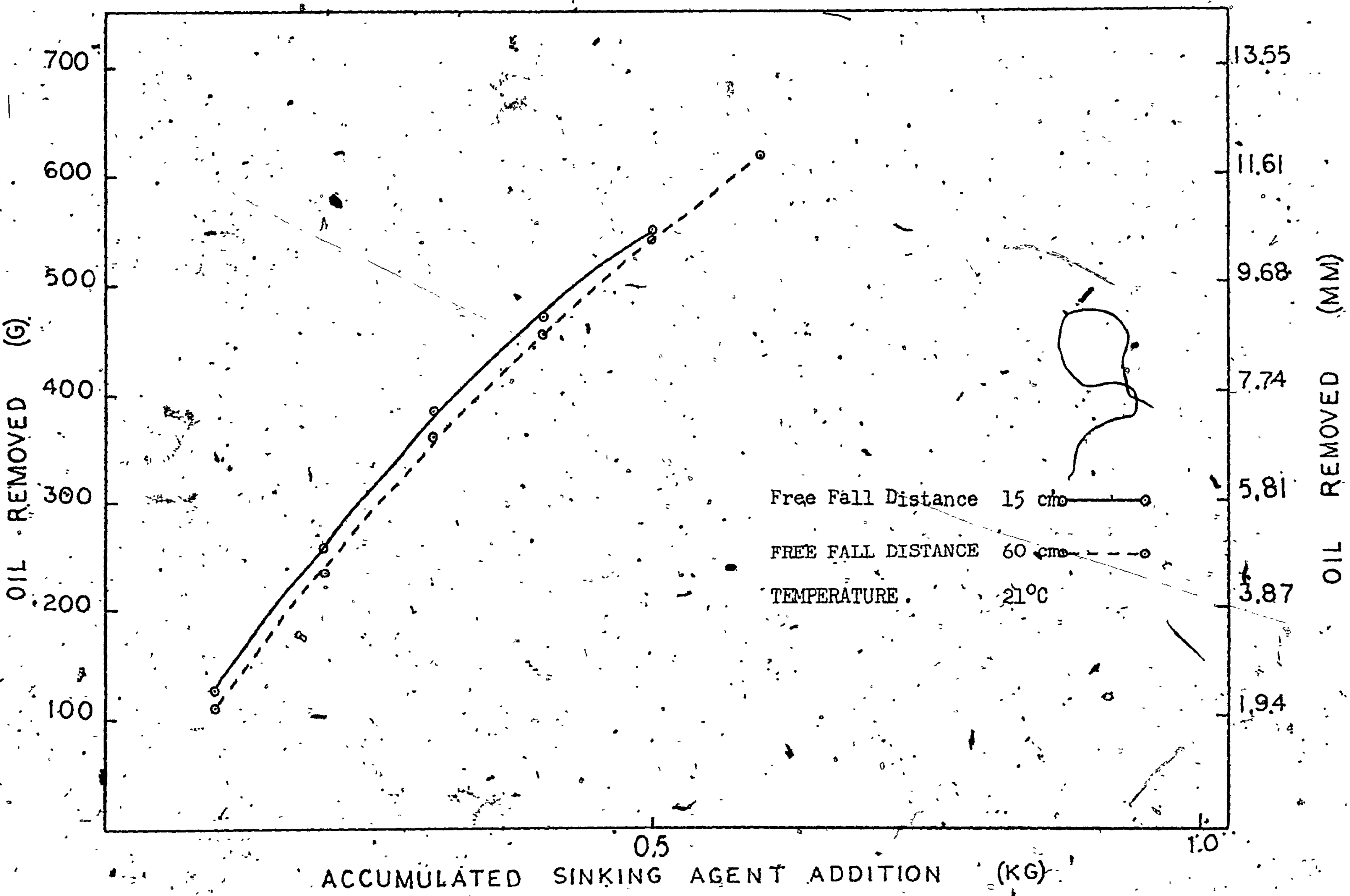

FIGURE 7-1 HI-DRI AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

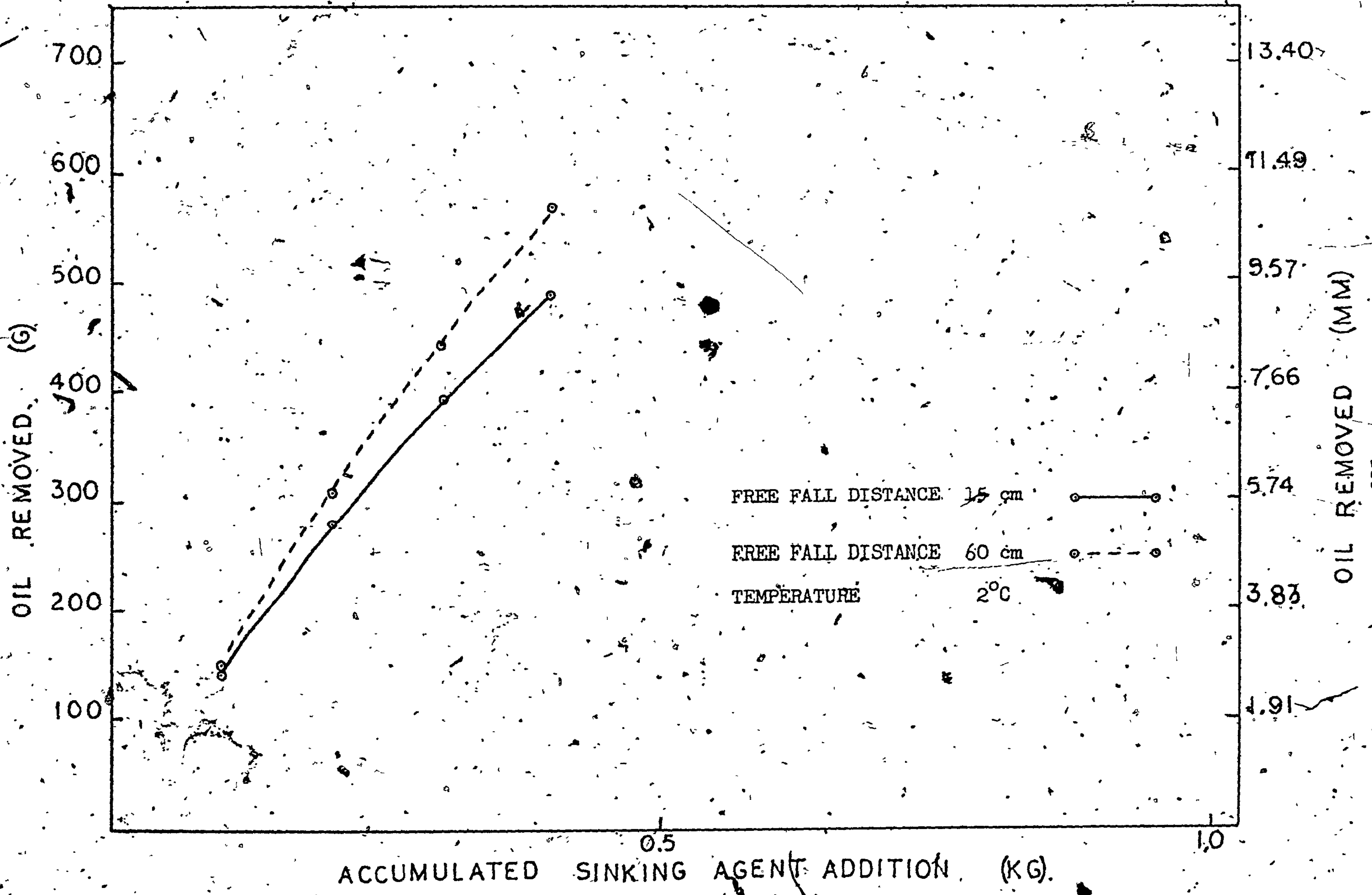

FIGURE 7-2 HI-DRI AND WESTERN CRUDE OIL - SINKING AGENT ADDED VS OIL REMOVED

TABLE 7-5

ANALYSIS OF RAW DATA - HI-DRI AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.72 mm (g)	Sinking Agent/Oil Ratio by Weight
12.39	500	551.2	0.91
9.91	400	423.1	0.95
7.35	300	290.9	1.03
4.93	200	166.9	1.20
3.26	100	79.6	1.26

* Free Fall Distance 15 cm Temperature 21°C

TABLE 7-6

ANALYSIS OF RAW DATA - HI-DRI AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.57 mm (g)	Sinking Agent/Oil Ratio by Weight
13.56	600	619.3	0.97
11.36	500	505.7	0.99
8.96	400	381.7	1.05
6.55	300	257.2	1.16
4.75	200	164.2	1.22
3.05	100	76.4	1.31

* Free Fall Distance 60 cm Temperature 21°C

TABLE 7-7

ANALYSIS OF RAW DATA - HI-DRI AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.82 mm (g)	Sinking Agent/Oil Ratio by Weight
11.12	400	485.6	0.82
8.36	300	341.5	0.88
5.77	200	206.3	0.97
3.62	100	94.0	1.06

* Free Fall Distance 15 cm Temperature 2°C

TABLE 7-8

ANALYSIS OF RAW DATA - HI-DRI AND WESTERN CRUDE OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.40 mm (g)	Sinking Agent/Oil Ratio by Weight
12.29	400	568.5	0.70
9.42	300	418.7	0.72
6.38	200	260.0	0.77
3.79	100	124.8	0.80

* Free Fall Distance 60 cm Temperature 2°C

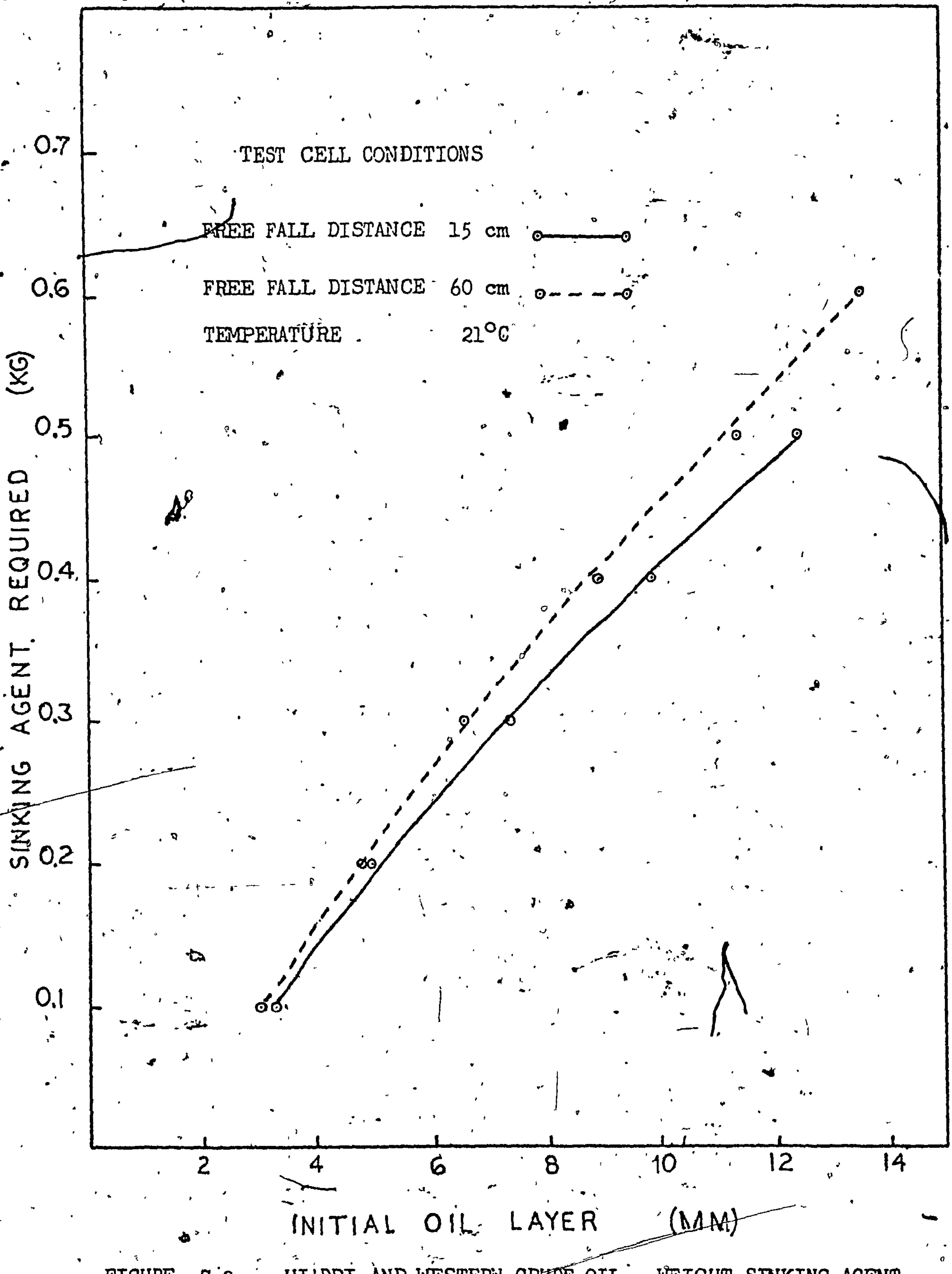

FIGURE 7-3 HI-DRI AND WESTERN CRUDE OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

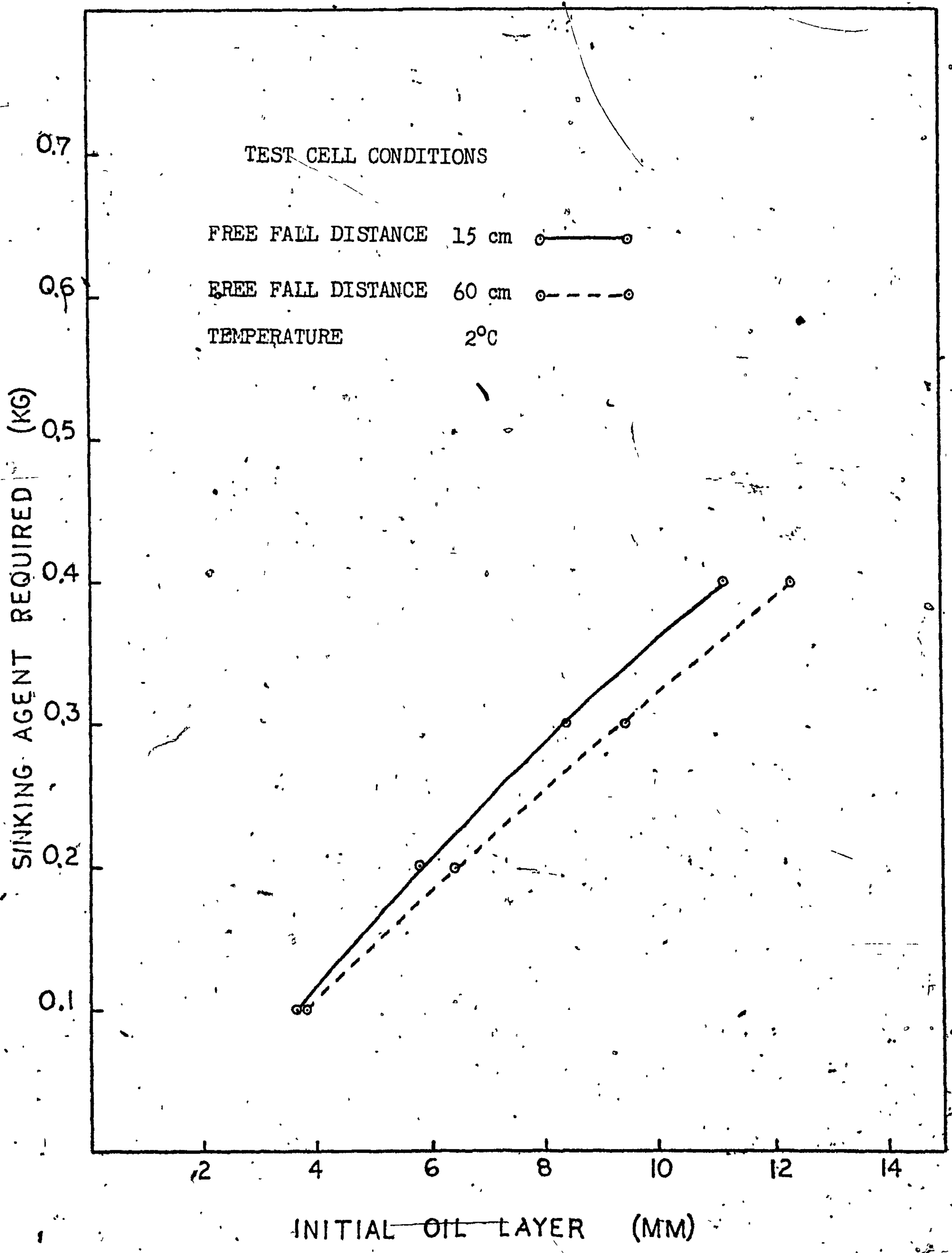

FIGURE 7-4 HI-DRI AND WESTERN CRUDE OIL – WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

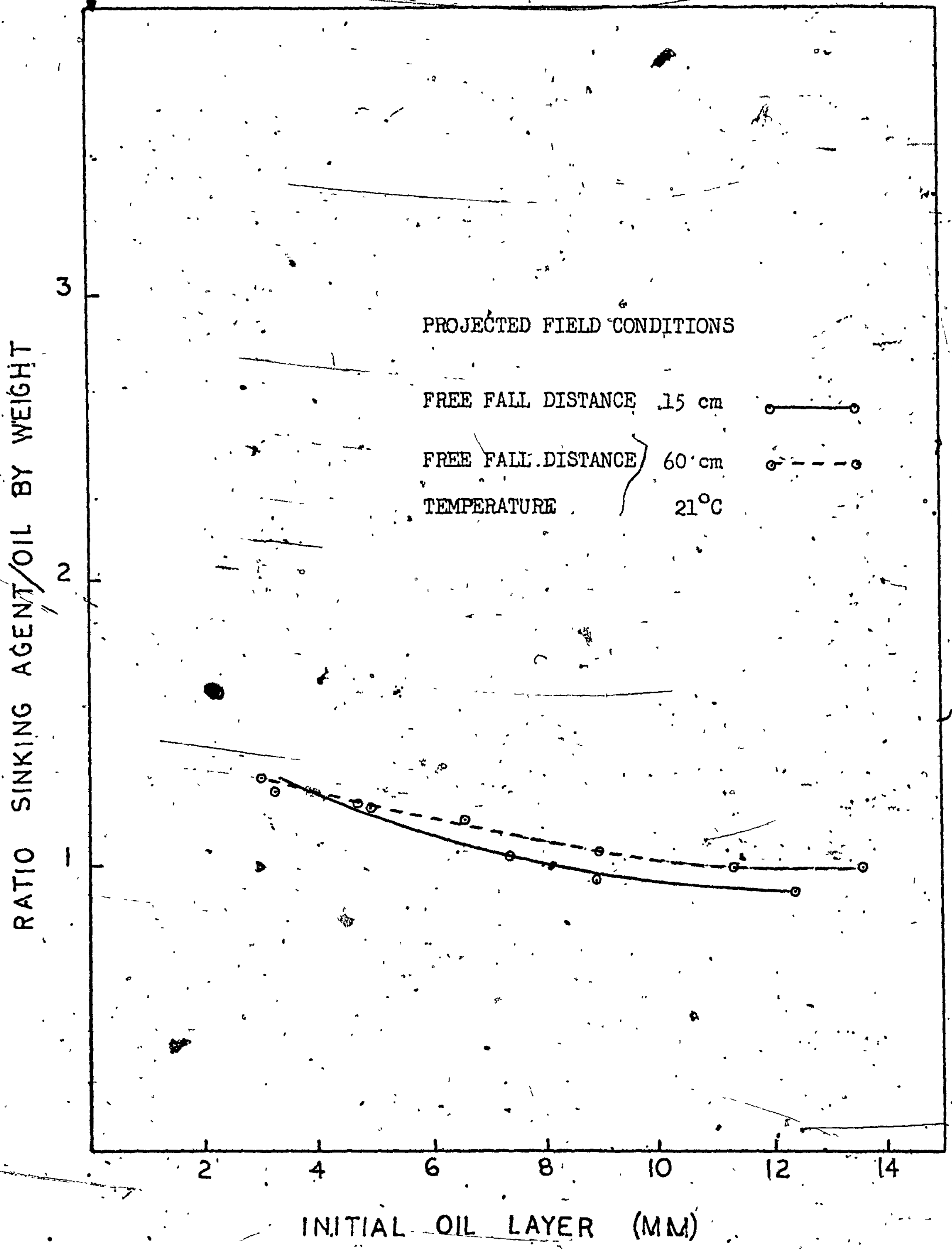

FIGURE 7-5 HI-DRI AND WESTERN CRUDE OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

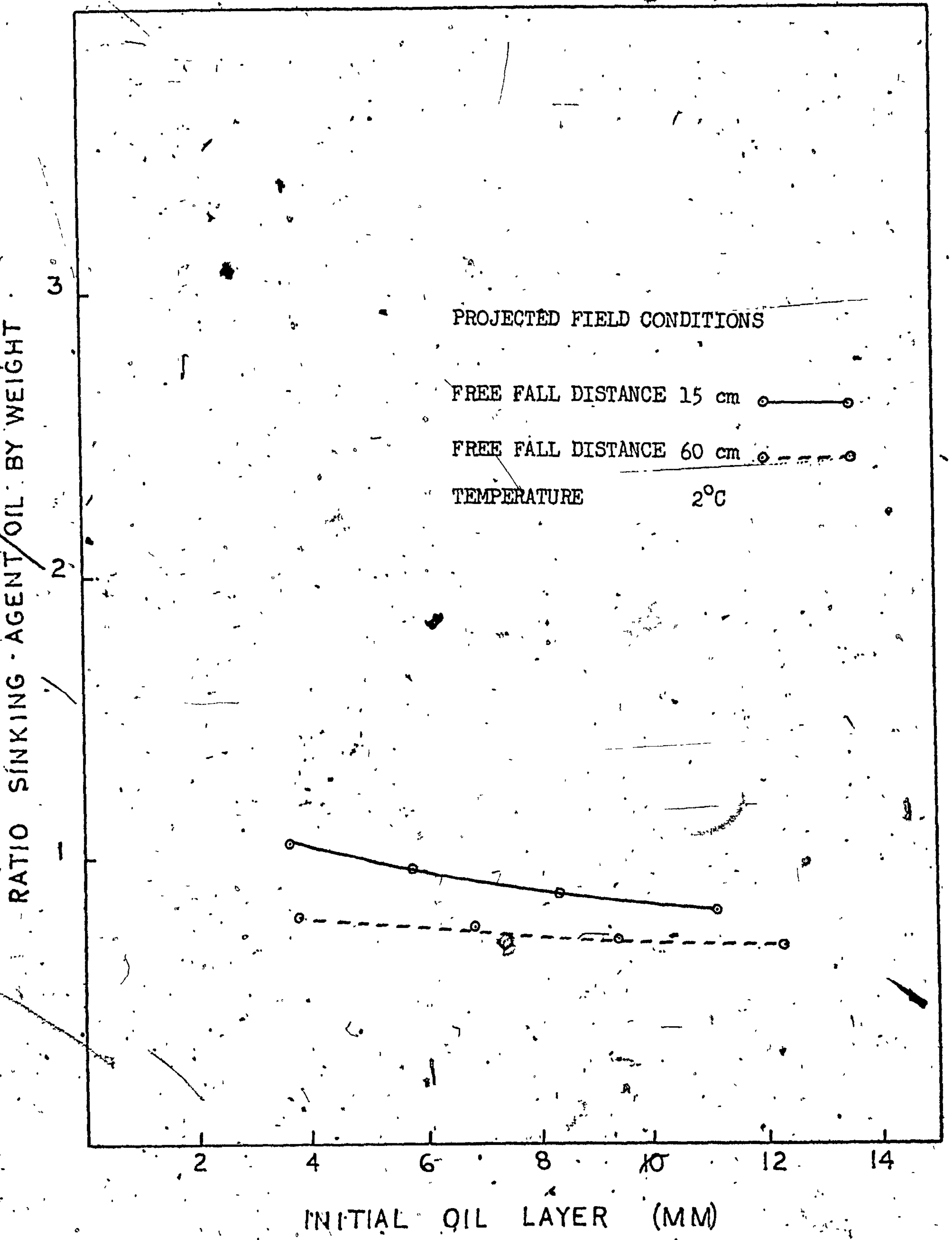

FIGURE 7-6 HI-DRI AND WESTERN CRUDE OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

APPENDIX VIII

HI-DRI AND NO. 2 FUEL OIL

EXPERIMENTAL DATA AND DATA ANALYSES

TABLE 8-1

RAW DATA – HI-DRI AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	9.34 (3)	± 0.03	–	–	–	–
1	6.9^{2} (3)	± 0.1^{4}	100	2.4^{2}	$126.^{5}$	$126.^{5}$
2	4.9^{7} (3)	± 0.1^{4}	200	1.9^{5}	$101.^{9}$	$228.^{4}$
3	3.60 (3)	± 0.05	300	1.3^{7}	$71.^{6}$	$300.^{0}$
4	2.09 (3)	± 0.1^{3}	400	1.5^{1}	$78.^{9}$	$378.^{9}$
5	1.0^{3} (3)	± 0.2^{5}	500	1.0^{6}	$55.^{4}$	$434.^{3}$
6	0.59 (3)	± 0.09	600	0.4^{4}	$23.^{0}$	$457.^{3}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight	487 g	Free Fall Distance	15 cm
Temperature	21°C		

TABLE 8-2

RAW DATA - HI-DRI AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	10.8^{3} (3)	± 0.1^{0}	-	-	-	-
1	8.6^{5} (3)	± 0.1^{0}	100	2.1^{8}	$114.^{0}$	$114.^{0}$
2	6.74 (3)	± 0.07	200	1.9^{1}	$99.^{8}$	$213.^{8}$
3	5.1^{4} (3)	± 0.1^{3}	300	1.6^{0}	$83.^{6}$	$297.^{4}$
4	3.6^{7} (3)	± 0.2^{1}	400	1.4^{7}	$76.^{8}$	$374.^{2}$
5	2.8^{9} (3)	± 0.1^{3}	500	0.7^{8}	$40.^{8}$	$415.^{0}$
6	2.1^{9} (3)	± 0.1^{0}	600	0.7^{0}	$36.^{6}$	$451.^{6}$
7	1.5^{9} (3)	± 0.2^{0}	700	0.6^{0}	$31.^{4}$	$483.^{0}$
8	1.1^{9} (3)	± 0.1^{9}	800	0.4^{0}	$20.^{9}$	$503.^{9}$
			WATER PATCH DISCONTINUITIES			

* Starting Oil Weight 566 g Free Fall Distance 60 cm

Temperature 21°C

TABLE 8-3

RAW DATA - HI-DRI AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking Agent (g)	Oil Layer Decrease (mm)	Oil Removed (g)	
	Average	Std. Devn.			Test	Accum.
Start	11.28 (3)	± 0.06	-	-	-	-
1	8.7^{0} (3)	± 0.1^{2}	100	2.5^{8}	$136.^{5}$	$136.^{5}$
2	6.5^{6} (3)	± 0.1^{0}	200	2.1^{4}	$115.^{2}$	$249.^{7}$
3	4.3^{1} (3)	± 0.1^{0}	300	2.2^{5}	$119.^{0}$	$368.^{7}$
4	2.00 (3)	± 0.09	400	2.3^{1}	$122.^{2}$	$490.^{9}$
5	0.6^{4} (3)	± 0.1^{8}	500	1.3^{6}	$71.^{9}$	$562.^{8}$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 615 g Free Fall Distance 15 cm

Temperature 2°C

TABLE 8-4

RAW DATA - HI-DRI AND NO. 2 FUEL OIL *

Test	Thickness (mm)		Accum. Sinking	Oil Layer	Oil Removed (g)	
	Average	Std. Devn.	Agent (g)	Decrease (mm)	Test	Accum.
Start	11.65 (3)	± 0.04	-	-	-	-
1	8.72 (3)	± 0.06	100	2.93	155.0	155.0
2	6.30 (3)	± 0.03	200	2.42	128.0	283.0
3	4.02 (3)	± 0.07	300	2.28	120.6	403.6
4	2.0^2 (3)	± 0.2^2	400	2.0^0	$106.^8$	$509.^4$
		WATER PATCH DISCONTINUITIES				

* Starting Oil Weight 620 g Free Fall Distance 60 cm

Temperature 2°C

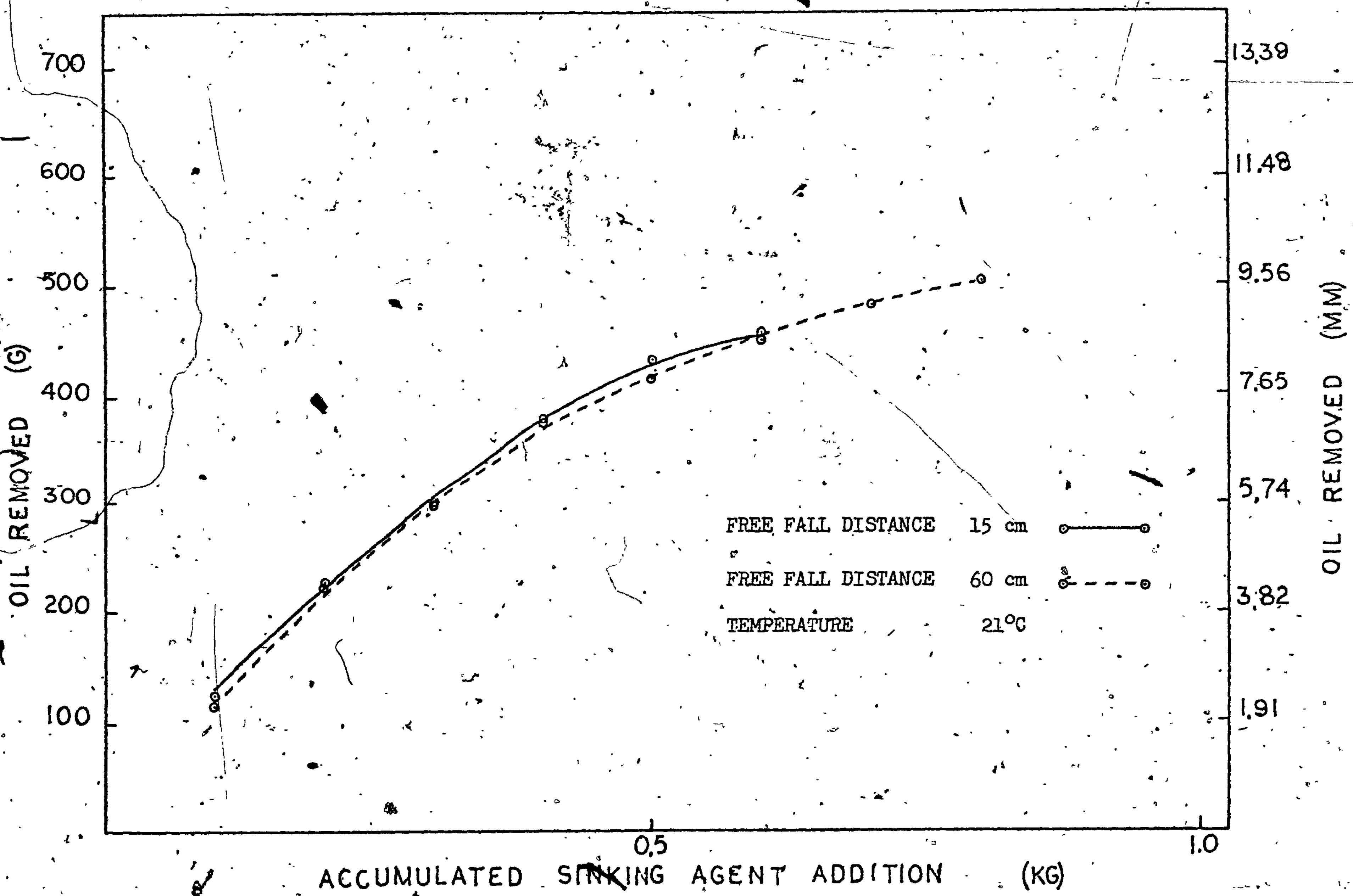

FIGURE 8-1 HI-DRI AND NO. 2 FUEL OIL - SINKING AGENT ADDED VS OIL REMOVED

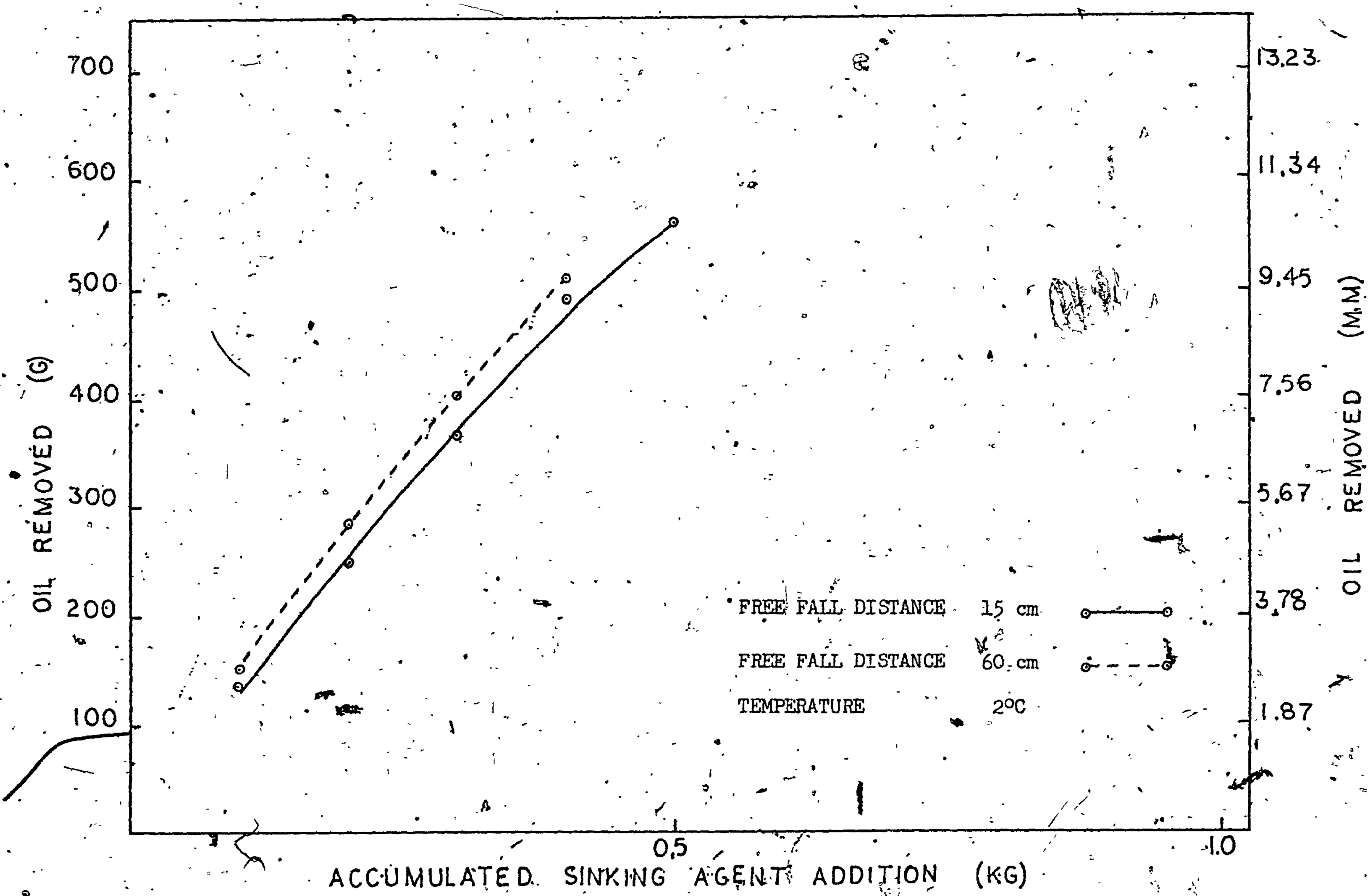

FIGURE 8-2 HI-DRI AND NO. 2 FUEL-OIL - SINKING AGENT ADDED VS OIL REMOVED

TABLE 8-5

ANALYSIS OF RAW DATA - HI-DRI AND NO. 2 FUEL OIL*

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.03 mm (g)	Sinking Agent/Oil Ratio by Weight
9.34	600	457.3	1.31
6.92	500	330.8	1.51
4.97	400	228.9	1.75
3.60	300	157.3	1.90
2.09	200	78.4	2.55
1.03	100	23.0	4.35

* Free Fall Distance 15 cm Temperature 21°C

TABLE 8-6

ANALYSIS OF RAW DATA - HI-DRI AND NO. 2 FUEL OIL*

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 1.19 mm (g)	Sinking Agent/Oil Ratio by Weight
10.83	800	503.9	1.59
8.65	700	389.9	1.79
6.74	600	290.1	2.07
5.14	500	206.5	2.42
3.67	400	129.7	3.08
2.89	300	88.9	3.37
2.19	200	52.3	3.82
1.59	100	20.9	4.78

* Free Fall Distance 60 cm Temperature 21°C

TABLE 8-7

ANALYSIS OF RAW DATA - HI-DRI AND NO. 2 FUEL OIL

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 0.64 mm (g)	Sinking Agent/Oil Ratio by Weight
11.28	500	562.8	0.88
8.70	400	426.3	0.94
6.56	300	313.1	0.96
4.31	200	194.1	1.03
2.00	100	71.9	1.39

* Free Fall Distance 15 cm   Temperature 2°C

TABLE 8-8

ANALYSIS OF RAW DATA - HI-DRI AND NO. 2 FUEL OIL *

Starting Oil Depth (mm)	Weight Sinking Agent (g)	Oil Removed to Depth of 2.02 mm (g)	Sinking Agent/Oil Ratio by Weight
11.65	400	509.4	0.78
8.72	300	354.4	0.85
6.30	200	226.4	0.88
4.02	100	105.8	0.95

* Free Fall Distance 60 cm   Temperature 2°C

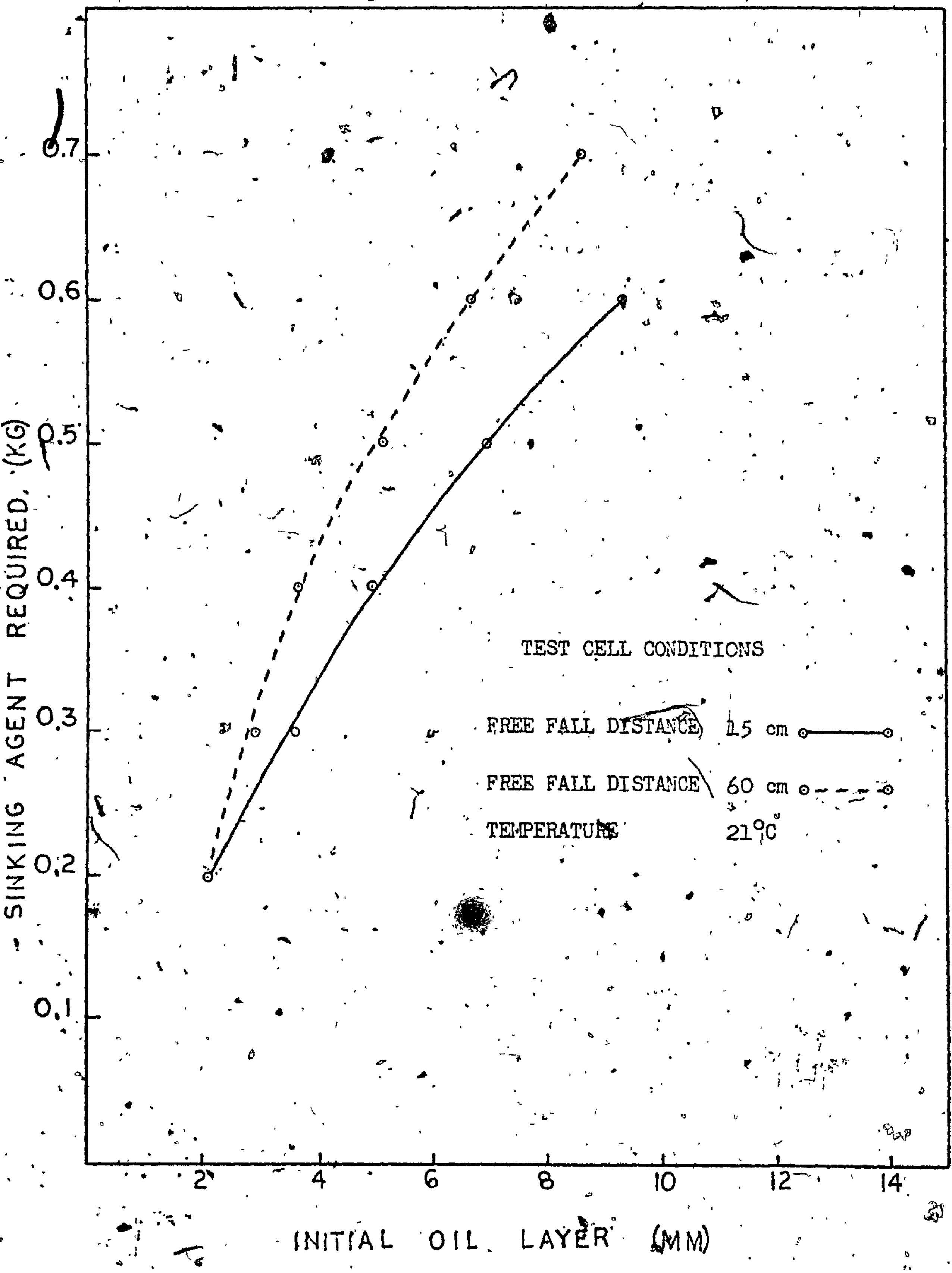

FIGURE 8-3 HI-DRI AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

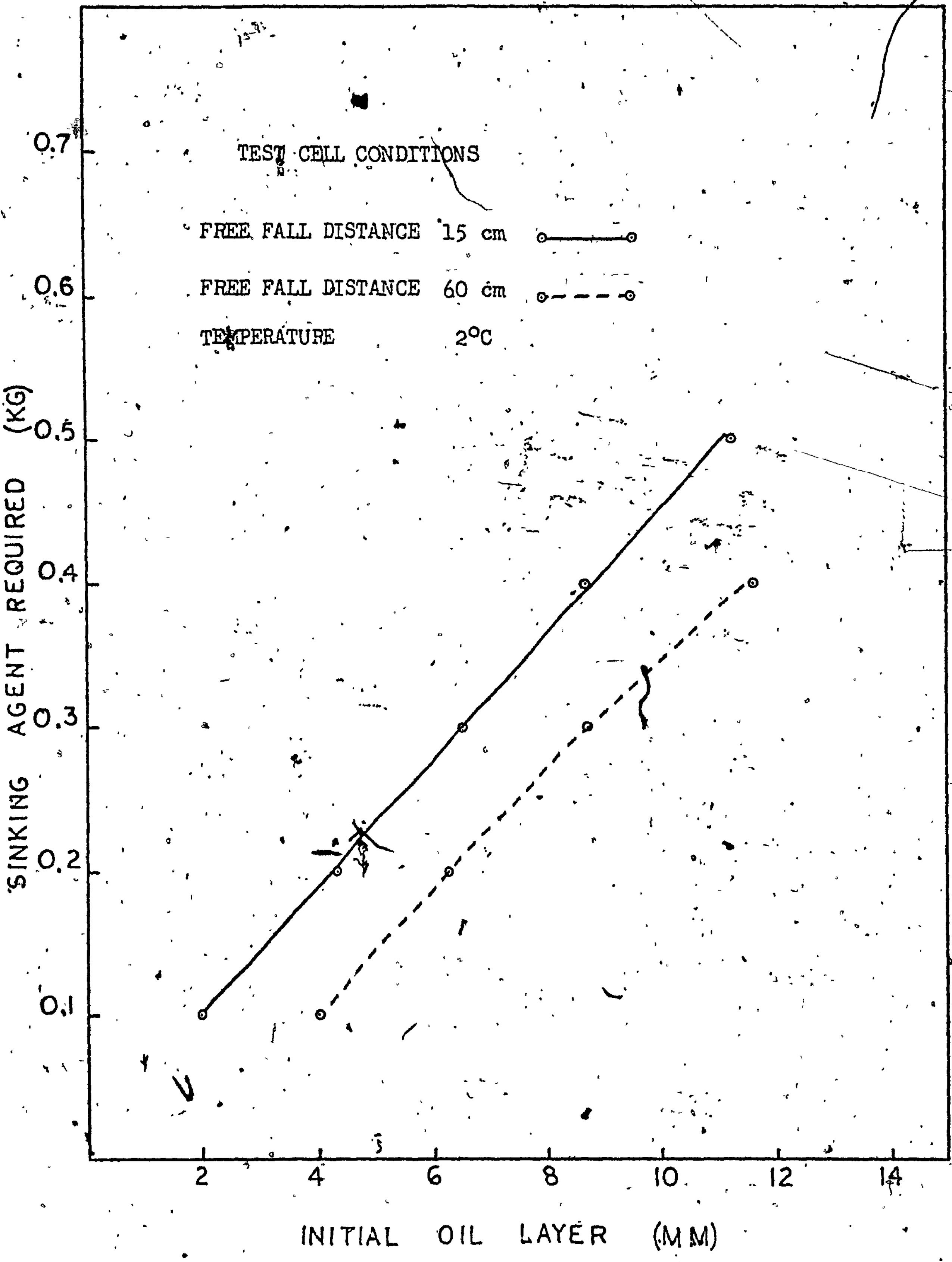

FIGURE 8-4 HI-DRI AND NO. 2 FUEL OIL - WEIGHT SINKING AGENT REQUIRED VS INITIAL OIL LAYER THICKNESS

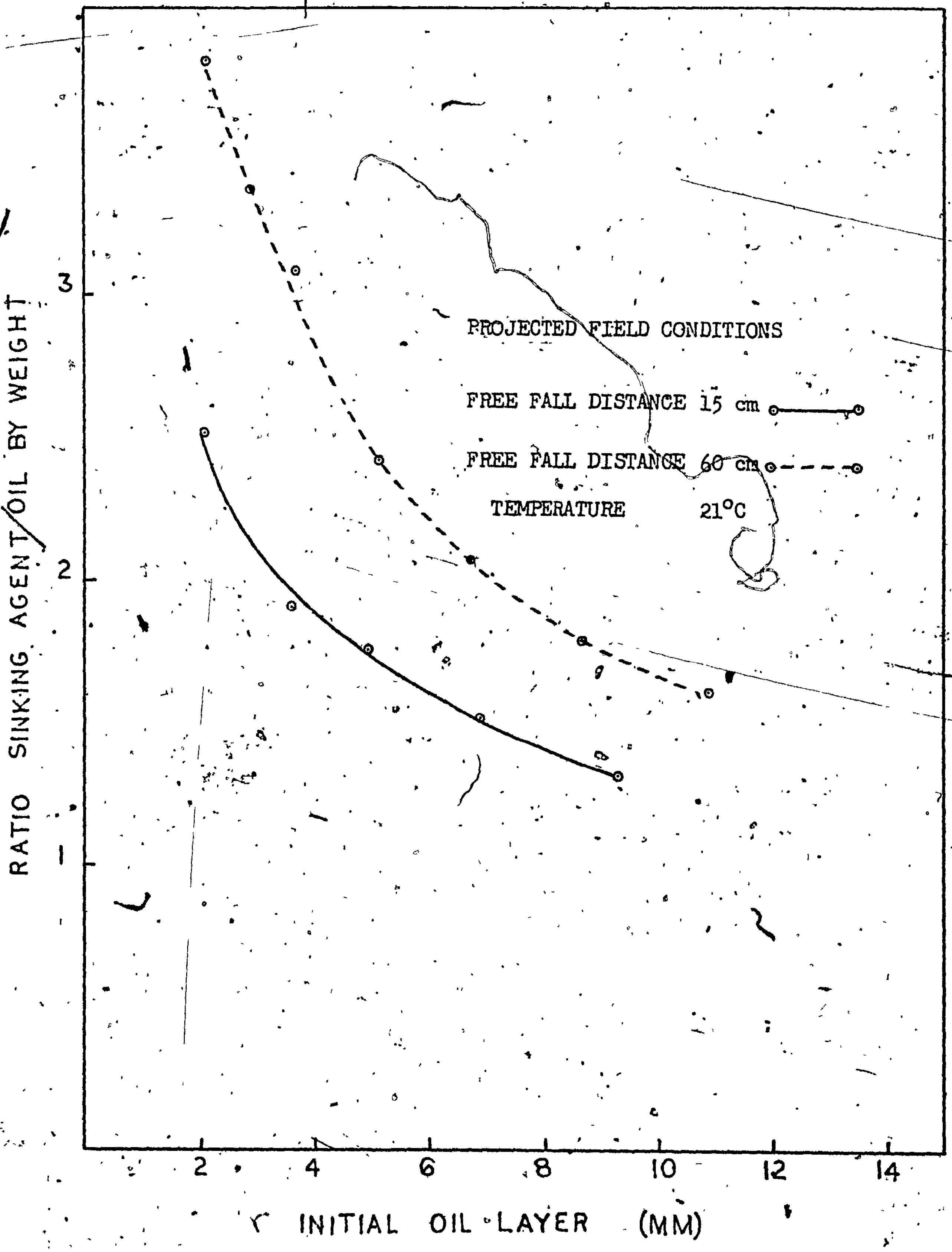

FIGURE 8-5 HI-DRI AND NO. 2 FUEL OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

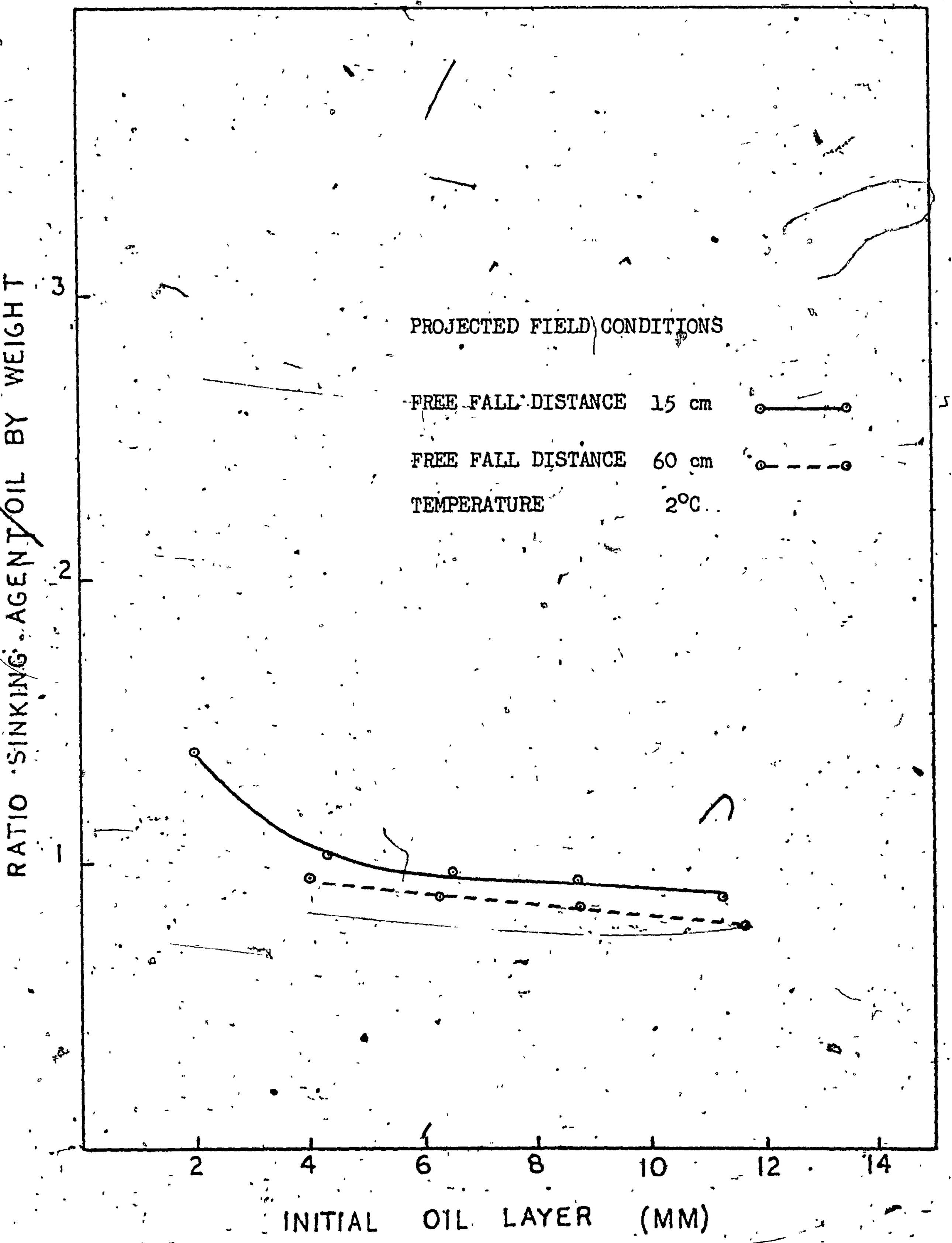

FIGURE 8-6 - HI-DRI AND NO. 2 FUEL OIL - RATIO SINKING AGENT/OIL BY WEIGHT VS INITIAL OIL LAYER THICKNESS

APPENDIX IX

OIL VOLATILITY LOSS TESTS

EXPERIMENTAL DATA

TABLE 9-1

VOLATILITY LOSS - WESTERN CRUDE OIL*

Test	Oil Layer Thickness (mm)		Weight	Total	Weight	Accum. Weight	Accum. Weight
	Average	Std. Devn.	Oil (g)	Time (h)	Loss (g)	Loss (g)	Loss (%)
Start	14.03 (3)	± 0.03	94.4	-	-	-	-
1	13.40 (3)	± 0.03	90.1	0.58	4.3	4.3	4.6
2	13.11 (3)	± 0.01	88.2	1.08	1.9	6.2	6.6
3	12.91 (3)	± 0.02	86.8	1.58	1.4	7.6	8.0
4	12.68 (3)	± 0.01	85.3	2.67	1.5	9.1	9.6
5	12.48 (3)	± 0.01	83.9	4.33	1.4	10.5	11.1
6	12.20 (3)	± 0.01	82.0	6.83	1.9	12.4	13.1
7	11.34 (3)	± 0.01	76.3	23.83	5.7	18.1	19.2
8	10.69 (3)	± 0.02	71.9	48.33	4.4	22.5	23.8
9	10.53 (3)	± 0.01	70.8	74.33	1.1	23.6	25.0
10	10.26 (3)	± 0.03	69.0	148.33	1.8	25.4	26.9

* Surface Area 81.03 ± 0.04 cm^2 Specific Gravity 0.830 ± 0.001

TABLE 9-2

VOLATILITY LOSS - NO. 2 FUEL OIL *

Test	Oil Layer Thickness (mm)		Weight	Total	Weight	Accum. Weight	Accum. Weight
	Average	Std. Devn.	Oil (g)	Time (h)	Loss (g)	Loss (g)	Loss (%)
Start	16.81 (3)	± 0.01	113.1	-	-	-	-
1	16.73 (3)	± 0.01	112.5	0.50	0.6	0.6	0.5
2	16.68 (3)	± 0.01	112.2	1.75	0.3	0.9	0.8
3	16.62 (3)	± 0.01	111.8	4.25	0.4	1.3	1.1
4	16.57 (3)	± 0.01	111.5	6.92	0.3	1.6	1.4
5	16.35 (3)	± 0.01	110.0	23.83	1.5	3.1	2.7
6	16.12 (3)	± 0.01	108.4	48.25	1.6	4.7	4.2
7	16.03 (3)	± 0.02	107.8	73.83	0.6	5.3	4.7
8	15.86 (3)	± 0.01	106.7	148.17	1.1	6.4	5.6

* Surface Area 80.08 ± 0.04 cm^2 Specific Gravity 0.840 ± 0.001

TABLE 9-3

VOLATILITY LOSS - NO. 6 BUNKER OIL *

Test	Oil Layer Thickness (mm)		Weight Oil (g)	Total Time (h)	Weight Loss (g)	Accum. Weight Loss (g)	Accum. Weight Loss (%)
	Average	Std. Devn.					
Start	19.01 (3)	± 0.02	147.3	-	-	-	-
1	18.89 (3)	± 0.03	146.4	0.50	0.9	0.9	0.6
2	18.82 (3)	± 0.07	145.8	1.58	0.6	1.5	1.0
3	18.62 (3)	± 0.08	144.3	4.08	1.5	3.0	2.0
4	18.45 (3)	± 0.07	143.0	6.83	1.3	4.3	2.9
5	18.24 (3)	± 0.03	141.4	23.92	1.6	5.9	4.0
6	18.16 (3)	± 0.03	140.7	48.17	0.7	6.6	4.5
7	18.08 (3)	± 0.04	140.1	73.42	0.6	7.2	4.9
8	17.89 (3)	± 0.07	138.6	148.17	1.5	8.7	5.9

* Surface Area 80.39 ± 0.04 cm² Specific Gravity 0.964 ± 0.001

APPENDIX X

OIL RETENTIVITY OF SINKING AGENTS

EXPERIMENTAL DATA

TABLE 10-1

OIL RETENTIVITY - OIL-LOK 501 AND WESTERN CRUDE OIL*

Test	Oil Layer (mm)		Accum. Time (h)			Weight Oil in	Volatility Loss (%)[1]		
	Average	Std. Devn.	dp	t	(dp-t)	Float (g)	V_{dp}	V_t	$V_{(dp-t)}$
Start	15.67 (3)	± 0.04	-	-	-	105.2	-	-	-
Delay	14.90 (3)	± 0.02	0.50	-	0.50	100.6 (T_o)	4.4	-	4.4
1	7.66 (3)	± 0.05	0.50	-	0.50	51.5 (I)	4.4	-	4.4
2	8.02 (3)	± 0.07	0.50	0.67	1.17	54.0 Mt	4.4	5.2	6.6
3	8.25 (3)	± 0.01	0.50	2.25	2.75	55.5 "	4.4	9.2	9.8
4	8.59 (3)	± 0.09	0.50	7.00	7.50	57.8 "	4.4	13.2	13.5
5	8.26 (3)	± 0.05	0.50	19.67	20.17	55.6 "	4.4	17.8	18.0
6	7.84 (3)	± 0.06	0.50	44.17	44.67	52.7 "	4.4	23.0	23.2
7	7.63 (3)	± 0.03	0.50	94.67	95.17	51.3 "	4.4	25.6	25.7
8	7.52 (3)	± 0.03	0.50	139.17	139.67	50.8 "	4.4	26.6	26.7

Released Oil R_t (g)	Oil in Sunken Mass (g)	Retained Oil OR_t (%)	Sinking Agent/Oil SA/O_t
-	-	-	-
-	-	-	-
-	49.1 (S_o)	-	3.58
3.8	45.3	92.2	3.88
7.2	41.9	85.3	4.20
10.8	38.3	78.0	4.59
12.5	36.6	74.5	4.81
12.8	36.3	73.9	4.84
12.9	36.2	73.7	4.86
13.1	36.0	73.3	4.89

* Surface Area 81.35 ± 0.04 cm^2 Temperature 21 ± 1 °C Free Fall Distance 15 cm

Total Weight of Sinking Agent (SA) 175.9 g Equations 45-49 Used for All Calculations

[1] Determined from Expanded Charts for Figures 43 and 44

TABLE 10-2

OIL RETENTIVITY - OIL-LOK 501 AND NO. 2 FUEL OIL *

Test	Oil Layer (mm)		Accum. Time (h)			Weight Oil in Float (g)	Volatility Loss (%) 1.		
	Average	Std. Devn.	dp	t	(dp+t)		V_{dp}	V_t	$V_{(dp+t)}$
Start	17.74 (3)	± 0.02	-	-	-	120.7	-	-	-
Delay	17.69 (3)	± 0.01	0.28	-	0.28	120.4(T_0)	0.23	-	0.23
1	8.54 (3)	± 0.08	0.28	-	0.28	58.1(I)	0.23	-	0.23
2	9.30 (2)	± 0.05	0.28	0.25	0.53	63.3 M_t	0.23	0.22	0.35
3	9.80 (3)	± 0.01	0.28	1.25	1.53	66.7 "	0.23	0.60	0.68
4	9.96 (3)	± 0.04	0.28	5.08	5.36	67.8 "	0.23	1.20	1.25
5	10.21 (3)	± 0.03	0.28	6.00	6.28	69.5 "	0.23	1.32	1.35
6	10.31 (3)	± 0.03	0.28	10.83	11.11	70.2 "	0.23	1.72	1.75
7	10.41 (3)	± 0.04	0.28	23.67	23.95	70.8 "	0.23	2.65	2.70
8	10.43 (3)	± 0.01	0.28	47.25	47.53	71.0 "	0.23	3.93	3.95
9	10.37 (3)	± 0.01	0.28	98.58	98.86	70.6 "	0.23	5.00	5.05
10	10.37 (3)	± 0.03	0.28	146.83	147.11	70.6 "	0.23	5.05	5.08

Released Oil R_t (g)	Oil In Sunken Mass (g)	Retained Oil OR_t (%)	Sinking Agent/Oil SA/O_t
-	-	-	-
-	-	-	-
-	62.2	-	3.41
5.3	56.9	91.5	3.73
8.9	53.3	85.7	3.98
10.4	51.8	83.3	4.10
12.1	50.1	80.5	4.24
13.1	49.1	78.9	4.32
14.3	47.9	77.0	4.43
15.4	46.8	75.2	4.53
15.7	46.5	74.8	4.56
15.75	46.45	74.7	4.57

* Surface Area 81.03 ± 0.04 cm² Temperature 21±1°C Free Fall Distance 15 cm
Total Weight Sinking Agent 212.2 g Equations 45f Used for All Calculations

1. Determined from Expanded Charts for Figure 45

TABLE 10-3

OIL RETENTIVITY - OIL-LOK 501 AND NO. 6 BUNKER OIL*

Test	Oil Layer (mm)		Accum. Time (h)			Weight Oil in	Volatility Loss (%)[1]		
	Average	Std. Devn.	dp	t	(dp-t)	Float (g)	V_{dp}	V_t	$V_{(dp-t)}$
Start	20.9^7 (2)	± 0.1^1	-	-	-	162.5	-	-	-
Delay	20.90 (3)	± 0.06	0.50	-	0.50	161.9(T_0)	0.35	-	0.35
1	12.93 (2)	± 0.02	0.50	-	0.50	100.2 (I)	0.35	-	0.35
2	13.17 (3)	± 0.05	0.50	0.83	1.33	102.1 M_t	0.35	0.45	0.62
3	13.67 (3)	± 0.08	0.50	1.83	2.33	105.9 "	0.35	0.75	0.85
4	14.3^9 (3)	± 0.1^6	0.50	20.42	20.92	111.5 "	0.35	2.55	2.58
5	14.43 (3)	± 0.04	0.50	70.25	70.75	111.8 "	0.35	4.57	4.60
6	14.51 (3)	± 0.04	0.50	115.00	115.50	112.5 "	0.35	5.45	5.47
7	14.5^0 (3)	± 0.1^4	0.50	162.83	163.33	112.4 "	0.35	5.83	5.84

Released Oil R_t (g)	Oil in Sunken Mass (g)	Retained Oil OR_t (%)	Sinking Agent/Oil SA/O_t
-	-	-	-
-	-	-	-
-	61.7	-	1.67
2.2	59.5	96.4	1.73
6.2	55.5	90.0	1.85
13.7	48.0	77.8	2.14
16.2	45.5	73.7	2.26
17.9	43.8	71.0	2.35
18.2	43.5	70.5	2.36

* Surface Area 80.39 ± 0.04 cm^2 Temperature 21-1°C Free Fall Distance 15 cm

Total Weight of Sinking Agent (SA) 102.8 g Equations 45-49 Used for All Calculations

[1] Determined from Expanded Charts for Figure 46

TABLE 10-4

OIL RETENTIVITY - ZORB-ALL AND WESTERN CRUDE OIL *

Test	Oil Layer (mm)		Accum. Time (h)			Weight Oil in	Volatility Loss (%) 1.		
	Average	Std. Devn.	dp	t	(dp+t)	Float (g)	V_{dp}	V_t	$V_{(dp+t)}$
Start	15.65 (3)	± 0.04	–	–	–	106.9	–	–	–
Delay	14.87 (3)	± 0.02	0.58	–	0.58	101.6(To)	5.0	–	5.0
1	5.23 (3)	± 0.04	0.58	–	0.58	35.7(I)	5.0	–	5.0
2	5.53 (3)	± 0.07	0.58	0.50	1.08	37.8 M_t	5.0	4.4	6.5
3	5.80 (3)	± 0.01	0.58	1.83	2.41	39.6 "	5.0	8.4	9.4
4	5.75 (3)	± 0.03	0.58	5.42	6.00	39.3 "	5.0	12.2	12.6
5	5.53 (3)	± 0.03	0.58	24.42	25.00	37.8 "	5.0	19.5	19.7
6	5.33 (2)	± 0.00	0.58	74.08	74.66	36.4 "	5.0	25.2	25.3
7	5.33 (3)	± 0.05	0.58	118.75	119.33	36.4 "	5.0	26.2	26.3

Released Oil R_t (g)	Oil in Sunken Mass (g)	Retained Oil OR_t (%)	Sinking Agent/Oil SA/O_t
–	–	–	–
–	–	–	–
–	65.9	–	1.48
2.7	63.2	95.9	1.54
5.8	60.1	91.2	1.62
6.9	59.0	89.5	1.65
8.4	57.5	87.2	1.69
9.5	56.4	85.6	1.73
10.0	55.9	84.8	1.74

* Surface Area 82.31 ± 0.04 cm² Temperature 21±1°C ; Free Fall Distance 15 cm.
Total Weight of Sinking Agent (SA) 97.4 g Equations 45f Used for All Calculations

1. Determined from Expanded Charts for Figures 43 and 44

TABLE 10-5

OIL RETENTIVITY - ZORB-ALL AND NO. 2 FUEL OIL *

Test	Oil Layer (mm)		Accum. Time (h)			Weight Oil in Float (g)	Volatility Loss (%) 1.		
	Average	Std. Devn.	dp	t	(dp+t)		V_{dp}	V_t	$V_{(dp+t)}$
Start	17.05 (3)	± 0.02	-	-	-	115.6	-	-	-
Delay	17.00 (3)	± 0.01	0.28	-	0.28	115.3(To)	0.23	-	0.23
1	6.36 (3)	± 0.08	0.28	-	0.28	43.1(I)	0.23	-	0.23
2	7.55 (3)	± 0.09	0.28	0.50	0.78	51.2 M_t	0.23	0.32	0.45
3	9.27 (3)	± 0.11	0.28	2.75	3.03	62.8 "	0.23	0.93	0.95
4	9.57 (3)	± 0.34	0.28	4.08	4.36	64.9 "	0.23	1.10	1.13
5	10.55 (3)	± 0.03	0.28	9.00	9.28	71.5 "	0.23	1.60	1.62
6	11.86 (3)	± 0.09	0.28	21.42	21.70	80.4 "	0.23	2.48	2.50
7	13.06 (3)	± 0.22	0.28	45.92	46.20	88.5 "	0.23	3.95	3.96
8	13.26 (3)	± 0.03	0.28	96.75	97.03	89.9 "	0.23	4.97	4.98
9	13.28 (3)	± 0.01	0.28	145.08	145.36	90.0 "	0.23	5.52	5.53
10	13.31 (3)	± 0.12	0.28	193.08	193.36	90.2 "	0.23	5.65	5.66

Released Oil R_t (g)	Oil in Sunken Mass (g)	Retained Oil OR_t (%)	Sinking Agent/Oil SA/O_t
-	-	-	
-	-	-	
-	72.2	-	1.10
8.2	64.0	88.6	1.24
20.1	52.1	72.2	1.53
22.3	49.9	69.1	1.60
29.2	43.0	59.6	1.85
38.8	33.4	46.2	2.39
48.0	24.2	33.5	3.29
50.1	22.1	30.6	3.61
50.6	21.6	29.9	3.69
50.9	21.3	29.5	3.74

* Surface Area 80.71 ± 0.04 cm^2 Temperature 21±1°C Free Fall Distance 15 cm
Total Weight Sinking Agent (SA) 79.7 g Equations 45f Used for All Calculations

1. Determined from Expanded Charts for Figure 45

TABLE 10-6

OIL RETENTIVITY - HI-DRI AND WESTERN CRUDE OIL *

Test	Oil Layer (mm)		Accum. Time (h)			Weight Oil in Float (g)	Volatility Loss (%) [1]		
	Average	Std. Devn	dp	t	(dp+t)		V_{dp}	V_t	$V_{(dp+t)}$
Start	16.19 (3)	± 0.02	-	-	-	107.6	-	-	-
Delay	15.59 (3)	± 0.03	0.25	-	0.25	104.4 (To)	3.0	-	3.0
1.	4.31 (3)	± 0.04	0.25	-	0.25	28.6 (I)	3.0	-	3.0
2	4.79 (2)	± 0.02	0.25	0.42	0.67	31.8 M_t	3.0	4.2	5.2
3	4.57 (2)	± 0.01	0.25	4.42	4.67	30.4 "	3.0	11.5	11.7
4	4.48 (2)	± 0.00	0.25	24.25	24.50	29.8 "	3.0	19.4	19.5
5	4.39 (3)	± 0.05	0.25	72.92	73.17	29.2 "	3.0	25.2	25.3
6	4.42 (3)	± 0.05	0.25	117.58	117.83	29.6 "	3.0	26.1	26.2

Released Oil R_t (g)	Oil in Sunken Mass (g)	Retained Oil OR_t (%)	Sinking Agent/Oil SA/O_t
-	-	-	-
-	-	-	-
-	75.8	-	1.09
3.9	71.9	94.8	1.15
4.6	71.2	93.9	1.16
6.7	69.1	91.2	1.19
8.2	67.6	89.2	1.22
9.0	66.8	88.1	1.23

* Surface Area 80.68 ± 0.04 cm^2 Temperature 21±1°C FreeFall Distance 15 cm
Total Weight Sinking Agent (SA) 82.4 g Equations 45f Used for All Calculations

[1] Determined from Expanded Charts for Figure 43 and 44

TABLE 10-7

OIL RETENTIVITY - HI-DRI AND NO. 2 FUEL OIL*

Test	Oil Layer (mm)		Accum. Time (h)			Weight Oil in Float (g)	Volatility Loss (%) [1.]		
	Average	Std. Devn.	dp	t	(dp+t)		V_{dp}	V_t	$V_{(dp+t)}$
Start	17.28 (3)	± 0.03	-	-	-	117.6	-	-	-
Delay	17.22 (2)	± 0.01	0.37	-	0.37	117.2(To)	0.27	-	0.27
1	10.35 (3)	± 0.16	0.37	-	0.37	70.4(I)	0.27	-	0.27
2	11.55 (2)	± 0.01	0.37	1.00	1.37	78.6 M_t	0.27	0.55	0.65
3	12.24 (3)	± 0.04	0.37	3.95	4.32	83.3 "	0.27	1.07	1.13
4	13.12 (3)	± 0.07	0.37	7.58	7.95	89.3 "	0.27	1.48	1.50
5	13.69 (3)	± 0.01	0.37	20.67	21.04	93.2 "	0.27	2.42	2.45
6	13.79 (3)	± 0.02	0.37	43.00	43.37	93.9 "	0.27	3.77	3.79
7	13.96 (3)	± 0.05	0.37	95.75	96.12	95.0 "	0.27	4.98	4.99
8	14.07 (2)	± 0.07	0.37	144.17	144.54	95.8 "	0.27	5.51	5.52
9	14.15 (3)	± 0.03	0.37	192.17	192.54	96.3 "	0.27	5.64	5.65

Released Oil R_t (g)	Oil in Sunken Mass (g)	Retained Oil OR_t (%)	Sinking Agent/Oil SA/O_t
-	-	-	-
-	-	-	-
-	46.8	-	1.06
8.5	38.3	81.8	1.30
13.6	33.2	70.9	1.50
19.9	26.9	57.4	1.85
24.6	22.2	47.4	2.24
26.5	20.3	43.4	2.45
28.6	18.2	38.9	2.73
29.9	16.9	36.1	2.94
30.6	16.2	34.6	3.07

* Surface Area 81.03 ± 0.04 cm^2 Temperature 21±1°C Free Fall Distance 15 cm
Total Weight of Sinking Agent (SA) 49.8 g Equations 45f Used for All Calculations

1. Determined from Expanded Charts for Figure 45

STUDIES IN CHEMISTRY

PART II

THE APPLICATION OF LAOCN 3 TO THE ANALYSIS OF OF THE PROTON MAGNETIC RESONANCE SPECTRA OF SEVERAL OLEFINIC ACETYLENES

Anatol Feldman

A THESIS
in the
Department of Chemistry

Presented in Partial Fulfillment of the Requirements
for the Degree of Master of Science at

Concordia University
Montreal, Canada

April, 1975

DEDICATION

With love, to my wife

ABSTRACT

PART II: THE APPLICATION OF LAOCN 3 TO THE ANALYSIS OF THE PROTON MAGNETIC RESONANCE SPECTRA OF SEVERAL OLEFINIC ACETYLENES

Anatol Feldman

Due to the computer limitations of a previous study, the experimental spectra of 25 olefinic acetylenes were re-analyzed using a CDC 6400 computer. The program used, LAOCN 3, was capable of adjusting the chemical shifts and coupling constants to give a best fit to observed sets of transitions. LAOCN 3 is the third revision of two previous LAOCN programs.

Because of the weak coupling found in many of the spectra, the X-approximation was used to disassemble complex spin systems into smaller parts.

The final revisions agreed well with the previous study.

ACKNOWLEDGEMENTS

The guidance of Dr. L.D. Colebrook during this investigation was appreciated.

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1 INTRODUCTION

The proton magnetic resonance spectra of 25 olefinic acetylenes were examined by means of the computer program, LAOCN 2, in a Ph.D. thesis by A.H. Turner (1) at the University of Rochester in 1964. Appendix I outlines the original experimental details. This study was hampered by the limits of the available computer, an IBM 7074. This computer had a word core of 10 000, whereas LAOCN 2 was designed for an IBM 7040 computer with a word core of 64 000. The direct calculation capacity of the first part of LAOCN 2 had to be reduced, and the second part of LAOCN 2 which compared calculated with experimental values in an iterative fashion could not be used.

Because of these limitations, it was necessary to match computed and experimental spectra visually, with the result that an error analysis was not possible. Further, because of the restricted capability of the modified version of LAOCN 2, approximate methods of analysis had to be used in a number of cases. Since plotting of the computer simulated spectra was not possible, it was necessary to hand plot the computed spectra in the form of stick diagrams and to visually match these to the experimental spectra, which limited the accuracy of the matching procedure.

In order to increase the accuracy of the analyses, it was decided to re-process the data, using Turner's results as the starting point. The spectra of the 25 olefinic acetylenes were examined on a CDC 6400 computer, capable of fully handling the third revision of the same program called LAOCN 3. LAOCN 3 is more computer efficient;

otherwise it differs little from the full LAOCN 2 program.

1.1 Division of the Analysis

The 25 olefinic acetylenes could be separated for analysis in order of difficulty. In each section some compounds were covered in detail if there was some advantage to be gained from their analysis.

1.1.1 Compounds with Less than Seven Spins.

This part of the study contained ten compounds of six spins or less which required only the straightforward application of LAOCN 3.

1.1.2 Compounds with Seven Spins.

The second part consisted of five compounds of seven coupled spins for which LAOCN 3, despite the claims of its authors A.A. Bothner-By and S.M. Castellano (2), proved inadequate. The compounds, because of the first order nature of their spectra, could be broken down by the X-approximation (3) into simpler moieties and then reconstructed. Further revision (4) of LAOCN 3 enabled this set to be handled as full seven-spin systems.

1.1.3 Compounds with More than Seven Spins.

The spectra of six compounds of eight spins or more were dismembered into a variety of simpler spin systems depending on their complexity.

1.1.4 Unsolved Problems.

The last part contained those problems which, for one reason or another, did not yield a profitable conclusion. The spectrum of one compound, because of excessive noise and poor resolution, could not be analyzed. One eight-spin compound deviated sufficiently from first order so that the X-approximation could not be applied. Two compounds were simple AB systems and their spectra were unavailable.

Table 1 contains the original data of the 25 olefinic acetylenes to be studied; only the compound numbers have been changed since the order in which they were handled was different.

2 DESCRIPTION OF LAOCN 3

The program LAOCN 3 was obtained from "Computer Programs for Chemistry, Volume 1", edited by Delos F. Detar (2) and was written by A.A. Bothner-By and S.M. Castellano.

It is the third revision of a program for the analysis of high-resolution NMR spectra. The program calculates transition energies (line positions) and intensities based on assumed chemical shifts and coupling constants and, if data are available, adjusts the chemical shifts and coupling constants to give a best fit to an observed set of transition energies.

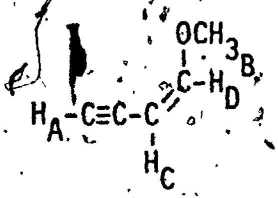
2.1 Direct Calculation

For input data LAOCN 3 required: a case number, the number of spin-coupled protons in the compound, an identifying legend, a range of frequencies and their minimum intensities, the isotopic variety of each nucleus (called the iso numbers), and a set of chemical shifts and coupling constants. The chemical shifts and coupling constants were the most important factors governing the appearance of the spectrum.

TABLE 1

NAME, STRUCTURE, AND ORIGINAL SPECTRAL DATA FOR 25 OLEFIN-ACETYLENES

Compound 1. 1-methoxy-*cis*-1-butene-3-yne



Solvent: neat

$\nu_A = 187.1$ Hz (6.88τ)

$\nu_B = 222.6$ (6.29τ)

$\nu_C = 267.3$ (5.55τ)

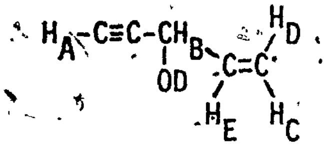
$\nu_D = 383.5$ (3.61τ)

$J_{AC} = -2.5$ Hz

$J_{AD} = 0.9$

$J_{CD} = 6.5$

Compound 2. 1-pentene-4-yne-3-ol



Solvent: $CDCl_3$

$\nu_A = 157.7$ Hz (7.37τ)

$\nu_B = 292.6$ (5.12τ)

$\nu_C = 313.3$ (4.78τ)

$\nu_D = 328.0$ (4.53τ)

$\nu_E = 357.5$ (4.05τ)

$J_{AB} = -2.2$ Hz

$J_{BC} = -1.4$

$J_{BD} = -1.5$

$J_{BE} = 5.4$

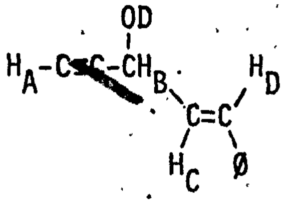
$J_{CD} = 1.1$

$J_{CE} = 10.35$

$J_{DE} = 16.95$

TABLE 1 continued

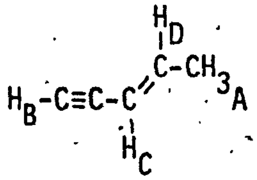
<u>Compound 3.</u> 1-phenyl-<u>trans</u>-1-pentene-4-yne-3-ol



Solvent: $CDCl_3$

$\nu_A = 154.0$ Hz (7.44τ) $J_{AB} = -2.2$ Hz
$\nu_B = 299.4$ (5.01τ) $J_{BC} = 5.8$
$\nu_C = 374.7$ (3.75τ) $J_{BD} = -0.5$
$\nu_D = 403.8$ (3.27τ) $J_{CD} = 15.8$

<u>Compound 4.</u> <u>trans</u>-2-pentene-4-yne

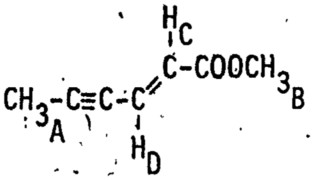


Solvent: $CDCl_3$

$\nu_A = 107.0$ Hz (8.23τ) $J_{AB} = -0.7$ Hz
$\nu_B = 165.2$ (7.24τ) $J_{AC} = -1.8$
$\nu_C = 328.4$ (4.52τ) $J_{AD} = 6.8$
$\nu_D = 374.6$ (3.76τ) $J_{BC} = -1.6$
$J_{CD} = 15.9$

TABLE 1 continued.

Compound 5. methyl trans-2-hexene-4-ynate

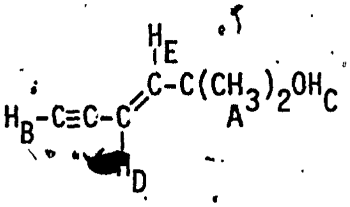

$CH_{3_A}-C\equiv C-\underset{H_D}{C}=\overset{H_C}{C}-COOCH_{3_B}$

Solvent: $CDCl_3$

$\nu_A = 120.4$ Hz (7.99τ)
$\nu_B = 223.1$ (6.28τ)
$\nu_C = 368.0$ (3.86τ)
$\nu_D = 402.9$ (3.28τ)

$J_{AC} = -0.6$ Hz
$J_{AD} = 2.4$
$J_{CD} = 16.2$

Compound 6. 5-methyl-trans-3-hexene-1-yne-5-ol


$H_B-C\equiv C-\underset{H_D}{C}=\overset{H_E}{C}-C(CH_{3_A})_2OH_C$

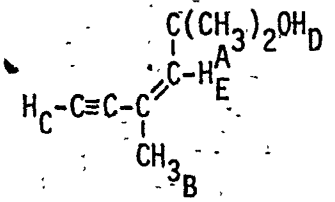
Solvent: $CDCl_3$

$\nu_A = 79.2$ Hz (8.68τ)
$\nu_B = 171.3$ (7.15τ)
ν_C ~~= 174.1~~ (7.10τ)
$\nu_D = 340.9$ (4.32τ)
$\nu_E = 379.9$ (3.67τ)

$J_{BD} = -2.3$ Hz
$J_{BE} = 0.6$
$J_{DE} = 16.1$

TABLE 1 continued

<u>Compound 7.</u> 3,5-dimethyl-<u>cis</u>-3-hexene-1-yne-5-ol



$\mathrm{H_C{-}C{\equiv}C{-}\underset{CH_{3_B}}{C}{=}\overset{C(CH_{3_A})_2OH_D}{C}{-}H_E}$

Solvent: $CDCl_3$

ν_A = 84.0 Hz (8.60τ) J_{BE} = -1.5 Hz

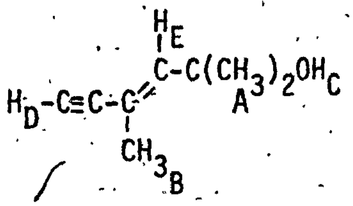
ν_B = 111.8 (8.14τ) J_{CE} = 0.8

ν_C = 202.0 (6.63τ)

ν_D = 226.0 (6.23τ)

ν_E = 355.5 (4.08τ)

<u>Compound 8.</u> 3,5-dimethyl-<u>trans</u>-3-hexene-1-yne-5-ol



$\mathrm{H_D{-}C{\equiv}C{-}\underset{CH_{3_B}}{C}{=}\overset{H_E}{C}{-}C(CH_{3_A})_2OH_C}$

Solvent: $CDCl_3$

ν_A = 84.6 Hz (8.59τ) J_{BE} = -1.6 Hz

ν_B = 112.9 (8.12τ) J_{DE} = 0.6

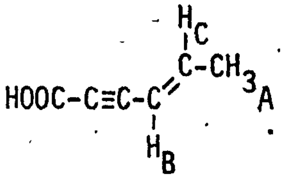
ν_C = 190.2 (6.84τ)

ν_D = 201.2 (6.65τ)

ν_E = 356.6 (4.05τ)

TABLE 1 continued

Compound 9. trans-4-hexene-2-ynoic acid



$\mathrm{HOOC{-}C{\equiv}C{-}\underset{H_B}{C}{=}\overset{H_C}{C}{-}CH_{3_A}}$

Solvent: $CDCl_3$

$\nu_A = 113.0$ Hz (8.12τ)

$\nu_B = 336.8$ (4.39τ)

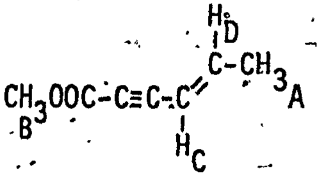
$\nu_C = 394.8$ (3.42τ)

$J_{AB} = -1.7$ Hz

$J_{AC} = 6.9$

$J_{BC} = 15.9$

Compound 10. methyl trans-4-hexene-2-ynate



$\mathrm{\underset{B}{CH_3}OOC{-}C{\equiv}C{-}\underset{H_C}{C}{=}\overset{H_D}{C}{-}CH_{3_A}}$

Solvent: $CDCl_3$

$\nu_A = 111.5$ Hz (8.14τ)

$\nu_B = 224.9$ (6.25τ)

$\nu_C = 335.4$ (4.41τ)

$\nu_D = 389.8$ (3.50τ)

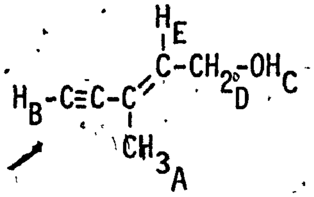
$J_{AC} = -1.8$ Hz

$J_{AD} = 6.9$

$J_{CD} = 15.9$

TABLE 1 continued

Compound 11. 3-methyl-trans-2-pentene-4-yne-1-ol

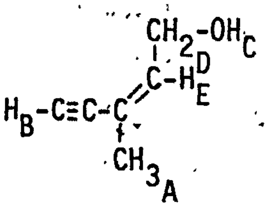


$H_B\text{-}C{\equiv}C\text{-}C(CH_{3_A}){=}C(H_E)\text{-}CH_{2_D}\text{-}OH_C$

Solvent: $CDCl_3$

ν_A = 108.9 Hz	(8.17τ)	J_{AD} = 0.8 Hz
ν_B = 171.4	(7.14τ)	J_{AE} = -1.5
ν_C = 192.8	(6.79τ)	J_{BD} = -0.3
ν_D = 251.6	(5.18τ)	J_{BE} = 0.6
ν_E = 363.2	(3.95τ)	J_{DE} = 6.7

Compound 12. 3-methyl-cis-2-pentene-4-yne-1-ol



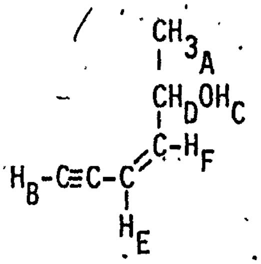
$H_B\text{-}C{\equiv}C\text{-}C(CH_{3_A}){=}C(H_E)\text{-}CH_{2_D}\text{-}OH_C$

Solvent: $CDCl_3$

ν_A = 113.9 Hz	(8.10τ)	J_{AD} = 1.2 Hz
ν_B = 194.2	(6.76τ)	J_{AE} = -1.5
ν_C = 234.3	(6.09τ)	J_{BE} = 0.8
ν_D = 259.5	(5.66τ)	J_{DE} = 6.6
ν_E = 356.4	(4.06τ)	

TABLE 1 continued

Compound 13. cis-3-hexene-1-yne-5-ol



Solvent: $CDCl_3$

ν_A = 78.0 Hz (8.70τ) J_{AD} = 6.5 Hz

ν_B = 198.6 (6.69τ) J_{BE} = -2.4

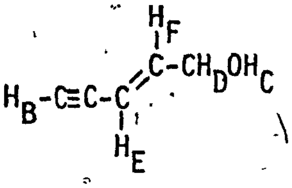
ν_C = 255.3 (5.75τ) J_{BF} = 0.9

ν_D = 289.9 (5.20τ) J_{DE} = -1.1

ν_E = 328.7 (4.52τ) J_{DF} = 8.2

ν_F = 363.1 (3.95τ) J_{EF} = 11.1

Compound 14. trans-3-hexene-1-yne-5-ol



Solvent: $CDCl_3$

ν_A = 76.0 Hz (8.73τ) J_{AD} = 6.5 Hz

ν_B = 174.6 (7.10τ) J_{BD} = -0.5

ν_C = 186.3 (6.89τ) J_{BE} = -2.3

ν_D = 259.6 (5.67τ) J_{BF} = 0.6

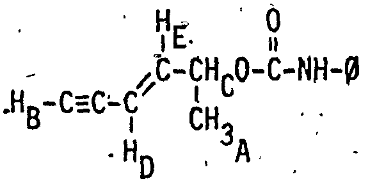
ν_E = 340.3 (4.33τ) J_{DE} = -1.4

ν_F = 375.5 (3.79τ) J_{DF} = 5.5

J_{EF} = 16.0

TABLE 1 continued

Compound 15. trans-3-hexene-1-yne-5-ol carbanilide

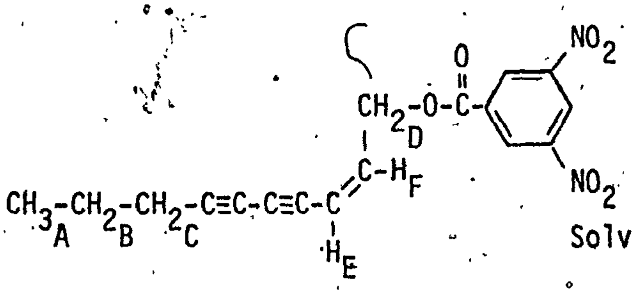


Solvent: $CDCl_3$

ν_A = 79.9 Hz (8.67τ)
ν_B = 174.3 (7.09τ)
ν_C = 322.2 (4.63τ)
ν_D = 341.8 (4.31τ)
ν_E = 371.7 (3.81τ)

J_{AC} = 6.5 Hz
J_{BD} = -2.2
J_{BE} = 0.6
J_{CD} = -1.4
J_{CE} = 6.1
J_{DE} = 16.0

Compound 16. cis-2-decene-4,6-diyn-1-yl-3,5-dinitrobenzoate



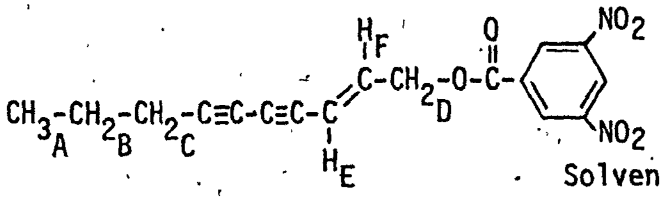
Solvent: $CDCl_3$

ν_A = 60.3 Hz (8.99τ)
ν_B = 94.9 (8.42τ)
ν_C = 138.6 (7.69τ)
ν_D = 312.0 (4.80τ)
ν_E = 349.8 (4.17τ)
ν_F = 374.6 (3.25τ)

J_{AB} = 7.2 Hz
J_{BC} = 6.5
J_{DE} = -1.2
J_{DF} = 6.4
J_{EF} = 10.9

TABLE 1 continued

Compound 17. trans-2-decene-4,6-diyn-1-yl-3,5-dinitrobenzoate



Solvent: $CDCl_3$

ν_A = 59.9 Hz (9.01τ)

ν_B = 94.6 (8.42τ)

ν_C = 138.6 (7.69τ)

ν_D = 299.0 (5.02τ)

ν_E = 354.4 (4.09τ)

ν_F = 382.6 (3.63τ)

J_{AB} = 7.1 Hz

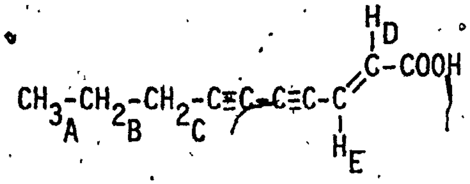
J_{BC} = 6.7

J_{DE} = -1.3

J_{DF} = 6.3

J_{EF} = 15.8

Compound 18. trans-2-decene-4,6-diynoic acid



$\mathrm{CH_{3_A}-CH_{2_B}-CH_{2_C}-C\equiv C-C\equiv C-\underset{H_E}{C}=\overset{H_D}{C}-COOH}$

Solvent: $CDCl_3$

ν_A = 60.0 Hz (9.00τ)

ν_B = 95.2 (8.41τ)

ν_C = 140.5 (7.66τ)

ν_D = 376.4 (3.72τ)

ν_E = 409.6 (3.18τ)

J_{AB} = 7.2 Hz

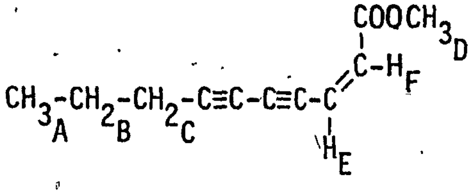
J_{BC} = 6.8

J_{CE} = 0.9

J_{DE} = 15.8

TABLE 1 continued

Compound 19. methyl cis-2-decene-4,6-diynate



$CH_{3_A}-CH_{2_B}-CH_{2_C}-C\equiv C-C\equiv C-C(H_E)=C(H_F)-COOCH_{3_D}$

Solvent: $CDCl_3$

ν_A = 60.1 Hz (9.00τ)

ν_B = 95.5 (8.41τ)

ν_C = 141.2 (7.65τ)

ν_D = 225.3 (6.25τ)

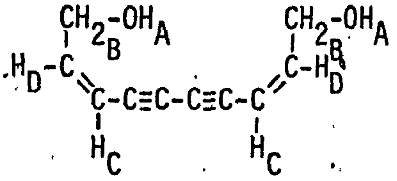
ν_E = 372.2 (3.80τ)

ν_F = 372.5 (3.80τ)

J_{AB} = 7.2 Hz

J_{BC} = 6.8

Compound 20. cis,cis-2,8-decadiene-4,6-diyne-1,10-diol



$H_D-C(CH_{2_B}-OH_A)=C(H_C)-C\equiv C-C\equiv C-C(H_C)=C(CH_{2_B}-OH_A)-H_D$

Solvent: CD_3COCD_3

ν_A = 246.0 Hz (5.90τ)

ν_B = 260.0 (5.66τ)

ν_C = 340.7 (4.32τ)

ν_D = 377.7 (3.70τ)

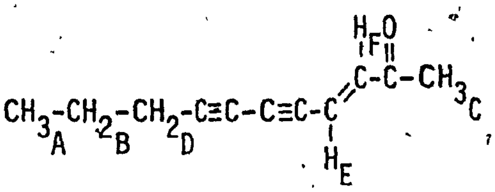
J_{BC} = -1.2 Hz

J_{BD} = 6.3

J_{CD} = 11.2

TABLE 1 continued

Compound 21. trans-3-undecene-5,7-diyne-2-one



$CH_{3_A}-CH_{2_B}-CH_{2_D}-C\equiv C-C\equiv C-\underset{H_E}{C}=\overset{H_F}{C}-\overset{O}{\overset{\|}{C}}-CH_{3_C}$

Solvent: $CDCl_3$

$\nu_A = 60.0$ Hz (9.00τ)

$\nu_B = 95.0$ (8.14τ)

$\nu_C = 134.2$ (7.76τ)

$\nu_D = 141.5$ (7.64τ)

$\nu_E = 393.9$ (3.44τ)

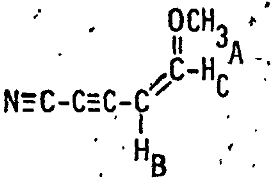
$\nu_F = 393.9$ (3.44τ)

$J_{AB} = 7.2$ Hz

$J_{BD} = 6.8$

$J_{EF} = 16.0$

Compound 22. 1-methoxy-4-cyano-cis-1-butene-3-yne



$N\equiv C-C\equiv C-\underset{H_B}{C}=\overset{OCH_{3_A}}{\overset{\|}{C}}-H_C$

Solvent: $CDCl_3$

$\nu_A = 230.7$ Hz (6.16τ)

$\nu_B = 275.2$ (5.41τ)

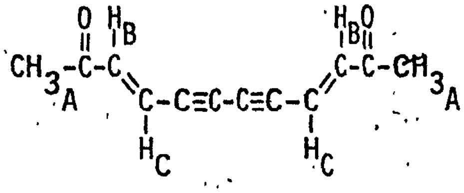
$\nu_C = 406.0$ (3.23τ)

$J_{BC} = 6.4$ Hz

$J_{AC13} = 146.2$

TABLE 1 continued

Compound 23. trans,trans-3,9-dodecadiene-5,7-diyne-2,11-dione



$\mathrm{CH_{3_A}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{H_B}{C}{=}\underset{H_C}{C}\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}\underset{H_C}{C}{=}\overset{H_B}{C}\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_{3_A}}$

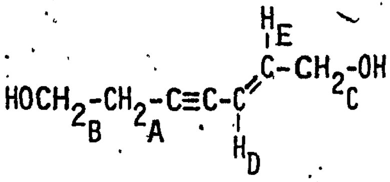
Solvent: $CDCl_3$

$\nu_A = 136.8$ Hz (7.72τ)

$\nu_B = 400.0$ (3.33τ)

$\nu_C = 400.0$ (3.33τ)

Compound 24. trans-2-heptene-4-yne-1,7-diol



$\mathrm{HOCH_{2_B}\text{-}CH_{2_A}\text{-}C{\equiv}C\text{-}\underset{H_D}{C}{=}\overset{H_E}{C}\text{-}CH_{2_C}\text{-}OH}$

Solvent: D_2O/CD_3COCD_3

$\nu_A = 151.7$ Hz (7.47τ)

$\nu_B = 219.9$ (6.34τ)

$\nu_C = 247.4$ (5.88τ)

$\nu_D = 343.7$ (4.27τ)

$\nu_E = 370.5$ (3.82τ)

$J_{AB} = 6.8$ Hz

$J_{AD} = 1.6$

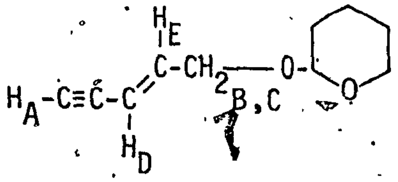
$J_{CD} = -1.2$

$J_{CE} = 5.0$

$J_{DE} = 16.0$

TABLE 1 continued

Compound 25. trans-2-pentene-4-ynyl tetrahydro-2-pyranyl ether.



Solvent: $CDCl_3$

ν_A = 172.5 Hz (7.13τ)
ν_B = 240.1 (6.00τ)
ν_C = 254.3 (5.76τ)
ν_D = 342.6 (4.29τ)
ν_E = 375.8 (3.74τ)

J_{AB} = - 0.8 Hz
J_{AC} = - 0.7
J_{AD} = - 2.3
J_{AE} = 0.6
J_{BC} = -14.6
J_{BD} = - 1.9
J_{BE} = 5.7
J_{CD} = - 1.9
J_{CE} = 4.9
J_{DE} = 16.0

NEW COMPOUND NUMBERS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
ORIGINAL COMPOUND NUMBERS	1	3	4	5	9	13	14	15	16	17	7	6	10	11	12	19	20	21	22	23	24	2	25	18	8

As output data, the program gave all input data plus two tables of transitions. The first table gave an identifying number for each transition, its frequency and its intensity. The second table contained the same data as the first but arranged in order of increasing frequency of transition. This ordered set had a maximum output of 300 lines. Lines in the trial data of the ordered set were matched with observed lines in the experimental spectrum in so far as possible.

2.2 Iterative Calculation

An iterative calculation required the same input data as in the trial direct calculation; in addition the sets of parameters of chemical shifts and coupling constants which were to be varied in fitting the spectrum had to be specified. Experimental frequencies corresponding to line numbers obtained in the preliminary trial direct calculation had to be fed in.

In the output of the iterated calculations the input data were returned and, in addition, the following:

1. A table of values of the adjusted chemical shifts and coupling constants.
2. A table of the probable errors associated with the values of each parameter.
3. Two tables of transitions. The first table contained, for each transition, the line identification number, the assigned experimental frequency (if any), the

calculated frequency and intensity, and the error in fitting, if an experimental frequency had been given. The second table contained the same data but arranged in order of increasing calculated frequencies.

4. The root mean square (RMS) error in fitting of assigned lines for the trial calculation.

The iterative process was halted if the RMS error was reduced by less than 1% on two successive iterations. If the RMS error was still too high, further matching or re-assignments were, if possible, continued and a second iterated calculation was performed. An RMS error below 0.1 was generally a sufficient indication of agreeable correspondance between the experimental spectrum and the calculated transition. The RMS error for most of the compounds in this work varied from 0.03 to 0.1.

Appendix II contains the data card information required for the LAOCN 3 program.

2.3 SHAPE

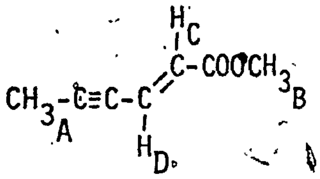
Another program, called SHAPE, needing as input information the range of transition frequencies and intensities bounding the spectrum, plotted the finished product. Appendix III contains the data card information required for the SHAPE program. Appendix IV contains a complete computer print-out for an analyzed sample, Compound 5, methyl trans-2-hexene-4-ynate.

Figure 1 shows a simplified flow diagram of how LAOCN 3 manufactures a synthetic facsimile of an experimental spectrum.

3 COMPOUNDS WITH LESS THAN SEVEN SPINS

Except for the simplest two- or three-spin coupled compounds the wealth of calculated lines that LAOCN 3 can produce far exceeds experimental observations. A very large number of transitions may sometimes contribute to a single spectral line.

3.1 Example: Analysis of Compound 5



$CH_{3_A}\text{-}C{\equiv}C\text{-}C(H_D){=}C(H_C)\text{-}COOCH_{3_B}$

methyl trans-2-hexene-4-ynate

Compound 5, presenting a spectrum of moderate noise, a five-spin system with 13 experimental lines which had to be fitted to 70 calculated lines, was chosen to investigate the problem of redundancy. The first experimental multiplet, due to the terminal acetylenic methyl group at 119.0 Hz, was attributable to 12 calculated lines as shown in Table 2.

The spread in frequency was not significant; numbers 52 to 155 clearly belonged to the experimental frequency of 119.0 Hz, but there was a wide spread of intensity. A proper choice of the exact calculated transition could be decided upon after, not only the position, but also the intensity was taken into consideration.

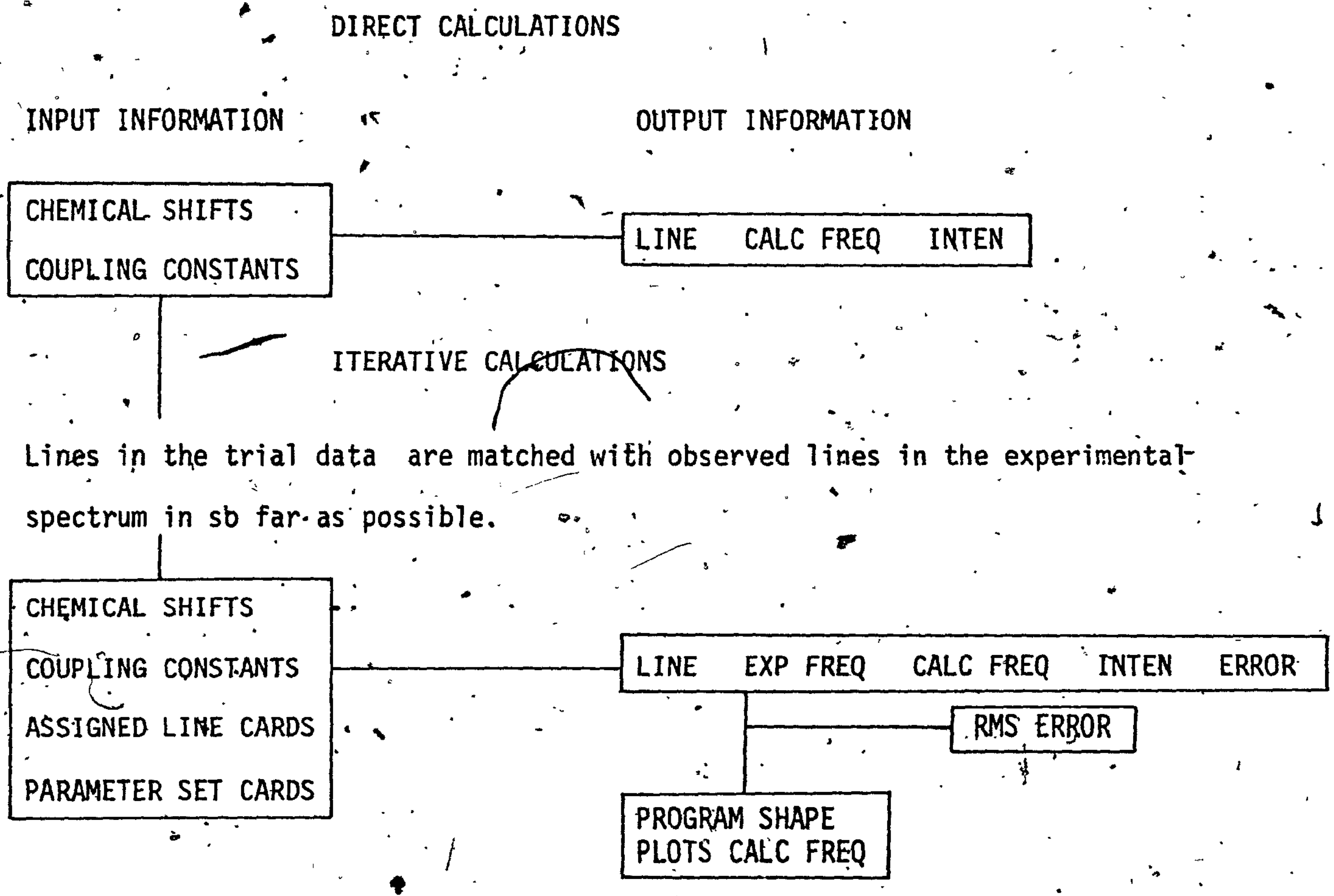


FIGURE 1 SIMPLIFIED FLOW DIAGRAM OF LAOCN 3.

TABLE 2

COMPOUND 5: COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED TRANSITIONS

LINE	EXP FREQ	CALC FREQ	INTEN
52	119.0	119.023	2.699
120		119.033	3.959
142		119.033	0.247
132		119.033	0.742
141		119.033	0.742
131		119.033	0.247
177		119.048	2.969
208		119.483	2.981
195		119.494	0.980
199		119.494	0.980
203		119.494	3.976
155		119.506	2.982
1	121.0	121.284	3.018
6		121.295	4.024

Compound 5 was analyzed in two ways, presented diagrammatically in Figure 2.

3.1.1 Method A: Group Assignment. In the direct calculation the lines produced were assigned on a group basis, as in Table 2. The iterated calculation had an RMS error of 0.155. Lines with the biggest error were removed. All cards with an error bigger than 0.1 were discarded. Hopefully, the remaining cards with the least error were those of the proper intensity. A second iterated calculation gave an RMS error of 0.081 which was within the bounds of acceptability.

3.1.2 Method B: Line-to-Line Matching. The lines produced were carefully chosen and assigned on a one-to-one basis to fit as closely as possible with the experimental results. Intensity of lines was taken into account in so far as ridiculous choices were avoided. For example, the line at 119.0 Hz in the experimental spectrum was the most intense line; yet in Table 2 the choice in intensity assignment lay between 3.976 and 0.247. The iterated calculations by this method had an RMS error of 0.145. Several lines were shifted to conform better with the experimental spectrum and a second iteration produced an RMS error of 0.089.

3.1.3 Comparison of Methods. Spectra were drawn for both methods from the full output decks produced by the second iterated calculations. Both calculated spectra matched well the experimental spectrum as can be seen in Figure 3.

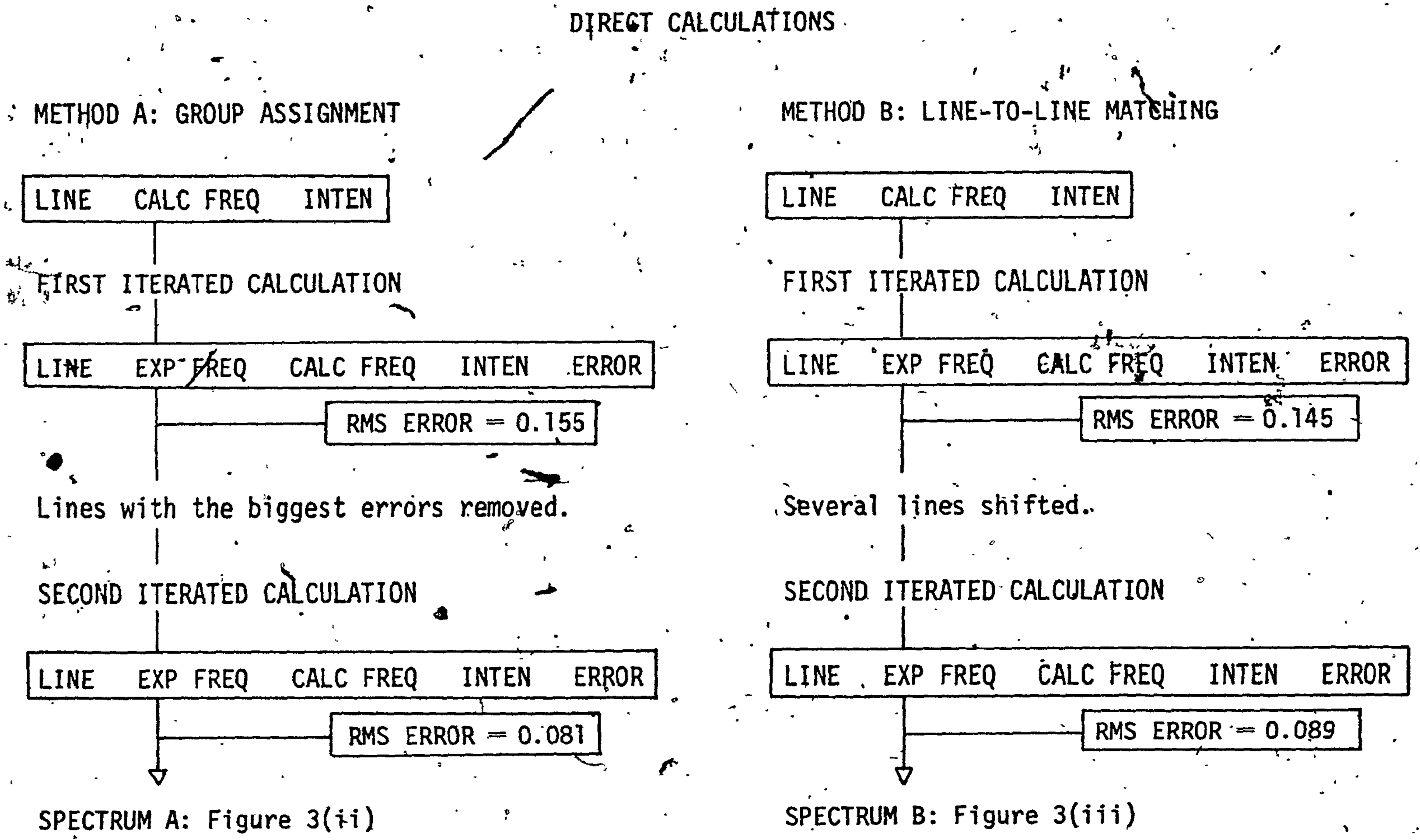


FIGURE 2 FLOW DIAGRAM OF THE ANALYSIS OF COMPOUND 5, METHYL TRANS-2-HEXENE-4-YNATE.

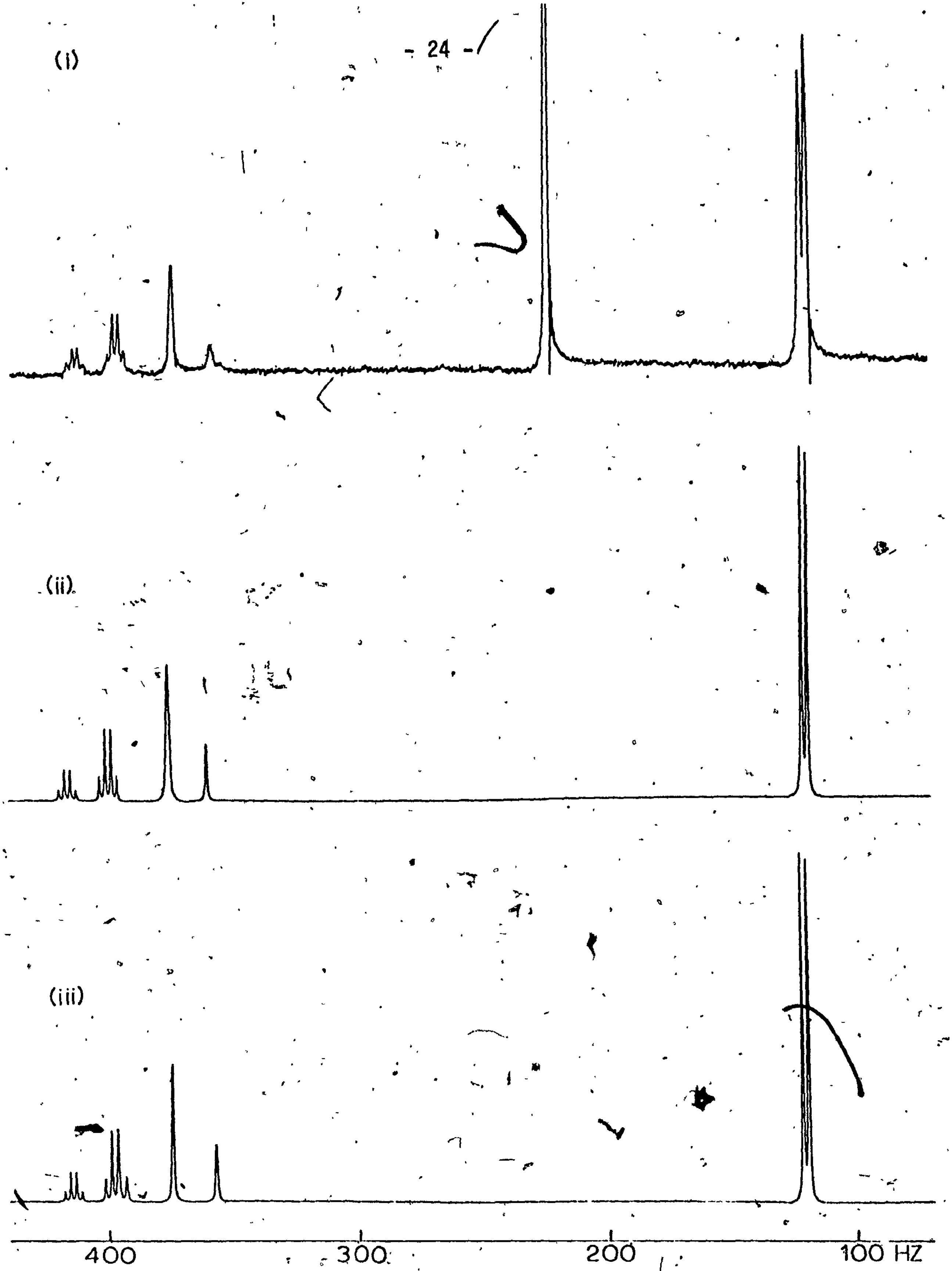


FIGURE 3 COMPOUND 6: METHYL TRANS-2-HEXENE-4-YNATE. COMPARISON OF EXPERIMENTAL AND COMPUTED SPECTRA.

In the figure, 3(i) presents the experimental spectrum; 3(ii) is the spectrum produced by method A, group assignment; 3(iii) is the spectrum produced by method B, line-to-line matching.

The slight shift of the multiplets in both calculated spectra was due to the fact that assignments were made from several experimental spectra at 100 Hz and are, therefore, probably more accurate than the main spectrum at 500 Hz sweep width. The strong line present at about 230 Hz was due to the isolated methoxy group, OCH_3.

The first more direct approach is preferred because it is simpler. Results are comparable with those produced by fitting, shifting, and re-assignment. Also, when dealing with noisy spectra, too few lines cause the RMS errors in the iterated calculations to diverge.

Table 3 contains the original and revised values of the chemical shift and coupling constants of the compounds with less than seven spins. The revised parameters are due to the fact that analysis was carried out more accurately for expanded spectra at 50, 100, or 250 Hz sweep width.

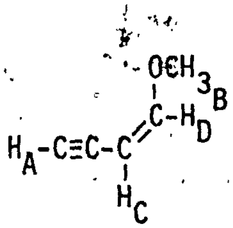
4 COMPOUNDS WITH SEVEN SPINS

The spectra of these compounds were studied in several ways. Because of the rapid growth in the number of possible transitions with each added proton, a seven-spin system had to be approached with respect, especially since LAOCN 3, as it was originally obtained, was incapable of solving seven-spin compounds.

TABLE 3

REVISED SPECTRAL DATA FOR COMPOUNDS WITH LESS THAN SEVEN SPINS *

Compound 1. 1-methoxy-*cis*-1-butene-3-yne



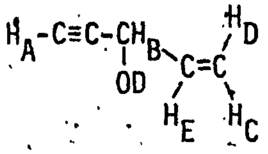
ORIGINAL DATA	REVISED DATA
ν_A = 187.1 Hz	ν_A = 185.421 ± 0.009 Hz
ν_B = 222.6	
ν_C = 267.3	ν_C = 265.755 ± 0.009
ν_D = 383.5	ν_D = 381.454 ± 0.009
J_{AC} = -2.5 Hz	J_{AC} = -2.537 ± 0.013 Hz
J_{AD} = 0.9	J_{AD} = 0.825 ± 0.013
J_{CD} = 6.5	J_{CD} = 6.427 ± 0.013

RMS Error = 0.019

* The numbers of significant figures in the revised values are as given in the computer print-out. It is not intended that they be published as such.

TABLE 3 continued

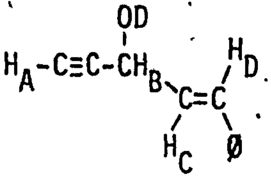
Compound 2. 1-pentene-4-yne-3-ol



ORIGINAL DATA	REVISED DATA
$\nu_A = 157.7$ Hz	$\nu_A = 154.779 \pm 0.014$ Hz
$\nu_B = 292.6$	$\nu_B = 290.371 \pm 0.014$
$\nu_C = 313.3$	$\nu_C = 310.668 \pm 0.016$
$\nu_D = 328.0$	$\nu_D = 325.333 \pm 0.016$
$\nu_E = 357.5$	$\nu_E = 354.951 \pm 0.017$
$J_{AB} = -2.2$ Hz	$J_{AB} = -2.214 \pm 0.020$ Hz
$J_{BC} = -1.4$	$J_{BC} = -1.320 \pm 0.021$
$J_{BD} = -1.5$	$J_{BD} = -1.559 \pm 0.021$
$J_{BE} = 5.4$	$J_{BE} = 5.288 \pm 0.021$
$J_{CD} = 1.1$	$J_{CD} = 1.090 \pm 0.021$
$J_{CE} = 10.35$	$J_{CE} = 10.252 \pm 0.023$
$J_{DE} = 16.95$	$J_{DE} = 17.045 \pm 0.021$
	RMS Error = 0.075

TABLE 3 continued

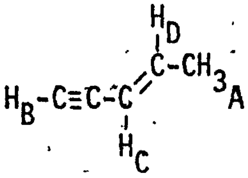
Compound 3. 1-phenyl-*trans*-1-pentene-4-yne-3-ol



ORIGINAL DATA	REVISED DATA
$\nu_A = 154.0$ Hz	$\nu_A = 152.838 \pm 0.012$ Hz
$\nu_B = 299.4$	$\nu_B = 298.695 \pm 0.012$
$\nu_C = 374.7$	$\nu_C = 372.646 \pm 0.014$
$\nu_D = 403.8$	$\nu_D = 401.734 \pm 0.014$
$J_{AB} = -2.2$ Hz	$J_{AB} = -2.131 \pm 0.016$ Hz
$J_{BC} = 5.8$	$J_{BC} = 5.999 \pm 0.019$
$J_{BD} = -0.5$	$J_{BD} = -1.448 \pm 0.019$
$J_{CD} = 15.8$	$J_{CD} = 15.879 \pm 0.017$
	RMS Error = 0.043

TABLE 3 continued

Compound 4. trans-2-pentene-4-yne

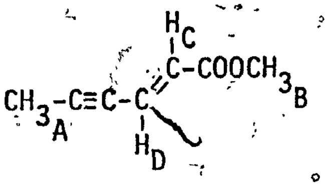


$H_B\text{-}C\equiv C\text{-}C(H_C)=C(H_D)\text{-}CH_{3A}$

ORIGINAL DATA	REVISED DATA
ν_A = 107.0 Hz	ν_A = 104.976 ± 0.018 Hz
ν_B = 165.2	ν_B = 163.055 ± 0.019
ν_C = 328.4	ν_C = 327.780 ± 0.011
ν_D = 374.6	ν_D = 373.995 ± 0.011
J_{AB} = -0.7 Hz	J_{AB} = -0.706 ± 0.010 Hz
J_{AC} = -1.8	J_{AC} = -1.882 ± 0.010
J_{AD} = 6.8	J_{AD} = 6.743 ± 0.011
J_{BC} = -1.6	J_{BC} = -1.561 ± 0.014
J_{CD} = 15.9	J_{CD} = 15.883 ± 0.016
	RMS Error = 0.073

TABLE 3 continued

Compound 5. methyl *trans*-2-hexene-4-ynate

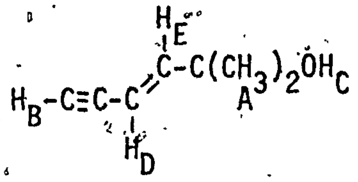


$CH_{3_A}-C\equiv C-C(H_D)=C(H_C)-COOCH_{3_B}$

ORIGINAL DATA	REVISED DATA
$\nu_A = 120.4$ Hz	$\nu_A = 120.000 \pm 0.017$ Hz
$\nu_B = 223.1$	
$\nu_C = 368.0$	$\nu_C = 368.756 \pm 0.028$
$\nu_D = 402.9$	$\nu_D = 404.105 \pm 0.015$
$J_{AC} = -0.6$ Hz	$J_{AC} = -0.364 \pm 0.022$ Hz
$J_{AD} = 2.4$	$J_{AD} = 2.432 \pm 0.012$
$J_{CD} = 16.2$	$J_{CD} = 16.032 \pm 0.025$
	RMS Error = 0.081

TABLE 3 continued

<u>Compound 6</u>. 5-methyl-<u>trans</u>-3-hexene-1-yne-5-ol



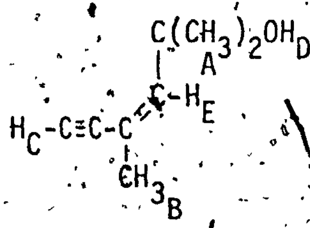
$H_B-C\equiv C-\underset{\substack{| \\ H_D}}{C}=\overset{\substack{H_E \\ |}}{C}-C(\underset{A}{CH_3})_2OH_C$

ORIGINAL DATA	REVISED DATA
ν_A = 79.2 Hz	
$\nu_{[illegible]}$ = 171.3	ν_B = 169.583 ± 0.015 Hz
ν_C = 174.1	
ν_D = 340.9	ν_D = 340.849 ± 0.016
ν_E = 379.9	ν_E = 379.733 ± 0.016
J_{BD} = -2.3 Hz	J_{BD} = -2.313 ± 0.022 Hz
J_{BE} = 0.6	J_{BE} = 0.547 ± 0.022
J_{DE} = 16.1	J_{DE} = 16.086 ± 0.021

RMS Error = 0.031

TABLE 3 continued

Compound 7. 3,5-dimethyl-cis-3-hexene-1-yne-5-ol



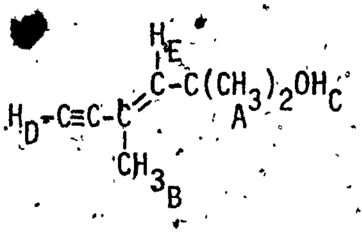
$H_C{-}C{\equiv}C{-}C(CH_{3_B}){=}C(H_E){-}C(CH_{3_A})_2OH_D$

ORIGINAL DATA	REVISED DATA
ν_A = 84.0 Hz	
ν_B = 111.8	ν_B = 110.912 ± 0.004 Hz
ν_C = 202.0	ν_C = 201.001 ± 0.005
ν_D = 226.0	
ν_E = 355.5	ν_E = 354.594 ± 0.005
J_{BE} = -1.5 Hz	J_{BE} = -1.518 ± 0.006 Hz
J_{CE} = 0.8	J_{CE} = 0.800 ± 0.007

RMS Error = 0.029

TABLE 3 continued

Compound 8. 3,5-dimethyl-trans-3-hexene-1-yne-5-ol

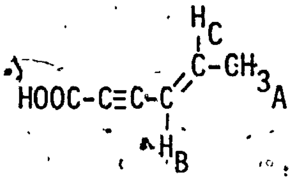


$H_D{-}C{\equiv}C{-}C(CH_{3_B}){=}C(H_E){-}C(CH_{3_A})_2OH_C$

ORIGINAL DATA	REVISED DATA
ν_A = 84.6 Hz	
ν_B = 112.9	ν_B = 111.052 ± 0.000 Hz
ν_C = 190.2	
ν_D = 201.2	ν_D = 199.401 ± 0.000
ν_E = 356.6	ν_E = 354.747 ± 0.001
J_{BE} = -1.6 Hz	J_{BE} = -1.300 ± 0.001
J_{DE} = 0.6	J_{DE} = 0.800 ± 0.001
	RMS Error = 0.001

TABLE 3 continued

Compound 9. trans-4-hexene-2-ynoic acid

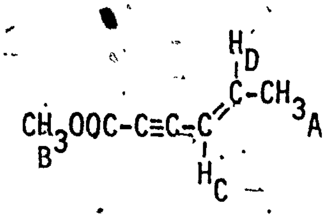


$HOOC{-}C{\equiv}C{-}C(H_B){=}C(H_C){-}CH_{3A}$

ORIGINAL DATA	REVISED DATA
ν_A = 113.0 Hz	ν_A = 112.480 ± 0.011 Hz
ν_B = 336.8	ν_B = 336.013 ± 0.013
ν_C = 394.8	ν_C = 394.103 ± 0.018
J_{AB} = -1.7 Hz	J_{AB} = -1.765 ± 0.013 Hz
J_{AC} = 6.9	J_{AC} = 6.871 ± 0.015
J_{BC} = 15.9	J_{BC} = 15.780 ± 0.023
	RMS Error = 0.081

TABLE 3 continued

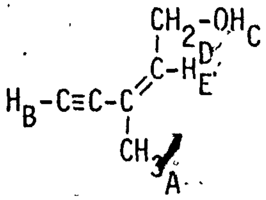
Compound 10. methyl *trans*-4-hexene-2-ynate



$$\underset{B}{CH_3}OOC-C\equiv C-\underset{H_C}{C}=\overset{H_D}{C}-CH_{3A}$$

ORIGINAL DATA	REVISED DATA
ν_A = 111.5 Hz	ν_A = 109.482 ± 0.009 Hz
ν_B = 224.9	
ν_C = 335.4	ν_C = 333.387 ± 0.009
ν_D = 389.8	ν_D = 388.041 ± 0.009
J_{AC} = -1.8 Hz	J_{AC} = -1.858 ± 0.010 Hz
J_{AD} = 6.9	J_{AD} = 6.882 ± 0.010
J_{CD} = 15.9	J_{CD} = 15.950 ± 0.013
	RMS Error = 0.055

4.1 Example: Analysis of Compound 12



3-methyl-*cis*-2-pentene-4-yne-1-ol

ORIGINAL VALUES

$\nu_A = 113.9$ Hz $J_{AD} = 1.2$ Hz
$\nu_B = 194.2$ $J_{AE} = -1.5$
$\nu_D = 259.5$ $J_{BE} = 0.8$
$\nu_E = 356.4$ $J_{DE} = 6.6$

4.1.1 First Attempt: Original Program. All seven spins were given the same iso numbers. The direct calculations produced two sets of lines. In the first set, each transition was given an identifying number. The second set, called the ordered set because the transitions were ordered in increasing frequency, had a maximum output of 300 transitions in the original version of LAOCN 3.

Seven-spin compounds can produce identifying sets larger in varying degrees from the ordered set. But the ordered set is the working set used for experimental matching. For compound 12 the identifying set of lines contained 372 transitions; the ordered set contained its maximum 300 lines.

The 72 missing lines, distributed throughout the ordered set, spoiled the proper correspondance between experimental and calculated frequencies. Assignments became more difficult with portions of the spectrum missing or under-represented. To compound the problem, the huge number of calculated lines that were produced often merged imperceptibly, so that clear-cut distinctions between transitions vanished.

In the direct calculations of compound 12 for experimental frequency 251.8 Hz, four calculated frequency lines were present in the unordered identifying set, but only one, namely 2437, was available in the ordered set.

LINE	EXP FREQ	CALC FREQ	INTEN
2437	251.80	254.414	1.930
2893		254.414	1.927
2902		254.195	1.917
2298		254.193	1.914

In the same spectrum, between experimental frequencies 347.3 and 348.0 Hz, again crucial lines were missing, as can be seen below.

LINE	EXP FREQ	CALC FREQ	INTEN
1481	347.30	349.705	1.145
2875		350.399	1.140
2883		350.383	1.140
2891	348.00	350.383	1.140
2363		351.181	1.128

The rest of the 68 missing lines were distributed throughout the ordered set. The size of a block of frequencies contibutes to the intensity; missing sections, therefore, may change the spectral intensity relationships. At the end of the ordered set of lines the program indicated overflow conditions by printing DC STORAGE FULL.

4.1.2 Second Attempt: Internal X-Approximation. The ratio $J/\Delta\nu$, coupling constant to chemical shift difference, indicates the interaction between the nuclei being considered.

For compound 12 the nuclei D and E give the ratio $J/\Delta\nu = 0.0686$ (coupling constant $J_{DE} = 6.6$ Hz, and chemical shift difference $\nu_D - \nu_E = 96.2$ Hz). The nuclei D and A produce a ratio $J/\Delta\nu = 0.00824$ (coupling constant $J_{AD} = 1.2$ Hz, and chemical shift difference $\nu_D - \nu_A = 145.6$ Hz). The former ratio exemplifies a stronger interaction between nuclei than the latter; that is, the methyl group behaves like a group of X-nuclei weakly coupled to its neighbours.

Compound 12 could tentatively be labelled as an AB_2MX_3 system. It was treated as an ordinary seven-spin system but the weakly coupled methyl group was given a different iso value. The intent was to reduce the number of combination transitions, relieving the overflow conditions. This was equivalent to an internal X-approximation.

This attempt was not successful, as intimated by the authors of the program (2). The number of transitions in the first set was still 372, and only 300 in the ordered set. Experimental lines previously missing were still missing. The only difference was that the immense block of lines of variable transition and intensity were replaced by the same sized blocks of more constant frequency and constant intensity.

4.1.3 Third Attempt: X-Approximation. To overcome these not inconsequential problems, what can be called an external X-approximation was then attempted (3,5,6).

In the X-approximation, a complex system that contains weakly-coupled and strongly-coupled nuclei can be broken down into subspectra. These subspectra have the coupling constants of the strongly-coupled parts, but the Larmor frequencies of the strongly-coupled nuclei are replaced by effective Larmor frequencies. Pople and Schaeffer (7) analyzed transitions in the systems ABX_q and ABR_pX_q. Diehl and Pople (8) extended the method to cover AB_2X_q and $AB_2R_pX_q$ and gave rules for the general $A_mB_n \ldots R_pX_q$ system. Retracing their path through "The Composite Particle Approach to NMR Analysis" (3), the specific systems AB, ABX, ABX_3, and AB_2, AB_2X, AB_2MX were examined as a prelude to simplifying an AB_2MX_3 system, compound 12.

The Composite Particle Approach treats a collection of magnetically equivalent nuclei as a simple particle of variable spin and is a shorthand effective method that enables otherwise formidable systems to be handled comfortably.

With hindsight came the realization that the model compounds investigated need not have been solved completely with every energy level fully worked out. It was sufficient merely to write down the first energy level of each system, and that, with a little bit of practice, could be done on sight. For example:

SYSTEM	FIRST ENERGY LEVEL	
AB	$\frac{1}{2}\nu_A + \frac{1}{2}\nu_B + \frac{1}{4}J_{AB}$	(1)
ABX	$\frac{1}{2}\nu_A + \frac{1}{2}\nu_B + \frac{1}{2}\nu_X + \frac{1}{4}J_{AB} + \frac{1}{4}J_{AX} + \frac{1}{4}J_{BX}$	(2)
ABX_2	$\frac{1}{2}\nu_A + \frac{1}{2}\nu_B + \nu_X + \frac{1}{4}J_{AB} + \frac{1}{2}J_{AX} + \frac{1}{2}J_{BX}$	(3)
AB_3MX	$\frac{1}{2}\nu_A + \nu_B + \frac{1}{2}\nu_M + \frac{1}{2}\nu_X + \frac{1}{2}J_{AB} + \frac{1}{4}J_{AM} + \frac{1}{4}J_{AX} + \frac{1}{2}J_{BM}$ $\frac{1}{2}J_{BX} + \frac{1}{4}J_{MX}$	(4)

In the simple AB system $+\frac{1}{2}$ is one of the possible eigenvalues of the spin angular momentum operator I_z of the A nucleus; $-\frac{1}{2}$ would be the other possible eigenvalue of I_z and so would give the lowest energy level as

$$-\frac{1}{2}\nu_A - \frac{1}{2}\nu_B + \frac{1}{4}J_{AB}$$

The energy levels of the mixed wave functions need not be taken into account.

If we designate the AB system by lower case letters and look again at the first energy levels of the ab and ABX systems, we see the algebraic substitutions required.

SYSTEM	FIRST ENERGY LEVEL	
ab	$\frac{1}{2}\nu_a + \frac{1}{2}\nu_b + \frac{1}{4}J_{ab}$	(5)
ABX	$\frac{1}{2}\nu_A + \frac{1}{2}\nu_B + \frac{1}{2}\nu_X + \frac{1}{4}J_{AB} + \frac{1}{4}J_{AX} + \frac{1}{4}J_{BX}$	(2)

We can switch from one to the other through

$$\nu_a = \nu_A + \tfrac{1}{2}J_{AX} \quad \text{and} \quad \nu_b = \nu_B + \tfrac{1}{2}J_{BX} \tag{6}$$

The strongly-coupled constant remains the same $J_{ab} = J_{AB}$.

But we still have the other eigenvalue of $-\frac{1}{2}$ to consider.

$$\nu_a = \nu_A - \tfrac{1}{2}J_{AX} \quad \text{and} \quad \nu_b = \nu_B - \tfrac{1}{2}J_{BX} \tag{7}$$

In general form the effective frequencies become

$$\nu_a = \nu_A + m_X J_{AX} \quad \text{and} \quad \nu_b = \nu_B + m_X J_{BX} \tag{8}$$

m_X gives the eigenvalues of the total spin angular momentum I_z of the X-nuclei.

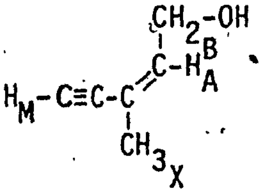
These same general formulas (8) can be applied to the systems ABX_2, AB_2X_2, AB_2X, AB_3X_4, etc. These equations are valid for all energy levels and completely transform one system into another.

If there are two weakly-coupled nuclei as in the AB_2MX system, complete representation into effective frequencies of the strongly-coupled nuclei is just as easy to obtain.

$$\begin{aligned} \nu_a &= \nu_A + m_M J_{AM} + m_X J_{AX} \\ \nu_b &= \nu_B + m_M J_{BM} + m_X J_{BX} \\ \nu_m &= \nu_M + m_A J_{AM} + m_B J_{BM} + m_X J_{MX} \end{aligned} \qquad (9)$$

These formulas (9) can be applied in full to compound 12, an AB_2MX_3 system.

4.1.3.1 Compound 12 relabelled.



3-methyl-*cis*-2-pentene-4-yne-1-ol

AB_2MX_3

$\nu_A = 356.4$ Hz $J_{BX} = 1.2$ Hz

$\nu_B = 259.5$ $J_{AX} = -1.5$

$\nu_M = 194.2$ $J_{AM} = 0.8$

$\nu_X = 113.0$ $J_{AB} = 6.6$

For practical considerations, an actual substitution can be carried out. Because J_{MX} and J_{BX} are zero, the formulas (9) are reduced to :

$$\begin{aligned} \nu_a &= \nu_A + m_M J_{AM} + m_X J_{AX} \\ \nu_b &= \nu_B + m_X J_{BX} \\ \nu_m &= \nu_M + m_A J_{AM} \end{aligned}$$

Only the eigenvalues of $m_M = +1/2$, $m_A = +1/2$, and $m_X = \pm 3/2, \pm 1/2$ were used to bring forth the sets of effective frequencies shown in Table 4. The strong coupling constants remain the same.

$$J_{ab} = J_{AB} = 6.6 \text{ Hz}$$
$$J_{am} = J_{AM} = 0.8$$
$$J_{bm} = J_{BM} = 0.0$$

These four systems were sufficient to obtain all the AB_2M lines in the spectrum. Combinations of m_M and m_A other than the ones chosen were not required. A complex seven-spin system AB_2MX_3 has been factorized into four much simpler four-spin systems $(ab_2m)X_3$.

The total output of all four systems was 96 calculated frequencies, a far smaller and more tractable number to confront. There was no problem with merging lines or missing sections. Assignments were carried out in confidence after the four separate sets were reconstituted. The first and last frequencies of each group of lines in the direct calculation output of each of Set A, B, C, and D were averaged. Table 5 shows the procedure.

The information from the Sets A, B, C, and D was brought together in Table 6.

The data were assembled, sorted according to frequencies, and matched with experimental lines, as shown in Table 7.

Three iterations were sufficient to bring the largest RMS error, namely for Set B, down to 0.064. All the other sets had lower

TABLE 4

COMPOUND 12: EFFECTIVE LARMOR FREQUENCIES (Hz)

SET A: $m_X = +3/2$	SET B: $m_X = +1/2$	SET C: $m_X = -1/2$	SET D: $m_X = -3/2$
$\nu_a = 354.55$ $\nu_b = 261.3$ $\nu_m = 194.6$	$\nu_a = 356.05$ $\nu_b = 260.1$ $\nu_m = 194.6$	$\nu_a = 357.55$ $\nu_b = 258.9$ $\nu_m = 194.6$	$\nu_a = 359.05$ $\nu_b = 257.7$ $\nu_m = 194.6$

TABLE 5

COMPOUND 12: AVERAGING OF LINES IN THE DIRECT CALCULATION ORDERED OUTPUT OF SET A

CALC FREQ	AVERAGE
194.199 Hz	194.6 Hz
194.199	
194.201	
194.201	
194.997	
194.997	
194.999	
194.999	
257.757	257.9
257.760	
258.016	
258.017	
264.374	264.4
264.576	
264.583	
264.584	
347.794	348.2
348.591	
354.151	354.7
354.620	
354.951	
355.416	
360.977	361.4
361.755	

TABLE 6

COMPOUND 12: THE AVERAGED CALCULATED FREQUENCIES IN THE SETS PRODUCED BY THE X-APPROXIMATION

SET A	SET B	SET C	SET D
194.6 Hz	194.6 Hz	194.6 Hz	194.6 Hz
257.9	256.7	255.5	254.3
264.4	263.3	262.1	260.8
348.2	349.7	351.2	352.6
354.7	356.3	357.8	359.2
361.4	362.9	364.3	365.8

TABLE 7

COMPOUND 12: MATCHING OF COMPOSITE CALCULATED FREQUENCIES WITH EXPERIMENTAL FREQUENCIES

SET	CALC FREQ	EXP FREQ
ABCD	194.6 Hz	191.2 Hz
D	264.3	251.8
C	255.5	253.0
B	256.7	254.1
A	257.9	255.2
D	260.8	258.4
C	262.1	259.6
B	263.3	260.8
A	264.4	262.0
A	348.2	346.0
B	349.7	346.8
C	351.2	347.3
D	352.6	348.0
A	354.7	352.4
B	356.3	353.0
C	357.8	353.8
D	359.2	355.0
A	361.4	359.3
B	362.9	360.0
C	364.3	360.8
D	365.8	361.6

errors. The error for Sets A and C was 0.049, and the error for the last set, Set D, was 0.050. The cards from each set were intermixed to produce a single ab_2m spectrum as shown in Figure 4.

Figure 4(i) represents the experimental spectrum; 4(ii) is the spectrum obtained by using the X-approximation; 4(iii) is the spectrum obtained by using the extended LAOCN 3 program (Section 4.1.4). With the X-approximation method, the X-lines do not appear in the spectrum. The calculated intensities only roughly approximate the the experimental spectrum.

4.1.4 Fourth Attempt: Extended LAOCN 3. In the original version of LAOCN 3 (2) the maximum number of calculated lines which could be accommodated was 300. In the extended version, this number was increased to 500. The change involved re-dimensioning all arrays (in all sub-programs) which store output data, and changing the statement which limits the size of the output data (statement 930, main program) (4).

Compound 12 was revisited with the extended LAOCN 3 program for seven-spin systems. Assignment of lines was aided by reference to the Sets A, B, C, and D from the X-approximation. All lines which had been missing before were now available. The new spectrum came much closer to realizing the experimental one. Refer to Figure 4(iii).

Table 8 contains the name, structure, and revised data for compounds with seven spins. The X-approximation gives a good match of chemical shifts and coupling constants with those produced by the extended LAOCN 3 program. The frequency of those lines treated as X-nuclei do not appear.

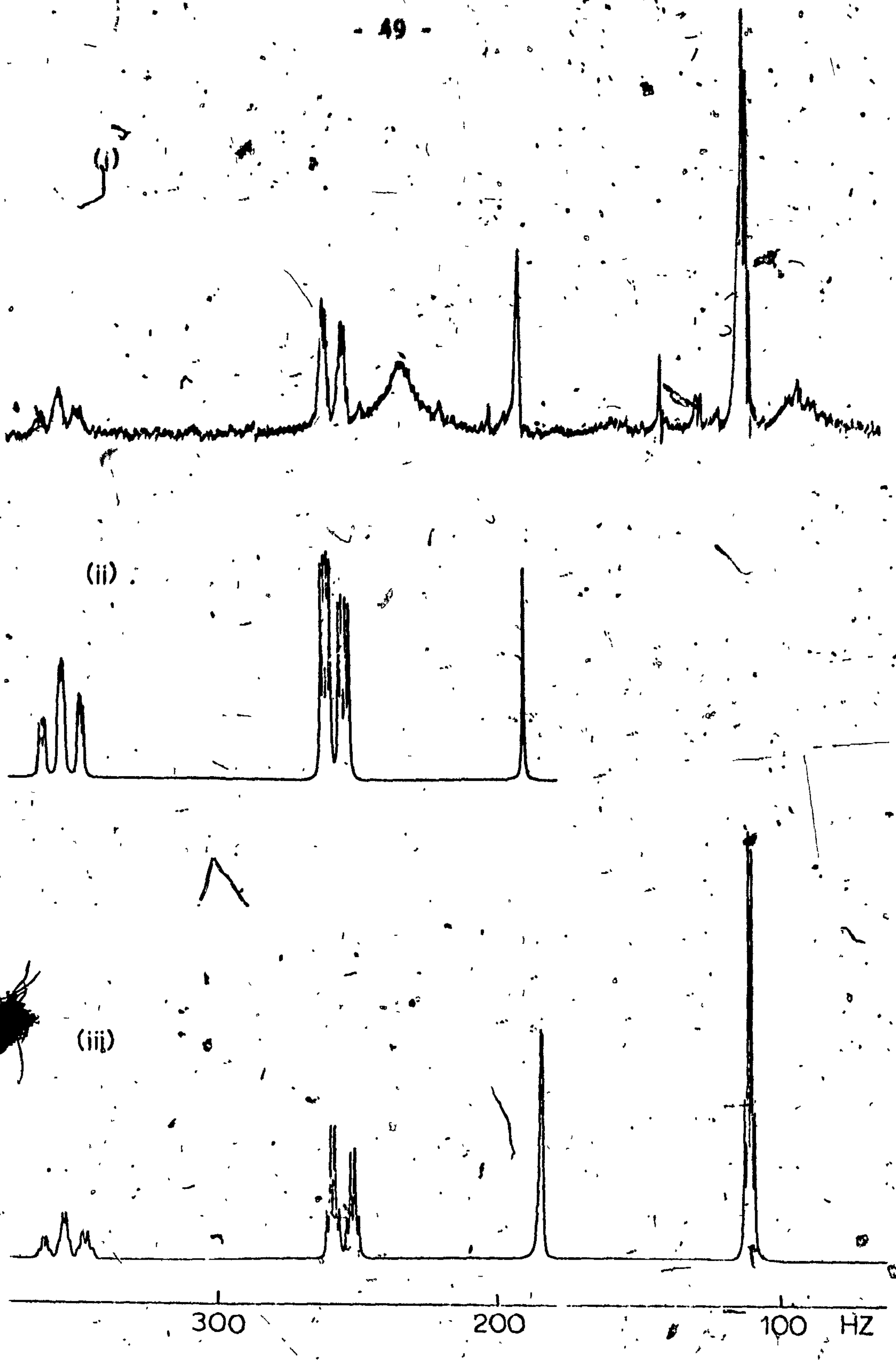
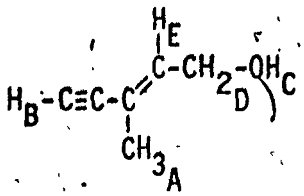


FIGURE 4 COMPOUND 12: 3-METHYL-CIS-2-PENTENE-4-YNE-1-OL.
COMPARISON OF EXPERIMENTAL AND COMPUTED SPECTRA.

TABLE 8.

REVISED SPECTRAL DATA FOR COMPOUNDS WITH SEVEN SPINS

<u>Compound 11</u>. 3-methyl-<u>trans</u>-2-pentene-4-yne-1-ol

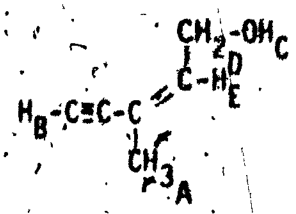


$H_B-C\equiv C-C(CH_{3_A})=C(H_E)-CH_{2_D}-OH_C$

ORIGINAL DATA	REVISED DATA	
	X-APPROX	EXT LAOCN
$\nu_A = 108.9$ Hz		$\nu_A = 106.583 \pm 0.006$ Hz
$\nu_B = 171.4$	$\nu_B = 169.080 \pm 0.014$ Hz	$\nu_B = 169.239 \pm 0.012$
$\nu_C = 192.8$		
$\nu_D = 251.6$	$\nu_D = 248.943 \pm 0.017$	$\nu_D = 249.000 \pm 0.008$
$\nu_E = 363.2$	$\nu_E = 360.403 \pm 0.017$	$\nu_E = 360.128 \pm 0.008$
$J_{AD} = 0.8$ Hz		$J_{AD} = 0.765 \pm 0.006$ Hz
$J_{AE} = -1.5$		$J_{AE} = -1.365 \pm 0.010$
$J_{BD} = -0.3$	$J_{BD} = 0.0 \pm 0.018$ Hz	$J_{BD} = -0.009 \pm 0.010$
$J_{BE} = 0.6$	$J_{BE} = 0.0 \pm 0.017$	$J_{BE} = 0.320 \pm 0.017$
$J_{DE} = 6.7$	$J_{DE} = 6.698 \pm 0.022$	$J_{DE} = 6.612 \pm 0.013$
	RMS Error = 0.052	RMS Error = 0.082

TABLE B continued

Compound 12. 3-methyl-*cis*-2-pentene-4-yne-1-ol

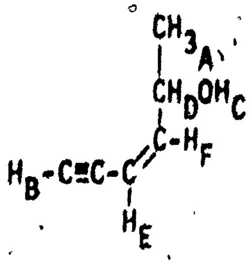


$H_B-C{\equiv}C-C(CH_{3A})=C(H_E)-CH_{2D}-OH_C$

ORIGINAL DATA	REVISED DATA	
	X-APPROX	EXT LAOCN
$\nu_A = 113.9$ Hz		$\nu_A = 110.843 \pm 0.007$ Hz
$\nu_B = 194.2$	$\nu_B = 191.200 \pm 0.015$ Hz	$\nu_B = 191.251 \pm 0.009$
$\nu_C = 234.3$		
$\nu_D = 259.5$	$\nu_D = 256.973 \pm 0.017$	$\nu_D = 256.976 \pm 0.009$
$\nu_E = 356.4$	$\nu_E = 354.464 \pm 0.017$	$\nu_E = 353.167 \pm 0.011$
$J_{AD} = 1.2$ Hz		$J_{AD} = 1.325 \pm 0.008$ Hz
$J_{AE} = -1.5$		$J_{AE} = -1.264 \pm 0.010$
$J_{BE} = 0.8$	$J_{BE} = 0.0 \pm 0.025$ Hz	$J_{BE} = 0.433 \pm 0.013$
$J_{DE} = 6.6$	$J_{DE} = 6.697 \pm 0.018$	$J_{DE} = 6.624 \pm 0.025$
	RMS Error = 0.050	RMS Error = 0.107

TABLE 8 continued

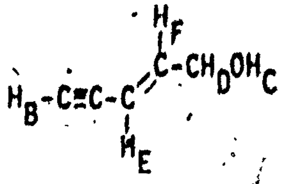
Compound 13. *cis*-3-hexene-1-yne-5-ol



ORIGINAL DATA	REVISED DATA	
	X-APPROX*	EXT. LAOCN
ν_A = 78.0 Hz		ν_A = 74.435 ± 0.014 Hz
ν_B = 198.6		ν_B = 195.739 ± 0.012
~~ν_C = 255.3~~		
ν_D = 289.9		ν_D = 286.815 ± 0.011
ν_E = 328.7		ν_E = 325.487 ± 0.012
ν_F = 363.1		ν_F = 359.934 ± 0.012
J_{AD} = 6.5 Hz		J_{AD} = 6.455 ± 0.012 Hz
J_{BE} = -2.4		J_{BE} = -2.329 ± 0.018
J_{BF} = 0.9		J_{BF} = 0.893 ± 0.018
J_{DE} = -1.1		J_{DE} = -1.073 ± 0.016
J_{DF} = 8.2		J_{DF} = 8.184 ± 0.016
J_{EF} = 11.1		J_{EF} = 11.056 ± 0.017
	* not done	RMS Error = 0.151

TABLE 8 continued

Compound 14. trans-3-hexene-1-yne-5-ol

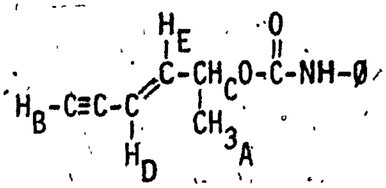


$H_B-C\equiv C-C(H_E)=C(H_F)-CH_DOH_C$

ORIGINAL DATA	REVISED DATA	
	X-APPROX	EXT LAOCN
ν_A = 76.0 Hz		ν_A = 76.028 ± 0.005 Hz
ν_B = 174.6	ν_B = 174.844 ± 0.030 Hz	ν_B = 174.842 ± 0.005
ν_C = 186.3		
ν_D = 259.6	ν_D = 259.580 ± 0.041	ν_D = 259.664 ± 0.005
ν_E = 340.3	ν_E = 340.099 ± 0.032	ν_E = 340.099 ± 0.005
ν_F = 375.5	ν_F = 375.370 ± 0.032	ν_F = 375.372 ± 0.005
J_{AD} = 6.5 Hz		J_{AD} = 6.488 ± 0.007 Hz
J_{BD} = -0.5	J_{BD} = -0.613 ± 0.050 Hz	J_{BD} = -0.468 ± 0.008
J_{BE} = -2.3	J_{BE} = -2.280 ± 0.044	J_{BE} = -2.278 ± 0.007
J_{BF} = 0.6	J_{BF} = 0.584 ± 0.044	J_{BF} = 0.586 ± 0.007
J_{DE} = -1.4	J_{DE} = -1.615 ± 0.049	J_{DE} = -1.510 ± 0.007
J_{DF} = 5.5	J_{DF} = 5.707 ± 0.049	J_{DF} = 5.570 ± 0.007
J_{EF} = 16.0	J_{EF} = 15.974 ± 0.042	J_{EF} = 15.972 ± 0.006
	RMS Error = 0.100	RMS Error = 0.058

TABLE 8 continued

Compound 15. trans-3-hexene-1-yne-5-ol carbanilide



ORIGINAL DATA	REVISED DATA	
	X-APPROX	EXT LAOCN
ν_A = 79.9 Hz		ν_A = 77.300 ± 0.005 Hz
ν_B = 174.3	ν_B = 171.706 ± 0.027 Hz	ν_B = 171.707 ± 0.006
ν_C = 322.2	ν_C = 319.382 ± 0.054	ν_C = 319.013 ± 0.015
ν_D = 341.8	ν_D = 338.649 ± 0.035	ν_D = 338.672 ± 0.008
ν_E = 371.7	ν_E = 368.951 ± 0.033	ν_E = 368.968 ± 0.007
J_{AC} = 6.5 Hz		J_{AC} = 6.782 ± 0.009 Hz
J_{BD} = -2.2	J_{BD} = -2.186 ± 0.045 Hz	J_{BD} = -2.199 ± 0.009
J_{BE} = 0.6	J_{BE} = 0.155 ± 0.042	J_{BE} = 0.173 ± 0.009
J_{CD} = -1.4	J_{CD} = -1.317 ± 0.060	J_{CD} = -1.337 ± 0.015
J_{CE} = 6.1	J_{CE} = 5.608 ± 0.056	J_{CE} = 5.814 ± 0.012
J_{DE} = 16.0	J_{DE} = 16.269 ± 0.052	J_{DE} = 16.189 ± 0.010
	RMS Error = 0.077	RMS Error = 0.074

4.2 General Observations

From these attempts some general principles can be formulated for solving complex spectra by LAOCN 3.

1. In the direct calculations it is not necessary nor desirable to assign every line in a large block of calculated lines. Thus if the assignments are poor, the errors produced have a smaller influence on the rest of the calculations and the RMS error. If the assignments are successful, reinforcements can always be brought in.

2. However, it is better to type more cards, i.e. assign more lines than less lines, for in noisy spectra where there may be a dearth of assignable lines the RMS error values, instead of converging to a minimum value, will diverge, increasing in error.

3. Large errors in the iterated calculations should be removed. They can be replaced, if possible, by more suitable neighbouring lines. This remedy is unfailing in reducing large RMS errors.

4. Since, after each iteration, new unassigned frequencies are born, it is appropriate to assign these where the error so produced is small.

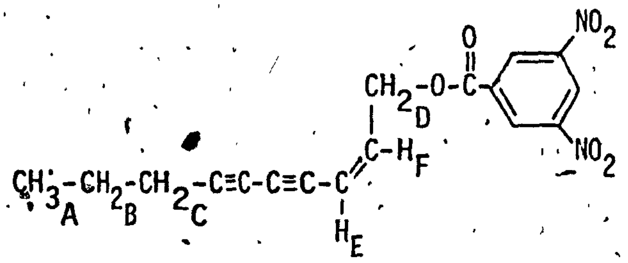
5. Once an iteration is completed, the whole output, or as much as possible, must be used. Plotting only the assigned lines produces on the whole very ill-fitting spectra. The computer knows best.

5 COMPOUNDS WITH MORE THAN SEVEN SPINS

It was possible to solve seven-spin compounds by breaking down these systems into simpler portions. By extrapolation, a similar procedure was employed for compounds with more than seven spins. It should be remembered that these complex compounds cannot be handled by even the extended LAOCN 3 program.

The spectra within this section were of poor quality, ill-resolved, and noisy. Few lines could be matched with any degree of certainty so that very often iterations were calculated on a bare minimum of experimental lines.

5.1 Example: Analysis of Compound 16



cis-2-decene-4,6-diyn-1-yl-3,5-dinitrobenzoate

ORIGINAL VALUES

$\nu_A = 60.3$ Hz $\quad J_{AB} = 7.2$ Hz
$\nu_B = 94.9 \quad J_{BC} = 6.5$
$\nu_C = 138.6 \quad J_{DE} = -1.2$
$\nu_D = 312.0 \quad J_{DF} = 6.4$
$\nu_E = 349.8 \quad J_{EF} = 10.9$
$\nu_F = 374.6$

Compound 16 was an eleven-spin compound consisting of two moieties not spin-coupled. Each was treated as an independent entity, one of seven spins and one of four spins, and then recombined. Internal normalization of spectral intensities in the LAOCN 3 program produced a spectrum in which the seven-spin part was too strong and the four-spin part almost vanished.

See Figure 5. Figure 5(i) represents the experimental spectrum; and 5(ii) is the first recombination attempt.

Another iterated calculation was performed on the separate parts in an attempt to correct this incongruity. All nuclei were given different iso values. In the internal X-approximation of compound 12, only a small part of the whole molecule was treated in this manner. The result of putting all the iso numbers different was to produce in the unordered and ordered sets frequencies of intensity 1 or 0.

The intensities for each group of nuclei at a particular

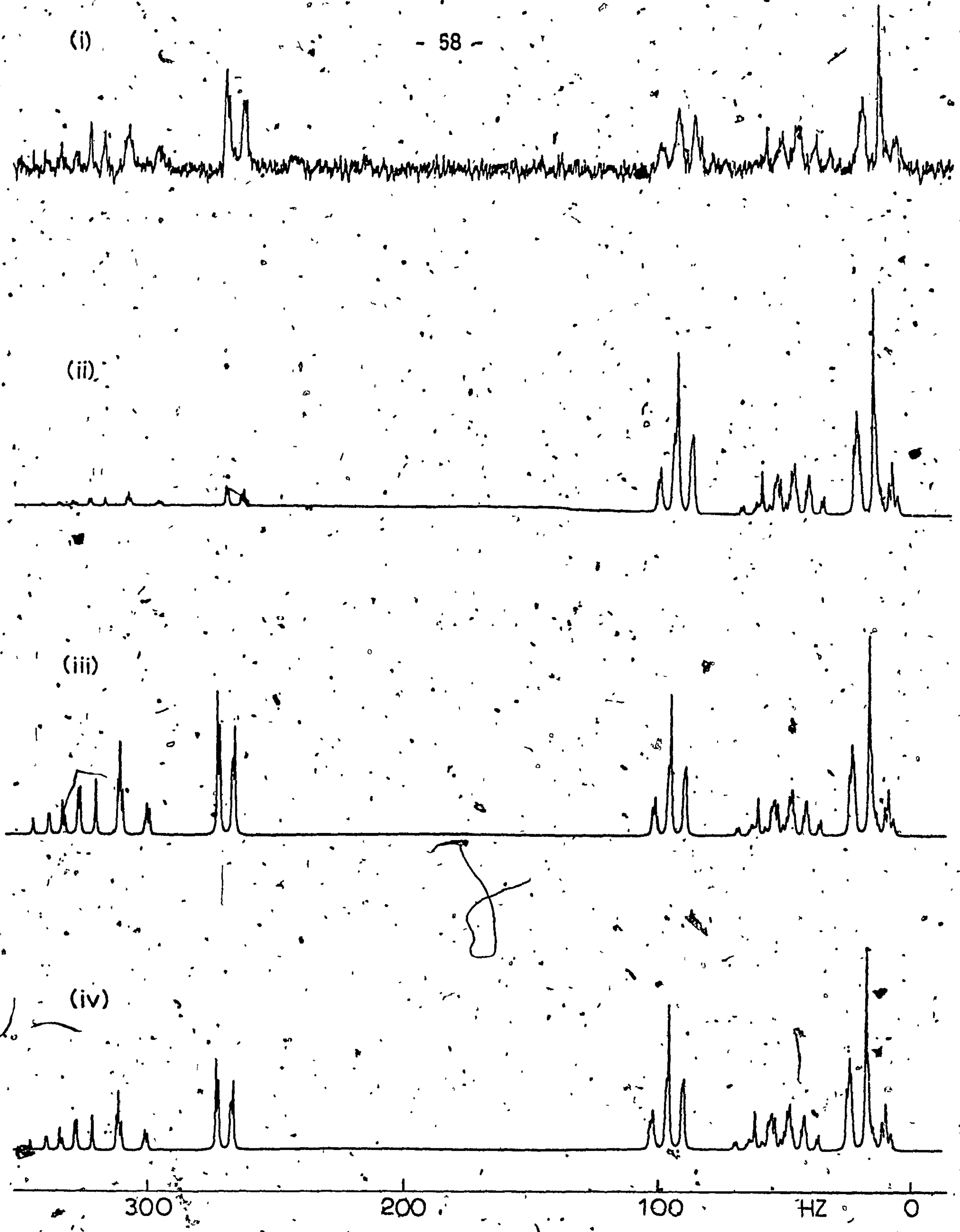


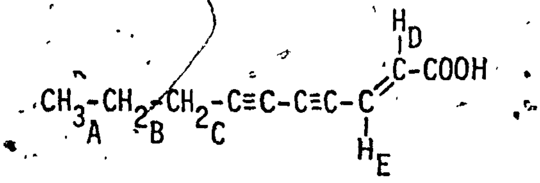
FIGURE 5 COMPOUND 16: CIS-2-DECENE-4,6-DIYN-1-YL-3,5-DINITROBENZOATE.
COMPARISON OF EXPERIMENTAL AND COMPUTED SPECTRA.

chemical shift value were totalled and divided by the number of protons in that group, as shown in Table 9.

It is seen that the seven-spin part has an intensity approximately eight times the strength of the four-spin part. A small program called MIRIAM was written that multiplied the output cards of the four-spin part by the appropriate factor, in this case 8.0125. The decks were again combined to present a spectrum that surprisingly increased the intensity of the four-spin part to a greater extent than expected. Figure 5(iii) shows the second recombination attempt, after correction with the factor 8.0125.

The situation was finally repaired by a straight-forward comparison of the experimental spectrum and the first LAOCN 3 spectrum. Actual measurements gave a factor of 5.0 for the ratio of experimental to calculated spectra, Figure 6. The combined spectrum thus produced approached gratifyingly the experimental one. The final spectrum can be found in Figure 5(iv), done with the correction factor of 5.000.

5.2 Example: Analysis of Compound 18



$$\underset{A}{CH_3}-\underset{B}{CH_2}-\underset{C}{CH_2}-C\equiv C-C\equiv C-\underset{H_E}{C}=\overset{H_D}{C}-COOH$$

trans-2-decene-4,6-diynoic acid

TABLE 9

COMPOUND 16: COMPARISON OF INTENSITIES

	7 Spin Part			4 Spin Part		
	A_3	B_2	C_2	D_2	E	F
Intensity	190	124	134	16	8	8
$\frac{\text{Intensity}}{\text{No. of Protons}}$	63.3	62	67	8	8	8
Average		64.1			8	

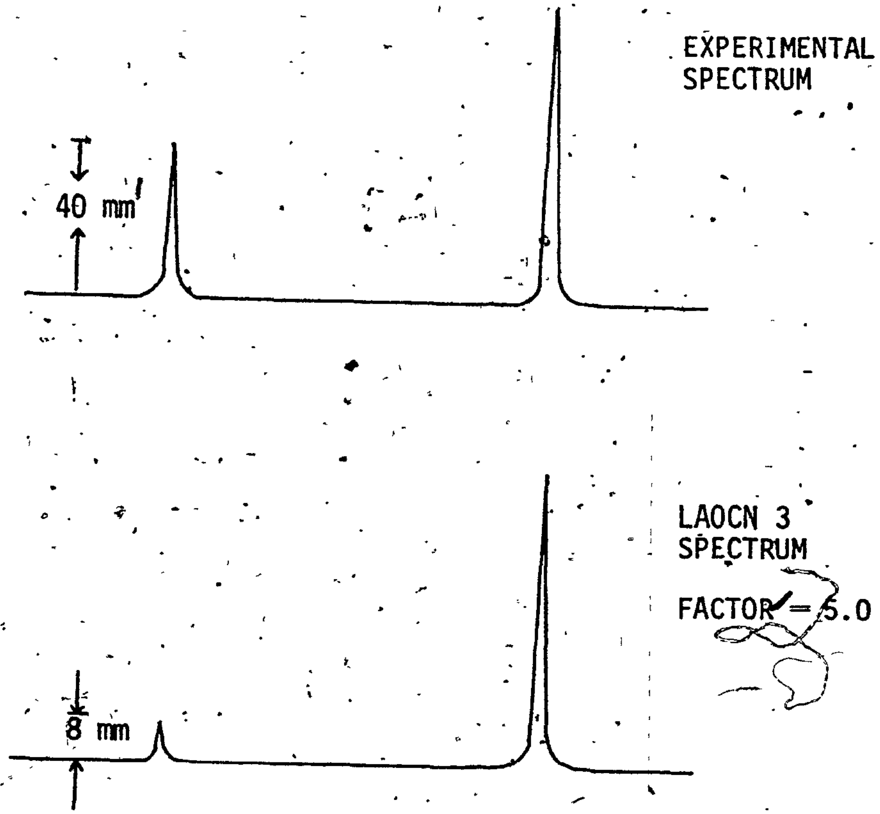


FIGURE 6 SYMBOLIC COMPARISON OF EXPERIMENTAL AND LAOCN 3 SPECTRA.

ORIGINAL VALUES

$\nu_A = 60.0$ Hz $\quad J_{AB} = 7.2$ Hz
$\nu_B = 95.2$ $\quad J_{BC} = 6.8$
$\nu_C = 140.5$ $\quad J_{CE} = 0.9$
$\nu_D = 376.4$ $\quad J_{DE} = 15.8$
$\nu_E = 409.6$

Compound 18, a nine-spin compound, required for its solution the techniques previously developed. Because of the small but finite coupling constant of 0.9 Hz transmitted through seven bonds, it could not easily be separated into two independent entities.

The last methylene group was weakly coupled to the protons past the extended seven-bond barrier, and seemed reasonably weakly coupled to its own ethyl group CH_3CH_2. Instead of confronting a nine-spin system $A_3B_2C_2ED$, we were dealing with a disguised $A_3B_2X_2ED$ combination, which could be separated into the siblings $A_3B_2X_2$ and X_2ED (i.e. A_2XY).

Using the X-approximation we obtained three $(a_3b_2)X_2$ spectra and three $X_2(ed)$ spectra. Recombination again produced a spectrum whose minor parts were too weak. Correction with program MIRIAM by comparison with the experimental spectrum gave the final product. The spectra are shown in Figure 7: 7(i) represents the experimental spectrum; 7(ii) is the calculated spectrum through the X-approximation. The X portion of the spectrum at about 150 Hz is absent.

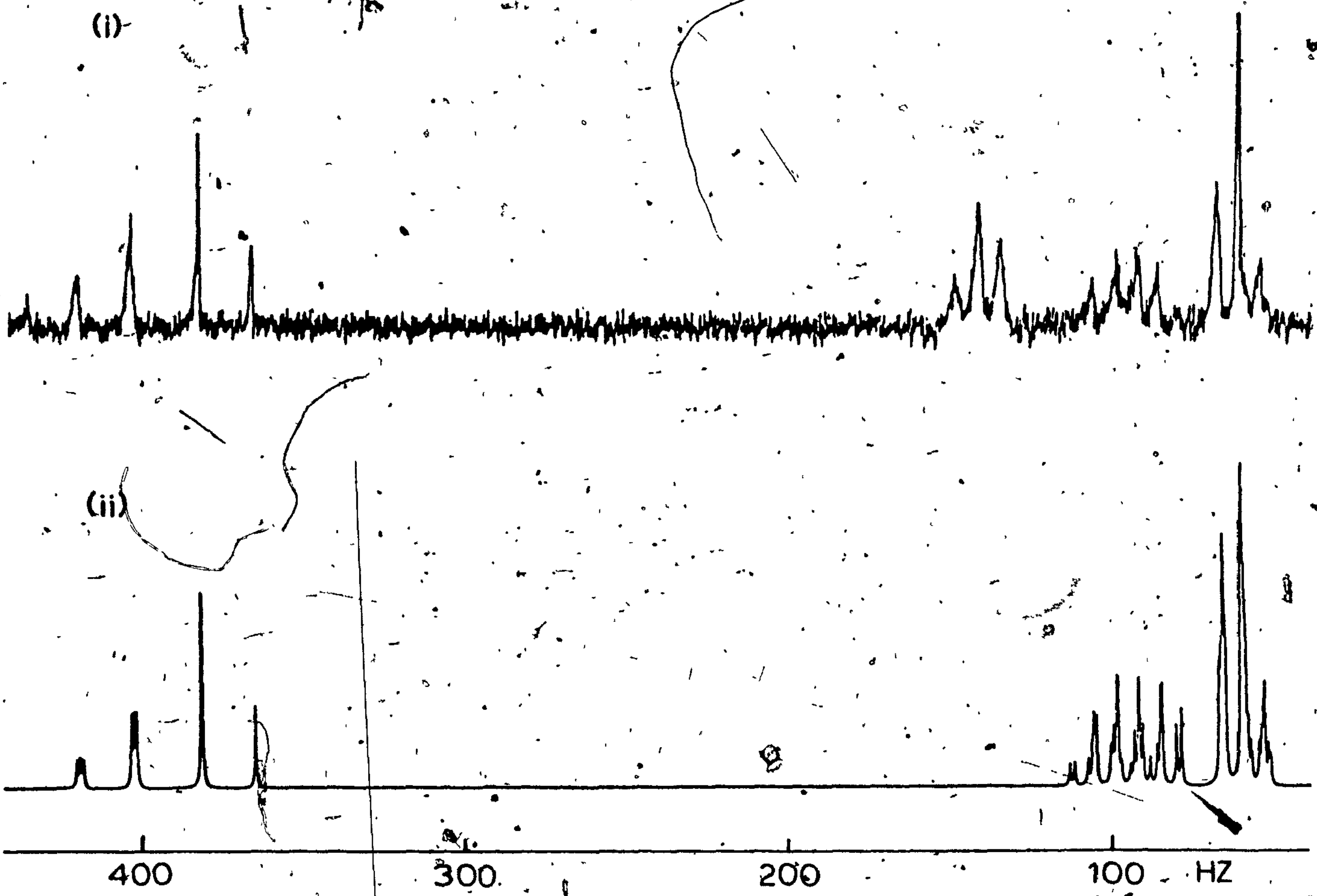
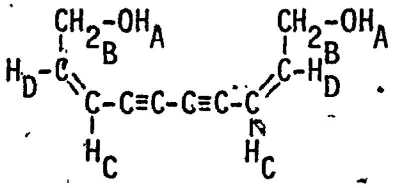


FIGURE 7 COMPOUND 18: TRANS-2-DECENE-4,6-DIYNOIC ACID. COMPARISON OF EXPERIMENTAL AND COMPUTED SPECTRA.

5.3 Example: Analysis of Compound 20



cis,*cis*-2,8-decadiene-4,6-diyne-1,10-diol

ORIGINAL VALUES

$\nu_A = 246.0$ Hz

$\nu_B = 260.0$

$\nu_C = 340.7$

$\nu_D = 377.7$

$J_{BC} = -1.2$ Hz

$J_{BD} = 6.3$

$J_{CD} = 11.2$

This eight-spin system folded into a four-spin coupled compound because of its symmetry and was easily resolved by the standard methods discussed.

Table 10 contains the name, structure, and spectral data for the compounds with more than seven spins.

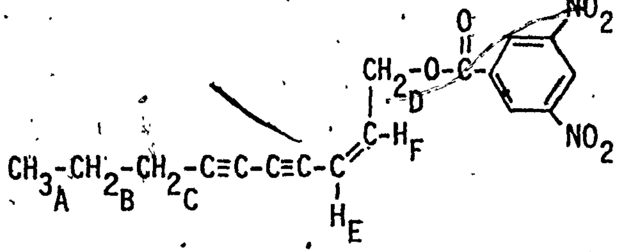
6 UNSOLVED PROBLEMS

The spectra of compounds 22 and 23 were missing; but as simple two-spin AB systems they would not have deserved analysis. In compound 24, an eight-spin system, the relationship between the chemical shift and coupling constant varied sufficiently from first order so as to make the X-approximation unusable. The spectrum of the last compound, 25, a relatively simple five-spin compound, was of such poor quality as to furnish insufficient data for analysis.

TABLE 10

REVISED SPECTRAL DATA FOR COMPOUNDS WITH MORE THAN SEVEN SPINS

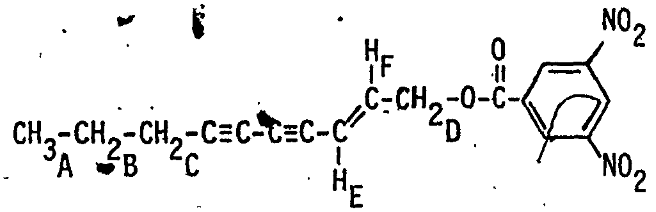
Compound 16. cis-2-decene-4,6-diyn-1-yl-3,5-dinitrobenzoate



ORIGINAL DATA	REVISED DATA
7 SPIN PART	
ν_A = 60.3 Hz	ν_A = 60.296 ± 0.002 Hz
ν_B = 94.9	ν_B = 94.913 ± 0.017
ν_C = 138.6	ν_C = 138.528 ± 0.012
J_{AB} = 7.2 Hz	J_{AB} = 7.150 ± 0.014 Hz
J_{BC} = 6.5	J_{BC} = 6.201 ± 0.044
	RMS Error = 0.030
4 SPIN PART	
ν_D = 312.0 Hz	ν_D = 312.504 ± 0.001 Hz
ν_E = 349.8	ν_E = 350.184 ± 0.001
ν_F = 374.6	ν_F = 375.354 ± 0.001
J_{DE} = -1.2 Hz	J_{DE} = -1.388 ± 0.001 Hz
J_{DF} = 6.4	J_{DF} = 6.625 ± 0.002
J_{EF} = 10.9	J_{EF} = 11.563 ± 0.002
	RMS Error = 0.000

TABLE 10 continued

<u>Compound 17</u>. <u>trans</u>-2-decene-4,6-diyn-1-yl-3,5-dinitrobenzoate



7 SPIN PART

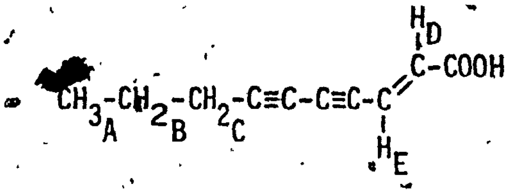
ORIGINAL DATA	REVISED DATA
ν_A = 59.9 Hz	ν_A = 59.999 ± 0.004 Hz
ν_B = 94.6	ν_B = 94.490 ± 0.007
ν_C = 138.6	ν_C = 138.503 ± 0.004
J_{AB} = 7.1 Hz	J_{AB} = 7.204 ± 0.007 Hz
J_{BC} = 6.7	J_{BC} = 6.692 ± 0.004
	RMS Error = 0.029

4 SPIN PART

ORIGINAL DATA	REVISED DATA
ν_D = 299.0 Hz	ν_D = 300.136 ± 0.033 Hz
ν_E = 354.4	ν_E = 355.649 ± 0.121
ν_F = 382.6	ν_F = 383.040 ± 0.091
J_{DE} = -1.3 Hz	J_{DE} = -0.637 ± 0.065 Hz
J_{DF} = 6.3	J_{DF} = 6.321 ± 0.065
J_{EF} = 15.8	J_{EF} = 16.010 ± 0.123
	RMS Error = 0.081

TABLE 10 continued

Compound 18. trans-2-decene-4,6-diynoic acid



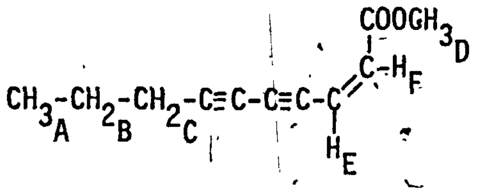
$\mathrm{CH_{3_A}\text{-}CH_{2_B}\text{-}CH_{2_C}\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}\underset{H_E}{C}{=}\overset{H_D}{C}\text{-}COOH}$

ORIGINAL DATA	REVISED DATA *
ν_A = 60.0 Hz	ν_A = 59.634 ± 0.009 Hz
ν_B = 95.2	ν_B = 94.754 ± 0.008
ν_C = 140.5	
ν_D = 376.4	ν_D = 375.048 ± 0.030
ν_E = 409.6	ν_E = 408.536 ± 0.030
J_{AB} = 7.2 Hz	J_{AB} = 6.672 ± 0.016 Hz
J_{BC} = 6.8	
J_{CE} = 0.9	
J_{DE} = 15.8	J_{DE} = 15.836 ± 0.036
	RMS Error = 0.025

* Revised by using the X-approximation in combination with the extended LAOCN 3 program.

TABLE 10 continued

<u>Compound 19</u>. methyl <u>cis</u>-2-decene-4,6-diynate

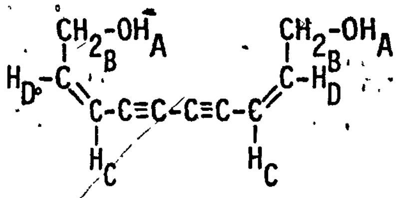


$CH_{3_A}-CH_{2_B}-CH_{2_C}-C\equiv C-C\equiv C-\underset{H_E}{C}=\overset{COOCH_{3_D}}{C}-H_F$

ORIGINAL DATA	REVISED DATA
ν_A = 60.1 Hz	ν_A = 58.494 ± 0.006 Hz
ν_B = 95.5	ν_B = 93.901 ± 0.008
ν_C = 141.2	ν_C = 139.781 ± 0.007
ν_D = 225.3	
ν_E = 372.2	
accidental degeneracy	
ν_F = 372.5	
J_{AB} = 7.2 Hz	J_{AB} = 7.260 ± 0.008 Hz
J_{BC} = 6.8	J_{BC} = 6.862 ± 0.007
	RMS Error = 0.066

TABLE 10 continued

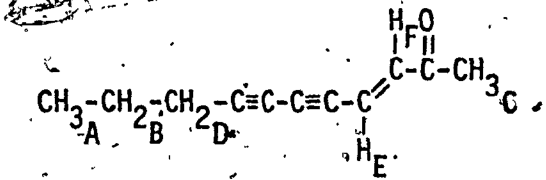
Compound 20. cis,cis-2,8-decadiene-4,6-diyne-1,10-diol



ORIGINAL DATA	REVISED DATA
$\nu_A = 246.0$ Hz	
$\nu_B = 260.0$	$\nu_B = 259.834 \pm 0.043$ Hz
$\nu_C = 340.7$	$\nu_C = 340.507 \pm 0.044$
$\nu_D = 377.7$	$\nu_D = 377.485 \pm 0.041$
$J_{BC} = -1.2$ Hz	$J_{BC} = -0.571 \pm 0.102$ Hz
$J_{BD} = 6.3$	$J_{BD} = 6.205 \pm 0.053$
$J_{CD} = 11.2$	$J_{CD} = 10.741 \pm 0.060$
	RMS Error = 0.093

TABLE 10 continued

Compound 21. trans-3-undecene-5,7-diyne-2-one



$$\underset{A}{CH_3}-\underset{B}{CH_2}-\underset{D}{CH_2}-C\equiv C-C\equiv C-\underset{H_E}{\underset{|}{C}}=\overset{H_F}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\underset{C}{CH_3}$$

ORIGINAL DATA		REVISED DATA
ν_A = 60.0 Hz		ν_A = 59.776 ± 0.016 Hz
ν_B = 95.0		ν_B = 94.998 ± 0.017
ν_C = 134.2		
ν_D = 141.5		ν_D = 141.992 ± 0.022
ν_E = 393.9	accidental degeneracy	
ν_F = 393.9		
J_{AB} = 7.2 Hz		J_{AB} = 7.246 ± 0.017 Hz
J_{BD} = 6.8		J_{BD} = 6.764 ± 0.020
J_{EF} = 16.0		

RMS Error = 0.154

The names and structures of these compounds, together with the original assignments, are listed in Table 11.

7 THE EFFECT OF STRUCTURE ON THE VINYL BOND AND COUPLING CONSTANTS

The strength of the various coupling constants and the observed shifts in the vinyl protons are affected by: intervening or side functional groups, the distance between the protons of interest, and their relative position. The observations are empirical in nature and no attempt was made to give a theoretical interpretation of the results.

The general conclusions reached in the original work were upheld. There was, for the most part, little difference between the original and revised values.

7.1 Vinyl Proton Chemical Shifts

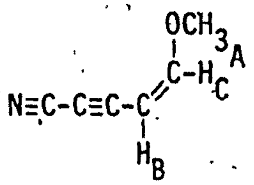
The chemical shifts of the vinyl protons clearly reflect structural changes; these changes are illustrated in Table 12. In the presence of oxygen, the A protons in the *trans* vinyl compounds absorb at an average value of 4.34 τ and the B protons at 3.69 τ. In the oxygenated *cis* vinyl case, compound 13, both the A and B protons are shifted upfield. In the *trans* compound without oxygen, compound 4, the A and B protons are again shifted upfield compared to the trans compounds with oxygen, but the B proton is not affected to the same extent.

With the replacement of proton A by a methyl group, proton B is shifted upfield. *Cis* and *trans* compounds are affected similarly. See Table 13.

TABLE 11

NAME AND STRUCTURE OF UNSOLVED COMPOUNDS

Compound 22. 1-methoxy-4-cyano-cis-1-butene-3-yne



$$N{\equiv}C{-}C{\equiv}C{-}\underset{H_B}{C}{=}\overset{OCH_{3A}}{C}{-}H_C$$

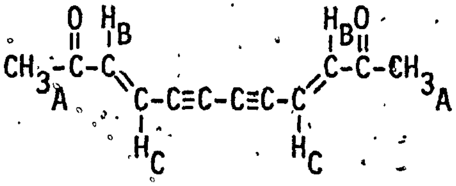
$\nu_A = 230.7$ Hz $J_{BC} = 6.4$ Hz

$\nu_B = 275.2$ $J_{AC^{13}} = 146.2$

$\nu_C = 406.0$

no spectrum available

Compound 23. trans,trans-3,9-dodecadiene-5,7-diyne-2,11-dione



$$CH_{3A}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H_B}{C}{=}\underset{H_C}{C}{-}C{\equiv}C{-}C{\equiv}C{-}\underset{H_C}{C}{=}\overset{H_B}{C}{-}\overset{O}{\overset{\|}{C}}{-}CH_{3A}$$

$\nu_A = 136.8$ Hz

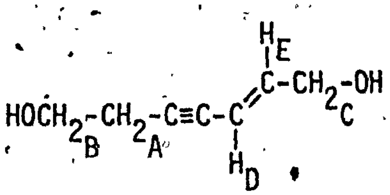
$\nu_B = 400.0$

$\nu_C = 400.0$

no spectrum available

TABLE 11 continued

Compound 24. trans-2-heptene-4-yne-1,7-diol



$$HOCH_{2_B}-CH_{2_A}-C\equiv C-C(H_D)=C(H_E)-CH_{2_C}-OH$$

$\nu_A = 151.7$ Hz $J_{AB} = 6.8$ Hz

$\nu_B = 219.9$ $J_{AD} = 1.6$

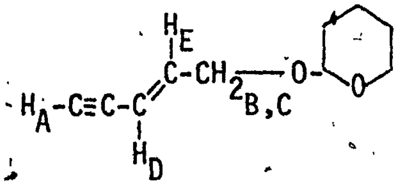
$\nu_C = 247.4$ $J_{CD} = -1.2$

$\nu_D = 343.7$ $J_{CE} = 5.0$

$\nu_E = 370.5$ $J_{DE} = 16.0$

no separation possible

Compound 25. trans-2-pentene-4-ynyl tetrahydro-2-pyranyl ether



$\nu_A = 172.5$ Hz $J_{AB} = -0.8$ Hz

$\nu_B = 240.1$ $J_{AC} = -0.7$

$\nu_C = 254.3$ $J_{AD} = -2.3$

$\nu_D = 342.6$ $J_{AE} = 0.6$

$\nu_E = 375.8$ $J_{BC} = -14.6$

$J_{BD} = -1.9$

$J_{BE} = 5.7$

TABLE 11 continued

Compound 25. continued

$J_{CD} = -1.9$ Hz
$J_{CE} = 4.9$
$J_{DE} = 16.0$

spectrum functionally unusable*

TABLE 12

THE PRESENCE OR ABSENCE OF OXYGEN

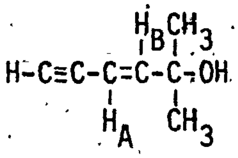
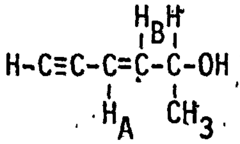
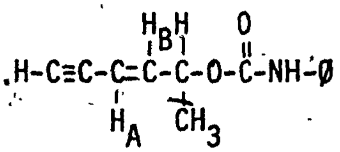
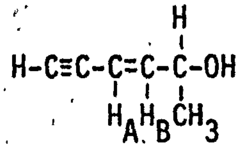
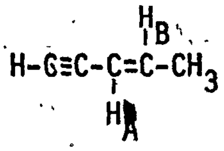
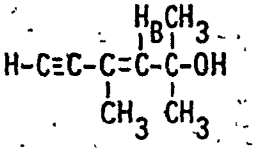
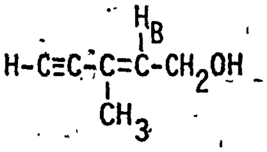
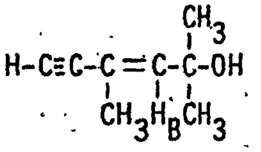
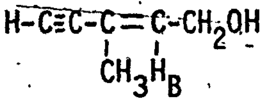
Compound	Structure	Original Values		Revised Values	
		τ_A	τ_B	τ_A	τ_B
	With Oxygen- trans				
6	 $\text{H-C}\equiv\text{C-C}(\text{H}_A)\text{=C}(\text{H}_B)\text{-C}(\text{CH}_3)_2\text{-OH}$	4.32	3.67	4.32	3.67
14	 $\text{H-C}\equiv\text{C-C}(\text{H}_A)\text{=C}(\text{H}_B)\text{-CH}(\text{CH}_3)\text{-OH}$	4.33	3.79	4.33	3.74
15	 $\text{H-C}\equiv\text{C-C}(\text{H}_A)\text{=C}(\text{H}_B)\text{-CH}(\text{CH}_3)\text{-O-C}(\text{=O})\text{-NH-}\emptyset$	4.31	3.81	4.36	3.65
	Average	4.32	3.76	4.34	3.69
	With Oxygen - cis				
13	 $\text{H-C}\equiv\text{C-C}(\text{H}_A)\text{=C}(\text{H}_B)\text{-CH}(\text{CH}_3)\text{-OH}$	4.52	3.95	4.57	4.00
	Without Oxygen - trans				
4	 $\text{H-C}\equiv\text{C-C}(\text{H}_A)\text{=C}(\text{H}_B)\text{-CH}_3$	4.52	3.76	4.54	3.77

TABLE 13

REPLACEMENT OF THE A-PROTON BY A METHYL GROUP

Compound	Structure	Original Values	Revised Values
		τ_B	τ_B
	With Oxygen - trans		
8	 $H\text{-}C\equiv C\text{-}\underset{CH_3}{C}=\overset{H_B}{C}\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH$	4.05	4.08
11	 $H\text{-}C\equiv C\text{-}\underset{CH_3}{C}=\overset{H_B}{C}\text{-}CH_2OH$	3.95	3.99
	Average	4.00	4.03
	With Oxygen - cis		
7	 $H\text{-}C\equiv C\text{-}\underset{CH_3}{C}=\underset{H_B}{C}\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH$	4.08	4.09
12	 $H\text{-}C\equiv C\text{-}\underset{CH_3}{C}=\underset{H_B}{C}\text{-}CH_2OH$	4.06	4.11
	Average	4.07	4.10

Addition of a second triple bond in conjugation with the first shifts the trans and cis A protons downfield to 4.16 τ and 4.07 τ, respectively. The cis and trans B protons are relatively little affected. This shift can be seen in Table 14.

The addition of conjugation on the B side of the double bond, compounds 5 and 18, produces a large diagnostically useful chemical shift in the A proton signals. Refer to Table 15. They absorb now at a lower field than the B proton. The relative positions of the A and B proton signals have been reversed.

In compound 1, a methoxy group is attached directly to the double bond and places the non-bonded electron pairs on the oxygen in conjugation with the π system. The result is to increase the chemical shift between the A and B protons without changing their relative positions. The A proton signal is shifted upfield to 5.57 τ. The B proton is relatively unmoved again and absorbs at 3.64 τ.

7.2 Magnitude of the Vinyl Coupling Constant

The most consistent coupling constant is that shown by the trans vinyl protons. It is always near 16.0 Hz, in spite of wide variations in the nature of the substituents in the rest of the molecule. Even where the substituent groups reverse the chemical shifts of the vinyl protons, as in compounds 5 and 18, the coupling constant remains remarkably close to 16.0 Hz. This relationship can be seen in Table 16. Through accidental degeneracy, no value can be assigned to the coupling constant in compound 21.

TABLE 14

ADDITION OF A SECOND CONJUGATED ACETYLENE UNIT

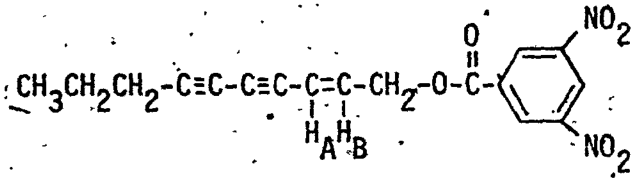
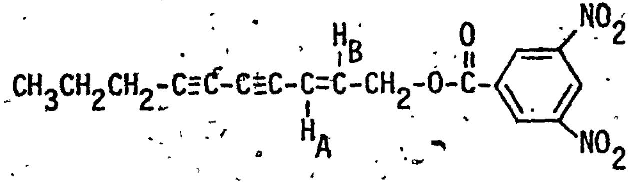
Compound	Structure	Original Values		Revised Values	
		τ_A	τ_B	τ_A	τ_B
	cis				
16		4.17	3.75	4.16	3.74
	trans				
17		4.09	3.63	4.07	3.61

TABLE 15

THE EFFECT OF CARBOXY, CARBOMETHOXY, AND METHOXY GROUPS

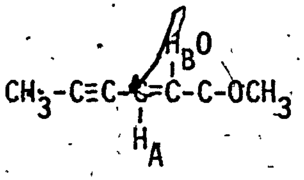
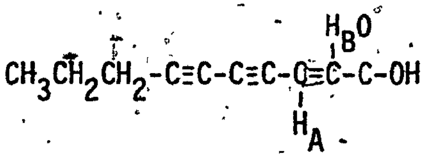
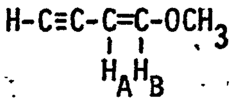
Compound	Structure	Original Values τ_A	Original Values τ_B	Revised Values τ_A	Revised Values τ_B
5	 $CH_3-C{\equiv}C-\underset{H_A}{C}=\overset{H_B}{C}-\overset{O}{C}-OCH_3$	3.28	3.86	3.26	3.85
18	 $CH_3CH_2CH_2-C{\equiv}C-C{\equiv}C-\underset{H_A}{C}=\overset{H_B}{C}-\overset{O}{C}-OH$	3.18	3.72	3.19	3.75
1	 $H-C{\equiv}C-\underset{H_A}{C}=\underset{H_B}{C}-OCH_3$	5.55	3.61	5.57	3.64

TABLE 16

TRANS COMPOUNDS

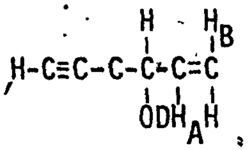
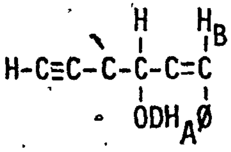
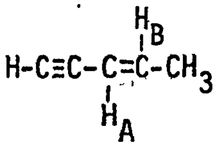
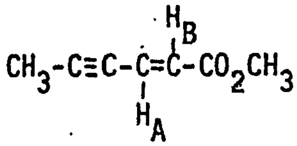
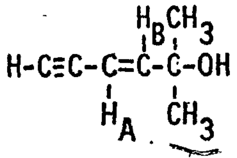
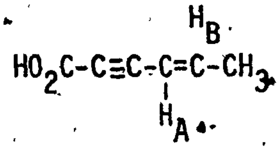
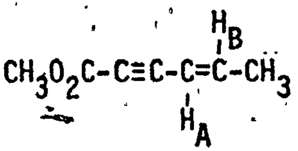
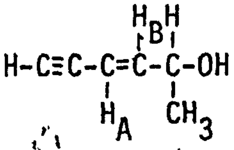
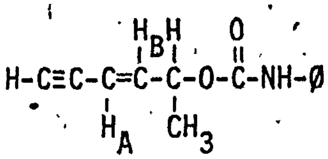
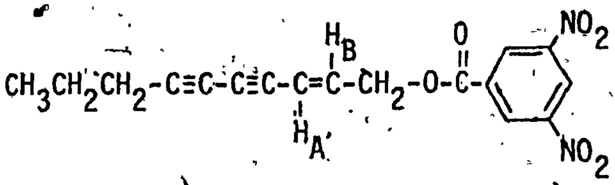
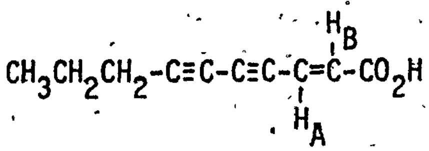
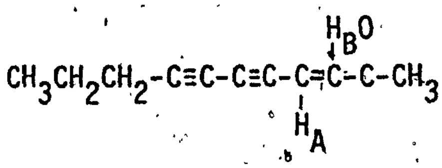
Compound	Structure	Coupling Constants	
		Original (Hz)	Revised (Hz)
2	 $H-C\equiv C-C-\underset{OD}{\overset{H}{C}}-\underset{H_A}{C}=\underset{H}{\overset{H_B}{C}}$	16.9	17.045
3	 $H-C\equiv C-C-\underset{OD}{\overset{H}{C}}-\underset{H_A}{C}=\underset{\text{Ø}}{\overset{H_B}{C}}$	15.8	15.88
4	 $H-C\equiv C-\underset{H_A}{C}=\overset{H_B}{C}-CH_3$	15.9	15.88
5	 $CH_3-C\equiv C-\underset{H_A}{C}=\overset{H_B}{C}-CO_2CH_3$	16.2	16.03
6	 $H-C\equiv C-\underset{H_A}{C}=\overset{H_B}{C}-\underset{CH_3}{\overset{CH_3}{C}}-OH$	16.1	16.08
9	 $HO_2C-C\equiv C-\underset{H_A}{C}=\overset{H_B}{C}-CH_3$	15.9	15.78
10	 $CH_3O_2C-C\equiv C-\underset{H_A}{C}=\overset{H_B}{C}-CH_3$	15.9	15.95

TABLE 16 continued

Compound	Structure	Coupling Constants Original (Hz)	 Revised (Hz)
14	 $H\text{-}C\equiv C\text{-}\underset{H_A}{C}=\overset{H_B}{C}\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}OH$	16.0	15.97
15	 $H\text{-}C\equiv C\text{-}\underset{H_A}{C}=\overset{H_B}{C}\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}O\text{-}\overset{O}{\overset{\Vert}{C}}\text{-}NH\text{-}\varnothing$	16.0	16.19
17		15.8	16.01
18	 $CH_3CH_2CH_2\text{-}C\equiv C\text{-}C\equiv C\text{-}\underset{H_A}{C}=\overset{H_B}{C}\text{-}CO_2H$	15.8	15.84
21	 $CH_3CH_2CH_2\text{-}C\equiv C\text{-}C\equiv C\text{-}\underset{H_A}{C}=\overset{H_B}{C}\text{-}\overset{O}{C}\text{-}CH_3$	-	-
	Average	16.0	16.06

Although the number of cis vinyl compounds is less, it is seen that they generally behave in the same systematic fashion as the trans compounds. This is shown in Table 17. The magnitude of the normal coupling constant in the cis vinyl compounds, excluding the methoxy compound, is 10.90 Hz. The methoxy group attached to the double bond in compound 1 reduces this value to 6.43 Hz. Compound 22 was not available for analysis, but the presence of the methoxy group gives a similar value of 6.4 Hz (original). Through accidental degeneracy, no value can be assigned to the coupling constant in compound 19.

7.3 Magnitude of the 1-4 Coupling Constant

The sign of the long range 1-4 coupling constant was originally determined by spin-tickling experiments and conformed with predicted theory: the coupling between even numbered bonds is negative, and that between odd numbered bonds is positive (9). Computer revisions effected only minor changes. The 1-4 coupling constant had an average value of -2.23 Hz, as can be seen in Table 18. In compounds 2 and 3, where the coupled proton is not directly attached to a vinyl bond, there is, nevertheless, little effect on the magnitude of the coupling constant. In compound 4, the absence of oxygen in the side chain creates the low value of -1.88 Hz.

7.4 Magnitude of the 1-5 Coupling Constant

The relatively weak 1-5 coupling constant between the acetylenic and the B vinyl protons seems to be susceptible to structural interference. See Table 19. The revised values in compounds 11, 12, and 15 are lower than the ones originally calculated. In

TABLE 17

CIS COMPOUNDS

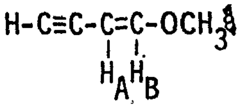
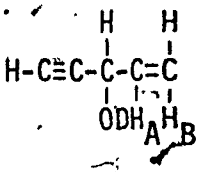
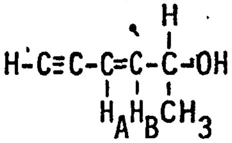
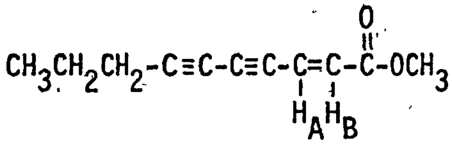
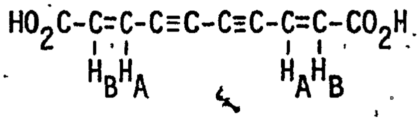
Compound	Structure	Coupling Constants	
		Original (Hz)	Revised (Hz)
1	 $\mathrm{H{-}C{\equiv}C{-}\underset{H_A}{C}{=}\underset{H_B}{C}{-}OCH_3}$	6.5	6.43
2	 $\mathrm{H{-}C{\equiv}C{-}\overset{H}{\underset{OD}{C}}{-}\underset{H_A}{C}{=}\overset{H}{\underset{H_B}{C}}}$	10.3	10.25
13	 $\mathrm{H{-}C{\equiv}C{-}\underset{H_A}{C}{=}\underset{H_B}{C}{-}\overset{H}{\underset{CH_3}{C}}{-}OH}$	11.1	11.06
19	 $\mathrm{CH_3CH_2CH_2{-}C{\equiv}C{-}C{\equiv}C{-}\underset{H_A}{C}{=}\underset{H_B}{C}{-}\overset{O}{\overset{\Vert}{C}}{-}OCH_3}$	-	-
20	 $\mathrm{HO_2C{-}\underset{H_B}{C}{=}\underset{H_A}{C}{-}C{\equiv}C{-}C{\equiv}C{-}\underset{H_A}{C}{=}\underset{H_B}{C}{-}CO_2H}$	11.2	10.74
	Average	10.9	10.90

TABLE 18

MAGNITUDE OF THE 1-4 COUPLING CONSTANT INVOLVING THE ACETYLENIC PROTON

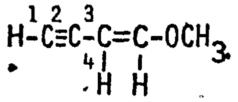
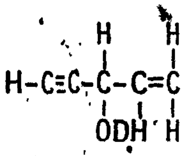
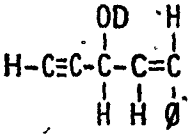
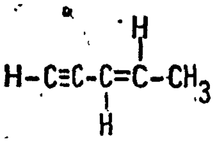
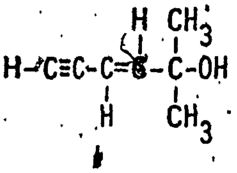
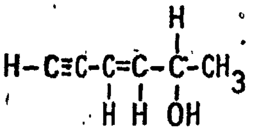
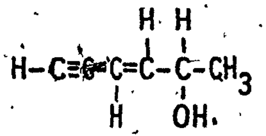
Compound	Structure	Original Values (Hz)	Revised Values (Hz)
1	 $\overset{1}{H}-\overset{2}{C}\equiv\overset{3}{C}-\underset{H}{\overset{4}{C}}=\underset{H}{C}-OCH_3$	-2.5	-2.54
2	 $H-C\equiv C-\underset{OD}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{\overset{H}{C}}$	-2.2	-2.21
3	 $H-C\equiv C-\underset{H}{\overset{OD}{C}}-\underset{H}{C}=\underset{\emptyset}{\overset{H}{C}}$	-2.2	-2.13
4	 $H-C\equiv C-\underset{H}{C}=\overset{H}{C}-CH_3$	-1.8	-1.88
6	 $H-C\equiv C-\underset{H}{C}=\overset{H}{C}-\underset{CH_3}{\overset{CH_3}{C}}-OH$	-2.3	-2.31
13	 $H-C\equiv C-\underset{H}{C}=\underset{H}{C}-\underset{OH}{\overset{H}{C}}-CH_3$	-2.4	-2.33
14	 $H-C\equiv C-\underset{H}{C}=\overset{H}{C}-\underset{OH}{\overset{H}{C}}-CH_3$	-2.3	-2.28

TABLE 18 continued

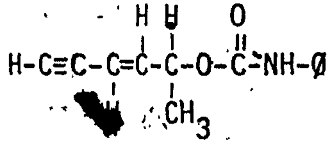
Compound	Structure	Original Values (Hz)	Revised Values (Hz)
15	 $H-C\equiv C-\underset{H}{C}=\overset{H}{C}-\underset{CH_3}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-NH-\text{Ø}$	-2.2	-2.20
	Average	-2.2	-2.23

TABLE 19

MAGNITUDE OF THE 1-5 COUPLING CONSTANT INVOLVING THE ACETYLENIC PROTON

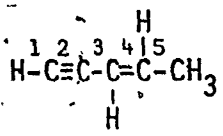
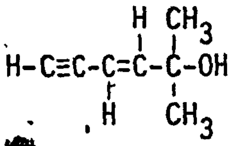
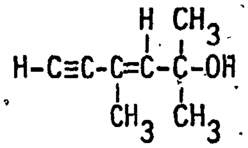
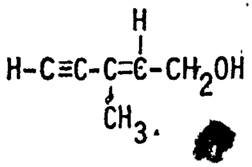
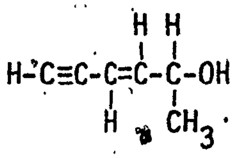
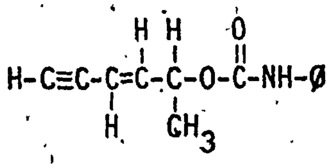
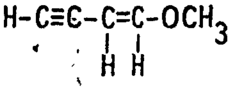
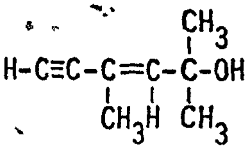
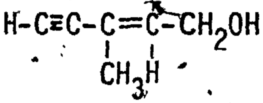
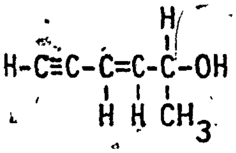
Compound	Structure	Original Values (Hz)	Revised Values (Hz)
	Trans Compounds		
4	 $\overset{1}{H}-\overset{2}{C}\equiv\overset{3}{C}-\underset{H}{\overset{4}{C}}=\overset{H}{\overset{5}{C}}-CH_3$	-	-
6	 $H-C\equiv C-\underset{H}{C}=\overset{H}{C}-\underset{CH_3}{\overset{CH_3}{C}}-OH$	0.6	0.54
8	 $H-C\equiv C-\underset{CH_3}{C}=\overset{H}{C}-\underset{CH_3}{\overset{CH_3}{C}}-OH$	0.6	0.80
11	 $H-C\equiv C-\underset{CH_3}{C}=\overset{H}{C}-CH_2OH$	0.6	0.32
14	 $H-C\equiv C-\underset{H}{C}=\overset{H}{C}-\underset{CH_3}{\overset{H}{C}}-OH$	0.6	0.58
15	 $H-C\equiv C-\underset{H}{C}=\overset{H}{C}-\underset{CH_3}{\overset{H}{C}}-O-\overset{O}{\overset{\|}{C}}-NH-\phi$	0.6	0.17
	Average	0.6	0.48

TABLE 19 continued

Compound	Structure	Original Values (Hz)	Revised Values (Hz)
	Cis Compounds		
1	 $H\text{-}C{\equiv}C\text{-}\underset{H}{C}{=}\underset{H}{C}\text{-}OCH_3$	0.9	0.82
7	 $H\text{-}C{\equiv}C\text{-}\underset{CH_3}{C}{=}\underset{H}{C}\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH$	0.8	0.82
12	 $H\text{-}C{\equiv}C\text{-}\underset{CH_3}{C}{=}\underset{H}{C}\text{-}CH_2OH$	0.8	0.43
13	 $H\text{-}C{\equiv}C\text{-}\underset{H}{C}{=}\underset{H}{C}\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}OH$	0.9	0.89
	Average	0.85	0.74

compound 4, the lack of an oxygen in the structure has removed any resolvable coupling. The 1-5 coupling constant with the B vinyl protons is about 0.48 Hz when the vinyl protons are trans, and about 0.74 Hz when the vinyl protons are cis to each other.

7.5 Magnitude of the 1-6 Coupling Constant

In all cases of 1-6 coupling with the acetylene proton, the coupled protons are trans. The revised magnitudes are still small and negative, as expected for even numbered bonds (9). The values are given in Table 20. Compounds 3 and 15, and the cis compounds, compounds 12 and 13, show no coupling; in the latter case it is the position, rather than distance, that seems to determine the magnitude of the coupling constant.

7.6 Magnitude of the 1-7 Coupling Constant

Possibly the longest coupling constant found in these compounds was a 1-7 coupling in compound 18, originally estimated at 0.9 Hz. But the only way to resolve this nine-spin coupled compound with LAOCN 3, was to split it into several independent parts with the X-approximation. In so doing, this coupling constant was lost. (See Section 5.2).

Several other compounds of similar structure, namely compounds 16, 17, 19, and 21, show a broadening in these two bands, but are not actually resolvable (see Table 10).

TABLE 20

MAGNITUDE OF THE 1-6 COUPLING CONSTANT INVOLVING THE ACETYLENIC PROTON

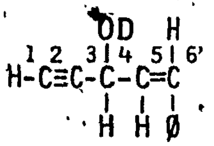
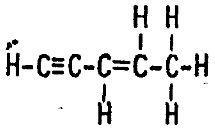
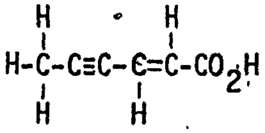
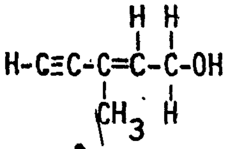
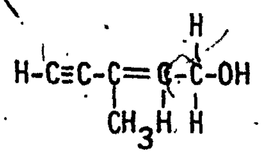
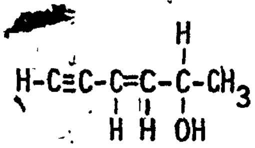
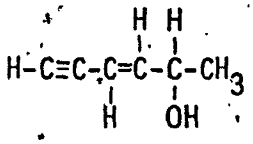
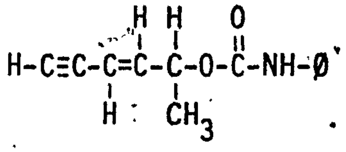
Compound	Structure	Original Values (Hz)	Revised Values (Hz)
3	 $\overset{1}{H}{-}\overset{2}{C}{\equiv}\overset{3}{C}{-}\underset{H}{\overset{OD}{C}}{-}\underset{H}{\overset{4}{C}}{=}\underset{\phi}{\overset{H}{C}}$ (1 2 3 4 5 6')	-	-
4	 $H{-}C{\equiv}C{-}\underset{H}{C}{=}\overset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}H$	-0.7	-0.71
5	 $H{-}\underset{H}{\overset{H}{C}}{-}C{\equiv}C{-}\underset{H}{C}{=}\overset{H}{C}{-}CO_2H$	-0.6	-0.36
11	 $H{-}C{\equiv}C{-}\underset{CH_3}{C}{=}\overset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}OH$	-0.3	-0.01
12	 $H{-}C{\equiv}C{-}\underset{CH_3}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}OH$	-	-
13	 $H{-}C{\equiv}C{-}\underset{H}{C}{=}\underset{H}{C}{-}\underset{OH}{\overset{H}{C}}{-}CH_3$	-	-

TABLE 20 continued

Compound	Structure	Original Values (Hz)	Revised Values (Hz)
14	 $H{-}C{\equiv}C{-}\underset{H}{C}{=}\overset{H}{C}{-}\overset{H}{\underset{OH}{C}}{-}CH_3$	-0.5	-0.47
15	 $H{-}C{\equiv}C{-}\underset{H}{C}{=}\overset{H}{C}{-}\overset{H}{\underset{CH_3}{C}}{-}O{-}\overset{O}{\overset{\Vert}{C}}{-}NH{-}\phi$	-	-
	Average	-0.5	-0.39

REFERENCES

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APPENDIX I

ORIGINAL EXPERIMENTAL DETAILS AND [illegible]SIS

APPENDIX I

ORIGINAL EXPERIMENTAL DETAILS AND ANALYSIS

All original spectra had been run at room temperature on a Varian A-60 spectrometer, using tetramethylsilane (TMS) as an internal standard. Dissolved oxygen was removed by flushing each solution for five minutes with nitrogen.

The amount and the solubility of the available samples had required the use of various solvents and concentrations. Three solvents were used:

chloroform-d
acetone-d_6
acetone-d_6/D_2O mixture

The solvent most often used was chloroform-d ($CDCl_3$). The sample tubes were the standard 5-mm tubes, filled to a minimum depth of 3 cm.

A 500-Hz sweep width was used to obtain the overall spectrum, and portions of interest were then expanded to 100 Hz or 50 Hz, whichever gave better resolution. D_2O was used on occasion to exchange the hydroxyl proton(s), to improve the resolution, or to shift the hydroxyl peak away from the peaks of interest.

Originally, since the core size of the IBM 7074 being used precluded the fit of computed to experimental spectrum, all such fitting was done by hand. It often required from 2 to 13 calculations to produce reasonably superimposable spectra.

The original information on these compounds was obtained in 1968. Since only the spectra and not the original compounds were available for the present study, it was not possible to re-run or alter any spectra for better resolution with more advanced instruments. In the intervening period the spectra of two compounds, namely compounds 22 and 23, became lost. In this re-analysis of the remaining spectra, only the actual information from readable spectra was used.

APPENDIX II

DATA CARDS FOR LAOCN 3 PROGRAM

APPENDIX II

DATA CARDS FOR LAOCN 3 PROGRAM

The data cards for LAOCN 3 were prepared as follows (2).

Card 1	FORMAT (2I3,10A6)		
	Columns	1 - 3	contain the case number (NC) 1-999
		4 - 6	the number of protons (NN) 2-7
		8 - 70	the identifying comments, name of compound
Card 2	FORMAT (3F10.3)		
	Columns	1 - 10	the lower limit of frequency range in Hz (FR1)
		11 - 20	the upper limit of frequency range in Hz (FR2)
		21 - 30	the minimum intensity of interest (AMIN)
Card 3	FORMAT (7I1)		
	Columns	1 - 7	This card contains isotope identification numbers; each nuclear species in the system is assigned an integer number from 1 to 9. e.g., A system of four nuclei all protons could be specified by a card punched 1111 (or 2222 or 4444, etc.). A five-spin system with two protons, 2 phosphorous-31 nuclei and 1 fluorine-19 nucleus could be specified by a card punched 11223 (or 44556, etc.).

Card 4 FORMAT (7F10.3)

The chemical shifts (W(1) ... W(NN)) of the nuclei in the same order as the isotope numbers are punched on this card.

Card 5 FORMAT (7F10.3)

This card contains the coupling constants A(1,2), A(1,3), ... A(1,NN) in that order.

Card 6 FORMAT (7F10.3)

This card contains the coupling constants A(2,3), A(2,4), ... A(2,NN).

Subsequent cards as required are used to feed in the remaining coupling constants up to

Card 3 + NN FORMAT (7F10.3)

This card contains the coupling constant A(NN - 1, NN).

Card 4 + NN FORMAT (7I1)

NI, NKTL(1) are punched on this card. NI is the number of iterations; if 0 no further cards are read for this problem. NKTL(1), if 0, no cards will be punched; if non-zero, calculated frequencies and intensities will be punched on cards.

ITERATIVE CALCULATION

Data cards 1 to 4 + NN are prepared for an iterative calculation exactly as above, except that the control variable NI is given a value > 0, usually 9. Further cards are then read as follows.

Assigned Line Cards FORMAT (I4,F20.3)

The assigned line cards are prepared by comparing the calculated spectrum obtained above with the experimental spectrum. For each line in the experimental spectrum which is matched with a line in the trial direct calculation, one data card is punched. One experimental line may, of course, be matched with more than one calculated transition.

Columns 1 - 4 contain the identification number from the trial direct calculation

6 - 12 the matched experimental frequency

First Terminator Card

A blank card is added to signal the end of the assigned line cards.

Parameter Set Cards FORMAT (6(I1,I1,2X))

Each card contains the specifications of the parameter or parameters which are to be varied together in attempting to fit the spectrum.

When two or more parameters are members of a single set, it is usually because of some symmetry in the molecule.
e.g., The chemical shifts of all protons in a single methyl group, or of the two ortho protons in a monosubstituted benzene, or the two ortho coupling constants in a para-disubstituted benzene form a set in each case.

One set may contain as few as one, but no more than six, parameters. The parameters are specified by two subscripts. The first subscript gives the number of the nucleus (same numbering as previously employed for the isotope numbers, chemical shift, and coupling constants). The second subscript is zero. In the case of the coupling constants, the two subscripts are the numbers of the nuclei coupled.

No more than 28 parameter set cards may be read. Each separate nucleus must appear no more than once.

Second Terminator Card

A blank card is added to signal the end of the parameter set cards.

Run Terminator Card

Data cards for several problems, both direct calculations and iterations, may be stacked sequentially. The end of the run is signified by adding one blank card to the end of the data deck.

APPENDIX III

DATA CARDS FOR SHAPE PROGRAMS

APPENDIX III

DATA CARDS FOR SHAPE PROGRAMS

These programs generate and plot Lorentzian lineshapes and/or stick diagrams from input frequencies and intensities.

SHAPE plots with high frequencies to the right. SHAPE 2 plots with high frequencies to the left.

Data cards are prepared as follows (4).

Item 1	NSPEC, IPLOT, NAME	FORMAT 2I3,7A10
	NSPEC	spectrum number. A zero or blank value for NSPEC will terminate the run.
	IPLOT	0 for Lorentzian lineshapes only
	IPLOT	1 for Lorentzian lineshapes and stick diagram
	IPLOT	2 for stick diagram only
Item 2	WIDTH, FREQL, FREQH	FORMAT 3F10.0
	WIDTH	width of Lorentzian line
	FREQL	low frequency limit of plot
	FREQH	high frequency limit of plot
Item 3	HSCALE, HEIGHT, ZAP	FORMAT 3F10.0
	HSCALE	horizontal scale of plot in mm/Hz
	HEIGHT	height (in mm) of highest peak. (HEIGHT $\leqslant$ 250.0 mm)
	ZAP	minimum effective resolution (Hz) for stick diagram. (Required only if one of the stick diagram options is selected.)

Item 4 FREQ(I), AMP(I) FORMAT (2F10.0)

I cards

FREQ(I) frequency (Hz) of ith line

AMP(I) intensity of ith line

Item 5

A blank card to signal the end if the item 4 data set.

Complete data sets (items 1 - 5) may be stacked one after another.

To terminate the run, add a further blank card. Note that there will be two blank cards at the end of the data deck.

The programs require the use of a magnetic tape.

APPENDIX IV

ILLUSTRATIVE EXAMPLE: COMPUTER PRINT OUT

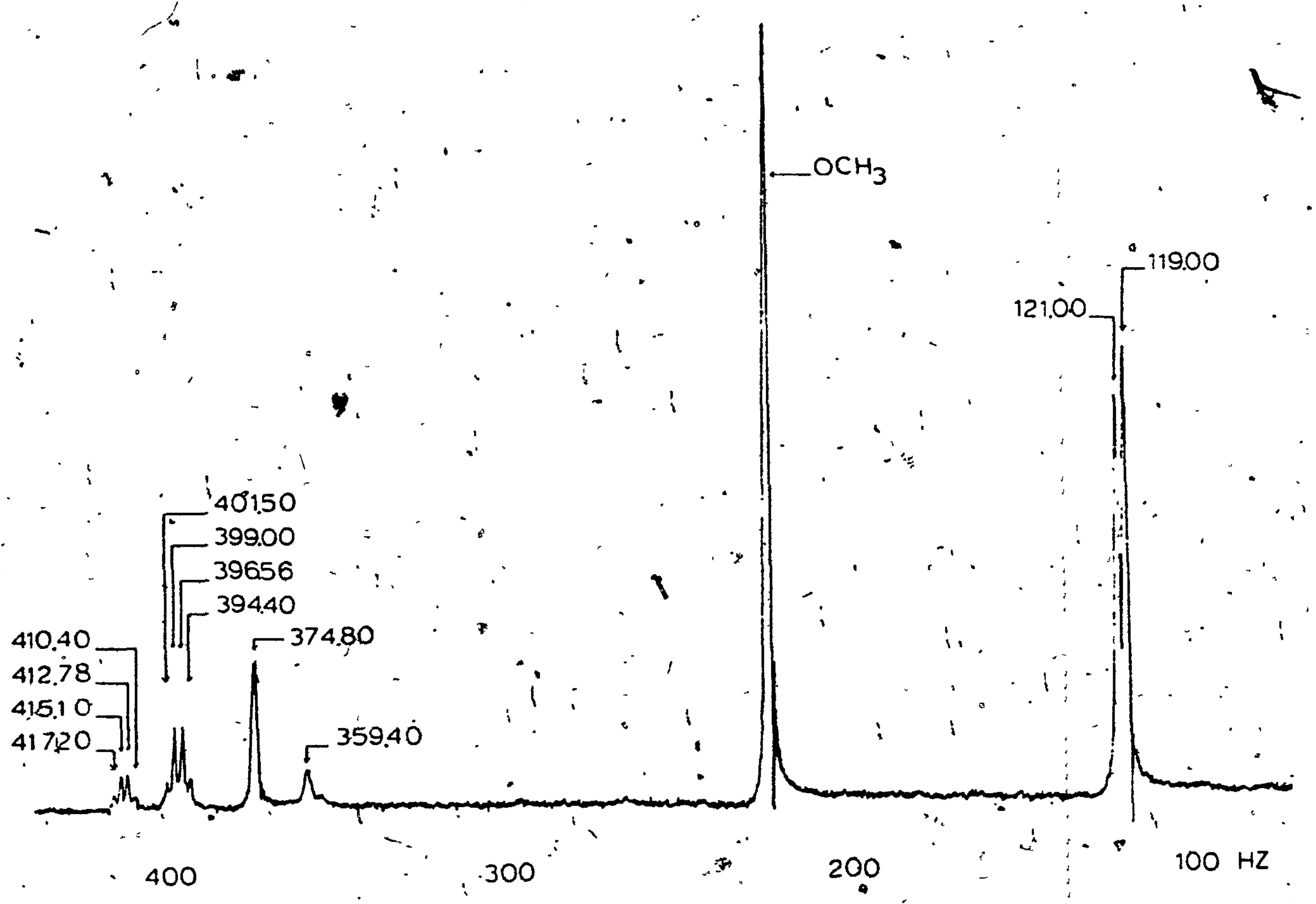

FIGURE 4.1. THE EXPERIMENTAL SPECTRUM OF COMPOUND 5: METHYL TRANS-2-HEXENE-4-YNATE.

A LINE AT 358.8 HZ IS NOT INDICATED.

```
LACCCON III

CASE 109   METHYL TRANS-2-HEXENE-4-YNATE

NN= 5  FREQUENCY RANGE    90.000   450.000  MINIMUM INTENSITY   .020

INPUT PARAMETERS

1          W(1)=  120.400
1          W(2)=  120.400
1          W(3)=  120.400
1          W(4)=  368.000
1          W(5)=  402.900
           A(1,2)=    -0.000
           A(1,3)=    -0.000
           A(1,4)=     -.600
           A(1,5)=     2.400
           A(2,3)=    -0.000
           A(2,4)=     -.600
           A(2,5)=     2.400
           A(3,4)=     -.600
           A(3,5)=     2.400
           A(4,5)=    16.200
           DEGENERACY
           DEGENERACY
           DEGENERACY
           DEGENERACY
           DEGENERACY
           DEGENERACY
           DEGENERACY
           DEGENERACY
```

```
CASE NO  109

LINE   EXP FREQ   CALC FREQ   INTEN   ERROR


  1                121.284    3.018
  4                373.600    1.382
  5                416.216     .600
  6                121.295    4.024
  9                374.081    1.407
 12                413.954     .587
 17                121.295     .673
 18                121.295     .333
 20                374.079    1.392
 23                413.926     .314
 24                413.926     .273
 27                121.295     .333
 28                121.295     .673
 31                374.079    1.392
 33                413.926     .273
 34                413.926     .314
 39                121.766    3.029
 45                400.017    1.352
 52                119.023    2.969
 55                357.401     .630
 56                121.305    3.019
 57                374.543    1.436
 60                411.692     .570
 68                374.540     .953
 69                374.540     .483
 71                411.665     .515
 72                411.665     .055
 78                374.540     .483
 79                374.540     .953
 81                411.665     .055
 82                411.665     .515
 87                121.756    4.039
 95                397.757    1.396
 98                121.756     .055
 99                121.756     .954
103                397.727     .106
104                397.727    1.291
108                121.756     .954
109                121.756     .055
113                397.727    1.291
114                397.727     .106
120                119.033    3.959
125                357.885     .597
131                119.033     .247
132                119.033     .742
133                357.879     .382
```

134	357.879	.215
141	119.033	.742
142	119.033	.247
143	357.879	.215
144	357.879	.382
155	119.506	2.982
156	374.979	1.470
157	409.435	.549
161	121.742	3.028
163	395.496	1.445
169	395.465	.509
170	395.465	.937
174	395.465	.937
175	395.465	.509
177	119.048	2.969
178	358.346	.561
184	358.341	.560
190	358.341	.560
195	119.494	.980
199	119.494	.980
203	119.494	3.976
206	393.237	1.499
207	358.781	.520
208	119.483	2.981

ORDERED LINES CASE 109

LINE	EXP FREQ	CALC FREQ	INTEN	ERROR
52	119.00	119.023	2.969	
120		119.033	3.959	
142		119.033	.247	
132		119.033	.742	
141		119.033	.742	
131		119.033	.247	
177		119.048	2.969	
208		119.483	2.981	
195		119.494	.980	
199		119.494	.980	
203		119.494	3.976	
155		119.506	2.982	
1	121.00	121.284	3.018	
6		121.295	4.024	
27		121.295	.333	
28		121.295	.673	
17		121.295	.673	
18		121.295	.333	
56		121.305	3.019	
161		121.742	3.028	
108		121.756	.954	
109		121.756	.055	
98		121.756	.055	
99		121.756	.954	
87		121.758	4.039	
39		121.766	3.029	
55	358.80	357.401	.630	
143		357.879	.215	
144		357.879	.382	
133		357.879	.382	
134		357.879	.215	
125		357.885	.597	
190	359.40	358.341	.560	
184		358.341	.560	
178		358.346	.561	
207		358.781	.520	
4	374.80	373.600	1.382	
31		374.079	1.392	
20		374.079	1.392	
9		374.081	1.407	
78		374.540	.483	
79		374.540	.953	
69		374.540	.483	
68		374.540	.953	

```
 57              374.543   1.436
156              374.979   1.470
206    394.40    393.237   1.499
170              395.465    .937
175    396.56    395.465    .509
169              395.465    .509
174              395.465    .937
163              395.496   1.445
113              397.727   1.291
103              397.727    .106
114    399.00    397.727    .106
104              397.727   1.291
 95              397.757   1.396
 45    401.50    400.017   1.352
157    410.40    409.435    .549
 82              411.665    .515
 72              411.665    .055
 81    412.78    411.665    .055
 71              411.665    .515
 60              411.692    .570
 33              413.926    .273
 23              413.926    .314
 34    415.10    413.926    .314
 24              413.926    .273
 12              413.954    .587
  5    417.20    416.216    .600

END OF CASE 109
```

```
LACCCON III

CASE 109    METHYL  TRANS-2-HEXENE-4-YNATE

NN= 5  FREQUENCY RANGE     90.000    450.000  MINIMUM INTENSITY    .020

INPUT PARAMETERS

1            W(1)=   120.400
1            W(2)=   120.400
1            W(3)=   120.400
1            W(4)=   368.000
1            W(5)=   402.900
             A(1,2)=      -0.000
             A(1,3)=      -0.000
             A(1,4)=       -.600
             A(1,5)=       2.400
             A(2,3)=      -0.000
             A(2,4)=       -.600
             A(2,5)=       2.400
             A(3,4)=       -.600
             A(3,5)=       2.400
             A(4,5)=      16.200

        PARAMETER SETS
1
        W(1)
        W(2)
        W(3)
2
        W(4)
3
        W(5)
4
        A(1,4)
        A(2,4)
        A(3,4)
5
        A(1,5)
        A(2,5)
        A(3,5)
6
        A(4,5)
             DEGENERACY
             DEGENERACY
             DEGENERACY
             DEGENERACY
             DEGENERACY
```

```
                DEGENERACY
                DEGENERACY
                DEGENERACY
      ITERATION  0  R M S ERROR =      .858
                DEGENERACY
                DEGENERACY
                DEGENERACY
                DEGENERACY
                DEGENERACY
      ITERATION  1  R M S ERROR =      .155
                DEGENERACY
                DEGENERACY
                DEGENERACY

                DEGENERACY
                DEGENERACY
                DEGENERACY
                DEGENERACY
      ITERATION  2  R M S ERROR =      .155
```

```
BEST VALUES CASE 109

1             W(1)=  119.999
1             W(2)=  119.999
1             W(3)=  119.999
1             W(4)=  368.631
1             W(5)=  404.140
              A(1,2)=    -0.000
              A(1,3)=    -0.000
              A(1,4)=     -.201
              A(1,5)=     2.341
              A(2,3)=    -0.000
              A(2,4)=     -.201
              A(2,5)=     2.341
              A(3,4)=     -.201
              A(3,5)=     2.341
              A(4,5)=    15.943

ERROR VECTORS AND STANDARD ERRORS
      .9805    .0049  -.0040   .1389    .1381  -.0126
              STANDARD ERROR=      .032
     -.0572    .8746   .1021   .2120    .1282  -.4001
              STANDARD ERROR=      .036
      .0109    .0561   .9274  -.0598    .0406   .3608
              STANDARD ERROR=      .033
     -.0372   -.1066   .0666   .8219   -.5523   .0477
              STANDARD ERROR=      .039
     -.1838   -.2316  -.0023   .5038    .8104   .0461
              STANDARD ERROR=      .037
     -.0049    .4072  -.3536   .0544    .0326   .8397
              STANDARD ERROR=      .054

PROBABLE ERRORS OF PARAMETER SETS

  1        .022
  2        .027
  3        .025
  4        .026
  5        .025
  6        .033
```

```
CASE NO  109

LINE   EXP FREQ   CALC FREQ   INTEN   ERROR


   1   121.000    121.056     3.022    -.056
   4   374.800    374.747     1.372     .053
   5   417.200    417.192      .606     .008
   6   121.000    121.065     4.030    -.065
   9   374.800    374.849     1.396    -.049
  12   415.100    414.967      .596     .133
  17   121.000    121.065      .704    -.065
  18   121.000    121.065      .304    -.065
  20   374.800    374.849     1.322    -.049
  21              374.849      .074
  23   415.100    414.940      .363     .160
  24   415.100    414.940      .234     .160
  27   121.000    121.065      .304    -.065
  28   121.000    121.065      .704    -.065
  30              374.849      .074
  31   374.800    374.849     1.322    -.049
  33   415.100    414.940      .234     .160
  34   415.100    414.940      .363     .160
  39   121.000    121.158     3.024    -.158
  45   401.500    401.250     1.347     .250
  52   119.000    118.830     2.975     .170
  55   358.800    358.805      .631    -.005
  56   121.000    121.074     3.023    -.074
  57   374.800    374.939     1.423    -.139
  60   412.780    412.737      .584     .043
  68   374.800    374.938  [illegible]008    -.138
  69   374.800    374.938     1.[illegible]15    -.138
  71   412.780    412.710      .137     .070
  72   412.780    412.710      .447     .070
  78   374.800    374.938     1.415    -.138
  79   374.800    374.938      .008    -.138
  81   412.780    412.710      .447     .070
  82   412.780    412.710      .137     .070
  87   121.000    121.154     4.032    -.154
  95   399.000    399.026     1.387    -.026
  98   121.000    121.154      .455    -.154
  99   121.000    121.154      .554    -.154
 103   399.000    398.998      .032     .002
 104   399.000    398.998     1.356     .002
 108   121.000    121.154      .554    -.154
 109   121.000    121.154      .455    -.154
 113   399.000    398.998     1.356     .002
 114   399.000    398.998      .032     .002
 120   119.000    118.835     3.966     .165
 125   358.800    358.909      .605    -.109
 131   119.000    118.835      .955     .165
 132   119.000    118.835      .036     .165
 133   358.800    358.906      .050    -.106
 134   358.800    358.906      .555    -.106
```

141	119.000	118.835	.036	.165
142	119.000	118.835	.959	.165
143	358.800	358.906	.555	-.106
144	358.800	358.906	.050	-.106
155	119.000	118.934	2.978	.066
156	374.800	375.013	1.454	-.213
157	410.400	410.504	.569	-.104
161	121.000	121.148	3.424	-.148
163	396.560	396.796	1.431	-.236
169	396.560	396.768	.103	-.208
170	396.560	396.768	1.329	-.208
174	396.560	396.768	1.329	-.208
175	396.560	396.768	.103	-.208
177	119.000	118.842	2.974	.158
178	359.400	358.999	.576	.401
184	359.400	358.996	.054	.404
185		358.996	.521	
189		358.996	.521	
190	359.400	358.996	.054	.404
194		118.924	.835	
195	119.000	118.924	.158	.076
199	119.000	118.924	.158	.076
200		118.924	.835	
203	119.000	118.924	3.970	.076
206	394.400	394.563	1.478	-.163
207	359.400	359.071	.544	.329
208	119.000	118.914	2.977	.086

```
ORDERED LINES CASE   109

LINE   EXP FREQ    CALC FREQ   INTEN      ERROR

  52   119.000     118.830     2.975      .170
 120   119.000     118.835     3.966      .165
 141   119.000     118.835      .036      .165
 131   119.000     118.835      .955      .165
 142   119.000     118.835      .955      .165
 132   119.000     118.835      .036      .165
 177   119.000     118.842     2.974      .158
 208   119.000     118.914     2.977      .086
 200               118.924      .835
 199   119.000     118.924      .158      .076
 195   119.000     118.924      .158      .076
 194               118.924      .835
 203   119.000     118.924     3.970      .076
 155   119.000     118.934     2.978      .066
   1   121.000     121.056     3.022     -.056
   6   121.000     121.065     4.030     -.065
  28   121.000     121.065      .704     -.065
  27   121.000     121.065      .304     -.065
  17   121.000     121.065      .704     -.065
  18   121.000     121.065      .304     -.065
  56   121.000     121.074     3.023     -.074
 161   121.000     121.148     3.024     -.148
  98   121.000     121.154      .455     -.154
  99   121.000     121.154      .554     -.154
 108   121.000     121.154      .554     -.154
 109   121.000     121.154      .455     -.154
  87   121.000     121.154     4.032     -.154
  39   121.000     121.158     3.024     -.158
  55   358.800     358.805      .631     -.005
 133   358.800     358.906      .050     -.106
 143   358.800     358.906      .555     -.106
 134   358.800     358.906      .555     -.106
 144   358.800     358.906      .050     -.106
 125   358.800     358.909      .605     -.109
 190   359.400     358.996      .054      .404
 189               358.996      .521
 185               358.996      .521
 184   359.400     358.996      .054      .404
 178   359.400     358.999      .576      .401
 207   359.400     359.071      .544      .329
   4   374.800     374.747     1.372      .053
  31   374.800     374.849     1.322     -.049
```

```
   30                  374.849      .074
   21                  374.849      .074
   20     374.800      374.849     1.322        -.049
    9     374.800      374.849     1.396        -.049
   78     374.800      374.938     1.415        -.138
   68     374.800      374.938      .008        -.138
   79     374.800      374.938      .008        -.138
   69     374.800      374.938     1.415        -.138
   57     374.800      374.939     1.423        -.139
  156     374.800      375.013     1.454        -.213
  206     394.400      394.563     1.478        -.163
  175     396.560      396.768      .103        -.208
  170     396.560      396.768     1.329        -.208
  174     396.560      396.768     1.329        -.208
  169     396.560      396.768      .103        -.208
  163     396.560      396.796     1.431        -.236
  103     399.000      398.998      .032         .002
  113     399.000      398.998     1.356         .002
  104     399.000      398.998     1.356         .002
  114     399.000      398.998      .032         .002
   95     399.000      399.026     1.387        -.026
   45     401.500      401.250     1.347         .250
  157     410.400      410.504      .569        -.104
   81     412.780      412.710      .447         .070
   71     412.780      412.710      .137         .070
   82     412.780      412.710      .137         .070
   72     412.780      412.710      .447         .070
   60     412.780      412.737      .584         .043
   34     415.100      414.940      .363         .160
   33     415.100      414.940      .234         .160
   23     415.100      414.940      .363         .160
   24     415.100      414.940      .234         .160
   12     415.100      414.967      .596         .133
    5     417.200      417.192      .606         .008

  END OF CASE 109
```

The boxed numbers represent cards that were removed because of large errors. See Sections 3.1 and 3.1.1.

For comparison between experimental and calculated spectra, see Figure 3.

```
LAOCCON III

CASE 109   METHYL TRANS-2-HEXENE-4-YNATE

NN= 5  FREQUENCY RANGE     90.000   450.000  MINIMUM INTENSITY   .020

INPUT PARAMETERS

1            W(1)=  120.400
1            W(2)=  120.400
1            W(3)=  120.400
1            W(4)=  368.000
1            W(5)=  402.900
             A(1,2)=    -0.000
             A(1,3)=    -0.000
             A(1,4)=     -.600
             A(1,5)=     2.400
             A(2,3)=    -0.000
             A(2,4)=     -.600
             A(2,5)=     2.400
             A(3,4)=     -.600
             A(3,5)=     2.400
             A(4,5)=    16.200

        PARAMETER SETS
1
        W(1)
        W(2)
        W(3)
2
        W(4)
3
        W(5)
4
        A(1,4)
        A(2,4)
        A(3,4)
5
        A(1,5)
        A(2,5)
        A(3,5)
6
        A(4,5)
             DEGENERACY
             DEGENERACY
```

```
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
         ITERATION  0  R M S ERROR =       .943
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
         ITERATION  1  R M S ERROR =       .081
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
                  DEGENERACY
         ITERATION  2  R M S ERROR =       .081
```

```
BEST VALUES CASE 109

1         W(1)=   120.000
1         W(2)=   120.000
1         W(3)=   120.000
1         W(4)=   368.756
1         W(5)=   404.105
          A(1,2)=    -0.000
          A(1,3)=    -0.000
          A(1,4)=      -.364
          A(1,5)=     2.432
          A(2,3)=    -0.000
          A(2,4)=      -.364
          A(2,5)=     2.432
          A(3,4)=      -.364
          A(3,5)=     2.432
          A(4,5)=    16.032

ERROR VECTORS AND STANDARD ERRORS
     .9613   -.0265   -.0617   -.0373   -.2612    .0432
          STANDARD ERROR=       .026
     .0360    .7480   -.1032   -.5046    .2124    .3590
          STANDARD ERROR=       .048
    -.1085    .0175    .7908   -.2216   -.5230    .1997
          STANDARD ERROR=       .021
    -.1065    .4486   -.1924    .6938   -.4481    .2611
          STANDARD ERROR=       .029
     .2259    .1667    .5565    .4617    .6285    .0670
          STANDARD ERROR=       .022
    -.0231   -.4588   -.1209    .0172    .1315    .8699
          STANDARD ERROR=       .037

PROBABLE ERRORS OF PARAMETER SETS

  1     .017
  2     .028
  3     .015
  4     .022
  5     .017
  6     .025
```

```
CASE NO  109

LINE    EXP FREQ    CALC FREQ    INTEN    ERROR

   1    121.000     121.019     3.021     -.019
   4    374.800     374.664     1.374      .136
   5    417.200     417.348      .605     -.148
   6    121.000     121.029     4.028     -.029
   9    374.800     374.919     1.399     -.119
  12    415.100     415.043      .594      .057
  17    121.000     121.029      .981     -.029
  18    121.000     121.029      .027     -.029
  20    374.800     374.918     1.359     -.118
  21                374.918      .040
  23                415.015      .021
  24                415.015      .573
  27    121.000     121.029      .027     -.029
  28    121.000     121.029      .981     -.029
  30                374.918      .040
  31    374.800     374.918     1.359     -.118
  33                415.015      .573
  34                415.015      .021
  39                121.274     3.027
  45    401.500     401.317     1.347      .183
  52                118.714     2.972
  55    358.800     358.633      .632      .167
  56    121.000     121.039     3.022     -.039
  57                375.158     1.427
  60    412.780     412.735      .580      .045
  68                375.157     1.427
  71    412.780     412.707      .554      .073
  72    412.780     412.707      .026      .073
  79                375.157     1.427
  81    412.780     412.707      .026      .073
  82    412.780     412.707      .554      .073
  87                121.268     4.036
  95    399.000     399.014     1.389     -.0[illegible]4
  98                121.268      .882
  99                121.268      .127
 103    399.000     398.983      .021      .017
 104    399.000     398.983     1.369      .017
 108                121.268      .127
 109                121.268      .882
 113    399.000     398.983     1.369      .017
 114    399.000     398.983      .021      .017
 120                118.721     3.962
 125                358.890      .603
 131                118.721      .035
 132                118.721      .956
 133                358.387      .570
```

134		358.887	.033	
141		118.721	.956	
142		118.721	.035	
143		358.887	.033	
144		358.887	.570	
155	119.000	118.971	2.979	.029
156		375.378	1.460	
157	410.400	410.427	.561	-.027
161		121.258	3.026	
163		396.706	1.436	
169	396.560	396.675	1.428	-.115
170	396.560	396.675	.008	-.115
174	396.560	396.675	.008	-.115
175	396.560	396.675	1.428	-.115
177		118.731	2.972	
178		359.129	.571	
184		359.126	.564	
190		359.126	.564	
194		118.960	.096	
195	119.000	118.960	.897	.040
199	119.000	118.960	.897	.040
200		118.960	.096	
203	119.000	118.960	3.972	.040
206	394.400	394.396	1.487	.004
207	359.400	359.347	.534	.053
208	119.000	118.948	2.978	.052

```
ORDERED LINES CASE  109

LINE    EXP FREQ    CALC FREQ    INTEN      ERROR

 52                 118.714      2.972
120                 118.721      3.962
132                 118.721       .956
142                 118.721       .035
131                 118.721       .035
141                 118.721       .956
177                 118.731      2.972
208     119.000     118.948      2.978      .052
195     119.000     118.960       .897      .040
194                 118.960       .096
200                 118.960       .096
199     119.000     118.960       .897      .040
203     119.000     118.960      3.972      .040
155     119.000     118.971      2.979      .029
  1     121.000     121.019      3.021     -.019
  6     121.000     121.029      4.028     -.029
 27     121.000     121.029       .027     -.029
 17     121.000     121.029       .981     -.029
 28     121.000     121.029       .981     -.029
 18     121.000     121.029       .027     -.029
 56     121.000     121.039      3.022     -.0[illegible]9
161                 121.258      3.026
 98                 121.268       .882
108                 121.268       .127
 99                 121.268       .127
109                 121.268       .882
 87                 121.268      4.036
 39                 121.274      3.027
 55     358.800     358.633       .632      .167
134                 358.887       .033
144                 358.887       .570
133                 358.887       .570
143                 358.887       .033
125                 358.890       .603
184                 359.126       .564
190                 359.126       .564
178                 359.129       .571
207     359.400     359.[illegible]47       .534      .053
  4     374.800     374.[illegible]4      1.374      .136
 30                 374.[illegible]18       .040
 31     374.800     374.918      1.359     -.118
 21                 374.918       .040
 20     374.800     374.918      1.359     -.118
  9     374.800     374.919      1.399     -.119
```

```
  79                   375.157     1.427
  68                   375.157     1.427
  57                   375.158     1.427
 156                   375.378     1.460
 206      394.400      394.396     1.487       .004
 175      396.560      396.675     1.428     -.115
 170      396.560      396.675      .008     -.115
 174      396.560      396.675      .008     -.115
 169      396.560      396.675     1.428     -.115
 163                   396.706     1.436
 104      399.000      398.983     1.369       .017
 114      399.000      398.983      .021       .017
 103      399.000      398.983      .021       .017
 113      399.000      398.983     1.369       .017
  95      399.000      399.014     1.389     -.014
  45      401.500      401.317     1.347       .183
 157      410.400      410.427      .561     -.027
  82      412.780      412.707      .554       .073
  81      412.780      412.707      .026       .073
  72      412.780      412.707      .026       .073
  71      412.780      412.707      .554       .073
  60      412.780      412.735      .580       .045
  33                   415.015      .573
  34                   415.015      .021
 124                   415.015      .573
  23                   415.015      .021
  12      415.100      415.043      .594       .057
   5      417.200      417.348      .605     -.148

 END OF CASE 109
```

```
PROGRAM SHAPE

LORENTZIAN LINESHAPE AND/OR STICK DIAGRAM PLOTTING PROGRAM


SPECTRUM NUMEER 109          -          METHYL TRANS-2-HEXENE-4-YNATE

LORENTZIAN LINESHAPE OPTION


PLOTTING PARAMETERS

SCALE =  1.00 MM/HZ       HEIGHT = 140.0 MM
FREQUENCY RANGE = 100.0 TO  420.0 HZ
      LINEWIDTH =  .5 HZ


 LINE  FREGUENCY  INTENSITY

   1    118.71       2.972
   2    118.72       3.962
   3    118.72        .956
   4    118.72        .035
   5    118.72        .035
   6    118.72        .956
   7    118.73       2.972
   8    118.95       2.978
   9    118.96        .897
  10    118.96        .096
  11    118.96        .096
  12    118.96        .897
  13    118.96       3.972
  14    118.97       2.979
  15    121.02       3.021
  16    121.03       4.028
  17    121.03        .027
  18    121.03        .981
  19    121.03        .981
  20    121.03        .027
  21    121.04       3.022
  22    121.26       3.026
  23    121.27        .882
  24    121.27        .127
  25    121.27        .127
  26    121.27        .882
  27    121.27       4.036
  28    121.27       3.027
  29    358.63        .632
```

```
   30     358.89          .033
   31     358.89          .570
   32     358.89          .570
   33     358.89          .033
   34     358.89          .603
   35     359.13          .564
   36     359.13          .564
   37     359.13          .571
   38     359.35          .534
   39     374.66         1.374
   40     374.92          .040
   41     374.92         1.3[illegible]
   42     374.92          .040
   43     374.92         1.359
   44     374.92         1.399
   45     375.16         1.427
   46     375.16         1.427
   47     375.16         1.427
   48     375.38         1.460
   49     394.40         1.487
   50     396.67         1.428
   51     396.67          .008
   52     396.67          .008
   53     396.67         1.428
   54     396.71         1.436
   55     398.98         1.369
   56     398.98          .021
   57     398.98          .021
   58     398.98         1.369
   59     399.01         1.389
   60     401.32         1.347
   61     410.43          .561
   62     412.71          .554
   63     412.71          .026
   64     412.71          .026
   65     412.71          .554
   66     412.74          .580
   67     415.01          .573
   68     415.01          .021
   69     415.01          .573
   70     415.01          .021
   71     415.04          .594
   72     417.35          .605


SUMMARY OF CALCULATIONS FOR PLOT NUMBER    1

LENGTH OF FREQUENCY AXIS (INCHES) =  13
   LENGTH OF FREGUENCY AXIS IN HZ =  330.[illegible]0
          FREQUENCY RANGE PLOTTED =  100.00 TO  419.86 HZ
         NUMEER OF POINTS PLOTTED = 2520
```