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LABORATORY STUDIES OF THE BEHAVIOUR AND FATE OF WAXY CRUDE OIL SPILLS

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EXECUTIVE SUMMARY

A series of small and mid-scale laboratory tests were undertaken to investigate the fate and behaviour of spills of waxy crude oils at sea. The results indicate that the behaviour of such oils will be very different from that of less viscous, conventional oils. This is concluded to be primarily due to the precipitation of waxes, asphaltenes and other unknown resinous compounds as the oil evaporates or as environmental temperatures drop.

The major characteristics of waxy oil spills are: firstly, very slow spreading or non-spreading behaviour, reduced evaporation rates, curtailed natural dispersion and anomalous emulsification. The end result of this unique behaviour is that waxy oil spills will likely survive considerably longer on the sea surface than equivalent non-waxy oils would.

Theoretical and empirical equations were developed to describe the behaviour of waxy (and non-waxy) oils and combined into a computer model capable of detailed predictions of the fate, behaviour and properties of waxy (and non-waxy) oil spills at sea. The model has the capability to deal with both blowouts and batch spills.

Preliminary, small-scale countermeasures tests indicated that although waxy oil forms could be contained by conventional booming systems, recovery of the oil using skimmers could prove difficult because of the semi-solid form of the oil and its lack of adhesion to oleophilic surfaces. Netting systems would also prove difficult to use since the gelled oil easily extrudes through mesh material at low pressures. A conventional chemical dispersant was completely ineffective on the waxy oils at temperatures below their pour point. Due to the slow weathering of waxy oils and the subsequent entrapment of volatile components they may burn more efficiently than conventional oils but may be more difficult to ignite.

RESUME

Une série d'essais en laboratoire a été entreprise afin d'investiguer le sort et le comportement des nappes d'hydrocarbures paraffiniques. Les résultats indiquent que le comportement de ces hydrocarbures sera très différent de celui des hydrocarbures conventionnels, moins visqueux. On conclue que ceci est due surtout à la précipitation de paraffines, d'asphaltènes et d'autres composés résineux inconnus à mesure que les hydrocarbures s'évaporent ou que les températures ambiantes baissent.

Les caractéristiques principaux des déversements d'hydrocarbures paraffiniques sont les suivantes: étalement très lent ou absent de la nappe, taux d'évaporation réduits, dispersion naturelle diminuée et émulsification anomale. Le résultat final de ce comportement est que les nappes d'hydrocarbures paraffiniques pourront survivre considérablement plus longtemps à la surface de la mer que les hydrocarbures non–paraffiniques.

Des équations théoriques et empiriques ont été développées afin de décrire le comportement des hydrocarbures paraffiniques (et non–paraffiniques) et ont été employées dans un modèle pour ordinateur ayant la capacité de prédire en détails le sort, le comportement et les propriétés des nappes d'hydrocarbures paraffiniques (et non–paraffiniques) à la surface de la mer. Ce modèle s'applique aux éruptions de puits extracôtiers ainsi qu'aux déversement en vrac.

Des essais préliminaires de contremesure menés à petite echelle ont indiqué que les hydrocarbures paraffiniques pourraient être retenues par des systèmes d'estacades conventionnels, mais que parcontre la récupération par écrémeurs d'hydrocarbures se montrera difficile à cause de la forme semi–solide de l'hydrocarbure et de son manque d'affinité aux surface oléophiliques. Les systèmes de fillets seront aussi difficile à employer, puisque l'hydrocarbure coagulé traverse facilement le filet, à basse pression. Un dispersant conventionnel n'a eu aucun effet sur les hydrocarbures paraffiniques à des témperature ambiants sous leur pointe d'écoulement.

A cause de l'évolution lente des hydrocarbures paraffiniques, les composés volatiles demeurent captés dans la nappe, ce qui pourra permettre une combustion plus efficace qu'avec les hydrocarbures conventionnels. Les hydrocarbures paraffiniques sont toutefois plus difficile à enflammer que les hydrocarbures conventionnels.

INTRODUCTION

A number of major hydrocarbon discoveries made off the East Coast of Canada over the past five years have involved so–called "waxy" crude oils. Preliminary work (S.L. Ross 1984a, 1985a, 1985b) with these oils has indicated that their oil spill behaviour is quite different from that of other crude oils and that this has significant implications with respect to countermeasures and environmental impacts.

Earlier studies with similar "waxy" oils from the North Sea also indicate that their behaviour, when spilled on water, is unique (WSL 1979 and 1981).

An earlier ESRF study on countermeasures for "waxy" crude oil spills also noted their unique behaviour when spilled at sea (S.L. Ross 1986a).

OBJECTIVE

The objective of this study was to perform a comprehensive investigation of the physical and chemical properties and behaviour of waxy crude oil spills. The purpose was to develop more information than is currently available and to use this information to predict potential impacts from waxy crude oil spills and to provide information useful in assessing appropriate cleanup measures.

REPORT FORMAT

This study was conducted in several independent phases at two different locations and involved some 10 individuals studying aspects of the behaviour and fate of waxy crude oil spills. Thus, this report is a compendium of studies rather than documentation of one study. As a result, the usual format of presenting the experimental methodology followed by results and discussion is not appropriate and a preferred format has been adopted of presenting each study individually. The individual study results are then combined into a revised oil fate and behaviour model to give an understanding of the spill behaviour of these unique oils.

The first section of the report deals with characterizing "waxy" crude oils in general and predicting their general spill behaviour using simple analytical and predictive methods. This includes a detailed analysis of the unique rheology of one waxy crude oil. The next section reports on experiments conducted to determine the near–source behaviour of waxy crude spills from both surface and subsea blowouts and from batch (i.e., tanker) spills. This is followed by a section discussing the results of experiments on the evaporation of waxy crude oil spills and the modification of existing equations to predict evaporation rates and subsequent property changes. The following section discusses the short term (up to one day) behaviour of waxy crude oil spills at sea, including emulsification, natural dispersion and particle formation. This section also discusses the results of a series of simple countermeasures tests conducted with the oils.

The final section of the report combines the results of the individual studies into a computerized oil fate prediction model to allow a comprehensive understanding of the behaviour of a spill of a particular oil over time. The conclusions and recommendations arising from the studies complete the report.

WAXY CRUDE OIL CHARACTERIZATION

INTRODUCTION

As experience has been gained with tests of oil spill behaviour in the laboratory and in field trials, and observations of actual oil spill incidents, it has become clear that different oils and petroleum products display widely varying behaviour. Some oils spread and evaporate rapidly, others form water–in–oil emulsions, while some form discrete pancakes, which are susceptible to periodic submergence by waves. It has become clear that there is a need to develop tests that can be applied to an oil to elucidate what type of behaviour to expect as a result of spillage. The incentives are (i) such a characterization provides advance warning of the adverse environmental effects leading to better environmental impact assessment, and (ii) it can lead to the deployment of more effective countermeasures.

Several groups have addressed this problem, notably that of CONCAWE (1983). In their report, "Characteristics of Petroleum and its Behaviour at Sea", they have documented the physical–chemical parameters of an oil and the effect which these parameters are believed to have on oil spill processes. Table 1 is reproduced from that report. Perhaps the most questionable feature of that table is the suggestion that viscosity does not effect spreading, since very viscous oils are unlikely to spread appreciably. Further, viscous oils are likely to experience retarded evaporation because of slowed diffusion in the oil phase. The CONCAWE group of experts assembled five oil groups, based on measurements of pour point and volatility, as shown on Table 2. The first group with high pour point, is expected to solidify rapidly at temperatures less than 10°C. There is thus recognition that this class of crude oil presents a unique problem for oil spill fate assessment and countermeasures deployment.

Mackay et al. (1983) reviewed this issue and developed a table, shown in Table 3, of phenomena, properties and suggested behaviour tests. It was acknowledged that, with the state of knowledge at that time, it was not possible to use only physical–chemical data to obtain estimates of oil spill behaviour. This is principally because the underlying mechanisms of oil spill processes are not sufficiently

Table 1 Physicochemical parameters of crude oil of importance for the individual processes

Process	Density	Spreading coefficient	Distillation curve	Viscosity	Pour point
Spreading	+	+			+
Evaporation	+ a)	+ a)	+		
Natural dispersion	+	+ b)		+	
Emulsification	+	+ c)		+	

a) Evaporation is only influenced indirectly by density and the spreading coefficient through their influence on spreading.

b) Only oil/water interfacial tension affects natural dispersion.

c) For emulsification the oil/water interfacial tension is important.

from CONCAWE (1983)

Table 2 Listing of groups

Group 1 Pour point >5-10°C			
. Argyll	. Cormorant	. Nigerian Light	. Soyo
. Auk	. Dunlin	. Ninian	. Suez Mix
. Brega	. Gamba	. Sarir	. Thistle
. Cabinda	. Lucina	. Schoonebeek	. Zueitina

Group 2 Evaporative loss 0-20 % (vol)	Group 3 Evaporative loss 20-40 % (vol)	Group 4 Evaporative loss 40-50 % (vol)	Group 5 Evaporative loss >50 % (vol)
PP 200+ >5-10°C	PP 200+ <5-10°C	PP 200+ <5-10°C	PP 200+ <5-10°C
. Lagunillas	. Arabian Heavy	. Arabian Light	. Zakum
. Tia Juana Pesado	. Champion Export	. Arabian Medium	
. West Nederland	. Khafji	. Basrah Light	PP 200+ >5-10°C
	. Nigerian Medium	. Danmark	. Abu Dhabi
	. Santa Maria	. Dubai	. Berri
		. Iranian Light	. Beryl
	PP 200+ >5-10°C	. Kuwait	. Brass River
	. Maya	. Nigerian Export Blend	. Brent Spar
		. Oman	. Ekofisk
		. Ural	. Kirkuk
			. Kole Marine
		PP 200+ >5-10°C	. Montrose
		. Buchan	. Murban
		. Es Sider	. Murchison
		. Flotta	. Nigerian Light Mobil
		. Forties	. Qatar Marine
		. Iranian Heavy	. Saharan Blend
		. Nigerian Light Gulf	. Sirtica
			. Statfjord

from CONCAWE (1983)

Table 3 Spill phenomena, properties influencing these phenomena, and suggested behavior tests

Phenomena	Basic properties influencing phenomena	Behavior tests
Spreading	Interfacial tensions, Viscosity	Tank test
Evaporation	Vapor pressure, Distillation curve	Tray evaporation, Gas stripping
Emulsification	Wax and asphaltene content	Rotating flask
Natural dispersion	Interfacial tension, Viscosity, Density	Modified Mackay-Nadeau-Steelman apparatus
Dissolution	Solubility	—
Reaction	Chemical nature	?
Sedimentation	Octanol-water partition coefficients, Solubility	?
Ice interaction	Viscosity, Oil-water interfacial tensions	?
Containment & recovery	Viscosity, Density	—
Combustion	Fire and flash point vapor pressure	—
Herding	Interfacial tensions	—
Chemical dispersion	Viscosity, Chemical nature	Mackay-Nadeau-Steelman apparatus
De-emulsification	Viscosity	—

from Mackay et al (1983)

understood. It is, therefore, necessary to use complementary tests designed to elucidate the susceptibility of the oil to the various phenomena.

These two studies suggest different approaches for considering oils that are unique in their properties and behaviour because of a property which is ill-defined but is generally referred to as "waxiness". The properties referred to by the term "waxiness" are non-Newtonian rheology at temperatures near the oil's pour point and the development of a "skin" on the oil as it cools and weathers. The CONCAWE approach is merely to group all these oils as one class in the expectation that experience gained on the behaviour of one member of the class can be applied to others. The Mackay approach has been to use physical, chemical, and behaviour tests. The difficulty with grouping is that, inevitably, some oils will lie on the boundaries between groups, and their behaviour may thus not be well characterized. As well, oils within this group may vary in "waxiness". The advantage is, of course, that the system is simple and immediately applicable. The proposed test system has a potential to be more accurate, but it cannot be fully applied with the present state of knowledge.

Waxy crude oils, such as those considered in this study, present a new dimension to the problem of oil spill prediction. There has been very limited experience of their behaviour in the laboratory or at sea. There is no adequate characterization of the "waxiness" of crude oils or of their unusual behaviour in water, or on water surfaces. This study thus attempts to address this issue by conducting and reporting experiments on selected waxy crude oils. Initially, it had been hoped that it would be possible to develop a simple test of "waxiness", but as a result of the investigations and gaining a greater appreciation of the properties of these oils, it became apparent that such a simple test is not likely to be feasible and could, indeed, be misleading. An alternative test scheme is, however, developed and presented later for consideration.

The established physical-chemical properties that are closest to characterizing "waxiness" are viscosity, pour point, and the content of waxes, asphaltenes, and resins. It has not, however, been clearly established if it is the waxes (as determined by a standard wax content test involving chilling the oil dissolved in solvent) that are the only, or even the principal, contributors to so-called "waxiness". Until recently, the ASTM pour point test, which provides an estimate of a temperature at which oil does not flow under the influence of gravity has been the only indicator of the presence of waxy character. It is known that certain waxy crude oils, with high pour points, i.e., in the range of 10 to 20°C, exhibit typical oil spill behaviour until the ambient temperature is about 10 degrees below the measured pour point (S.L. Ross 1985a). It is also known that sample handling can affect pour points by up to 10°C, and no correlation can be established between pour point and wax content. It is important to understand the reasons for these observations and phenomena.

The program of studies which is described here evolved as the project proceeded with major decisions being taken in conjunction with the Scientific Advisers. The prinicpal effort was a detailed study of the rheology of one oil, using state–of–the–art equipment. It was hoped, and indeed it transpired, that this study would elucidate the intricacies of behaviour of the oil and demonstrate the effects of temperature, gelation time, and shear rate. This study could then be used as a template to suggest simpler, less expensive studies for other waxy oils. A limited study of the properties of all the candidate oils, using conventional measurement techniques was also conducted.

TEST OILS

In order to investigate waxy oil characteristics, five oils were selected to represent the range of waxiness in Canadian oils. These crude oils were Mixed Sweet Western (MSW), Hibernia B–27, Hibernia C–96, Avalon J–34 and Terra Nova K–08/DST1. The latter four are oils discovered on the Grand Banks and represent the range of oils likely to be produced from this region, the first is a pipeline blend of Western Canada oils. Table 4 lists the standard physical properties of the oils.

Based on the recommendation of the Scientific Advisers the characterization studies concentrated on four oils, MSW, Hibernia B–27, Hibernia C–96 and Avalon J–34, the subsequent fate and behaviour studies utilized three oils, MSW, Hibernia B–27 and Avalon J–34, and only one oil, Avalon J–34 oil was selected for a detailed rheological study.

TABLE 4

PROPERTIES OF TEST OILS

	MIXED SWEET WESTERN	HIBERNIA B–27	HIBERNIA C–96	AVALON J–34	TERRA NOVA K–08
DENSITY (kg/m^3)					
@ 10°C	874	878	844	880	850
@ 20°C	866	870	837	871	842
@ 30°C	857	862	830	864	834
VISCOSITY (mPa.s)**					
@ 15°C	18	240	*	*	*
@ 20°C	17	80	90	220	*
@ 25°C	16	25	30	40	*
POUR POINT (°C)***	<–17	9	18	18	27
WAX CONTENT (% mass)	2.9	9.7	7.4	3.5	11.8
ASHPHALTENE CONTENT (% mass)	4.0	1.2	3.2	3.2	7.7

* below pour point

** at a shear rate of approximately 10 s^{-1} using a Brookfield concentric cylinder viscometer

*** as determined by ASTM D97–66

RHEOLOGY

It is appropriate at this point to review briefly the nature of the rheology of Newtonian liquids, such as crude oils above their pour points. When a fluid is stressed, i.e., velocity or momentum is applied to part of the fluid, the momentum is transmitted through the fluid to other locations. In a solid, the transmission of momentum is essentially complete, i.e., when one part of the solid body is moved, all other parts follow. In a fluid, the transmission of momentum is inefficient, in that there is some loss of momentum due to viscous dissipation in the fluid. The fundamental property that causes momentum transport is a difference in velocity of fluid at two points or, more specifically, the velocity gradient, which is measured in units of (m/s)/m, or reciprocal seconds (s^{-1}). This is referred to as the "shear rate", and essentially expresses the magnitude of velocity variation in the fluid. The momentum transferred through this gradient is dissipated and measured as a force (Newtons (N)) per unit area, and thus has units of pressure (Pascal, Pa). The proportionality constant between the pressure or stress generated and the velocity gradient which causes the transfer of momentum, is the viscosity and has unit of Pascal seconds (Pa.s)

$$\text{Stress (Pa)} = \text{Viscosity (Pa.s)} \times \text{Shear Rate } (s^{-1})$$

High viscosity implies a high efficiency in transmitting momentum and stress, thus the fluid is more "solid" in character.

For many fluids this simple proportionality breaks down, and more complex rheological behaviour occurs. This can be viewed as a dependence of viscosity on shear rate and other factors, and such fluids are classified as non–Newtonian fluids.

A first deviation from Newtonian behaviour occurs in waxy crude oils because of the possibility of precipitation of certain high molecular weight components, such as waxes, asphaltenes, and resins. The nature of these precipitates is not well understood, but it is known that the asphaltenes are capable of forming colloidal suspensions which may aggregate into relatively large "particle structures". These "particles" appear to be capable of forming a fairly rigid structure, which resists deformation until a certain minimum stress is applied to the fluid. The fluid can then be referred to as having "gelled" or "set". Having been stressed beyond failure, the fluid starts to flow at a yield stress. Generally, oils that have a condition below the yield stress behave as semi–solids or gels, and those that are in a condition exceeding the yield stress behave as liquids. The magnitude of the yield stress is thus an important characteristic of the oil.

The formation of this "solid structure" is profoundly affected by temperature, presumably because of the marked dependence of solubility of the precipitating material on temperature.

A second deviation from Newtonian behaviour is that the apparent viscosity depends on the shear rate of the oil. In the class of fluids discussed here, as a fluid is increasingly sheared, the apparent viscosity tends to decrease. This is referred to as "shear thinning" or pseudo–plastic behaviour. It is believed to be caused by a steady state being achieved between the competitive processes of association of precipitated material to form a rigid solid structure and a break up of that structure by shear. Oils that are at a high shear rate are presumed to have a spectrum of smaller particle sizes of solid material, resulting in less structure and a lower viscosity.

As a consequence of this rheological behaviour, the condition of an oil at any point in time is a function, not only of the present shearing status, but also of its recent shearing history. An oil that has previously been at a high shear rate and is not sheared at present may be in the process of building up a solid structure, and will generally still have a lower viscosity than one that has been allowed to remain quiescent for a prolonged time period.

There is a possibility that the precipitation process may actually result in bulk phase separation. Samples of oil must thus be handled with extreme care to avoid inadvertent phase separation. The best way of assuring this is to store the oil at high temperature and mix it regularly. Another problem is the potential loss of volatile material in the oil. The volatile low molecular weight hydrocarbons play a crucial role in controlling the oil rheology. If there is loss of even a small proportion of the volatile material, there may be a marked increase in oil viscosity because these hydrocarbons are believed to be the most efficient solvents for substances such as asphaltenes. Particularly important are the light aromatics, such as benzene, toluene, and xylenes. It is thus essential to ensure that the oil samples are not subjected to evaporation and are carefully reconstituted before each measurement.

A comment is appropriate about the units of viscosity used in this section of the report. Shear rates will be consistently expressed in units of reciprocal seconds, and shear stresses in Pascals. Viscosity is thus reported in units of Pascal·seconds. The most commonly used unit is still the CGS unit, the centipoise, which is equivalent to one milliPascal·second. Water has a viscosity of about 1 centipoise or 0.001 Pa.s. An oil of viscosity 1000 centipoise, thus has a viscosity of one Pa.s. The reader can convert the reported viscosities in units of Pascal seconds to centipoise by multiplying all reported numbers by 1000.

RHEOLOGY OF AVALON J–34: PROCEDURES

Given this background, it was decided to study, in some detail, the rheological behaviour of one of these oils, Avalon J–34. The study consisted of the following components.

1. measurements in the temperature range from 4° to 60°C to evaluate the oil's apparent viscosity as a function of the shear rate between 0.87 and 348 s^{-1};
2. an evaluation of the yield stress as a function of temperature in the range from 0° to 22°C; and
3. a study of the dependence of the apparent viscosity on the shear history at a temperature of 0° and 10°C.

As discussed earlier, when studying the rheology of waxy crude oils it is crucial that all samples are identical in composition. To this end the Avalon J–34 crude was heated to 50°C in a closed 5–litre metal can and kept at this temperature for 2 hours. During this time the crude was shaken repeatedly to ensure that any precipitates would dissolve and the oil would become fully homogenized. Sealing from the atmosphere ensured that, but no evaporation would take place.

About 100 vials each with a volume of 20 cm^3 were then filled with about 15 cm^3 of warm oil and subsequently closed with screw caps with an aluminum liner; about 200 vials with a volume of 2 cm^3 were filled with about 1.5 cm^3 of warm oil and closed in the same way. The vials were stored at room temperature.

The oil in the large vials was used for measurements with the Haake Rotovisco RV12 Viscometer; the oil in the smaller vials for measurements with the Haake PK100 Cone–and–Plate Viscometer.

Apparent Viscosity Between 4° and 60°C

Procedure. The apparent viscosity of the oil between 4° and 60°C was measured with a Haake Rotovisco RV12 Viscometer using the NV sensor system. This system is a coaxial concentric cylinder type with a sample volume of 9 cm^3. Due to the shrinkage of the crude sample during its cooling in the measuring chamber, the concentric cylinder geometry is less convenient than the cone–and–plate geometry for fluids that exhibit a yield stress. As the sensitivity of the RV12 system was ten times greater than that of the cone–and–plate PK 100 it was decided to perform these measurements with the Rotovisco RV12 Viscometer, so as to facilitate measurements over the full temperature range from 4° to 60°C without changing the sensor system. This is of critical importance when comparing the rheology of the oil at different temperatures.

For each temperature a fresh oil sample was used. Prior to each measurement series the oil sample was reconditioned in its vial at a temperature of 50°C for 30 minutes.

The measurement procedure at each temperature was as follows:

1. the temperature of the NV sensor system was set at 50°C using a thermostat bath;

2. an oil sample of 9 cm^3 was taken from a vial using a syringe and a needle and gently injected into the sensor system;
3. the temperature of the sensor system was switched immediately to the measurement temperature;
4. the sample was kept at the measurement temperature for 5 minutes without shearing; at low temperatures this allowed the oil to gel;
5. the shearing was initiated at its lowest value, 0.87 s^{-1}; when the shear stress reached a constant value the apparent viscosity was determined. In cases where the value of the shear stress was still changing after 10 minutes of constant shearing, the value at that time was used to determine the apparent viscosity;
6. the shear rate was then increased to the next higher value and the procedure for determining the apparent viscosity was repeated. The increase between two consecutive shear rate values was usually a factor of two;
7. measurements were performed at increasing values of the shear rate up to the value of 87 s^{-1}. At this shear rate the sample was sheared until a constant value of the shear stress was reached, but not longer than 30 minutes;
8. subsequently, measurements were performed at decreasing values of the shear rate until the lowest value of 0.87 s^{-1} was again reached;
9. the measurements were repeated with increasing shear rates as described before up to a value of 348 s^{-1};
10. finally the sensor system was taken apart and cleaned thoroughly to prepare for the next sample.

Results and Discussion. The results of the measurements are shown in Figure 1, the value of the apparent viscosity is plotted as a function of the shear rate for sample temperatures from 4.0° to 60.0°C. The points marked A, B, C and D on the curves represent shear rates of 0.87, 87, 0.87 and 348 s^{-1} respectively.

The curves for temperatures of 25°C and higher show pseudoplastic behaviour, i.e., the apparent viscosity decreases with increasing shear rate. All values measured for these temperatures became constant within a few minutes of shearing and no dependence on the shear rate history was observed. The curves for

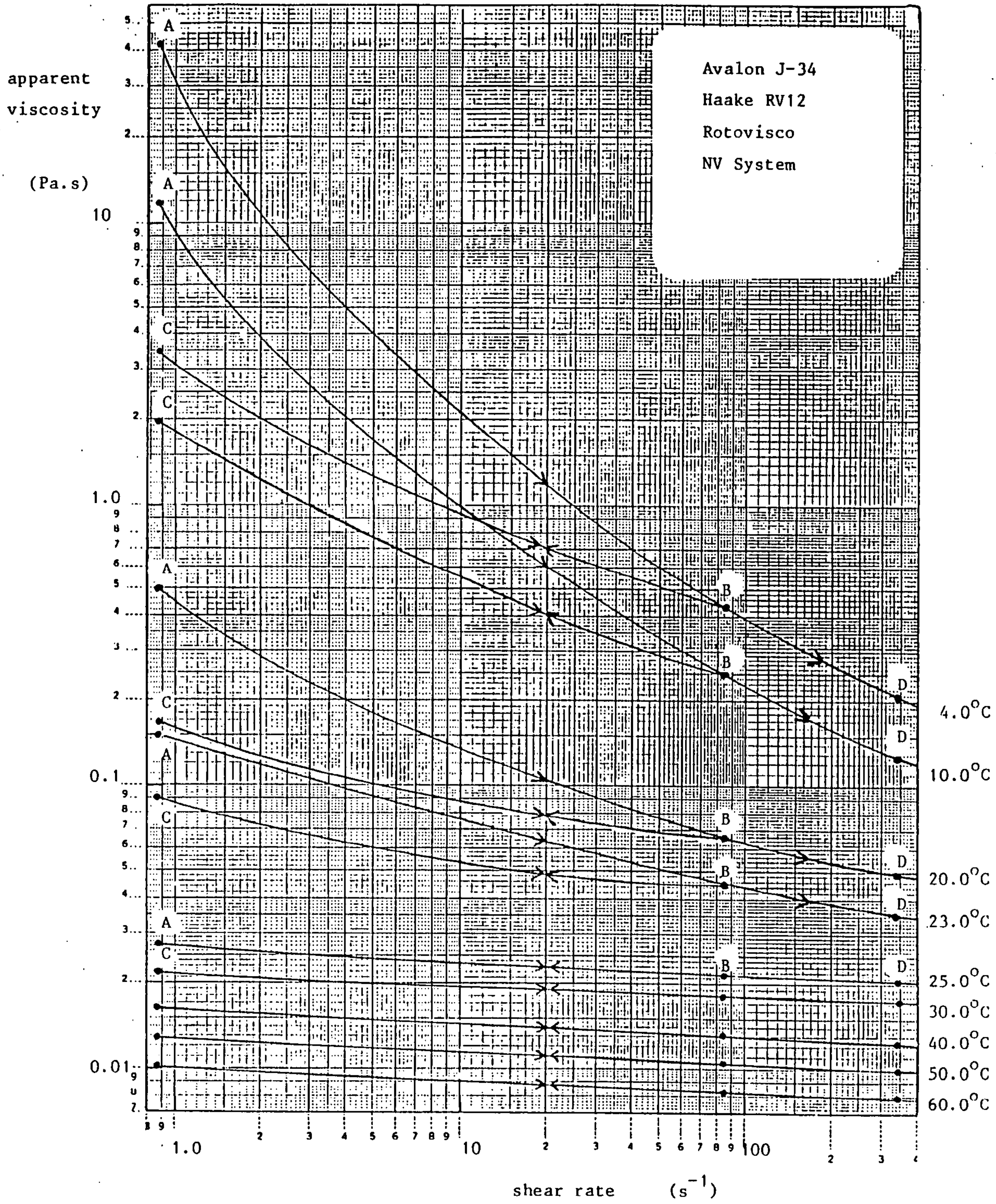


FIGURE 1 Apparent viscosity as a function of shear rate at temperatures from 4.0° to 60.0°C.

temperatures of 23°C and lower show thixotropic behaviour, i.e., the apparent viscosity also depends on the shear history. For example, at 20°C a value for the apparent viscosity of 0.49 Pa.s was observed at the lowest shear rate of 0.87 s^{-1} when sheared for the first time (point A). Increasing the shear rate gradually up to 87 s^{-1} the apparent viscosity drops to 0.066 Pa.s (point B). If the next shear rate is gradually lowered back to the starting value of 0.17 Pa.s or about 35% of its previous value at this shear rate. If we next increase the shear rate back up to 87 s^{-1} and then down again to 0.87 s^{-1} no hysteresis is observed between the lowest and the highest shear rate (points C and B).

No attempt was made to measure the values of the apparent viscosity after shearing at the highest shear rate of 348 s^{-1}, however it is probable that a further reduction of the apparent viscosity at lower shear rates would have resulted. In practice, most situations encounter shear rates in the range between 1 and 100 s^{-1}.

At the lower temperature range, where the crude shows a yield stress, the concentric cylinder configuration of the Haake Rotovisco RV12 Viscometer system was considered to be less accurate. This is attributed to the shrinkage of the oil at temperatures below the pour point, which causes voids in the sample and slip at the oil–cylinder interfaces. Due to the much smaller sample volumes involved, a cone–and–plate configuration is much less sensitive to shrinkage problems and therefore the PK100 Cone–and–Plate system was used for the remainder of the study.

Yield Stress Between 0° and 22°C

Procedure. The behaviour of the crude oil Avalon J–34 at temperatures below 25°C points to the existence of a yield stress that increases at lower temperatures. A study of the yield stress in this temperature range was carried out with the Haake PK100 Cone–and–Plate Viscometer to minimize the effects of shrinkage during the gelation of the samples during cooling. The cone used had a cone angle of 1° and a diameter of 50 mm. A sample volume of 0.9 cm^3 was used and each measurement was carried out with a fresh sample. Prior to each measurement the sample was reconditioned in its vial for 30 minutes at a temperature of 50°C.

The measurement procedure at each temperature consisted of the following steps:

1. the temperature of the cone–and–plate system was set at the intended measuring temperature with the use of a thermostat bath;
2. an oil sample of 0.9 cm^3 was taken from a vial using a syringe and a needle and gently ejected onto the surface of the plate, the cone was raised just prior to the application of the oil;
3. the cone was slowly lowered back onto the plate avoiding premature shearing of the sample;
4. the sample was kept at the measurement temperature for 5 minutes without shearing to allow the oil to build up its gel structure;
5. shearing was initiated at the lowest available shear rate (0.06 s^{-1}) and the shear stress was recorded as a function of time on a stripchart recorder;
6. the peak value of the recorded shear stress was identified as the value of the yield stress.

Results and Discussion. Figure 2 shows a typical example of a stripchart record used for the determination of the yield stress at a temperature of 0.1°C. The graph essentially consists of three regions: From A to B the sample is unsheared; at point B shearing starts at the rate of 0.06 s^{-1} and the shear stress builds up linearly with time until it reaches a maximum value at point C. After this the shear stress levels off and eventually reaches a constant value. There is no flow in the region up to point C at which the oil yields. The value of the shear stress at point C (its maximum value) is taken to be the yield stress.

When the measurements were repeated at higher values for the shear rate, identical values for the yield stress were found although the transient character of the shear stress signal made it more difficult to correctly identify its peak value at higher values of the shear rate.

In Figure 3 the value of the yield stress of the Avalon J–34 oil is shown as a function of the temperature between 0° and 22°C. For temperatures higher than 22°C the value of the yield stress was too low to be measured with acceptable accuracy with the PK100 cone–and–plate system. The yield stress was clearly a

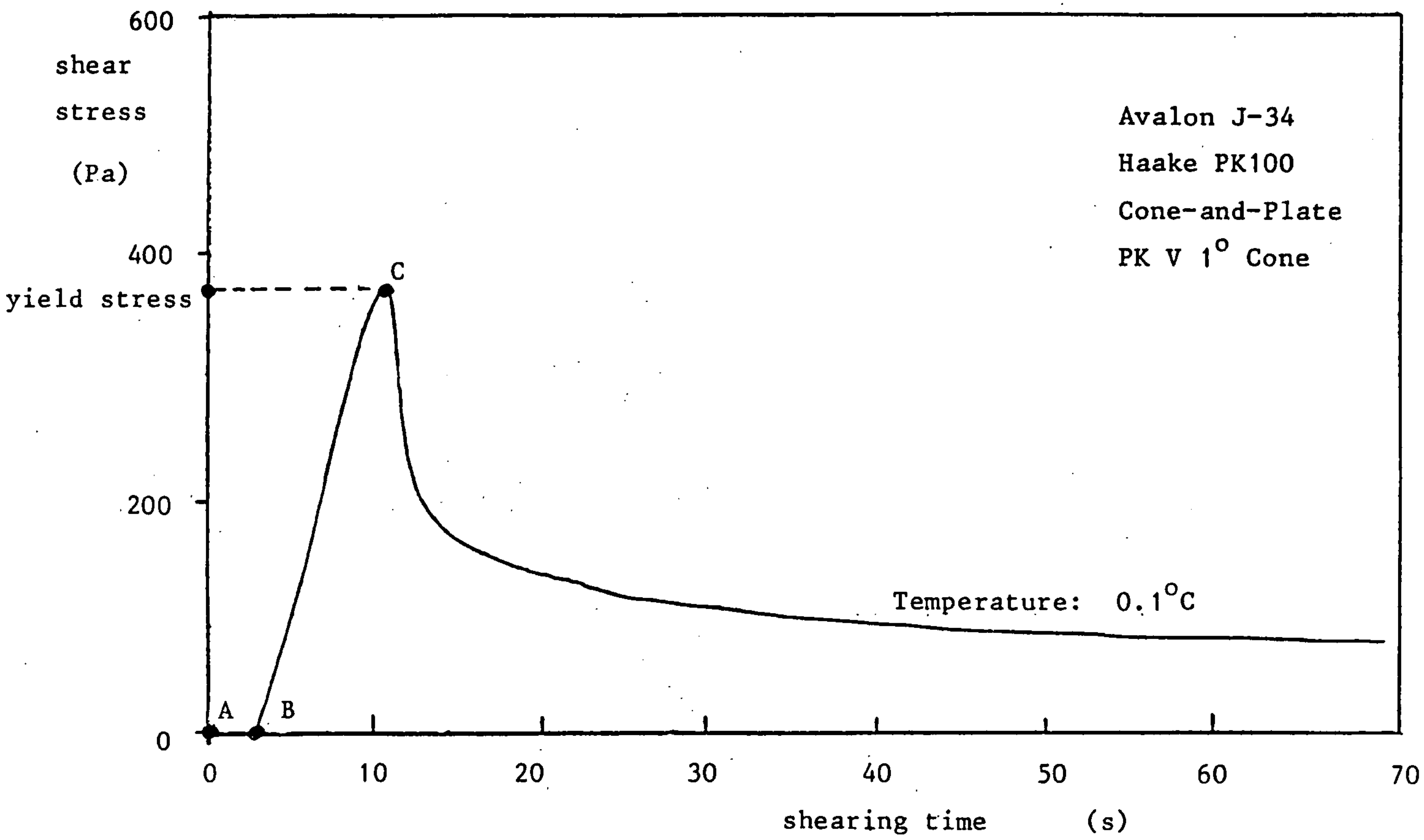


FIGURE 2 Shear stress as a function of time during the determination of the yield stress using a shear rate of 0.06 s^{-1}.

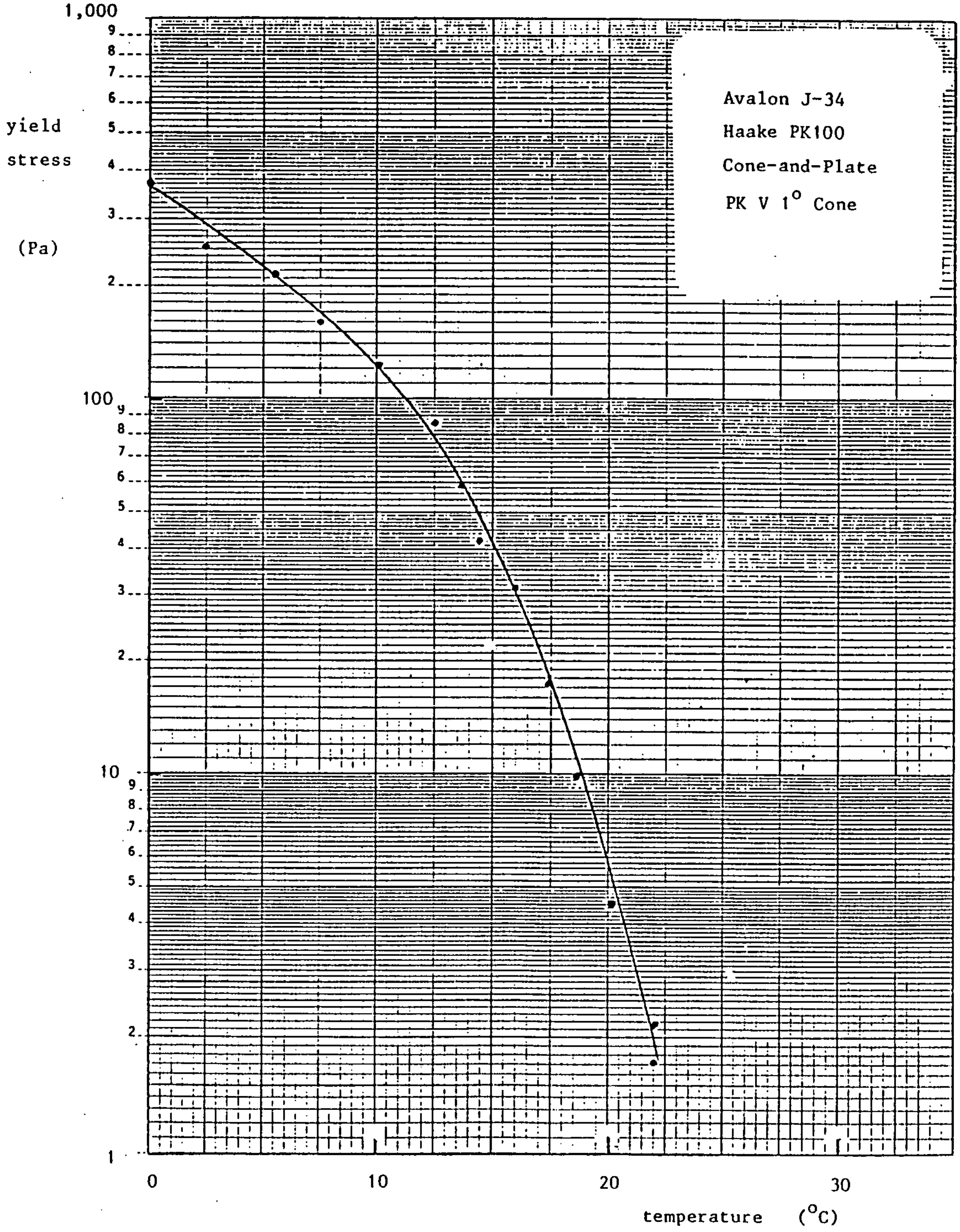


FIGURE 3 Yield stress as a function of temperature.

strong function of the temperature. At 0°C the value was 370 Pa. With increasing temperature the value dropped gradually until at about 14°C a value of 50 Pa was reached. A further increase in temperature resulted in a more significant decrease; at the pour point of the Avalon J–34 oil (18°C) the yield stress had dropped to 14 Pa. At 22°C the value of the yield stress was only 2 Pa.

Dependence of the Yield Stress and Apparent Viscosity on Gelation Time

The results reported in the previous sections clearly show that the rheological behaviour of the waxy crude oil Avalon J–34 at temperatures below 25°C is complicated and depends upon the shear history of the sample. The yield stress presumably originates from the precipitation of waxes and the colloidal asphaltenes. As a result, the value of the yield stress depends to a large extent on the temperature history of the sample.

A series of measurements was carried out to determine the influence of the gelation time (i.e., the duration of the time for which the oil was allowed to stabilize before shearing) on the value of the yield stress. For these tests the measurement procedure as outlined earlier was followed. However, the gelation time of 5 minutes was now varied between 1 and 1000 minutes.

In Figure 4 the value of the yield stress for oil temperatures of 0.2° and 10.2°C is shown as a function of the gelation time. The results for 10.2°C show a strong dependence of the yield stress on the gelation time. After 1 minute the value of the yield stress has built up to 76 Pa; with increasing time this value increases steadily to reach a value of 320 Pa after 1000 minutes of gelation time. This result is even higher than the initial value for the yield stress at the much lower temperature of 0.2°C after the shortest build–up period of 1 minute, which is only 290 Pa. At this lower temperature the increase of the value in the yield stress with time is much slower and after 1000 minutes a value of 590 Pa results.

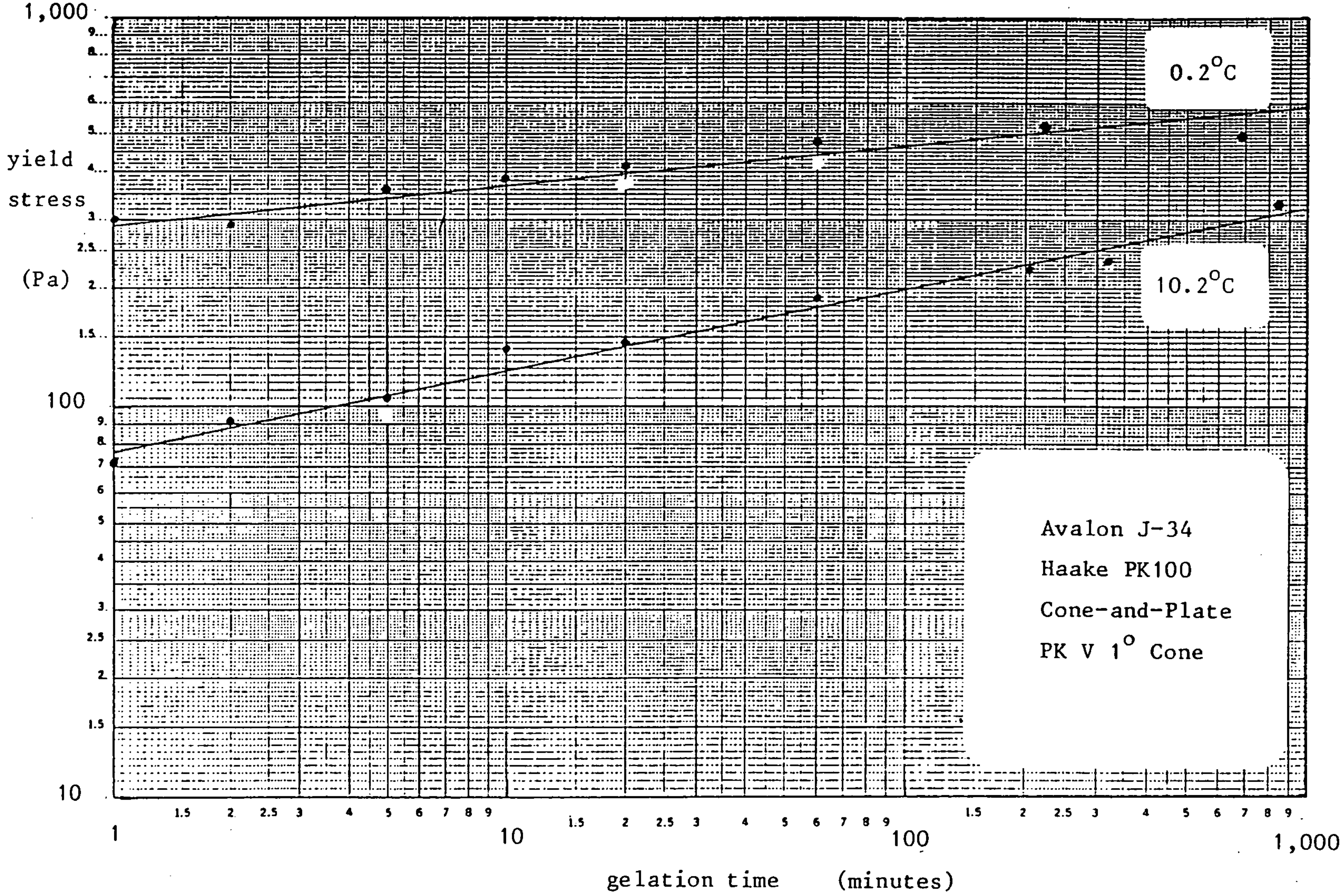


FIGURE 4 Yield stress as a function of isothermal gelation time for temperatures of 0.2^{o} and 10.2^{o}C.

The graphs for the different temperatures suggest that it is in this temperature region (0° – 10°C) that after a sufficiently long gelation period the yield stress of the Avalon J–34 oil will be strongly dependent on the gelation time and less dependent on the temperature.

From the results reported above it is expected that the apparent viscosity will also be dependent on the gelation time. To investigate this further a series of measurements at both 0.2° and 10.2°C was carried out to determine the equilibrium value of the apparent viscosity of a previously unsheared sample. The gelation time was again varied between 1 and 1000 minutes and a shear rate of 0.96 s^{-1} was used throughout the investigation.

The measurement procedure was virtually identical to the one described previously:

1. the temperature of the cone–and–plate system was set at the required measuring temperature with the use of a thermostat bath;
2. an oil sample of 0.9 cm^3 was taken from a vial using a syringe and a needle and gently ejected onto the surface of the plate, the cone was raised just prior to the application of the oil;
3. the cone was slowly lowered back onto the plate avoiding premature shearing of the sample;
4. the sample was kept at the measurement temperature for a time between 1 and 1000 minutes without shearing to allow the oil to build up its gel structure;
5. shearing was initiated at a shear rate of 0.96 s^{-1} and the value of the shear stress was recorded as a function of time on a stripchart recorder;
6. the value of the shear stress after 10 minutes of continuous shearing was used to calculate the value of the apparent viscosity. Usually a stable reading was reached after only 1–3 minutes of shearing.

Prior to each measurement the oil sample was reconditioned in its vial at a temperature of 50°C for 30 minutes. A fresh sample was used for each measurement. In Figure 5 the influence of the gelation time on the value of the apparent viscosity for a shear rate of 0.96 s^{-1} is shown for temperatures of 0.2° and 10.2°C. In

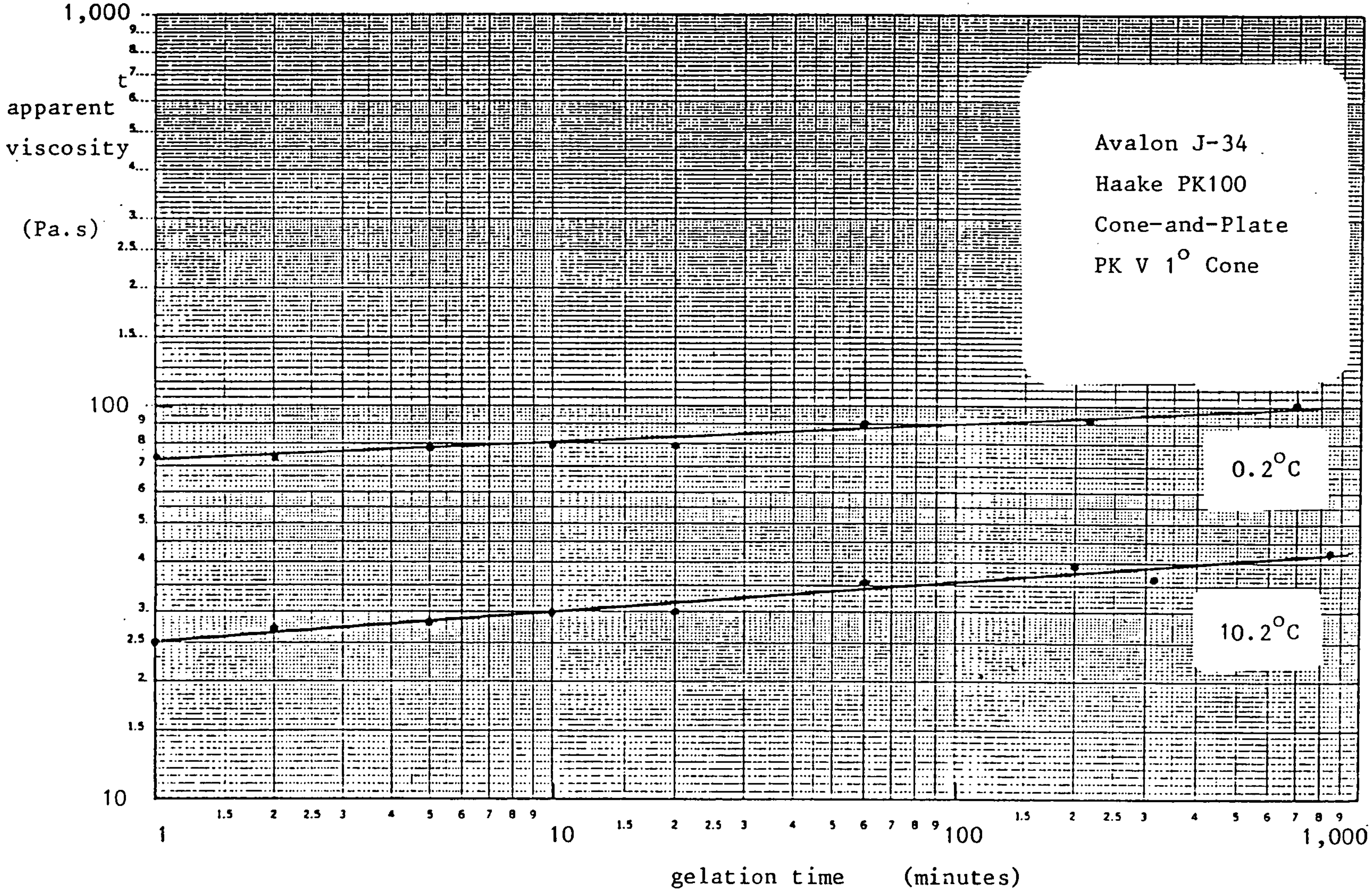


FIGURE 5 Apparent viscosity for a shear rate of 0.96 s^{-1} as a function of isothermal gelation time for temperatures of 0.2° and 10.2°C.

contrast to the results for the yield stress, the values for the apparent viscosity show less dependence on the gelation time. After a period of 1000 minutes the value of the apparent viscosity at 10.2° increases from 25 Pa.s (value after 1 minute) to 43 Pa.s. At 0.2°C the increase is even less: from 72 Pa.s after 1 minute to 100 Pa.s after 1000 minutes of gelation time.

Influence of the Shear History on the Apparent Viscosity

To evaluate further the influence of the shear history on the apparent viscosity of the Avalon J–34 oil, two measurement series were carried out at temperatures of 10.2 and 0.2°C respectively. The Haake PK100 Cone–and–Plate Viscometer was used for these measurements because the concentric cylinder system was found to be inaccurate at temperatures at which the oil shows a yield stress. This is caused by "slippage" between the oil and the walls of the concentric cylinders.

A standardized shear rate program was selected as shown schematically in Figure 6. The preparation for each measurement was the same as that described in Steps 1 through 4 of the yield stress measurements. The value of the shear stress was recorded as a function of time on a stripchart recorder for the total duration of the measurement program which took 75 minutes to complete for each run. In the top part of Figure 6 the values of the shear rate applied are shown as a function of time, while the bottom part shows schematically the recorded values of the shear stress, again as a function of time.

A complete measurement program consisted of each of the 8 numbered phases shown in Figure 6:

1. During Phase 1 the sample was allowed to gel without shearing for 5 minutes. The value of the shear stress during this phase was zero.
2. During Phase 2 the sample was sheared at the selected shear rate value SR for 10 minutes. During this phase the shear stress decreased from the value A to the equilibrium value B. A constant value was usually attained within 2–5 minutes. The value of the apparent viscosity at this shear rate

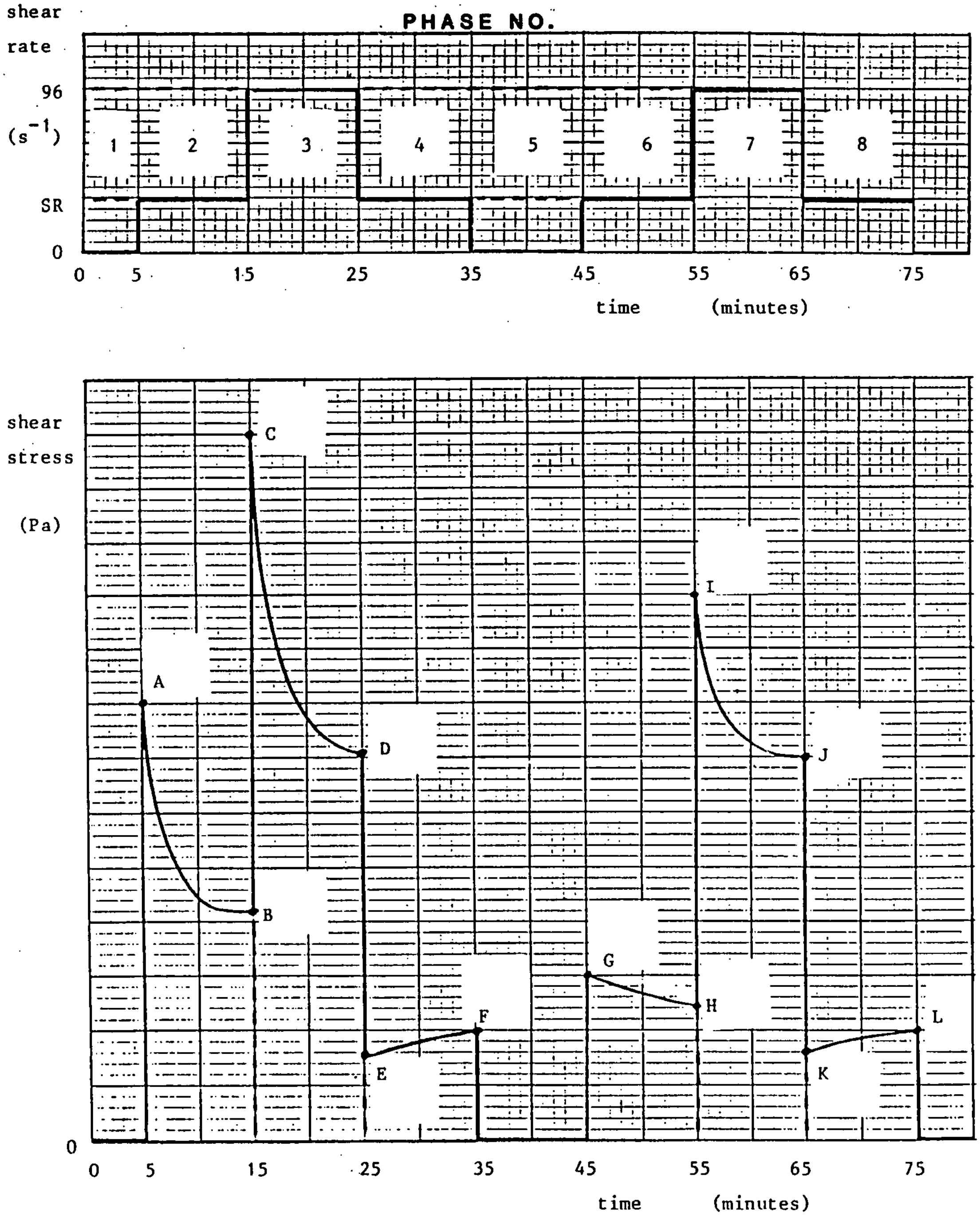


FIGURE 6 Shear rate program for the detailed rheological study consisting of 8 phases.

value was then calculated from the value of the shear stress at the end of Phase 2.

3. During Phase 3 the shear rate was increased to the "standard" high value of 96 s^{-1}. Figure 7 shows an example of a typical record of the apparent viscosity of a sample at a temperature of 0.2°C during this phase of the program; a steady value is reached after just a few minutes of shearing.
4. During Phase 4 the shear rate was restored to the originally selected shear rate value SR. As the sample has now experienced a period of high shear rate, the gel structure has been broken down partially and the values of the shear stress are much lower than during Phase 2. This indicates that the build-up of the gel structure is only partial. An experiment where the duration of this phase was extended to 60 minutes showed an equilibrium value that was only slightly higher than the value recorded after just 10 minutes.
5. During Phase 5 the shear rate was reduced to zero and the sample was allowed to re-gel under no-shear conditions.
6. During Phase 6 the sample was sheared again at the selected shear rate value SR. As a yield stress had been built up during Phase 5, the value of the shear stress now decreased with time and the value after 10 minutes was only slightly higher than the final value during Phase 4.
7. Phase 7 was the same as Phase 3; the equilibrium value of the shear stress at the end of these phases was found to be about equal.
8. Phase 8 was the same as Phase 4; the records of the shear stress during these phases were found to be nearly identical.

From the general shape of the shear stress records during the measurement program it was concluded the value of the apparent viscosity of the sample after shearing for 10 minutes at the standardized high shear rate of 96 s^{-1} can be found from the average of the shear stress values at the end of Phases 4 and 6.

Figure 8 shows a typical record of the apparent viscosity of a sample at a temperature of 0.2°C during these phases for a selected shear rate SR of 0.96 s^{-1}. The values of the recorded shear stress have been converted to apparent viscosity values. The build-up of the apparent viscosity during Phase 4 was still not completed after 10 minutes of shearing. The results during Phase 6 showed that the

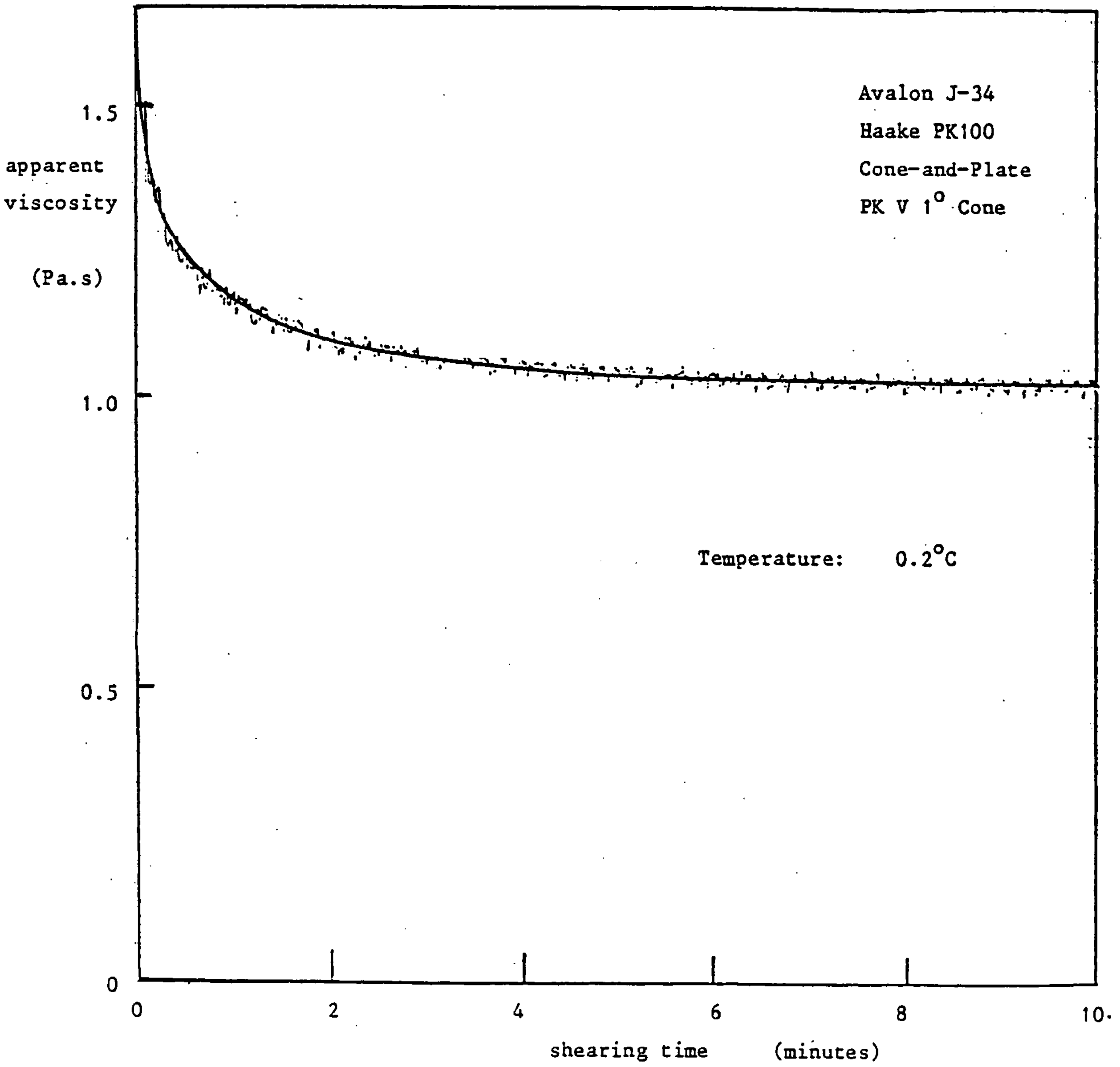


FIGURE 7 Apparent viscosity of an oil sample during phase 3 as a function of shearing time at a shear rate of 96 s^{-1} and a temperature of 0.2°C.

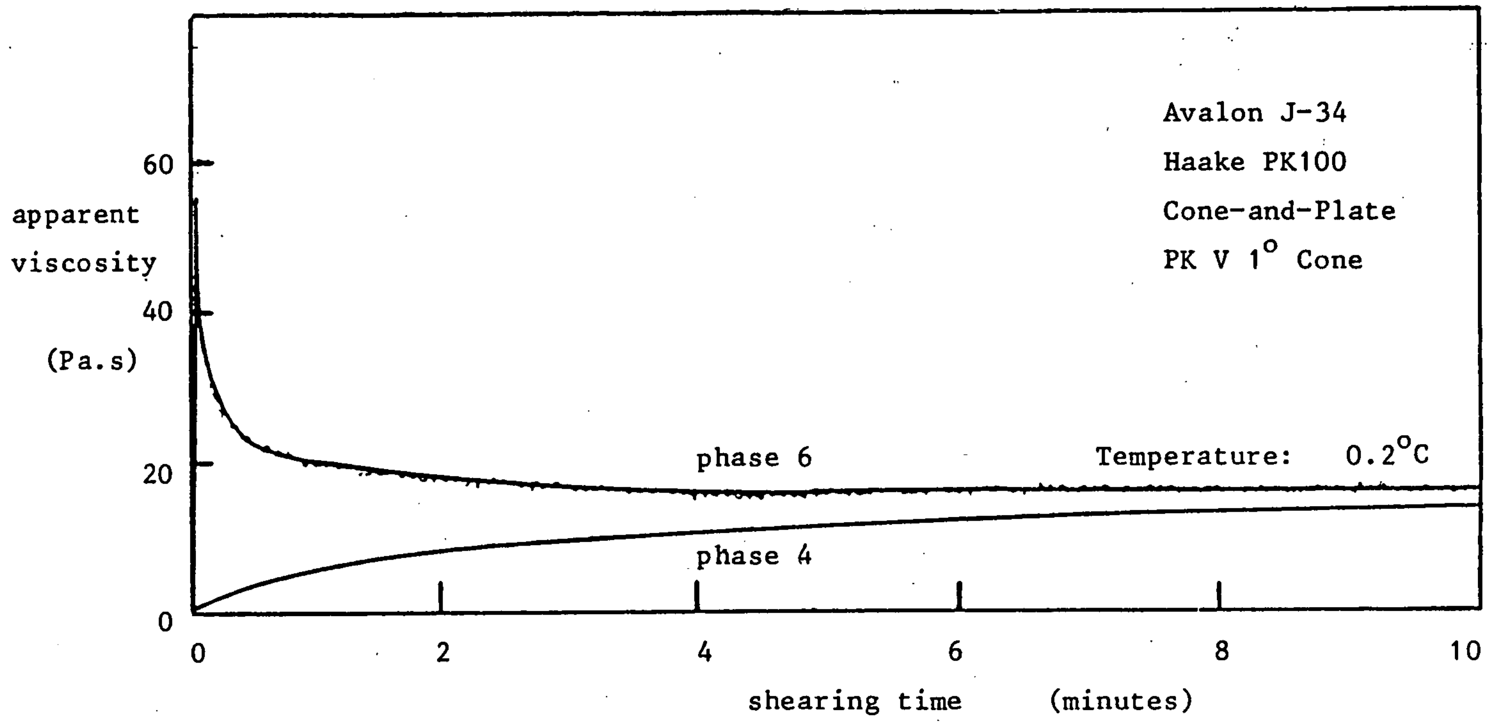


FIGURE 8 Apparent viscosity of an oil sample during the phases 4 and 6 as a function of shearing time at a shear rate of 0.96 s^{-1} and a temperature of 0.2°C.

oil had built up a considerable yield stress during the 10 minute unsheared rest period of Phase 5; it took less than 1 minute to break down the structure and after 2 minutes of renewed shearing the equilibrium value for the apparent viscosity is attained.

In Figure 9 the results for the measurement series at 0.2°C are represented as apparent viscosity values. The two curves show the values before and after shearing for 10 minutes at the standardized high shear rate of 96 s^{-1}. In Figure 10 the results for the measurements at a temperature of 10.2°C are presented. The results show the strong influence of shear history on the apparent viscosity at these temperatures. For example, at a temperature of 10.2°C and a shear rate of 1 s^{-1} the apparent viscosity for a previously unsheared sample is 29 Pa.s and 10 minutes shearing at a shear rate of 96 s^{-1} reduces this value to 6.6 Pa.s at the same shear rate of 1 s^{-1}. For a temperature of 0.2°C the apparent viscosity at a shear rate of 1 s^{-1} for a previously unsheared sample is 73 Pa.s, which value reduces to just 14 Pa.s after being sheared for 10 minutes at a shear rate of 96 s^{-1}. Comparison of the results at 10°C in Figure 1 with the results for an oil temperature of 10.2°C in Figure 10 reveal that the measurements with the Haake PK100 Cone–and–Plate Viscometer lead to considerably higher values for the apparent viscosity than measurements with the Haake Rotovisco RV12 concentric cylinder Viscometer. This had been expected and the result is attributed to the shrinkage problems for fluids with a yield stress which causes voids in the oil sample in the concentric cylinder configuration at temperatures below the pour point. As a result, the values for the apparent viscosity for temperatures below 25°C shown in Figure 1 are largely underestimated and should be considered as indicative only.

General Discussion and Conclusions

A program of rheological investigation was designed and carried out for the waxy crude oil Avalon J–34 in the temperature range from 0° to 60°C using the Haake Rotovisco RV12 Viscometer with the NV sensor system. In the temperature range from 25° to 60°C the oil is slightly shear thinning, i.e. the apparent viscosity decreases with increasing shear rate. No dependence upon the shear history was found. The shear rates applied varied from 0.96 to 348 s^{-1}. In the temperature

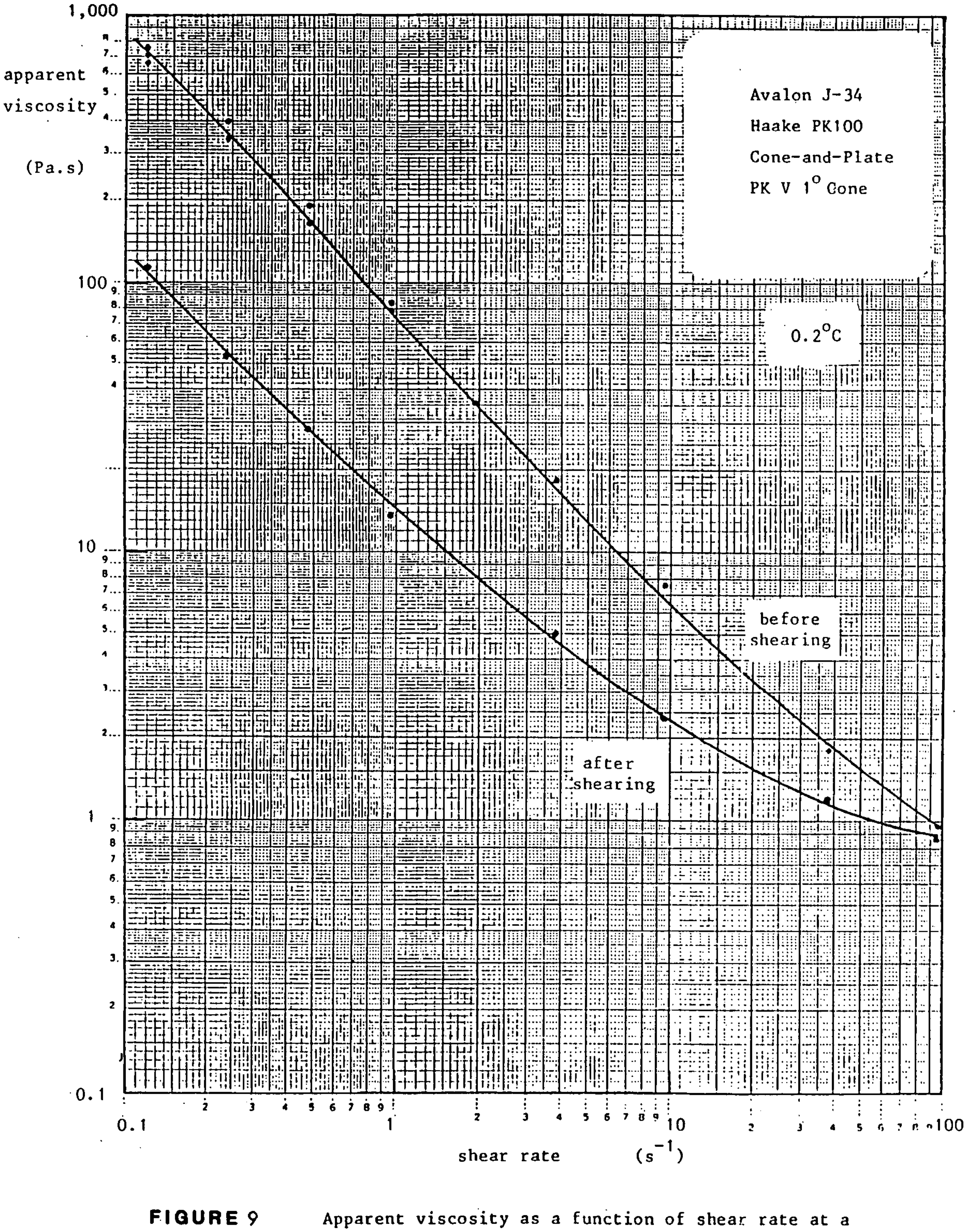


FIGURE 9 Apparent viscosity as a function of shear rate at a temperature of 0.2°C both before and after shearing at a shear rate of 96 s^{-1}.

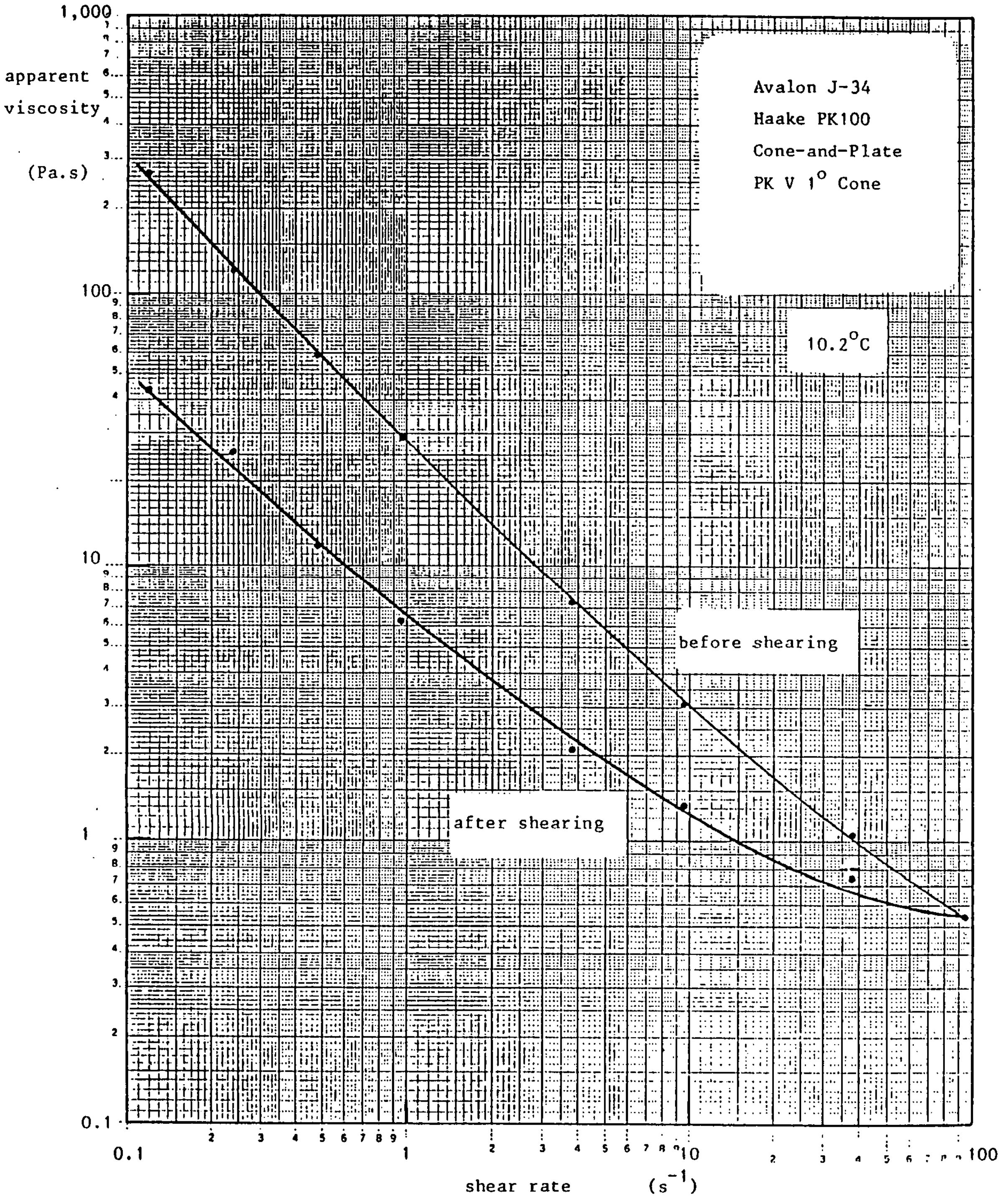


FIGURE 10 Apparent viscosity as a function of shear rate at a temperature of 10.2°C both before and after shearing at a shear rate of 96 s^{-1}.

range from 0° to 25°C the oil developed a yield stress that was strongly temperature dependent. The yield stress also increased with increasing gelation time. The apparent viscosity of previously unsheared oil increased, as well, with increasing gelation time. Gelation times from 1 to 1000 minutes were used. A standard gelation time of 5 minutes was selected for further measurement.

A standard measurement program was developed for subsequent rheological studies in the temperature range from 0° to 25°C using the Haake PK100 Cone–and–Plate Viscometer with the PKV1° cone because of the previously described problems with the concentric cylinder configuration in this temperature range. After a 5 minute gelation period the viscosity of the previously unsheared oil was calculated. Next, the sample was sheared for 10 minutes at a standardized shear rate of 96 s^{-1} after which the apparent viscosity at the selected shear rate was determined for this now pre–sheared sample. The shear rates used varied between 0.96 and 96 s^{-1}. The apparent viscosity of both previously unsheared and pre–sheared samples was measured at 0.2° and 10.2°C.

The apparent viscosity, as measured with the Cone–and–Plate system, was consistently higher than the values determined with the concentric cylinder system for the temperature range between 0° and 25°C. The difference is attributed to the shrinkage problems that occur with the latter system for samples with a yield stress.

The general picture of the fluid which emerges from these studies is that, for the purposes of oil spill rheology, the crude oil can be considered as having the properties of a two–phase system. One phase is a relatively low viscosity hydrocarbon "solvent" phase which may contain dissolved waxes and asphaltenes, colloids, or aggregations of relatively high molecular weight. This fluid is relatively well behaved in a rheological sense. The other phase is a solid precipitate of high molecular weight material, probably waxes, colloidal aggregations of asphaltenes, and resins which impart structure and pseudosolid character to the fluid.

At temperatures exceeding 23°C, there is essentially complete dissolution of the solid phase in the solvent, and the fluid behaves fairly ideally. At lower temperatures, there is increasing precipitation of solids, resulting in the establishment of a yield stress which rises to 40 Pa at 15°C, 120 Pa at 10°C, 230 Pa at 5°C, and 380 Pa at 0°C. The integrity of the solid structure is thus much greater at low temperature, when more solid material is present. The curvature of the yield stress versus temperature graph, presented earlier in Figure 3, suggests that there may be a limited amount of solid material available for precipitation from the oil. The data suggest that, in the range 15 – 20 °C, the amount of solid material appears to be controlled by the solubility of the solid in the solvent, and the slope of the yield stress temperature curve probably reflects the temperature coefficient of solubility of the solid material in the solvent. At low temperatures of 0 – 5°C, the slope is much reduced, possibly because most or much of the solid material has precipitated. Thus, further drops in temperature have less effect.

When both phases are present, the viscosity is affected by the amount of solid material present and its particle size, which influences the structural integrity. At high shear rates, the particle size of the solids appears to be reduced, thus the viscosity is reduced. The results shown in Figures 9 and 10 for temperatures of 0.2 and 10.2°C respectively, demonstrate that this effect is very significant, and can alter the viscosity by a factor of up to 7. Above 25°C, the viscosity is fairly constant regardless of shear rate. Thus, in the range of 0 – 25°C, there is a regime in which a dynamic steady state is achieved in which viscosity is primarily controlled by the amount of solid material and its particle size, the latter being affected by a balance between the associating tendency of the solid material and the tendency to break it down by shear. The oil thus displays a marked increase in shear–thinning behaviour at low temperatures.

The status of the solid phase is influenced by kinetic considerations, i.e., the time taken for the solids to develop. This time is surprisingly long, since the data presented above indicate the process continuing for at least 1000 minutes, and probably longer.

The rheology of waxy crude oils is thus exceedingly complex and depends on a large number of variables. Even at one temperature, viscosity may vary by a factor of 7. A relatively small change in temperature of 5°C can cause a profound change in yield stress and oil can be converted from a near–solid gel to a fairly mobile fluid. This is certain to cause the behaviour of spills of waxy crude oils to be very different from that of conventional oils. For example, a near solid waxy oil, if subjected to warming and turbulent wave action, may start to flow and spread rapidly.

It is not necessary or practical for every oil to be subjected to as complete a rheological analysis as has been done here for Avalon J–34, but this work suggests that a minimum program of rheological determinations should be undertaken. The following is a suggested program.

1) The yield stress should be measured as a function of temperature to determine the magnitude of the yield stress and its sensitivity to temperature. This is essentially a sophisticated pour point measurement. For most oils, the yield stress will be low, and the oil can be considered to remain fluid at all temperatures. For waxy oils, a high yield stress is expected, and a high temperature sensitivity is expected.

2) If a yield stress significant at a relevant environmental temperature of 5°C is found, it should also be measured as a function of gelation time at this temperature. This will provide information on the time behaviour of the oil.

3) Viscosities should be measured at standardized shear rates of 1 and 10 s^{-1} over a range of environmental temperatures after prolonged shearing, for example about 10 minutes.

4) Documentation should be provided of the combination of temperature and shear rate behaviour, which results in the oil establishing a viscosity exceeding about 3 Pa.s.

5) Furthermore it is also useful to make viscosity measurements using conventional instruments, such as a Brookfield viscometer, and to measure pour point using the ASTM method, to provide comparison with other oils.

CONCLUSIONS

The phenomenon of "waxiness" is, we believe, best characterized by the yield stress temperature curve. Waxy oils will display a significant yield stress and a marked temperature dependence of yield stress in the range of environmentally relevant temperatures. For example, for Avalon J–34, there is clear onset of waxy behaviour if the oil is cooled below 20°C. In the range of 20 – 10°C, there are profound changes in oil behaviour as a result of phase separation. In region 0–10°C, the oil has developed a very high viscosity, which ranges from 1–1000 Pa.s with that viscosity being strongly affected by shear rate. The conditions under which the oil becomes very viscous, i.e., above 3 Pa.s, are shear rates less than about 10 s^{-1}, and temperatures less than 10°C. In this range, it can be expected that the oil, if allowed to remain reasonably quiescent, will set up and form solid masses.

It is concluded that:

- yield stress measurements must be conducted with a cone and plate type viscometer because of the slippage problem identified with concentric cylinder type viscometers;
- because of the sensitivity of the rheology to oil evaporation and condition that a standardized protocol is necessary to treat oil samples and thus obtain reproducible results; and
- standardized shear rate and shear–thinning procedures must be used for viscosity measurements (e.g., shear at 10 s^{-1} for 10 minutes then measure viscosity at 1 s^{-1}).

In conclusion, this part of the study has provided insights into the rheology of a waxy crude oil, has identified the nature of the phenomenon of "waxiness", and has resulted in a suggested characterization scheme. The scheme includes measurements of the yield stress as a function of temperature and the apparent viscosity before and after shearing at a high shear rate to reveal the breakdown of the gel structure.

A STUDY OF THE FEASIBILITY OF OIL CHARACTERIZATION USING A MATRIX APPROACH

INTRODUCTION

In common with most crude oils, waxy oils are subject to considerable property changes as a result of (i) evaporation (preferential loss of volatile components); (ii) temperature change; (iii) water uptake to form emulsions, and, possibly, also by dissolution and photolysis. The result is that, as the oil resides on the sea surface, its properties change, often dramatically, and its susceptibility to various remedial actions is altered. Further, its environmental impact, for example on fish and planktonic organisms, changes as a result of loss of the more volatile soluble hydrocarbons. Its density may approach that of water, thus making the oil masses susceptible to episodes of submergence and thus enhanced oil—water contact.

There is a need to quantify these processes and the relationship between the rates of these processes and the changing properties of the oil, preferably in a manner compatible with current oil behaviour prediction models. Currently available computer programs can calculate the changing location and dimensions of an oil slick, and they may be used prospectively or retrospectively to assess past or potential future damage of oil spills. They may be used to design countermeasures systems and to draw conclusions about economic, social, and ecological damages.

A major difficulty in such assessments is quantifying the property changes of the oil and the subsequent effect of the changes on the various processes, such as spreading, evaporation, and dissolution. In its simplest form, these properties can be expressed as functions of temperature and extent of weathering, by fitting parameters to suitable empirical equations. Unfortunately, this process is inherently unsatisfactory because there are dangers of extrapolation, and interactions between various competing processes may not be adequately treated.

APPROACH

In this project this issue was addressed by devoting a small exploratory effort to further development of a concept termed the "matrix method". In this method, the oil composition is expressed by elements in a matrix. The columns of the matrix consist of selected chemically distinct structural groups. For example, it could include the normal alkanes, the iso– and cyclo–alkanes, the isoprenoids, the aromatics, and polar substances. The rows consist of groups of hydrocarbons of similar volatility or vapour pressure, as indicated by their position or retention time on a capillary column gas chromatogram. For example, it may be convenient to define a group containing all the hydrocarbons between the peak for n–octane up to, but not including, that for n–nonane. This group could be termed the "C–8" group. The model has been developed in other studies to treat the problem of oil degradation in soils, and as part of this project, we examined its potential application to waxy crude oils. For waxy oils, it may be necessary to establish separate elements for waxes and asphaltenes, because these substances may play a key role in determining oil properties.

The essential concept is that, if the relevant properties of volatility, solubility, density, viscosity, molecular weight, etc. can be assigned to the individual elements in the matrix, then the properties of the mixture can be computed using some "mixing rule" to combine the individual element properties. The rate of the loss of each element can be calculated, for example by applying Raoult's Law for evaporation, using the individual mole fraction and the pure matrix element vapour pressure properties. As a result, the changing composition of the matrix can be computed over time as evaporation proceeds, and the net effect of that composition change on bulk oil property changes can be computed.

This method, when fully developed, may provide the most satisfactory description of oil properties. It has the potential to describe changes of volatility, solubility, density, and possibly also viscosity of the oil as a function of time, extent of weathering, and temperature. It should also be capable of relating the oil properties to readily accessible analytical information, for example, gas chromatographic or high pressure liquid chromatographic analyses of the oil, and to distillation curves, ratios of isoprenoid to normal alkane hydrocarbons, and other indicators of the status of the oil.

There are four scientific hurdles to be overcome. First, is the issue of developing suitable analytical methods for determining the initial composition of the matrix. There seems little doubt that this will ultimately be a combination of HPLC and GC analysis, with selective use of mass spectrometry, but the exact conditions of these analysis or the method of quantifying the results is not entirely established.

Second, it is necessary to establish properties for each of the individual matrix elements. This could be done by determining which hydrocarbons dominate each element. For example, element #46 may contain naphthalene, and thus the properties of naphthalene may be used for this element. This probably requires a certain amount of coupled gas–chromatography mass spectroscopic analysis, in order to determine the presence of hydrocarbons in each element. This is a difficult problem because there is a lack of physical–chemical property data for many hydrocarbons, especially those with higher molecular weight.

Third, oils contain groups of hydrocarbons, such as the asphaltenes, resins, etc., that are of doubtful structure and that may not fall into the convenient categories indicated earlier. Even the composition of the waxes is in some doubt. For oils such as waxy crudes, with properties which tend to be dominated by the presence of such groups, it is critically important that their element properties be well expressed. At present, it is not entirely clear how this can be accomplished.

Fourth, there is a need to develop mixing rules, such as Raoult's Law, in order to calculate the properties of the oil from that of the individual components. For properties such as density and volatility, this is relatively straightforward. However, for properties such as viscosity, it is a formidable problem. The reason for this is that the properties of waxy crude oils are dominated by the exceptionally high viscosity in liquid state of relatively low concentrations of the waxy materials. Further, these waxy and asphalteric materials are apparently present both in solution in the oil and in suspension as colloids or aggregates of colloids. To reliably quantify the changing viscosity as a function of composition thus requires treatment of the varying proportions of material in solution and suspension, and possibly even a characterization of the particle size or mean molecular weight of the material in suspension. It was not recognized that these difficulties would be encountered when work started on this project, and it was not until the full rheology of the oil has been investigated and the extent of variation of viscosity established for oil samples of identical composition and temperature that the severity of the problem of estimating viscosity was fully realized.

Experimental

Only a brief account of the experimental work undertaken is presented here because, as is concluded later, insufficient progress was made, given the available effort. More details may be found in Appendix 1. The primary concern was the effect of evaporation on changing properties. Dissolution or solubility of the oil was not regarded as being an important property at this stage. It was decided to simplify the system and avoid separating the aromatics, alkanes, and polars, and merely treat the oil as consisting of one column, that is all the chemically different groups would be considered one group for the purposes of this study.

The oil was subjected to gas chromatographic analysis on a Hewlett–Packard GC Model 5077A, equipped with a flame ionization detector. The column was 60 m long and was 0.075 cm in internal diameter; gas capillary tubing was coated with SPB5 from Supelco. Initial oven temperature was set at 50°C with a post ejection time of 8 minutes. The oven was temperature programmed to 220°C at a rate of 5°C per minute. The areas were recorded by a Hewlett–Packard 33908 Integrator. The sample injection volume was 0.5 uL with a split ratio of 50:1. The segregation was by carbon number, i.e., C6, C7, C8.

To characterize the oil's volatility by distillation, 200 mL of the J–34 crude oil were poured into a 500 mL distillation flask and distilled to collect various fractions of distillate. A thermocouple was inserted so that the tip extended below the surface of the crude oil.

The gas chromatograms were obtained for the crude oil and for various distilled fractions.

When interpreting the gas chromatograms to establish amounts, some difficulty was experienced due to the presence of a considerable "hump" under the gas chromatogram. This hump is not always adequately integrated using the integrating system, and a method was devised whereby its area, and hence the amount of material in it, was estimated by simple geometric area measurement on the gas chromatogram trace. There is some difficulty in translating these areas into amounts of hydrocarbon because the response factor of the hydrocarbons present in the hump are not known.

The aim of the series of experiments was generally to establish the feasibility of the matrix method. Therefore, the first approach was to take a fresh crude oil, batch distill it, and take off two separate fractions, leaving the bottom fraction. As a result, the oil was split into three fractions. Gas chromatography was done on the fresh oil and these three fractions, and matrix compositions were estimated from the gas chromatographs. Molecular weights, densities, vapour pressures, and viscosities were then estimated for the various elements in the vector of the matrix. Table 5 gives the values of the data used. These values were mainly obtained from literature sources and represent the real properties of these hydrocarbons. Total density of the mixture was then calculated as the density of each component, multiplied by the volume fraction of that component. The viscosity was calculated by multiplying the mole fraction of each component by the natural logarithm of the viscosity of that component. The sum of these terms was equal to the natural logarithm of the viscosity of the mixture.

When applying these data, there is considerable doubt about the molecular weight, viscosity, and density of the residual material, i.e., the material higher in carbon number than C16. These values were, therefore, "fitted" to the results.

Table 5
The Alkanes and their Molecular Weights, Viscosities and Densities

Carbon #	M.W. (g/mol)	Viscosity (mPa.s)	Density (kg/m^3)
<C6	72	0.22	627
C6	86	0.30	659
C7	100	0.41	683
C8	114	0.55	702
C9	128	0.72	718
C10	142	0.93	731
C11	156	1.20	743
C12	170	1.51	752
C13	184	1.88	761
C14	198	2.31	768
C15	212	2.80	774
C16	226	3.36	780
>C16	240	2.20E+04	785

Results and Discussion

It proved to be possible to calculate the density of the crude oil and its various distilled fractions with an accuracy of about +/−5%. This is not regarded as a particularly challenging task. The distilling temperature, as calculated using vapour pressures and Antoine constants, and the compositions agreed reasonably well. The viscosity calculations were, not surprisingly, unsatisfactory. First, there is some doubt as to which viscosity to use for these calculations. From a consideration of the results, we believe that it is feasible to estimate the viscosity of the fresh and weathered oil at temperatures well in excess of the pour point where the oil is behaving in a reasonably predictable rheological manner. At present, there is little prospect of calculating the behaviour of the oil in the region of environmental temperatures, i.e. 0 to 15°C.

Some effort was devoted to attempting to devise rheological models in which modifications were made to the mixing rules for the component viscosities, and an attempt was made to quantify and model the dissolved and colloidal material. However, the task proved to be beyond our present capabilities.

Conclusions

It is concluded that, with the present state of knowledge, it is not possible to apply the matrix model concept to oils of a waxy nature. The preferred approach is to apply it first to petroleum distillates, such as gasoline and diesel fuel, which are more predictable in their behaviour and consist of a higher proportion of well characterized components with fairly Newtonian rheologies. Only when the matrix method has been successfully applied to these types of hydrocarbons is there any justification for attempting to apply it to very complex mixtures such as waxy crude oils. This result was disappointing, but it is believed that the insights obtained from the modest effort devoted to exploring the applicability of the matrix method to crude oil have been worthwhile. Further programs, involving this approach can now be better designed or even avoided.

WEATHERED OIL PROPERTY DETERMINATIONS

INTRODUCTION

It is desirable to have knowledge of the extent to which oil properties change as a result of weathering. Accordingly an experimental program was undertaken to measure certain properties as a function of extent of evaporation. In assessing the results the reader should note that when oils become very viscous "waxy", they become difficult to handle experimentally. Small air bubbles may become trapped and thus affect density measurements. The thermal history of the sample affects the viscosity. There is thus potential for considerable error, and it can be seen that certain properties such as viscosity reported in the earlier chapter on oil rheology do not "agree" with properties reported in this chapter using a different viscometer and smaller sample volumes.

EXPERIMENTAL

The density and viscosity of four crude oils at different degrees of weathering were measured at 15°C, 20°C and 25°C. The weathering of the oil was achieved using batch distillation.

About 250 mL of fresh oil was poured into a 500 mL boiling flask and was weighed. The oil was stirred using a teflon–coated stirrer bar and was heated using a heating jacket. The top part of the boiling flask was insulated to minimize heat loss. The liquid temperature was measured using a thermocouple. The condensate was collected in a 50 mL graduated cylinder. The volume of condensate was recorded. The residue (weathered oil) was cooled and weighed.

The density and viscosity of the weathered oil samples were measured using a hydrometer and a Brookfield viscometer, respectively. The pour point of the fresh oil was measured. The temperature was controlled using a temperature bath at 15°C, 20°C, or 25°C.

The results are given in Table 6. It proved to be impossible to determine reproducible viscosities near or below the pour point, thus the data are all for conditions in which the oil was fairly fluid. The effect of increasing temperature was consistently to reduce viscosity as expected. The densities also decreased as expected, but it should be noted that the error in density measurement was often considerable due to the difficulty of ensuring that the hydrometer was truly at an equilibrium condition. The densities quoted should be viewed as only approximate and in individual cases can be subject to error of perhaps 3%.

Anomalous viscosity behaviour was evident in some samples, where weathering caused an apparent reduction in viscosity, especially at low temperatures. This was attributed to variation in oil conditioning prior to and during viscosity determination and the problem associated with concentric cylinder viscometers (of which the Brookfield is one) in measuring viscosities near the fluid's pour point. As a result, the viscosities quoted are subject to variation of a factor of up to 3 at the low temperatures. Accuracy improves at 25°C, but this condition is not likely to be encountered environmentally.

TABLE 6

WEATHERED OIL PROPERTIES

Oil	Degree Weathering (by volume)	Pour Point	Viscosity (mPa.s)/Density (kg/m^3) 15°C	20°C	25°C
J–34	0%	18°C	68/0.8690	52/0.8640	28/0.8620
	8.8%	–––	60/0.8980	42/0.8920	39/0.8880
	15.2%	–––	212/0.9090	136/0.9060	82/0.9020
C–96	0%	18°C	138/0.8940	49.6/0.8770	19/0.8680
	10.8%	–––	below pour pt	234/0.9030	46/0.8930
	15%	–––	below pour pt	308/0.9100	56/0.8980
B–27	0%	9°C	40.6/0.8620	18/0.8510	10/0.8420
	6%	–––	82/0.8700	28.0/0.8650	14/0.8620
	10.8%	–––	110/0.8740	62/0.8700	29/0.8660
MSW	0%	<–17°C	13.5/0.8590	10/0.8440	8.0/0.8400
	11.2%	–––	20/0.8720	15.7/0.8700	12/0.8660
	15.6%	–––	22.3/0.8775	17.4/0.8740	15/0.8710

CONCLUSION

The general conclusion from this limited study was that, at 25°C, when the oils are about 10°C above their pour point, they displayed fairly ideal rheological behaviour with fresh oil viscosities in the range 8 to 28 mPa.S. Weathering to lose 6 to 11% of the oil, as will occur fairly rapidly from a slick, increased the viscosities by a factor of 1.5 to 2. Further weathering to about 15% caused a further increase of the magnitude. The pour point rose on weathering and as it approached the measurement temperature, the oil rheology became very erratic and viscosities may rise by a factor of 10. In this region, measured viscosity values are of little significance as indicators of oil flow behaviour in the environment.

There is some merit in obtaining viscosity and density in the regime of fairly ideal rheological behaviour, to provide comparison data between oils, to assist with interpretation of spreading behaviour, and to delineate the boundaries of this regime in terms of temperature and weathering status, but regrettably such data are of limited value for environmental prediction purposes.

NEAR SOURCE SPILL BEHAVIOUR

The behaviour and ultimate fate of an oil spill is strongly dependent on the type of oil release; blowouts result in initially thin, wide slicks involving relatively small flowrates of oil; batch spills (i.e., tanker releases) sometimes involve large quantities of oil released over short time periods resulting in initially thick oil slicks.

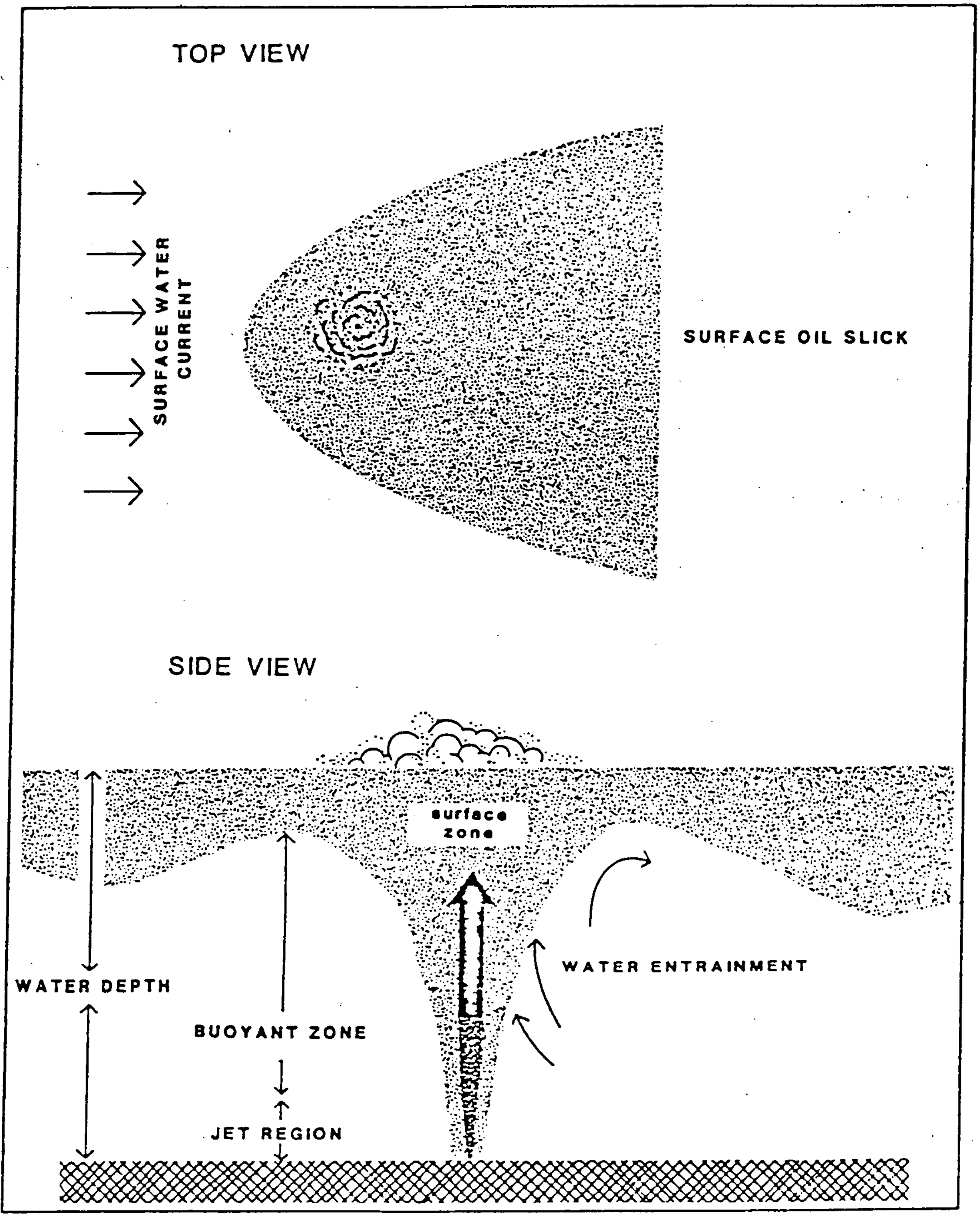
SOURCE CHARACTERISTICS

There are two possible sources of major offshore oil spill; a blowout (either subsea or from a platform) or a batch spill (such as from a tanker or storage accident).

Subsea Blowouts

Subsea blowouts (and "live" pipeline ruptures) involve two fluids: natural gas and oil. The natural gas, is responsible for atomizing the oil as it exits the well–head. The oil droplets, ranging in size up to a few millimetres in diameter, are pumped to the surface in the water entrained by ascending gas bubbles. The hot oil droplets cool as they rise. As the water plume nears the surface it spreads outwards in a radial layer. The oil droplets rise out of this horizontal layer of water and, for typical oils, coalesce into a slick on the surface. In the presence of a surface current the oil is swept out of the surface zone, forming a conic slick profile (see Figure 11). Sufficient turbulence may be present, as the oil coalesces into a surface slick, to cause the formation of a water–in–oil emulsion. Radiated heat from the burning gas (if ignited) may promote this emulsification by flashing off the light ends in the oil thus increasing the concentration of asphaltenes and waxes, and rendering the oil more susceptible to emulsification (Young and Buist 1984, Ross et al. 1979).

FIGURE 11 SCHEMATIC VIEWS OF A SUB-SEA BLOWOUT



If a waxy crude oil is released by a subsea blowout several unusual phenomena may occur. Firstly, if the oil is cooled and gelled sufficiently as it rises to the surface, the droplets may not coalesce to form a slick, but remain as a stream of droplets. This probably depends on the oil's "waxiness", droplet size, the entrained water temperature, the oil temperature, the heat transfer coefficients and the plume rise velocity. Recently, an equation to predict atomized droplet size distribution was adapted for blowouts (S.L. Ross 1985c). The model results agree will with experimental data (Topham 1975, Dickins and Buist 1981). A heat transfer model has been converted (S.L. Ross 1985a) to predict droplet cooling in subsea blowouts. The model (Figure 12) compares the time for a droplet to cool to within 1°C of ambient temperature with the droplet rise time for a blowout at a given water depth. Experimental studies of the behaviour of oil droplets in a rising plume were conducted in a vertical water tunnel at the University of Toronto for this project.

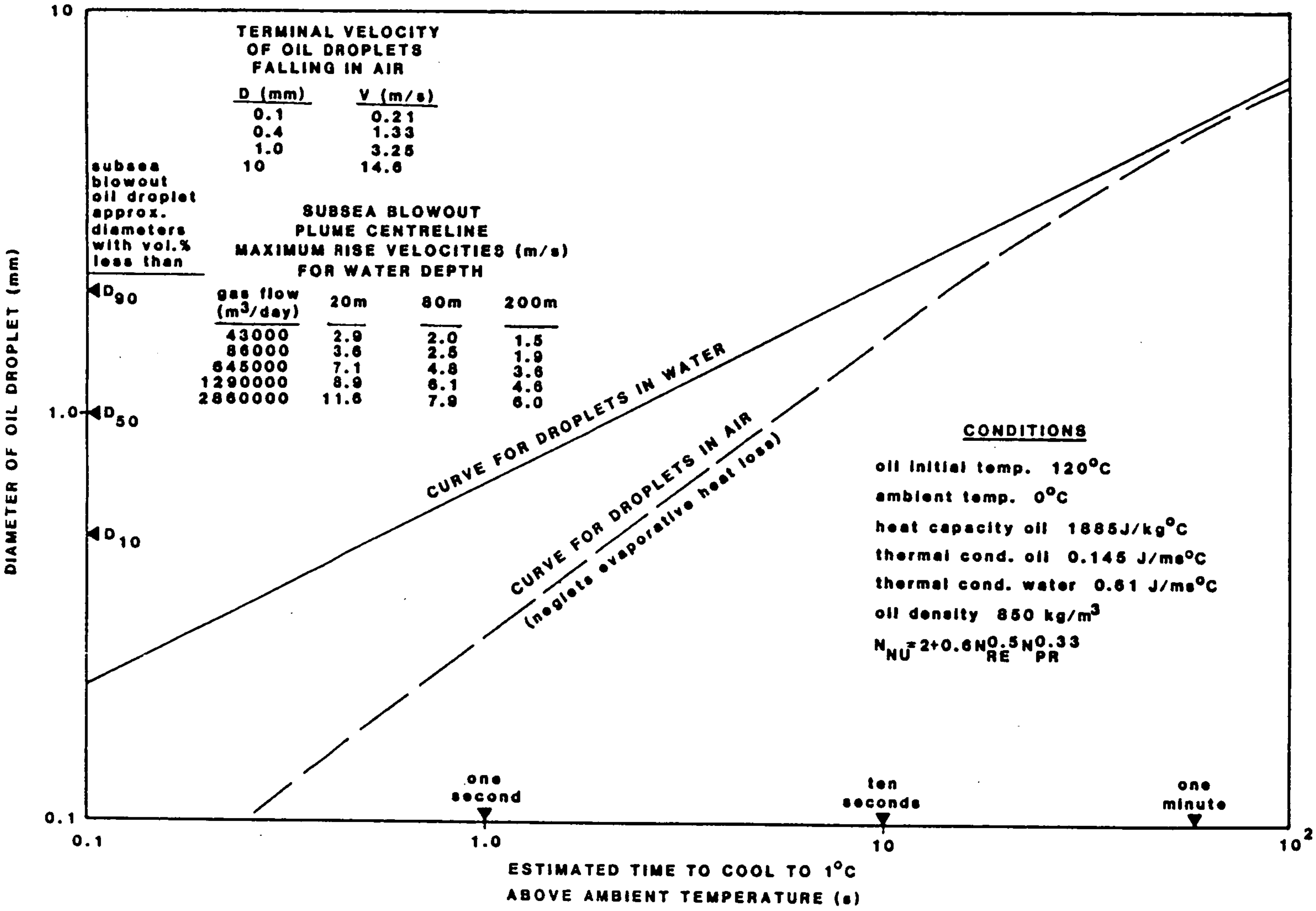
Platform Blowouts

Platform (or surface) blowouts also result in droplets of oil, in this case "raining" from the gas plume to fall on the sea surface (Figure 13). Oil droplets of a typical oil would then spread, coalesce and form a slick. If a waxy oil is involved, the droplets could cool sufficiently through radiative, convective and evaporative heat loss, to be non-spreading once they hit the water (see Figure 12). Studies of the cooling and evaporation of individual oil drops suspended in a wind tunnel were conducted at the University of Toronto to elucidate this phenomena. They are described later in the section on droplet evaporation.

Batch Spills

Batch spills differ from blowouts, with respect to spill behaviour, primarily in that batch slicks are initially many times thicker than blowout slicks. Normally a large batch spill, such as from a tanker accident, starts with a thickness of many centimetres and spreads and thins according to its physical properties and the spreading forces as proposed by Fay 1969. This spreading continues until the slick breaks up into thick and thin portions. The thick (about 1 mm) patches contain

FIGURE 12 COOLING OF OIL DROPLETS FROM A BLOWOUT



TERMINAL VELOCITY OF OIL DROPLETS FALLING IN AIR

D (mm)	V (m/s)
0.1	0.21
0.4	1.33
1.0	3.25
10	14.6

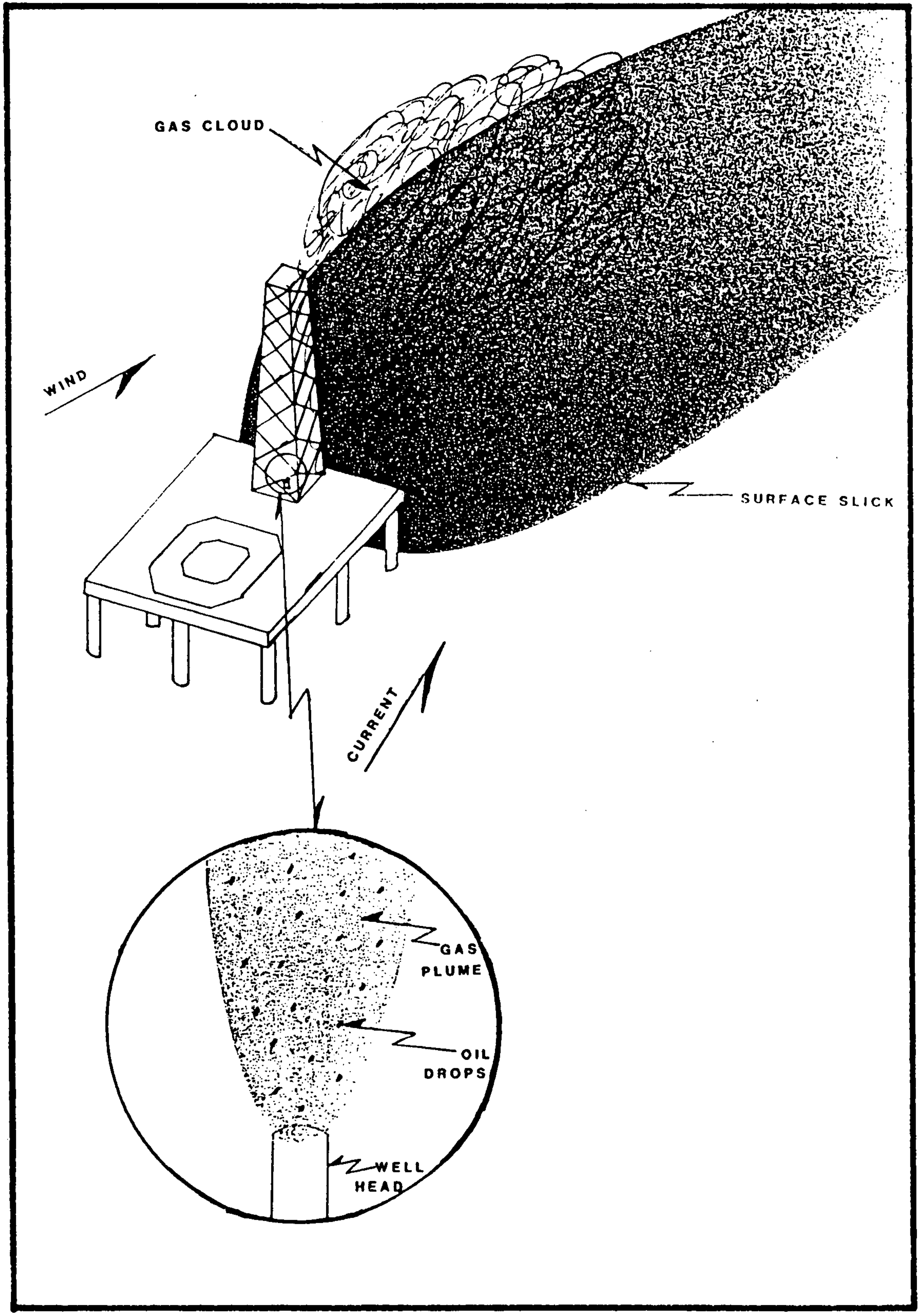
SUBSEA BLOWOUT PLUME CENTRELINE MAXIMUM RISE VELOCITIES (m/s) FOR WATER DEPTH

gas flow (m^3/day)	20m	80m	200m
43000	2.9	2.0	1.5
86000	3.6	2.5	1.9
645000	7.1	4.8	3.6
1290000	8.9	6.1	4.6
2860000	11.6	7.9	6.0

CONDITIONS

oil initial temp. 120°C
ambient temp. 0°C
heat capacity oil 1885J/kg°C
thermal cond. oil 0.145 J/ms°C
thermal cond. water 0.61 J/ms°C
oil density 850 kg/m^3
$N_{NU} = 2 + 0.6 N_{RE}^{0.5} N_{PR}^{0.33}$

FIGURE 13 SCHEMATIC OF A SURFACE BLOWOUT



about 90% of the oil's volume and are surrounded by a thin (1–10 um) sheen making up about 90% of the surface area of the slick.

Waxy crudes behave differently. Based on the results of sea trials in the U.K. (WSL 1979 and 1981), waxy crudes spilled on water spread normally until they cool below their "gelation" point. The slick then fragments into mats (5–10 cm thick) and globules (1–5 cm in diameter) which do not spread further surrounded with sheen (1–2 um thick). Experimental studies on the spreading of thick "waxy" crude oil slicks on water were carried out in Ottawa.

OIL DROPLET BEHAVIOUR IN A RISING WATER PLUME

A series of experiments was carried out in a vertical water tunnel to examine the behaviour of oil from a subsea blowout. Since the rise time of oil droplets in a plume can be several minutes, it was considered desirable to observe the behaviour of drops over a time period of up to 5 minutes. It was not feasible to construct a deep exposure vessel, thus the approach taken was to construct a vertical water tunnel, in which water flowed downward at a velocity controlled to match that of the rising oil drops. Oil drops were thus maintained in stationary condition, relative to laboratory coordinates. After being maintained in this condition for some minutes, the oil was allowed to rise to the free water surface. It should be noted that considerable effort was devoted to designing, testing, and modifying this system. To our knowledge, the system is unique in performance and capabilities. It was then desired to simulate the behaviour of the oil as it resided for some hours at the sea surface. Various systems were tried in an attempt to accomplish this, including a use of hoop type apparatus. However, after some experimentation, it was decided to collect some of the oil and place it on the surface of the water in a 25 cm diameter bowl, which was magnetically stirred at the bottom. This resulted in the oil remaining observable on the water surface for a period of days after release from the blowout. The bowl was kept in a cold room at the required temperature.

APPARATUS

A schematic diagram of the vertical water tunnel is shown in Figure 14. An insulated 1000 L water storage tank with a level indicator was connected to a 3/4 HP centrifugal pump. The water flow rate was controlled by a flow control valve and measured with a rotameter type flowmeter with a range of 0–2.5 L/s. A 50 mm I.D. plastic tubing connection brought the water flow into the top water chamber of the tunnel. The top part of this chamber consisted of a transparent acrylic cylinder with an I.D. of 160 mm and was open to the atmosphere at the top to create a free water surface where the spreading behaviour of the crude oil could be observed. The bottom part of the top chamber consisted of a clear acrylic cylinder with an I.D. of 100 mm and was attached to the tapered holding section by means of a flange

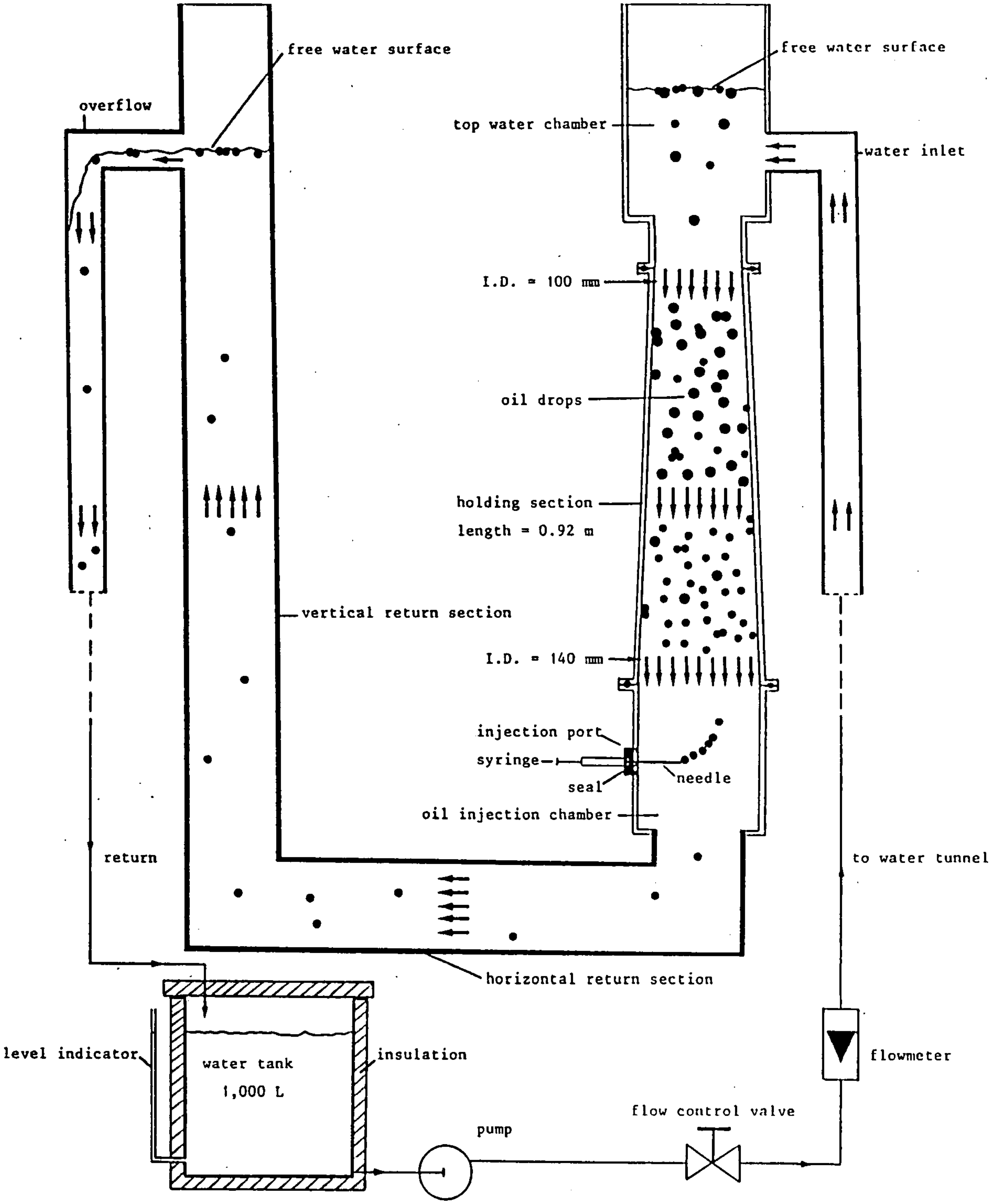


Figure 14. Schematic diagram of the vertical water tunnel.

and an O–ring. The tapered holding section was constructed of 2 mm clear acrylic to facilitate observation of the oil drops while they were kept suspended in this part of the water tunnel. The holding section was 0.92 m long with an I.D. of 100 mm at the top increasing to an I.D. of 140 mm at the bottom of the section. The water velocity in this viewing section was adjusted by means of the flow control valve. The velocity in the top part of the tapered section was about twice that in the bottom part, which made it possible to observe drops of different diameters during a single test run. This was necessary both because of the range of droplet diameters produced during oil injection and the coalescence and break–up of these droplets. Drops of different diameters had different rise velocities and remained suspended in that part of the tapered holding section where the local downwards water velocity equalled their individual rise velocity.

The bottom part of the holding section was connected to the oil injection chamber by means of a flange and an O–ring. In this way the water tunnel could easily be taken apart for cleaning. The injection chamber consisted of a clear acrylic cylinder with an I.D. of 140 mm; a male tube adaptor fitted with a rubber seal welded to the cylinder served as the oil injection port. Oil could be injected into the injection chamber section of the water tunnel by piercing the rubber seal with a hypodermic needle and injecting the oil from an oil–filled syringe. The injection velocity of the oil was determined with a stopwatch, measuring the time needed to empty the syringe. Droplet size distribution could be changed by changing the injection velocity and the size of the needle.

Water flowing downwards through the transparent parts of the vertical water tunnel left the injection chamber through a horizontal 100 mm I.D. PVC pipe section and then flowed upwards through a vertical return section. This section consisted of a 100 mm I.D. PVC pipe section that was open at its top, the water returned to the tank through an overflow in the wall of this section. The water temperature in the storage tank and in the injection chamber of the vertical water tunnel was monitored by means of the thermocouples and a datalogger. The water temperature in the tank was adjusted prior to each test run by adding a suitable amount of ice to reach the required temperature.

PROCEDURE

Prior to the experiments the oil was reconstituted by keeping it at a temperature of 50°C for 2 hours in a closed container. During this time the oil was shaken repeatedly to ensure a uniform composition. A volume of oil, typically 40 cm^3 was then drawn into a plastic syringe from this container and the syringe was placed in a thermostatted water bath set at the required injection temperature for at least 30 minutes prior to the test to ensure thermal equilibrium.

The desired temperature in the water storage tank was adjusted by adding ice and the water flow was started and adjusted to the required flow rate. A typical value for the water velocity at the top of the tapered section was 56 mm/s. During any test run, the water temperature did not vary more than 1°C.

Oil was then injected over a period of 10 – 20 s (an injection rate of 2 – 4 cm^3/s). This corresponds to a velocity in the 1.2 mm and 1.8 mm I.D. nozzles of 1 – 4 m/s. At oil injection temperatures of 60°C this amounts to Reynolds numbers in the nozzles of about 100 – 400. At injection temperatures lower than 60°C, the values of the Reynolds numbers were considerably lower so that laminar flow in the nozzles was present during all experiments.

The swarm of oil drops thus generated was observed and recorded on videotape and still photographs. After a typical simulated rise period of 5 minutes the flow was stopped and the oil drops were allowed to rise to the water surface and their behaviour upon surfacing was studied. Following surfacing the drops were collected and transferred to the water surface of a stirred bowl. Transfer was either by scooping them up with a soup ladle or by draining the top of the water tunnel through a ball valve into a bucket.

The behaviour of the oil slick or the drops in the stirred bowl was observed over a period of 24 hours in an attempt to predict the long term behaviour of oil on the surface of the ocean. Originally it had been intended to use a hoop apparatus as a means of simulating ocean exposure, but this proved to be difficult because the hoop system could not accommodate more than one sample at any time. Hence the simpler system of the stirred bowls was used. The stir bar was rotated at a low speed of about 160 rpm using a magnetic stirrer. The system consisted of 4 stirred bowls so that 4 samples could be accommodated simultaneously. This enabled comparison between different samples. The system was set up in a cold room that was kept at a constant temperature during the whole procedure, equal to the temperature of the water in the water tunnel during the test.

Table 7 summarizes the experimental work and the conditions. Figures 15 – 21 present typical results of oil drop formation at the nozzle, oil drop behaviour in the water tunnel and spreading behaviour of the drops upon surfacing. Following is a detailed description of observations during the test runs. Videotapes are also available for viewing.

Experiments I, II and III. The first experiments were performed mainly to examine the behaviour of the oil drop formations produced from the nozzles. Three oil types were used, Avalon J–34, Hibernia B–27 and Mixed Sweet Western.

In experiment I–1 Avalon J–34 was injected, at 60°C through a small nozzle with a 1.2 mm I.D., into the injection chamber. The water temperature in the tunnel was kept at 10°C and the water velocity at the top of the tapered section of the tunnel was set at 3.4 cm/s. A swarm of fine oil drops was generated with sizes ranging from 0.1 to 3 mm. As expected the smaller drops with a diameter of less than about 1 mm were washed out and only the larger drops were retained in the tapered vertical section of the tunnel. During the holding period of 5 minutes some of the oil drops collided and formed "duplets". When the flow was stopped after the holding period, the oil drops rose to the free surface as discrete drops and upon surfacing no spreading was observed i.e., the drops remained completely spherical. The oil drops were then transferred to a stirred bowl in the climatized room at 10°C. After 24 hours the oil remained as a cluster of oil drops and no spreading was observed.

Table 7
Water Tunnel Tests

Run #	Twater °C	Toil °C	Oil	Drop Size mm	Minimum Flow cm/s	Duration minutes
I-1	10	60	Av J-34	mist+ 1-3	3.4	5
I-2	10	60	Av J-34	2-5	4.7	5
I-3	10	60	Av J-34	4-10	7.6	5
II-1	10	60	Hi B-27	1-2	4.3	5
II-2	10	60	Hi B-27	2-5	5.6	5
II-3	10	60	Hi B-27	3-8	7.5	5
III-1	10	60	MSW	1.5-2	4.3	5
III-2	10	60	MSW	2-5	5.6	5
III-3	10	60	MSW	3-10	7.5	5
IV-1	10	80	Av J-34	2-6	5.6	5
IV-2	10	80	Hi B-27	2-6	5.6	5
V-1	10	60	Av J-34	2-6	5.6	5
V-2	10	40	Av J-34	2-6	5.6	5
V-3	10	20	Av J-34	2-6	5.6	5
V-4	10	0	Av J-34	3-8	5.6	5
VI-1	10	60	Av J-34	3-6	5.6	1
VI-2	10	60	Av J-34	3-6	5.6	2
VI-3	10	60	Av J-34	3-6	5.6	5
VI-4	10	60	Av J-34	3-6	5.6	10
VII-1	10	60	Av J-34	0.3-3	0	0
VII-2	10	60	Av J-34	1-4	0	0
VII-3	10	60	Av J-34	7-9	0	0
VIII-1	2	60	Av J-34	2-6	0	0
VIII-2	2	60	Av J-34	9	0	0
VIII-3	2	60	Av J-34	2-6	5.6	1
VIII-4	2	60	Av J-34	2-6	5.6	5
IX-1	2	60	Hi B-27	3-6	0	0
IX-2	2	60	Hi B-27	8	0	0
IX-3	2	60	Hi B-27	2-6	5.6	1
IX-4	2	60	Hi B-27	2-6	5.6	5
X-1	2 S	60	Av J-34	2-6	0	0
X-2	2 S	60	Av J-34	9	0	0
X-3	2 S	60	Av J-34	2-6	5.6	1
X-4	2 S	60	Av J-34	2-6	5.6	5
XI-1	2 S	60	MSW	1-5	0	0
XI-2	2 S	60	Hi B-27	2-6	0	0
XII-2	2 S	60	Hi B-27	7	0	0
XII-3	2 S	60	Hi B-27	2-4	5.6	1
XII-4	2 S	60	Hi B-27	2-6	5.6	5
XIII	10	0	Av J-34	strands	0	0

S = seawater

Figure 15 – Injection of Avalon J–34 at a high shear rate

Figure 16 – Injection of Avalon J–34 at a low shear rate

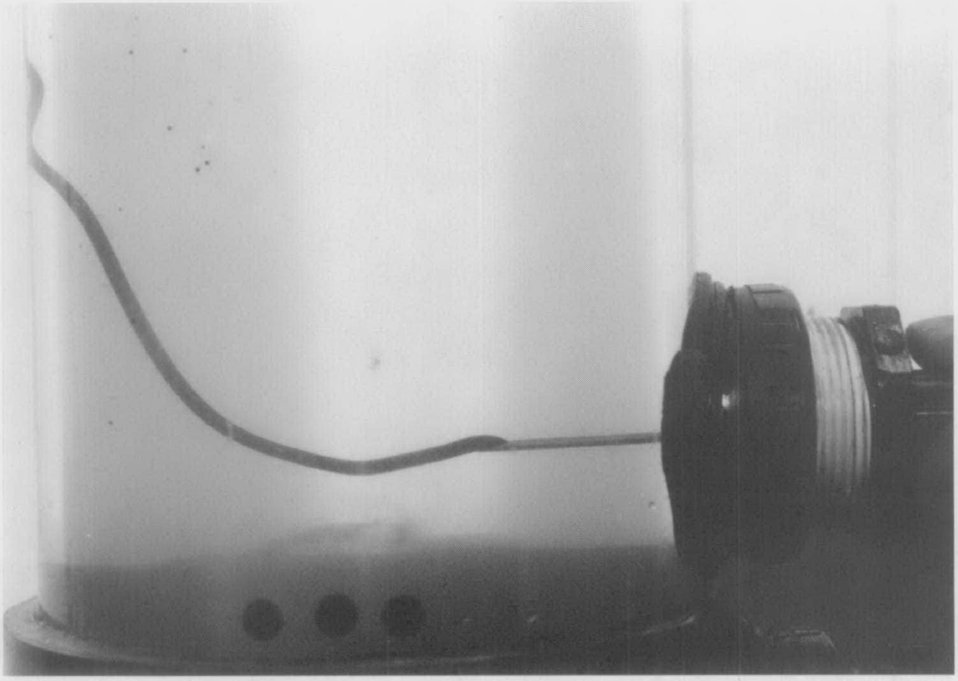


Figure 17 – Injection of waxy oil through small nozzle into water at 2°C

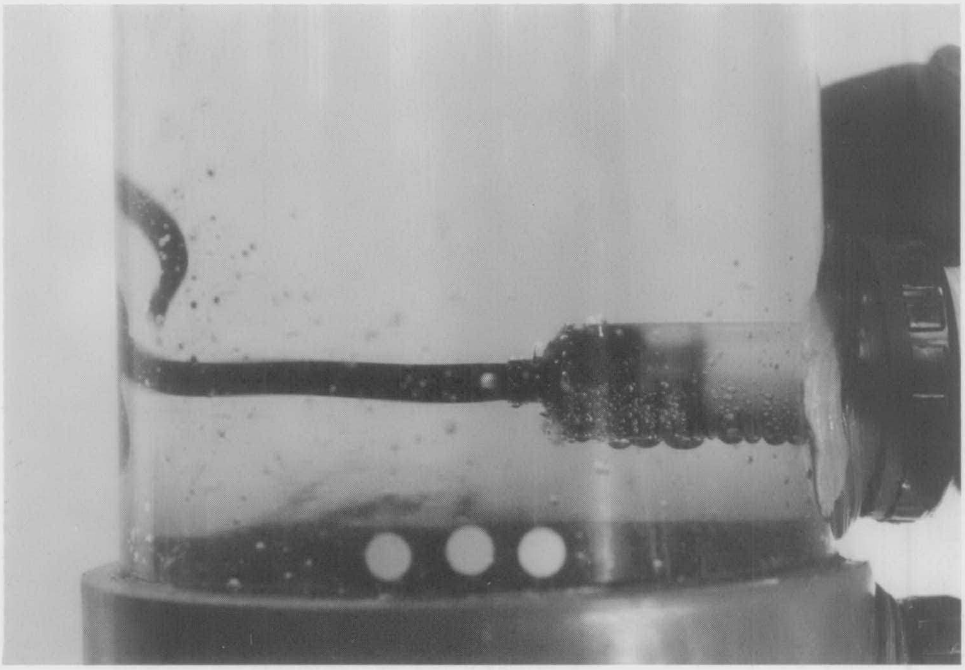


Figure 18 – Injection of waxy oil through large nozzle into water at 2°C

Figure 19 – Oil drops floating in the water tunnel

Figure 20 – Oil drops on the water surface

Figure 21 – Transfer of oil drops to the stirred bowl

In experiment I–2 larger drop sizes were generated using the same oil, Avalon J–34 at 60°C. The oil was injected through a large nozzle with 1.8 mm I.D. under identical circumstances as in the previous experiment. To hold the larger drops in the tapered vertical section the water velocity was increased to 4.7 cm/s. The size of the oil drops produced was 2–5 mm. During the holding period, many of these drops stuck together to form clusters of duplets, triplets and multiplets. Upon surfacing after 5 minutes no spreading was observed; the individual drops remained completely spherical. After 24 hours in the stirred bowl the oil remained as a cluster of oil drops.

In experiment I–3 Avalon J–34 was again injected through the large nozzle at 60°C but the water velocity was further increased to 7.6 cm/s. By lowering the oil injection rate, still larger oil drops were produced with diameters ranging from 4 – 10 mm. It was noted that the larger drops were markedly non–spherical. During the holding period of 5 minutes large clusters of individual drops were formed which tended to stick to the wall. Upon surfacing the clusters retained their structure and the individual drops retained their shapes. No spreading was observed. After 24 hours in the stirred bowl the drops remained as clusters and no spreading took place.

In experiment II–1 another oil, Hibernia B–27 was used. The oil was injected at 60°C through the small nozzle with a water velocity of 4.3 cm/s. Oil drops were generated in the range of 1 – 2 mm diameter; a small fraction of finer drops that were also generated were washed out at the beginning of the holding period of 5 minutes. During this period some oil drops stuck together forming clusters that mostly stuck to the wall of the tunnel. Upon surfacing after the holding period no spreading occurred and the drops retained their spherical shape. After 24 hours in the stirred bowl the drops did not change shape and remained in clusters. No spreading was observed. The water temperature was kept at 10°C.

In experiment II–2 Hibernia B–27 at 60°C was injected through the large nozzle to generate larger drops. The water velocity was 5.6 cm/s and the temperature 10°C. Oil drops were produced with sizes ranging from 2 – 5 mm. During the 5 minute holding period duplets, triplets and clusters were formed and some of them stuck to the wall of the tunnel. Upon surfacing after the holding period only the drops with sizes from 2 – 3 mm appeared; the larger ones remained stuck to the tunnel wall in the tapered section. The surfaced drops did not spread, but were slightly non–spherical. After 24 hours in the stirred bowl no change in appearance was noticed. The clusters remained clusters and no spreading occurred.

In experiment II–3 Hibernia B–27 oil was injected at 60°C through the large nozzle with the water flow rate adjusted to establish a water velocity of 7.5 cm/s. The water temperature was 10°C. Oil drops were produced in the size range of 3 – 8 mm. During the holding period of 5 minutes multiplets and clusters were formed and most of the clusters got smeared onto the wall forming a thin layer. Upon surfacing the clusters retained their shapes though most of them remained stuck onto the wall in the tapered section. The larger drops were markedly flattened. No spreading occurred. After 24 hours in the stirred bowl no change in appearance occurred.

In experiment III–1 a non–waxy crude oil, Mixed Sweet Western was injected at 60°C through the small nozzle into the injection chamber. The water velocity was 4.3 cm/s and the water temperature was kept at 10°C, as in the previous runs. Very fine oil drops were generated with sizes ranging from 0.1 – 2 mm. The very small drops were washed out and after a short time only the sizes between 1.5 – 2 mm remained in the tapered holding section. During the holding period of 5 minutes some drops merged forming larger drops whilst others hit the tunnel wall and remained there forming a smear. Upon surfacing the drops broke through the surface, flattened out and spread, forming a continuous slick. After 24 hours in the stirred bowl in the cold room at 10°C a thin layer of oil slick continued to cover the water surface.

In experiment III–2 Mixed Sweet Western oil was injected at 60°C through the large nozzle with the water velocity set at 5.6 cm/s and the water temperature at 10°C. Oil drops were produced in the size range 2 – 5 mm; the finer drops were flushed away with the water stream. During the holding period of 5 minutes a very large oil drop was observed near the top of the tapered tunnel section. The size and shape of this drop changed continuously while smaller drops merged with it and separated from it. Drops that hit the wall remained there as a smeared layer. Some drops managed to reach the free water surface and formed an oil slick. After the flow was stopped the drops rose to the surface, spread and formed a slick. After 24 hours in the stirred bowl in the cold room no change in behaviour was observed and the oil slick remained as before.

In experiment III–3 still larger drops were produced by injecting Mixed Sweet Western at 60°C through the large nozzle with the water velocity set at 7.5 cm/s. In this way oil drops in the range of 3 – 10 mm were produced. During the holding period, at surfacing and during the stirred bowl test in the cold room the behaviour of the oil was basically identical to that during the experiment with the smaller drops, experiment III–2.

Experiment IV. A second series of experiments was carried out to examine the effect of the temperature of the injected oil on drop formation and behaviour upon surfacing. Two oil types, Avalon J–34 and Hibernia B–27, were injected through the large nozzle with the water velocity at 5.6 cm/s and the water temperature at 10°C. Both oils were injected at an oil temperature of 80°C; attempts to inject at still higher oil temperatures failed because of excessive vapour generation.

In experiment IV–1 Avalon J–34 was injected and drops were produced in the range of 2 – 6 mm. During the holding period of 5 minutes no duplets or multiplets were formed, but some drops stuck to the wall and formed clusters there. Upon surfacing the drops spread and interconnected to form a thick slick with openings. When transferred to the stirred bowl the oil spread and formed sheen and oil slick. After 24 hours in the cold room at 10°C the sheen layer broke up into fragments and the slick gelled.

In experiment IV–2 Hibernia B–27 was injected and drops were produced again in the range of 2 – 6 mm. During the holding period of 5 minutes some very large globs were formed with a diameter of 10 – 20 mm. The globs originated through merging of smaller globlets which in turn originated from drops merging together. The globs continued to capture smaller drops. Upon surfacing the drops and globs formed an interconnected discontinuous slick in which the individual drop outlines could still be noticed. No complete spreading took place. Upon transferring to the stirred bowl the oil spread out to form a sheen layer and slick. After 24 hours in the cold room at 10°C the sheen had broken up forming fragments and the slick had gelled.

Experiment V. In order to evaluate further the influence of the oil temperature at injection upon the behaviour of the oil in the water tunnel during the holding period and upon surfacing, as well as upon the behaviour in the stirred bowl, a series of four experiments was carried out with Avalon J–34. Injection temperatures were chosen at 60, 40, 20 and 0°C. The large nozzle was used to create medium size drops at a water velocity 5.6 cm/s and a water temperature of 10°C.

In experiment V–1 the oil was injected at a temperature of 60°C and drops were produced in the range of 2 – 6 mm. This experiment was essentially a duplication of run I–2 with a slightly higher value of the water velocity. During the holding period of 5 minutes some of the drops collided and formed duplets and triplets. Upon surfacing no spreading occurred but the larger drops sagged out somewhat to form discs. Upon transfer to the stirred bowl the drops spread out and formed a sheen and a slick.

In experiment V–2 the oil temperature was lowered to 40°C before injection. Drops were generated between 2 – 6 mm in diameter. During the holding period of 5 minutes some drops collided and formed duplets, triplets and clusters that predominantly clung to the walls of the tapered section. Upon surfacing the drops remained spherical and the clusters remained unchanged. Upon transfer to the stirred bowl the drops spread out and formed a sheen and oil slick.

In experiment V–3 the oil temperature was lowered further to 20°C. As before, drops were generated in the range of 2 – 6 mm. Some of the larger drops were not spherical but had an ellipsoidal shape. The large drops escaped to the surface during the 5 minute holding period and spread to form a slick. After the holding period the remaining drops rose to the surface and flattened out to form individual "pancakes" separated from each other. When transferred to the stirred bowl the oil again spread further to form sheen and slick.

In experiment V–4 the oil was injected at a temperature of 0°C. As the pour point of the Avalon J–34 oil was determined to be 18°C, the oil in the syringe was actually gelled and considerable force was needed to squeeze the oil through the nozzle. During the injection short strands of "spaghetti" were formed as well as drops in the range of 3 – 8 mm. During the holding period some of the "spaghetti" strands and the larger drops rose to the surface where they spread out to form a slick. As well, some of the oil drops smeared onto the wall of the tunnel. After the holding period the remaining oil rose to the surface and spread to form a slick. The unexpected spreading behaviour at this low injection temperature is attributed to the fact that during the injection through the nozzle shear rates of about 8000 s^{-1} were used. As a consequence the gelled structure was destroyed and the oil attained a relatively low apparent viscosity throughout the holding period.

Experiment VI. Another series of experiments was carried out to determine the influence of the holding time on the behaviour of the oil. Again Avalon J–34 was used and the injection temperature was chosen at 60°C. The water velocity was set again at 5.6 cm/s and the water temperature at 10°C. Holding times of 1, 2, 5 and 10 minutes were selected with drop sizes ranging from 3 – 6 mm.

In experiment VI–1 the holding time was kept at 1 minute. Upon surfacing the smaller drops remained spherical but the larger ones flattened out to form discs with a sheen around them.

In experiment VI–2 the drops were held in the water tunnel for 2 minutes. Many of the larger drops formed clusters that stuck to the wall and as a result not many drops rose to the surface once the flow was stopped. These drops appeared to be flattened with a sheen around them.

In experiment VI–3 the holding time was 5 minutes so this run was almost identical to the runs I–2 and V–1. The observations were similar to those in the previous run VI–2.

In experiment VI–4 the holding time was 10 minutes. During the holding period many drops collided and formed agglomerates of spherical drops. The clusters tended to stick to the wall of the tunnel and only a small fraction of the oil actually kept clear from the tunnel wall. Upon surfacing after the holding period the drops were perfectly spherical and the clusters retained their shape. The drops had a small ring of sheen around them.

Experiment VII. Another series of experiments was carried out with no flow in the water tunnel. The drops formed at the nozzle were allowed to rise to the surface. The rise time varied from 10 – 20 s. By varying the injection rate drops of different sizes were generated. As before, Avalon J–34 was used at an injection temperature of 60°C and the water temperature in the tunnel was kept at 10°C.

In experiment VII–1 drops in the range of 0.3 – 3 mm were produced. The larger drops reached the water surface first, where they flattened out to form discs. The medium size drops of 1 – 2 mm reached the surface as spheres but flattened out to form discs after a short time. The small drops of 0.3 – 0.5 mm rose slowly to the surface and retained their spherical shape once at the surface.

In experiment VII–2 larger drops in the range of 1 – 4 mm were produced. The largest drops spread upon surfacing and formed a slick. The smaller ones got stuck underneath the slick and retained their spherical shape.

In experiment VII–3 an attempt was made to generate very large drops. Drops with diameters from 7 – 9 mm were produced. The time required to reach the surface was about 12 s. Upon surfacing the drops spread to form individual "pancakes" of oil.

Experiments VIII and IX. In these experiments the water temperature in the tunnel was lowered to 2°C to study the influence of the water temperature on the behaviour of oil. Both Avalon J–34 and Hibernia B–27 were studied. The injection temperature was kept at 60°C and the large nozzle was used. The holding times were set at 0, 1 and 5 minutes. The average drop sizes were taken as 2 – 6 mm, except for the free rise experiments where larger drops of 8 – 9 mm were studied as well. The water velocity in the tunnel was 5.6 cm/s.

In experiment VIII–1 Avalon J–34 was injected and drops in the size range of 2 – 6 mm were allowed to rise to the surface, i.e., the holding time was 0 minutes. Upon surfacing the drops remained predominantly spherical. The drop part above the water surface sagged out and formed a flat cap, while the submerged part remained spherical. No spreading occurred. When transferred to the stirred bowl no change in the shape of the drops took place.

In experiment VIII–2 Avalon J–34 was again injected and drops with diameters of about 9 mm were produced and allowed to rise to the surface. Though the drops were significantly larger than in the previous experiment, the observed behaviour was very similar to that in run VIII–1.

In experiment VIII–3 Avalon J–34 was injected and drops ranging from 2 – 6 mm were kept in the water tunnel for a holding period of 1 minute. During the holding period some of the drops collided and formed clusters. Duplets and triplets were formed as well. Upon surfacing all drops retained their spherical shapes and the clusters remained unchanged.

In experiment VIII–4 Avalon J–34 was injected, drops ranging from 2 – 6 mm were generated and the holding time was set at 5 minutes. As before many duplets, triplets and clusters were formed during the holding period with the large clusters sticking to the walls of the tunnel. Only about 20 –40 single drops remained after the holding period. Upon surfacing the drops remained spherical and the clusters did retain their structures. After transferring to the stirred bowl the drops were kept for 24 hours in the cold room at 2°C. No change in shape or size of the drops and clusters occurred.

In experiment IX–1 Hibernia B–27 oil was injected to form drops with sizes of 3 – 6 mm. The holding period was 0 minutes. This run was essentially a repetition of run VIII–1 but with Hibernia B–27 instead of Avalon J–34 oil. The behaviour of the Hibernia B–27 oil drops was identical to that of Avalon J–34 in run VIII–1.

In experiment IX–2 Hibernia B–27 oil was again injected but an attempt was made to create large drops of about 8 mm diameter. The drops were allowed to rise freely, i.e., the holding period was 0 minutes. It was noted that the rising drops were not perfectly spherical but more ellipsoidal with the short axis vertical. Upon surfacing this shape was retained.

In experiment IX–3 Hibernia B–27 oil was injected to form drops with sizes of 2 – 6 mm and the holding time was 1 minute. During the holding period duplets, triplets and clusters formed in the tunnel with some clusters sticking to the walls. Upon surfacing the small drops remained spherical and the large ones that were ellipsoidal in shape in the tunnel did not change their shape either. No spreading occurred.

In experiment IX–4 Hibernia B–27 oil was injected to form oil drops with sizes of 2 – 6 mm; the holding period was 5 minutes. The Hibernia B–27 oil behaved similar to the Avalon J–34 oil in the identical experiment VIII–4 with that oil.

<u>Experiments X, XI and XII</u>. In these experiments the influence of simulated sea water at 2°C on the oil was studied. For this purpose NaCl was added to the water to a concentration of 2.5 kg/m^3. The series X runs were basically identical to the series VIII with Avalon J–34 except for the salt water. In the series XI Mixed Sweet Western oil was studied during free rise to the surface. Series XII was identical to series IX with Hibernia B–27.

In experiment X–1 Avalon J–34 oil was injected through the large nozzle and drops were generated in the size range 2 – 6 mm. The drops were allowed to rise freely; the holding time was zero minutes. As the drops rose, some of them collided and formed duplets and triplets. Upon surfacing the smaller drops remained spherical while the large ones flattened above the water surface but remained spherical for the underwater part. When transferred to the stirred bowl the shape of the drops did not change and no spreading was observed.

In experiment X–2 larger drop sizes of 9 mm diameter of Avalon J–34 oil were produced and allowed to rise freely to the surface. The oil behaved the same as during experiment VIII–2, the only difference between the two experiments was the addition of the salt to the water.

In experiment X–3 Avalon J–34 was injected to create drops in the range 2 – 6 mm. The holding period was set at 1 minute, the oil temperature was 60°C and the water temperature 2°C. The water velocity was 5.6 cm/s. During the holding period many drops formed duplets, triplets and clusters. Upon surfacing the clusters and drops retained their shapes and identity and no spreading occurred. Upon transfer to the stirred bowl no changes were observed and no spreading took place.

In experiment X–4 the holding period was set at 5 minutes and drop sizes of 2 – 6 mm of Avalon J–34 oil were generated. During the run most of the drops stuck together in clusters, many of which got attached to the wall. Upon surfacing no changes in shape were observed. When transferred to the stirred bowl no spreading took place and the drops and clusters retained their shapes.

In experiment XI–1 Mixed Sweet Western oil was injected to form drops with sizes of 1 – 5 mm diameter. The drops were allowed to rise freely in the salt water. Upon surfacing both the small and large drops broke through the surface and spread to form a continuous oil slick.

In experiment XI–2 Mixed Sweet Western oil was injected and large drops with a diameter of 7 mm were produced. The drops were allowed to rise freely to the water surface. During their ascent the drops acquired an ellipsoidal shape. Upon surfacing they spread and formed a continuous oil slick.

In experiment XII–1 Hibernia B–27 oil was used. Apart from the salt water, this was identical to experiment IX–1 and the results were nearly identical.

In experiment XII–2 Hibernia B–27 oil was used, the only difference with experiment IX–2 was that in the present run the water was salt. The results did not differ from each other.

In experiment XII–3 again Hibernia B–27 oil was used and the results were identical to those of run IX–3, the only difference in circumstances being the salt water.

In experiment XII–4 once again Hibernia B–27 oil was used. The circumstances were identical to those during run IX–4 apart from the salt water and no differences in the behaviour of the oil were observed.

Experiment XIII. During experiment V–4 with the Avalon J–34 oil injected at a temperature of 2°C in water of 10°C the behaviour of the oil was not as expected. Upon surfacing the oil spread and formed a slick instead of emerging as gelled drops. It was concluded that the high shear rate of about 8000 s^{-1} the during injection through the nozzle had destroyed the gel structure. To test this conclusion the experiment was repeated but this time the oil was injected through a nozzle with an I.D. of 6.5 mm instead of the previous 1.8 mm. As a consequence the shear rate during injection was only 500 s^{-1} and the gel structure was only partly destroyed. During the injection in the water tunnel this time strands of oil were produced that were allowed to rise freely in the stagnant water. During the ascent the strands twisted and upon surfacing they sagged out and formed a discontinuous oil paste on the surface. The outlines of the original strands remained visible. No spreading took place.

Heat Transfer Tests

It was expected that the oil drops would achieve thermal equilibrium with the water in the tunnel in a relatively short period of time. This was confirmed by some exploratory experiments in which approximate measurements were made of the temperature of oil droplets as a function of time in water using a fine thermocouple under fairly quiescent conditions. Oil droplets were prepared with diameters ranging from 1 to 10 mm and the change in temperature observed. Generally, the equilibrium time was of the order of 1 to 5 minutes. Thus, the oil essentially reached the temperature of the surrounding water during its residence in the water tunnel. The actual equilibrium time depends on the drop diameter, the thermal conductivity, the heat capacity of the oil, and the characteristics of the water boundary layer around the oil. In the intensely turbulent conditions which exist at the sea bottom where the oil plume is discharged into the water phase, it is likely that rapid heat transfer occurs and thermal equilibrium is established quite quickly. There is thus little prospect that the oil reaching the surface of the water will be at other than the water temperature, i.e., it will not retain the "memory" of its reservoir temperature.

CONCLUSIONS

This has been an exploratory study of oil behaviour in a rising plume; emphasis was placed on obtaining qualitative results, i.e., determining what processes were occurring. It is likely that oil from a sub–sea blowout will be at a relatively high temperature (i.e., above 50°C), and it will have experienced a recent history of high shear. It will, therefore, be in a situation of relatively low apparent viscosity. As it enters the water, the oil jet will be disintegrated into a spectrum of oil particle sizes ranging from a few micrometers to a few millimeters. These oil droplets rapidly equilibrate to the water temperature. In the case of waxy oils, this equilibrium temperature may be below the pour point and in the region where the oil exhibits a relatively high yield stress. The oil droplets will gel over a period of some minütes, as they rise through the water column.

There is a possibility that, in some cases, the gelling process may be sufficiently slow that the oil will have reached the water surface before gelling is complete. However, this is difficult to investigate, because it involves controlling the oil's history prior to injection. Oils that are still fluid and of a non–waxy character may experience some drop–to–drop coalescence in which two oil drops will associate and form one larger oil drop. In waxy oils, some coalescence may occur, but the resulting particles will tend to be duplets, triplets, or multiplets of oil particles, i.e., the drops will retain their original size and merely stick together. This is, presumably, because the oil has established a yield stress at its surface which is sufficient to overcome the surface energy forces that are tending to minimize the oil–water interfacial area.

A conventional non–waxy oil tends to form a slick at the surface. These waxy oils tend to form "peppercorn" type oil at the surface, in which the oil retains its droplet integrity.

Under certain conditions, it was possible to form strands or spaghetti–like masses of oil. This will tend to occur when the oil is injected into the water relatively slowly under fairly low shear conditions (such as from a pipeline containing "dead" oil), and the oil cools to a temperature at which it has a relatively high yield stress, and is thus able to resist the process of drop to drop separation which normally occurs in turbulent jets. "Strands" or "strips" of oil may thus be generated which will tend to retain their shape and arrive at the water surface, forming masses of inter–connected oil, but probably not a homogeneous slick.

The principal conclusion from this work is that, from an oil spill countermeasures and behaviour point of view, operators should be prepared to face slicks that consist of accumulations of small oil particles, or peppercorns, or strands of oil rather than continuous homogeneous slicks. The countermeasures implication of this possibility are discussed in a later section.

EVAPORATION OF OIL DROPLETS IN AIR

PROCEDURES

The five oils used in this study were Avalon J–34, Hibernia B–27, Hibernia C–96, Terra Nova K 08–DSTI, and Mixed Sweet Western. A series of exploratory tests was undertaken in order to determine the optimal method of exposing small oil drops to an air current, thus simulating transit through the atmosphere. The general approach favoured was to hold a small drop on a wire in an air stream, measuring its mass periodically. The size of oil droplets that could be handled experimentally were in the range of 1 to 3 mm. It was believed that oil droplet velocities would be about 3 m/s. Thus, the wind tunnel was adjusted to give approximately this condition.

A measurement system was developed in which a very thin wire was bent to form a hoop of about 2 mm diameter. An oil drop was then attached to this hoop and was suspended in the air flow of the 30 cm x 30 cm square wind tunnel. The initial mass of the oil drops used in this system ranged from about 4 to 8 mg. Five runs were undertaken for each oil, each run lasting 10–15 minutes. The mass of the oil drops was measured at various intervals, and plots were then obtained of the mass of oil lost on a percentage basis vs. time.

In order to provide some calibration, it was desired to evaporate a liquid of known vapour pressure. 2–methyl naphthalene was used for this purpose. However, the drop tended to solidify as a result of evaporative cooling. Efforts to find a more suitable liquid were unsuccessful, as the liquid had to be fairly viscous (and preferably possess some yield stress!) in order that it remain on the wire. Normal alkanes were not suitable, nor were most common solvents: the small drops which were feasible were too low in mass to weigh accurately with the micro–balance.

Precautions were taken to heat and shake the oil prior to sampling to redissolve any precipitated material. It should be noted that the amounts of oil being weighed were relatively small. Thus, a high experimental error was inevitably present in the percentage of loss. All the runs were done at 20°C.

RESULTS

Figure 22 gives the results for the crude oils. No evaporation of the Terra Nova K08 DST–1 oil was observed. The mass loss of the 2–methyl naphthalene was, as expected, near linear, amounting to 50% in one hour. It had been hoped to calculate a mass transfer coefficient from this data, but the uncertainties in vapour pressure are too large to permit this to be done accurately.

The most useful data from these tests are believed to be:

i) mass loss percent after 2 minutes, which represents the probable extent of evaporation in a well blow–out. It is likely that the actual drops will be smaller and transit time greater, thus the data are likely conservative.

ii) the time to a mass loss of 50% of that at 2 minutes. This gives an impression of the rapidity of evaporation.

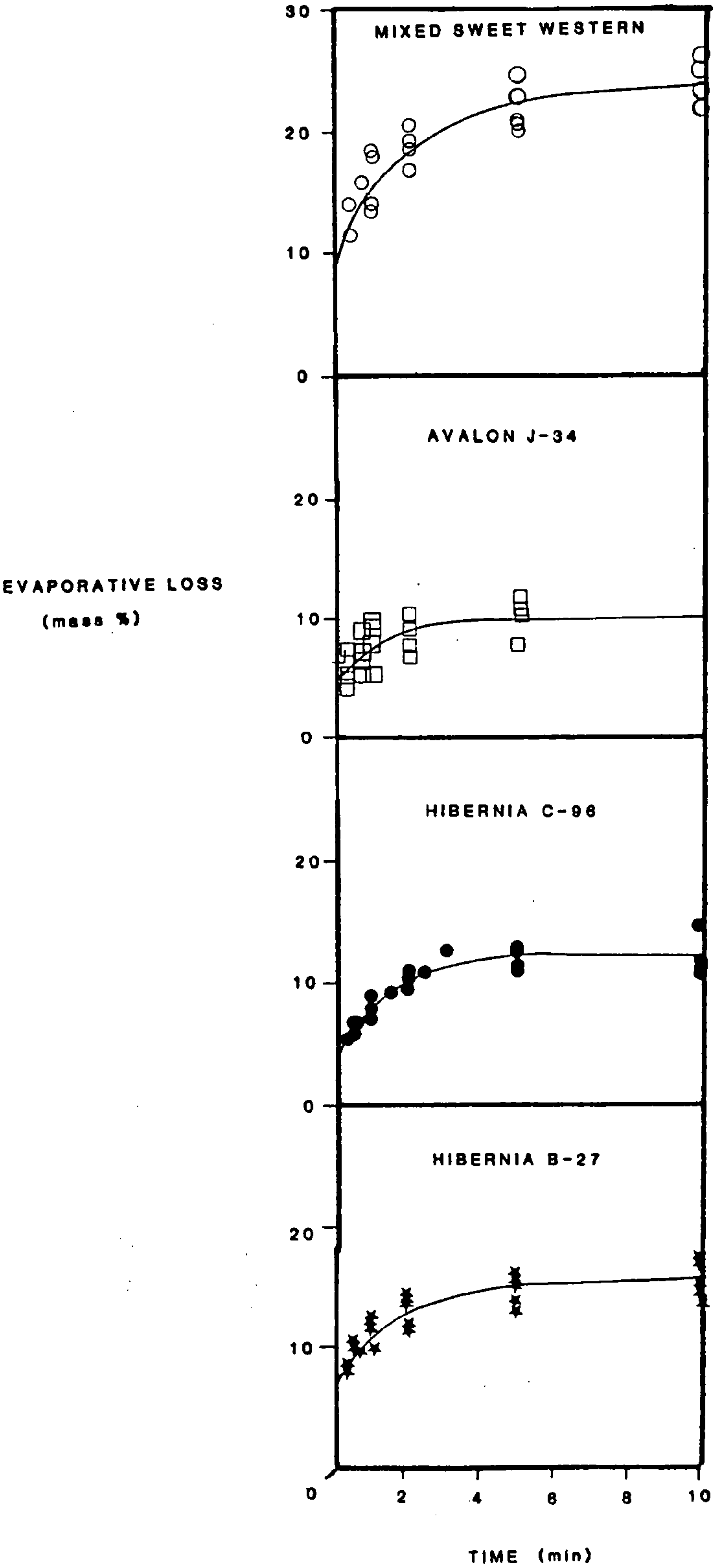
These data are summarized below.

	Mass loss at 2 min. %	Time to 50% (of mass lost at 2 minutes)
Avalon J–34	9 ± 1.5	0.1 – 0.4
Hibernia B–27	13 ± 2	0.1 – 0.3
Hibernia C–96	10.5 ± 1.5	0.2 – 0.5
Mixed Sweet Western	19 ± 3	0.1 – 0.2
Terra Nova K08 DSTI	0	N/A

Three waxy oils gave similar results, losing 4 to 6% of their mass in 0.1 to 0.4 minutes (6 to 24 seconds), this increasing to 9 to 13% after 2 minutes.

FIGURE 22

EVAPORATION OF OIL DROPS IN AIR



THEORETICAL DISCUSSION

The aim of this section is to outline the theoretical approach to quantifying droplet evaporation and to develop order–of–magnitude estimates of evaporation rates from droplets in air compared to rates from surface slicks.

The rate of evaporation of an oil droplet in air depends on two groups of factors. First is the inherent volatility of the oil, which can be expressed in terms of vapour pressure. The second is the mass transfer characteristics, which apply to the contact between the oil droplet and the air stream. There have been numerous studies of mass transfer between droplets and air streams, as reviewed, for example, in the text by Sherwood et al. (1973). The most common approach is to calculate the Reynolds number and Schmidt number for the drop, and from this, calculate the Sherwood number. The Sherwood number is a dimensionless representation of a mass transfer coefficient. For conditions as existed in this system and as expected offshore, a Reynolds number of the order of 200 is expected. This corresponds, using established correlations, to Sherwood numbers of about 10 and thus to mass transfer coefficients of the order of 10 cm/s or 0.1 m/s. A typical oil slick mass transfer coefficient is about 0.3 cm/s, thus as expected, there is more intense or intimate contact between an oil drop in air, than between an oil slick and air.

Stiver and Mackay (1983) introduced the concept of evaporative exposure for oil in which exposure is expressed as the product of mass transfer coefficient multiplied by area multiplied by time divided by volume of the oil. In the case of a 1 mm oil droplet, under conditions discussed here, the mass transfer coefficient is believed to be of the order of 0.1 m/s, the volume to area ratio is 3×10^{-4} m, (i.e., one third the radius of the drop). Thus, the evaporative exposure is approximately 300 x t, where t is in seconds. Thus, in a period of 1 hour, exposures of the order of 1,000,000 are expected. This is a faster rate of oil exposure than occurs to an oil slick, in which a mass transfer coefficient for evaporation of the order of 10 m/h is expected. It thus appears that, under conditions of droplet movement through the atmosphere, evaporation is occurring at a rate of exposure some 100 times greater than that which exists on the sea surface, i.e., the amount of evaporation which will take place with a 1 mm diameter drop in a period of one minute, corresponding to about 100 minutes for a 1 mm oil slick residing on the water surface or in a pan in a wind tunnel. This is confirmed by the experimental data. In almost all cases, the evaporative process had gone to a high level of completion, completion being loosely defined as the amount evaporated after 2 minutes of exposure. There will thus be intense mass loss of volatile material from the oil spray into the atmosphere, and by the time the oil reaches the water surface, it will be in a highly weathered condition. It will likely also be at a temperature corresponding to the air through which it is moving, and that temperature may be well below the oil's pour point. It should be noted that evaporation results in an increase in pour point, thus, there is a probability that the oil particles, when landing on the water surface, will retain their integrity as particles, i.e., they will have a yield stress that exceeds the spreading forces which would otherwise tend to cause them to spread and form a slick. Obviously, the exact conditions of residence time in the atmosphere and extent of evaporation will depend on factors such as the height to which the oil is ejected into the atmosphere, the air temperature, and the fall velocity. There is also a possibility that, if there is intense ejection of oil into the atmosphere, there could be established a condition in which a back pressure of volatile material in the atmosphere will be formed which could retard evaporation, i.e., the atmosphere could locally become saturated with volatile hydrocarbons. It is believed that this is only likely in the immediate vicinity of the oil discharge in which the ratio of air volume to oil volume is still fairly low.

In the event that the oil is ejected hot and the air is fairly warm, the evaporation rate will, of course, be enhanced.

CONCLUSIONS

These experiments have confirmed, in semi–quantitative terms, the intuitively held view that, when a crude oil is sprayed into the atmosphere as a mist of droplets of diameter of the order of 1 mm, that oil will evaporate very rapidly and typically lose 10 – 20% of its mass within a few minutes and, presumably, prior to reaching the water surface. The oil properties will thus have changed profoundly. In the case of waxy oils, the pour point will have risen, a yield stress will have been established, and the oil is unlikely to be subject to spreading.

BATCH SLICK SPREADING

This section of the report covers a series of thick slick spreading experiments undertaken to evaluate the initial spreading rates of both waxy and non–waxy batch oil spills.

APPARATUS

One–dimensional spreading tests were conducted with fresh Mixed Sweet Western, Hibernia B–27 and Avalon J–34 crude oils in a water–filled trough 3 m long by 10 cm wide (Figure 23). Two water temperatures (5° and 10°C) and two initial slick thicknesses were used for each oil. Oil spreading was recorded by a video camera; the tape was subsequently analyzed to give the distance down the trough of the leading edge of the slick (as determined from a scale on the side of the trough) as a function of time (from the VCR display timer overlain on the video picture).

PROCEDURE

Prior to each run the test oil was reconstituted by heating it's container to about 50°C in a hot water bath and periodically shaking the container over a period of 30 minutes. Appropriate volumes (300 cm^3 for a 1 cm initial thickness, 600 cm^3 for a 2 cm initial thickness) were drawn from the container and placed behind a removable rubber dam placed 30 cm from one end of the trough. The oil was allowed to cool to the water temperature, the video was turned on and the rubber dam was gently and quickly lifted from the trough. Video recording continued until no further movement of the oil could be detected for a period of at least 20 seconds.

RESULTS AND DISCUSSION

Figures 24 and 25 give the results of the spreading tests (length vs. time) for initial slick thicknesses of 1 and 2 cm respectively. One fact is obvious; the more viscous the oil the slower it spreads and the sooner it stops spreading.

This is further borne out by Table 8 which gives the final slick thickness for each of the runs. In the case of the Mixed Sweet Western oil the slick spreads until it virtually fills the trough (spreading eventually ceases before the end of the trough because a sheen emanating from the slick reaches the end first and stops the bulk of the oil from spreading). As the oil viscosity increases the oil stops spreading sooner (resulting in thicker final slicks). The final slick thicknesses are much greater than could be accounted for by the sheen stopping oil spreading.

Figure 26 shows the spreading results plotted using the non–dimensional format of Fay (1969); again the effect of increasing oil viscosity (either reduced temperature or increasing waxiness) on reducing slick spreading is apparent. Figure 27 shows the results replotted against a modified derivation of Fay's (1969) model in which viscous dissipation is assumed to occur in the oil slick itself rather than in the underlying water layer. This results in the viscosity and density terms in the equation being that of oil, rather than water as in the original derivation. As can be seen from Figure 27, this new derivation removes the effects of temperature on spreading rate for each oil. Although there are differences amongst oils, particularly between Avalon J–34 and the Mixed Sweet Western, this discrepancy lies in the value of the viscosity used for the waxy, non–Newtonian rheology crudes. An estimate of the shear rate during spreading (spreading velocity divided by slick thickness) was used to estimate the oil viscosity for the waxy crudes; since the viscosity of these oils is a strong function of shear rate; higher shear rates would result in much lower viscosities (see Rheology) and a better fit of the data to the model.

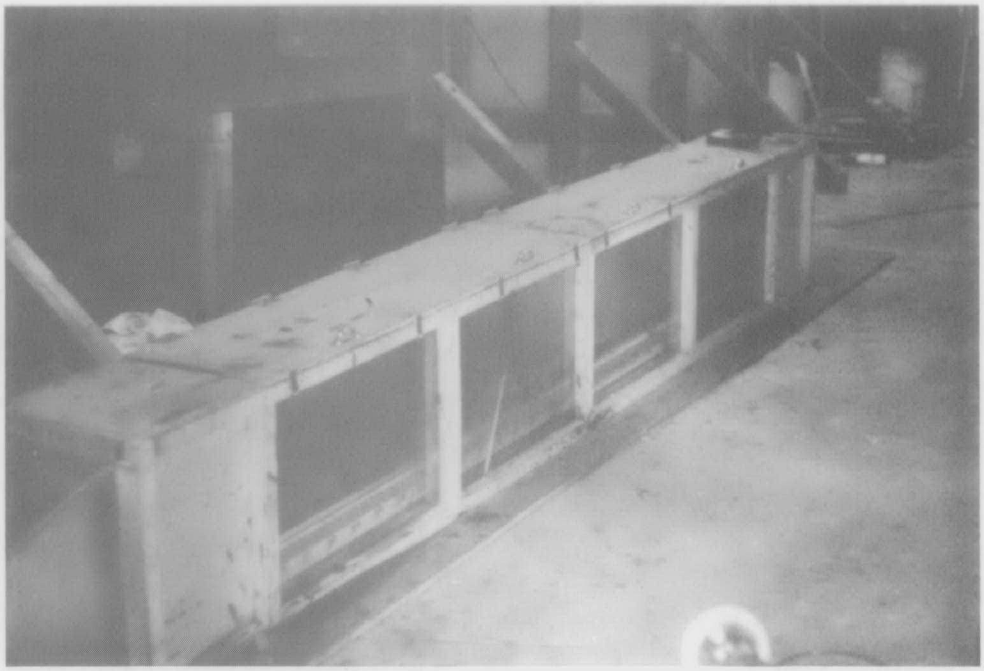


Figure 23
Batch slick spreading test apparatus

FIGURE 24

SPREADING OF 1 cm THICK SLICKS

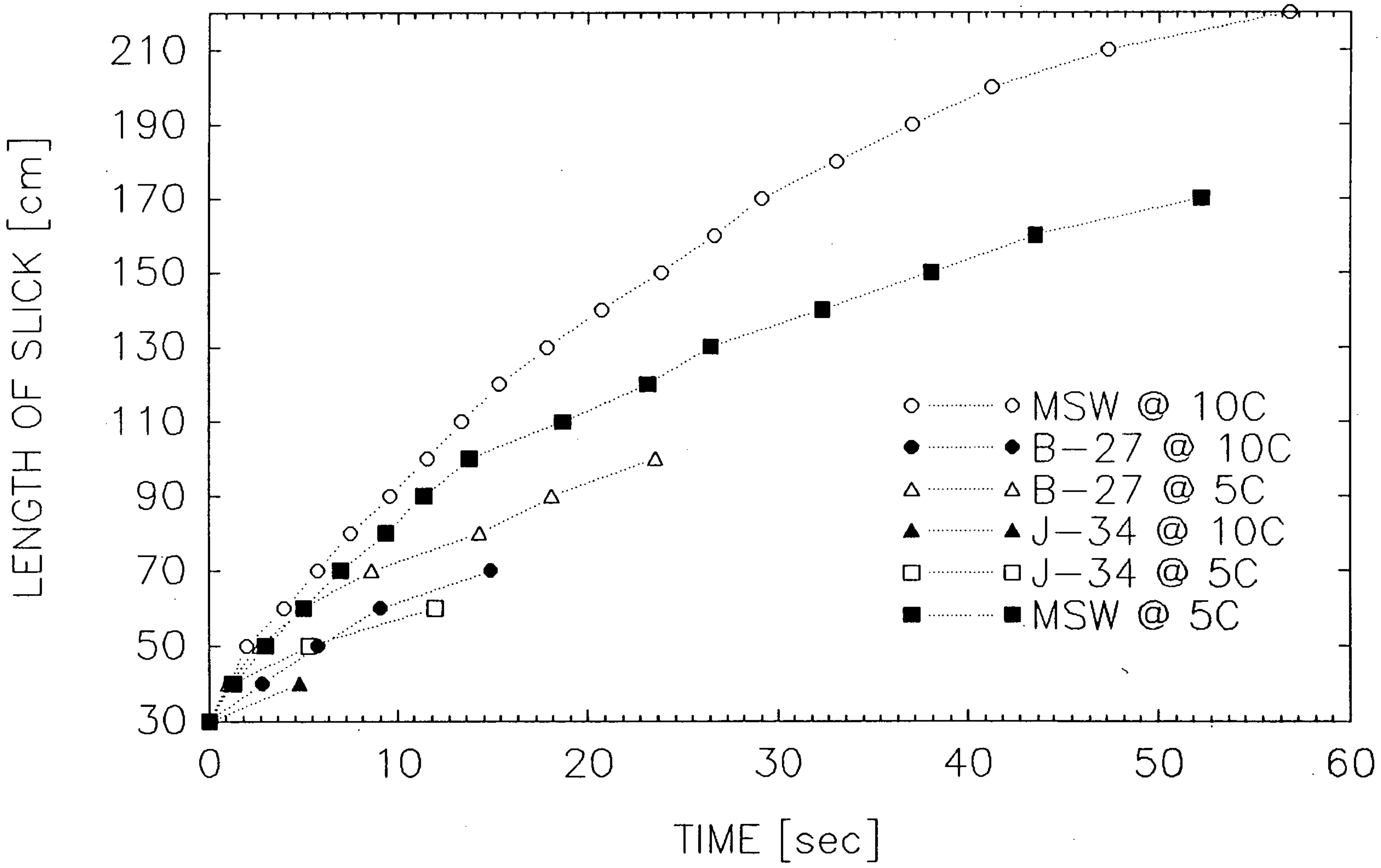


FIGURE 25
SPREADING OF 2 cm THICK SLICKS

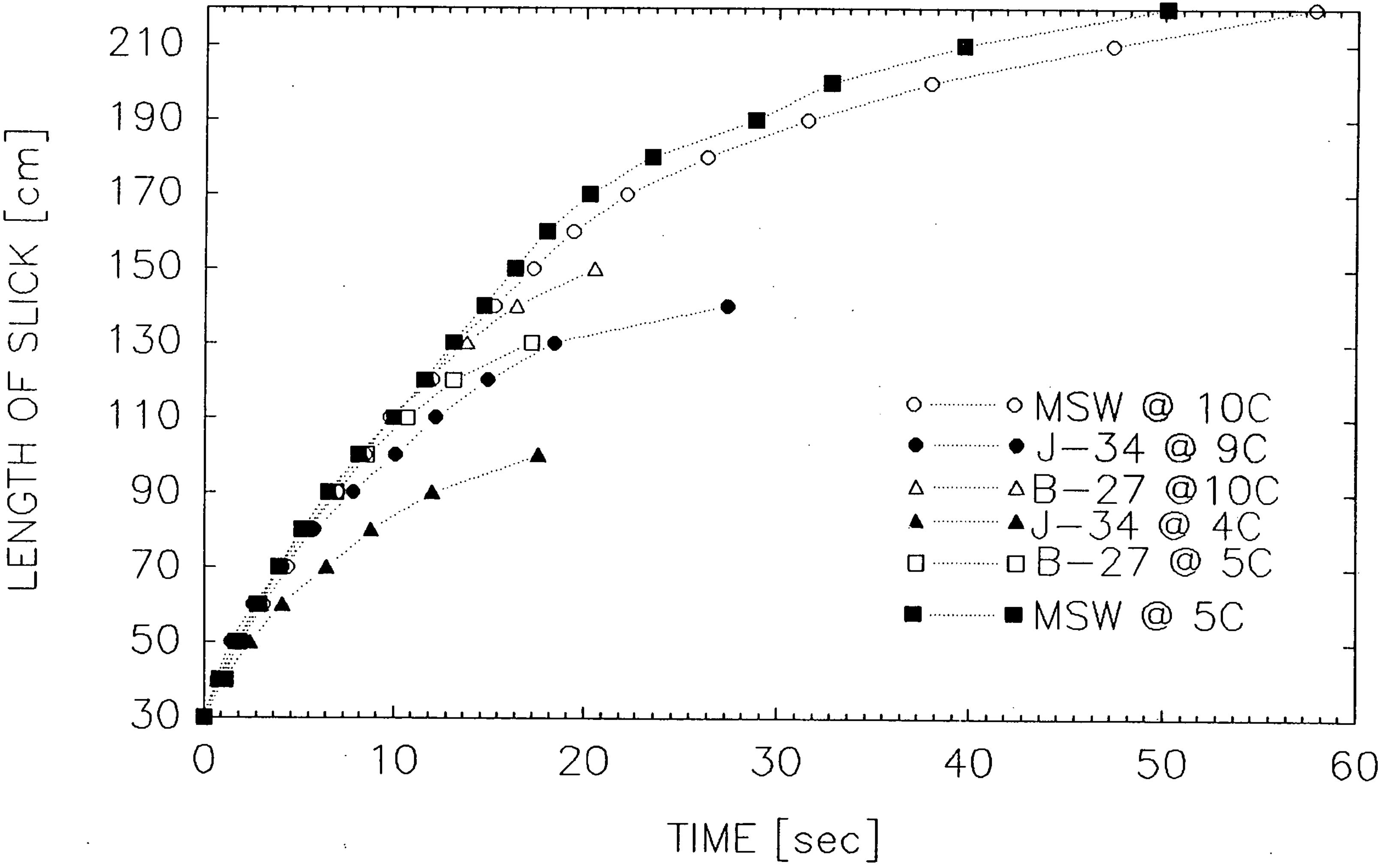


FIGURE 26

NON-DIMENSIONAL SPREADING

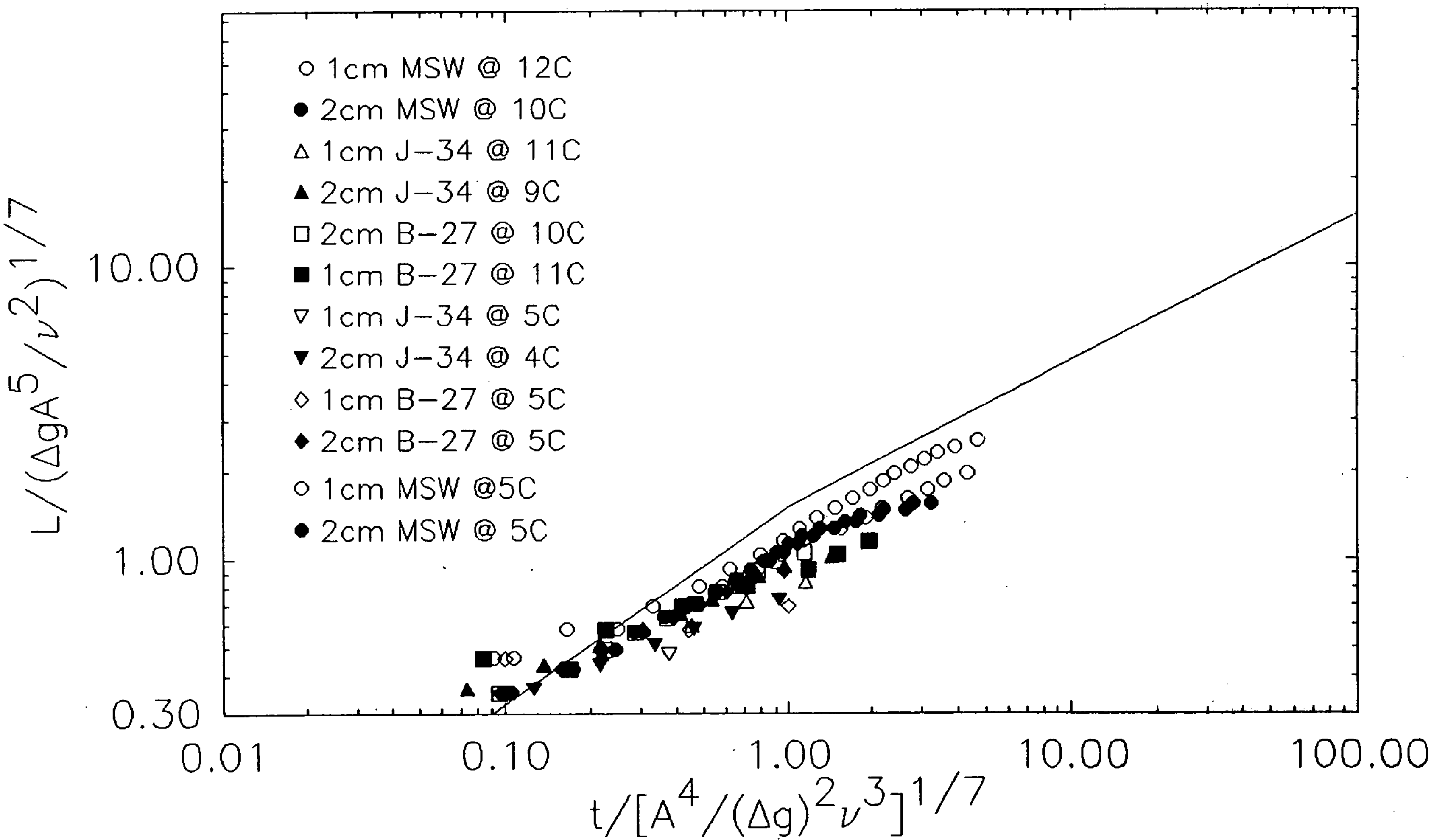


FIGURE 27

CORRECTED NON-DIMENSIONAL SPREADING

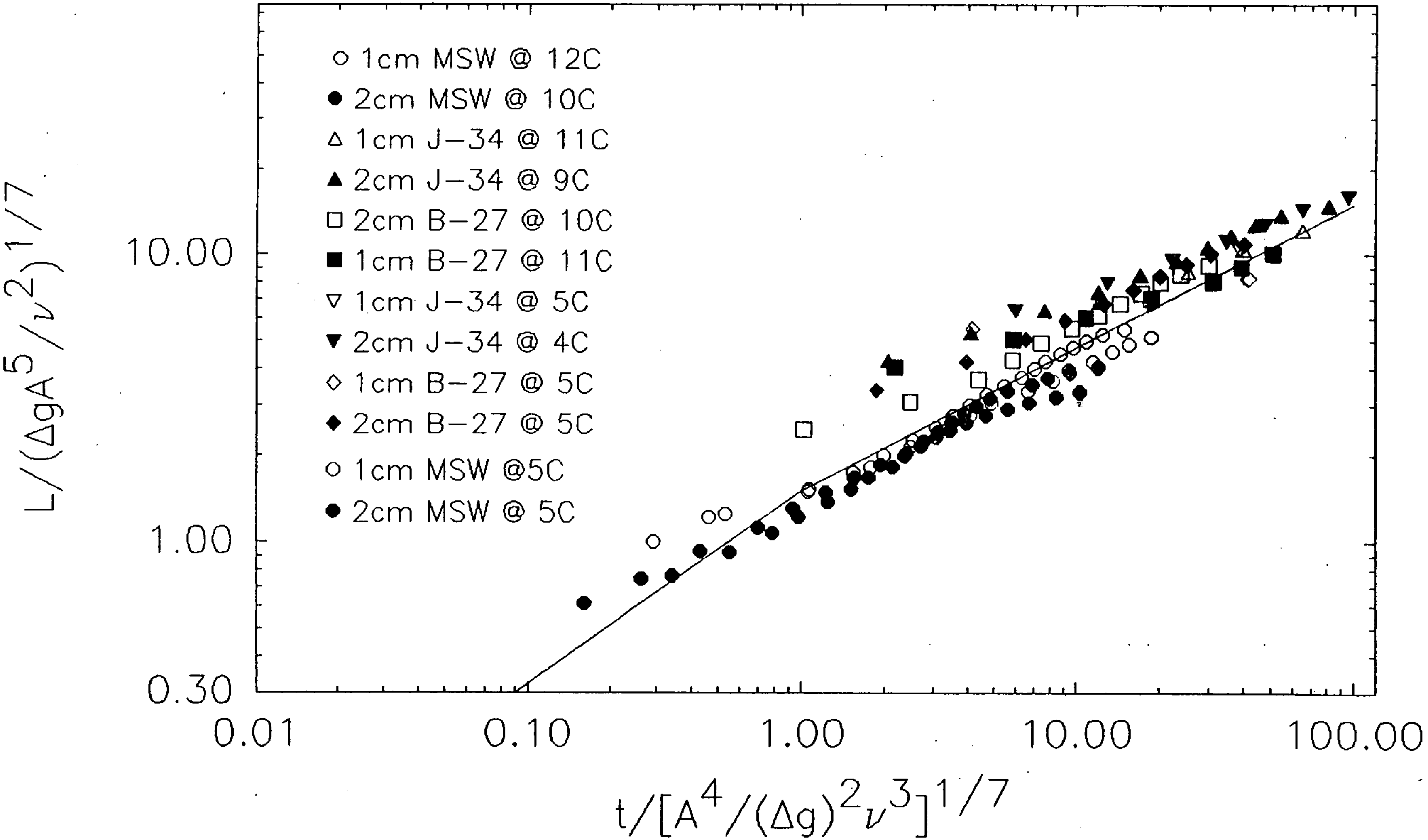


Figure 28 shows the equilibrium slick thickness data for the Avalon oil (Table 8) plotted in various manners. Figure 28a shows equilibrium slick thickness plotted against the oil's yield stress. Two values of oil depth are used: slick thickness and freeboard (or height of the oil above the water surface). Figure 28b shows the same data except that the thicknesses have been converted to pressures (P = gh or gh for thicknesses and freeboard respectively).

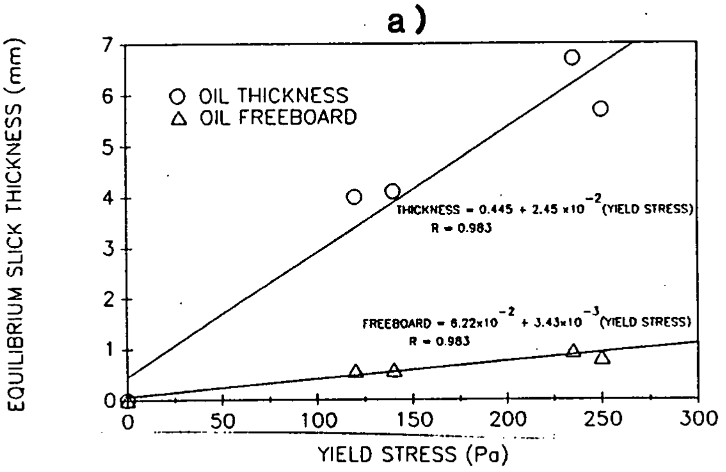
The results do not show the theoretically correct relationship of pressure = yield stress, however it must be remembered that these data involved the cessation of spreading of initially very thick slicks, rather than the thickness at which the oil begins to spread. Figure 28c shows the relationship between equilibrium slick thickness and the temperature difference between the three oils pour points and the water temperature. The empirical best fit equation relating equilibrium thickness to temperature difference is given.

TABLE 8
Final Slick Thickness
(mm)

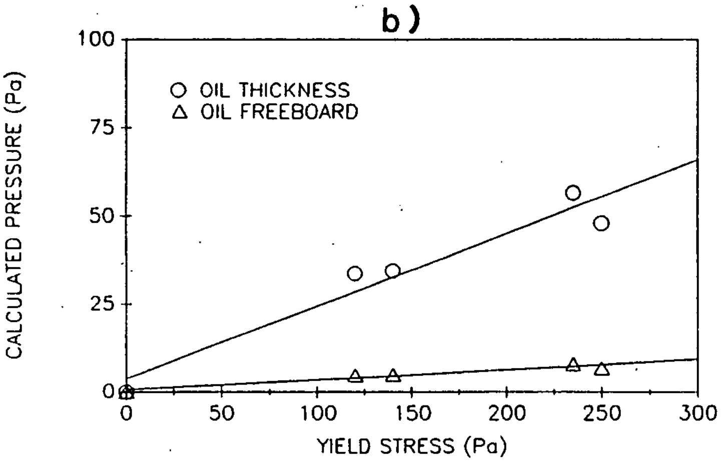
OIL TYPE	TEMPERATURE			
	10°C		5°C	
	1 cm	2 cm	1 cm	2 cm
MSW	1.34	2.7	1.9	2.7
B–27	2.8	3.9	4.6	4.4
J–34	4.0	4.1	6.7	5.7

FIGURE 28

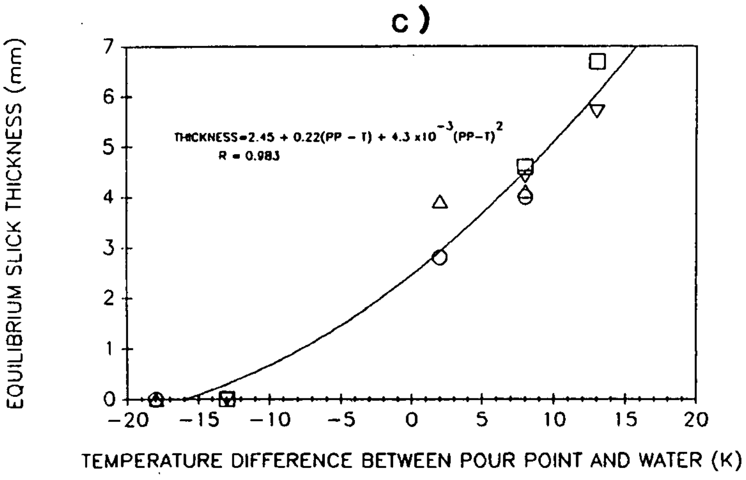
FINAL SLICK THICKNESS OF AVALON OIL vs. YIELD STRESS



COMPARISON OF CALCULATED SLICK PRESSURE WITH YIELD STRESS



CESSATION OF SPREADING



CONCLUSION

It is concluded that waxy crude oils will exhibit very different spreading characteristics than non–waxy oils. Batch spills of waxy oils will spread slowly and reach equilibrium thicknesses much greater than those for equivalent spills of non–waxy oils. The spreading rate of waxy oils can be modelled by using oil viscosity, as opposed to water viscosity, in Fay's (1969) spreading equations. The equilibrium thickness of batch spills of waxy oils has been modelled empirically by relating equilibrium thickness to the difference between the oil's pour point and the water temperature.

EVAPORATION

Evaporation of the volatile components of an oil spill is one of the three key natural processes that remove oil from the sea surface (natural dispersion and dissolution being the others). Evaporation is also one of the two primary natural processes that result in changes in oil properties with time (emulsification being the other).

The volatilization of components from an oil slick is normally a function of many variables, the most important of which are: the component's vapour pressure, the oil's temperature and thickness, and the wind speed. The lighter components of a typical slick evaporate first until, after a few days at sea, up to 50% of the oil has evaporated leaving behind a heavy residue. Ambient temperature, slick thickness and wind speed combine to determine the rate at which evaporation occurs. The "evaporative exposure" approach of Mackay is the preferred technique for predicting environmental evaporation rates for normal oils (Stiver and Mackay 1983). These simple equations permit the correlation of experimental data from different tests and the extension of the results to environmental conditions. The required numerical factors can be determined from a standardized test (a modified ASTM distillation).

Unfortunately, the technique cannot account for the unusual evaporation behaviour of waxy oils (S.L. Ross 1984a and 1985b) for two reasons. The first is that waxy crude spills will likely exist at sea as mats, droplets and globules, not as continuous slicks (a fundamental assumption of the existing model). This feature of waxy oil spills has implications that affect evaporation.

The surface area of droplets is much greater than that of a slick. For example, per unit volume, although 1 mm droplets have 3 times the surface area than that of a slick, only 25% of each droplet's surface is exposed to the atmosphere while 75% is immersed in water. This means that the surface area of oil droplets exposed to the air is only 0.75 times that for slicks. The surface area of oil exposed to water is 2.25 times greater for droplets than for slicks. Dissolution of volatile components followed by their evaporation from water may be a more important weathering process for waxy oils than it is for normal oils.

The second reason for the unusual evaporation behaviour of waxy crude oils is the formation of a skin or crust on the surface of the oil. This phenomenon was found to occur on samples of waxy crude oils evaporated in wind tunnel tests (S.L. Ross 1984a and 1985b). After 48 hours exposure to air (independent of temperature or slick thickness) a shiny layer appeared on the surface of the oil samples (Figure 29). It is surmised that this layer consists of waxes which precipitate as the relative concentration of higher molecular weight compounds in the surface layer increases by virtue of the loss of the lower molecular weight compounds through evaporation. This crust, probably in combination with the high viscosity of the bulk oil, is thought to introduce additional resistance to internal mass transfer not accounted for in the evaporative exposure model. This is illustrated in Figure 30, which shows the fit of data to the evaporative exposure model for normal and waxy crude oils. Two facts are obvious: normal oils evaporate much faster than waxy oils, and the evaporative exposure model fits normal oils, but not waxy oils.

Since evaporation is one of the major processes that changes oil properties, the unusual behaviour of waxy crude oils has secondary effects. One of these is the fact that the adhesiveness of the oil surface decreases dramatically (S.L. Ross 1985b). Figure 31 shows the amount of waxy crude oil retained on sorbent pads as a function of weathering. The dramatic initial decrease is associated with the formation of the surface crust. It is interesting to note that this surface crust is only about 100 um thick, and encapsulates relatively fresh oil.

Finally, oils that do not exhibit waxy behaviour when fresh can, with evaporation, reach a point where they begin to behave as waxy oils. This is analogous to increases in pour points with increased exposure. It is important to be able to predict at what degree of evaporation an oil will start to behave as a waxy oil. It is possible that most crude oils eventually evaporate to this point.

Three series of experiments were carried out to investigate evaporation of waxy oils: slick evaporation studies both in wind tunnels in Ottawa and at the University of Toronto, wind/wave tank studies in Ottawa, and droplet evaporation studies in a wind tunnel at the University of Toronto.

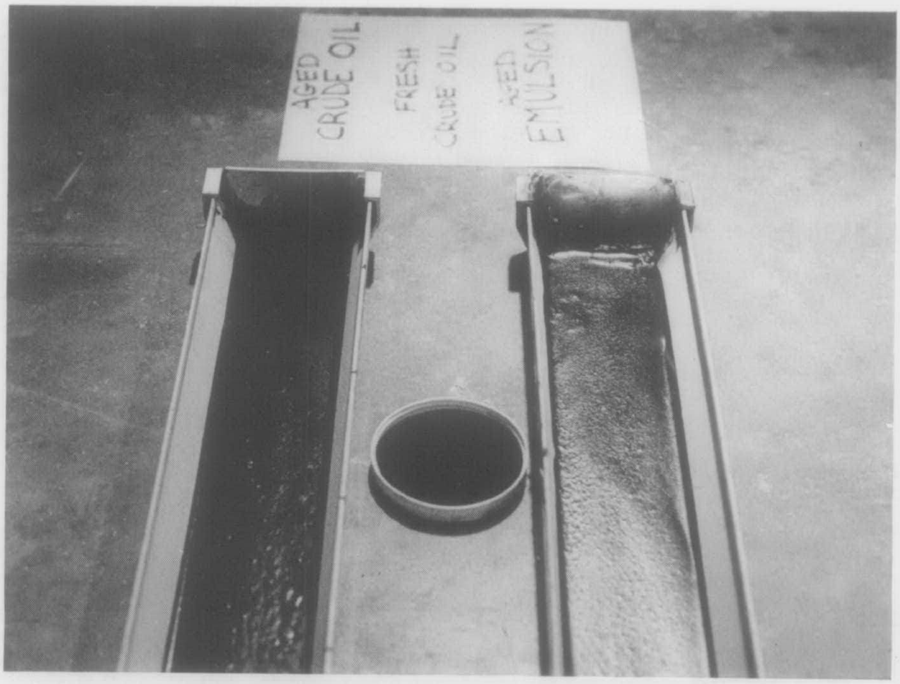


FIGURE 29 - Comparison of surface appearance of fresh and weathered oil

FIGURE 3 0- EVAPORATIVE LOSS

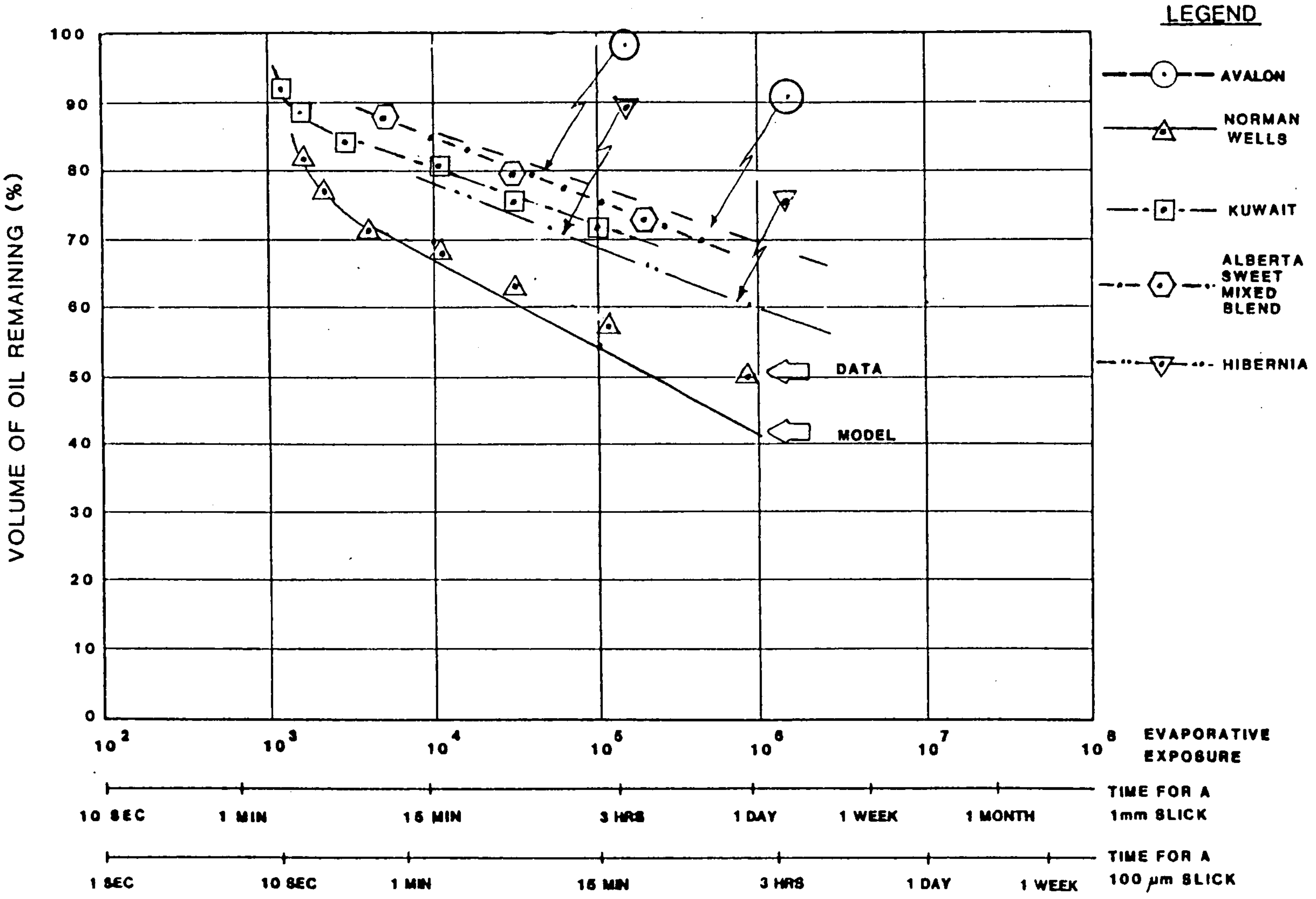
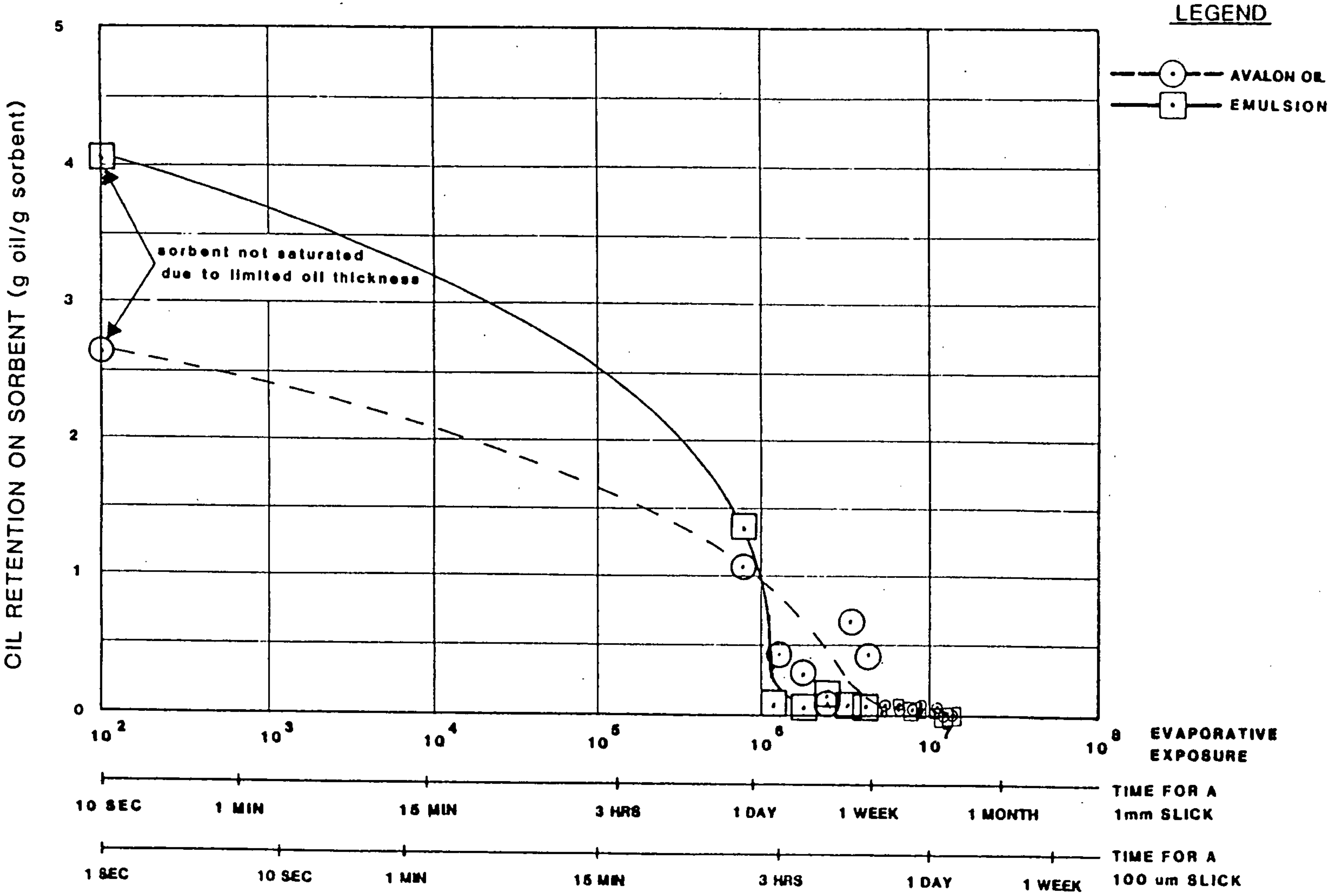


FIGURE 31 - SORBENT TESTS IN TROUGH



(from S L Ross 1986)

TROUGH EVAPORATION STUDIES

EQUIPMENT AND PROCEDURES

Slicks of the Mixed Sweet Western, Hibernia B–27 and Avalon J–34 crudes were placed in troughs (3m x 10 cm x 1 cm) in a wind tunnel for two weeks. Three initial thicknesses were used for each oil: 1, 3 and 5 mm. Wind speed was maintained at 6–8 m/s with an average temperature of 17°C throughout the test period. Each trough was removed from the wind tunnel periodically and weighed to determine oil mass loss. At the time of each weighing two samples of the oil were taken: a bulk sample of approximately 20 ml incorporating the full depth of the oil and a crust sample, containing only the top layer of the oil. These latter samples were diluted with hexane. All these samples were shipped to the University of Toronto for G.C. and physical property analyses.

Figure 32 shows the mass loss curve for the non–waxy Mixed Sweet Western crude oil. Also shown are the results for a gas sparging experiment and the prediction based on a modified ASTM distillation (Stiver and Mackay 1983) for the Mixed Sweet Western (S.L. Ross and D.F. Dickins 1987). All the data correlate well with the model prediction, with the exception of the 1 mm thick slick (this is likely due to measurement (weighing) errors since the weight of the 1 mm oil makes up only a small fraction of the weight of the trough).

Figure 33 shows the equivalent results for the Hibernia B–27 oil. Although not unmistakable, there seems to be a trend in the data (discounting the poor accuracy data point for the 1 mm thick oil) of increased evaporation for the 5 mm oil compared with the 3 mm oil at exposures above 5×10^5. This runs contrary to common sense (i.e., one would expect thinner slick to evaporate faster) and the evaporative exposure model which for normal oils (see Figure 32) removes the effect of thickness through the evaporative exposure coefficient.

The unusual trend is further illustrated in Figure 34 for the Avalon J–34 crude evaporation. In this case the effect of slick thickness on evaporation is quite pronounced.

FIGURE 32

EVAPORATION OF MSW SLICKS

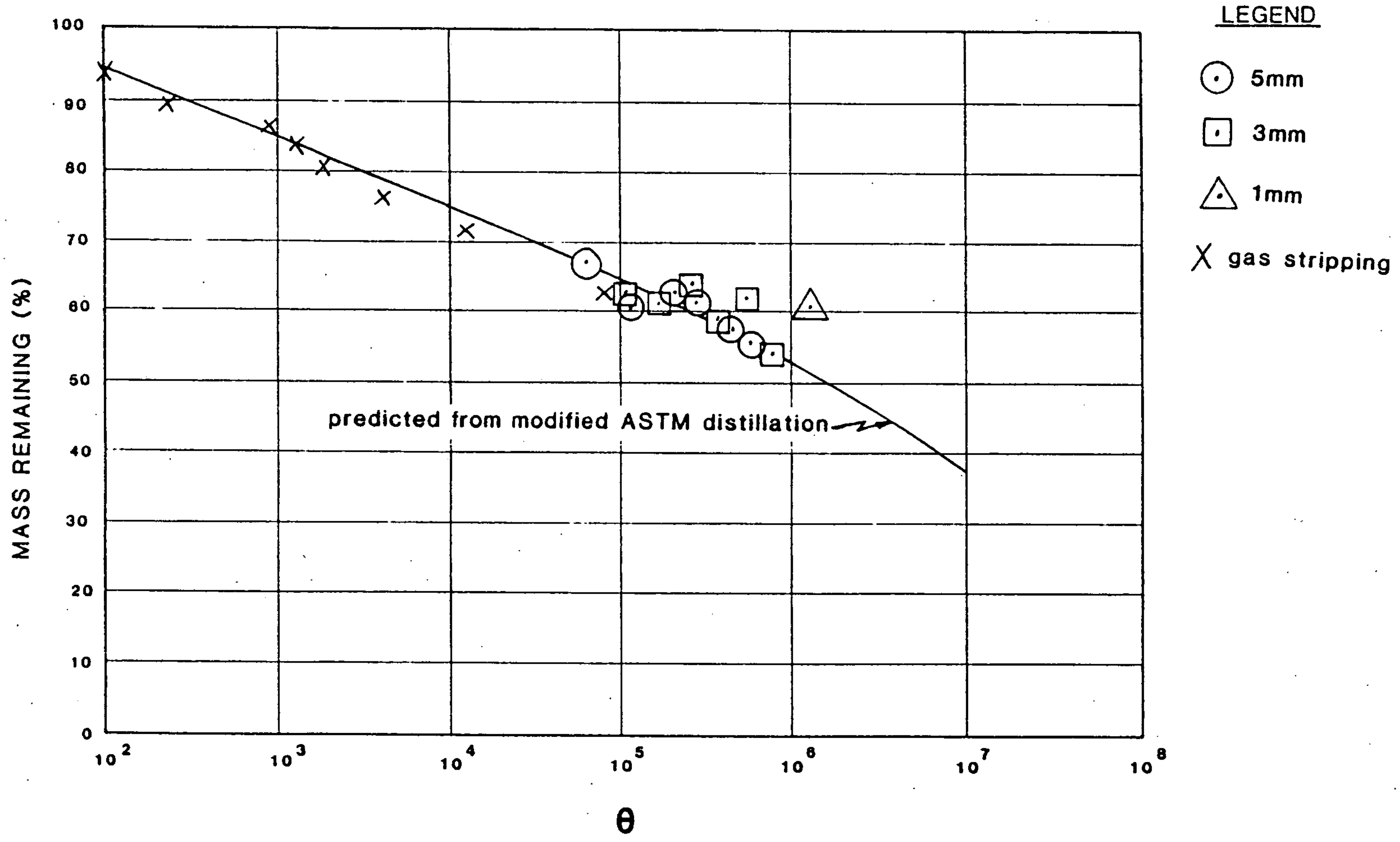


FIGURE 33

EVAPORATION OF B27 SLICKS

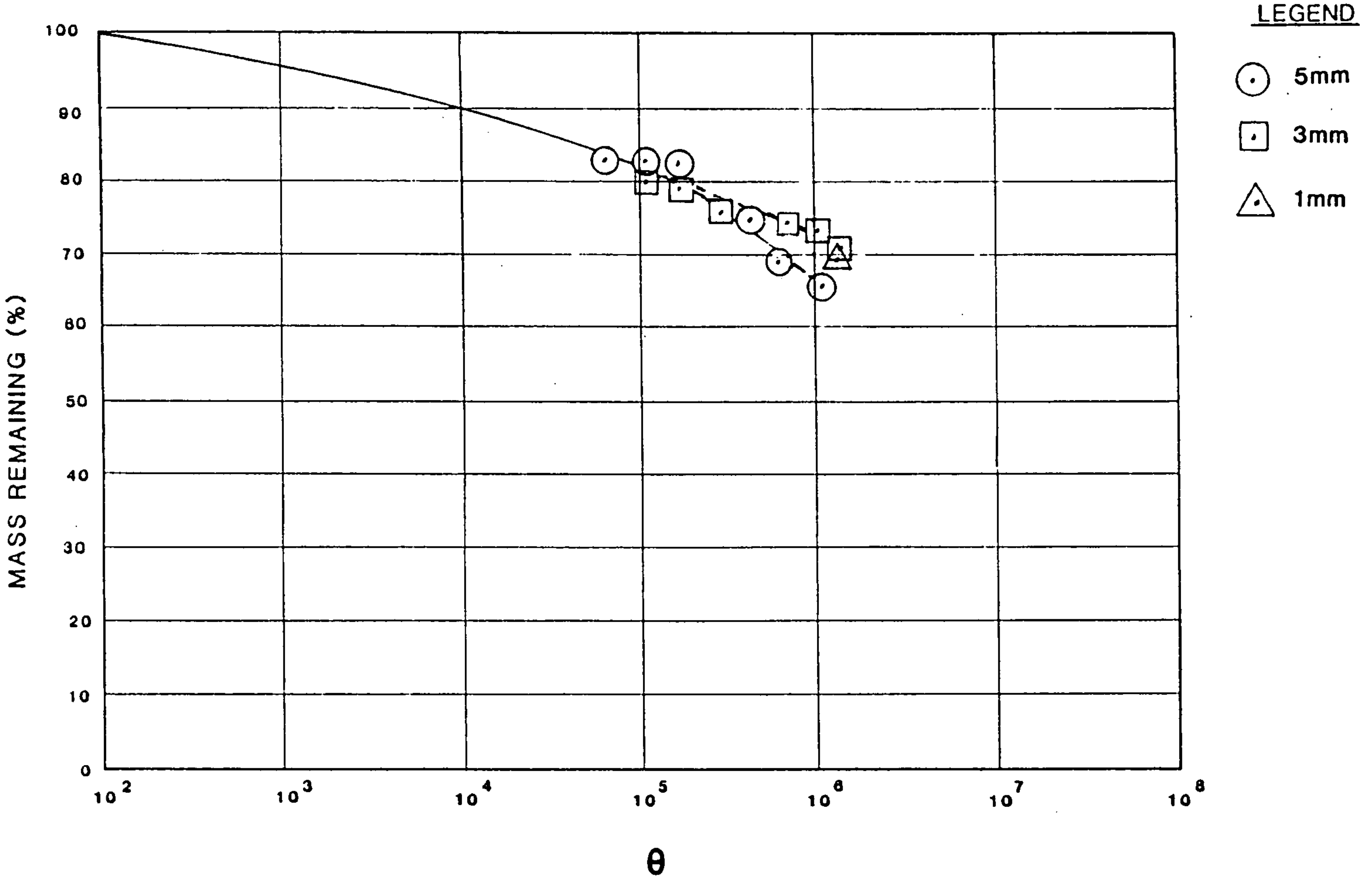
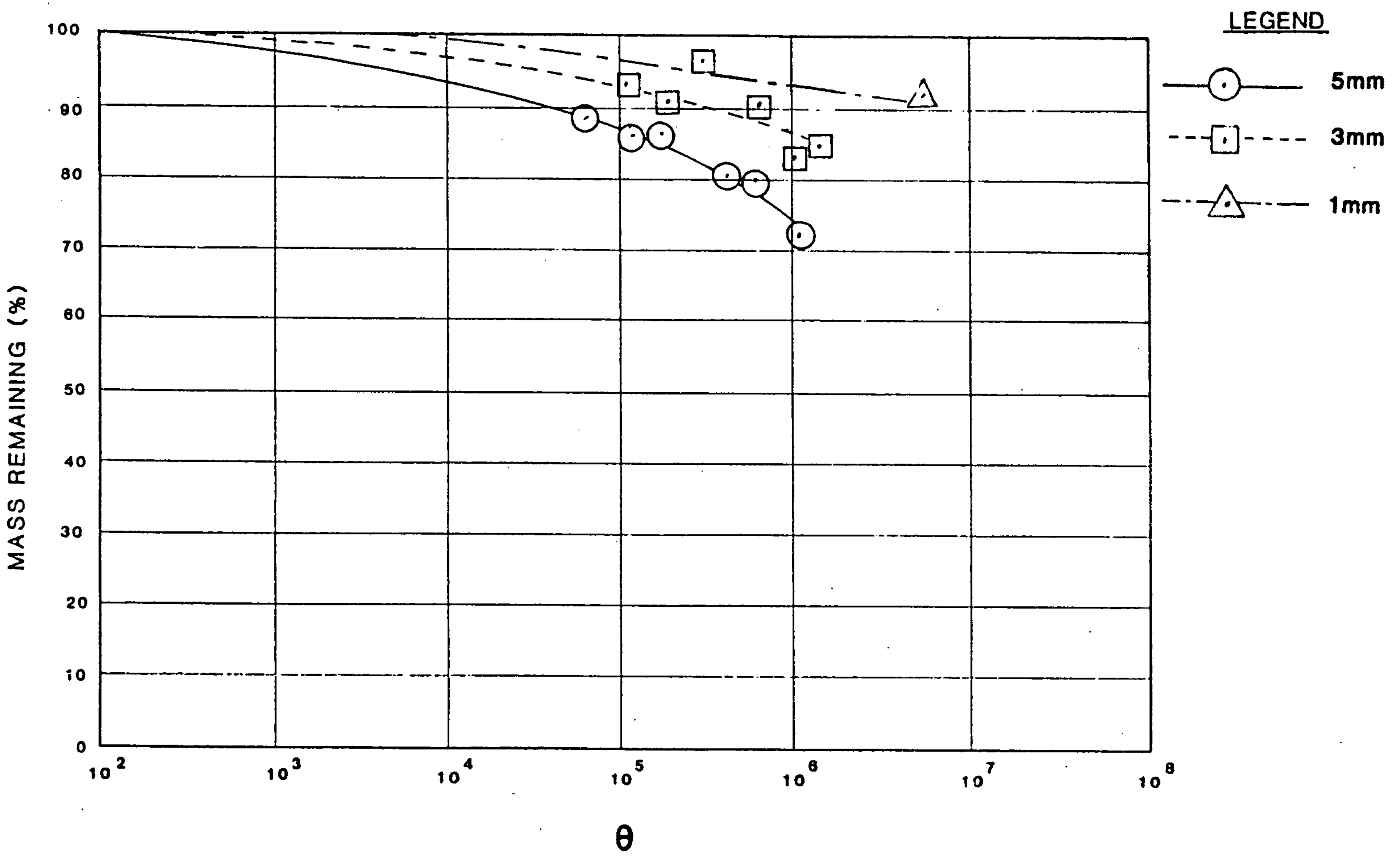


FIGURE 34

EVAPORATION OF J34 SLICKS



It is likely that the crust that forms on waxy oils as they evaporate plays a role in this phenomenon. Unfortunately, the crust samples taken from the troughs were too diluted with hexane to give good G.C. traces, thus a second wind tunnel evaporation experiment was run with the Avalon J–34 oil at the University of Toronto to investigate this crust and its effect on evaporation rates.

Tray Evaporation Experiment

A volume of 50 ml of oil (Avalon J–34) was placed onto a tray and weighed. The thickness of the oil was approximately 5 mm. The tray was placed into a wind tunnel and subjected to a wind speed of 10 m/s at 20°C. Samples were taken from the surface of the oil and the bulk of the oil and run on gas chromatography daily. The tray was also weighed every day. The length of the experiment was 15 days. Log (Cn/C16) versus evaporation time was plotted for each carbon atom (C8–C15) (Figures 35, 36 and 37). Evaporation times when log (Cn/C16) is –1 (C_9, C_{10}, C_{11}, C_{12}) were obtained from the plots (Figure 38).

Theoretical

The conventional treatment of oil evaporation assumes that the entire resistance to evaporation lies in the vapour phase (Stiver and Mackay 1983). In reality the oil phase is not perfectly mixed and in the case of waxy oils, a waxy "crust" may form which offers a resistance to diffusion. We develop here a theory to treat this situation and use it to analyse the experimental data.

Conventionally, the flux of an oil component is given by:

$$N_i = - V dC_i/dt = KAP_i/RT$$

where: N_i is the flux (mol/h)
V is the oil volume (m^3)
C_i is the concentration of i (mol/m^3)
t is time(s)

FIGURE 35

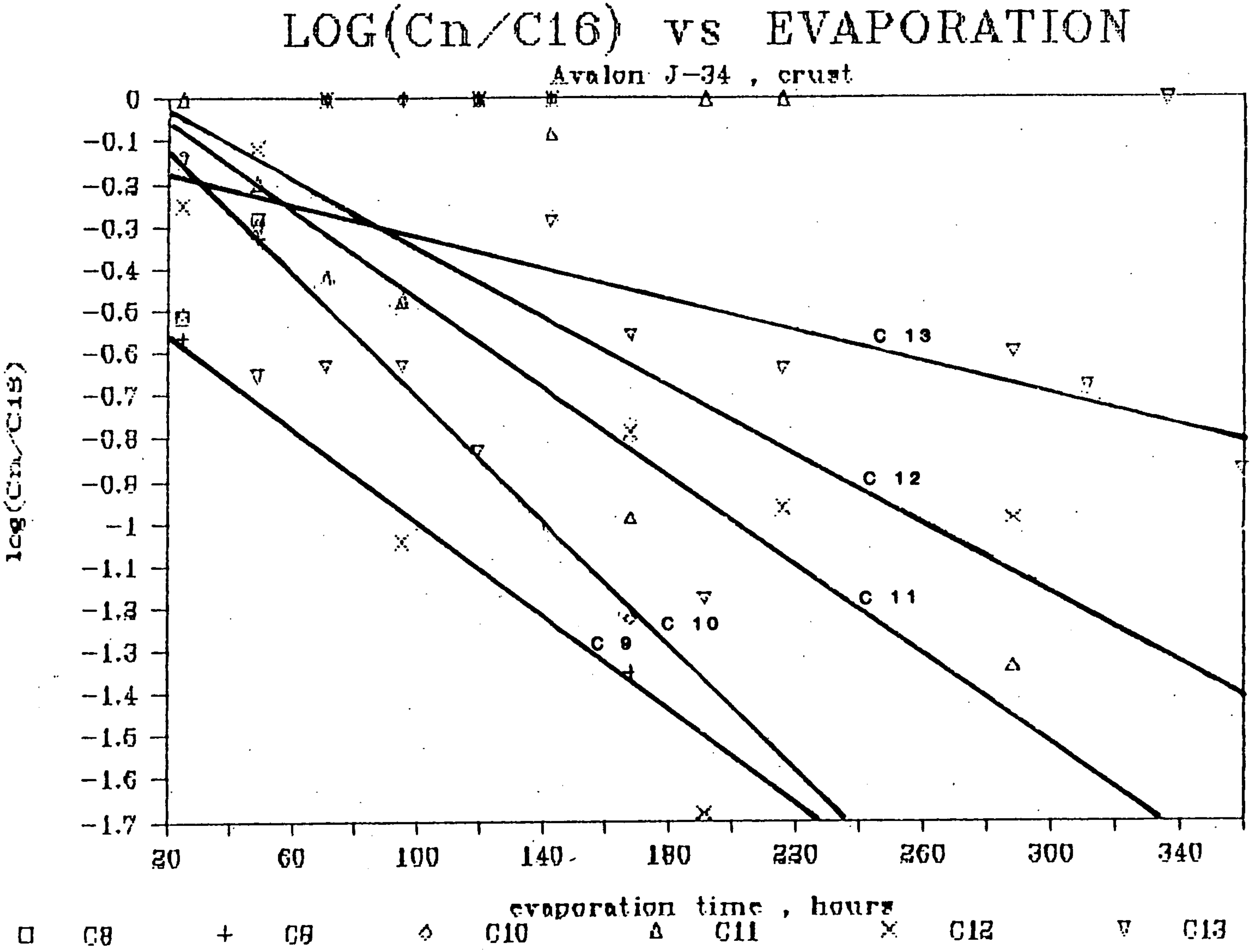

LOG(Cn/C16) vs EVAPORATION
Avalon J-34 , crust
log(Cn/C16)
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
-1.7
20
60
100
140
180
220
260
300
340
evaporation time , hours
C 13
C 12
C 11
C 10
C 9
□ C8
+ C9
◇ C10
△ C11
× C12
▽ C13

FIGURE 36

LOG(Cn/C16) vs EVAPORATION

Avalon J-34 , crust

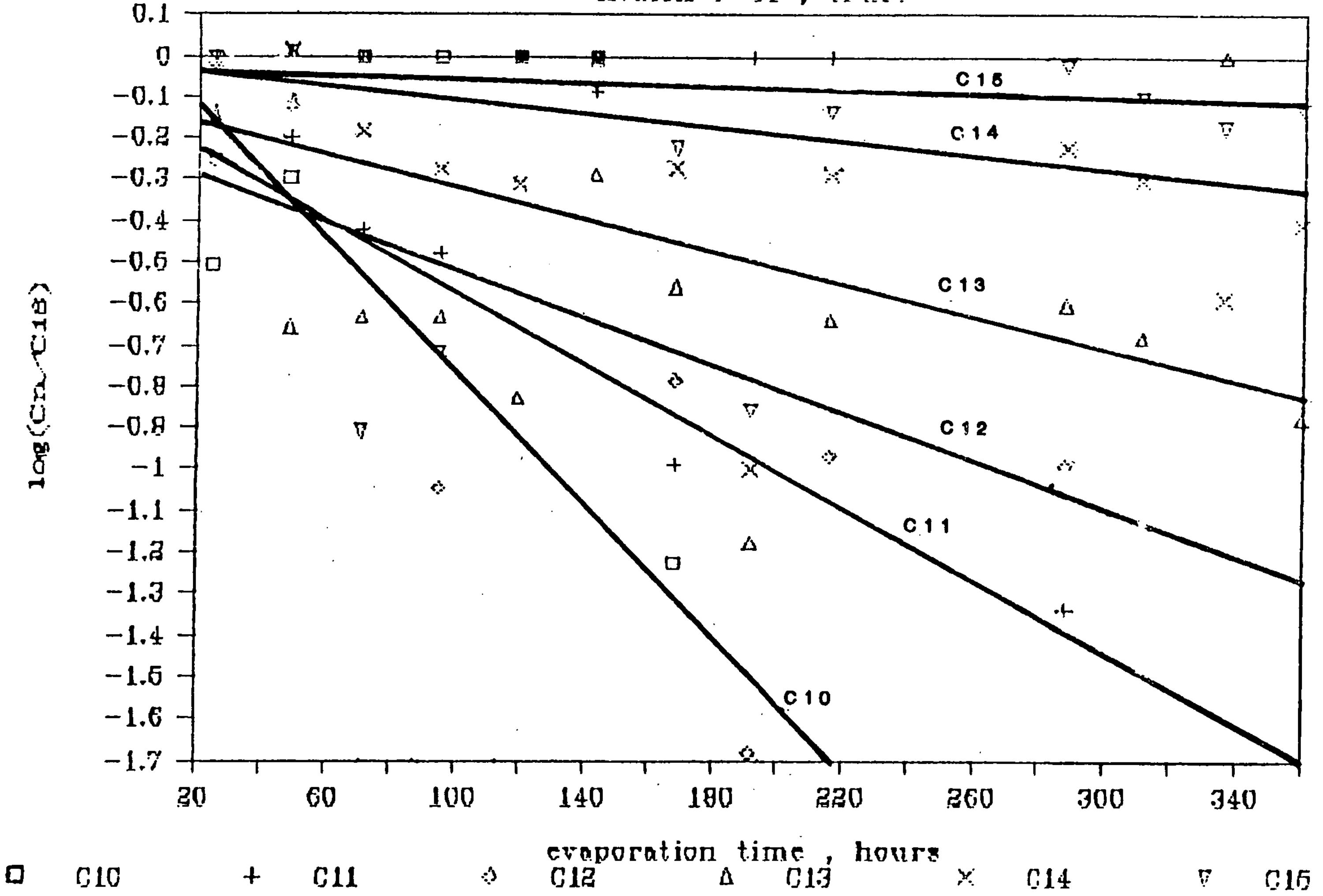


FIGURE 37

LOG(Cn/C16) vs EVAPORATION

Avalon J-34 ,crust

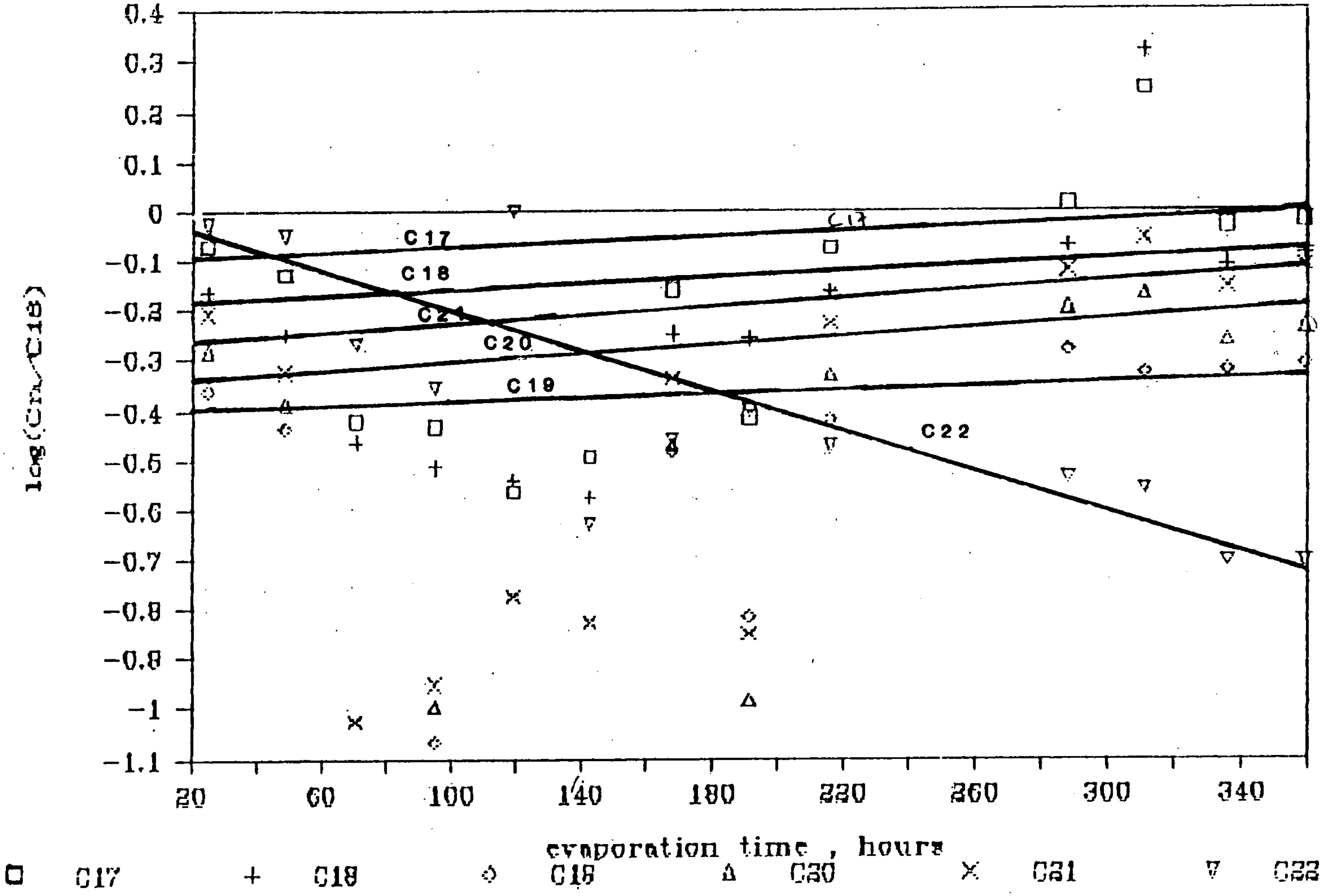
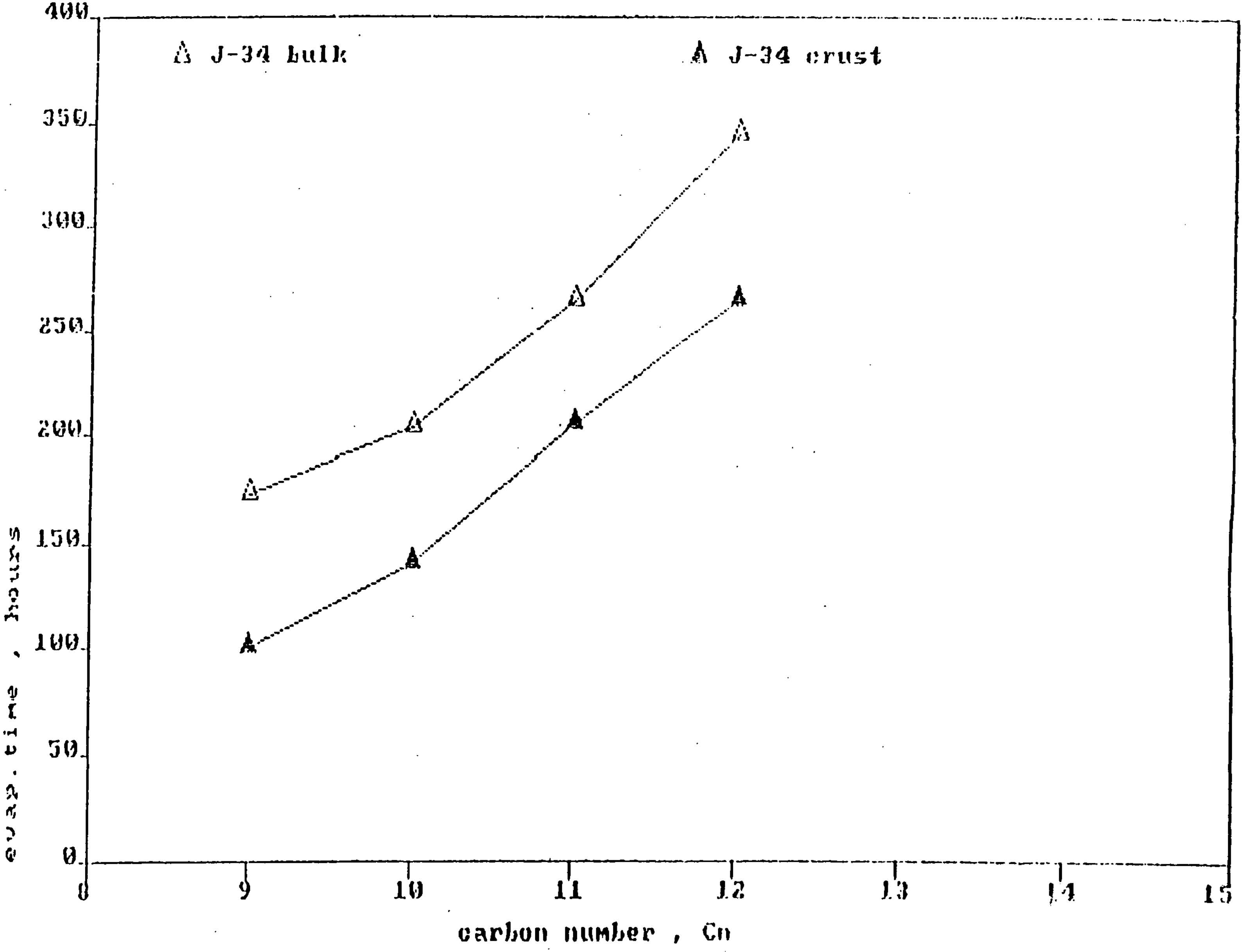


FIGURE 38

EVAP.TIME vs CARBON NUMBER when log(Cn/C16) = -1



K is the mass transfer coefficient (m/h)
A is the area (m^2)
P_i is the partial pressure of i (Pa)
R is the gas constant (8.314 Pa m^3/mol)
T is temperature (°K)

The group P_i/RT is then the concentration of i in the vapour phase at the surface. Now P_i can be related to the concentration of the component and its vapour pressure P^s using Raoults Law.

i.e., $P_i = x_i P^s_i$

where: x_i is mole fraction but
$x_i = C_i v$

where: v is molar volume of the hydrocarbons (m^3/mol)

thus: $dC_i/dt = (KA/V)(P^s{}_i v/RT)^{Ci}$

The group ($P^s iv/RT$) is a dimensionless Henrys Law Constant H i.e., (mol i/m^3 air)/(mol i/m^3 oil)

Integrating gives:

$$Ci = Cio \exp \quad (-(KAt/V)(P^s{}_i v/RT))$$

$$= Cio \exp \ (-\ \theta H) \ = Cio \exp\ (-k_t t)$$

where θ is a dimensionless evaporative exposure and is the ratio of the volume of air saturated with i to the volume of oil, i.e., (KAt/V).

The rate constant k_t is thus:

$$k_t = (KA/V)(P^s{}_i v/RT)$$

This constant can be determined experimentally from plots of concentrations of i versus time. k is the reciprocal of the time taken for Ci to fall to exp (−1) of its initial volume i.e. 0.308. It should be a linear function of vapour pressure. For high vapour press hydrocarbons is it observed (as is discussed later) for the bulk oil that k_t is fairly constant at approximately 3.8×10^{-3} h^{-1} (Figure 39).

We postulate that this is equal to the crust resistance and that we can include this resistance in series using an expression of the form

$$Z_t = Z_c + Z_v$$

or

$$1/k_t = 1/k_c + 1/k_v$$

where Z is a resistance, k the rate constant and subscripts t,c and v refer to total, crust and vapour

The vapour rate constant is:

$$K_v = (K_v A/V)(P^s{}_i v/RT)$$

The unknown is K_v which can be estimated, by rearranging the equations to give

$$RTV/(Av(1/k_t - 1/k_c)) = K_v P^s{}_i$$

A plot of $RTV/(Av(1/k_t - 1/k_c))$ or $RTH/(v(1/k_t - 1/k_c))$ (where h is oil thickness or ratio of volume to area) versus $P^s{}_i$ for each hydrocarbon should give a straight line of slope K_v. This is shown in Figure 40 and gives a value of 9.2 m/h which is in reasonable accord with observed values of evaporative mass transfer coefficients.

FIGURE 39

CORRECTED RATE CONSTANT k VS CARBON NUMBER

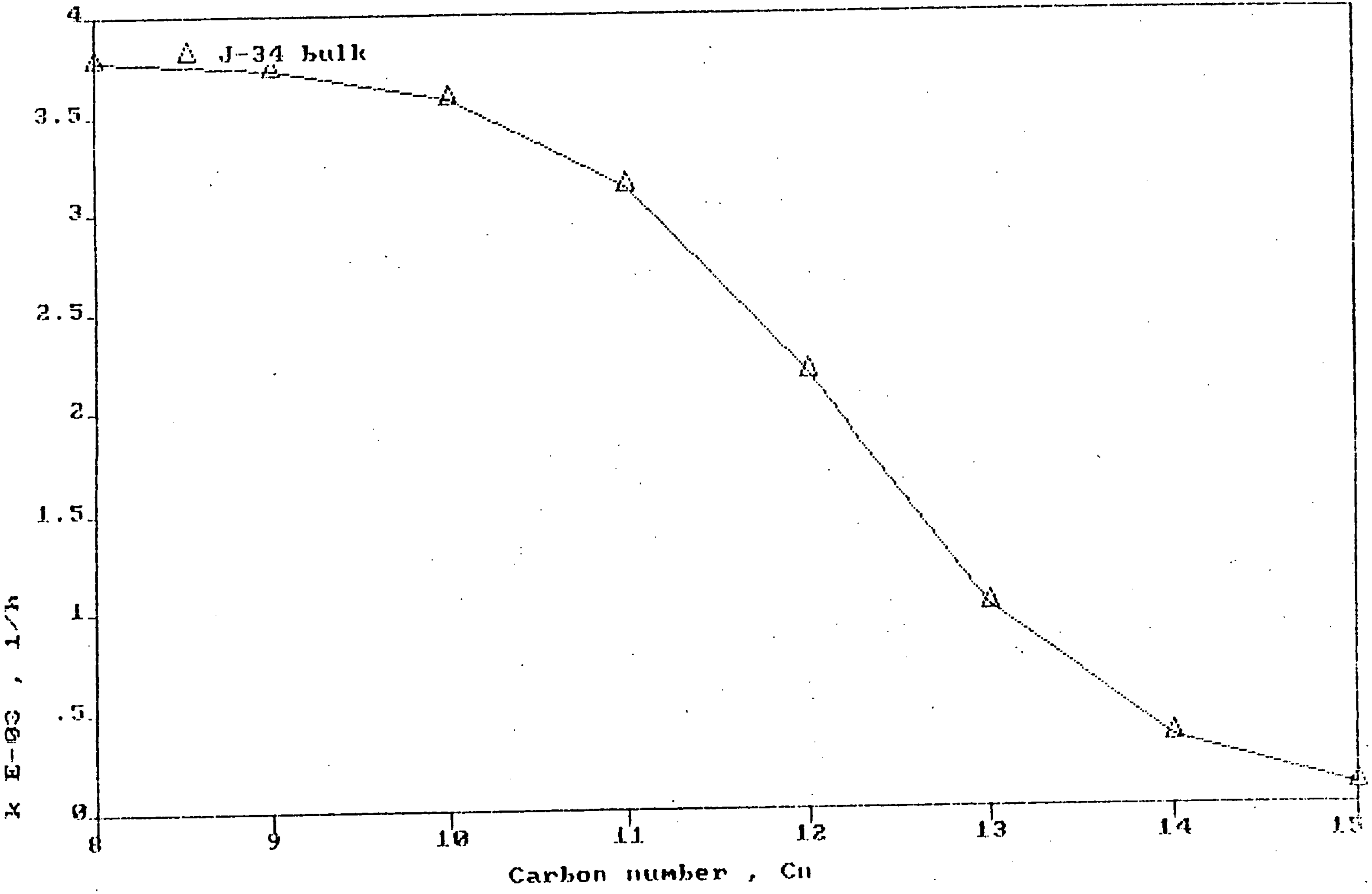
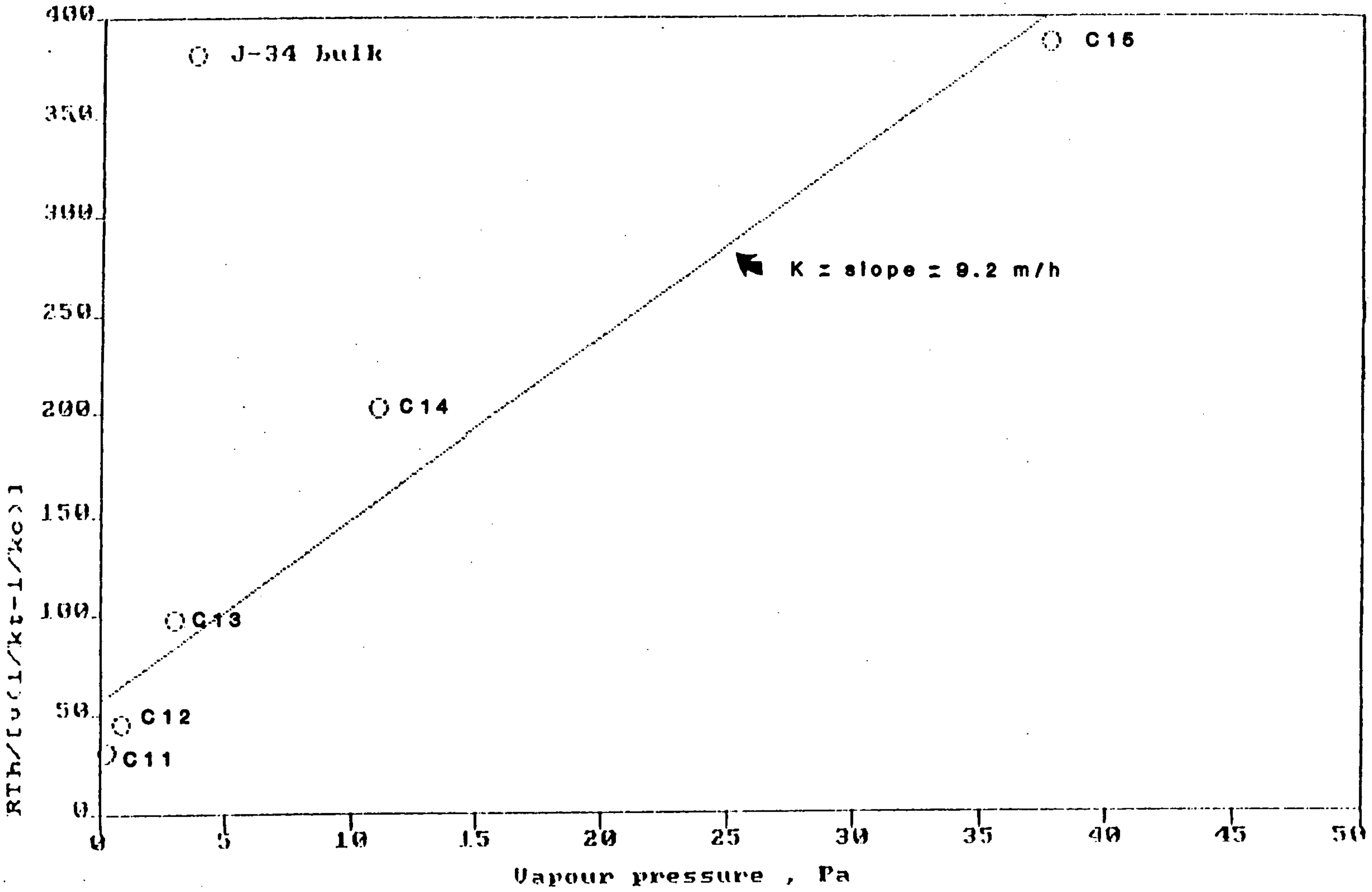


FIGURE 40

MASS TRANSFER CONSTANT K



The overall expression for concentrations of i in the bulk of the oil is thus

$$Ci = Cio \exp(-k_t t)$$

where $1/k_t = 1/k_c + 1/k_v$

and $k_c = 3.8 \times 10^{-3}$

$$k_v = (9.2/h)(P^s{}_i v/RT)$$

The crust resistance is thus most significant for hydrocarbons of large $P^s{}_i$, i.e., large k_v or small Z_v for which k_t approaches k_c.

We thus have, for the first time, developed an equation expressing crust resistance and have quantified that resistance for a waxy crude oil. It is only significant for the volatile hydrocarbons which experience a large value of k_v and thus become rapidly depleted from the crust. Less volatile hydrocarbons evaporate more slowly thus they have more time to diffuse through the crust, thus the crust resistance is less important.

Equal crust and evaporation resistance occur when k_c and k_v are equal i.e.:

$$3.8 \times 10^{-3} = 9.2(P^s iv/hRT)$$

or $P^s{}_i v = 3.8 \times 10^{-3}\ hRT/9.2$

For T of 294 K and h of 0.005 m the right hand side is 5.05×10^{-3}. Since v is typically 3.74×10^{-4} m^3/mol this corresponds to a $P^s{}_i$ of 13 Pa which is approximately the vapour pressure of C_{12} at 20°C.

The absolute magnitude of k_c is of interest. If we regard it as a diffusion resistance then from Fick's Law, the diffusion rate N(mol/h) is given by:

$$N = D\Delta CA/h_c$$

where D is a diffusivity m^2/h, h_c is the crust thickness and ΔC is the concentration difference. If all the resistance is in the crust, as almost occurs for volatile hydrocarbons, ΔC approaches C_i and,

$$-VdC_i/dt = DC_iA/h_c$$

or

$$C_i = C_{io} \exp \frac{-DAt}{Vh_c} = C_{io} \exp(-k_ct)$$

thus k_c is essentially DA/Vh_c or D/h_oh_c, where h_o is the oil slick thickness, i.e., 5 mm.

We have no information about D or h_c, but their ratio D/h_c, which can be regarded as a mass transfer coefficient, is of the order of k_ch_o or 2×10^{-5} m/h. If h_c is 0.1 mm or 10^{-4} m then D must be 2×10^{-9} m^2/h or approximately 5×10^{-9} cm^2/s which is a very low value and possibly characteristic of a waxy film.

It is believed that the fundamentally correct correlating and scaling approach is to use this experimentally determined value of 2×10^{-5} m/h as a liquid phase resistance mass transfer coefficient designated K_c. The rate constant K_c/h_o, or k_c is then approximately 3.8×10^{-3}. We can now invoke the familiar two resistance mass transfer coefficient model which can be written in terms of an overall vapour phase transfer coefficient K_t as:

$$1/K_t = 1/K_v + H/K_c$$

This is essentially a reformulation of the summation of the rate constant equations wth the substitutions:

$$K_t = k_th_o/H$$
$$K_c = k_ch_o$$
$$K_v = k_vh_o/H$$

This equation can be used with typical values of 2×10^{-5} m/h for K_c and 9 m/h for K_v, but these values will vary considerably with wind speed, temperature and the nature of the oil.

To illustrate this approach for a waxy crude oil the data for Avalon J–34 evaporation from troughs was replotted as a function of evaporative exposure θ

including the redefined mass transfer coefficient. The essential point is that 0 is defined in terms of K_t which previously was equated to K_v. By including the group H/K_c, K_t and 0 are reduced thus the equations correctly express the retardation of evaporation due to the crust. An estimate of H is needed, a convenient source being the equation developed by Stiver and Mackay (1983) using the ASTM distillation procedure, namely:

$$H = \exp (6.3 - 10.3 (T_o + T_G F_v)/T)$$

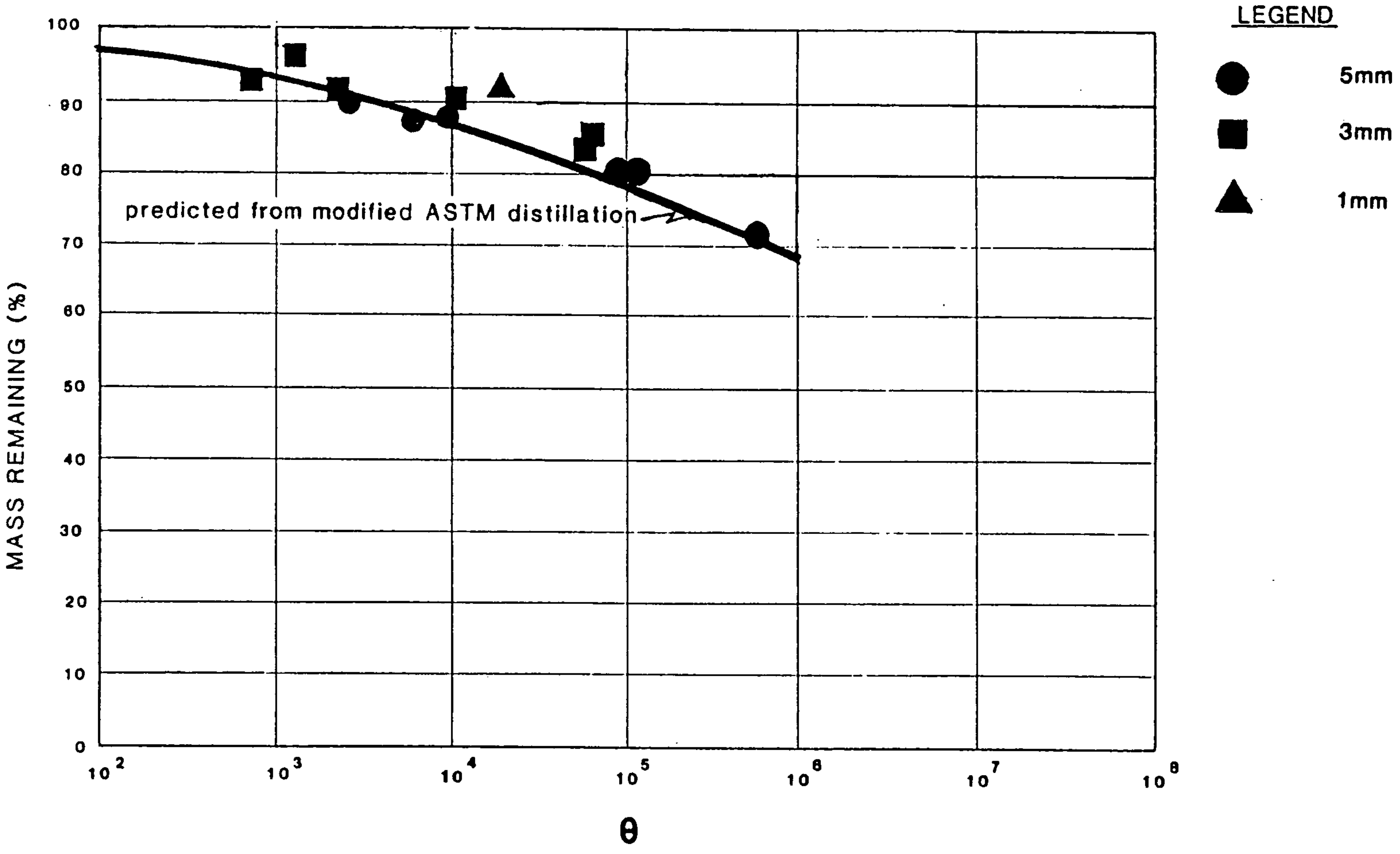
where T_o = initial boiling point (°K)
T_G = slope of the boiling curve (°K)
F_v = fraction volatilized
T = ambient temperature (°K)

In the simulation the following values of K_v and K_c were used:

$K_v = 4.4 \times 10^{-3}$ m/s (from toluene evaporation measurements)
$K_c = 10^{-6} h_o$ m/s, i.e., assuming k_c to be $10^{-6}\ s^{-1}$ or $3.8 \times 10^{-3} h^{-1}$

The results are shown on Figure 41 compared to the original results and the ASTM distillation model. Discounting the 1 mm slick data point, the fit of the data to the model is reasonable and the dependance of evaporation on thickness is adequately removed through the modified exposure coefficient.

FIGURE 4 1
CORRECTED EVAPORATION OF J34 SLICKS



WIND/WAVE TANK EVAPORATION EXPERIMENTS

A series of wind/wave tank experiments were conducted with varying thicknesses of the Mixed Sweet Western, Hibernia B–27 and Avalon J–34 crude oils. These tests are described fully in the next section. One part of the experiments was the sampling of the slicks to determine evaporative loss in more realistic conditions. Samples of each slick were taken after 60, 180 and 420 minutes in the tank, diluted with hexane and sent to the University of Toronto for G.C. analysis. Evaporative loss was determined by comparing the G.C.'s of the samples with G.C.'s of samples weathered by gas sparging to a known degree. Unfortunately, some of the samples were too diluted in hexane to make correlation possible and the accuracy of the remainder is questionable.

BATCH SLICK EVAPORATION

Figure 42 shows the results plotted against evaporative exposure (using the modified technique for the waxy oils) compared to the predictions from the modified ASTM distillations. Although the data fit is poor (because of the difficulty in determining weathering discussed previously, and the problem of determining the slick thickness) the trends in the results are broadly consistent with the prediction.

DROPLET EVAPORATION

Figure 43 shows the results from a series of wind/wave tank runs using 1 mm oil droplets. In this case the modified evaporative exposure is calculated using a "thickness" determined by drop area divided by drop volume (which equals the drop diameter divided by six). The data, taking into account the errors in determining evaporation discussed previously, is in general agreement with the prediction based on the modified ASTM distillation (Stiver and Mackay 1983) and the results for the batch slicks.

FIGURE 42

CORRECTED EVAPORATION OF SLICKS ON WATER

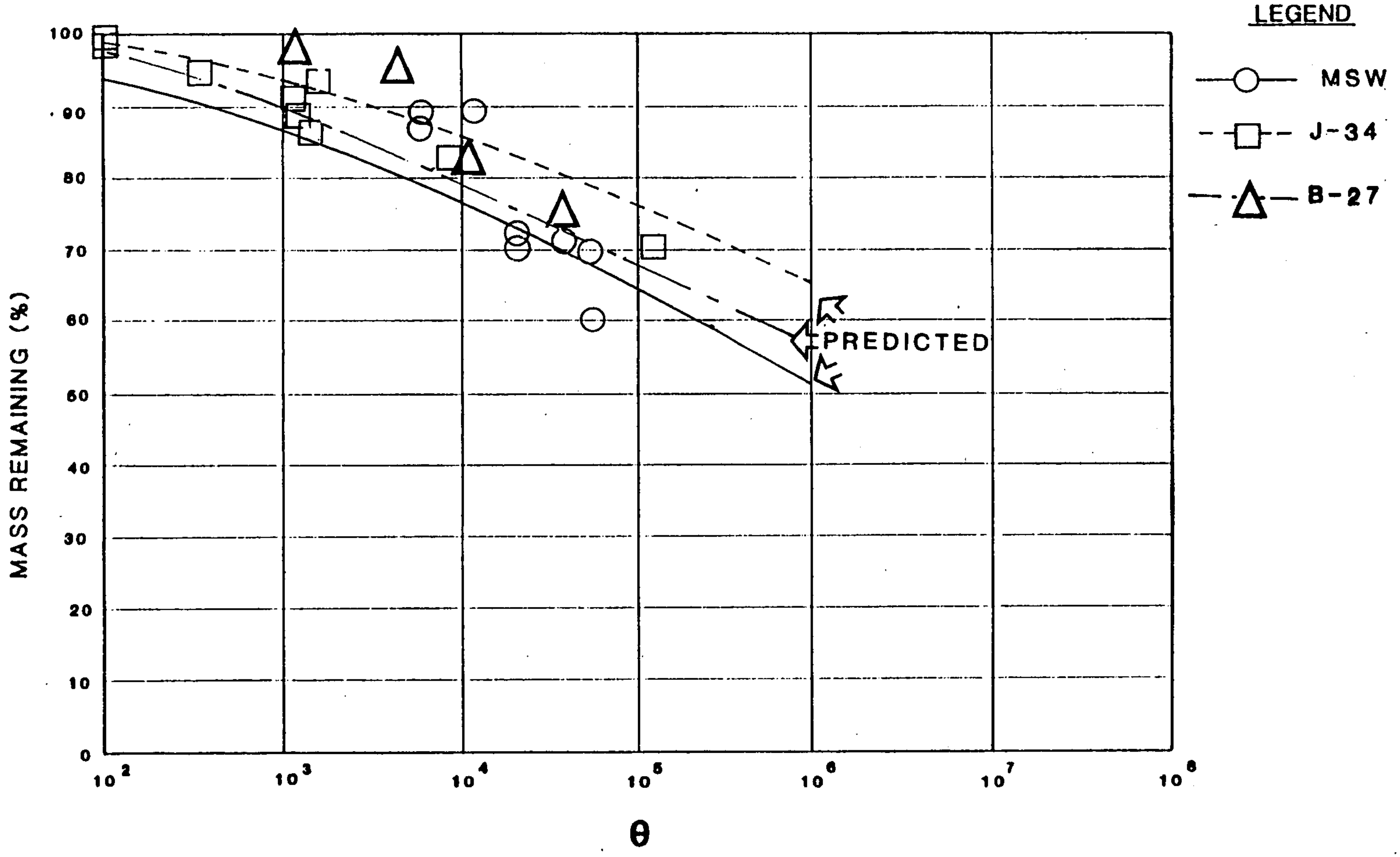
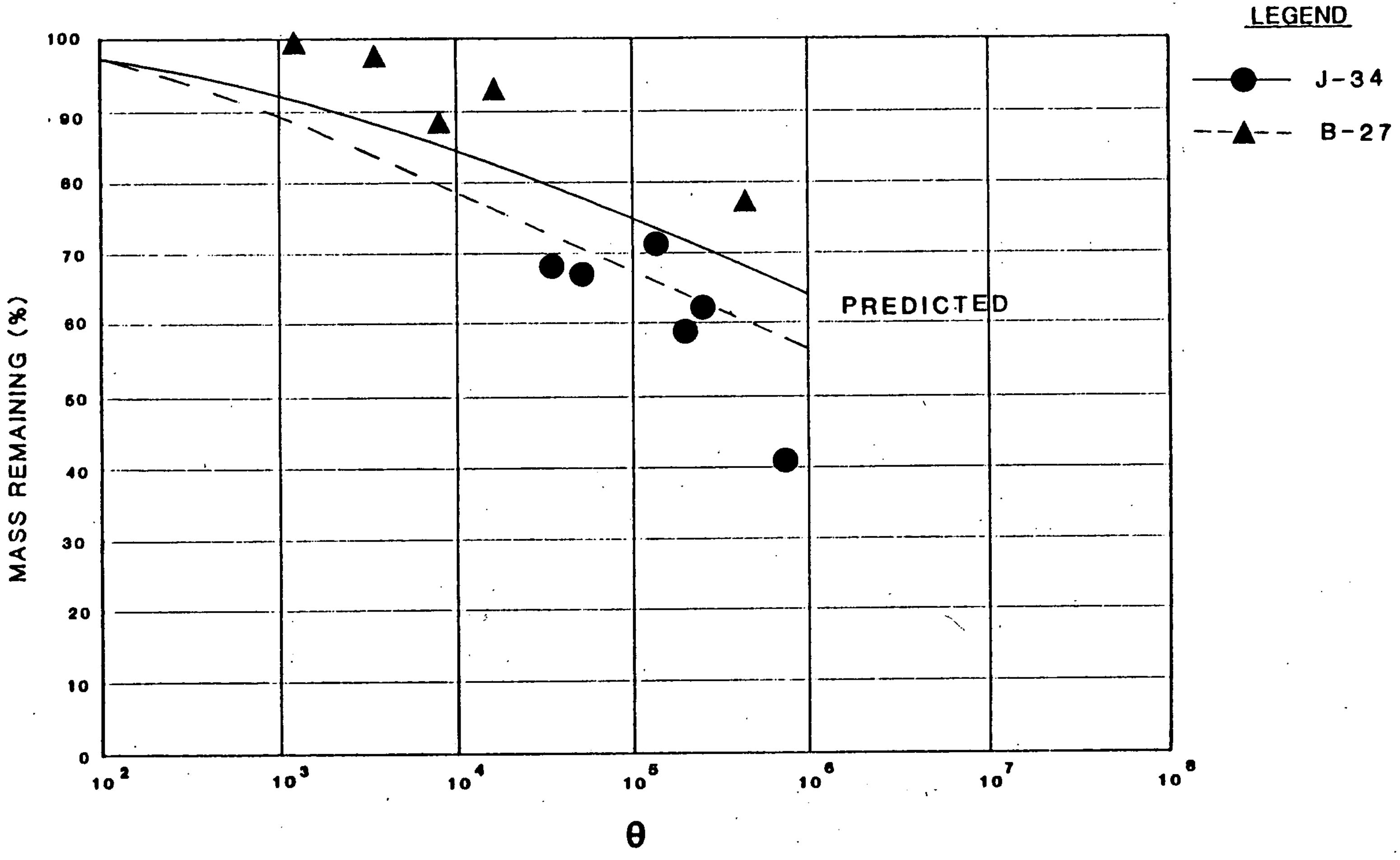


FIGURE 4 3
CORRECTED EVAPORATION OF OIL DROPS ON WATER



This implies that the droplets evaporate at the same rate as a slick of equivalent thickness (or more correctly surface area per unit volume). Since much of the surface area of the droplet is submerged this means that, at least initially the dissolution mass transfer coefficient is approximately the same as the coefficient for evaporation.

Mackay (1985) gives the dissolution mass transfer coefficient as approximately 10^{-2} m/h (1 cm/h) for oil slicks. Assuming that the internal (crust) resistance to mass transfer affects dissolution as well as evaporation the total dissolution mass transfer coefficient is:

$$1/K_{DT} = (1/K_D) + (1/K_{ow}K_c)$$

where

K_{ow} = octanol/water partition coefficient which can be assumed to be approximately equal to the oil–water partition coefficient

which, for the fresh Avalon oil at 5°C yields (assuming $K_{OW} = 10^4$)

$$K_{DT} = 8 \times 10^{-3} \text{ m/h}$$

the evaporative coefficient is

$$K_{ET} = 1/((H/K_c) + (1/K_v))$$

$$= 2 \times 10^{-2} \text{ m/h}$$

Thus, initially evaporation and dissolution would start at approximately the same rate; as the oil is leached of its light ends evaporation would greatly predominate over dissolution. Due to the data scatter and the difficulties in determining oil/water partition coefficients it is not possible to say whether or not the droplets are simply evaporating or dissolving and then evaporating. Regardless, the trend seems to indicate that droplets lose light ends at a rate roughly equal to the rate of a slick with the same surface area per unit volume.

CONCLUSIONS

All previous accounts of oil evaporation have made the assumption that the oil film is well mixed, or equivalently that there is no diffusive resistance in the oil phase.

In this study we have assembled for the first time, a theoretical framework which can address this issue quantitively. Experimental data have been gathered and interpreted which demonstrate convincingly that the "crust" resistence is real and can be appreciable. All existing oil spill models will thus appreciably overestimate the evaporation rate of volatile hydrocarbons for waxy oils. Essentially, the development of a waxy crust "traps" the volatile hydrocarbons in the oil mass retarding evaporation. These findings and modelling procedures may have applications in other areas of oil spill research and countermeasures.

SPILL BEHAVIOUR STUDIES

In this section two types of tests on the spill behaviour of waxy oils are discussed. The first tests involved investigating the emulsification behaviour of the three selected test oils in rotating flasks, the second series of tests comprised observations and measurements of slick behaviour, emulsification and natural dispersion over a period of hours in a wind/wave tank.

EMULSIFICATION

Background

An emulsion is formed when oil incorporates water into itself. This water is in the form of droplets which can range in size from millimeters down to microns. An emulsion usually contains from 50–90% water by volume, thus drastically increasing the volume of the spill.

Emulsion viscosity can be several orders of magnitude greater than the parent oil. This can make clean–up methods (i.e., skimming, pumping) difficult or impossible. Also, the emulsion resists both natural and chemical dispersion. Therefore a stable emulsion could survive a long time on the ocean surface.

Therefore, two characteristics of an oil that have a significant influence over the success of clean–up operations are the tendency of an oil to emulsify and the stability of the resulting emulsion. Mackay and Zagorski (1982) developed a simple bench–scale test that generates indicators for these two properties: F_0 is a measure of the tendency of the oil to emulsify, whether stable or not; and F_{00} is a measure of the stability of the emulsion formed. These indicators are interpreted as follows: 0 to 0.25 – low tendency or stability; 0.25 to 0.75 – moderate tendency or stability; 0.75 to 1.0 – high tendency or stability.

Test Design

Emulsification testing was carried out using the Zagorski apparatus (Mackay and Zagorski 1982). Water (300 ml) and oil (30 ml) were placed in a closed glass cylinder which was mounted in a frame and rotated end–over–end at 65 rpm for one hour.

The cylinder was then left to settle, in an upright position, for 30 minutes before height measurements (total, oil and emulsion, oil) were taken. This cycle of mix, settle, measure was then repeated three more times. Final measurements were taken after the fluids had settled for 24 hours. Viscosities of the emulsions at four hours were measured using a Brookfield viscometer at the lowest shear rate (0.3 rpm).

Results

The results are summarized in Table 9. F_0 is the volume fraction of oil in the emulsion at time zero. It is calculated by extrapolating back to t=0 using the values of emulsion oil content measured at 1.5 and 6 hrs during the test. As mentioned before, F_0 indicates the tendency of an emulsion to form. F_{∞} is the volume fraction of oil in the emulsion at infinite time and an indicator of the stability of the emulsion. In this test, 24 hours was considered to represent infinite time.

Discussion

Tendency and Stability. At 5°C, all three oils are very susceptible to emulsion formation despite the fact that 5°C is below the pour points of both Avalon J–34 and Hibernia B–27. The emulsions formed from the waxy crudes were very stable whereas the MSW emulsion was only moderately stable.

At 15°C, the MSW had a moderate tendency to produce an unstable emulsion. The waxy crudes had a high tendency to emulsify and the resulting emulsions were moderately to very stable.

TABLE 9

RESULTS OF EMULSIFICATION TESTING

Temperature	Oil	F_o	F_{oo}	H_20 in Stable[1] Emulsion (vol. %)	Viscosity of Stable Emulsion (mPa.s)	Colour of Emulsion	Viscosity Fresh Oil (mPa.s)
5°C	MSW	1.0	0.66	93.86	60,750	black	18.5
	J–34	1.0	1.0	89.17	120,000	mid brown	140,000*
	B–27	1.0	1.0	90.14	41,750	dark brown to black	72,000*
15°C	MSW	0.42	0.11	97.83	39,500	black	13.5
	J–34	1.0	1.0	89.41	84,250	mid brown	60,000*
	B–27	0.96	0.66	86.40	17,750	dark brown to black	62,000*

Note: For comparison purposes: viscosity of water: 1 mPa.s
viscosity of peanut butter: 150,000 mPa.s @20°C

* below pour point

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1. "Stable emulsion" is the emulsion that existed at 24 hours.

The effect of entrained water droplet size could be seen. The Avalon J–34 emulsion appeared to have the smallest drop size and was the most stable. The Hibernia B–27 emulsion was moderately stable and contained a significant number of large water drops.

Temperature Effect. All emulsions had a greater tendency to form at the lower temperature, and the emulsions were more stable as well.

Viscosity. Viscosity is a function of temperature, and as expected the emulsions were more viscous at the lower temperature. However, the emulsions made from the waxy crude oils did not show as dramatic an increase in viscosity as that shown by the typical MSW. The MSW emulsions were in the range of 3000 times more viscous than fresh MSW. The waxy crude emulsions, however, had viscosities comparable to their fresh oil counterparts. The measurements using the Brookfield viscometer at temperatures at or near the pour point are, however, questionable (see Rheology). The viscosity of the waxy crude emulsions ranged from 0.29 to 1.25 times the viscosity of the parent oil.

Water Uptake. The emulsions had water contents between 86 and 98%. The J–34 emulsion appeared to contain the smallest droplet size, and the B–27 emulsion had drops that were quite large and could be easily seen.

Colour and Appearance. The J–34 emulsion was uniform in appearance and brown in colour. It had the characteristics of typical "chocolate mousse". The B–27 emulsion was very dark brown, nearly black, in colour, but it did not appear uniform because of the large number of large water drops throughout. The MSW formed a black emulsion, appearing to be a typical emulsion that was stable only because of the temperature. The water drops were visible, but not overly large.

Conclusions

Under the conditions tested (5°C, 15°C and 65 rpm mixing energy), the waxy crude oils form stable emulsions and do so fairly quickly. The J–34 oil produced the most viscous emulsion which had the appearance of true "chocolate mousse".

At 5°C, the emulsions were very viscous and very stable. This decreased somewhat at 15°C. Water uptake was consistently in the 90% range at both temperatures.

The most interesting aspect of the test was that the viscosities of the emulsions of the waxy crudes were not significantly different from the viscosity of the parent oils and in three of four cases were actually lower. This is in stark contrast to the 3000-fold increase in the MSW emulsion.

Recommendations

A correlation between sea states and the mixing energies of the Zagorski apparatus should be investigated. The Zagorski apparatus provides a simple mixing system but since emulsion formation and stability are closely related to input energy, a real-world meaning to "65 rpm" is needed.

WIND/WAVE TANK TESTS

A series of tests were carried out in the wind/wave tank of the S.L. Ross laboratory. The purpose of the tests was to observe the behaviour of both batch and blowout slicks over a seven-hour period, and to investigate the applicability of several types of countermeasures. The following sections describe the test facility, the general test procedure, and a summary of each test run. Following that are the results and a discussion of the countermeasures portion of the experiments.

Test Facility

The wind/wave tank, Figure 44, is 11 m long by 1.2 m wide by 1.2 m deep. A variable speed paddle at one end provides wave action; at the opposite end a high speed fan delivers outside air, opposing the waves and thus keeping a slick stationary. The top of the tank is covered with hoods, some of which have entry-ways to permit sample-taking and one of which has a clear plexiglass cover to allow

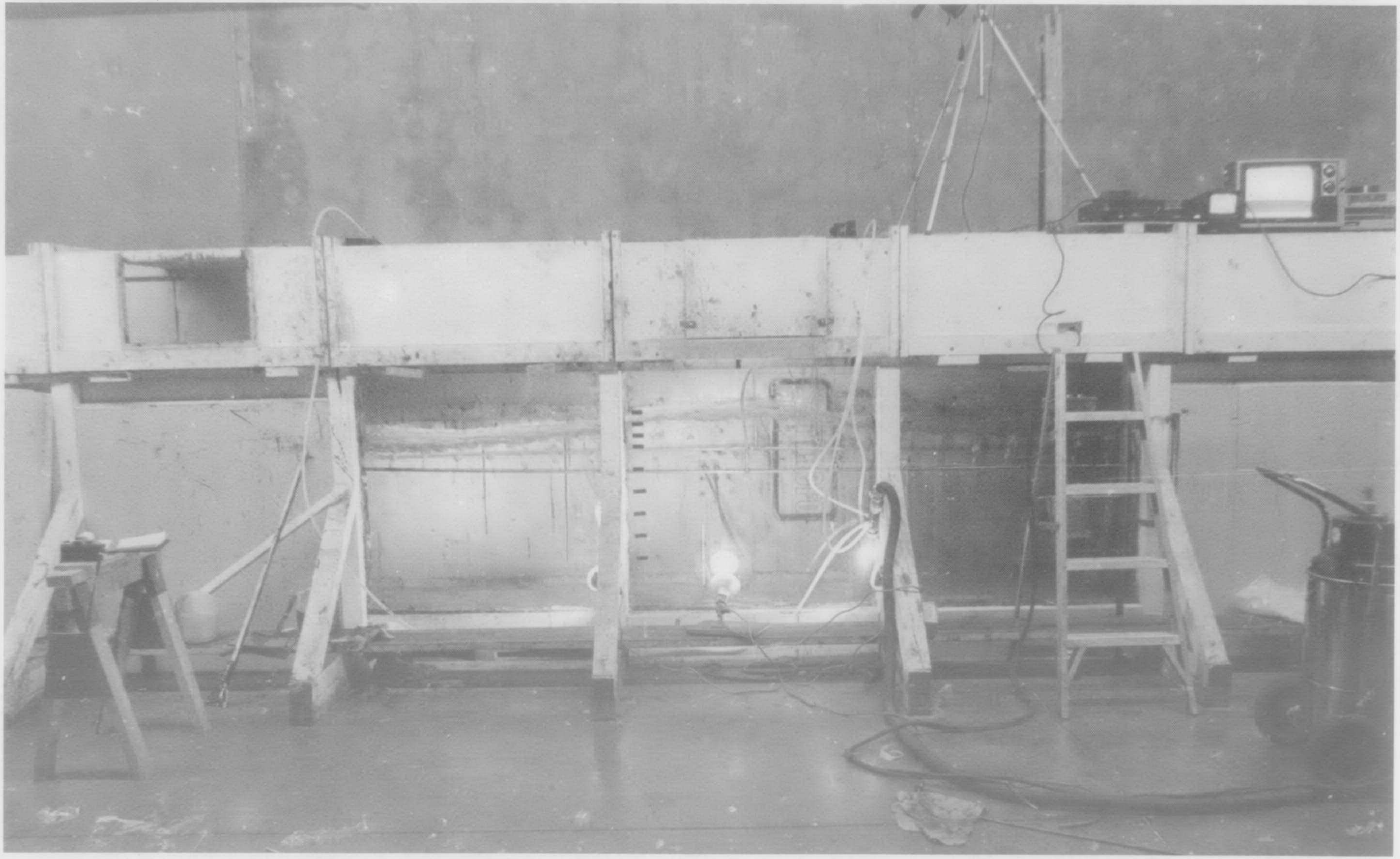


FIGURE 44 - Wind/wave tank

overhead observation and video-taping. As well, three central sections of the tank have glass walls to allow direct observation of the slick and underlying water.

General Test Procedure

The test matrix comprised three oils (Mixed Sweet Western (MSW), Hibernia B-27 and Avalon J-34), two water temperatures (5° and 15°C), two wind/wave energies (denoted as low and high energy), two spill types (batch and blowout), and two slick thicknesses for the "batch" spills. For each oil and water temperature combination, the tank was filled with fresh water and chilled to the desired temperature using ice. The oil was heated prior to pouring to allow uniform application in the tank.

For the batch-type spills, a measured amount of oil was poured into the water within a containing ring, producing a slick of approximately uniform thickness. The oil volume corresponded to an average slick thickness of 1 or 5 mm. Several minutes were allowed for the oil temperature to equilibrate with that of the water, after which the containing ring was removed.

For the blowout-type spills, the heated oil was discharged through a nozzle, driven by air pressure, positioned near the tank bottom. After some experimentation with various nozzles and different air pressures, fairly uniform droplets of 1 mm diameter (representing drops from a subsea blowout) were produced. The oil discharge line and nozzle were enclosed in a jacket that contained warm water to prevent the waxes in the oil from precipitating prior to discharge. A gentle wave action was applied to the tank during the oil droplet discharge; this dispersed the plume of droplets as it left the nozzle and prevented the droplets from recoalescing during their rise to the surface.

For both spill types, following the presentation of oil as described above, the tank hoods were re-installed and the wind and waves were started. For a period of seven hours, the wind and waves were maintained at a constant level, corresponding to high or low energy, except for occasional adjustments made to re-centre the slick in the tank.

Observations of the tests included:

- visual observations of slick behaviour;
- (overhead) video record of slick behaviour and fragmentation;
- surface samples for emulsified water content and weathering (determined by GC); and
- dispersed oil concentration at depth.

A description of each test run is presented in Appendix II.

Following most test runs, countermeasures tests were performed on the surface slick that remained. The countermeasures tests included tests of the oil's ability to be sorbed with PVC surfaces or synthetic sorbent pads, tests of the oil's ability to be burned in–situ, and tests of the oil's behaviour when concentrated with conventional containment booms and net–type booms. The procedures used and the results are fully described in a section following the test run descriptions.

Summary of Wind/Wave Tank Tests

Mixed Sweet Western. MSW was used in the testing as a standard non–waxy crude oil for the purposes of comparison. Its observed behaviour was as expected, exhibiting fluid properties when fresh and slightly weathered, dispersing into the water column (especially at the higher energy used), and forming a viscous water–in–oil emulsion.

In the tests with thin slicks (1 mm), the slick eventually broke up into patches of emulsion 5 to 20 mm in diameter. The emulsion, while viscous, was still fluid, but the patches did not recoalesce with each other. With the thicker slicks (5 mm), the fragmentation process was more gradual; the slick developed long finger–like patches that were broken down over time to patches up to 100 mm in diameter. In the tests with droplets, the oil droplets quickly recoalesced, at both temperatures tested, to form a batch slick that behaved in a manner similar to the 1 mm and 5 mm slicks.

Dispersed oil concentrations were low for the low energy tests, measured in the range of 5 to 20 ppm, and slightly higher for the high energy tests, measured in the range of 10 to 40 ppm for the droplet and 1 mm batch slicks and 40 to 70 ppm for the 5 mm batch slick. Water–in–oil emulsification was substantial, with no great difference according to wave energy or temperature: emulsified water contents were generally in the range of 50 to 70% by volume.

Hibernia B–27. This oil was used as a representative moderately waxy crude oil. As its pour point is about 9°C, it behaved quite differently in the tests carried out at 5°C than in the 15°C series. In the 15°C tests, the oil behaved in a similar manner to the non–waxy MSW. Both thin and thick slicks at this temperature quickly broke up to form small patches of extremely viscous emulsion. In the "blowout" test, the droplets quickly recoalesced and behaved similar to a batch slick.

In the 5°C tests, behavioural differences were immediately obvious. For one, when poured onto the water surface, the oil failed to fill the spill containing ring as it had in the higher temperature tests and in all MSW tests. During the pouring of the oil, the leading edge of the advancing slick appeared to gel and resist further spreading. Secondly, when the wave action was started, the slick quickly shattered, resulting in irregularly shaped patches of oil. These patches developed a greater thickness over time; at low energy this appeared to be caused by the collision of patches, giving them rounded, built–up edges (Figure 45), and at high energies the patches appeared to be balling–up into clumps. In the "blowout" tests at 5°C, the droplets matted together but did not immediately coalesce (Figure 46). In time, and particularly at high energy, these mats tended to lose their textured appearance as each mat consolidated into a thick clump (Figure 47).

Dispersed oil concentrations were very low for the low energy tests and the high energy tests at 5°C, generally less than 10 ppm, and slightly higher for the high energy tests at 15°C, 20 to 35 ppm for the 1 mm batch slick and 10 ppm increasing with time to 100 ppm for the 5 mm slick. Water–in–oil emulsification was substantial, with no apparent difference according to wave energy, or initial slick conditions: emulsified water contents were in the range of 20 to 50% by volume in the 15°C tests, and 40 to 60% in the 5°C tests.

Figure 45: Consolidation of oil patches against boom (run B7)

Figure 46: Agglomeration of oil droplets, five minutes after discharge (run B10)

Figure 47: Oil clumps, after three hours (run B11)

Avalon J–34. This oil had the highest pour point of the three tested. Its pour point was about 18°C and, as with the B–27 oil, it behaved quite differently at 5°C than in the 15°C series.

In the 15°C tests, the oil behaved, at least initially, in a manner similar to the other two oils. This may be a result of poor reconstitution of the oil prior to these tests. The slick fragmented into patches of viscous emulsion, patches that would not recoalesce with each other.

In the 5°C tests, as with the B–27 oil, the oil did not spread uniformly when it was initially poured onto the water surface. When the wave energy was started, the oil slick immediately shattered like a pane of glass, resulting in irregularly shaped patches of oil. These patches appeared to be semi–solid, and at high energy, tended to form thick clumps as the result of collision between patches (Figure 48).

In the droplet tests at 15°C, the droplets quickly recoalesced to form a slick that behaved similar to the previous batch–type slicks. At 5°C, the droplets retained their individual shape for a few hours, but in the first few minutes they agglomerated, but did not recoalesce, to form mats 20 to 100 mm in diameter (Figure 49). Initially, these mats had a textured appearance as the droplets retained their individual shape. Over time, these mats tended to ball–up, forming clumps 10 to 15 mm thick and 10 to 30 mm in diameter and with a more rounded appearance (Figure 50).

Dispersed oil concentrations were low for all tests with J–34, less than 10 ppm in the low energy tests, 5 to 15 ppm in the high energy tests at 5°C, and 10 to 30 ppm in the high energy tests at 15°C. Water–in–oil emulsification was also much lower than for the other two oils: at 15°C, emulsified water contents were measured in the range of 15 to 40% by volume, and at 5°C, at high energy, nine measurements revealed only six with emulsification (in the range of 4 to 16%), and at low energy, nine measurements yielded only two with emulsification (measured at 9%). These results contradict those obtained in the Zagorski apparatus; energy level obviously plays a strong role in emulsification of waxy oils.

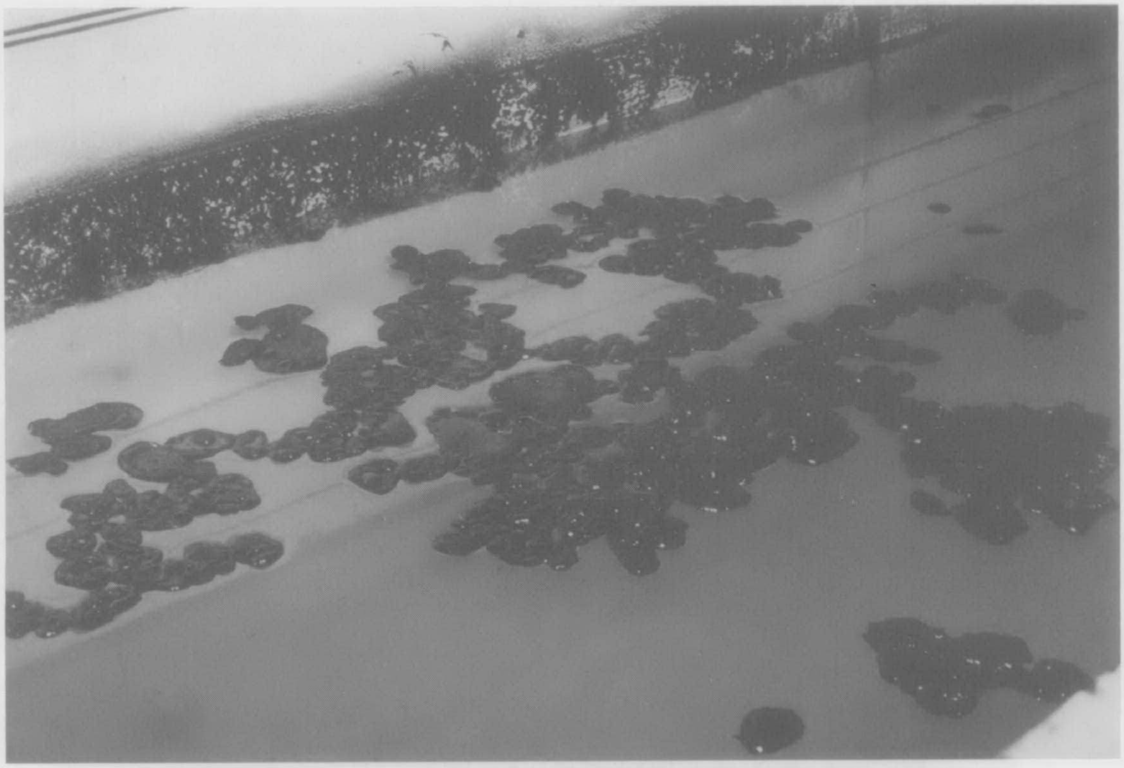


Figure 48: Patches of J–34 oil, after seven hours (run B13)
(waxy skin is apparent)

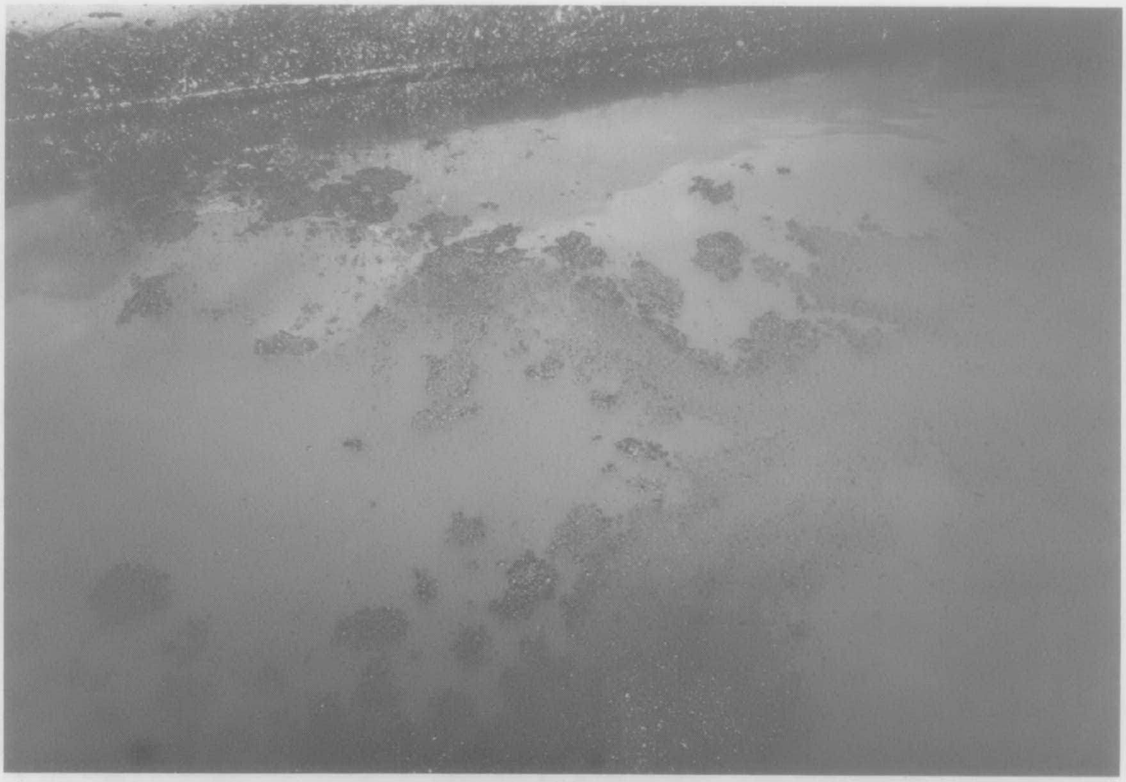


Figure 49: Agglomeration of oil droplets, five minutes after discharge (run B17)

Figure 50: Clumping of matted oil droplets, 15 minutes after discharge (run B17)

COUNTERMEASURES TESTS

In this section, the results of a series of simple countermeasures tests are described. The intent of the tests was to determine the applicability of the main conventional response techniques to waxy oils that have been weathered for several hours.

The five countermeasures techniques examined were containment with conventional booms, sorbing with PVC and synthetic sorbent pads, in–situ burning, containment with net–type booms, and chemical dispersion. All except chemical dispersion were carried out in the wind/wave tank at the completion of a test run, usually one involving a 5 mm batch slick due to the volume of oil required. Chemical dispersion testing was carried out separately in a hoop–tank apparatus, using fresh oil.

CONTAINMENT WITH CONVENTIONAL BOOMS

Three methods were used to simulate conventional containment techniques and their applicability to the test oils. These were: collecting the oil by towing a floating barrier along the length of the tank; using the tank's wind system to drive the oil against a fixed barrier perpendicular to the air flow; and using wind to drive the oil against a fixed barrier angled at 45° to the wind (as might be the case with a V–shaped booming system with a skimmer). All three oils were tested with two or more of these methods.

In booming tests with MSW, the patches of oil stuck together to form a viscous mass when forcibly confined. It was clear that the patches did not truly coalesce, for when released from the boom, most of the patches broke free and took their original form. This observation was demonstrated more clearly when the patches were blown against a barrier; with less confining force, the patches retained their original form among the confined slick and when released from the barrier, they floated free as distinct patches.

In booming tests with B–27, the lack of recoalescence was more distinct. Even when forcibly confined within the containment barrier, the patches resisted complete agglomeration and open areas of water and light sheen were visible between the patches. When released, the patches floated freely.

In booming tests with J–34, the lack of recoalescence was even more distinct than with the B–27 (for example see Figure 48). The oil patches resembled and behaved as semi–rigid "ice floes". The ice floe analogy is apt, considering the irregular shapes of the oil patches and their poor consolidation when confined with a boom. When the containment barrier was fixed at a 45° angle to the tank wall and wind was applied to drive the oil patches against the barrier, the patches jammed against one another in a manner similar to an ice jam. This prevented the patches from consolidating, and prevented their flowing to the downwind end of the boom. In a real–life situation, this phenomenon could seriously hamper a conventional boom and skimmer operation, because a V–shaped containment system would not receive a continuous feed of oil.

Sorbents

The use of sorbents was tested to determine the applicability of oleophilic type skimmers to waxy oils.. It was suspected that waxy oils, and particularly the waxy crust formed on the surface of such oils, could inhibit efficient adsorption.

Sorbent tests were carried out with B–27 and J–34, using PVC plastic (as is used in many oleophilic disc skimmers) and a synthetic sorbent pad (manufactured by Sorbent Products Co., represents material used in oleophilic belt skimmers). With each sorbing material a 100 by 100 mm sample was used. With the PVC material, the PVC was slowly pushed vertically down through the mass of oil, as it would be in the case of a disc or drum skimmer. The sorbent pad was placed on the oil slick, applying gentle pressure to allow the oil's buoyancy to aid adhesion onto the pad. In each case, the sorbent material was cooled to the test temperature (15°C or 5°C) prior to use; this was particularly important for the tests with weathered J–34 because a "hot" sorbent surface would cause the waxy skin on the oil to "melt", causing the oil to slide off the surface.

In tests carried out at 15°C, both oils were sorbed effectively by both sorbent materials. The PVC surface sorbed 18 g and 15 g of B–27 and J–34, respectively, and the pad sorbed 25 g and 28 g, each per 10^4 mm^2 of surface area.

In the tests carried out at 5°C, the B–27 oil produced a similar result, 19 g on PVC and 21 g on the sorbent pad.

However, in three tests using the PVC and J–34 oil, the oil being the result of a droplet test, a low energy batch slick test, and a high energy one, no oil was sorbed. In one case, some oil appeared to initially stick to the PVC but it quickly dripped off, despite gentle handling and the previously mentioned precautions with respect to sorbent temperature. The sorbent pad fared slightly better, sorbing 35 g of oil that resulted from the droplet test run. However, in the two other tests with J–34, very little oil was sorbed. The poor results with both the PVC and the sorbent pad on the J–34 oil reflect the oil's higher wax content and its formation, over time, of a waxy surface crust that resists sorption.

Burning

Four in–situ burning tests were carried out in the wind/wave tank following test runs A8, A13 (B–27 and J–34, each a 5 mm slick, low energy, 15°C), B9, and B15 (B–27 and J–34, each a 5 mm slick, high energy, 5°C). In each burning test, the oil remaining from the test run was contained within an aluminum containing ring in the middle of the wind/wave tank (Figure 51). The oil was then further concentrated within the ring; the contained area was typically 0.11 m^2 and the initial oil thickness up to 10 mm. Diesel soaked sorbent pads were used to ignite the oil. During the burning, the tank's fan was used periodically to exhaust smoke from the laboratory. However, this was used sparingly as it had an adverse effect on the flames in all but one of the test burns. The tests were videotaped to provide a record of flame spread and burn times. Burning efficiencies were estimated visually, and compared to pre– and post–burn slick thicknesses. Relative comparisons (i.e., test to test) could also be made using the product of burn time and area.

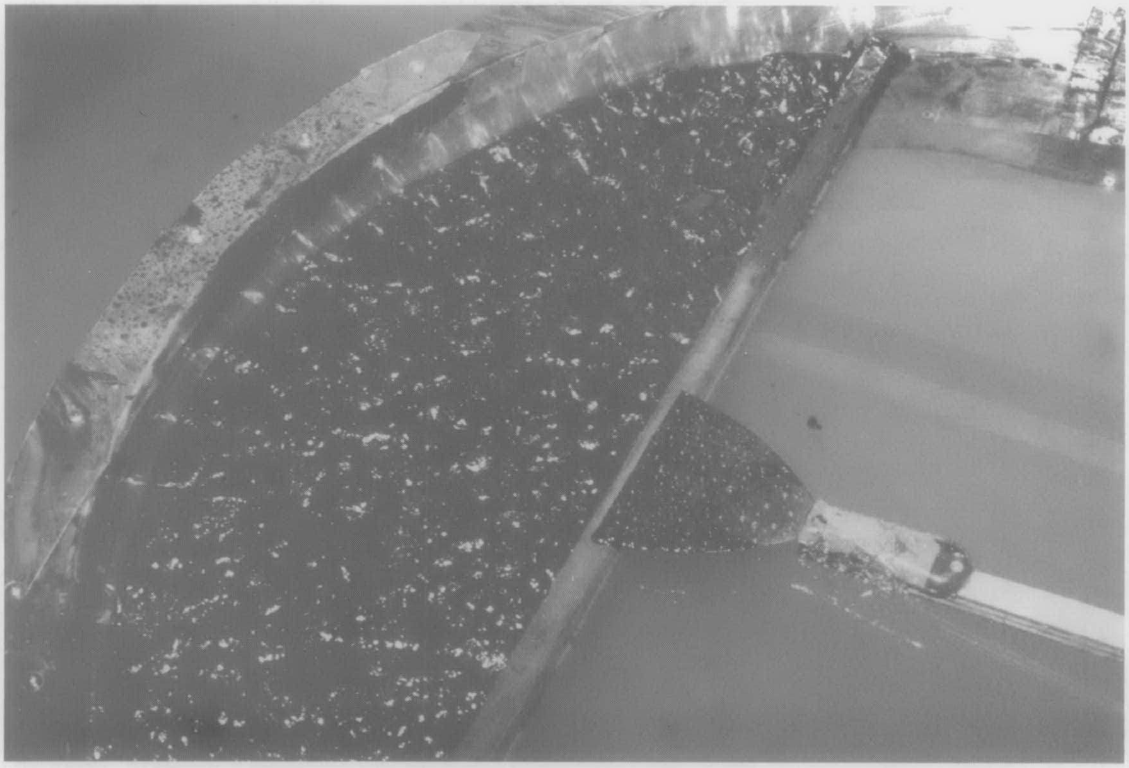


Figure 51: Oil confined within ring for burning tests

The two tests carried out at 15°C were moderately successful. Ignition of each oil was achieved without great difficulty, but burn efficiencies of only 15% for the B–27 and 25% for the J–34 were estimated. The burning test of B–27 at 5°C was slightly better. Two successive burns were conducted, the second after the remainder from the first was rethickened into a smaller area. A total of about 40% of the oil was burned, the majority of which was burned in the initial attempt.

The test with J–34 at 5°C was much more successful. Compared with the previous three tests, this one proceeded in a similar manner for about two minutes after which the flame increased greatly in intensity and the fire appeared to continue at a much higher rate. What appeared to happen was that during the early stages of the burn, the heat from the fire was burning through the waxy crust that covered the oil. Once the crust was consumed, essentially unweathered oil (the evaporation rate at 5°C was much slower than at 15°C) was exposed and this oil burned much more readily. The overall burn efficiency was estimated to be about 90%.

Netting

The use of porous nets has been proposed as a method of containing and collecting waxy crude oils. Previous researchers (Thomas and Morris 1983) have done experiments that measured the extrusion of oils of varying viscosities through such nets. Their findings indicate initial extrusion at about 5 g/cm^2 applied pressure, with leak rates ranging from 0.2 to 10 ml/min as pressure is increased to 35 g/cm^2.

An apparatus similar to that used in the above referenced work was used to determine the applicability of MSW, B–27 and J–34 oils. Briefly, a piece of "Westnet" netting from Jackson U.K. Ltd. with 2–3 mm pores (Thomas and Morris 1983) was fitted over the end of a piece of plastic pipe. A layer of oil was placed in the pipe against the net, and water pressure slowly applied on top of against the oil.

The results were comparable to the previous work, although the pressures at which extrusion began were slightly lower. Extrusion commenced at pressures as low as 0.5 g/cm^2 (0.007 psi = 0.5 cm of H_20). Crude measurements of leak rates were obtained at pressures up to 2.5 g/cm^2 (0.035 psi = 2.5 cm of H_20); they ranged from 0.9 to 2 ml/min through a net area of 44 cm^2.

Chemical Dispersion

In order to assess the preliminary viability of chemical dispersants as a countermeasures option for waxy oil spills a series of small-scale dispersant effectiveness tests were conducted. A hoop tank (S.L. Ross 1987) filled with 35 ppt salt water was used to carry out the tests at temperatures of 5 and 15°C. The hoop oscillation rate was 80 rpm. A conventional concentrate dispersant, Corexit 9527, was applied to 1 mm thick slicks of each oil as 200 um diameter drops at a dispersant-to-oil ratio of 1:20. Table 10 shows the results. The dispersant was quite effective on the Mixed Sweet Western oil at both temperatures, marginally effective on the Hibernia B-27 oil at 15°C and ineffective on the Hibernia B-27 at 5°C and the Avalon J-34 oil at both temperatures. At temperatures below the oil's pour point dispersants are ineffective even in laboratory tests

TABLE 10
CHEMICAL DISPERSANT TESTING

	PERCENTAGE DISPERSED at	
OIL	15°C	5°C
Mixed Sweet Western	92	80
Hibernia B–27	35	6
Avalon J–34	4	2

FATE AND BEHAVIOUR SUMMARY AND MODELLING

In this section the results of the individual studies are summarized and combined with existing spill behaviour process equations into a computer model to predict the fate and behaviour of waxy (and non–waxy) oil spills at sea. Some predictions of large spill behaviour and fate are presented.

CHARACTERIZING WAXY CRUDES

Although considerable effort was expended, no simple method of characterizing the behaviour and fate of waxy oils was found. The most accurate, currently–available technique of characterizing when an oil will begin to exhibit waxy oil behaviour is sophisticated rheological studies measuring yield stresses as a function of temperature, time and weathering. Unfortunately this type of study is not readily available in most laboratories and requires considerable time and expense to conduct. As well, it is not a major improvement in the state of the art since it alone will not predict other behaviour characteristics of an oil when it is spilled.

As such, the simplest existing measure of waxiness, the pour point, must be retained as a measure of an oils tendency to exhibit waxy behaviour as a function of temperature and weathering. It should be noted that the pour point test, as described by ASTM, is really a measure of the temperature range (3°C) at which the oil develops a certain yield stress.

In subsequent sections, the pour point is thus used to delineate the point at which an oil begins to behave as a waxy oil. As is described later, certain behavioural aspects of a waxy oil do not occur until the ambient temperature is below the oil's pour point by a certain amount.

NEAR SOURCE BEHAVIOUR

As discussed earlier, large marine oil spills can result from two sources: blowouts (either sub–sea or surface) or batch spills (such as tanker accidents, storage leaks etc.).

Blowouts

Subsea. Blowouts which occur at the seabed involving waxy oils whose pour point (fresh) is above ambient temperature will result in non–spreading droplets on the water surface rather than a surface slick. This has implications for both subsequent oil behaviour and countermeasures (see below).

The behaviour of subsea blowouts was modelled using two independent sets of equations. The first of these describes the hydrodynamics of a subsea blowout, using the equations of Fannelop and Sjoen (1980) as described in S.L. Ross (1982). Gas flowrates, surface currents and well depths are used to calculate surface slick dimensions, most importantly thickness and width at a distance downstream of the blowout where the outflow of entrained plume water no longer dominates over oil spreading forces.

The second set of equations use the model of Deysson and Karian (1978) as presented in S.L. Ross (1985c) to estimate the oil drop size produced by the blowout. If the oil's pour point is above ambient water temperature, these droplets neither spread on the surface nor recoalesce into a slick; subsequent evaporation, natural dispersion and emulsification is based on droplet size and properties (see below).

Above Sea. In an above sea blowout the oil is atomized and rains from the plume to form a slick. The slicks from an above–sea blowout are usually much narrower and thicker than those from an equivalent sub–sea blowout. In the case of waxy (or nearly–waxy) oils the pour point, when it reaches the water surface, may be above ambient temperatures and the droplets may retain their shape rather than coalesce to form a slick. The dimensions of the slick resulting from such a blowout have been modelled using Turner's (1970) atmospheric dispersion equations as described in S.L.

Ross (1982). The slick thickness, width and initial length are calculated from oil flowrate, gas–to–oil–ratio (GOR), plume rise, wind speed, surface current and atmospheric stability considerations. The oil drop size distribution is calculated using a version of the model described for subsea blowouts.

Evaporation of the light ends of the oil from the small oil droplets as they fall through the air is rapid; this has been modelled using the modified evaporative exposure model for droplets in air presented earlier. The oil property changes resulting from this evaporation are calculated (see below) and, if the pour point exceeds the ambient water temperature the droplets will not coalesce into a slick and subsequent behaviour and fate predictions are based on droplet properties.

Batch Spills

The near–source behaviour of batch spills is very different than that of blowouts. Batch spills usually involve large quantities of oil discharged over short times resulting in initially thick slicks as opposed to the relatively long–term, low flowrate, thin slicks usually associated with blowouts.

In modelling the initial characteristics of a batch spill the approach of Mackay et al. (1980) has been followed; the thick oil is arbitrarily given an initial thickness of 2 cm from which a thick slick area is calculated. The thin slick is arbitrarily assigned a thickness of 1 um and an initial area of 8 times that of the thick slick; a thin slick volume is then calculated.

If the equilibrium slick thickness calculated for the oil at environmental temperature is greater than 2 cm (see Figure 28) the thick slick ceases spreading at this point.

SLICK BEHAVIOUR

In the preceding discussion the initial characteristics of a waxy (or non–waxy) oil slick were summarized and their characteristics predicted. In this section the subsequent fate and behaviour of these slicks will be addressed in the categories of spreading, evaporation, natural dispersion and emulsification.

Spreading

Waxy oils, when spilled on water spread more slowly than less viscous conventional oils and tend to cease spreading as thick slicks at much greater thicknesses. Both these facts are a result of the rheology of waxy crudes (high viscosity and the development of a yield stress as temperatures drop or state of weathering increases).

Batch. The spreading of the thick portion of batch slicks has been modelled using the equations of Fay (1969) for the gravity–viscous regime modified, as presented earlier, to include oil (or emulsion) viscosity (and emulsion density). The thin slick (sheen) is spread according to the surface tension–viscous regime of Fay (1969) modified to include oil viscosity.

Blowouts. Blowout slick spreading is dealt with in a slightly different manner. A section of the slick of width and thickness as calculated in the near–source behaviour section and length equal to 100 s (the model time step) times the current speed is selected. This section of the surface slick spreads only laterally and is used for all subsequent behaviour calculations. This Lagrangian approach (following one part of the slick) assumes that the slick emanating from the blowout is continuous and unchanging. In reality, after some unknown period of time (likely days) the slick will break up into a series of slicklets under the influence of oceanic turbulence and the slick can then spread radially, not just laterally.

The thick portion of the slick is spread according to the "point–source" or one–dimensional surface tension viscous spreading law of Fay (1969) modified to include oil or emulsion viscosity. At the beginning of the spreading calculations the thin slick is arbitrarily given an area of 1 m^2 and a thickness of 1 um; this is the case since the initial generation of the slick (droplets raining from the air or entrained water spreading) is assumed to evenly spread the oil across the calculated width of the slick resulting in an even thickness of oil. Subsequent thin slick spreading is based on the one-dimensional surface tension-viscous spreading law of Fay (1969), modified to incorporate oil properties.

In the case of a waxy oil with a pour point greater than ambient temperature the droplets would not coalesce into a slick and thick slick spreading is halted, although the droplets still generate a sheen as described above. The model checks which is larger, the slick thickness or droplets and uses the greater for subsequent calculations.

The turbulent horizontal diffusion of these droplets (and mats, globs and fragments) of waxy oil is a subject requiring future research.

Cessation of Spreading. Thick slick spreading ceases when the slick thickness falls to the equilibrium value calculated using the difference between weathered oil pour point and the water temperature (see Figure 28); thin slick spreading ceases when the spreading coefficient (Fay 1969) of the slick oil drops to 0 or becomes negative.

Evaporation

Waxy crude oils evaporate more slowly than conventional crudes because of the resistance to diffusion of the lower molecular weight components presented by the crust formed on evaporation.

This is accounted for in the model by incorporating a crust mass transfer coefficient and Henry's Law constant into the calculation of the evaporative exposure. This is instituted when the pour point of the oil exceeds environmental temperatures by 5°C, estimated based on observations in the weathering experiments and wind/wave tank studies.

In the case of slicks, the overall mass transfer coefficient, elapsed time and slick thickness are used to calculate evaporative exposure; volume losses to evaporation are subsequently calculated using the modified ASTM distillation based equation of Stiver & Mackay (1983). For droplets on water the same technique is used except the drop volume per unit surface area, calculated from the volume median diameter, is substituted for slick thickness.

In the special case of droplets raining from an above–sea blowout the evaporative exposure is calculated using the mass transfer coefficient determined experimentally. The volume lost to evaporation in the time it takes the volume median diameter droplet to fall from the plume rise height to the sea surface (using a Stoke's Law terminal velocity) is calculated using the approach of Stiver & Mackay (1983).

Thin slicks emanating from thicker oil are initially evaporated a fixed 30% (to prevent the finite difference form of the evaporative loss equation for these thin slicks from blowing up); in subsequent iterations the evaporative loss is the sum of the incremental evaporation from 30% to that predicted plus the incremental evaporation of the volume of oil from the thick slick that feeds the sheen.

Natural Dispersion

Oil on the water surface, in the presence of turbulence, forms droplets, some of which are small enough to be permanently entrained in the water column. Waxy oils, because of their higher viscosity and gelation at ambient temperatures disperse naturally at much slower rates than conventional oils.

The equation used to predict natural dispersion for slicks is that given in S.L. Ross (1985a) which empirically incorporates oil density and viscosity, wind speed (i.e., sea state) and slick thickness. For thick oil if emulsification has occurred, emulsion properties are used; for the thin slick the thin, weathered oil properties are used regardless of whether the thick slick has emulsified.

In the case of waxy oils, natural dispersion is stopped once the oil's pour point exceeds the ambient water temperature by 15°C. This is based on measurements in the wind/wave tank experiments.

If non–spreading droplets are present, as in the case of blowouts, no natural dispersion is allowed to take place based on observations in the wind/wave tank. This is likely an overly conservative assumption since some of the droplets generated by a blowout will be in the size range small enough to be permanently dispersed, particularly in the case of an above–sea blowout. Although the droplet size distribution resulting from a blowout can be reasonably estimated (e.g., S.L. Ross 1985c) little is known about the size of buoyant drop that can be retained below the surface as a function of sea state. It seems likely that, given a blowout that generates very small droplets, say 50 um, a large fraction of the drops, if they do not coalesce to form a slick would be rapidly dispersed by reasonably energetic seas. Further research is required to elucidate this.

Emulsification

Emulsification of oil spills is a very poorly understood process and even less so for waxy oils. State–of–the–art tests which reasonably predict the emulsification behaviour of conventional oils do not predict the behaviour of waxy oils. It seems likely that oil rheology, turbulence levels and slick thickness play an important role in controlling the emulsification process and its competition with natural dispersion for these atypical oils.

Regardless, the simple equation proposed by Mackay et al. (1979) has been used to model emulsification. Once an oils pour point exceeds the ambient water temperature by 15°C (based on the wind/wave tank test results) emulsification ceases.

It is unfortunate that this simple approach is all that is currently available since emulsification is a key process that controls the long–term fate and behaviour of oil at sea by reducing natural dispersion rates and dramatically altering oil properties, subsequent oil behaviour and possibly impact on seabirds and marine mammals. Research on this subject should be a high priority.

Property Changes

Two spill behaviour processes act to change oil properties: evaporation and emulsification. Oil properties are also a function of environmental temperatures.

Evaporation, through the depletion of light ends, increases oil density, viscosity and pour point and reduces interfacial tensions and oil solubility. These changes result in reduced spreading, natural dispersion and dissolution and increased emulsification.

Emulsification, through the incorporation of water into the oil, results in dramatic increases in spill volume (and hence thickness), fluid density and viscosity. All of these result in reduced spreading and natural dispersion and increase the survival time of a slick on the ocean.

The effects of evaporation on oil property changes were modelled with the equations proposed by Mackay et al. (1983) using evaporation vs. property data determined experimentally for each of the subject oils (MSW, Avalon J–34 and HIbernia B–27). The effects of emulsification on property changes were modelled using the simple procedures proposed by Mackay et al. (1979). Again, there is a pressing need to research the effects of emulsification on key behaviour–controlling properties such as oil viscosity since the available equations cannot account for such parameters as pour point, water droplet size etc. This need is acute for waxy oils since the data from this study indicates that emulsification may actually reduce the viscosity of very waxy oils.

MODEL RESULTS

The computer model (see Appendix III for a complete listing) was written in PASCAL and is suitable for use on an IBM–PC compatible micro–computer. Figure 52 shows the typical inputs required for the model which include physical properties of the fresh oil (stored as a file in the program) the type (in this case batch) and conditions of the spill, environmental conditions and behaviour and property rate constants (as discussed previously).

FIGURE 52

TYPICAL MODEL INPUT DATA

```
                             3200 m3 Hibernia Batch


        The spill is from a batch spill.

  Fresh oil properties

     Emulsification delay (theta)                       0.0
     Density (kg/m3)                                  837.00
     Standard density temperature (K)                 293.00
     Viscosity (mPas)                                  11.40
     Standard viscosity temperature (K)               288.00
     Pour point (K)                                   279.00
     Aqueous solubility (g/m3)                         16.92
     Flash point (K)                                  287.00
     Oil-water interfacial tension (N/m)                0.02
     Oil-air interfacial tension (N/m)                  0.029

  Spill conditions

     Duration of spill (100sec)                         1.00
     Volume of oil spilled (m3)                      3200.00


  Environmental Conditions

     Windspeed (m/s)                                    5.00
     Air temperature (K)                              290.00
     Water temperature (K)                            290.00


  Constants

     Density constant 1                               234.0000000
     Density constant 2                                 0.6000000
     Viscosity constant 1                              14.3700000
     Viscosity constant 2                           20738.00
     Pour point constant                                0.2500000
     Solubility constant                                0.0000000
     Flash point constant                               0.0000000
     Oil-water int. tension constant                    0.0000000
     Oil-Air int. tension constant                      0.0000000
     ASTMA constant                                   580.00
     ASTMT constant                                   402.00
```

Figure 53 illustrates the type of numeric output from the model. For each chosen output time (in this case 2 hours) the program documents the dimensions of the slick (area and thickness), volume remaining on the surface and the cumulative volumes of oil evaporated and dispersed naturally for the thick, thin and total spill. The properties of the thick oil and emulsion (if any) at the indicated time are also documented, including density, viscosity, water content, emulsion thickness and fraction evaporated. The value of theta, the exposure coefficient, and a record of the weathered oil's pour point and the ambient water temperature are also recorded. Additional property information can easily be output by simple changes to the program.

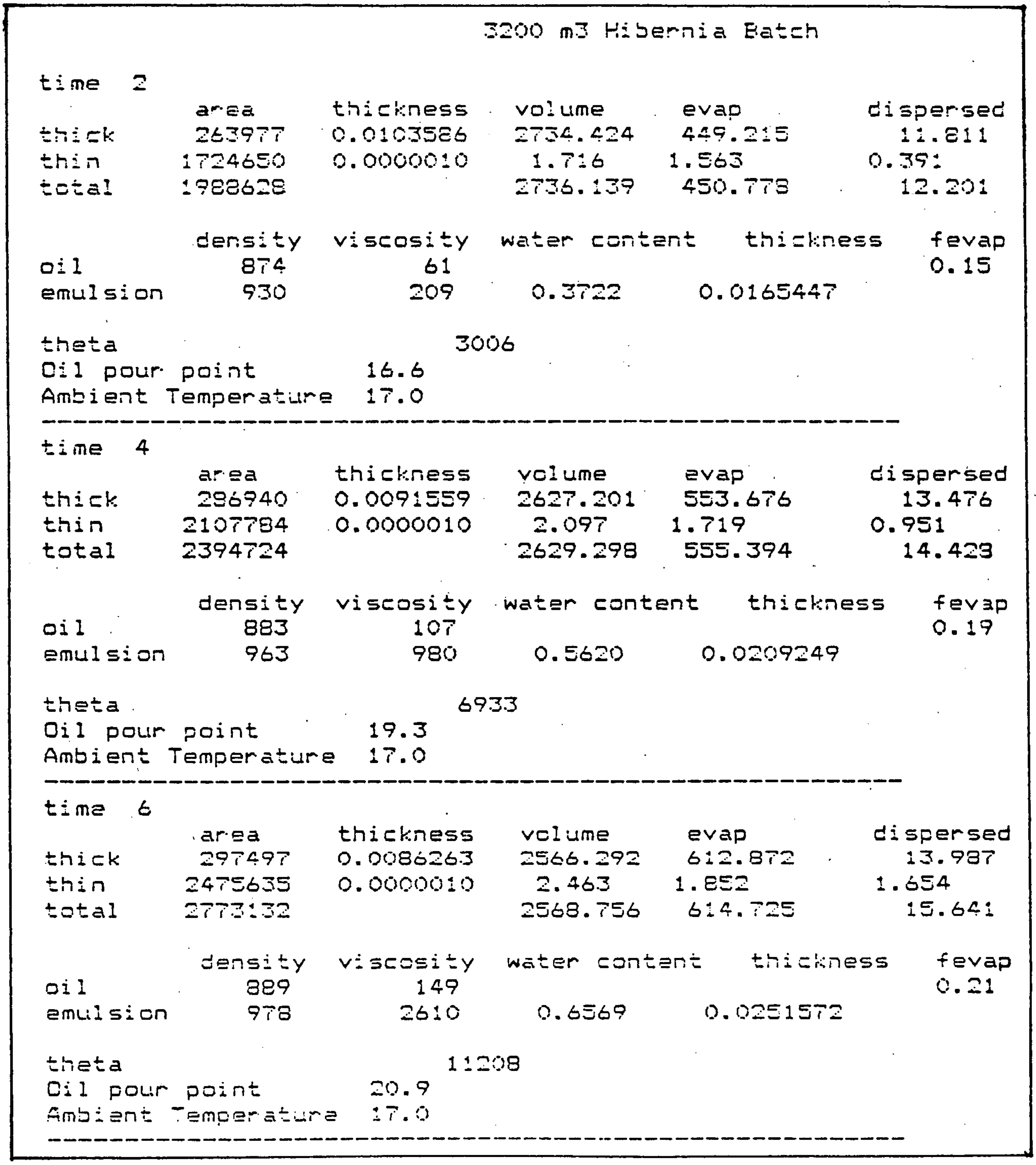
Figure 54 shows a typical graphic output from the model. The volumes of oil in the slick, evaporated and naturally dispersed as well as thick slick thicknesses, water content, density and viscosity are plotted against the run time (either to extinction of the thick slick or as selected by the operator).

Figure 55 illustrates the effect of temperature on the model prediction, in this case a 3200 m^3 (20,000 bbl) batch spill of Hibernia B–27 oil in a 5 m/s wind at 0 and 17°C. Though the differences are subtle, the oil at lower temperatures spreads, evaporates and disperses more slowly at 0°C than at 15°C because of its increased viscosity and the larger difference between the oil's pour point and ambient temperature.

Figure 56 compares the model predictions for 3200 m^3 batch spills at 17°C under identical conditions for three different oil types: Hibernia B–27, Mixed Sweet Western and Amauligak. In this and subsequent model runs the MSW is assigned a pour point of –8°C (Bobra and Chung 1987) and thus represents a slightly waxy oil. The Amauligak oil, from the Beaufort Sea, has a very low pour point and low viscosity at low temperatures. Comparison of the three graphic outputs shows that the Hibernia oil spreads much more slowly than either of the less waxy oils (note the change in thickness scale for the Mixed Sweet Western and Amauligak oils from 0 – 80 mm to 0 – 24 mm) and evaporates and disperses much more slowly. Of particular interest is the fact that the MSW and Amauligak oils do not begin to emulsify for 15 and 23 hours respectively and the subsequent effects on oil properties and natural dispersion rates.

FIGURE 53

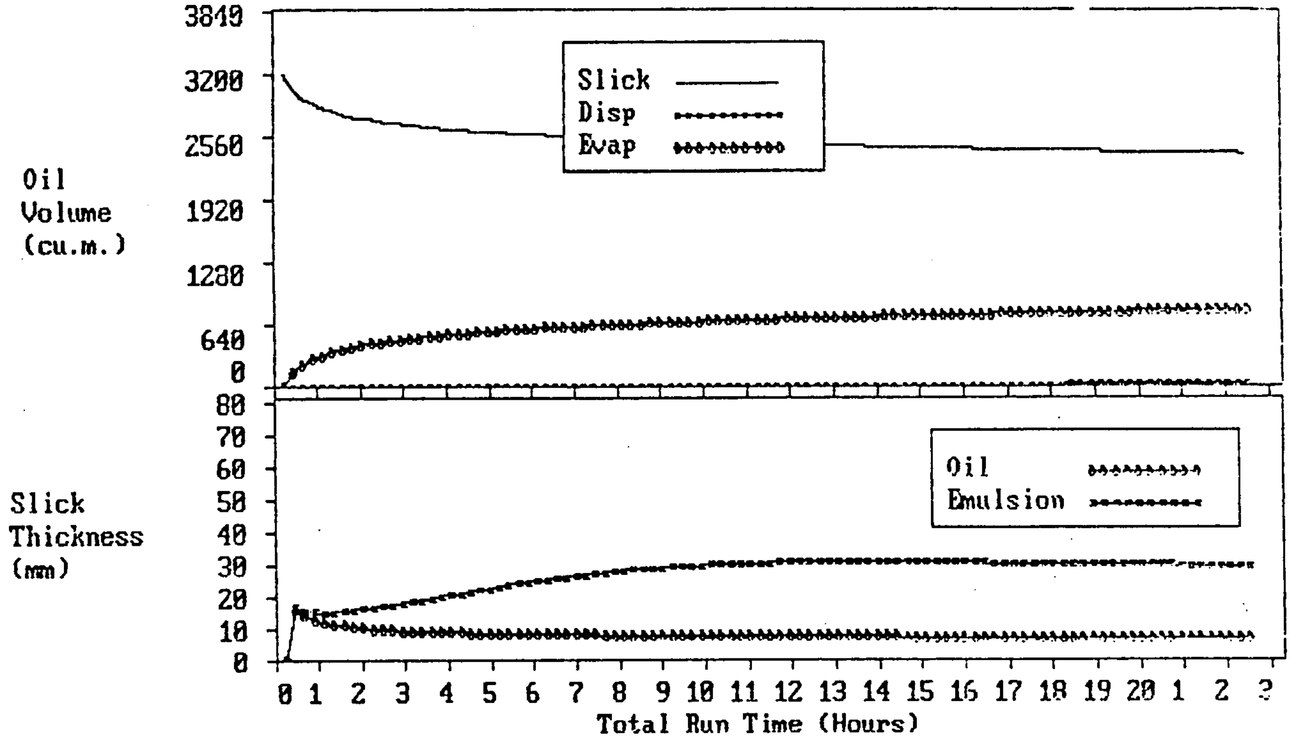
EXAMPLE NUMERIC OUTPUT



```
                             3200 m3 Hibernia Batch

time  2
          area     thickness   volume     evap        dispersed
thick     263977   0.0103586   2734.424   449.215       11.811
thin     1724650   0.0000010    1.716    1.563        0.391
total    1988628               2736.139   450.778       12.201

          density  viscosity  water content   thickness    fevap
oil          874        61                                0.15
emulsion     930       209     0.3722     0.0165447

theta                      3006
Oil pour point       16.6
Ambient Temperature  17.0
--------------------------------------------------------
time  4
          area     thickness   volume     evap        dispersed
thick     286940   0.0091559   2627.201   553.676       13.476
thin     2107784   0.0000010    2.097    1.719        0.951
total    2394724               2629.298   555.394       14.423

          density  viscosity  water content   thickness    fevap
oil          883       107                                0.19
emulsion     963       980     0.5620     0.0209249

theta                      6933
Oil pour point       19.3
Ambient Temperature  17.0
--------------------------------------------------------
time  6
          area     thickness   volume     evap        dispersed
thick     297497   0.0086263   2566.292   612.872       13.987
thin     2475635   0.0000010    2.463    1.852        1.654
total    2773132               2568.756   614.725       15.641

          density  viscosity  water content   thickness    fevap
oil          889       149                                0.21
emulsion     978      2610     0.6569     0.0251572

theta                     11208
Oil pour point       20.9
Ambient Temperature  17.0
--------------------------------------------------------
```

FIGURE 54

EXAMPLE GRAPHIC OUTPUT


3200 m3 Hibernia Batch

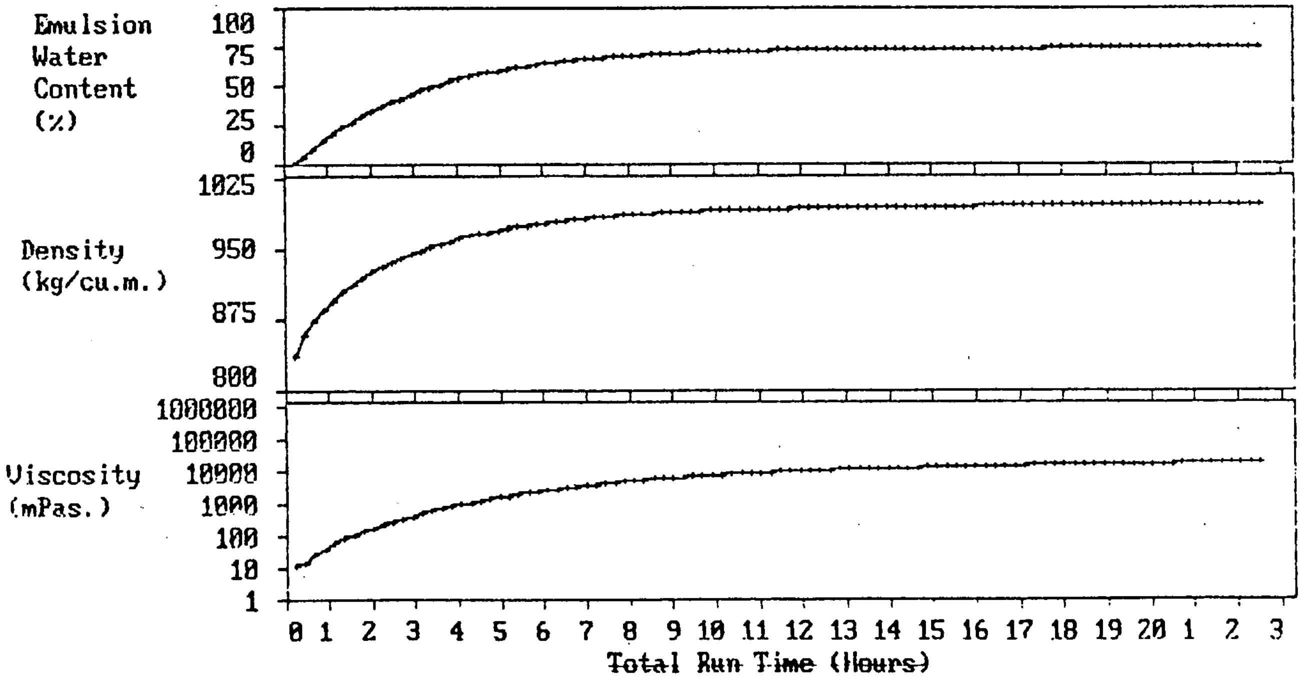

3200 m3 Hibernia Batch

FIGURE 55

EFFECT OF TEMPERATURE ON MODEL PREDICTIONS

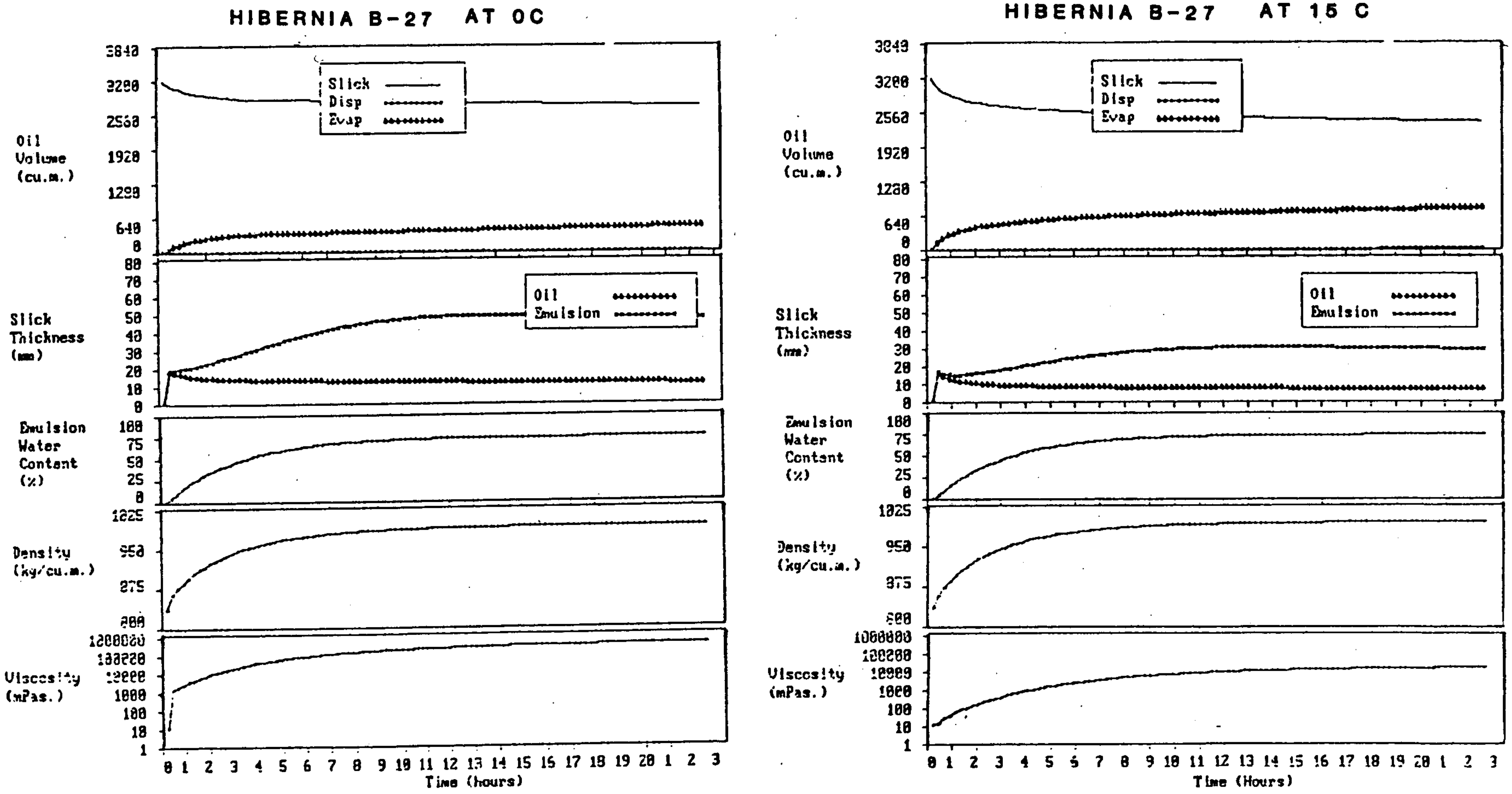


FIGURE 56

COMPARISON OF BATCH MODEL PREDICTIONS FOR THREE OILS

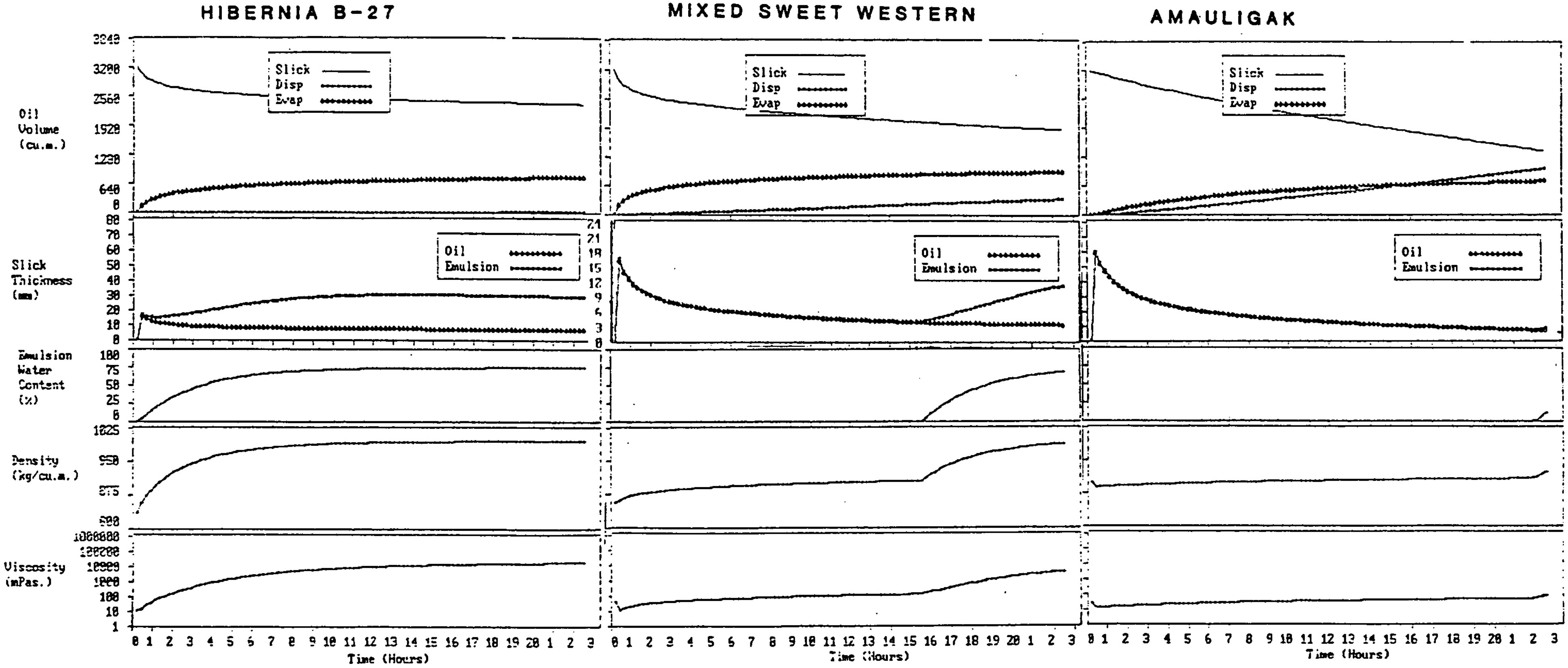


Figure 57 shows a comparison of the model outputs for identical sub–sea blowouts (20,000 BOPD; GOR = 200:1; water depth = 50 m) involving the three different oil types at 17°C. The evaporation rates are almost identical, because the slicks are initially very thin (80 um) and evaporation of the light ends occurs rapidly regardless of oil type. The major difference is in the rates of natural dispersion. The less viscous the oil, the greater its dispersion rate. The rate of slick thickness decline is also different. Both the Hibernia B–27 and Mixed Sweet Western oils are initially weathered and emulsified enough to dramatically curtail thick slick spreading whereas the Amauligak oil (note the slick thickness scale change from 0–240 um to 0–80 um) has not initially emulsified and thus continues to spread rapidly for several hours.

Figure 58 compares the model predictions for surface blowouts of the three oils (20,000 BOPD; GOR = 200:1; plume rise = 50 m). In the case of the Hibernia B–27 oil and the Mixed Sweet Western, the oil pour points have been raised sufficiently by evaporation as they rain down from the flume that the droplets do not coalesce into a slick. Subsequent changes are slow and driven by dispersion losses of the sheen generated by the droplets. The Amauligak oil is predicted to behave quite differently since it's pour point is not raised sufficiently to gel the droplets. Subsequent depletion of the surface slick is much faster than for the gelled oils.

One failing of the equations used to develop the model is evident in Figure 58. The equation used to predict oil viscosity as a function of temperatures and weathering cannot account for the true viscosity of the oil at environmental temperatures below the oil's pour point. In the case of the Hibernia and MSW oils the viscosities should be in the 10,000+ mPa.s range. The development of equations to better predict rheological characteristics of oils near or below their pour point is required before this shortfall can be rectified.

FIGURE 57

COMPARISON OF SUB SEA BLOWOUT MODEL PREDICTIONS FOR THREE OIL TYPES

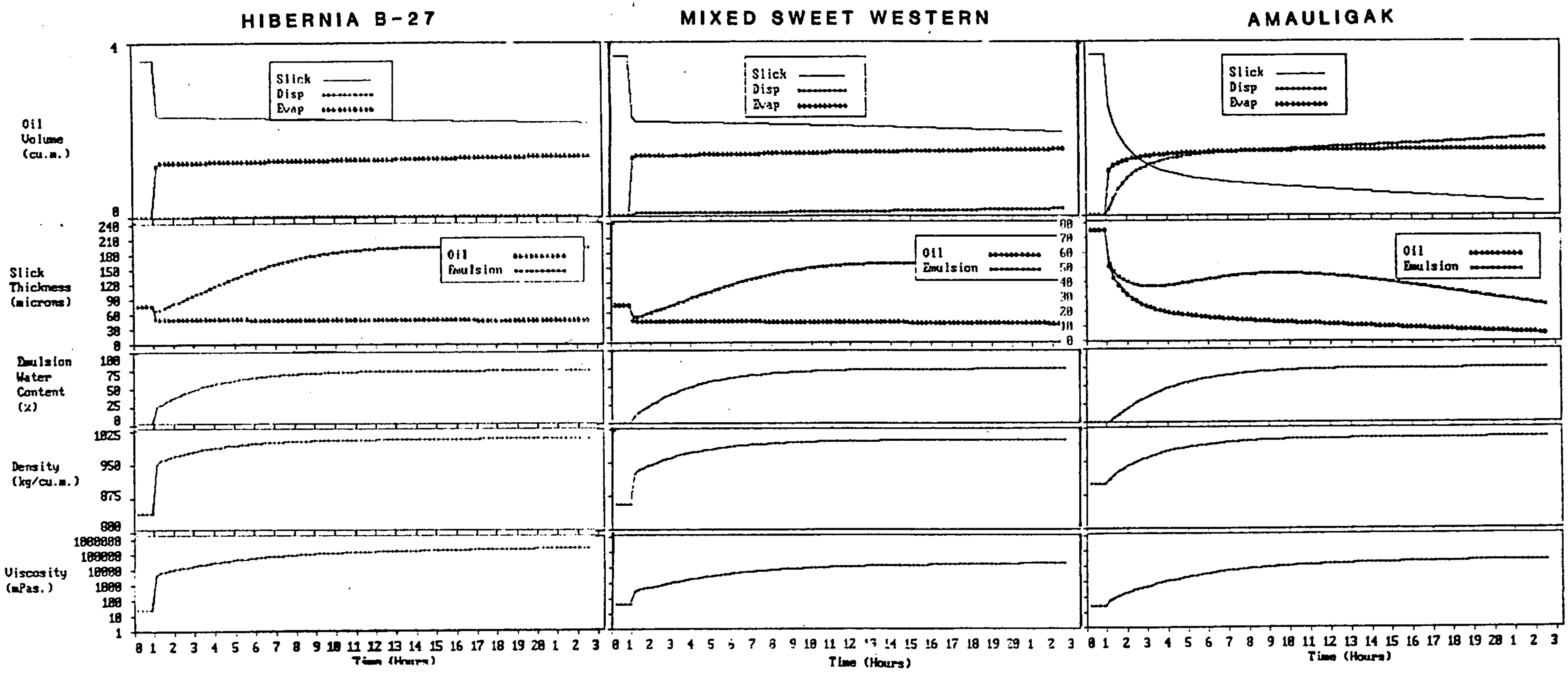
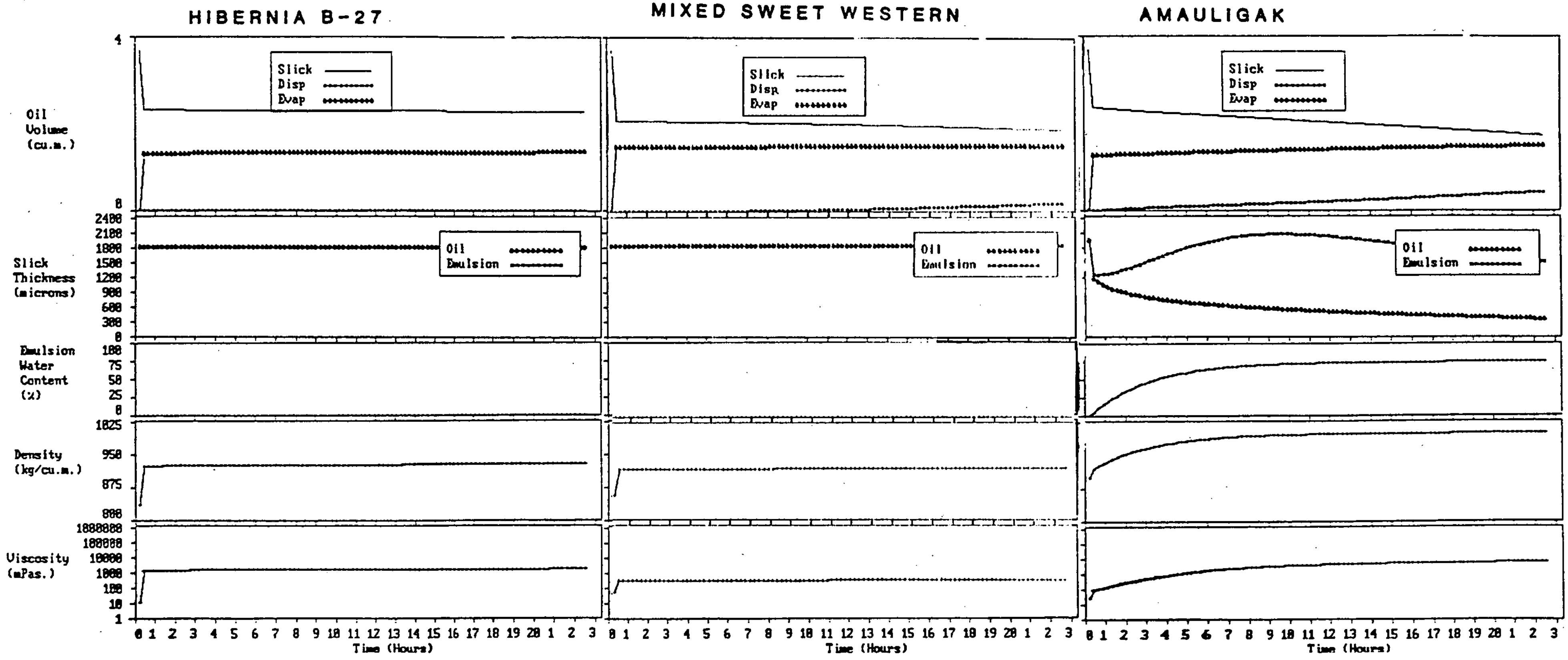


FIGURE 58

COMPARISON OF SURFACE BLOWOUT MODEL PREDICTIONS FOR THREE OIL TYPES



CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The fate and behaviour of waxy crude oil spills is dramatically different from that of less waxy crude oils. Waxy oils, when spilled on water spread very slowly (if at all), gel and then fracture into mats and blobs at environmental temperatures below their pour point, initially evaporate very slowly due to the internal resistance to mass transfer offered by their gel–like structure, emulsify and disperse into the water column very slowly. Waxy oils spilled from blowouts may result in streams of individual, non–coalescing, gelled oil droplets, rather than a continuous slick of oil, depending on the pour point of the oil and environmental temperature differences.

The main reason for this unique behaviour is likely related to the precipitation of waxy, asphaltic and resinous compounds from solution in the oil and the subsequent equilibrium between the formation of solid particles or lattices and their breakdown by turbulence. The precipitation, or gelling, occurs as temperatures decline or as evaporation of lighter ends reduces the solvent available for the precipitates. The result is the development of a temperature and time–dependent yield stress in the oil and the onset of complex non–Newtonian rheology involving thixotropic and shear history–dependent viscosity.

Despite considerable effort, no simple analytical technique was found to characterize waxy oils. The best available approach was determined to be studies of the rheology of the oil, in particularly the development of a yield stress, as a function of temperature and weathering. Until further progress is made the pour point is the best, simple test of waxiness.

Based on theoretical considerations and experimental data the following mathematical models were developed to predict the behaviour and fate of waxy oil spills.

* the slow spreading of waxy viscous oils on water can be adequately described

by incorporating oil viscosity, rather than water viscosity, in Fay's (1969) equations;

- the large equilibrium slick thickness displayed by waxy oils can be related empirically to a difference between the oil's pour point and environmental temperatures;
- the very slow evaporation rates exhibited by waxy oils are due to the development of an internal resistance to mass transfer (i.e., a crust) and can be modelled by incorporating this resistance into a modified evaporative exposure equation combined with a modified ASTM distillation. Models for droplets in air and on water were also derived.

These, and other spill process equations for natural dispersion and emulsification modified to reflect waxy oil behaviour, were combined into a comprehensive spill fate and behaviour prediction model on a micro–computer.

Based on a series of small– and mid–scale tests the emulsification behaviour of waxy oils is anomalous. At temperatures near and above the oil's pour point they behave as do conventional oils; at temperaturres below their pour point they may not emulsify at all (depending on mixing energy levels) and if they do, the emulsion viscosity may be less than that of the parent waxy oil.

Countermeasures for waxy oil spills on water were tested on a preliminary basis. Containment of waxy oil spills on water by conventional booms is feasible, however the gelled oil particles once concentrated are not adhesive and larger mats jam together (much like ice floes) preventing their flow to areas for skimming.

Waxy oils, at temperatures below their pour point, do not adhere well to oleophilic surfaces and thus skimmers operating on this principle are not likely to be efficient in waxy oil recovery operations at cold temperatures. Waxy oils, at environmental temperatures below their pour point are extremely resistant to chemical dispersants. Despite the fact that weathered waxy oils develop a yield stress this is insufficient to prevent their extrusion through typical oil spill net material at very low pressures.

In–situ burning, however, does seem to offer a viable spill response technique. In fact, waxy oils may burn more efficiently than comparable less waxy oils because of the reduced loss of volatile compounds from gelled waxy oils. They may however, for the same reason, be somewhat harder to ignite.

RECOMMENDATIONS

Further study of waxy oil spill behaviour is recommended in the areas of:

- characterization;
- rheology, especially mathematical models for oil rheology near and below the pour point;
- evaporation and dissolution of droplets on water;
- emulsification and its effects;
- spreading of gelled oil forms over a long time period (i.e., surface horizontal turbulent eddy diffusion);
- countermeasures techniques, particularly recovery technology; and
- potential environmental impacts of gelled oil forms, particularly on seabirds.

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APPENDIX I

THE MATRIX APPROACH

APPENDIX I

DISTILLATION EXPERIMENTS

The MATRIX Model

The Original MATRIX Model. The rate of a process such as evaporation, dissolution, or biodegradation affecting a hydrocarbon mixture in the environment is estimated by summing the individual rates applicable to each hydrocarbon. Consequently, calculating a value for a substance such as crude oil poses a problem because crude oil consists of thousands of compounds, many of which cannot be identified. A solution, introduced in a mathematical model called MATRIX (Mackay et al. 1985), groups the hydrocarbon constituents of crude oil into classes which have similar properties of volatility, solubility and degradability.

The columns of the matrix are formed by the structural groups: n-alkanes, iso- and cyclo- alkanes, isoprenoids, aromatics and polars. The rows are groups of similar volatility or vapour pressure are indicated by position on the capillary column gas chromatogram. For example, the class C-8 is n-octane and all subsequent peaks up to, but not including, n-nonane. This model has the capacity to quantify not only the fate of diesel oil in soil, but also other petroleum products and crude oils in other environmental matrices.

The Modified MATRIX Model. The MATRIX model used in this report was modified to consist of one column only, the n-alkane column. The rows are groups of compounds having a vapour pressure similar to the n-alkane.

The vapour pressure for each n-alkane, shown in Table A1, is determined by the Antoine equation:

$$\text{Vapour pressure (Pa)} = ((10\ \ (A-B/(T+C)))/760) * 101325$$

where A, B, and C are Antoine equation constants specific to each alkane and T is the temperature in Celsius degrees.

Total pressure is calculated in two steps. First, partial pressures are obtained by applying Raoult's Law to each of the vapour pressures of the component alkanes. For each alkane:

Partial pressure = mole fraction * vapour pressure.

Next, the partial pressures are summed and, according to Dalton's Law, the total pressure is equal to this sum.

Table A1
The Alkanes and Their Vapour Pressures

Carbon #	Vapour Pressure at 20C (Pa)
<C6	5.66E+04
C6	1.62E+04
C7	4.74E+03
C8	1.41E+03
C9	4.12E+02
C10	1.21E+02
C11	3.47E+01
C12	1.00E+01
C13	2.68E+00
C14	7.31E−01
C15	1.91E−01
C16	4.58E−02
>C16	1.31E−02

Experimental Method

Distillation. The distillation apparatus was arranged as in Figure A1 (Linstromberg and Baumgarten 1980). Standard–taper glassware was used. Approximately 200 ml of crude oil was poured into the 500 ml distillation flask. Glass vials, placed at the tip of the adapter, were used to collect distillate.

The thermocouple was inserted through the upper stopper in the distillation flask so that the tip extended below the surface of the crude oil. A heating mantle connected to a rheostat was used to effect boiling.

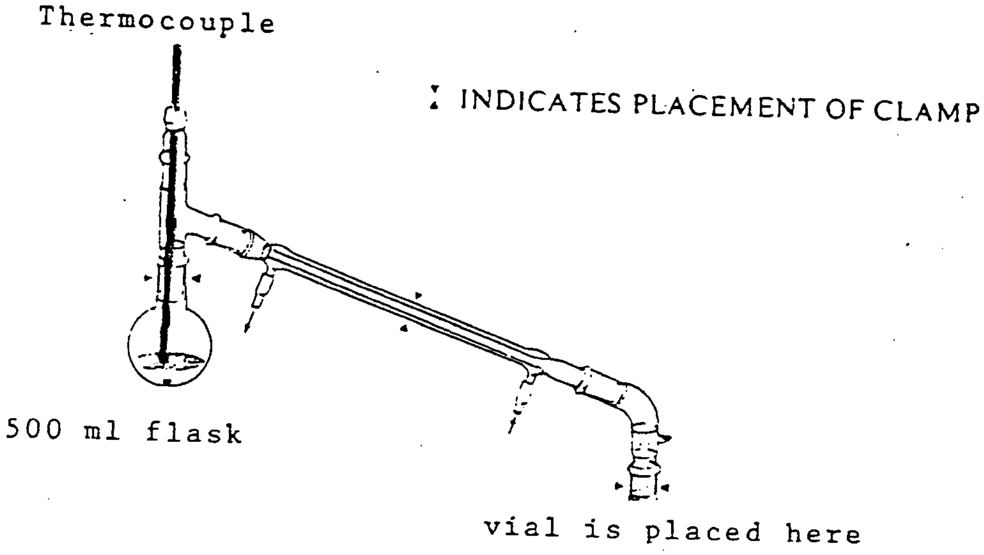


Figure A1: The Distillation Assembly

Gas Chromatographic Analysis. Analysis of the fresh crude oil and the fractions was effected on a Hewlett–Packard GC Model 5700A equipped with a flame ionization detector. The column was 60 m long, 0.075 cm ID glass capillary tubing coated with SPB–5 (Supelco). The initial oven temperature was set at 50°C with a post injection time of 8 minutes. The oven was then temperature programmed to 220°C at a rate of 5°C per minute. The peak areas were recorded by the Hewlett–Packard 3390A integrator. Sample injection volume was 0.5 microlitres with a split ratio of 50:1 (1).

Density Measurement. The densities of the crude oil and of the fractions were obtained with 10–ml and 5–ml pycnometers.

Viscosity Measurement. Viscosities were obtained using Ostwald viscometers.

The MATRIX Model

The crude oil was specified to be composed of alkanes between C–5 and C–17. Alkanes below C–5 were assigned to carbon number 5 and alkanes above C–16 were assigned to carbon number 17. The composition data was obtained from a chromatogram of the crude oil. For example, the class C–8 was n–octane and all subsequent peaks up to but not including n–nonane. Each class was assigned the properties of its alkane constituent.

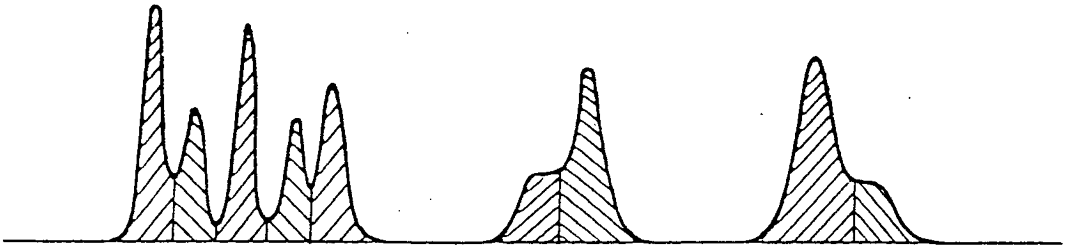
On some chromatograms, a "hump" of unresolved hydrocarbons was observed. In these cases, the peak above the hump was integrated all the way down to the baseline as shown in Figure A2.

The molecular weights and the densities at 20°C, shown in Table A2, were calculated for each component, using the following equations, with I equal to carbon number:

$$\text{Molecular weight (g/mol)} = I*12.01 + 2*(I+1)*1.008$$

$$\text{Density (g/ml)} = I/(2.268 + I*1.1403)$$

(Reid et al. 1977).



Vertical Division Process

Figure A2: The Integration of the "Hump"

Total density was equal to the density of each component multiplied by the volume fraction of that component in the bottle.

The viscosity for each component, shown in Table A2, was calculated using the following equation (Reid et al 1977):

Viscosity (cP) = 10 (BU*((1/T) – (1/TU))) with T = 293 K
where, if I < 17:
BU = 24.79 + 66.885*I–1.3173*I 2–0.00377*I 3
and TU = 28.86 + 37.439*I–1.3547*I 2+0.02076*I 3
and, if I = 17, then BU = 1800 and TU = 1000.

To obtain LNU = ln (viscosity of the mixture), the mole fraction of each component was multiplied by the ln of the viscosity of that component. The sum of these terms was equal to LNU. Therefore, the viscosity of the mixture was equal to e raised to the power of LNU (Reid et al. 1977).

Table A2
The Alkanes and their Molecular Weights, Viscosities and Densities

Carbon #	M.W. (g/mol)	Viscosity (cP)	Density (g/cm^3)
<C6	72	0.22	0.627
C6	86	0.30	0.659
C7	100	0.41	0.683
C8	114	0.55	0.702
C9	128	0.72	0.718
C10	142	0.93	0.731
C11	156	1.20	0.743
C12	170	1.51	0.752
C13	184	1.88	0.761
C14	198	2.31	0.768
C15	212	2.80	0.774
C16	226	3.36	0.780
>C16	240	2.20E+04	0.785

Results

Density: Experimental and MATRIX. Table A3 shows the experimental and MATRIX densities for fresh J–34 and its fractions. See the appendix for calculations.

Table A3
Density: Experimental and MATRIX

Sample	Measured Density	MATRIX
Fresh J–34	0.865	0.815
Fraction 1	0.715	0.723
Fraction 2	0.747	0.744
Bottoms	0.894	0.833

Viscosity: Experimental and MATRIX. Table A4 shows the experimental and MATRIX viscosities for fresh J–34 and its fractions. Please see the appendix for calculations.

Table A4
Viscosity: Experimental and MATRIX

Sample	Measured Viscosity	MATRIX
Fresh J–34	29	30
Fraction 1	0.421	0.311
Fraction 2	0.548	0.393
Bottoms	110	103

Discussion

Density: Experimental and MATRIX. Experimental and MATRIX densities showed good agreement. MATRIX densities were closer to the actual densities for fractions 1 and 2 than for the fresh oil and the bottoms. Percent error, equal to (actual value – MATRIX value)/actual value, is shown in Table A5.

Table A5
Density: Percent Error

Sample	Percent Error
Fresh J–34	5.8
Fraction 1	–1.1
Fraction 2	0.4
Bottoms	6.8

Viscosity: Experimental and MATRIX. Experimental and MATRIX viscosities did not agree as well as densities. MATRIX viscosities for fresh oil and the bottom were much closer to actual values than MATRIX viscosities for fractions 1 and 2. Percent error for each sample is shown in Table A6.

Table A6
Viscosity: Percent Error

Sample	Percent Error
Fresh J–34	–4.6
Fraction 1	26.2
Fraction 2	28.3
Bottoms	5.9

Conclusions

The MATRIX method can be used to estimate the properties of crude oil when evaporation is the major process. Densities calculated with MATRIX show good agreement with measured densities. MATRIX viscosities for fresh J–34 and for the bottoms are in closer agreement with measured viscosities than MATRIX viscosities for fractions 1 and 2.

Summary of Data and Calculated Values

Chromatograms

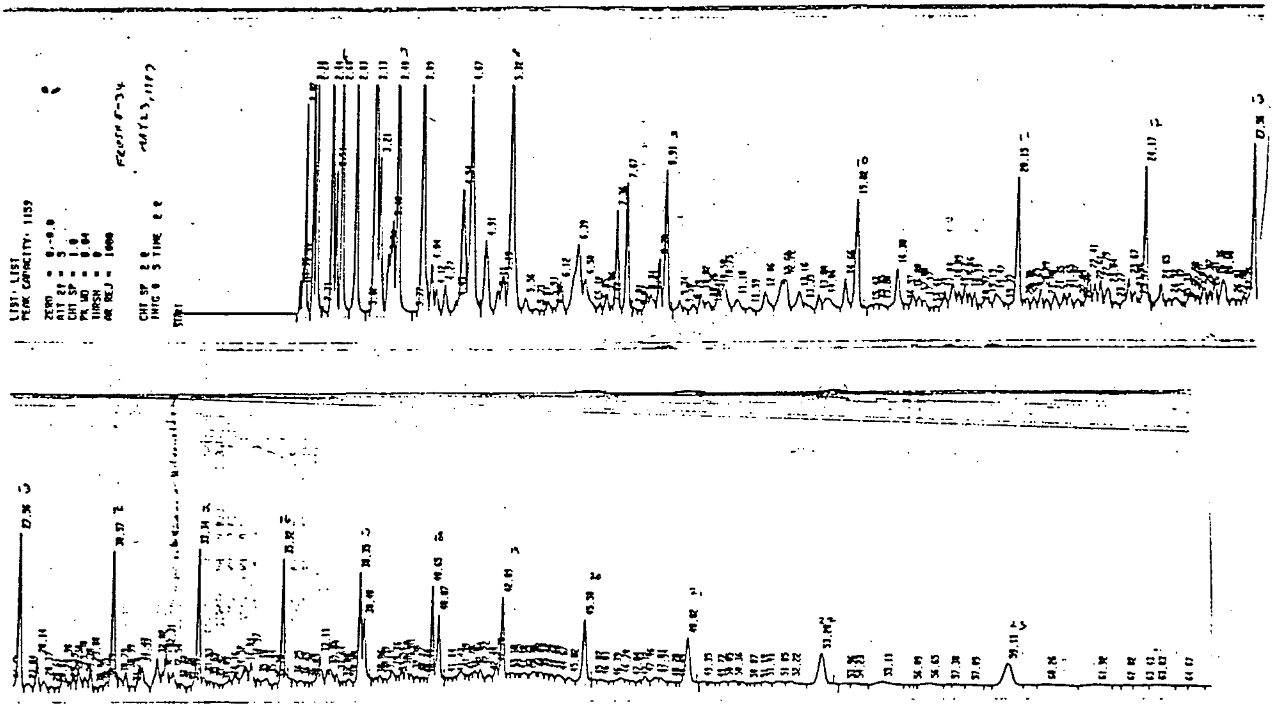


Figure 7.1: Chromatogram of J-34 Fresh Crude Oil

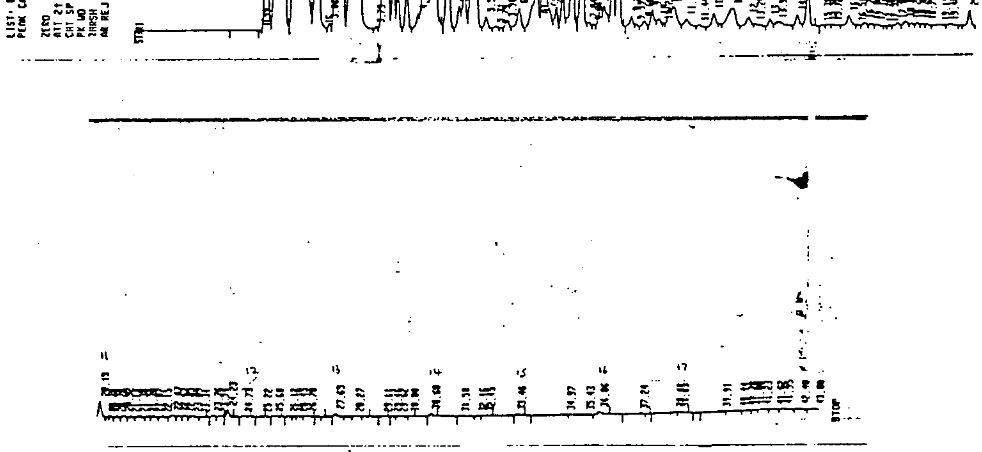


Figure 7.2: Chromatogram of J-34: Fraction 1

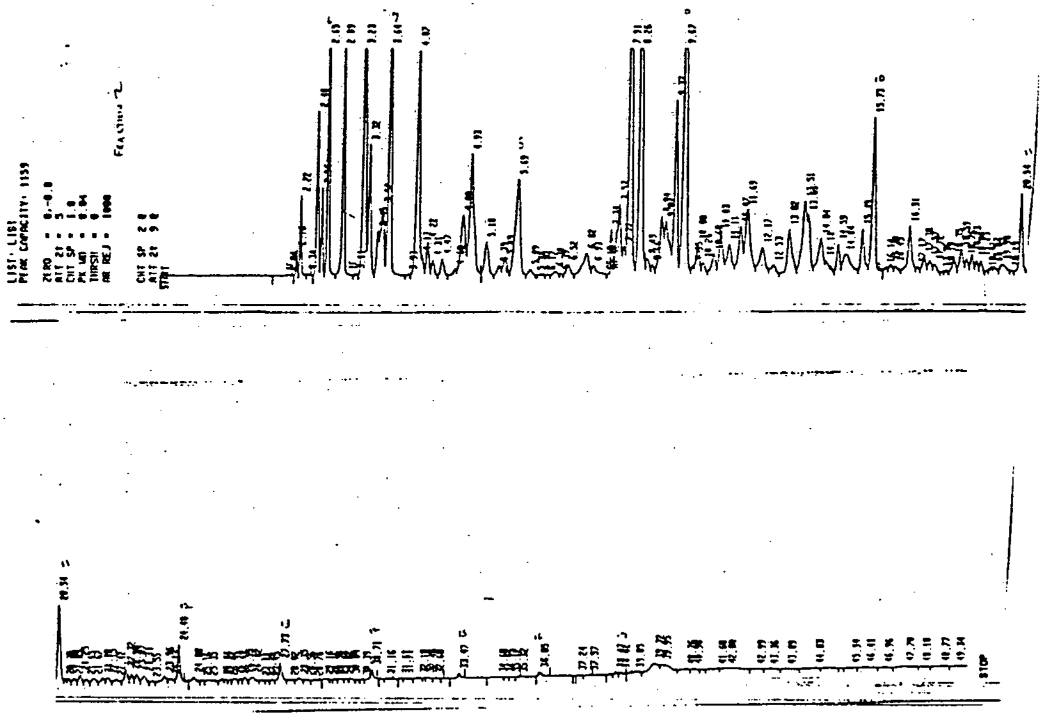


Figure 7.3: Chromatogram of J-34: Fraction 2

Figure 7.4: Chromatogram of J-34: Bottoms

Data Tables: J-34

Vapour Pressure Calculations

Carbon #	Antoine Equation Constants			Vapour Pressure at 20C (Pa)
	A	B	C	
< C6	6.87632	1075.78	233.205	5.66E+04
C6	6.87024	1168.72	224.21	1.62E+04
C7	6.89385	1264.37	216.636	4.74E+03
C8	6.90940	1349.82	209.385	1.41E+03
C9	6.93440	1429.46	201.820	4.12E+02
C10	6.96375	1508.75	195.374	1.21E+02
C11	6.97220	1569.57	187.700	3.47E+01
C12	6.99795	1639.27	181.835	1.00E+01
C13	7.00756	1690.67	174.220	2.68E+00
C14	7.01300	1740.88	167.720	7.31E-01
C15	7.02359	1789.95	161.380	1.91E-01
C16	7.02857	1830.51	154.450	4.58E-02
> C16	7.0143	1865.1	149.2	1.31E-02

Raw J-34: Composition Calculations

Carbon #	GC Results (Mass Units or M.U.)				Ratio to C19 peak (g)	Std. Dev.	Error Bars	
	Run 1	Run 2	Run 3	Average			Low	High
< C6	3042174	3069606	2808992	2973591	3.27	0.13	3.15	3.40
C6	4247099	4483838	4073739	4268225	4.70	0.19	4.52	4.89
C7	5476602	5778093	5280781	5511825	6.07	0.23	5.84	6.29
C8	5397746	5545508	5256175	5399810	5.95	0.13	5.82	6.08
C9	5087326	5283884	4962833	5111348	5.63	0.15	5.48	5.77
C10	4404935	4614920	4330955	4450270	4.90	0.13	4.77	5.03
C11	4367411	4602767	4378889	4449689	4.90	0.12	4.78	5.02
C12	3769310	4155747	3939439	3954832	4.36	0.17	4.18	4.53
C13	4412560	4639744	4389990	4480765	4.93	0.12	4.81	5.06
C14	4351420	4625510	4357130	4444687	4.89	0.14	4.75	5.04
C15	4092880	4394890	4141330	4209700	4.64	0.15	4.49	4.78
C16	3871607	4259643	3829639	3986963	4.39	0.21	4.18	4.60
> C16	29572650	32602900	31009813	31061788	34.21	1.36	32.84	35.57
	82093720	88057050	82759705	84303491	92.84		89.61	96.06

Average C19 peak = 908083 mass units

Raw J-34: Density Calculations

Carbon #	Mass (g)	Density : 20C(g/ml)	Volume (ml)	Total Density at 20C (g/ml)
5	3.27	0.627	5.22	0.029
6	4.70	0.659	7.14	0.041
7	6.07	0.683	8.89	0.053
8	5.95	0.702	8.47	0.052
9	5.63	0.718	7.84	0.049
10	4.90	0.731	6.71	0.043
11	4.90	0.740	6.62	0.043
12	4.36	0.749	5.82	0.038
13	4.93	0.756	6.53	0.043
14	4.89	0.762	6.42	0.043
15	4.64	0.768	6.04	0.041
16	4.39	0.773	5.68	0.039
17	34.21	0.777	44.00	0.300
	92.84		125.35	0.815

Total density = sum(volume fraction*density at 20C*1.1)
Actual density = 0.865 g/ml
Percent error = 5.8%

Raw J-34: Viscosity Calculations

Carbon #	Mass (g)	Density : 20C(g/ml)	Volume (ml)	TU	BU	Viscosity (cP)	Volume fraction * ln u
5	3.27	0.627	5.22	185	327	0.22	-0.06
6	4.70	0.659	7.14	209	379	0.30	-0.07
7	6.07	0.683	8.89	232	430	0.41	-0.06
8	5.95	0.702	8.47	252	477	0.55	-0.04
9	5.63	0.718	7.84	271	523	0.72	-0.02
10	4.90	0.731	6.71	289	566	0.93	-0.00
11	4.90	0.740	6.62	304	606	1.20	0.01
12	4.36	0.749	5.82	319	644	1.51	0.02
13	4.93	0.756	6.53	332	680	1.88	0.03
14	4.89	0.762	6.42	344	713	2.31	0.04
15	4.64	0.768	6.04	356	744	2.80	0.05
16	4.39	0.773	5.68	366	773	3.36	0.06
22	34.21	0.794	43.08	1000	1800	2.20E+04	3.46
	9.28E+01		124.43				3.41

Total viscosity = 30 cP
Actual viscosity = 29 cP
Percent error = -4.6%

Weathered J-34 (Bottoms): Composition Calculations

Carbon #	GC Results (Mass Units or M.U.)			Ratio to C19 peak	Std.	Error Bars	
	Run 1	Run 2	Average	(g)	Dev.	Low	High
< C6	27057	16966	22012	0.02	0.01	0.02	0.03
C6	382843	384448	383646	0.40	0.00	0.40	0.40
C7	2014634	2049712	2032173	2.12	0.02	2.10	2.14
C8	3574423	3722939	3648681	3.81	0.08	3.73	3.88
C9	4222335	4434531	4328433	4.52	0.11	4.41	4.63
C10	3895634	4170202	4032918	4.21	0.14	4.06	4.35
C11	4091439	4352851	4222145	4.41	0.14	4.27	4.54
C12	3821290	4039457	3930374	4.10	0.11	3.99	4.21
C13	4073620	4563540	4318580	4.51	0.26	4.25	4.76
C14	4349940	4573380	4461660	4.66	0.12	4.54	4.77
C15	4254590	4401850	4328220	4.52	0.08	4.44	4.59
C16	4259060	4243096	4251078	4.44	0.01	4.43	4.44
> C16	35371420	34295120	34833270	36.35	0.56	35.78	36.91
	74338285	75248092	74793189	78.04		76.42	79.67

Average C19 peak = 958375 mass units

Weathered J-34: Density Calculations

Carbon #	Mass (g)	Density : 20C(g/ml)	Volume (ml)	Total Density at 20C (g/ml)
5	0.02	0.627	0.04	0.000
6	0.40	0.659	0.61	0.004
7	2.12	0.683	3.10	0.023
8	3.81	0.702	5.42	0.041
9	4.52	0.718	6.29	0.048
10	4.21	0.731	5.76	0.045
11	4.41	0.740	5.95	0.047
12	4.10	0.749	5.48	0.044
13	4.51	0.756	5.96	0.048
14	4.66	0.762	6.11	0.050
15	4.52	0.768	5.88	0.048
16	4.44	0.773	5.74	0.047
17	36.35	0.777	46.75	0.388
	78.04		103.08	0.833

Total density = sum(volume fraction*density at 20C*1.1)

Actual density = 0.894 g/ml

Percent error = 6.8%

Weathered J-34 (Bottoms): Viscosity Calculations

Carbon #	Mass (g)	Density : 20C(g/ml)	Volume (ml)	TU	BU	Viscosity (cP)	Volume fraction * ln u
5	0.02	0.627	0.04	185	327	0.22	-0.00
6	0.40	0.659	0.61	209	379	0.30	-0.01
7	2.12	0.683	3.10	232	430	0.41	-0.03
8	3.81	0.702	5.42	252	477	0.55	-0.03
9	4.52	0.718	6.29	271	523	0.72	-0.02
10	4.21	0.731	5.76	289	566	0.93	-0.00
11	4.41	0.740	5.95	304	606	1.20	0.01
12	4.10	0.749	5.48	319	644	1.51	0.02
13	4.51	0.756	5.96	332	680	1.88	0.04
14	4.66	0.762	6.11	344	713	2.31	0.05
15	4.52	0.768	5.88	356	744	2.80	0.06
16	4.44	0.773	5.74	366	773	3.36	0.07
22	36.35	0.794	45.78	1000	1800	2.20E+04	4.48
	7.80E+01		102.11				4.64

Total viscosity = 103 cP

Actual viscosity = 110 cP

Percent error = 5.9%

Fraction 1: Composition Calculations

Carbon #	GC Results (Mass Units or M.U.)				Std.	Error Bars	
	Run 1	Run 2	Run 3	Average	Dev.	Low	High
< C6	7413451	7007579	6878053	7099694	228074	6871620	7327768
C6	7445081	7013510	6936602	7131731	223785	6907946	7355516
C7	4364627	4167672	4133939	4222079	101733	4120346	4323812
C8	1550059	1478338	1465673	1498023	37156	1460867	1535180
C9	476719	462459	457094	465424	8282	457142	473706
C10	142439	140981	139369	140930	1254	139676	142184
C11	46361	48201	47837	47466	796	46671	48262
C12	12848	11556	11510	11971	620	11351	12592
C13	4207	3378	3362	3649	395	3254	4044
C14	4765	3149	3166	3693	758	2936	4451
C15	0	0	0	0	0	0	0
C16	14239	8989	9100	10776	2449	8327	13225
> C16	21309	17306	15618	18078	2387	15691	20464
	21496105	20363118	20101323	20653515		20045827	21261203

Fraction 1: Density Calculations

Carbon #	Mass (g)	Density : 20C(g/ml)	Volume (ml)	Total Density at 20C (g/ml)
5	7099694	0.627	11316203	0.248
6	7131731	0.659	10828107	0.250
7	4222079	0.683	6182391	0.148
8	1498023	0.702	2132886	0.052
9	465424	0.718	648010	0.016
10	140930	0.731	192922	0.005
11	47466	0.740	64112	0.002
12	11971	0.749	15988	0.000
13	3649	0.756	4826	0.000
14	3693	0.762	4844	0.000
15	0	0.768	0	0.000
16	10776	0.773	13941	0.000
17	18078	0.777	23254	0.001
	20653515		31427483	0.723

Total density = sum(volume fraction*density at 20C*1.1)
Actual density = 0.715 g/ml
Percent error = -1.1%

Fraction 1: Viscosity Calculations

Carbon #	Mass (g)	Density : 20C(g/ml)	Volume (ml)	TU	BU	Viscosity (cP)	Volume fraction * ln u
5	7099694	0.627	11316203	185	327	0.22	-0.54
6	7131731	0.659	10828107	209	379	0.30	-0.41
7	4222079	0.683	6182391	232	430	0.41	-0.18
8	1498023	0.702	2132886	252	477	0.55	-0.04
9	465424	0.718	648010	271	523	0.72	-0.01
10	140930	0.731	192922	289	566	0.93	-0.00
11	47466	0.740	64112	304	606	1.20	0.00
12	11971	0.749	15988	319	644	1.51	0.00
13	3649	0.756	4826	332	680	1.88	0.00
14	3693	0.762	4844	344	713	2.31	0.00
15	0	0.768	0	356	744	2.80	0.00
16	10776	0.773	13941	366	773	3.36	0.00
22	18078	0.794	22769	1000	1800	2.20E+04	0.01
	20653515		31426998				-1.17

Total viscosity = 0.311 cP
Actual viscosity = 0.421 cP
Percent error = 26.2%

Fraction 2: Composition Calculations

Carbon #	GC Results (Mass Units or M.U.)				Std.	Error Bars	
	Run 1	Run 2	Run 3	Average	Dev.	Low	High
< C6	1927674	1927743	1945878	1933765	8565	1925200	1942330
C6	6790383	6844827	6902608	6845939	45822	6800117	6891762
C7	6862623	6900999	6932281	6898634	28487	6870147	6927121
C8	3207002	3203234	3242824	3217687	17841	3199845	3235528
C9	1265479	1259313	1276828	1267207	7254	1259953	1274461
C10	485277	482012	485603	484297	1621	482676	485919
C11	212920	209314	212433	211556	1598	209958	213153
C12	89800	86687	89157	88548	1342	87206	89890
C13	40902	38387	39858	39716	1032	38684	40747
C14	18228	13113	16093	15811	2098	13714	17909
C15	4207	3715	3709	3877	233	3644	4110
C16	12212	11616	13046	12291	586	11705	12878
> C16	21787	16161	17569	18506	2390	16115	20896
	20938494	20997121	21177887	21037834		20918964	21156704

```
Fraction 2:  Density Calculations
==========   ====================

          Mass    Density :  Volume Total Density at 20C
Carbon #   (g)    20C(g/ml)    (ml)   (g/ml)
--------  ----    ---------  ------   ------
       5  1933765    0.627  3082228    0.068
       6  6845939    0.659 10394190    0.242
       7  6898634    0.683 10101670    0.244
       8  3217687    0.702  4581342    0.114
       9  1267207    0.718  1764332    0.045
      10   484297    0.731   662966    0.017
      11   211556    0.740   285745    0.007
      12    88548    0.749   118255    0.003
      13    39716    0.756    52529    0.001
      14    15811    0.762    20738    0.001
      15     3877    0.768     5048    0.000
      16    12291    0.773    15901    0.000
      17    18506    0.777    23804    0.001
         =========          =================
         21037834           31108749   0.744
                                 Total density = sum(volume fraction*density at 20C*1.1)
                                 Actual density =     0.747 g/ml
                                 Percent error =        0.4%
```

```
Fraction 2:  Viscosity Calculations
==========   ======================

          Mass    Density :  Volume      TU       BU Viscosity  Volume fraction * ln u
Carbon #   (g)    20C(g/ml)    (ml)                     (cP)
--------  ----    ---------  ------      --       -- ---------  ----------------------
       5  1933765    0.627  3082228     185      327      0.22   -0.15
       6  6845939    0.659 10394190     209      379      0.30   -0.40
       7  6898634    0.683 10101670     232      430      0.41   -0.29
       8  3217687    0.702  4581342     252      477      0.55   -0.09
       9  1267207    0.718  1764332     271      523      0.72   -0.02
      10   484297    0.731   662966     289      566      0.93   -0.00
      11   211556    0.740   285745     304      606      1.20    0.00
      12    88548    0.749   118255     319      644      1.51    0.00
      13    39716    0.756    52529     332      680      1.88    0.00
      14    15811    0.762    20738     344      713      2.31    0.00
      15     3877    0.768     5048     356      744      2.80    0.00
      16    12291    0.773    15901     366      773      3.36    0.00
      22    18506    0.794    23308    1000     1800 2.20E+04    0.01
         =========          =========                         =========
         21037834           31108252                            -0.93
                                              Total viscosity =    0.393 cP
                                              Actual viscosity =   0.548 cP
                                              Percent error =       28.3%
```

APPENDIX II

SUMMARY OF INDIVIDUAL SPILL BEHAVIOUR IN THE WIND/WAVE TANK

Summary of Individual Tests

A1 – MSW, 1 mm slick, low energy, 15°C

A 1 mm slick of MSW was placed on the water surface. After 30 minutes of wind/wave action, the oil was present as numerous patches 20–80 mm in diameter with a sheen between the patches. During the succeeding hours, the patches or slicklets became progressively smaller and very little of the sheen was dispersed into the water. Dispersed oil concentrations were fairly constant at about 5 ppm during the seven–hour test run. At the end of the seven–hour run, the oil was in numerous emulsified patches, ranging in diameter from 5 to 20 mm, with the sheen (approximate thickness 20 um) representing about 10% of the amount originally spilled. Water content of the emulsified oil was about 50%.

A2 – MSW, 5 mm slick, low energy, 15°C

A 5 mm slick of MSW was placed on the water surface. Immediately upon removing the spill containing ring, the slick area increased from the initial area of 0.82 m^2 to about 2 m^2; the slick remained fairly continuous and homogeneous with only a few thick patches and bare patches. After two hours of wind/wave action, the remaining oil was in 5 to 20 mm diameter patches and one 1 m^2 thick slick. After four hours, several "fingers" of open water were visible in the main slick; these fingers would open and close as a wave passed through the slick, but, while the oil appeared to be fluid, the slick edges of the fingers did not recoalesce even when they met in a wave trough. Dispersed oil concentrations were low (less than 10 ppm) throughout the test run. Emulsified water content was 50% after the first hour, increasing to the 60–65% range in the succeeding hours.

A3 – MSW, 1 mm slick, high energy, 15°C

Within five minutes of starting the test run, the oil formed a thick sheen with some patches of 5 – 10 mm diameter. After 90 minutes, much of the sheen had agglomerated into patches of diameter 5 – 50 mm with most in the 10 – 20 mm range. The patches did not recoalesce with each other even when they met and collided. Little change was noted over the next 4½ hours. At the completion of the test run (7 hrs) the patch size had reduced slightly, with most in the 5 – 10 mm diameter range. The patches appeared to remain distinct even when moved to the end of the tank with a towed containment boom. Dispersed oil concentrations were slightly greater than in the low energy test, reaching a range of 10 – 20 ppm. Emulsified water contents were fairly constant in the 64 – 68% range through the seven–hour run.

A4 – MSW, 5 mm slick, high energy, 15°C

A 5 mm slick was placed on the water surface. After removing the spill containing ring, the oil spread to cover an area of about 2 m^2. During the first hour of the test run, several long "fingers" and patches, 10 to 50 mm diameter, had formed. Over the next few hours, the patches became gradually smaller until after six hours, the small patches had fully disintegrated and all that was left were several large patches resulting from the initial "fingers". These large patches appeared to be resistant to further breakage from the waves. After seven hours, when the wind and waves were stopped, there was some recoalescence of these large patches. Dispersed oil concentrations were substantially higher than in the previous tests, and were in the 40 to 70 ppm range. Emulsified water contents were comparable to those in the previous "high energy" run, and were 64 to 72%.

A5 – MSW, droplets, low energy, 15°C

Using the "blowout" apparatus, 2 l of MSW was injected at the bottom of the tank, in droplet form. When the droplets reached the water surface they immediately recoalesced, forming a continuous slick 2 to 3 m^2 in area. Over the next seven hours of wind/wave action, little difference was noted compared with the previous low energy batch slicks. Dispersed oil concentrations were in the range of 5–20 ppm; emulsified water contents increased from 40% up to 70% through the test.

A6 – MSW, droplets, high energy, 15°C

As in A5, the droplets recoalesced to form a continuous slick when they reached the surface. The slick behaved in a similar fashion to the previous high energy batch slicks, developing into several large patches with sheen in between. Emulsified water contents through the test run were in the 55–70% range.

A7 – B–27, 1 mm slick, low energy, 15°C

Upon placing the slick on the water surface, it was apparent that this oil would behave differently than the MSW, even though the water temperature was only near the oil's pour point and not below it. As the oil was poured onto the water surface, it cooled and did not spread to the edges of the spill containing ring. Within minutes of starting the wave paddle, the slick was broken into 100 mm diameter plates, and had the appearance of a shattered pane of glass. These plates became progressively smaller under the influence of the wind/wave action, and were about 50 mm or less in diameter after the two hours, and 10 to 20 mm after six hours. Dispersed oil concentrations were close to negligible through the test run. Emulsified water contents were low, about 6% at one and three hours and 19% at seven hours.

A8 – B–27, 5 mm slick, low energy, 15°C

During the first three hours of low energy wind/wave action, the oil remained fluid, breaking into patches and long slicklets that would recoalesce upon contact. By four hours, recoalescence was lessening and 100 mm diameter patches were forming, patches that became progressively smaller until after seven hours they were in the 10 to 50 mm range with most about 25 mm in diameter. Dispersed oil concentrations were low (less than 10 ppm) throughout the test. Emulsified water contents increased through the test from 41% at one and three hours to 52% at seven hours.

A9 – B–27, 1 mm slick, high energy, 15°C

Within 10 minutes of starting the wind and waves, all oil was in patches that were less than 30 mm diameter. Through the test run, losses to dispersion and to the tank walls were high. After three hours, what little oil was left was patches less than 10 mm diameter. Dispersed oil concentrations were about 20 ppm during the first three hours, increasing to about 30 – 35 ppm by the end of the test at seven hours. Emulsified water content was measured at 35 and 37% at one and three hours, respectively, and 58% at seven hours.

A10 – B27, 5 mm slick, high energy, 15°C

Within 15 minutes of starting the test, the slick broke into plates that were of a maximum diameter of 80 mm. Over time they became progressively smaller, ranging from 5 to 70 mm after five hours, to less than 20 mm (most less than 10 mm) after seven hours. Dispersed oil concentrations were 10 to 20 ppm at one hour, 25 to 35 ppm at three hours, and about 100 ppm at seven hours. Emulsified water contents were in the range of 35 to 45%.

A11 – B–27, droplets, low energy, 15°C

When the droplets, injected at depth, reached the water surface they spread to form a 2 m^2 slick (average thickness 1 mm) with some sheen. The sheen ceased spreading after a few minutes. With the start of the wind and wave action, the slick broke into long fingers (20 by 200 mm) and patches with some sheen between them. After two hours, the sheen had dispersed and the oil was present as 5 to 20 mm diameter patches. Dispersed oil concentrations reached a maximum of 5 to 10 ppm at seven hours. Emulsified water contents were in the range of 25 to 40% through the test. As the droplets quickly recoalesced into a slick that behaved similar to the previously tested "batch" slick, the droplet test was not repeated at high energy.

A12 – J–34, 1 mm slick, low energy, 15°C

A 1 mm slick of J–34 was placed on the surface; it quickly spread to cover twice the original area. Within five minutes of low energy wind/wave action, the slick was broken into five windrows, 50 mm by 500 mm, and several patches 50 mm in diameter. Slick fragmentation continued at a much slower rate, eventually resulting in 10 to 20 mm diameter patches after four hours with a light sheen between the patches for the first two hours of the run. Dispersed oil concentrations were less than 10 ppm; emulsified water contents were 32% at one hour and 37% at four hours. Due to apparatus problems, the test was ended at four hours.

A13 – J–34, 5 mm slick, low energy, 15°C

A 5 mm slick of J–34 was placed on the water surface within a spill containing ring. When the spill ring was removed, the slick area increased three to fourfold. After 30 minutes of wind/wave action, slick fragments were up to 200 mm in diameter, with most in the 50 to 100 mm range. After one hour, the patches were in the 10 to 50 mm diameter range, with some light sheen between them. Fragmentation continued over the next six hours, resulting finally in 10 to 20 mm diameter patches. Dispersed oil concentrations were low throughout the test run, never exceeding 5 ppm. The maximum emulsified water content was 30%, measured at seven hours.

A14 – J–34, 1 mm slick, high energy, 15°C

Once the spill containing ring was removed, the slick increased in area to 2 to 3 m^2 (average thickness 0.3 to 0.4 mm). After 10 minutes of wind/wave action, the oil was in long windrows that behaved as a fluid slick. After 15 minutes, the windrows and patches were not recoalescing, and little sheen was observed between them; most oil was in patches of diameter greater than 100 mm. After three hours, most oil was in patches 50 to 100 mm in diameter, with a few small patches and no sheen. After seven hours, the patches would not recoalesce, even when forced together with a containment boom. Dispersed oil concentrations were only slightly higher than the low energy tests, reading 10 to 20 ppm. Emulsified water contents were comparable, in the 15 to 25% range.

A15 – J–34, 5 mm slick, high energy, 15°C

After five minutes of wind/wave action, the slick area had increased to 3 to 4 m^2 (average thickness 1.0 to 1.3 mm) and was in fairly continuous windrows with few patches and little sheen. Slick fragmentation started after 15 minutes, when long "fingers" developed, ranging in size from 20 by 200 mm to 50 by 500 mm. After one hour, most oil was in 50 to 100 mm diameter patches, with a few 50 by 200 mm fingers and very little sheen. The size range of patches increased over the next hour to the 20 to 100 mm range, with most about 50 mm range. Little change was noted during the next two hours (four hours total) when the test ended due to failure of the wave paddle. Dispersed oil concentrations were in the 15 to 30 ppm range; emulsified water content was measured at 32% and 33% at one and three hours.

A16 – J–34, droplets, low energy, 15°C

Two litres of oil was injected as droplets near the tank bottom. On the water surface, the droplets agglomerated and then recoalesced to form a 20 by 1000 mm slick. After 90 minutes of wind/wave action, the slick had broken into discrete, non–recoalescing patches 5 to 50 mm in diameter. Little change was noted during the remainder of the test run (seven hours total). Dispersed oil concentrations were less than 10 ppm throughout the test. Emulsified water contents were measured at 30% and 38% at one and three hours, respectively. As the droplets quickly recoalesced to form a batch slick with behaviour similar to that observed in the previous test, the droplet test was not repeated at high energy.

B1 – MSW, 1 mm slick, low energy, 5°C

After one hour of low energy wind/wave action, the slick had broken into 50 mm diameter patches with a sheen in between them. After three hours, the patches were slightly smaller, 35 to 50 mm diameter, and covered a total area of about 4 m^2. The patch size was fairly stable over the next four hours. At the end of the test run, the patches were confined with a barrier against a wind–driven surface current, causing them to stick together but not recoalesce. When released from the barrier, the patches separated to roughly their pre–confinement form. Dispersed oil concentrations were measured in the 10 to 25 ppm range. Emulsified water content was in the range of 62 to 76%.

B2 – MSW, 5 mm slick, low energy, 5°C

When the spill containing ring was removed, the oil spread to form a continuous 3 m^2 slick (average thickness about 1.3 mm). After one hour, almost all of the oil was in a continuous 2 m^2 slick, with some patches and long finger–like slicks at its edges. At this time, the first signs of slick fragmentation were observed as the large slick developed "fingers" about 100 mm in width. Changes during the remainder of the test run were gradual; after seven hours, most of the oil was still in a fairly continuous slick that comprised several long fingers (50 by 500 mm) with a few small patches around the perimeter. Dispersed oil concentrations were measured in the 7 to 20 ppm range. Emulsified water content was measured in the range of 74 to 78%.

B3 – MSW, 1 mm slick, high energy, 5°C

Within ten minutes of starting the wind/wave action, the slick broke into patches, about 50 mm in diameter, with sheen between them. Unfortunately, the small amount of oil used combined with the high wave energy caused most of the oil to be deposited on the tank walls within the first hour of testing. Dispersive losses were also high in the first hour; dispersed oil concentrations were measured at 43 ppm near the water surface and 30 ppm further down. What little oil was left was in small, discrete patches with very little sheen. The maximum emulsified water content was measured at 51% at seven hours.

B4 – MSW, 5 mm slick, high energy 5°C

Slick fragmentation was similar to that observed in the A4 test (same parameters at 15°C): the slick progressively developed long "fingers" that broke onto 50 to 100 mm diameter patches. After two to three hours, the patches appeared to be well–defined and non–recoalescing, and no sheen was observed. Dispersed oil concentrations were fairly constant through the test, and were in the 40 to 50 ppm range. Emulsified water content was measured at 46% and 43% at one and three hours, and 82% at seven hours. At the completion of the test run, booming the patches with a barrier caused them to consolidate without completely coalescing; when freed, most broke free to form discrete patches as before the booming.

B5 – MSW, droplets, 5°C

Using the "blowout" apparatus, 2 l of MSW was injected in droplet form at the bottom of the tank. When the droplets reached the surface, they immediately recoalesced forming a continuous slick. Rather than duplicating the previous "batch" slick runs, the test was terminated.

B6 – B–27, 1 mm slick, low energy, 5°C

As the oil was poured onto the water surface, it appeared to gel slightly and it failed to fill the spill containing ring; initial slick area was about 400 by 700 mm (average thickness about 3 mm) with a trace of sheen at its edges. When the waves were started, the slick quickly broke into three large pieces, which were in turn broken into smaller pieces. The pieces broke in the following manner: the trailing edge (relative to the waves) of the piece submerged at the wave crest, was bent back–and–forth in successive waves until it broke free. After a few minutes, the pieces were in the 200 to 400 mm diameter range. After 15 minutes, most of the oil was in patches about 100 mm in diameter, and after one hour all of the patches had broken to the 10 to 50 mm diameter range. At the end of the test run, at seven hours, most of the original oil was stuck to the tank walls, what little oil was left was in small patches 10 to 20 mm in diameter. Dispersed oil concentrations were 10 to 15 ppm; three measurements of emulsified water content were between 40 and 48%.

B7 – B–27, 5 mm slick, low energy, 5°C

As in the B6 test, the oil gelled as it was poured onto the water surface and did not completely fill the spill containing ring: initial slick thickness was about 6 mm with some thin patches. With the start of waves, the oil immediately broke into 200 mm diameter patches that had jagged edges. Further breakage was more gradual over the next hour; after one hour, the oil was in discrete patches (50 to 100 mm diameter) that had rounded, built–up edges similar to old pack ice floes. When confined with a containment barrier at the end of the test run (seven hours), the patches consolidated, but did not coalesce (Figure 45), and floated freely and discretely again once released. Dispersed oil concentrations were in the 5 to 10 ppm range through the test run; emulsified water content was similar to the B6 results, and were in the 44 to 48% range.

B8 – B–27, 1 mm slick, high energy, 5°C

Initial spreading observations were similar to the B6 and B7 tests. Within 30 seconds of starting the waves, the slick had broken into 100 mm diameter pieces. After one hour, little oil was left on the water surface, the majority having been deposited on the walls of the tank. What was left was present as 20 mm blobs that appeared to be the result of slightly larger patches "balling–up" under the influence of the waves. After three hours, the only oil left was a number of small blobs, 5 to 20 mm in diameter. As in the previous B6 and B7 tests, dispersed oil concentrations were low, below 10 ppm throughout the test. Emulsified water contents were higher, measured at 50% at one hour and 56 and 55% at three and seven hours.

B9 – B–27, 5 mm slick, high energy, 5°C

Initial slick coverage was similar to the B7 test; initial oil thickness was about 6 mm with some thin patches. Immediately after starting the waves, the slick broke into patches. Within one minute, the patches were 10 to 100 mm in diameter and up to 10 mm thick with most 20 to 50 mm in diameter. Within 10 minutes, the patches were "balling–up" to form blobs 50 to 100 mm in diameter, which gradually broke up to form 50 to 20 mm diameter blobs over the next hour. Little change was noted over the next seven hours except that more smaller blobs were observed. Dispersed oil concentrations were in the 10 to 20 ppm range. Emulsified water contents were higher than the previous B–27 runs, and were measured at 61 to 74%.

B10 – B–27, droplets, low energy, 5°C

Using the blowout apparatus, 2 l of B–27 was injected through a nozzle near the tank bottom. When the droplets reached the water surface, they agglomerated (but did not coalesce) to form 50 to 100 mm diameter mats of droplets (Figure 46). After one hour of wind/wave action, the textured appearance of the mats was gone as the mats were consolidated into clumps. These clumps continued relatively unchanged through the remainder of the seven–hour test. Dispersed oil concentrations were low, less than 10 ppm throughout the test run. Emulsified water contents were comparable to the previous B–27 "batch" slick tests, measured at 56 to 63%.

B11 – B–27, droplets, high energy, 5°C

Initial oil droplet behaviour was similar to that observed in B10: the droplets rose to the water surface and formed mats of droplets, the mats then balling–up to form clumps soon after wave energy was applied. Figure 47 shows the oil clumps at three hours. After seven hours of wind/wave action, these clumps, which were 10 to 50 mm in diameter, remained discrete and would not agglomerate or recoalesce even when forced together by the wind. As in the previous B–27 tests, dispersed oil concentrations were low (less than 10 ppm throughout the test run). Emulsified water contents were also comparable, measured in the 54 to 59% range.

B12 – J–34, 1 mm slick, low energy, 5°C

As with the B–27 batch slicks, the J–34 oil, when poured onto the water surface, gelled and failed to fill the spill containing ring. Average initial oil thickness was about 1.2 mm, with some slightly thicker areas within the slicks. After one hour of wind/wave action, the oil was in floe–like mats, most of which were less than 100 mm in diameter with two mats about 150 mm diameter. After seven hours, the oil was virtually unchanged in appearance; the size range of patches was, in the main, 10 to 50 mm diameter, with several patches about 100 mm diameter. Dispersed oil concentrations were less than 10 ppm throughout the test run. No water–in–oil emulsification was observed.

B13 – J–34, 5 mm slick, low energy, 5°C

As compared with the B12 run, the slick broke up more quickly initially, but followed virtually the same progression of fragmentation. The final slick conditions can be seen in Figure 48, which shows the patches of oil immediately after they have been confined against a barrier by wind forces. The patches are 10 to 50 mm in diameter, and they do not coalesce although they do stick together somewhat when forced against one another. Dispersed oil concentrations were low, less than 5 ppm throughout the test. No water–in–oil emulsification was observed.

B14 – J–34, 1 mm slick, high energy, 5°C

As the oil was poured onto the water surface, it gelled and covered only about half the spill ring area (average initial thickness about 2 mm). The slick was quickly fragmented as a result of wave action; after two minutes, the slick fragments were less than 100 mm diameter, with most 10 to 50 mm. After 10 minutes, they were about 20 mm in diameter, and after one hour they were about 10 mm in diameter. Little change was observed over the next six hours. Dispersed oil concentrations were slightly higher than the previous J–34 tests, and were in the 5 to 15 ppm range. Emulsified water contents were low, measured at 16% and 15% at one and three hours, and 8% at seven hours.

B15 – J–34, 5 mm slick, high energy, 5°C

As with the previous J–34 tests, the oil, when poured onto the water surface, gelled and failed to cover the area within the spill containing ring: initial average slick thickness was about 6 mm. When the wind/wave energy was started, the slick quickly broke into pieces. After two minutes, the pieces were as large as 300 mm diameter, after 10 minutes they were all less than 100 mm diameter with most in the 10 to 50 mm range. After one hour, the larger pieces had broken further, and there were also thick clumps – 20 to 50 mm diameter and up to 20 mm thick – that had formed as a result of two or more pieces colliding in a wave trough. Little change was observed over the next six hours. Dispersed oil concentrations were low, in the 5 to 10 ppm range. No water–in–oil emulsification was observed.

B16 – J–34, droplets, low energy, 5°C

Using the blowout apparatus, 2 l of J–34 was injected through a nozzle near the tank bottom. When the droplets reached the water surface, they agglomerated (but did not recoalesce) to form 20 to 100 mm diameter mats, covering a total area of 3 to 4 m^2. The mats had a pebbled appearance, indicating that the droplets had retained their individual integrity. Over the first two hours, the mats tended to "ball–up" under the influence of wave energy, resulting in clumps 20 to 50 mm diameter, and a few millimetres thick. Little change was observed for the balance of the seven-hour test run. Dispersed oil concentrations were very low, less than 5 ppm throughout the test. Emulsified water content was also very low, measured at 9% at one and seven hours, and zero at three hours.

B17 – J-34, droplets, high energy, 5°C

Initial oil droplet behaviour was similar to that observed in the B16 test. The droplet mats, measured 50 to 100 mm diameter and were irregularly shaped initially. Figures 49 and 50 show the oil droplets, five and 15 minutes after discharge. Their thickness appeared to be fairly uniform, 1 to 2 mm (i.e., one to two droplets thick). During the first hour of wind/wave action, the mats tended to "ball-up", forming clumps that were 10 to 15 mm thick and 10 to 30 mm in diameter. They were more rounded, and more rounded still at seven hours when they were of fairly uniform size, 10 to 20 mm diameter. Dispersed oil concentrations were very low, less than 5 ppm throughout the test. Emulsified water content was also very low, measured at 4% at one and three hours, and 6% at seven hours.

APPENDIX III

COMPUTER PROGRAM LISTING

```
{$R+}
program waxfate;
      {
      **********************************************************************
      *       Most recent revision: Nov  5, 1987                          *
      **********************************************************************
      *                                              Nov 3,1987            *
      *     Added option of cutting off the model run after a certain     *
      * amount of time. Module 'HowLong.inc' added and module 'Question   *
      * .inc' added to.                                                    *
      **********************************************************************
      *                                              Oct 30, 1987          *
      *     Added output to take up continuous spill section generation   *
      * time on the graphs. Time is now fairly accurate.                   *
      *     Added a header on the printer output.                          *
      *                                                                    *
      **********************************************************************
      *                                              Oct 22, 1987          *
      *     SubSea has been made to work. Major readjustment of the new   *
      * SpillType logic was necessary in order to get a realistic batch   *
      * start from the SubSea input.                                       *
      *                                                                    *
      **********************************************************************
      *                                              Sept 17, 1987         *
      *     Oilfate is becoming WAXFATE. Addition of blowouts, both       *
      * above and below sea, necessitates the rearrangement of the menu   *
      * system.                                                            *
      *                                                                    *
      **********************************************************************
      *                                              June, 1987            *
      *     OilFate has now been modified to enable the running of other *
      * programs from within it and hardcoded to run MakeGraf from within *
      * it. These options are available from the main menu.               *
      *     In order to leave room for the loading of other programs,     *
      * OilFate must be compiled using the O)ptions choices:               *
      *         C)om file                                                  *
      *         mAximum dynamic memory = 0100                              *
      *         mInimum dynamic memory = 0100                              *
      *     This insures that OilFate does not take all of available      *
      * memory for it's own. In future modifications of OilFate it may be *
      * necessary to increase the values from 0100. This would be signaled*
      * by the 'stack-heap collision' error from Turbo.                   *
      *                                                                    *
      **********************************************************************
      }

const
   min_thick:real = 1e-6;
   fract_vol:real = 0.05;       {the RUN limits - how far do we take it?}

   tstep = 100;                 {The basic 'heart-beat' of the model - in
                                                               seconds}
   ShortStep:integer = 36;      {step size for running the Sub and AboveSea
                                initialization procedures}
   Size = 42;                   {number of variables in the 'fateinit' file}
                                { Used by UT-MOD00 and UT-MOD03
                                                   to define an array size}

   FF = 12;

   G = 9.81;
```

```
   Pi = 3.14159;

   Hour2Sec = 3600.0;
   Day2Sec = 86400.0;
   Week2Sec = 604800.0;

   MaxInt =  32767;
   MinInt = -32767;
   MaxReal = 1e+37;
   MinReal = 1e-37;

{ * TURBO-UT.PAS ram/rom *                  }
{ * by Don Ramsey and Larry Romero *        }
{ * March-April-May 1984 *                  }
{ * Modified by J. Morrison - July, 1987 - by the addition of 'Size' * }
{ *   and again             - Nov,  1987 - by the addition of Memory_scr[2] * }
type
  str255     =   string[255];
  str80      =   string[80];
  str20      =   string[20];
  str5       =   string[5];
  screen     =   array[1..4000] of char;

var
  Ch              : Char;
  Answer,S        : str255;
  Template        : str80;
  P,Filvar        : array[1..Size] of str80; { menu Prompts }
     {Note that 'Size' is now a visible constant, declared in the major
      program. This is done for ease of expansion.}
  InsertOn,Exit,
  Escape,
  F1,F3,
  Use_Default,
  First_Run       : Boolean;
  Video_Scr1      : array[1..4000] of char absolute $B000:$0000;
  Video_Scr2      : array[1..4000] of char absolute $B800:$0000;
    { video_scr1 is mono screen & video_scr2 is color graphics }
    { Note that these do not require space in the data segment }
  Memory_Scr      : array[1..2] of screen;
    { Memory_scr is the memory image of the video }

{ * Modified by JDM - Nov, 1987 - to use multiple screen images in SaveScreen
                                                        and FlashScreen}

procedure Msg(MsgString: str255; Col,Row: integer);
   { Print a message at location Col,Row }
 begin
    gotoXY(Col,Row);  write(MsgString);
 end;

procedure Center(S: str255; Col,Row,L: integer);
  { Center a string on a line of L length beginning at position Col,Row }
  {** (Col,Row) is row and column to center on **}
  {** L is the length of the line to center on **}
var I: integer;
 begin
    gotoXY(Col,Row);
    for I:= 1 to L do write(' ');
    gotoXY(Col+(L-Length(S)) div 2,Row); write(S);
```

```
 end;

procedure InvVideo( InvStr: str255);
    { print a string in inverse video }
 begin
   textBackground(15);textcolor(0); write(InvStr);
   textBackground(0) ;textcolor(7);
 end;

procedure Color(BackGnd,Txt: integer);
   { change the background & text color }
 begin
   textBackGround(BackGnd); textColor(Txt);
 end;

function UpcaseStr(S : Str80) : Str80;
   { convert a string to UpperCase }
var
  P : Integer;
begin
  for P := 1 to Length(S) do
    S[P] := Upcase(S[P]);
  UpcaseStr := S;
end;

function ConstStr(C : Char; N : Integer) : Str80;
  (*  ConstStr returns a string with N characters of value C *)
var
  S : string[80];
begin
  if N < 0 then
    N := 0;
  S[0] := Chr(N);
  FillChar(S[1],N,C);
  ConstStr := S;
end;

function fmt_real(num : real; len,dec: integer): str20;
   { Sstring is string[20] }
   { format a real number to length len (len is total length of string
     including commas and decimal), with dec decimal places }
 var  s1,s2,Temp : string[20];
      C,I,J,K,Cd : integer;
  begin
    str(num,S1);
    S1 := copy(S1,pos('+',S1)+1,2);
    val(S1,C,cd); str(num:C:dec,S1);
    S2 := copy(S1,pos('.',S1)+1,dec);
    S1 := copy(S1,1,pos('.',S1)-1);
    J:=1; K:=0;
    for I := length(S1) downto 1 do
      begin
       if ((j mod 3) = 0) and (I <> 1) then
         begin
           if (I=2) and (copy(s1,1,1)='-') then S1:=S1 else
           s1:=copy(s1,1,length(s1)-j-k)+','+copy(s1,i,length(s1)-i+1);
           k:=k+1;
         end;
       J:=J+1;
      end;
```

```
    Temp := S1+'.'+S2;
    if length(Temp) > len then Temp:='%'+Temp;
    if length(Temp) < len then
      begin
       repeat Temp:=' '+Temp; until length(Temp)=len;
      end;
    Fmt_real := Temp;
  end;

procedure Box(C1,R1,C2,R2,M: integer);
 { Draw a box with a dividing line }
 {* (C1,R1) is upper left of box, (C2,R2) is lower rt of box *}
 {* M is the row of the dividing line (2nd line) of box      *}
 var I,J,K: integer;
  begin
    K:= C2-C1-1; HighVideo;
    GotoXY(C1,R1); write('Ö');
    for I:=1 to K do write('á');
    write('¢');
    for I:=R1+1 to R2-1 do
    begin
      GotoXY(C1,I); write('°');
      if I = M then begin
        for J:=1 to K do write('á');
      end;
      GotoXY(C2,I); write('°');
    end;
    GotoXY(C1,R2); write('â');
    for I:=1 to K do write('á');
    write('ì'); LowVideo;
  end;

procedure Option;
   { Read a keyboard character & convert to upper-case }
 begin
    read(kbd,Ch);  Ch:=UpCase(Ch);
 end;

procedure StripSpaces(S: str255; var NewStr: str255);
    {strip spaces from the end of a string}
 begin
   S:=S+'  '; NewStr := copy(S,1,pos('  ',S)-1);
 end;

procedure ClrWnd(C1,R1,C2,R2: integer);
   { Clear a selected portion of the screen }
   {** (C1,R1) & (C2,R2) are upper left and lower rt of window **}
 var I,J,K: integer;
 begin
   K:=C2-C1-1;
   for I:=R1 to R2 do
     begin
       gotoXY(C1,I); for J:= 1 to K do write(' ');
     end;
 end;

procedure SaveScreen(Num:integer);
    { save an image of the video in memory }
 var mono: boolean;
  begin
```

```
    if (mem[0000:1040] and $30) = $30 then Mono:=true else Mono:=false;
    if mono then move(video_scr1[1],memory_scr[Num,1],4000)
    else         move(video_scr2[1],memory_scr[Num,1],4000);
  end;

procedure FlashScreen(Num:integer);
    { redisplay a memory image of a video display }
 var mono: boolean;
  begin
    if (mem[0000:1040] and $30) = $30 then Mono:=true else Mono:=false;
    if mono then move(memory_scr[Num,1],video_scr1[1],4000)
    else         move(memory_scr[Num,1],video_scr2[1],4000);
  end;


{Modified by JDM to use the 'Esc' key both to clear input and, if pressed
 twice, to jump back a level in the menu}

procedure Beep(Tone,Duration : integer);
 begin
   Sound(Tone); Delay(Duration); NoSound;
 end;

procedure Say_Cap_Num;
   { Display Caps, Num, Insert in inverse video on line 25 of Video }
 var  Value  : integer;
 begin
     Value := Mem[0000:1047];      { test for caps, numbers, & cursor cntrl }
     gotoXY(65,25);
     Case Value of
       0   : begin LowVideo; write('               '); Inserton:= false; end;
       32  : begin LowVideo; write('     '); InvVideo('NUM');
                   Clreol; InsertOn:= false; end;
       64  : begin InvVideo('CAPS'); Clreol;
                   InsertOn:= false; end;
       96  : begin InvVideo('CAPS'); write(' '); InvVideo('NUM');
                   Clreol; InsertOn:=false; end;
       128 : begin LowVideo; write('         ');
                   InvVideo('Insert');InsertOn:=true; end;
       160 : begin LowVideo; write('     '); InvVideo('NUM');write(' ');
                   InvVideo('Insert'); InsertOn:=true; end;
       192 : begin InvVideo('CAPS'); write('     ');
                   InvVideo('Insert'); InsertOn:=true; end;
       224 : begin InvVideo('CAPS'); write(' ');InvVideo('NUM'); write(' ');
                   InvVideo('Insert'); InsertOn:= true; end;
     end; { Case }
  end;

procedure Set_Cap_Num(Caps,Num,Insert : Char);
   { Set the Cap Lock, Number Lock, and Ins Keys as desired }
 var J : integer;
 begin
  if Insert='I' then J:=128 else J:=0;
  Case Caps of
    'C': begin if Num='N' then  MemW[0000:1047]:= 96+J
                else            MemW[0000:1047]:= 64+J;
          end;
    ' ': begin if Num='N' then  MemW[0000:1047]:= 32+J
                else            MemW[0000:1047]:=  0+J;
          end;
```

```
  end; { Case }
 end;

{.pa}
procedure Ck_edit_key(var Ch: Char);
   { test for an IBM Cursor control or Function key }
begin
  read(kbd,Ch);
  begin {see if IBM specific key pressed}
    case Ch of
      'H': Ch:=^E    ;  { up-arrow   }
      'P': Ch:=^X    ;  { dn-arrow   }
      'M': Ch:=^D    ;  { rt-arrow   }
      'K': Ch:=^S    ;  { left-arr   }
      'S': Ch:=#127  ;  { Del        }
      'R': Ch:=^V    ;  { insert     }
      'G': Ch:=^G    ;  { Home       }
      'O': Ch:=^O    ;  { End        }
      'I': Ch:=^R    ;  { Pg-Up      }
      'Q': Ch:=#00   ;  { Pg-Dn      }
      ';': Ch:=^a    ;  { F1         }
      '<': Ch:=^b    ;  { F2         }
      '=': Ch:=^c    ;  { F3         }
      '>': Ch:=^d    ;  { F4         }
      '?': Ch:=^e    ;  { F5         }
      '@': Ch:=^f    ;  { F6         }
      'A': Ch:=^g    ;  { F7         }
      'B': Ch:=^h    ;  { F8         }
      'C': Ch:=^i    ;  { F9         }
      'D': Ch:=^j    ;  { F10        }
    end;   {Case Ch}
  end;   {IBM check}
end;  {Ck_edit_key}

procedure Get_Template(Template_num:integer; var template: str80);
   { Templates are specified by the Programmer }
 begin
  Case Template_num of
    1 : template := '(___) ___-____';
    2 : template := '__/__/__';
  end;
 end;

procedure Input(Typ: Char          ;    { Type of input        }
                Default: str255   ;    { Default string       }
                Col,Row: integer   ;    { Where start line     }
                Mlen: integer      ;    { Max length           }
                UpperCase:Boolean  ;    { True if auto Upcase  }
           var  F1,F3,                { Returned true if F1 or F3 }
                ESC: Boolean )     ; { Returned true if 'Esc' }

   {-- requires
       Global procedures:
         Say_Cap_Num, Set_Cap_Num, Color, Ck_edit_key, Beep, Get_template }
var
  X,J,LastValue: integer;
  OkChars,temp : set of Char;
  DF           : Boolean;

{.pa}
```

```
{-------------------------- local procedures --------------------------}
  procedure GotoX;
   begin
     GotoXY(X+Col-1,Row);
   end;

  procedure Ck_Cap_Num; { test for caps, numbers, & cursor cntrl }
   var Value : integer;
   begin
      repeat
        Value := Mem[0000:1047];
        if LastValue<>value then
          begin LastValue:=Value; Say_Cap_Num; GotoX; end;
      until keypressed;
   end;

  procedure PosX;
    begin
      while copy(template,X,1)<>#95 do
       begin
         Answer:=Answer + copy(template,X,1); X:=X+1; GotoX;
       end;
    end;

  procedure Del_Ans;
    begin
      Answer:=''; X:=1; GotoX;
      write(template);  GotoX; PosX;
    end;
{------------------------ end local procedures ------------------------}

begin
  if Typ='A'then  OKChars:=[' '..'}']
  else OKChars:=['0'..'9','+','-','.'];
  Temp := OKChars;  color(7,0); DF:= false;
  Case Typ of
    'A','N','$': begin  fillchar(template,80,#95);
                        template:=copy(template,1,Mlen);
                        if Typ='$' then
                         begin
                           X:=0; GotoX; HighVideo; write('$');
                         end;
                 end;
    'F':         begin
                   Get_template(Mlen,template); Mlen := length(template);
                   if copy(template,1,1)<>#95 then DF:= true;
                 end;

  end;

  if Typ = 'A' then if uppercase then Set_Cap_Num('C',' ','I')
                    else Set_Cap_Num(' ',' ','I')
  else Set_Cap_Num(' ','N',' ');
  Color(7,0);
  Answer := ''; F1:=false; F3:=false;
  if Default<>'' then
    begin
      X:=1; GotoX; write(template); GotoX; write(default);
      Answer:=Default;
    end
```

```
  else Del_Ans;
  LastValue:=Mem[0000:1047]; Say_Cap_Num; GotoX;

  ESC:= false;
  repeat
    Ck_Cap_Num; read(kbd,Ch);  Color(7,0);
    if (keypressed) and (Ch<>'p') and (Ch<>'q') then Ck_edit_key(Ch);
    if (Typ='F') and (X=1) and (Default<>'') and (Ch<>^I) and (Ch<>#13)
     then Del_Ans;
    if ESC and (ch = ^[) then         {ESC pressed twice}
     Exit:= true
    else
     case Ch of
       ^[: begin Del_Ans;
                ESC:= true
           end;     { ESC pressed once  }

       ^D: begin { Move cursor right : rt-arr }
             X:=X+1;
             if (X>length(Answer)+1) or (X>Mlen) then X:=X-1;
             GotoX;
           end;

       ^S: begin { Move cursor left : left-arr }
             if Typ='F' then Del_Ans  else
             begin
               X:=X-1; if X<1 then X:=1;
               GotoX;
             end;
           end;
       ^O: begin { Move cursor to end of line }
              X:=Length(Answer)+1; if X>Mlen then X:=Mlen; GotoX;
           end;
       ^G: begin { Move cursor to beginning of line }
             X:=1; GotoX;
           end;
       ^H: begin { Delete left char: BS }
             if Typ='F' then Del_Ans
             else
               begin
                 X:=X-1;
                 if (Length(Answer)>0) and (X>0)  then
                   begin
                     Delete(Answer,X,1); GotoX;
                     Write(copy(Answer,X,(Length(Answer)-X+1)),#95);
                     GotoX;
                   end
                 else X:=1;
             end; { Typ <> 'F' }
           end;
       #127: begin { Delete }
               Delete(Answer,X,1);
               Write(copy(Answer,X,Length(Answer)-X+1),#95); GotoX;
             end;
        ^a : begin  { F1 pressed }
               F1 := true; Exit := true; Answer:= default;
             end;
        ^M : Exit := true;
        ^c : begin F3 := true; Exit := true; Answer := default; end;
```

```
    else
    if (length(Answer)+1 <= Mlen) or (not InsertOn) then
    begin   { non-IBM char }
        if Ch in OkChars  then
         begin
          if InsertOn then
          begin
           if length(Answer) < Mlen then
           begin             { OK to insert }
             insert(Ch,Answer,X);
               Case Typ of
                'A','N','$' : write(copy(Answer,X,Length(Answer)-X+1));
                'F'         : Write(Ch);
               end; {Case}
           end;        { OK to insert }
          end else     { end InsertOn }
          if X <= Mlen then
          begin
             write(Ch);
             if X>length(Answer) then Answer:=Answer+Ch
             else Answer[X]:=Ch;
          end;  { processing this key }
          if X+1 <= Mlen then X:=X+1;
          if (X > Length(Answer)) and (template[X]<>#95) then PosX;
         end { OkChars }
         else if (Ch<> ^V) then Beep(300,150);
             { beep if invalid char and ch is not Insert key }
        GotoX;
    end;   { non IBM key }
    if (typ<>'F') and (length(Answer)+1 > Mlen) and (Ch <> ^V)
     then  beep(600,100);
   end;    {    CASE!!!    } {and 'not(ESC and ch = ^[)}
  until Exit = true;
 if not (ch = ^[) then ESC:= false;  {ensure that the right value is passed}
 Color(0,15); X:=1; gotoX; write(Answer);
      { erase part of template that is left }
 X:=length(Answer)+1; GotoX;
 for J:= 1 to Mlen-x+1 do write(' ');
 Exit := false; Color(0,7);
 if (DF) and (length(Answer)=1) then
  begin
    gotoXY(col,row); write(' '); Answer:='';
  end;
end;           { end Input Procedure }

procedure Prompt(Line1,Line2 : str255);
    { Display prompt lines on bottom 2 lines of Video }
  begin
    gotoXY(1,23); ClrEol; writeln(Line1); ClrEol; write(Line2);
  end;

procedure Say_Prompt(Prompt_num : integer);
   { Programmer defined prompts for bottom 2 lines of Video }
 var Line1,Line2 : string[80];
 begin
   Line2 := 'Press <F1> to change previous entry';
   Case Prompt_num of
     1 : Line1 := '';
     2 : begin
           Line1 := 'Edit highlighted value and press <RETURN>';
```

```
         end;
     3 : Line1 := 'This is the second prompt';
     4 : Line1 := 'All prompts are programmer defined';
     5 : Line1 := 'This is the last prompt';
   end;
   prompt(Line1,Line2);
 end;

procedure Get_Default(Default_num : integer; var Default : str80);
  { Default values for the Input_Handler are handled here }
 begin
 end;

procedure Do_Validation(Valid_num : integer; var Valid : boolean);
   { Validation of user inputs is done here }
 var S : str80;
  Cd,I : integer;
     N : Real;
 begin
   Valid := true;
   Case Valid_num of
     1 : ;
     2 :begin
         val(copy(Answer,4,2),I,Cd); if I>31 then Valid := false;
        end;
     3 :begin
        end;
   end; { case }
 end;   { procedure }


procedure Input_Handler(IpCode: str5; var Escape: boolean);
  { Handles all input and editing for a page of inputs }
  { requires procedures
               Say_Prompt, Do_Validation, Get_Default
          global variables
               Filvar: array of [1..Size] of string[80] }
 label  100;

 var Typ,IpType,uppercase     : Char;
     Default,Template         : str80;

     Row,Col,Mlen,I,Code,Count,
     First_var_num,Last_var_num,
     Filvar_num,
     Default_num,Prompt_num,Validation_num  : integer;
     F1,F3,Valid,UCase,
     ESC : boolean;

  procedure Get_Var;
    begin
      val(copy(P[count],1,2), Col,Code);
      val(copy(P[count],3,2), Row,Code);
      Typ := copy(P[count],5,1);
      val(copy(P[count],6,3), Mlen,Code);
      val(copy(P[count],9,2), Filvar_num,Code);
      upperCase := copy(P[count],11,1);
      val(copy(P[count],12,2),Default_num,Code);
      val(copy(P[count],14,2),Prompt_num,Code);
      val(copy(P[count],16,2),Validation_num,Code);
```

```
      if upperCase= 'T' then UCase:= true else UCase:= false;
    end;

  procedure Display_Rec;
   var I : integer;
   begin
     HighVideo;
     for I:= first_var_num to last_var_num do
      begin
        if iptype <> 'N' then
        begin
          Count:= I; Get_Var;
          gotoXY(col,row); write(Filvar[Filvar_num]);
        end;
      end; { for loop }
   end;

 begin
   IpType := copy(IpCode,1,1);
   val(copy(IpCode,2,2),First_Var_num,Code);
   val(copy(Ipcode,4,2),Last_var_num,Code);
   Case IpType of
     'N' : for I:= 1 to Size do Filvar[I] := '';
     'C' : ;
   end; { Case }
   count := First_var_Num;
   F1:=false;
   F3:=false;
   ESC:= false;
   if IpType = 'D' then Display_rec
   else
   begin
    if iptype='C' then
     begin
      gotoxy(1,25);clreol;
      invVideo('Press <F3> to exit or <ESC> to delete');
      say_cap_num;
     end;
     repeat
       Get_Var; template:='';
 100:  Default := Filvar[count];
       HighVideo; Say_Prompt(Prompt_num);

       Input(Typ,Default,Col,Row,Mlen,UCase,F1,F3,ESC);
           { F1 and F3 is returned from Input }

       if (IpType = 'C') and (F3) then
         begin Exit := true; F3:= false; end
       else
       if ESC then Exit:= true
       else
        begin
         Do_validation(Validation_num,Valid);
         {Valid returned from Do_Validation: if not Valid then entry is redone}
         if not valid then
          begin
            Default:=''; Filvar[count]:='';  Beep(350,150);
            goto 100;   { 100 is the input procedure above (in this procedure) }
          end;     { do not use default }
         Filvar[count] := Answer;
```

```
         if F1 then
         begin
           gotoXY(col,row); HighVideo;
           if Filvar[count]<>''then write(Filvar[count])
            else write(template);
           count:=count-1; F1:=false;
         end else  count:=count+1;
         if count<First_var_num then count:=last_var_num else
         if count>Last_var_num  then count:=first_var_num;
       end;
     until Exit = true;
     if count > first_var_num then Escape:= false;
     if F3 or ESC then escape:=true;
     if IpType = 'C' then begin gotoXY(1,25); clreol; end;
   end; { typ <> 'D' }
   Exit:=false;
 end;

procedure Hmenu(C,R:integer;Status:str255; var Ch: char);
var
  MenuLen     : integer;
  Menustr     : string[79];
  MenuLtrs    : string[12];
  I           : array[1..20] of string[8];  { menu Items }
  counter     : integer;
begin
  Counter := 0; Set_Cap_Num(' ',' ',' ');

       {**** build menu Item and Prompt arrays ****}
  repeat
    Counter := Counter + 1;
       {** locate menu Item in Prompt string and assign it to I[Counter **}
    I[Counter] := Copy(P[Counter],1,Pos('.',P[Counter])-1);
       {** trim trailing blanks , if any from newly formed menu Item ** }
    I[Counter] := Copy(I[Counter],1,Pos(' ',I[Counter]+' ')-1);
       {** delete menu Item from from Prompt string **}
    Delete(P[Counter],1,Pos('.',P[Counter]));
  until (P[Counter] = ' ') or (P[Counter] = '');
       {**** last menu Item and Prompt completed ****}

  Menulen  := Counter-1;
  MenuStr  := '';
  MenuLtrs := '';
  for Counter := 1 to Menulen do
    begin
        {** the  + ' '  below controls space between menu items **}
      MenuStr := MenuStr  + I[Counter] + '  ';
      MenuLtrs:= MenuLtrs + Copy(I[Counter],1,1);
    end;

{.pa}
        {**** begin display of Hmenu ****}
  Counter := 1;
        {** write Status string in top right corner **}
  gotoXY(1,1); clreol; GotoXY(79-length(status),1);
  textbackground(15);textcolor( 0);write(status);
  textbackground( 0);textcolor(15); writeln; clreol;
  lowvideo;
  repeat
    GotoXY(C,R);
```

```
    lowvideo;
    writeln (Menustr); {** Write menu choices string in low video **}
    clreol;
       {** find location for and write highlighted menu choice **}
    GotoXY((C-1) + pos(I[counter],MenuStr),R);
    textbackground(15);textcolor( 0);write(I[Counter]);
    textbackground( 0);textcolor(15);
        {** write Prompt for highlighted Item **}
    GoToXY(C,R+1); clreol; writeln ( P[Counter] );
    GotoXY(80,1);
        {**** get keyboard input ****}
    Read(kbd,Ch);
    if KeyPressed then Ck_edit_key(Ch);
    Ch := UpCase(Ch);
    case Ch of
      #13       : Ch      := Copy(MenuLtrs,Counter,1);    {'Return'}
      ^D,^E,#32 : Counter := Counter + 1;        {'up-arrow','right-arrow',?}
      ^S,^X     : Counter := Counter - 1;        {'down-arrow','left-arrow'}
      ^G        : Counter := 1;                  {'Home'}
      ^O        : Counter := MenuLen;            {'End"}
    end; {case Ch}
    if Pos(Ch,MenuLtrs) <> 0 then Counter := Pos(Ch,MenuLtrs)
     else if not (Ch in [#13,^D,^E,#32,^S,^X,^G,^O,^[]) then beep(350,200);
    if Counter < 1  then Counter := MenuLen;
    if Counter > MenuLen  then Counter := 1;
  until (Pos(Ch,MenuLtrs) <> 0) or (ch = ^[);          {'Escape'}
  lowvideo;
 end;

type
   String16 = string[16];
   string20 = string[20];
   string25 = string[25];
   initfile=record
              cond:array[1..Size] of string[25];
            end;
   physprop=record
              vlost,
              sumvevap,
              sumvdis,
              volume,
              area,
              fevap,
              vevap,
              fdis,
              vdis,
              width,
              thickness:real;
            end;
   chemprop=record
              density,
              viscosity:real;
            end;


const
    OutFileName: string20 = 'fategraf.dta';
    RunStatsFileName: string20 = 'fatestat.dta';
```

```
var
   r:array[1..Size] of real;
   Run_Stats: text;
   Out_file: text;
   init_value : file of initfile;
   initial : initfile;
   sTitle: string25;
   i,code:integer;
   thickspread,
   thinspread,
   change,
   OilPicked,
   ESC: boolean;

procedure CentrePrint(title:str80);     {assume an 80 column printer}

var
   i,
   offset:integer;

begin
   offset:= (80 - length(title)) div 2;
   for i:= 1 to offset do
      write(lst,' ');
   writeln(lst,title);
   writeln(lst)
end;

function exist(filename : str20): boolean;

   var
    fil:   text;

 begin
   assign(fil,filename);
   {$I-}
   reset(fil);
   {$I+}
   exist:=(ioresult=0);
 end;

var
   initfilename:string16;              {set by PickOil}

procedure readinitfile;
 begin
   assign(init_value,initfilename);
   if exist(initfilename) then
    begin
     reset(init_value);
     read(init_value,initial);
     close(init_value);
     for i:=1 to (Size-1) do
        begin
         initial.cond[i]:=initial.cond[i]+' ';
         filvar[i]:=copy(initial.cond[i],1,pos(' ',initial.cond[i])-1)
        end;
     sTitle:= initial.cond[Size]
    end;
   end;
```

```
procedure writeinitfile;
 var
     s:string[20];

 begin
   assign(init_value,initfilename);
   if exist(initfilename) then
      reset(init_value)
    else rewrite(init_value);
   for i:=1 to (Size-1) do
    begin
      s:=filvar[i]+'          ';
      initial.cond[i]:=copy(s,1,10);
    end;
   initial.cond[Size]:= copy(sTitle,1,25);
   write(init_value,initial);
   close(init_value);
end;

procedure pstring;
 begin
   p[1]:='6013A01001-000101';     {Type of spill (A,B,S)                    }
   p[2]:='';
   p[3]:='6007N01003-000201';     {Emuls delay (theta)    \                 }
   p[4]:='6008N01004-000101';     {Density (kg/m3)         \                }
   p[5]:='6009N01005-000101';     {Standard dens temp (K)   \               }
   p[6]:='6010N01006-000101';     {Viscosity (mPas)          \              }
   p[7]:='6011N01007-000101';     {Standard Visc temp (K)     > used in all }
   p[8]:='6012N01008-000101';     {Pour point (K)            /              }
   p[9]:='6013N01009-000101';     {Aqueous solubility (g/m3)/               }
   p[10]:='6014N01010-000101';    {Flash point (K)         /                }
   p[11]:='6015N01011-000101';    {Oil-water ift (N/m)    /                 }
   p[12]:='6016N01012-000101';    {Oil-air ift (N/m)     /                  }
   p[13]:='6017N01013-000101';    {Gas/oil ratio            - A & S         }
   p[14]:='6018N01014-000101';    {Gas density (kg/m3)      - A             }
   p[15]:='6019N01015-000101';    {Oil/gas ift (N/m)        - A             }
   p[16]:='';
   p[17]:='6007N01017-000101';    {Windspeed (m/s)        \                 }
   p[18]:='6008N01018-000101';    {Air temp (K)            > used in all    }
   p[19]:='6009N01019-000101';    {Water temp (K)         /                 }
   p[20]:='6010N01020-000101';    {Surface current (m/s)    - A & S         }
   p[21]:='6011A01021-000101';    {Stability Class (A,D,F)  - A             }
   p[22]:='';
   p[23]:='6007N01023-000101';    {Duration of spill (100s) - B             }
   p[24]:='6008N01024-000101';    {Volume spilled (m3)      - B             }
   p[25]:='6007N01025-000101';    {Oil discharge rate (BOPD) - S            }
   p[26]:='6008N01026-000101';    {Well depth (m)           - A & S         }
   p[27]:='6009N01027-000101';    {Pipe diameter (m)        - A             }
   p[28]:='6010N01028-000201';    {Plume rise (m)           - A             }
   p[29]:='6011N01029-000101';    {Mixing zone height (m)   - A             }
   p[30]:='6012N01030-000101';    {Oil discharge rate (BOPD) - A            }
   p[31]:='6007N01031-000201';    {Density con1         \                   }
   p[32]:='6008N01032-000101';    {Density con2          \                  }
   p[33]:='6009N01033-000101';    {Viscosity con1         \                 }
   p[34]:='6010N01034-000101';    {Viscosity con2          \                }
   p[35]:='6011N01035-000101';    {Pour point               \               }
   p[36]:='6012N01036-000101';    {Solubility                > used in all  }
   p[37]:='6013N01037-000101';    {Flash point              /               }
   p[38]:='6014N01038-000101';    {Oil-water ift constant  /                }
```

```
   p[39]:='6015N01039-000101';    {Oil-Air ift constant   /                }
   p[40]:='6016N01040-000101';    {ASTMA constant        /                 }
   p[41]:='6017N01041-000101';    {ASTMT constant       /                  }
 end;


procedure dis_gen_msg(msgtyp:char);   {messages shared by all spills}
 begin
   case msgtyp of

     'O':begin                                              {array index #}
           msg('Emulsification delay (theta)',20,7);          {3}
           msg('Density (kg/m3)',20,8);                       {4}
           msg('Standard density temperature (K)',20,9);      {5}
           msg('Viscosity (mPas)',20,10);                     {6}
           msg('Standard viscosity temperature (K)',20,11);   {7}
           msg('Pour point (K)',20,12);                       {8}
           msg('Aqueous solubility (g/m3)',20,13);            {9}
           msg('Flash point (K)',20,14);                      {10}
           msg('Oil-water interfacial tension (N/m)',20,15);  {11}
           msg('Oil-air interfacial tension (N/m)',20,16);    {12}
         end;
     'E':begin
           msg('Windspeed (m/s)',20,7);                       {17,WindSp}
           msg('Air temperature (K)',20,8);                   {18,AirT}
           msg('Water temperature (K)',20,9);                 {19,WaterT}
          end;
     'C':begin
           msg('Density constant 1',20,7);                    {31}
           msg('Density constant 2',20,8);                    {32}
           msg('Viscosity constant 1',20,9);                  {33}
           msg('Viscosity constant 2',20,10);                 {34}
           msg('Pour point constant',20,11);                  {35}
           msg('Solubility constant',20,12);                  {36}
           msg('Flash point constant',20,13);                 {37}
           msg('Oil-water int. tension constant',20,14);      {38}
           msg('Oil-Air int. tension constant',20,15);        {39}
           msg('ASTMA constant',20,16);                       {40}
           msg('ASTMT constant',20,17);                       {41}
         end;
    end;
 end;{dis_msg}

procedure dis_batch_msg(msgtyp:char);   {messages used for batch spills only}
 begin
   case msgtyp of
     'S':begin    {batch}
           msg('Duration of spill (100sec multiples)',20,7);  {23}
           msg('Volume of oil spilled (m3)',20,8);           {24}
          end;
   end   {case}
 end;     {proc}

procedure dis_above_msg(msgtyp:char);   {messages used for above sea blowouts}
 begin
   case msgtyp of
     'O':begin
           msg('Gas/Oil ratio (dimensionless)',20,17);        {13}
           msg('Gas density (kg/m3)',20,18);                  {14}
           msg('Oil/gas interfacial tension (N/m)',20,19);    {15}
```

```
          end;
     'E':begin    {above}
           msg('Surface current (m/s)',20,10);                   {20}

(*         msg('Stability class (A, D or F)',20,11);             {21}
     Nailed down to 'D'   *)

          end;
     'S':begin    {above}
           msg('Well depth (m)',20,8);                           {26}
           msg('Pipe diameter (m)',20,9);                        {27}
           msg('Plume rise (m)',20,10);                          {28}
           msg('Mixing zone height (m)',20,11);                  {29}
           msg('Oil discharge rate (BOPD)',20,12);               {30}
          end;
   end   {case}
 end;     {proc}

procedure dis_sub_msg(msgtyp:char);   {messages used for subsea blowouts}
 begin
   case msgtyp of
     'O':begin
           msg('Gas/Oil ratio (dimensionless)',20,17);           {13}
          end;
     'E':begin    {sub}
           msg('Surface current (m/s)',20,10);                   {20}
          end;
     'S':begin    {sub}
           msg('Oil discharge rate (b/d)',20,7);                 {25}
           msg('Well depth (m)',20,8);                           {26}
          end;
   end   {case}
 end;     {proc}

 procedure dis_source_msg(msgtyp:char);
   begin
    case msgtyp of
      'P':begin
         msg('Above sea blowout',20,10);
         msg('Subsea blowout',20,11);
         msg('Batch spill',20,12);
         msg('chose A, S or B',25,13);                           {1}
        end;
    end   {case}
 end;

procedure initcond;

   procedure Title;

   begin
      clrscr;
      highvideo;
      center('Set title for this run',0,5,80);
      lowvideo;
      prompt('Use normal edit keys','and <Enter> when finished');
      Input('A',                 {alphabetical}
            sTitle,              {the current title}
            25,10,               {screen position}
            25,                  {length accepted}
```

```
            false,            {Caps returned?}
            F1,               {true if F1 was pressed}
            F3,               { "   "  F3 "     "    }
            ESC);             {true if 'Esc' was pressed}
      sTitle:= Answer
   end;

   procedure gen_oil_prop;
    begin
     clrscr;lowvideo;
      pstring;
      highvideo;center('Fresh oil properties',0,5,80);lowvideo;
      dis_gen_msg('O');
    end; {oilprop}

   procedure batch_oil_prop;
    begin
      highvideo; center('Batch Spill',00,3,80);lowvideo;
      dis_batch_msg('O');
      input_handler('D0312',escape);
      input_handler('C0312',escape);
    end; {oilprop}

   procedure Above_oil_prop;
    begin
      highvideo;center('Above Sea Blowout',0,3,80);lowvideo;
      dis_Above_msg('O');
      input_handler('D0315',escape);
      input_handler('C0315',escape);
    end; {oilprop}

   procedure Sub_oil_prop;
    begin
      highvideo;center('SubSea Blowout',0,3,80);lowvideo;
      dis_Sub_msg('O');
      input_handler('D0313',escape);
      input_handler('C0313',escape);
    end; {oilprop}

   procedure Gen_Spill_cond;
    begin
     clrscr;lowvideo;
      pstring;
      highvideo;center('Spill conditions',0,5,80);lowvideo;
      dis_gen_msg('S');
    end; {env_cond}

   procedure Batch_Spill_cond;
    begin
      highvideo; center('Batch Spill',00,3,80);lowvideo;
      dis_batch_msg('S');
      input_handler('D2324',escape);
      input_handler('C2324',escape);
    end; {env_cond}

   procedure Above_Spill_cond;
    begin
      highvideo;center('Above Sea Blowout',0,3,80);lowvideo;
      dis_above_msg('S');
      input_handler('D2630',escape);
```

```
     input_handler('C2630',escape);
   end; {env_cond}

  procedure Sub_Spill_cond;
   begin
     highvideo;center('SubSea Blowout',0,3,80);lowvideo;
     dis_sub_msg('S');
     input_handler('D2526',escape);
     input_handler('C2526',escape);
   end; {env_cond}

  procedure Gen_Env_cond;
   begin
    clrscr;lowvideo;
     pstring;
     highvideo;center('Spill conditions',0,5,80);lowvideo;
     dis_gen_msg('E');
   end; {env_cond}

  procedure Batch_Env_cond;
   begin
     highvideo; center('Batch Spill',00,3,80);lowvideo;
     dis_batch_msg('E');
     input_handler('D1719',escape);
     input_handler('C1719',escape);
   end; {env_cond}

  procedure Above_Env_cond;
   begin
     highvideo;center('Above Sea Blowout',0,3,80);lowvideo;
     dis_above_msg('E');
     input_handler('D1720',escape);
     input_handler('C1720',escape);
   end; {env_cond}

  procedure Sub_Env_cond;
   begin
     highvideo;center('SubSea Blowout',0,3,80);lowvideo;
     dis_sub_msg('E');
     input_handler('D1720',escape);
     input_handler('C1720',escape);
   end; {env_cond}

  procedure Constant;
   begin
    clrscr;lowvideo;
     pstring;
     highvideo;center('For all spill sources',0,3,80);
     center('Values of constants',0,5,80);lowvideo;
     dis_gen_msg('C');
     input_handler('D3141',escape);
     input_handler('C3141',escape);
   end; {constant}


   procedure get_Main;
    begin
      p[1]:='Title      .Set title for this run';
      p[2]:='Pick       .Pick the source of the spill';
      p[3]:='Batch      .Define the conditions of a batch spill';
```

```
      p[4]:='Above      .Define the conditions of an above sea blowout';
      p[5]:='SubSea     .Define the conditions of a subsea blowout';
      p[6]:='Quit       .Save present parameters and exit to main menu';
      p[7]:='';
    end;

   procedure get_var;
    begin
      p[1]:='Oil_prop   .Define initial oil properties';
      p[2]:='Environ    .Define environmental conditions';
      p[3]:='Spill_cond .Set spill conditions';
      p[4]:='Constants  .Set values of constants';
      p[5]:='Quit       .Save present parameters and exit to main menu';
      p[6]:='';
    end;

procedure Get_Batch;
 begin
  repeat
   clrscr;lowvideo;
   prompt('Use arrow keys and <RETURN>','Or first letter of key word');
   get_var; hmenu(1,2,'Batch spill conditions',ch);
   case ch of
    'O':begin
         gen_oil_prop;
         batch_oil_prop
        end;
    'E':begin
         gen_env_cond;
         batch_env_cond
        end;
    'S':begin
         gen_spill_cond;
         batch_spill_cond
        end;
    'C':Constant;
    ^[,'Q':exit:=true;
   end; {case}
  until exit=true;
 exit:=false;
end; {initcond}

procedure Get_Above;
 begin
  repeat
   clrscr;lowvideo;
   prompt('Use arrow keys and <RETURN>','Or first letter of key word');
   get_var; hmenu(1,2,'Above sea blowout conditions',ch);
   case ch of
    'O':begin
         gen_oil_prop;
         Above_oil_prop
        end;
    'E':begin
         gen_env_cond;
         Above_env_cond
        end;
    'S':begin
         gen_spill_cond;
         Above_spill_cond
```

```
         end;
     'C':Constant;
     ^[,'Q':exit:=true;
    end; {case}
   until exit=true;
   exit:=false;
 end; {initcond}

 procedure Get_Sub;
  begin
   repeat
    clrscr;lowvideo;
    prompt('Use arrow keys and <RETURN>','Or first letter of key word');
    get_var; hmenu(1,2,'SubSea blowout conditions',ch);
    case ch of
     'O':begin
          gen_oil_prop;
          Sub_oil_prop
         end;
     'E':begin
          gen_env_cond;
          Sub_env_cond
         end;
     'S':begin
          gen_spill_cond;
          Sub_spill_cond
         end;
     'C':Constant;
     ^[,'Q':exit:=true;
    end; {case}
   until exit=true;
   exit:=false;
 end;

    procedure pick_source;
    begin
     clrscr;lowvideo;
      pstring;
      highvideo;center('Possible Spill sources',0,5,80);lowvideo;
      dis_source_msg('P');
      input_handler('D0101',escape);
      input_handler('C0101',escape);
    end; {oilprop}

 begin             {initcond}
   readinitfile;
   repeat
    clrscr;lowvideo;
    prompt('Use arrow keys and <RETURN>','Or first letter of key word');
    get_Main; hmenu(1,2,'Input Routine',ch);

    case ch of
     'T':Title;
     'B':Get_batch;
     'A':Get_Above;
     'S':Get_Sub;
     'P':Pick_Source;
     ^[,'Q': begin
               writeinitfile;
               exit:=true;
```

```
          end;
    end; {case}
   until exit=true;
  exit:=false;
 end; {initcond}



function pwr(mantissa:real;exponent:real):real;
 begin
   pwr:= exp(ln(mantissa)*exponent)
 end;


procedure SEZ(var Target:String16);          {StripExtraZero to deal with
                                               Borland's stupidity}
                                              {Ammended - my stupidity:
                                              Turbo-87 uses 3 digits of exp
var                                           in reals - Turbo uses 2}
   i:integer;

begin
   i:= 1;
   while not (Target[i] in ['E','e']) and (i < 16) do
      i:= i + 1;
   if i < 16 then begin
      if Target[i+1] in ['+','-'] then begin
         if Target[i+2] = '0' then
            delete (Target,i+2,1)  end
      else
         if Target[i+1] = '0' then
            delete(Target,i+1,1);
   end
end;
   {******************** Above Sea Blowout Calcs ****************************}


procedure fatemodel;

 label
   abort;
 var
   thick,
   thin,
   totslick:physprop;

   oil,
   init,
   emul,
   thnoil:chemprop;

   Astma,
   Astmt,
   SpillDur,
   SpillVol,
   WindSp,
   AirT,
   WaterT,
```

```
  tcount,                    {time count}
  SaveCount,                 {save the duration of first run}
  tcountstop,                {run until this time limit(sec)}
  DataFreq,                  {seconds between Graphic records}
  dfevtn,                    {differential fraction evaporated thin}
  dfevtk,                    {     "           "         "      thick}
  vtotn,                     {volume thick to thin in one pass}
  estop,                     {?}
  water_content,             {yup}
  DensCon1,                  {density constant 1}
  DensCon2,                  {density constant 2}
  DensT,                     {standard density temperature}
  VisCon1,                   {Viscosity constant 1}
  VisCon2,                   {viscosity constant 2}
  ViscT,                     {standard viscosity temperature}
  ttke,                      {theta thick emulsion}
  zthick,                    {emulsion thickness}
  ttk,                       {theta thick slick}
  sigma,                     {Thin slick spreading constant}
  dvol,                      {differential volume}
  OWintCon,                  {oil/water interfacial constant}
  InitOWint,                 {initial oil/water interfacial tension}
  owint,                     {oil/water interfacial tension}
  OAintCon,                  {oil/air intefacial constant}
  InitOAint,                 {initial oil/aair interfacial tension}
  oaint,                     {oil/air interfacial tension}
  PPCon,                     {pour point constant}
  InitPP,                    {Initial oil pour point}
  oilpp:real;                {oil pour point}

  RecCount,                  {count the records being saved to file}
  OutC,                      {number of passes between outputs of data}
  PointNum,                  {number of records output for graphing}
  i,
  cnt,
  passcount:integer;

  GraphFlag,                 {saving data to file?}
  DoubleRun,                 {making a calibration run?}
  ScreenData,                {doing screen writes?}
  PrintData,                 {doing printer output?}
  FirstRun,                  {etc}
  StopShort,                 {Has operator called for non-completion of run}
  Done:Boolean;

{added for introduction of SubSea and Surface blowouts}
  SpillType: char;
  Water_Depth,
  Pipe_Diam,
  OGint,
  Oil_Flow_Rate,
  Oil_Density,
  Surface_Current,
  AvThickness,
  UpStream,
  Volume,
  lenSection,
  VMD,
  Width:real;
  droplets:boolean;
```

```
Procedure ModSauter(var diam:real);

   Const
      Gas_Density:real = 0.75;          {kg/cu m}
      MeanDiamFact = 1.2;

   var
      GOR,
      Sauter,
      Gas_Flow_Rate,
      Max_Diam,
      Gas_Vel,                          {m/s}
      Mass_Gas_Flow_Rate,
      Mass_Oil_Flow_Rate:real;

   begin
      Oil_Density:= r[4];
      Water_Depth:= r[26];
      Pipe_Diam:= r[27];
      OGint:= r[15];
      GOR:= r[13];
      Gas_Flow_Rate:= Oil_Flow_Rate * GOR;
      Gas_Vel:= 4 * Gas_Flow_Rate/Pipe_Diam/Pipe_Diam/Pi
                                                * 10/(Water_Depth + 10);
      if Gas_Vel > 517 then Gas_Vel:= 517;
      Mass_Gas_Flow_Rate:= Gas_Flow_Rate * Gas_Density;
      Mass_Oil_Flow_Rate:= Oil_Flow_Rate * Oil_Density;
      Sauter:= 0.8/Gas_Vel * sqrt(OGint/Oil_Density)
               * pwr(1 + 2.75 * (Mass_Oil_Flow_Rate/Mass_Gas_Flow_Rate),2/3);
      Diam:= Sauter * MeanDiamFact;
   end;


procedure Above_Sea(var DRT,                     {slick thickness}
                        tcount,                  {how long did it take}
                        volume,
                        Plume_Width,
                        x:real);


const
   ROA = 1.3;                       {Reynold's Number for air}
type
   Class = (A,D,F);

var
   Dep_Rate,
   Conc: real;
   Full: Boolean;
   DT,                                 {delta time}
   PSVel,
   dummy,                              {a place to test an extreme exponent}
   Y,
   Z,
   GOR,
   Source_Strength,
   Init_Wind_Vel,
   Plume_Rise,
   Mixing_Zone_Height,
```

```
   Part_Diam,
   Part_Dens,
   Surface_Current,
   Vel,
   Dep_Rate_old,
   PW_old,
   DRT_old:real;
   StabChar:char;
   Stability_Class:Class;
   Corr_Fact,
   Sauter_Hold:real;                    {dimensionless fudge factor}
   Assumed_Fallout,
   X_Incr:real;
   check:real;

{functions}
{
function ALOG(x:real):real;
begin
   ALOG:= exp(x * ln(10))
end;
not needed }

function ASIGY(X:real):real;
begin
   ASIGY:= exp(0.86947 * ln(X) + 5.371)
end;

function ASIGZ(X:real):real;
begin
   if X > 0.3 then
      if X > 0.5 then
         ASIGZ:= exp(2.1216 * ln(X) + 6.1245)
      else
         ASIGZ:= exp(1.5323 * ln(X) + 5.7161)
   else
      ASIGZ:= exp(1.1215 * ln(X) + 5.2214)
end;

function DSIGY(X:real):real;
begin
   DSIGY:= exp(0.89965 * ln(X) + 4.15)
end;

function DSIGZ(X:real):real;
begin
   if X > 1.0 then
      DSIGZ:= exp(0.58584 * ln(X) + 3.4965)
   else
      DSIGZ:= exp(0.85576 * ln(X) + 3.4965)
end;

function FSIGY(X:real):real;
begin
   FSIGY:= exp(0.882606 * ln(X) + 3.496)
end;

function FSIGZ(X:real):real;
begin
   if X > 1.0 then
```

```
      if X > 10.0 then
         FSIGZ:= exp(0.30103 * ln(X) + 3.157)
      else
         FSIGZ:= exp(0.496 * ln(X) + 2.708)
   else
      FSIGZ:= exp(0.81436 * ln(X) + 2.708)
end;

function SVEL(Part_Diam,Part_Dens,ROA:real):real; {Settling velocity}

var
   CD,
   CD2,
   temp,
   RYN: real;
   Done: Boolean;

begin
   CD:= 0.4;
   Done:= false;
   while not Done do begin
      temp:= sqrt(4/3 * Part_Diam * G * ((Part_Dens - ROA)/ROA)/CD);
      RYN:= temp * Part_Diam * 1.3/1.7e-05;
      if RYN > 680 then
         Done:= true;
      CD2:=(sqrt (RYN * 3/16 + 1)) * 24/RYN;
      if (CD2 - CD) < 0.1 then
         Done:= true;
      CD:= CD2;
      SVEL:= temp
   end
end;

begin          {PXV}
   {Initialize}
   Init_Wind_Vel:= r[17];
   Plume_Rise:= r[28];
   Mixing_Zone_Height:= r[29];
   Part_Dens:= r[4];
   Source_Strength:= Oil_Flow_Rate * Part_Dens * 1000;    {gm/s}
   Oil_Density:= Part_Dens;
   Part_Diam:= VMD;
   StabChar:= 'D';                   {copy(Filvar[10],1,1);}
   Corr_Fact:= 1.0;
   Case StabChar of
      'A':  Stability_Class:= A;
      'D':  Stability_Class:= D;
      'F':  Stability_Class:= F;
      else  Stability_Class:= D;
   end;
   Surface_Current:= r[20];

   Vel:= Init_Wind_Vel;
   PSVel:= SVEL(Part_Diam,Part_Dens,ROA);
   Assumed_Fallout:= Plume_Rise/PSVel * Vel/1000 * 2.67;
   X_Incr:= Assumed_Fallout/1000;
   DT:= X_Incr * 1000/Vel;
   X:= X_Incr;
   Full:= false;
   Dep_Rate_old:= 0;
```

```
   PW_old:= 0;
   DRT_old:= 0;
{end init}

   while not Full and (X <= Assumed_Fallout) do begin
         case Stability_Class of
            A: begin Y:= ASIGY(X);
                     Z:= ASIGZ(X)  end;
            D: begin Y:= DSIGY(X);
                     Z:= DSIGZ(X)  end;
            F: begin Y:= FSIGY(X);
                     Z:= FSIGZ(X)   end;
            else
         end;
         Plume_Width:= 2.67 * Y;
         if Z > (0.47 * Mixing_Zone_Height) then
            Full:= true
         else begin
            dummy := -0.5 * sqr((Plume_Rise - X * 1000.0 * PSVel/Vel)/Z);
            if dummy < -70 then
               Conc:=0.0
            else
            Conc:= Source_Strength/(2 * Pi * Y * Z * Vel)
                   * (exp(dummy));
            Dep_Rate:= Conc * PSVel;
            DRT:= (((Dep_Rate + Dep_Rate_old)/2 * DT)/Part_Dens/1000)
                  + DRT_old * PW_old/Plume_Width;
            X:= X + X_Incr;
         end;                                  {else Z...}
         if DRT_old > DRT then
            Full:=true;
         Dep_Rate_old:= Dep_Rate;
         PW_old:= Plume_Width;
         DRT_old:= DRT;
   end;                                     {while not Full}
   tcount:= round(10*X/Vel) * 100;
   Volume:= tstep * Oil_Flow_Rate;          {cu m}
   Corr_Fact:= Oil_Flow_Rate/Surface_Current/Plume_Width/DRT;
   DRT:= DRT * Corr_Fact;
end;
  {********************** End of Above Sea Blowout Calcs *******************}


  {********************** SubSea Blowout Calcs ******************************}
procedure Sub_Sea(var Slick_Thickness,       {Plume}
                      tcount,
                      volume,
                      Slick_Width,
                      UpStream_Extent:real);
Const
   Alpha = 0.1;           {stats        }
   Beta = 0.06;           {   fudge     }
   Lambda = 0.65;         {      factors }
var
   {Inputs}
   Well_Depth,                {m}
   Current_Speed,             {M/Sec}
   Oil_Discharge_Rate:real;   {Barrels/Day}
   Oil_Flow_Rate:real;        {Cu m/sec}
```

```
var
   {Internal}
   Hi_Mark,
   Lo_Mark,
   XX,
   B,
   W,
   OG,
   Radius,
   Plume_Velocity,
   Depth_of_Calc,
   GOR,
   BW:real;

begin
   Oil_Flow_Rate:= r[25] * 0.159/Day2Sec;                   {cu m/sec}
   Oil_Discharge_Rate:= Oil_Flow_Rate;
   Current_Speed:= r[20];
   Well_Depth:= r[26];
   GOR:= r[13];

   Hi_Mark:= Well_Depth - 5;
   Lo_Mark:= Well_Depth + 10;
   XX:= Hi_Mark/Lo_Mark;
   if XX <= 0.6 then begin
      XX:= 0.6;
      Hi_Mark:= Lo_Mark * XX
   end;
   Depth_of_Calc:= Well_Depth - Hi_Mark;
   B:= (3.0/5.0 * XX) * (1.0 - (XX/13.0) - (7.0 * sqr(XX/13.0)));
   W:= Pwr(25.0/12.0,0.3333)/Pwr(XX,0.3333) *
                                (1 + 11.0 * XX/39.0 + (255.5 * sqr(XX/39.0)));
   OG:= Oil_Discharge_Rate * GOR;
   Radius:= 2.0 * Alpha * Lo_Mark * B;
   Plume_Velocity:= Pwr(((sqr(Lambda) + 1) * OG * G)/(2.0 * Pi * sqr(Alpha)
                                                      * Lo_Mark),0.3333) * W;
   BW:= Radius * Plume_Velocity;
   Slick_Thickness:= sqrt(Beta/2.0) * Oil_Discharge_Rate/(BW * Pi);
   UpStream_Extent:= sqrt(2.0/Beta) * BW/(2.0 * Current_Speed);
   Slick_Width:= Pi * sqrt(2.0/Beta) * BW/Current_Speed;
   volume:= tstep * Oil_Discharge_Rate;
   tcount:= Hour2Sec;                    { one hour }
end;

   {******************* End of SubSea Blowout Calc **************************}

procedure evap(tstep:real;
               var dftk,        {differential fraction evaporated thick slick}
                   dftn,        {     "          "         "      thin   "   }
                   fevtk,       {fraction evaporated thick slick}
                   fevtn,       {   "          "         thin    "  }
                   ththk:real;  {theta (evaporative exposure) thick slick}
                   zthick,      {thickness of thick slick}
                   winds,       {wind speed}
                   zthin,       {thickness of thin slick}
                   astma,
                   astmt,
                   airt:real);  {air temperature}
 var
    drop,
```

```
     H,                         {Henry's Law constant}
     dttk,
     dttn,
     rk:real;

 begin
   rk:=0.0015*pwr(winds,0.78);
   if oilpp >=(waterT + 15.0) then
      H:= exp(6.3 -10.3*(ASTMT + ASTMA * fevtk)/airT)
   else
      H:=0.0;
   if droplets then
      drop:= 6.0
   else
      drop:= 1.0;
   dttk:=tstep/zthick/(H * drop/(1e-6 * thick.thickness) + (1.0/rk));
   ththk:=ththk+dttk;
   dttn:=rk*tstep/zthin;
   dftk:=dttk*exp((6.3-(10.3/airt*(astmt+astma*fevtk))));
   dftn:=dttn*exp((6.3-(10.3/airt*(astmt+astma*fevtn))));
   fevtk:=fevtk+dftk;
   fevtn:=fevtn+dftn;
 end;

procedure spread(var athick,      {thick area}
                     athin:real;  {thin area}
                     sigma,       {0.7 - oil/water interfacial tension - oil/air
                                                      interfacial tension}
                     zthick,      {thick thickness}
                     oilpp,       {pour point}
                     watert:real);{water temperature}

 var
     thinfact,
     spreadfact,
     dthin,
     dthick:real;

 begin
   thinfact:= 4.55 * pwr(sigma/sqrt(oil.density * oil.viscosity / 1000.0),1/3);
   if thinfact < 0.0 then
      thinfact:= 0.0;
   if not thinspread then
      dthin:=0.0
   else
      dthin:= thinfact * pwr(athin,0.33)*exp(-0.003/zthick)*tstep;
   spreadfact:= 2.2 * pwr((1025 - emul.density)*
                           g/sqrt(emul.density * emul.viscosity / 1000.0),2/3);
   if spreadfact < 0.0 then
      spreadfact:= 0.0;
   if not thickspread then
      dthick:=0.0
   else
      dthick:=spreadfact * pwr(zthick,1.33)*pwr(athick,0.33) *
                                             tstep-(1.0E-6*dthin/zthick);
   athick:=athick+dthick;
   athin:=athin+dthin;
 end;
```

```
procedure TwoDSpread(var athick,      {thick area}
                         athin,       {thin area}
                         wthick,      {thick width}
                         wthin:real;  {thin width}
                         tcount,
                         emulv,
                         current_speed,
                         sigma:real);      {0.7 - owint - oaint; the spreading
                                                               coefficient}

 var
     dArea,
     dWidthn,
     dWidth:real;

 begin
   if sigma < 0.0 then
      sigma:=0;
   dWidth:= 3/4 * (sqrt(sigma)/pwr((emul.density * emul.viscosity / 1000.0
                                                       * tcount),1/4)) * tstep;

   wthick:= wThick + dWidth;
   dWidthn:= dWidth * pwr((emul.density * emul.viscosity /
                                              oil.density * oil.viscosity),1/4);
   wthin:= wthin + dWidthn;
   dArea:= dWidth * current_speed * tstep;
   athick:=athick + dArea;
   athin:=athin + dArea;
 end;

procedure dispers(tstep:real;
                  var fdtk,          {fraction of thick dispersed}
                      fdtn:real;     {     "     "   thin     "      }
                      winds,         {wind speed}
                      emuld,         {emulsion density}
                      oild,          {oil density}
                      owint,         {oil/water interfacial tension}
                      emulv,         {emulsion viscosity}
                      zthick,        {thick thickness}
                      zthin,         {thin thickness}
                      tnoilv:real); {thin oil viscosity}
 const
  C1=2.4E+3;
  C2=1.0E-3;
  C3=1.16E-6;
  C4=1025;
 var
     shut,
     drho1,
     drho2,
     wss,
     dum:real;

 begin
      drho1:=c4-emuld;
      drho2:=c4-oild;
      wss:=winds/8.0;
      dum:=sqr(wss)*c1*c2*c3/(owint*emulv*drho1);
      if (waterT > oilpp - 15.0) and not droplets then
         fdtk:=dum/zthick*tstep
```

```
      else
         fdtk:= 0.0;
      fdtn:=dum/zthin*tstep*emulv*drhol/(drho2*tnoilv);
 end;

procedure emulsion(tstep:real;
                   var zthick,      {thick thickness}
                       emulv,       {emulsion viscosity}
                       emuld,       {emulsion density}
                       ww:real;     {water content}
                       winds,       {wind speed}
                       oild,        {oil density}
                       oilv,        {oil viscosity}
                       ttk,         {theta (evaporative exposure) thick slick}
                       ttke:real);  {theta thick emulsion}

 var
     dww:real;                      {delta water content}

 begin
   if (ttk<ttke) or droplets then
    begin
      emulv:=oilv;
      emuld:=oild;
    end
   else
    begin
      dww:=2.0E-6*sqr(winds+1.0)*(1-1.33*ww)*tstep;
      ww:=ww+dww;
      emulv:=oilv*exp(2.5*ww/(1.0-0.65*ww));
      emuld:=oild*(1.0-ww)+1025*ww;
      zthick:=zthick/(1.0-ww);
    end;
   end;


procedure OilProp;
{calculate new oil properties}

begin
    {density}
       oil.density:=init.density+DensCon1*thick.fevap-DensCon2*(WaterT-DensT);
    {viscosity}
       oil.viscosity:=init.viscosity*exp(VisCon1*thick.fevap) *
                      exp(VisCon2*(1/WaterT-1/ViscT));
       thnoil.viscosity:=init.viscosity*exp(VisCon1*0.5)*
                         exp(VisCon2*(1/WaterT-1/ViscT));
    {pour point}
       oilpp:= InitPP*(1+PPCon*thick.fevap);
       if oilpp >= WaterT then
          thickspread:= false;
    {interfacial tension}
       owint:= InitOWint*(1+OWintCon*thick.fevap);
       oaint:= InitOAint*(1+OAintCon*thick.fevap);
       sigma:= 0.07-oaint-owint;
       if sigma <= 0.0 then
          thinspread:= false
 end;
 procedure SlickChar;
 {calculate new slick characteristics}
```

```
begin
   {evaporation}
      if thick.fevap>0.3 then estop:=0.3 else estop:=thick.fevap;
      thin.vevap:=dfevtn*thin.volume+vtotn*(0.3-estop);
      with thin do
       begin
         vdis:=fdis*volume;
         vlost:=vevap+vdis;
         if vlost>volume then
          begin
            vdis:=vdis*(volume/vlost);
            vevap:=vevap*(volume/vlost);
            vlost:= vevap + vdis;
          end;
       end;
      thick.vevap:=dfevtk*thick.volume;
      totslick.vevap:=thin.vevap+thick.vevap;
      with thick do sumvevap:=sumvevap+vevap;
      with thin do sumvevap:=sumvevap+vevap;
      with totslick do sumvevap:=sumvevap+vevap;
   {dispersion}
      thick.vdis:=thick.fdis*thick.volume;
      totslick.vdis:= thin.vdis+thick.vdis;
      with thick do sumvdis:=sumvdis+vdis;
      with thin do sumvdis:=sumvdis+vdis;
      with totslick do sumvdis:=sumvdis+vdis;
   {volume}
      with thick do begin
         volume:=volume-vevap-vdis-vtotn;
         if volume <= 0.0 then begin
            volume:= 0.0;
            area:= 0.0
         end;
         zthick:= thickness;
         thickness:=volume/area;
         if thickness <= 0.0 then
            thickness:= 0.0;
         if droplets then begin
            thickness:= AvThickness;
            if (VMD > thickness) then
               thickness:= VMD
         end;
      end;
      with thin do begin
         vtotn:=thin.area*thin.thickness-thin.volume;
         volume:=volume+vtotn-vlost
      end;
      totslick.area:=thick.area+thin.area;
      totslick.volume:=thin.volume+thick.volume
end;

procedure dataout(var dev:text);

  begin
    writeln(dev,'time',tcount/3600:3:0);
    case SpillType of
       'A',
       'S':begin
          writeln(dev,
```

```
            '          width    thickness   volume     evap        dispersed');
          with thick do
             writeln(dev,'thick    ',width:7:0,'   ',thickness:7:7,'   ',volume:
                   '   ',sumvevap:6:3,'       ',sumvdis:6:3);
          with thin do
             writeln(dev,'thin    ',width:8:0,'   ',thickness:7:7,'   ',volume:6
                   '   ',sumvevap:6:3,'       ',sumvdis:6:3);
          with totslick do
             writeln(dev,'total   ',(thick.width+thin.width):8:0,'
                '   ',sumvevap:6:3,'       ',sumvdis:6:3);
          end;
       'B':begin
          writeln(dev,
             '          area     thickness   volume     evap        dispersed');
          with thick do
             writeln(dev,'thick    ',area:7:0,'   ',thickness:7:7,'   ',volume:6
                   '   ',sumvevap:6:3,'       ',sumvdis:6:3);
          with thin do
             writeln(dev,'thin    ',area:8:0,'   ',thickness:7:7,'   ',volume:6:
                  '   ',sumvevap:6:3,'       ',sumvdis:6:3);
          with totslick do
             writeln(dev,'total   ',area:8:0,'           ',
                   volume:6:3,'   ',sumvevap:6:3,'       ',sumvdis:6:3);
        end
        else  {nothing}
    end;   {case}
    writeln(dev);
    writeln(dev,'         density  viscosity  water content   thickness    fevap
    writeln(dev,'oil         ',oil.density:5:0,'   ',oil.viscosity:8:0,
       '                              ',thick.fevap:5:2);
    writeln(dev,'emulsion   ',emul.density:5:0,'   ',emul.viscosity:8:0,
            '   ',water_content:5:4,'     ',zthick:7:7);
    writeln(dev);
    writeln(dev,'theta                  ',ttk:10:0);
    writeln(dev,'Oil pour point         ',(oilPP - 273):1:1);
    writeln(dev,'Ambient Temperature    ',(AirT - 273):1:1);
    writeln(dev,'----------------------------------------------------------');
  end;


function SaveData:Boolean;
 begin
   Clrscr; Center('Do you require the saving of model-run data? ',1,8,80);
   highvideo; Center('Answer (Y/N) ',1,10,80); lowvideo;
   repeat
     Option; if not (Ch in ['Y','N']) then beep(350,150);
   until Ch in ['Y','N'];
   SaveData:= (Ch in ['Y'])
 end;

function ScreenOut:Boolean;
 begin
   Center('Do you require screen output for data? ',1,11,80);
   highvideo; Center('Answer (Y/N) ',1,13,80); lowvideo;
   repeat
     Option; if not (Ch in ['Y','N']) then beep(350,150);
   until Ch in ['Y','N'];
   ScreenOut:= (Ch in ['Y'])
 end;
```

```
function PrintOut:Boolean;
 begin
   Center('Do you require printer output for data? ',1,14,80);
   highvideo; Center('Answer (Y/N) ',1,16,80); lowvideo;
   repeat
     Option; if not (Ch in ['Y','N']) then beep(350,150);
   until Ch in ['Y','N'];
   PrintOut:= (Ch in ['Y'])
 end;
procedure HowOften(var OutC:integer);

var
   Result,
   vCh:integer;

begin
   Center('How often should data be put to screen? ',1,16,80);
   highvideo; Center('Answer (Hours:1->9) ',1,18,80); lowvideo;
   repeat
     Option; if not (Ch in ['1'..'9']) then beep(350,150);
   until Ch in ['1'..'9'];
   val(Ch,vCh,Result);
   OutC:= vCh*3600 div tstep;
   OutC:=OutC                 {Get the debugger to stop here}
end;

procedure ResetGraphFile;

begin
     assign(Out_File,OutFileName);
   {  if Exist(OutFileName) then
        reset(Out_File)
     else
    }    rewrite(Out_File)
end;

function Completion:Boolean;
 begin
   Clrscr; Center('Run the model to completion? ',1,8,80);
   highvideo; Center('Answer (Y/N) ',1,10,80); lowvideo;
   repeat
     Option; if not (Ch in ['Y','N']) then beep(350,150);
   until Ch in ['Y','N'];
   Completion:= (Ch in ['Y'])
 end;


function HowLong:real;

var
   Done:Boolean;
   mult:real;
   Scale:str80;
   dum,
   i:integer;

   procedure pstring;
      begin
         p[1]:= '6013A01001-000101';     {time scale: weeks,days,hours}
         p[2]:= '6015N01002-000101';     {how many}
```

```
      end;

   procedure disp_msg;
      begin
         msg('Do you want to limit the run in weeks, days or hours?',5,13);
         msg('How many days, weeks or hours?',5,15);
      end;

   procedure get_limits;
      begin
         clrscr; lowvideo;
         pstring;
         highvideo;
         center('Set run time limit',0,3,80);
         disp_msg;
         input_handler('D0102',escape);
         input_handler('C0102',escape);
      end;

begin     {HowLong}
   Done:= false;
   filvar[1]:= '';
   filvar[2]:= '';
   repeat
      get_limits;
      val(filvar[2],mult,code);
      Scale:= Filvar[1];
      dum:= length(Scale);
      for i:= 1 to dum do
         Scale[i]:= upcase(Scale[i]);
      if Scale = 'WEEKS' then begin
         HowLong:= Week2Sec * mult;
         Done:= true;
      end
      else if Scale = 'DAYS' then begin
         HowLong:= Day2Sec * mult;
         Done:= true;
      end
      else if Scale = 'HOURS' then begin
         HowLong:= Hour2Sec * mult;
         Done:= true;
      end
      else begin
         clrscr;
         highvideo;
         center('Error in scale input.',0,14,80);
      end;
   until Done;
end;

procedure SaveGraphicData;

var
   vevap,
   vdisp,
   vice,
   vsurf,
   sthkness,
   ethkness,
   w_c,
```

```
   density,
   viscosity: string[16];

begin
   RecCount:= RecCount + 1;
     {turn the reals into strings}
        str(TotSlick.sumvevap:10,vevap);
        str(TotSlick.sumvdis:10,vdisp);
        str(0.0:10,vice);
        str(TotSlick.volume:10,vsurf);
        str(thick.thickness:10,sthkness);
        str(zthick:10,ethkness);
        str(water_content * 100:10,w_c);
        str(emul.density:10,density);
        str(emul.viscosity:10,viscosity);
     {and get rid of the extra digit in the exponent}
{don't use this if the receiving routine expects 3-digit exponentiation
   i.e. compiled by Turbo-87
}
        SEZ(vevap);
        SEZ(vdisp);
        SEZ(vice);
        SEZ(vsurf);
        SEZ(sthkness);
        SEZ(ethkness);
        SEZ(w_c);
        SEZ(density);
        SEZ(viscosity);

    writeln(Out_File,'Record #',RecCount:1);
    writeln(Out_File,vevap:16,vdisp:16,vice:16,vsurf:16);
    writeln(Out_File,sthkness:16,ethkness:16,w_c:16,density:16,viscosity:16)
end;

procedure SaveRunStats(DataFreq,
                       Vinit:real;
                       PointNum:integer;
                       sTitle:string25);

var
   sDataFreq,
   sVinit,
   sPointnum: string[16];

begin
   str(DataFreq:10,sDatafreq);
   str(Vinit:10,sVinit);
   str(PointNum:10,sPointnum);
{  Eliminate one digit of exponentiation to make acceptable to
   the VAL routine when used in MAKEGRAF
   }
   SEZ(sDataFreq);
   SEZ(sVinit);
   SEZ(sPointnum);

   writeln(Out_File);
   writeln(Out_File,sTitle);
   writeln(Out_File,sDataFreq:16);
   writeln(Out_File,sVinit:16);
   writeln(Out_File,sPointnum:16)
```

```
end;


procedure PrintHeader(var dev:text);

begin
   writeln(dev);
   writeln(dev,'          --------------------------------------------------');
   writeln(dev);
   writeln(dev,'The continuous spill section is:');
   writeln(dev,'                            ',width:2:0,' meters wide,');
   writeln(dev,'                            ',Surface_Current*tstep:2:0,
                                                              ' meters long,');
   writeln(dev,'                        and ',AvThickness*1e6:2:0,
                                                            ' microns thick.');
   writeln(dev,'It initially had a volume of ',SpillVol:10:3,' cu m');
   writeln(dev,'                   of which  ',Totslick.sumvevap:6:3,
                                                           ' cu m evaporated');
   writeln(dev,'                         and ',Totslick.sumvdis:6:3,
                                                           ' cu m dispersed ');
   writeln(dev,'during the time required for the plume to reach the above width.
                                                                           ');
   writeln(dev);
   writeln(dev,'          --------------------------------------------------');
   writeln(dev);
end;

procedure SaveDummyData;

var
   vevap,
   vdisp,
   vice,
   vsurf,
   sthkness,
   ethkness,
   w_c,
   density,
   viscosity: string[16];

begin
        if droplets and (VMD > AvThickness) then
           AvThickness:= VMD;
        str(0.0:10,vevap);
        str(0.0:10,vdisp);
        str(0.0:10,vice);
        str(SpillVol:10,vsurf);
        str(AvThickness:10,sthkness);
        str(AvThickness:10,ethkness);
        str(0.0:10,w_c);
        str(r[4]:10,density);
        str(r[6]:10,viscosity);
        SEZ(vevap);
        SEZ(vdisp);
        SEZ(vice);
        SEZ(vsurf);
        SEZ(sthkness);
        SEZ(ethkness);
        SEZ(w_c);
        SEZ(density);
```

```
        SEZ(viscosity);

    writeln(Out_File,'Record #',RecCount:1);
    writeln(Out_File,vevap:16,vdisp:16,vice:16,vsurf:16);
    writeln(Out_File,sthkness:16,ethkness:16,w_c:16,density:16,viscosity:16)
end;

begin         {fatemodel}
   OutC:= 36;                             {give it a non-zero value in case the
                                           user doesn't}
   if not Completion then
      begin
         StopShort:= true;
         tcountstop:= HowLong;
      end
   else
      begin
         StopShort:= false;
         tcountstop:= MaxReal
      end;
   if SaveData then
      begin
         DoubleRun:= true;
         if ScreenOut then
               ScreenData:=true
         else
            begin
               ScreenData:= false;
               clrscr;
            end;
         if PrintOut then begin
            PrintData:=true;
            clrscr
         end
         else
            PrintData:= false;
         if ScreenData or PrintData then begin
            HowOften(OutC);
            clrscr
         end;
         if not ScreenData then begin
               clrscr;
               textcolor(14+blink);
               Center('Doing calibration run with no screen output.',1,12,80);
               textcolor(14)
         end
      end
   else
      begin
         DoubleRun:= false;
         ScreenData:= true;
         PrintData:= true;
         HowOften(OutC);
         Center('Running..........wait..',1,22,80)
      end;
   FirstRun:= true;
   GraphFlag:= false;
   Done:= false;

   repeat                             {until Done = true}
```

```
{ initialize for oil fate model run }
   ReadInitFile;
   SpillType:= upcase(copy(Filvar[1],1,1));
   for i:=1 to Size do val(filvar[i],r[i],code);
   ttke:=r[3];
   Oil_Flow_Rate:= r[30] * 0.159/Day2Sec;                     {cu m/sec}

   init.density:=r[4];
   emul.density:=init.density;
   oil.density:=init.density;
   DensCon1:= r[31];
   DensCon2:= r[32];
   DensT:= r[5];

   init.viscosity:=r[6];
   emul.viscosity:=init.viscosity;
   oil.viscosity:=init.viscosity;
   thnoil.viscosity:=init.viscosity;
   VisCon1:= r[33];
   VisCon2:= r[34];
   ViscT:= r[7];

   InitPP:= r[8];
   PPCon:= r[35];
   oilpp:= InitPP;

   water_content:=0.0;
   ttk:=0.0;

   InitOWint:= r[11];
   OWIntCon:= r[38];
   owint:=InitOWint;
   InitOAint:= r[12];
   OAIntCon:= r[39];
   oaint:=InitOAint;

   sigma:=0.07-oaint-owint;

   WindSp:=r[17];
   AirT:= r[18];
   WaterT:= r[19];
   Surface_Current:= r[20];

   SpillDur:= 100*r[23];
   SpillVol:= r[24];

   Astma:= r[40];
   Astmt:= r[41];

 { Initialize for First Pass }

   with thick do
     begin
       width:= 0.0;
       thickness:=0.02;
       fevap:=0.0;
       fdis:=0.0;
       vevap:=0.0;
       sumvevap:=0.0;
```

```
          vdis:=0.0;
          sumvdis:=0.0
        end;
      with thin do
        begin
          width:= 0.0;
          thickness:=0.000001;
          fevap:=0.3;
          fdis:=0.0;
          vdis:=0.0;
          sumvdis:=0.0;
        end;
      with totslick do
        begin
          width:= 0.0;
          fdis:=0.0;
          vevap:=0.0;
          sumvevap:=0.0;
          vdis:=0.0;
          sumvdis:=0.0;
        end;

      thinspread:= true;
      thickspread:= true;
      droplets:= false;

      case SpillType of
         'A':begin
               Water_Depth:= 0.0;
               ModSauter(VMD);
               Above_Sea(AvThickness,tcount,SpillVol,Width,lenSection);
               thick.thickness:= AvThickness;
               thin.thickness:= 0.000001;
               thin.area:= 1;
               thick.area:= width * Surface_Current * tstep;
               ttk:= 0.6 * tcount / VMD;
               thick.fevap:=Ln(1.0 + 10.3 * astma * ttk *
                                exp(6.3 - 10.3 * astmt / airt) / airt) /
                                (10.3 * astma / airt);
               thin.fevap:= thick.fevap;
               cnt:= round(tcount/100.0);
               for i:= 1 to cnt do begin
                  OilProp;
                  if oilpp >= WaterT then begin
                     droplets:= true;
                     if VMD > thick.thickness then
                        thick.thickness:= VMD
                  end;
                  emulsion(tStep,thick.thickness,emul.viscosity,emul.density,
                           water_content,WindSp,oil.density,oil.viscosity,ttk,
                           ttke);
                  dispers(tStep,thick.fdis,thin.fdis,WindSp,emul.density,
                           oil.density,owint,emul.viscosity,thick.thickness,
                           thin.thickness,thnoil.viscosity);
                end;
                thick.thickness:= AvThickness;
             end;
         'B':begin
               dvol:=SpillVol*(tstep/SpillDur);
               totslick.volume:=dvol;
```

```
         thick.area:=totslick.volume/(thick.thickness+8.0*thin.thickness);
         thin.area:=8.0*thick.area;
         tcount:=tstep;
      end;
   'S':begin
         ModSauter(VMD);
         Sub_Sea(AvThickness,tcount,SpillVol,Width,UpStream);
         thick.thickness:= AvThickness;
         thin.thickness:= 0.000001;
         thin.area:= 1;
         thick.area:= width * Surface_Current * tstep;
         ShortStep:= 1;
         if oilpp >= WaterT then begin
            droplets:= true;
            if VMD > thick.thickness then
               thick.thickness:= VMD
         end
         else
            thick.thickness:= AvThickness * (1 + Width/UpStream)/2;
         for i:= 1 to 60 do begin
            evap(shortstep,dfevtk,dfevtn,thick.fevap,thin.fevap,ttk,
                 thick.thickness,WindSp,thin.thickness,ASTMA,ASTMT,AirT);
            OilProp;
            emulsion(ShortStep,thick.thickness,emul.viscosity,
                emul.density,water_content,WindSp,oil.density,
                oil.viscosity,ttk,ttke);
            dispers(ShortStep,thick.fdis,thin.fdis,WindSp,emul.density,
                oil.density,owint,emul.viscosity,thick.thickness,
                thin.thickness,thnoil.viscosity);
         end;
         ShortStep:= 60;
         for i:= 2 to 60 do begin
            evap(shortstep,dfevtk,dfevtn,thick.fevap,thin.fevap,ttk,
                 thick.thickness,WindSp,thin.thickness,ASTMA,ASTMT,AirT);
            OilProp;
            emulsion(ShortStep,thick.thickness,emul.viscosity,
                emul.density,water_content,WindSp,oil.density,
                oil.viscosity,ttk,ttke);
            dispers(ShortStep,thick.fdis,thin.fdis,WindSp,emul.density,
                oil.density,owint,emul.viscosity,thick.thickness,
                thin.thickness,thnoil.viscosity);
         end;
         thick.thickness:= AvThickness;
      end;
   else begin
         clrscr;
         textcolor(14 + blink);
         Center('Undefined spilltype passed to model - halting',
                                                              1,13,80);

         delay(3000);
         goto Abort;
      end
end;  {case}
totslick.area:=thin.area+thick.area;
thick.width:= width;
with thick do begin
   volume:= thickness * area;
   vevap:= volume * fevap;
   sumvevap:= vevap;
   vdis:= fdis * volume;
```

```
         sumvdis:= vdis;
         volume:= volume - vdis - vevap;
      end;
      thin.width:= 1/(tstep*Surface_Current);
      with thin do begin
         volume:= thickness * area;
         vevap:= volume * fevap;
         sumvevap:= vevap;
         vdis:= fdis * volume;
         sumvdis:= vdis;
         volume:= volume - vdis - vevap;
      end;
      totslick.sumvevap:= thick.sumvevap + thin.sumvevap;
      totslick.vdis:= thick.vdis + thin.vdis;
      vtotn:=thin.volume;
      passcount:=round(tcount/tstep);  {start passcount after the section
                                          has been formed}
    {end general init for each run}

      if (not FirstRun) and DoubleRun then
         begin
            PointNum:= 100;
            OutC:= trunc(SaveCount/PointNum/tstep);         {steps per output}
            DataFreq:= OutC*tstep;      {seconds per data output}
            ScreenData:= false;
            PrintData:= false;
            GraphFlag:= true;
            clrscr;
            Center('Doing graphic data run - wait.......',1,12,80);
            ResetGraphFile;
            SaveRunStats(DataFreq,SpillVol,PointNum,sTitle);
            RecCount:= PassCount div outc;    {preset the time wasted in prep}
            if RecCount < 1 then
               RecCount:= 1;
            for i:= 1 to RecCount do
               SaveDummyData;
         end
      else
         {do first run};
      SaveCount:= tcount;     {save tcount in case we need it for section
                               spill calculations}


   { Repeat until done, first or second run }
      while (thick.volume > Fract_Vol * SpillVol)
            and (thick.thickness > Min_Thick)
                and (tcount < tcountstop) do
       begin
          if SpillType = 'B' then
             if tcount<SpillDur then
               begin
                 thick.volume:=thick.volume+dvol;
                 thick.thickness:=thick.thickness+dvol/thick.area;
               end;
          tcount:=tcount+tstep;
          passcount:=passcount+1;
          evap(tstep,dfevtk,dfevtn,thick.fevap,thin.fevap,ttk,thick.thickness,
             WindSp,thin.thickness,ASTMA,ASTMT,AirT);
          case SpillType of
            'A',
```

```
         'S':TwoDSpread(thick.area,thin.area,thick.width,thin.width,tcount,
                        emul.viscosity,surface_current,sigma);
         'B': spread(thick.area,thin.area,sigma,thick.thickness,InitPP,
                       WaterT)
       end;  {case}
       OilProp;
       emulsion(tstep,thick.thickness,emul.viscosity,emul.density,
          water_content,WindSp,oil.density,oil.viscosity,ttk,ttke);
       dispers(tstep,thick.fdis,thin.fdis,WindSp,emul.density,oil.density,
          owint,emul.viscosity,thick.thickness,thin.thickness,
          thnoil.viscosity);
       SlickChar;

       if outc < 1 then begin
          clrscr;
          TextColor(14 + blink);
          center('OutC is zero or negative - halting',1,13,80);
          delay(3000);
          goto Abort;
       end
       else if (passcount mod outc) = 0 then
          begin
             if ScreenData then begin
                clrscr;
                dataout(CON)
             end;
             if PrintData then begin
                if passcount = outc then begin
                   CentrePrint(sTitle);
                   case SpillType of
                   'A','S':PrintHeader(LST)
                   end    {case}
                end;
                dataout(LST)
             end;
             if GraphFlag then
                SaveGraphicData
       end;
  end;            {while}
  SaveCount:= tcount;

{finish output}
   if PrintData then begin
      dataout(LST);
      writeln(lst,'Passes = ',Passcount:0,'  Time (sec) = ',tcount:0:0);
      if StopShort then begin
         writeln(lst);
         CentrePrint('Run aborted early on operator''s direction');
      end;
      writeln(lst,chr(FF))
   end;
   if ScreenData then
   if DoubleRun then begin
      clrscr;
      dataout(CON);
      gotoXY(1,23);
      writeln('Passes = ',Passcount:0,'  Time (sec) = ',tcount:0:0);
      if StopShort then begin
         Center('Run aborted early on operator''s direction',1,24,80);
         delay(5000)
```

```
         end;
      end
      else begin
         gotoXY(1,22);
         writeln('Passes = ',Passcount:0,'  Time (sec) = ',tcount:0:0);
         writeln('Ending run - no graphic output.');
      end;
      if GraphFlag then begin
         SaveGraphicData;
         close(Out_File)
      end;
      if (not FirstRun) or (not DoubleRun) then
         Done:= true;
      FirstRun:= false
   until Done;
   writeln('model complete',passcount);
abort:end;


{****************** Procedures for using external programs *****************}

procedure NameError(i:integer);

begin
   write('Error - ',i,' :');
   case i of
      1: writeln('Invalid function');
      2: writeln('File/Path not found');
      8: writeln('Not enough memory to load program');
     10: writeln('Bad environment (greater than 32k)');
     11: writeln('Illegal .EXE file format')
   end
end;

{ EXEC.PAS version 1.3

  This file contains 2 functions for Turbo Pascal that allow you to run other
  programs from within a Turbo program.  The first function, SubProcess,
  actually calls up a different program using MS-DOS call 4BH, EXEC.  The
  second function, GetComSpec, returns the path name of the command
  interpreter, which is necessary to do certain operations.  There is also a
  main program that allows you to test the functions.

  Revision history
  ----------------
  Version 1.3 works with MS-DOS 2.0 and up, TURBO PASCAL version 1.0 and up.
  Version 1.2 had a subtle but dangerous bug: I set a variable that was
              addressed relative to BP, using a destroyed BP!
  Version 1.1 didn't work with Turbo 2.0 because I used Turbo 3.0 features
  Version 1.0 only worked with DOS 3.0 due to a subtle bug in DOS 2.x

     -  Bela Lubkin
        Borland International Technical Support
        CompuServe 71016,1573
}

Type
  Str66=String[66];

Function SubProcess(CommandLine: Str255): Integer;
```

```
  { Pass this function a string of the form
      'D:\FULL\PATH\NAME\OF\FILE.TYP parameter1 parameter2 ...'

    For example,
      'C:\SYSTEM\CHKDSK.COM'
      'A:\WS.COM DOCUMENT.1'
      'C:\DOS\LINK.EXE TEST;'
      'C:\COMMAND.COM /C COPY *.* B:\BACKUP >FILESCOP.IED'

    The third example shows several things.  To do any of the following, you
    must invoke the command processor and let it do the work: redirection;
    piping; path searching; searching for the extension of a program (.COM,
    .EXE, or .BAT); batch files; and internal DOS commands.  The name of the
    command processor file is stored in the DOS environment.  The function
    GetComSpec in this file returns the path name of the command processor.
    Also note that you must use the /C parameter or COMMAND will not work
    correctly.  You can also call COMMAND with no parameters.  This will allow
    the user to use the DOS prompt to run anything (as long as there is enough
    memory).  To get back to your program, he can type the command EXIT.

    Actual example:
      I:=SubProcess(GetComSpec+' /C COPY *.* B:\BACKUP >FILESCOP.IED');

    The value returned is the result returned by DOS after the EXEC call.  The
    most common values are:

       0: Success
       1: Invalid function (should never happen with this routine)
       2: File/path not found
       8: Not enough memory to load program
      10: Bad environment (greater than 32K)
      11: Illegal .EXE file format

    If you get any other result, consult an MS-DOS Technical Reference manual.

    VERY IMPORTANT NOTE: you MUST use the Options menu of Turbo Pascal to
    restrict the amount of free dynamic memory used by your program.  Only the
    memory that is not used by the heap is available for use by other
    programs. }

  Const
    SSSave: Integer=0;
    SPSave: Integer=0;

  Var
    Regs: Record Case Integer Of
            1: (AX,BX,CX,DX,BP,SI,DI,DS,ES,Flags: Integer);
            2: (AL,AH,BL,BH,CL,CH,DL,DH: Byte);
          End;
    FCB1,FCB2: Array [0..36] Of Byte;
    PathName: Str66;
    CommandTail: Str255;
    ParmTable: Record
                 EnvSeg: Integer;
                 ComLin: ^Integer;
                 FCB1Pr: ^Integer;
                 FCB2Pr: ^Integer;
               End;
    I,RegsFlags: Integer;
```

```
  Begin
    If Pos(' ',CommandLine)=0 Then
     Begin
      PathName:=CommandLine+#0;
      CommandTail:=^M;
     End
    Else
     Begin
      PathName:=Copy(CommandLine,1,Pos(' ',CommandLine)-1)+#0;
      CommandTail:=Copy(CommandLine,Pos(' ',CommandLine),255)+^M;
     End;
    CommandTail[0]:=Pred(CommandTail[0]);
    With Regs Do
     Begin
      FillChar(FCB1,Sizeof(FCB1),0);
      AX:=$2901;
      DS:=Seg(CommandTail[1]);
      SI:=Ofs(CommandTail[1]);
      ES:=Seg(FCB1);
      DI:=Ofs(FCB1);
      MsDos(Regs); { Create FCB 1 }
      FillChar(FCB2,Sizeof(FCB2),0);
      AX:=$2901;
      ES:=Seg(FCB2);
      DI:=Ofs(FCB2);
      MsDos(Regs); { Create FCB 2 }
      ES:=CSeg;
      BX:=SSeg-CSeg+MemW[CSeg:MemW[CSeg:$0101]+$112];
      AH:=$4A;
      MsDos(Regs); { Deallocate unused memory }
      With ParmTable Do
       Begin
        EnvSeg:=MemW[CSeg:$002C];
        ComLin:=Addr(CommandTail);
        FCB1Pr:=Addr(FCB1);
        FCB2Pr:=Addr(FCB2);
       End;
      InLine($8D/$96/ PathName /$42/  { <DX>:=Ofs(PathName[1]);  }
             $8D/$9E/ ParmTable /     { <BX>:=Ofs(ParmTable);    }
             $B8/$00/$4B/             { <AX>:=$4B00;             }
             $1E/$55/                 { Save <DS>, <BP>          }
             $16/$1F/                 { <DS>:=Seg(PathName[1]);  }
             $16/$07/                 { <ES>:=Seg(ParmTable);    }
             $2E/$8C/$16/ SSSave /    { Save <SS> in SSSave      }
             $2E/$89/$26/ SPSave /    { Save <SP> in SPSave      }
             $FA/                     { Disable interrupts       }
             $CD/$21/                 { Call MS-DOS              }
             $FA/                     { Disable interrupts       }
             $2E/$8B/$26/ SPSave /    { Restore <SP>             }
             $2E/$8E/$16/ SSSave /    { Restore <SS>             }
             $FB/                     { Enable interrupts        }
             $5D/$1F/                 { Restore <BP>,<DS>        }
             $9C/$8F/$86/ RegsFlags / { Flags:=<CPU flags>       }
             $89/$86/ Regs );         { Regs.AX:=<AX>;           }
      { The messing around with SS and SP is necessary because under DOS 2.x,
        after returning from an EXEC call, ALL registers are destroyed except
        CS and IP!  I wish I'd known that before I released this package the
        first time... }
      If (RegsFlags And 1)<>0 Then SubProcess:=AX
      Else SubProcess:=0;
```

```
     End;
  End;

Function GetComSpec: Str66;
  Type
    Env=Array [0..32767] Of Char;
  Var
    EPtr: ^Env;
    EStr: Str255;
    Done: Boolean;
    I: Integer;

  Begin
    EPtr:=Ptr(MemW[CSeg:$002C],0);
    I:=0;
    Done:=False;
    EStr:='';
    Repeat
      If EPtr^[I]=#0 Then
       Begin
        If EPtr^[I+1]=#0 Then Done:=True;
        If Copy(EStr,1,8)='COMSPEC=' Then
         Begin
          GetComSpec:=Copy(EStr,9,100);
          Done:=True;
         End;
        EStr:='';
       End
      Else EStr:=EStr+EPtr^[I];
      I:=I+1;
    Until Done;
  End;

procedure UseDos;

Var Command: Str255;
    I: Integer;

Begin
  ClrScr;
  WriteLn('Enter a * to quit.');
  Repeat
    Write('-=-=->');
    ReadLn(Command);
    If Command<>'*' Then
       If Command<>'' Then
        Begin
         Command:=GetComSpec+' /C '+Command;
         I:=SubProcess(Command);
         If I<>0 Then NameError(I)
        End;
  Until Command = '*'
End;

procedure RunGraph;

{Simply call MakeGraf.com using Bela Lubkin's routine: SubProcess}

var
   Command:Str255;
```

```
   I:integer;

begin
    ClrScr;
    Command:= GetComSpec+' /c MakeGraf';
    I:= SubProcess(Command);
    if I<>0 then
       begin
          NameError(I);
          writeln('Press a key to continue');
          repeat until KeyPressed
       end
end;

{*************************** End of EXEC routines ****************************}


procedure ListInputs;

var
   s1,s2,s3,s4,s5,s6,s7,s8,s9,s10,s11,s12,s13,s14,s15,s16,s17,s18,s19,s20,
   s21,s22,s23,s24,s25,s26,s27,s28,s29,s30,
   s31,s32,s33,s34,s35,s36,s37,s38,s39,s40,s41,s42:real;
   i:integer;
   source,class:char;

begin
   readinitfile;
   for i:=1 to Size do val(filvar[i],r[i],code);
   source:= upcase(copy(Filvar[1],1,1));          {write 'upcase'}
   s2:= r[2];
   s3:= r[3];
   s4:= r[4];
   s5:= r[5];
   s6:= r[6];
   s7:= r[7];
   s8:= r[8];
   s9:= r[9];
   s10:= r[10];
   s11:= r[11];
   s12:= r[12];
   s13:= r[13];
   s14:= r[14];
   s15:= r[15];
   s16:= r[16];
   s17:= r[17];
   s18:= r[18];
   s19:= r[19];
   s20:= r[20];
   class:= upcase(copy(Filvar[21],1,1));
   s22:= r[22];
   s23:= r[23];
   s24:= r[24];
   s25:= r[25];
   s26:= r[26];
   s27:= r[27];
   s28:= r[28];
   s29:= r[29];
   s30:= r[30];
   s31:= r[31];
```

```
   s32:= r[32];
   s33:= r[33];
   s34:= r[34];
   s35:= r[35];
   s36:= r[36];
   s37:= r[37];
   s38:= r[38];
   s39:= r[39];
   s40:= r[40];
   s41:= r[41];
   CentrePrint(sTitle);
   writeln(lst);
   write(lst,'         The spill is from');
   case source of
    'A':writeln(lst,' an above sea blowout.');
    'B':writeln(lst,' a batch spill.');
    'S':writeln(lst,' a subsea blowout.');
   end;
   writeln(lst);
   writeln(lst,'Fresh oil properties');
   writeln(lst);
   writeln(lst,'   Emulsification delay (theta)           ',s3:8:1);
   writeln(lst,'   Density (kg/m3)                        ',s4:8:2);
   writeln(lst,'   Standard density temperature (K)       ',s5:8:2);
   writeln(lst,'   Viscosity (mPas)                       ',s6:8:2);
   writeln(lst,'   Standard viscosity temperature (K)     ',s7:8:2);
   writeln(lst,'   Pour point (K)                         ',s8:8:2);
   writeln(lst,'   Aqueous solubility (g/m3)              ',s9:8:2);
   writeln(lst,'   Flash point (K)                        ',s10:8:2);
   writeln(lst,'   Oil-water interfacial tension (N/m)    ',s11:8:2);
   writeln(lst,'   Oil-air interfacial tension (N/m)      ',s12:9:3);
   case source of
     'B': {do nothing};
     'A': begin
            writeln(lst,'   GOR (dimensionless)                    ',s13:8:2);
            writeln(lst,'   Gas Density (kg/m3)                    ',s14:8:2);
            writeln(lst,'   Oil/Gas interfacial tension (N/m)      ',s15:8:2);
          end;
     'S':   writeln(lst,'   GOR (dimensionless)                    ',s13:8:2)
   end;
   writeln(lst);
   writeln(lst,'Spill conditions');
   writeln(lst);
   case source of
     'B': begin
            writeln(lst,'   Duration of spill (100sec)             ',s23:8:2);
            writeln(lst,'   Volume of oil spilled (m3)             ',s24:8:2);
          end;
     'A': begin
            writeln(lst,'   Well Depth (m)                         ',s26:8:2);
            writeln(lst,'   Pipe diameter (m)                      ',s27:8:2);
            writeln(lst,'   Plume rise (m)                         ',s28:8:2);
            writeln(lst,'   Mixing zone height (m)                 ',s29:8:2);
            writeln(lst,'   Oil discharge rate (g/s)               ',s30:8:2);
          end;
     'S': begin
            writeln(lst,'   Oil discharge rate (barrels/day)       ',s25:8:2);
            writeln(lst,'   Well Depth (m)                         ',s26:8:2);
          end;
   end;
```

```
   writeln(lst);
   writeln(lst);
   writeln(lst,'Environmental Conditions');
   writeln(lst);
   writeln(lst,'   Windspeed (m/s)                        ',s17:8:2);
   writeln(lst,'   Air temperature (K)                    ',s18:8:2);
   writeln(lst,'   Water temperature (K)                  ',s19:8:2);
   case source of
     'B': {do nothing};
     'A': begin
            writeln(lst,'   Surface current (m/s)                  ',s20:8:2);
            writeln(lst,'   Stability class (A, D or F)            ',class);
          end;
     'S':   writeln(lst,'   Surface current (m/s)                  ',s20:8:2);
   end;
   writeln(lst);
   writeln(lst);
   writeln(lst,'Constants');
   writeln(lst);
   writeln(lst,'   Density constant 1                     ',s31:13:7);
   writeln(lst,'   Density constant 2                     ',s32:13:7);
   writeln(lst,'   Viscosity constant 1                   ',s33:13:7);
   writeln(lst,'   Viscosity constant 2                   ',s34:8:2);
   writeln(lst,'   Pour point constant                    ',s35:13:7);
   writeln(lst,'   Solubility constant                    ',s36:13:7);
   writeln(lst,'   Flash point constant                   ',s37:13:7);
   writeln(lst,'   Oil-water int. tension constant        ',s38:13:7);
   writeln(lst,'   Oil-Air int. tension constant          ',s39:13:7);
   writeln(lst,'   ASTMA constant                         ',s40:8:2);
   writeln(lst,'   ASTMT constant                         ',s41:8:2);
   writeln(lst,char(FF));
end;


procedure PickOil;
 const
     LastOil = 3;                {set this for the number of REAL oils defined}
     OilName: array[1..LastOil] of string25 = ('Hibernia',
                                               'Mixed Sweet Western',
                                               'Amauligak');
     OilFile: array[1..LastOil] of string16 = ('Hibernia.dta',
                                               'MSW.dta',
                                               'Amauliga.dta');

 var I,Tab: integer;
     Okchoices: set of char;
     newinitfilename:string16;
  begin
    if not OilPicked then
       OilPicked:= true;
    ClrScr; HighVideo;
    center('OILS CURRENTLY DEFINED',0,4,80);
    for I:= 1 to 4 do  writeln('');
    Tab:= 25;
    for i:= 1 to LastOil do
       writeln('':Tab,'<',chr(i+48):1,'> ',OilName[i]);
    Box(20,2,60,LastOil + 11,6);writeln('');
    Highvideo; Center('Press Your Selection',21,LastOil + 9,38);
    Center('<ESC> to quit',21,LastOil + 10,38); LowVideo;
    OKchoices:=['1'..'7',^[];
```

```
    repeat
      Option; if not (Ch in OKchoices) then Beep(350,150);
    until Ch in OKchoices;
    if Ch <> ^[ then
       initfilename:= OilFile[(ord(Ch)-48)]
  end;


procedure ProgramExit;
 begin
   Clrscr; Center('This Program is about to end',1,11,80);
   highvideo; Center('Verify Ok (Y/N)',1,13,80); lowvideo;
   repeat
     Option; if not (Ch in ['Y','N',^[]) then beep(350,150);
   until Ch in ['Y','N'];
 end;

procedure MainMenu;
 var I,Tab: integer;
     Okchoices: set of char;
  begin
   if First_run then
    begin
     ClrScr; HighVideo;
     center('S. L. ROSS ENVIRONMENTAL RESEARCH',0,4,80);
     center('WAXY OIL OILFATE MODEL',0,5,80);
     for I:= 1 to 4 do  writeln('');
     Tab:= 25;
     writeln('':Tab,'<1> Define initial conditions ');
     writeln('':Tab,'<2> Run oilfate model ');
     writeln('':Tab,'<3> List the input parameters');
     writeln('':Tab,'    to the model (to print)');
     writeln('':Tab,'<4> Graph the results ');
     writeln('':Tab,'<5> Pick an oil ');
     writeln('':Tab,'<6> Use DOS commands '); writeln('');
     writeln('':Tab,'<7> Exit the Program');
     Box(20,2,60,20,6);writeln('');
     SaveScreen(1); First_run:=false;
    end else FlashScreen(1);
    Highvideo; Center('Press Your Selection',21,19,38); LowVideo;
    OKchoices:=['1'..'7',^[];
    repeat
      Option; if not (Ch in OKchoices) then Beep(350,150);
    until Ch in OKchoices;
    case Ch of
      '1' : begin
               if not OilPicked then
                  PickOil;
               initcond;
            end;
      '2' : begin
               if not OilPicked then
                  PickOil;
               fatemodel;
            end;
      '3' : begin
               if not OilPicked then
                  PickOil;
               ListInputs;
            end;
```

```
      '4' : RunGraph;
      '5' : PickOil;
      '6' : UseDOS;
      ^[,'7' :  begin                   {include 'Esc' as an exit}
               ProgramExit;
               if Ch in ['Y',^[] then Exit := true;
                   {'Esc' not working at this level}
             end;
    end; { case }
  end;

{**********************************************************}
{*              Program Starts Execution                 *}
{**********************************************************}

begin
  ClrScr; Exit:=false; First_run:=true;
  OilPicked:= false;
  repeat
    MainMenu;
  until Exit = true;
  Set_Cap_Num(' ',' ',' ');        {Turn of the bloody settings!!!}
  ClrScr
end.
```