

A STUDY TO EVALUATE THE
COMBUSTIBILITY AND OTHER PHYSICAL AND
CHEMICAL PROPERTIES OF AGED
OILS AND EMULSIONS

A Study to Evaluate the Combustibility and
Other Physical and Chemical Properties
of Aged Oils and Emulsions

by

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SUMMARY

The extent of environmental damage created by marine oil spills and the effectiveness of operations devoted towards their cleanup are dictated primarily by the environment of the spill, and by the physical and chemical properties of the spilled oil. Several important processes of oil aging (evaporation, dissolution, atmospheric oxidation, and bacterial oxidation, for example) and the formation of water-in-oil (W/O) emulsions have been known to alter significantly the characteristics of spilled oil in various marine locations. It is desirable to establish the effects of oil aging as a function of the time, and the change in oil characteristics as a consequence of emulsification with water. Little systematic experimental work has been done on oil aging in an arctic environment, or towards the formation and properties of W/O emulsions. This report describes research performed in Waterloo, Ontario during the winter of 1978/79 which was devoted to the study of both of these areas and especially their effects on oil combustibility. The report is divided into two parts concerning oil aging and the formation of W/O emulsions.

Part I of this report is concerned with the aging of Bunker-C fuel, marine diesel fuel, and six crude oils under conditions similar to the arctic spring climate. For aging intervals of up to four weeks, several physical and chemical properties of the oils were monitored. In addition, the oils aged for the intervals concerned with subjected to wicking and in situ combustion tests, in order to establish the suitability of sorbent and combustion techniques for their disposal. From this work, it was noted that the majority of volatile hydrocarbons in the crude oil layers were lost within the first two days of aging. The evaporative losses from Bunker-C and marine diesel fuel oils were negligible, even for aging intervals of up to 4 weeks. It was noted that crude oils increased significantly in viscosity as a consequence of oil aging, and this observation accounts for the fact that aged crude oils were not wicked up by a sorbent as well as fresh crude oils. Although the combustibility of the crude oils was reduced (as noted by increased flash and fire point values) as a result of aging, the in situ combustion of oil slicks consisting of aged crude oils is possible. With assistance provided by adding fresh crude oil as a priming agent, the minimum ignitable thicknesses for slicks of crude oils aged for up to 4 weeks (and for slicks of marine diesel fuel) ranged between 3 and 4 mm, when a solid fuel igniter was employed to initiate in situ combustion. For the same igniter (and with the priming assistance provided by adding fresh crude oil), the minimum ignitable thicknesses for Bunker-C fuel oil appear to range between 4 and 5.5 mm. With the use of a solid fuel igniter and without the addition of fresh crude oil, the minimum ignitable thicknesses for the aged crude oils are considered to be approximately 5 mm, and the minimum ignitable thickness for Bunker-C fuel oil is estimated to be approximately 10 mm.

Part II of the report is concerned with the formation of W/O emulsions (with varying water contents) with several crude oils. The physical properties of these emulsions were determined, as well as the effectiveness of in situ combustion and wicking methods for their disposal. It was found that stable W/O emulsions could be formed with water contents of up to 80 percent for the heavy crude oils (Weyburn-Midale and Lloydminster crudes),

and partially-stable W/O emulsions could be formed with water contents of up to 60 percent with the medium crude oils (Alberta Sweet Blend and Norman Wells crudes). In general, the mixing energy required to form a stable W/O emulsion increased with water content. For a given oil type, higher water contents resulted in increased viscosity values for the W/O emulsion. Because of this fact (and also because of the water-repelling nature of the sorbent itself), emulsions with high water contents were not wicked by the sorbent as well as those with lower water contents. As expected, the combustibility of a given crude oil (as noted by increased flash and fire point values) was reduced with increased contents of emulsified water. The in situ combustion of W/O emulsions was found to be possible (W/O emulsions with fresh oils having water contents of 20 percent were easily ignited by a match), but W/O emulsions with higher water contents required a much stronger ignition source (incorporating a flame with a minimum diameter of 0.5 m) in order for the flame to spread over the entire slick surface. Since W/O emulsions must be separated before the oil can be effectively burned, flame propagation over the emulsion surfaces was much slower than with slicks of non-emulsified oil. Once fully developed, the combustion of W/O emulsion layers was very intense (due to micro explosions probably associated with boiling water), and the residual oil layer thicknesses were similar to those remaining following the in situ combustion of non-emulsified oils. Emulsions formed with Lloydminster crude oil tended to foam during the combustion process, resulting in a suppression of the flames. For an emulsion of Lloydminster crude oil with a 50 percent water content, the foam generation was so intense that in situ combustion was not possible (even when fresh crude oil was added in an effort to assist combustion).

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INTRODUCTION

In the Canadian Arctic, the possibility of marine oil spills and underwater well blowouts is an environmental threat that grows with increased offshore drilling operations and the future increase in traffic expected in this region. The aging (or "weathering") of oil spills is an extremely complex phenomenon, and may involve up to ten major processes (described in Chapter 1 of Part I), many of which could occur simultaneously. The extent of environmental damage caused by an oil spill and the effectiveness of a given cleanup technique is dictated by the environment of the oil spill (land, ice, or open water), as well as by the physical and chemical properties of the oil itself.

Oil spilled in an arctic marine environment could take any of the following forms:

- (i) oil under ice
- (ii) oil on melt pools
- (iii) oil on ice
- (iv) oil under or in snow
- (v) oil on open water.

For oil under ice, only hydrocarbon dissolution is important, and sinking, bacterial removal, and water currents may have smaller effects. No extensive countermeasure techniques are presently available for this situation. For oil on melt pools, evaporation and dissolution are two important processes, and atmospheric oxidation and the formation of water-in-oil emulsions (probably largely as a result of rainfall) may also be possible. In situ combustion has been considered as a possible primary countermeasure in this situation. For oil on ice, the important processes are evaporation, atmospheric oxidation, and the formation of water-in-oil emulsions. In situ combustion is a suggested countermeasure in this situation. For oil under and in snow, the formation of water-in-oil emulsions during snow melting and evaporation (to a limited extent) would be the most important processes. Incineration and in situ combustion are the suggested countermeasures in this situation. For oil on water, the four most important processes would be evaporation, dissolution, the formation of water-in-oil emulsions, and natural dispersion. The main cleanup options in this situation are the usual ones for open water--mechanical removal and chemical dispersion.

In a given arctic environment, the previously mentioned processes would mostly occur over a much different time scale than they would for oil spilled in a more southerly location.

The study described in Part I was devoted towards determining the hydrocarbon composition, physical properties, and chemical properties of eight oils (Bunker-C fuel, marine diesel fuel, three medium crude oils, and three heavy crude oils), primarily as a function of evaporative loss. The

oils were aged under Southern Ontario winter conditions for six discrete aging intervals (ranging from 6 hours to 4 weeks). Following the aging intervals, the oils were subjected to laboratory analyses, and the evaporative losses were determined. Laboratory analyses were also performed with these oils in their fresh states. Wicking tests and in situ combustion tests were carried out with the oils, in order to establish their relative effectiveness. A review of several oil aging processes is presented in Chapter 1. The experimental approach and results are presented in Chapters 2 and 3, respectively. The conclusions of the study are presented in Chapter 4. Chapter 5 outlines future research suggestions.

The study described in Part II of this report deals with the formation and characteristics of water-in-oil (W/O) emulsions. In this work, W/O emulsions were prepared with various water contents (ranging between 20 and 80 percent by volume). In Phase #1, the W/O emulsions were prepared with marine diesel fuel, three heavy crude oils, and three medium crude oils. The stability of these emulsions during their aging (under Southern Ontario winter conditions) was observed from a qualitative point of view. In Phase #2, W/O emulsions were prepared with two medium crude oils and two heavy crude oils, and were subjected to laboratory analyses. Wicking tests and in situ combustion tests were also carried out with the emulsions. A review of emulsions in general, and W/O (petroleum) emulsions is presented in Chapter 1. The experimental approach and results are described in Chapters 2 and 3, respectively. Conclusions are presented in Chapter 4, and future research suggestions are outlined in Chapter 5.

PART I: A STUDY TO INVESTIGATE THE COMBUSTIBILITY AND
PHYSICAL/CHEMICAL PROPERTIES OF AGED OILS

1 A REVIEW ON THE AGING OF MARINE OIL SPILLS

Recent research concerning the environmental effects of marine oil spills has given rise to a small (but growing) body of literature on the fate of spilled oil. In this section, some of this published literature is reviewed, and related to this study. The majority of the papers and reports reviewed here deal with the behaviour of real and simulated oil slicks on the sea. The prime purpose of most research has been to study the fate of crude oil in order to establish its possible toxic effects upon a marine environment. Taken in this context, the "fate" of spilled oil involves many processes of dispersion, as well as those processes that might be included in terms of "aging" or "weathering" (Berridge et al., 1968 and Feldman, 1973). Ten such process (Berridge et al., 1968) have been listed:

- Evaporation
- Atmospheric Oxidation
- Bacterial Degradation
- Formation of Oil-in-Water Emulsions
- Formation of Water-in-Oil Emulsions
- Dissolution
- Sinking
- Adsorption by Particulate Matter
- Spreading
- Mechanical Transport by Wind, Tides, and Current.

The object of this study was to examine the effect of exposure time and environmental conditions upon the properties that determine the handling and burning characteristics of spilled fuel oil and crude oil. Since the experiments deal with oil samples confined in open pans, only the processes of evaporation, atmospheric oxidation, possibly bacterial degradation, and the formation of water-in-oil emulsions (as a result of atmospheric precipitation) are considered relevant. These four processes are essentially the main aspects of oil aging (or "weathering"), as opposed to oil dispersion. For this reason, much of the research that has been surveyed does not bear directly upon this study, but would provide peripheral information that may enable the interpretation of results from this study in a broader context.

Hydrocarbon evaporation is the only significant mechanism for weight loss in the oil layer during the aging intervals (up to 4 weeks) incorporated in this study. Even in warm water, microbial degradation and chemical reactions could yield significant changes in the oil only over a time scale of 1 year (Blumer et al., 1973). On the other hand, hydrocarbon evaporation can remove

the light fractions from a slick in a matter of hours (Sivadier/Mikolaj, 1973, Smith/MacIntyre, 1973, McAuliffe, 1976, and McAuliffe, 1976a). Although the subject of considerable attention in the literature, hydrocarbon dissolution in the water layer was not considered in the experimental design of this study. These subjects are discussed in more detail in the following sections of the review. The formation of water-in-oil emulsions is discussed in the literature review in Part II of this report.

1.1 Hydrocarbon Evaporation

Hydrocarbon evaporation is a diffusion-controlled process, by which the lighter (more volatile) components are lost to the atmosphere, while the heavier components remain in the oil layer. By one definition (Pilpel, 1968), the volatile components of oil consist of the paraffinic, naphthalenic, and aromatic fractions having boiling points up to 150°C, with chains consisting of up to 10 carbon atoms. Hydrocarbon evaporation ultimately results in a decrease in the volume and volatility of an oil spill and an increase in the density and viscosity of the oil. The evaporation rate from a marine oil spill is dependent upon the initial composition (or volatility) of the spilled oil, temperature, the extent of solar heating, the extent of precipitation, and the presence of wave action. Evaporation rates for single-component liquids have been investigated for small oil slicks (Blokke, 1964). In this work, the change in oil volume with time (dV/dt) was estimated for two different geometries. For slicks in channels (assuming a wind blowing lengthwise),

$$\frac{dV}{dt} = - K_{ev} \mu \alpha b \ell^{1-\beta} p M$$

and for circular slicks,

$$\frac{dV}{dt} = - \frac{\pi}{4} K_{ev} \mu \alpha D^{2-\beta} p M$$

where: V = liquid volume (m^3)

μ = wind speed (m/s)

D (or ℓ) = the diameter (or length) of the oil spill (m)

b = the width of the oil spill (m)

p = the vapour pressure of the single-component oil
(mm of Hg)

M = the molecular weight of the oil

t = time (min)

K_{ev} = evaporative mass transfer coefficient (a constant value of 1.2×10^{-8} for a neutral atmosphere and a temperature of 2°C)

$\alpha = 0.78$ (for a neutral atmosphere)

$\beta = 0.11$ (for a neutral atmosphere).

Although this equation has not necessarily been proven applicable for large slicks of crude or fuel oils, it provides a general mathematical expression for hydrocarbon evaporation.

Solar heating would warm up an oil layer, consequently reducing the viscosity and surface tension of the oil. These two property changes would promote the spread of an unconfined slick (thereby increasing the surface contact of oil with both air and water layers), which would enhance the evaporation rate (Garrett, 1973). In the case of oil confined in open pans, however, the effect of solar heating (or increased temperatures) is primarily a thermodynamic one. As the oil temperature rises, the vapour pressures of the volatile hydrocarbon fractions also increase and the potential for evaporation is consequently increased. Another possible effect of increased oil temperatures is the increase of mass transfer rates within the oil layer by convection and diffusion.

The importance of mechanical effects can be discussed with reference to several studies (Sivadier/Mikolaj, 1973, Smith/MacIntyre, 1973, McAuliffe, 1976, and Harrison et al., 1975), from which it was observed that the appearance of white caps dramatically increased the weight loss rate from a oil slick. However, little effort has been devoted towards explaining this effect. One suggestion for this observation is that wave action (or white caps) serves to increase the surface area of an oil slick, and may therefore accelerate hydrocarbon evaporation rates. Another possibility is that water turbulence serves to drive oil droplets from the oil layer into the water column, resulting in the formation of oil-in-water emulsions or colloidal suspensions. Also, a possibly important consequence of wave action is the formation of oil aerosols (airbourne mists of oil droplets produced by wind-stripping and the splashing of wave crests). This phenomenon may be supported by the fact that wave action can create salt aerosols in the atmosphere. Finally, the turbulent mixing of the oil near white caps may increase the mass transfer rates in the oil layer.

Aside from the creation of water turbulence, wind velocity plays an important role in hydrocarbon evaporation, since the evaporation rate is directly proportional to the removal of hydrocarbon vapours from the area adjacent to the oil/air interface (McMinn, 1972). Theoretically, the convective mass transfer coefficient between the slick and the ambient air is increased with higher wind velocities. This effect has been combined with the thermodynamic effects of slick temperatures, and the resulting effect on evaporation rates has been presented in convenient charts (Mackay/Nadeau, 1978), in which the weight losses for several types of oil are expressed as a function of time, slick area, slick thickness, and slick temperature. The correlations are based upon the evaporation studies described in two earlier papers (Mackay/Matsugu, 1973 and Goodwin et al., 1976).

Another computer model for the evaporation of an oil slick has been reported in detail, and the computer program has been described (Wang et al., 1976). Experiments were performed as part of the study to provide the empirical constants required in the equation for the evaporation rate. However, it is felt that the final model developed must be treated with suspicion, since it predicts that the evaporation rate decreases with increasing wind speed at a constant temperature (Figure 14 of this reference), and decreases with increasing air temperature at a constant wind speed (Figure 13 of this reference). These two trends are exactly opposite to what was predicted in the previous model (Mackay/Nadeau, 1968), as well as what would be expected according to the theory of mass transfer.

Experimental results (described by Kolpack et al., 1973) have been obtained for the evaporative loss of hydrocarbons from various oils. The evaporative loss of hydrocarbons from a slick of Cook Inlet crude oil over aging intervals of 3 and 8 hours was determined by Kinney et al. (1969), and is presented in Table #1A. In this work, the wind speed was established at 9.12 knots (16.89 km/h), and the air and water temperatures were 5.9°C. For an unspecified crude oil under simulated field conditions, the evaporative losses were determined for aging intervals up to 21 days (Kreider, 1971). The results are presented in Table #1B. The oil film thickness in this work was 0.5 mm. From both of these investigations, it appears that hydrocarbon components ranging from C_6 to C_{14} are extremely volatile, and may be lost from crude oil spills over aging intervals up to several days.

1.2 Hydrocarbon Dissolution

For a marine oil spill, it appears that the water layer does not serve as a sink for the dissolution of hydrocarbon fractions. Instead, hydrocarbon dissolution seems to be an intermediate process leading to enhanced evaporation of certain fractions (that are not extremely volatile), so that the equilibrium solubility of these fractions in water is never attained. Such fractions dissolve in water at the oil/water interface, are advected with the water, and evaporate at the water/air interface (Smith/MacIntyre, 1973, McAuliffe, 1976, and McAuliffe, 1976a). This phenomenon can be explained by the fact that these fractions have high activity coefficients when dissolved in water. These high activity coefficients (in turn) produce high partial pressures of the active fractions in the vapour in equilibrium with the solution. Since the evaporation rates of oil slicks are sufficiently low (so that they are limited by thermodynamics rather than by heat or mass transfer processes), the high partial pressures lead to relatively high evaporation rates for these fractions (Mackay/Wolkoff, 1973 and Mackay/Shiu, 1976). In a general sense, the water layer provides a path for the evaporation of hydrocarbon fractions that would not readily evaporate from the bulk of an oil slick.

It is important to note which hydrocarbon fractions are most soluble in water. The solubilities of sixty-five hydrocarbons have been determined at room temperature (McAuliffe, 1966). In this reference, it was noted that paraffin, olefin, and acetylene hydrocarbons are increasingly water-soluble when their structures contain branched chains. McAuliffe has claimed that the increased solubilities of these hydrocarbons was apparently due to

TABLE #1A

EVAPORATIVE LOSS OF HYDROCARBONS FROM COOK INLET
CRUDE OIL REPORTED BY KINNEY ET AL (1969)*

Carbon Number	Evaporative Loss (%)	
	Aging Interval	
	3 Hours	8 Hours
C ₆	100	100
C ₇	80	100
C ₉	70	85
C ₁₁	40	55
C ₁₂	30	35
C ₁₄	1	2

* The data was obtained from a report prepared by Kolpack et al. (1973). The data was interpreted from a graph, with no estimation of the surface area presented.

Conditions of above data:

- a) Interpreted from a graph.
- b) Wind = 9-12 knots.
- c) Water temperature and air temperature = 5.9°C.
- d) No estimation of slick surface area or thickness.

TABLE #1B

EVAPORATIVE LOSS OF HYDROCARBONS FROM CRUDE OIL REPORTED BY KREIDER (1971)*

Carbon Number	Evaporative Loss (%)						
	Aging Interval						
	1 Day	2 Days	3 Days	4 Days	7 Days	10 Days	21 Days
C ₁₂	98	100	100	100	100	100	100
C ₁₃	75	91	98	100	100	100	100
C ₁₄	38	52	80	92	100	100	100
C ₁₅	12	18	40	55	84	95	100
C ₁₆	1	2	15	27	52	74	88
C ₁₇	0	0	5	11	25	40	58
C ₁₈	0	0	0	0	8	24	35
C ₁₉	0	0	0	0	5	13	-
C ₂₀	0	0	0	0	0	3	-

*The data was obtained from a report prepared by Kolpack et al. (1973). The data was interpreted from a graph, and based upon a film thickness of 0.5 mm.

their increased vapour pressures, as opposed to their structural features. For a given carbon number, the presence of a ring was noted to increase water solubility. An increase in the unsaturation of a hydrocarbon chain or ring was also noted to increase the solubility of a hydrocarbon molecule in water. From other work (Blumer et al., 1973), it was reported that aromatic and heterocyclic hydrocarbons are the most water-soluble components in oil mixtures. The maximum concentration values for many hydrocarbons dissolved in water have not been thoroughly investigated. However, a general idea of the extent of oil dissolution in water can be gathered from previous work. Oil concentrations from areas subjected to varying degrees of oil pollution were noted by Gordon et al. (1976). From polluted seawater samples taken from Boston Harbour, Halifax Harbour, Bedford Basin, Chedabucto Bay, and the Halifax-Bermuda section, the hydrocarbon concentrations ranged in value from 1 to 800 μg per litre. In other work (Lu/Polak, 1973), the solubilities of western crude oil (38.6 API gravity), No. 2 fuel oil, and Bunker oil in water were determined under laboratory conditions. The maximum solubilities of the oils were determined by two different methods (dissolution curves and static equilibrium methods), with each method yielding similar results for each oil. At a temperature of 25°C (based upon the data obtained from dissolution curves), the maximum solubilities of western crude oil, No. 2 fuel oil, and Bunker oil were 44 ppm, 9.7 ppm, and 2.4 ppm, respectively.

1.3 Biochemical Oxidation

In the literature, the terms biochemical oxidation, microbial degradation, and bacterial degradation have been discussed with respect to oil spills, all of which refer to the consumption and metabolism (or biochemical oxidation) of hydrocarbons by various bacteria or microorganisms. Although this process was not monitored in this study, it has been noted that biochemical oxidation of hydrocarbon components (under suitable conditions) is possible with a variety of petroleum-metabolizing microorganisms. The rate of biochemical oxidation appears to be greater for oil-in-water emulsions, oil adsorbed on solids, and thin oil films over water than for large, coherent masses of oil (McLeod/McLeod, 1974). Microorganisms serving this function may be classified into several groups, based upon the hydrocarbon components that they are capable of oxidizing (Pilpel, 1968). One classification (Osnitskaya, 1946 and Zobell, 1963) describes four major groups of hydrocarbon-oxidizing microorganisms:

- microorganisms that oxidize paraffinic hydrocarbons
- microorganisms that oxidize aromatic hydrocarbons
- microorganisms that oxidize naphthalenic hydrocarbons
- microorganisms that oxidize petroleum or refined petroleum products.

It has been noted (Blumer et al., 1973) that the ease of bacterial degradation decreases with the following order of hydrocarbon components:

Normal alkanes (straight chain paraffins) > iso-alkanes (branched paraffins) > cyclo-alkanes > aromatic hydrocarbons

The literature in this area has not dealt with this process under Arctic conditions. However, it can be generally assumed that biochemical oxidation would not be a rapid process with arctic marine oil spills, in view of the low temperatures and low nutrient levels that would be encountered in the Arctic. Some experimental work concerning biochemical oxidation is presented in the following paragraphs.

In experiments performed with Louisiana and California crude oils (Miget et al., 1969), microorganisms were planted in oil slicks. It was noted that normal paraffin hydrocarbons through C_{26} were degraded by two types of microorganisms; those that grew only in the oil phase and those that grew only in the water phase. In this work, 6 out of 50 mixed cultures of active hydrocarbon degrading marine microorganisms were studied. It was reported that between 35 and 55 percent of the dichromate oxidizable crude oil was degraded by microbial action in enriched seawater within 60 hours. Emulsification of the crude oil also occurred, reportedly through the production of surfactants in many of the enriched microorganism cultures.

Crude oils from California, Louisiana, Oklahoma, Pennsylvania, and Texas oilfields have been studied in microbial degradation experiments (ZoBell/Prokop, 1966, and ZoBell, 1969). All of the crude oils in this study (in which the volatiles were absent) were degraded by mixed enrichment cultures (at temperatures between 21° and 28°C) within a period of 12 weeks. When 1 gram (approximate) of volatile-free crude oil was added to 100 ml of aerated seawater (enriched with potassium phosphate and ammonium nitrate), it was observed that between 26 and 98% of the oil was degraded by mixed cultures (at 25°C) within a period of 30 days. In this work, theoretical BOD (Biochemical Oxygen Demand) values for several crude oils and pure hydrocarbons were determined. It was estimated that the complete oxidation of 1 mg of hydrocarbon to CO_2 and H_2O would require 3 to 4 mg of oxygen.

In experiments carried out at Chesapeake Bay, marine sediment microorganisms cultured in natural seawater and salt solutions (supplemented with nitrate and phosphate) were assessed for their ability to degrade a variety of petroleum hydrocarbons (Walker et al., 1976). In this work, it was observed that microorganisms cultured in Chesapeake Bay water were capable of degrading between 5 and 80 percent of a total mixture of petroleum hydrocarbons. The significant factors controlling their performance in this study were:

- incubation temperature
- source of inoculum
- source of the Chesapeake Bay water used
- the type of petroleum hydrocarbon degraded.

1.4 Atmospheric Oxidation

Liquid hydrocarbons in a marine oil spill may be oxidized in the presence of atmospheric oxygen. In the literature, this process has been referred to as chemical oxidation, autooxidation, photochemical oxidation, and hydrocarbon photolysis. Although this process was not monitored during this study, it was expected to occur with the oils to a certain extent. This process involves the initiation of free radical chain reactions (by sunlight or ultraviolet light) to form hydroperoxide intermediates. It has been reported (Pilpel, 1968) that these intermediates can either (a) polymerize into hard, dense substances, or (b) break down to yield alcohols, acids, aldehydes (as well as ketones) and carbon dioxide and water. With reference to path (b), it was reported that this process results primarily in the production of aliphatic and aromatic acids, with the production of alcohols and phenols to a lesser extent (Hansen, 1975 and McAuliffe, 1976). However, it has also been postulated (Feldman, 1973a) that the active intermediates created during such oxidation could be degraded (or utilized for synthesis) by the biota.

Since the oxidation products from path (b) are polar molecules, they would be more water-soluble than the original hydrocarbon components. In the case of a marine oil spill, it is therefore possible for various hydrocarbon components to dissolve in the water layer (or water column) following their oxidation. This is suggested from experimental work performed by Frankenfeld (1973), in which the concentration of oxygenated compounds in the aqueous phase was determined during the weathering of slicks consisting of Lagunillas crude oil and No. 2 fuel oil. After selected weathering periods, it was noted that the concentrations of oxygenates in the aqueous phase were significantly greater than in the case of unweathered oil. Other experimental results with slicks of No. 2 fuel oil (Frankenfeld, 1973a) indicated that the concentration of dissolved organics in the aqueous phase was greater when the oil layer was subjected to radiation from a UV light and a sunlamp.

ZoBell (1963) claims that all constituents of oils are subject to autooxidation, and that emulsions of oil or thin films are more susceptible to this process than large, coherent oil masses. It has been mentioned that this process can be catalysed by light and certain metals, but inhibited by various constituents in the oil, such as phenols, hydroquinones, and sulfur-containing compounds (Horowitz et al., 1969 and Mesrobain/Tobolsky, 1961). Various organic compounds have been identified as "sensitizers", which are capable of accelerating autooxidation. One such agent has been identified as 1-naphthol (Kelin/Pilpel, 1974 and McAuliffe, 1976). In recent publications (Gesser/Turner, 1977 and 1978), a variety of additional sensitizing agents have been noted.

At the present time, it is felt that insufficient experimental work has been carried out in this area for conclusions to be made. The rates and final effects of autooxidation with an arctic marine oil spill have not yet been established.

1.5 Summary

This review of the literature of "weathering" of crude oil spills leads to several conclusions relevant to the present project.

1. On the time scale of the present study, evaporation is the only significant weathering process.
2. The effects of weather, namely wind, sun, and precipitation during the test must be taken into account in interpreting the results.
3. The effects of weather on the properties of crude oil as observed in this study can be expected to be qualitatively similar to the effects of weathering of real spills in the Arctic. However, the time in which a particular change in properties might emerge will depend on the actual conditions experienced by the sample and by the spill. For example, oil in a melt pool should behave fairly similarly to test samples if it is exposed to similar weather conditions. On the other hand, a slick floating on a calm sea might age more quickly because it has a higher surface area per unit volume in contact with the air above and the water below. Finally, a slick on a choppy or rough sea might break up by mechanical processes and disappear before the weathering process by evaporation has been completed.

2 EXPERIMENTAL APPROACH

The following oils were studied in this project:

- (a) Norman Wells Crude
- (b) Lloydminster Blended Crude
- (c) Bow River Blended Crude
- (d) Sweet Blended Crude
- (e) Sour Blended Crude
- (f) Weyburn-Midale Crude
- (g) Marine Diesel Fuel
- (h) Bunker-C Fuel.

Norman Wells crude was obtained directly from the battery at the Norman Wells field, N.W.T. The rest of the oils were obtained from the Research Department of Imperial Oil Ltd. (Sarnia, Ontario). Each of the above oils were allowed to age under Southwestern Ontario winter conditions (late October to December of 1978) for the following intervals:

- (i) 0 Hours
- (ii) 6 Hours
- (iii) 1 Day (24 Hours)
- (iv) 2 Days
- (v) 1 Week (7 Days)
- (vi) 2 Weeks
- (vii) 4 Weeks.

The temperatures during this period were obtained from the weather office at the Waterloo-Wellington Airport (near Breslau, Ontario). Additional meteorological data (precipitation, hours of sunlight, air temperatures, and wind velocities) were determined at the Elora Gorge Research Station, and supplied by the Department of Land Resource Science at the University of Guelph. The data obtained from both locations were recorded for each day of a given aging interval (Table #1 of Appendix "A"). For each aging interval, the weather parameters were summarized by the methods described in Appendix "A", and presented in Table #2 and Figure #2. For a given aging interval, the oils were not all aged at the same time. This was to allow the oils to be exposed to a variety of weather parameters for each aging interval and to maximize the use of the pans and storage area.

During their aging, the oils were confined to an area of 0.836 m^2 (1 square yard) by means of metal pans. A photograph of the oil aging facility is shown in Figure #1. For the first five aging intervals (excluding the interval of 4 weeks and 2 weeks), the initial oil layers formed were approximately 1 cm in thickness. This thickness was obtained by pouring 10 litres of fresh oil into each pan. For the aging intervals of 2 weeks and 4 weeks, the initial layers of the crude oils, marine diesel fuel and Bunker-C fuel were formed with approximate thicknesses of 1 cm and 2 cms (however, the evaporative losses were determined only from the oil layers having an initial thickness of approximately 1 cm). In the case of Bunker-C fuel, the initial oil layer thickness was approximately 1 cm for the two-week and four-week aging intervals.

Following each aging interval, the oils were recovered from the pans, and stored in containers. The evaporative losses were determined by measuring the remaining oil volumes during the recovery operation, and expressing the lost volume as a function of the original (fresh) oil volume. Oil was later withdrawn from the containers for laboratory tests (described in Sections 2.1 to 2.7), wicking tests (described in Section 2.8) and in situ combustion tests (described in Section 2.9).

2.1 Flash and Fire Point Determinations

The flash and fire points of the oil samples were determined by means of the Cleveland Open Cup Apparatus (ASTM method of test, designation D92-72). The flash point of an oil was defined as the lowest oil temperature at which a small test flame (when swept across the oil layer's surface) was capable of igniting the vapours coming off the oil surface. The fire point of an oil was defined as the lowest temperature at which a small test flame (when swept across the oil layer's surface) was capable of igniting the surface vapours from the oil, and to subsequently result in these vapours burning for a minimum period of 5 seconds. For most of the fresh oil samples, it was necessary to cool the oil to below room temperatures for an accurate determination of their flash and fire points.

Flash and fire points were also determined for various residual oil samples obtained from the in situ combustion tests.

2.2 Procedure for Gas Chromatography Analysis

Samples of the oils (0.2 cm^3 volumes) were analysed by a Chromalytics MP-3 Multipurpose Thermal Analyser, which incorporated a flame ionization detector. A 6-ft. (OU - 3% on Chromosorb W-HP 80/100 mesh, 1/8 inch) column was employed. The chromatogram ranged from C_1 to C_{20} , and the temperature program for each analysis was as follows:

- 2 minutes at 50°C
- increased at a rate of 40°C per minute up to 300°C

- 2 minutes at 300°C.

Helium was employed as the carrier gas (at an approximate flow rate of 30 cm³ per minute). The approximate flow rates of air and hydrogen during the analyses were 110 cm³ per minute and 25 cm³ per minute, respectively. During these analyses, the detector temperature was 340°C, and the temperature at the injection port was 310°C.

2.3 Procedure for Distillation Analysis

Oil distillation analyses were carried out by a method modified from ASTM test methods D86-67 and DZ85-62. For each analysis, an empty distillation flask was weighed, charged with 100 cm³ of the oil, and then reweighed. During the distillation process, heat was applied at a uniform rate, regulated so that the first drop of condensate fell from the condenser (the temperature at which this happened was considered the initial boiling point) within 5 to 10 minutes after the heating was initiated. The heating was then regulated so that oil was distilled at a uniform rate of 5 cm³ per minute. The temperature readings from the distillation thermometer were recorded after each 10 cm³ increment of distilled oil had been collected. The heating was continued until a temperature of 410°C was indicated by the thermometer. The distillation flask was then cooled and reweighed. The residue (by weight) was reported as the weight of the undistilled oil, expressed as a percentage of the weight of the original 100 cm³ sample. The difference between the original oil volume (100 cm³) and the volume of the residue following distillation was expressed as a percentage of the original oil volume, and was reported as the distillation loss.

These analyses were performed by an independent commercial laboratory (Chem. Search Laboratories, Ltd. of Toronto).

2.4 Determination of Specific Gravity Values

Specific gravity values were determined for the samples at room temperature. These values were obtained by weighing a known volume of an oil sample.

2.5 Determination of Interfacial Tension Values and Spreading Coefficients

The tension values at both oil/air and oil/water interfaces (σ_{OA} and σ_{OW} , respectively) were determined for the oil samples. A Fisher Surface Tensiometer (model 21) was used to obtain these values.

Assuming that the interfacial tension between water and air (σ_{WA}) is 72.5 dynes/cm, it was possible to calculate the spreading coefficient (or force) of oil on water. The spreading coefficient of the oil samples was calculated by the following formula (Glasstone, 1958):

$$\text{spreading coefficient (dynes/cm)} = \sigma_{WA} - \sigma_{OA} - \sigma_{OW}.$$

2.6 Determination of Viscosity Values

The viscosity of the oil samples at 0, 10, and 20°C were obtained with a Saybolt viscosimeter. The viscosity readings (in Saybolt Universal seconds) were converted into centipoise units.

2.7 Determination of Pour Point Values

Pour point determinations for the oils were performed by a method modified from ASTM test method D97-66. For each determination, the oil was poured into a test jar (to a height between 2 and 2.25 inches), and the test jar was tightly sealed by a cork. A test thermometer (inserted through the cork) was placed so that its bulb was embedded in the oil. The test jar was placed in a cooling bath. At various intervals, the test jar was removed from the bath, and tilted just enough to ascertain if the oil around the thermometer remains as a liquid, and replaced in the bath (the complete operation of removal and replacement would require no longer than 3 seconds). At a point where the oil around the thermometer showed no movement, the test jar was held in a horizontal position for exactly 5 seconds. During this time span, the lowest reading of the test thermometer at which the oil surrounding the thermometer showed any movement was recorded as the pour point.

These determinations were carried out by an independent commercial laboratory (Chem. Search Laboratories, Ltd. of Toronto).

2.8 Wicking Test Procedure

The wicking tests were performed at room temperature with confined oil slicks having initial thicknesses of 0.5 cm. 3M Brand Oil Sorbent sheets (type 157) were used as the wicking materials. In each test, the wicking materials (cut to an area of approximately 100 cm²) were allowed to float on the oil layer for a period of 15 minutes. After this period, the materials were removed from the oil slicks, and placed over a wire screen for approximately one minute, so that any unabsorbed oil could be allowed to drip away from the material. By means of a wringer roll (and/or manual squeezing), most of the absorbed oil was extracted from the sorbent sheets, and this volume was measured. For some of these tests, the weight of the unrecoverable oil (the oil that could not be extracted from the sorbent) was established by determining the difference in weight between the sorbent sheet when dry and after the oil extraction. As noted in Table #12, the average weight of a dry sorbent sheet (before the wicking test) was approximately 37 grams, and the average weight of unrecoverable oil in the sorbent was approximately 103 grams (which corresponds to an average oil volume between 110 and 120 cm³).

Several of the wicking tests were performed under outdoor conditions, at near-room temperatures. It is felt that the results obtained from these tests are comparable to the results from the tests carried out indoors. Due to the oleophilic nature of 3M Brand Oil Sorbent, it was found that essentially no water was collected by the sorbent sheets during any of the wicking tests.

2.9 Procedure for In Situ Combustion Tests

The combustion tests were performed at the North Campus Research Station (in North Waterloo). Slicks of the oils were burned over a large pool of water, approximately 3 ft. deep. By means of a metal square partially suspended in the water, the slicks were confined to an area of 1 m². The fresh oils were applied as slicks having initial thicknesses of 1 cm (10 litres of oil poured within the pan's area) for the burning tests. The aged oil samples were applied as slicks with initial thicknesses of 0.5 cm (5 litres poured within the pan's area) for these tests. The tests were performed with ambient air temperatures ranging between +10 and -20°C.

The oil slicks were ignited by means of a solid fuel igniter, which had been developed in previous work by this organization (Energetex, 1978). This type of igniter was capable of floating on water indefinitely, and had been proven capable of preheating and igniting oil slicks. This igniter consists of two wooden floats securing a sheet metal enclosure. The solid fuel is secured by wire screen which is in turn secured about 1/2" above the surface by the sheet metal enclosure. Flame propagation protrudes the 2 sides of the igniter by six to ten inches over the surface of the oil. In the case of an ignition failure, up to 1.0 litre of fresh crude were added to assist ignition. For each test run, the following parameters were determined:

- Preheating time
- Ignition time
- Combustion time
- The volume, weight, specific gravity, and thickness of the residue remaining.

The remaining residues were also analysed by means of gas chromatography, in the same manner described in Section 2.2.

3 RESULTS AND DISCUSSION

3.1 Weather Parameters and Evaporative Loss of Hydrocarbons

The aging intervals, weather parameters, and evaporative losses (by volume) for each oil are shown in Table #2. The aging intervals and the weather parameters encountered during each interval are also presented in Figure #2. Graphs of evaporative loss vs. aging interval are presented in Figures #3A and #3B.

For an aging interval in which the oils were not all aged at the same time, it can be seen that various oils were subjected to different weather parameters. The daily wind speeds were the most consistent weather parameters during the aging intervals, with the average daily wind speeds ranging between 10 and 19 km/h, and the maximum daily wind speeds ranging from 18 to 53 km/h. The wind-speed data for November 13 was not considered here, since it was obtained at a different location (the Waterloo-Wellington Airport) to the other wind speed values. Depending upon the oil aging interval concerned, maximum temperatures as high as 19°C and minimum temperatures as low as -10.6°C were attained, and average daily air temperatures during the intervals ranged between -0.3 and 7.7°C. In general, values for total bright sunlight hours and total solar radiation increased in proportion to the length of the aging interval. During some of the aging intervals (especially for those of 1 week, 2 weeks, and 4 weeks), significant volumes of rain and snow fell onto the oil layers, and significant amounts of water became entrained in the oil layers in this manner. Although water (and ice) was separated from the oil layers following periods of heavy precipitation, the real values for oil volumes remaining after intervals greater than one week were established only after the recovered oil had thawed for several days indoors (during which most of the entrained water had separated from the oil). Due to the entrained water in the oil layers, the error encountered in measuring oil volumes aged for two weeks and four weeks was estimated to be within 15% (of the initial oil volume), whereas the error encountered in measuring oil volumes aged for shorter aging intervals was estimated to be within 5% (of the initial oil volume).

The evaporative losses from Bunker-C fuel oil were negligible for aging intervals of up to four weeks. This was as expected, since this fuel contained few volatile components. The evaporative losses from marine diesel fuel were negligible for aging intervals of up to two weeks. After aging intervals of two weeks and four weeks, only small evaporative losses by volume (7 and 8 percent, respectively) were noted for marine diesel fuel. Most of the volatile hydrocarbons in the crude oils had evaporated within the first two days of aging under Southern Ontario winter conditions. The evaporative losses from the medium crude oils (Norman Wells, Sweet Bl., and Sour Bl.) were slightly higher than the evaporative losses from the heavy crude oils (Bow River, Lloydminster, and Weyburn-Midale). As shown by Figure #3A, the evaporative losses from the medium crude oils (Norman Wells, Sweet Bl. and Sour Bl.) were greater than those predicted for light and medium crude oils (for a given aging interval) with the model developed by Mackay and Nadeau. This discrepancy could be attributed to the following factors:

(a) The model (described further in Appendix "B") is based upon average values of ambient temperature (approximated to within the closest 5°C) and wind speed. Short peaks of higher temperatures (greater than the average temperature) were known to have occurred during the aging intervals, resulting in accelerated hydrocarbon evaporation. A wide range of wind speeds were also encountered during a given aging interval (especially for intervals of 1 day or longer), and consequently, an average value of wind speed may not have served as an adequate parameter.

(b) The model does not differentiate between light and medium crude oils. The evaporative losses (encountered in this study) that were compared to the model were from medium crude oils.

3.2 Flash and Fire Point Data

Flash and fire point data are presented in Table #3. Graphs of flash and fire point vs. aging interval for the crude oils and marine diesel fuel are presented in Figures #4A to #4G. For each of the crude oils, graphs of fire point vs. aging interval are presented in Figure #5.

For Bunker-C fuel and marine diesel fuel, the aging interval had little significance on their flash and fire points. This may be expected, since the evaporation of volatile components from these oils was either negligible, or relatively small. For all of the fresh crude oils, the flash points were below 12°C, and fire points were below 22°C. During the first two days of aging, however, the flash and fire points of these oils were significantly increased. As shown by Figure #5, and fire points of crude oils aged for two days ranged between 70 and 113°C. Beyond this aging interval, the flash and fire points of the crude oils increased, but to a relatively smaller degree. Depending upon the crude oil, the fire points ranged between 105 and 159°C after an aging interval of four weeks.

Under these weather conditions, it was noted that the ignitability of the crude oils was significantly reduced after aging intervals of up to two days. However, the data also suggest that slicks of Bunker-C fuel, marine diesel fuel, and each of the six crude oils could be ignored (and burned in situ to some extent) after aging intervals of up to four weeks, provided a sufficiently powerful ignition source was employed.

3.3 Gas Chromatography Data

Gas chromatography analyses for the six crude oils and marine diesel fuel oil are presented in Figures #6-1 to #6-8. Gas chromatography analysis of Bunker-C fuel oil was not possible.

The fresh crude oils contained hydrocarbon components ranging from C_4 to C_{20} . During the first 6 hours of aging, the majority of hydrocarbon components in the C_4 to C_{10} range were lost from the crude oils. This observation agrees closely with the evaporative loss values for C_6 , C_7 and C_9 hydrocarbons from crude oils aged for 3 and 8 hours in previous experimental work (Kinney et al., 1969, discussed in Section 1.1, and shown in

Table #1A). After an aging interval of 2 days, hydrocarbon components up to C_8 had generally vanished from the crude oils, and a significant reduction in the proportion of C_9 to C_{14} hydrocarbons had occurred. After aging for 2 days, continued evaporation resulted only in the slight loss of hydrocarbons in the C_{14} to C_{20} range. In situ combustion of the crude oils left a residue that was composed of hydrocarbons in the C_{15} to C_{20} range.

As shown in Figure 6-4, fresh marine diesel fuel was composed primarily of hydrocarbons in the C_{14} to C_{20} range. Since these hydrocarbons were relatively non-volatile, little evaporative loss occurred from this oil during the aging intervals. As with the crude oils, in situ combustion of marine diesel fuel oil left a residue that consisted of hydrocarbons in the C_{15} to C_{20} range.

3.4 Distillation Data

Distillation data for Bunker-C fuel, marine diesel fuel, and each of the crude oils is presented in Table #4A to #4H. Distillation curves are shown in Figures #7A to #7H.

For each of the crude oils, the rapid loss of volatile hydrocarbons during the first two days of aging may be noted by comparing the initial boiling points of fresh and aged crude oils. Depending upon the crude oil, the initial boiling points ranged between 45 and 75°C for fresh crudes, between 55 and 196°C for crudes aged 2 days, and between 90 and 215°C for crudes aged 4 weeks. As shown in Figures #7A to #7F, the reduction in the concentration of volatile components in the crude oils is generally shown by the shifting of the distillation curves upwards and to the left with increased aging interval.

As shown in Figure #7G and Table #4G, the distillation characteristics for marine diesel fuel oil were not significantly altered by the aging intervals. As noted in Table #4H and Figure #7H, the aging intervals had little effect upon the distillation characteristics of Bunker-C fuel oil.

3.5 Specific Gravity Values

The values of specific gravity (at room temperature) for the crude oils, marine diesel fuel oil, and Bunker-C fuel oil are presented in Table #5. Graphs of specific gravity vs. aging interval are shown in Figures #8A and #8B.

The specific gravity values for fresh samples of the heavy crude oils (Bow River, Lloydminster, and Weyburn-Midale) ranged between 0.89 and 0.9, whereas the specific gravity value for fresh samples of the medium crude oils (Norman Wells, Sweet Bl., and Sour Bl.) was 0.83. From Figures #8A and #8B, it was noted that the specific gravities of all crude oils increased significantly during aging intervals of up to 1 week. After the aging interval of 1 week, the specific gravities of most of the crude oils (except in the case of Bow River and Sour Bl. crudes) continued to increase slightly over intervals of 2 weeks and 4 weeks. The specific gravities of the crude oils aged for 4 weeks ranged between 0.87 and 0.99.

From Figure #8B, a slight increase in the specific gravity of marine diesel fuel oil during aging intervals of up to 2 days (0.83 to 0.85) was noted. No further increase in the specific gravity of this oil was observed with increased aging intervals.

No change was observed in the specific gravity of Bunker-C fuel oil, which remained at 0.99 for aging intervals of up to 4 weeks.

3.6 Interfacial Tension Data and Oil Spreading Coefficients

Oil/air and oil/water interfacial tension values for each oil type are shown in Tables #6 and #7, respectively. Using the procedure described in Section 2.5, oil spreading coefficients (for oil over a water surface in air) were calculated, and are presented in Table #8. This data is applicable for room temperatures only.

For all oil types, little correlation between aging interval and oil/air interfacial tension values was observed. The values ranged between 11.5 and 26 dynes/cm for crude oils, between 6.3 and 22 dynes/cm for marine diesel fuel, and between 27 and 32 dynes/cm for Bunker C fuel.

For each oil type, it was generally noted that oil/water interfacial tension values increased slightly with increased aging intervals. These values ranged between 26.8 and 34.5 dynes/cm for crude oils, between 30.7 and 32.3 dynes/cm for marine diesel fuel oil, and between 39.8 and 43.5 dynes/cm for Bunker-C fuel oil.

Oils having positive oil spreading coefficients will tend to spread on water surfaces, and oils having negative oil spreading coefficients will tend to reach a limiting thickness. Based upon this parameter, it can be noted (from a theoretical point of view) that marine diesel fuel oil and the six crude oils aged for intervals of up to 4 weeks are capable of spreading on a water surface at room temperature. Bunker-C fuel oil (fresh and 1 week aged) shows less tendency to spread on water than do the other oils, and Bunker-C fuel oil aged for 4 weeks does not appear to be capable of spreading on water.

3.7 Oil Viscosity Data

Viscosity values for each oil type at 0, 10, and 20°C are presented in Table #9. Graphs of viscosity (at 0°C) vs. aging interval for marine diesel fuel oil and the crude oils are presented in Figures #9A and #9B. The

viscosity of Bunker-C fuel oil (at 0, 10 and 20°C) is shown in Figure #10.

At 0°C fresh samples of the medium crude oils (Norman Wells, Sweet Bl., and Sour Bl.) had viscosity values between 14.2 and 26.7 centipoise, and fresh samples of the heavy crude oils (Bow River, Lloydminster, and Weyburn-Midale) had viscosity values between 74 and 126 centipoise. For all of the crude oils, a very rapid increase in oil viscosity was observed during aging intervals of up to 2 days. Depending upon the crude oil, viscosities (at 0°C) following a 2-day aging interval ranged between 440 and 38,500 centipoise. In general, significant increases in crude oil viscosities occurred with aging intervals longer than 2 days, but to a lesser extent with Norman Wells, Bow River, Lloydminster, and Weyburn-Midale crude oils.

As shown in Figure #9B, a slight increase in the viscosity of marine diesel fuel oil (at 0°C) was observed with increased aging intervals. The viscosity values ranged between 13.6 centipoise (for fresh fuel oil) and 31 centipoise (for oil aged 4 weeks).

The viscosity of Bunker-C fuel (at 0°C) was relatively unchanged over aging intervals of 2 weeks and 4 weeks. Fresh Bunker-C fuel oil had a viscosity of 2.87×10^7 centipoise, and the same oil aged for 4 weeks had a viscosity of 2.89×10^7 centipoise.

3.8 Pour Point Data

Pour point data for each of the oils are presented in Table #10.

For each of the crude oils, it was noted that the pour point values increased significantly with increased aging intervals. The pour points ranged between -85 and -27°C for fresh crude oils, between -33 and -10°C for crude oils aged 2 days, and between -3 and +12°C for crude oils aged 4 weeks. The data suggests that crude oils aged for intervals as short as 6 hours may attain pour points that could make their handling difficult in Arctic temperatures.

In the case of marine diesel fuel and Bunker C fuel oils it was observed that aging intervals of up to 4 weeks did not significantly increase their pour points. Pour points for marine diesel fuel oil ranged between -15 and -8°C, and those for Bunker-C fuel oil ranged between +6 and +12°C.

3.9 Wicking Test Data

The recoverable oil volumes obtained from the wicking tests are shown in Table #11. Oil sorption capacities for 3M Brand Oil Sorbent are presented (along with the results of an earlier study) in Table #12. It should be noted that the wicking test data was obtained at temperatures close to room temperature.

Although perfect trends were not observed from the results of the wicking tests, it appears that the recoverable crude oil volumes wicked

by the sorbent is greater with fresh crudes, and least in comparison with crudes aged 4 weeks. Weyburn-Midale crude oil was least amenable to the wicking process, due probably to its relatively high viscosity (see Table #9 and Figure #9A). The data in Table #11 and #12 suggests that the sorption capacity for the other five crude oils is inversely dependent upon the length of their aging intervals. The calculated sorption capacities of 3M Brand Oil Sorbent range between 5.3 and 12.4 (the sorbent was capable of absorbing between 5.3 and 12.4 times its weight in oil), and agree with oil sorption capacities reported with this sorbent in earlier work (Robertson et al., 1976).

The recoverable volumes of marine diesel fuel oil wicked up by this sorbent were not altered significantly by increased aging intervals. For 3M Brand Oil Sorbent, the oil sorption capacity was established at an approximate value of 12.6.

3.10 In Situ Combustion Data

Results from the in situ combustion of each oil are presented in Tables #13A to #13H. Combustion data for thin slicks of several oils is presented in Table #14.

With the exception of 1-week aged Lloydminster crude oil, all crude oils aged for intervals of up to 4 weeks were ignitable (by means of a solid fuel igniter) as slicks of 5 mm thickness. Slicks of the fresh crude oils (10 mm thick) burned with negligible preheating times and ignition times, whereas slicks of aged oils (5 mm in thickness) burned with relatively longer preheating and ignition times. For crude oils aged 2 days, the preheating times ranged between 40 sec for Lloydminster and 4 min 55 sec for Sour Bl. Crude and ignition times ranged between 47 sec for Lloydminster and 4 min 35 sec for Sour Bl. Crude. For crude oils aged 4 weeks, the preheating times ranged between 1 min 27 sec for Weyburn-Midale Crude and 4 min 52 sec for Sour Bl. Crude, and ignition times ranged between 1 min 34 sec for Weyburn-Midale Crude and 4 min 51 sec for Sour Bl. Crude. For a given crude oil, a distinct correlation between the aging interval and the residual oil layer thickness was not observed. In general, the residual oil layer thicknesses ranged between 0.32 mm and 0.85 mm following the combustion of the crude oils. For the aged oil, the amount of residue left was less than for fresh oils, but the difference was quite small.

The residual oils remaining had specific gravity values between 0.90 and 0.97 (at room temperatures). For a given crude oil type, no trend between the aging interval and the specific gravity values of the residual oils were noted. The minimum ignitable thickness for layers of crude oil (aged for intervals between 1 day and 4 weeks) was estimated to range between 3 and 4 mm, when solid fuel igniters were employed and up to one litre of fresh crude was added (depending on the age of the crude) to promote slick ignition. It is felt that a thickness within the 3-4 mm range would also be the minimum ignitable thickness of these oils when a solid propellant igniter is employed. Without the assistance of fresh crude oil, the approximate value of minimum ignitable thickness for these oils would be 5 mm when a solid fuel igniter is employed to initiate in situ combustion. During these tests, it was noted that the aged crude oils (most of which contained varying amounts of entrained water) burned with more intense flames than did the fresh crude oils, and that the combustion of the aged crude oils

left behind thinner layers of residual oil than did the combustion of the fresh crude oils. This was explained by the fact that micro-explosions (detected by "popping" sounds) occurred during the combustion of the aged crude oils, which undoubtedly increased the rate of oil atomization and vapourization during the combustion process. Steam released during the micro-explosions would also enhance the combustion process (to a limited extent). It was therefore assumed that the micro-explosions generated far more intense flames during combustion (which led to increased thermal radiation from the flame to the oil layer) and resulted in a slight increase in the volumes of oil that could be effectively burned away by in situ combustion.

For a fresh slick of 10 mm thickness, marine diesel fuel burned with a negligible preheating time. In general, slicks of aged marine diesel fuel oil (5 mm thick) burned with longer ignition and preheating times than did slicks of aged crude oils. The residual oil layers following the combustion of marine diesel fuel oil ranged between 0.52 mm and 0.75 mm.

Bunker-C fuel oil was successfully burned in situ, but was more difficult to ignite than marine diesel fuel and the crude oils. Preheating times for 10 mm thick layers of Bunker-C fuel oil ranged between 4 and 22 minutes. The residual oil layer thickness following the combustion of Bunker-C fuel ranged between 1.63 and 2.63 mm. The specific gravity value of the residual oil was 0.99 (at room temperature). When a solid fuel igniter was employed (and when fresh crude oil was added to promote slick ignition), the minimum ignitable thickness for a layer of Bunker-C fuel oil appeared to range between 4 and 5.5 mm. If a more powerful igniter (i.e., a solid propellant igniter) was employed, the minimum ignitable thickness for this type of oil would also range between these two values but with a shorter preheating time. Without assistance provided by the addition of fresh crude oil, it is felt that the minimum ignitable thickness for Bunker-C fuel oil would be approximately 10 mm when a solid fuel igniter is employed to initiate in situ combustion.

FIGURE #2 (A)

AGING INTERVALS AND WEATHER PARAMETERS FOR NORMAN WELLS, SWEET BL., SOUR BL., AND BOW RIVER CRUDE OILS

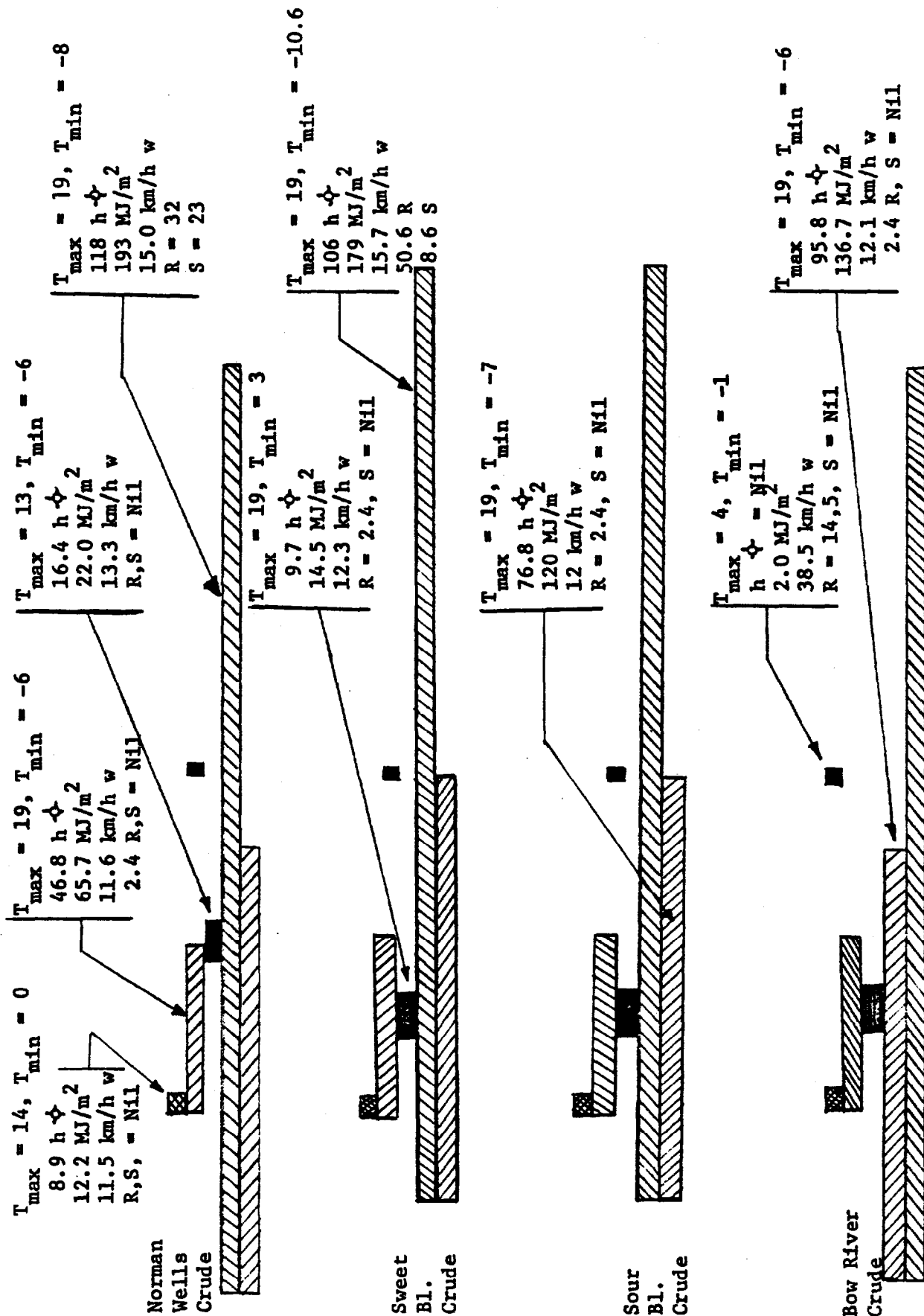


FIGURE #2 (B)

AGING INTERVALS AND WEATHER PARAMETERS FOR WEYBURN-MIDALE/LLOYDMINSTER CRUDE OILS
AND MARINE DIESEL/BUNKER-C FUEL OILS

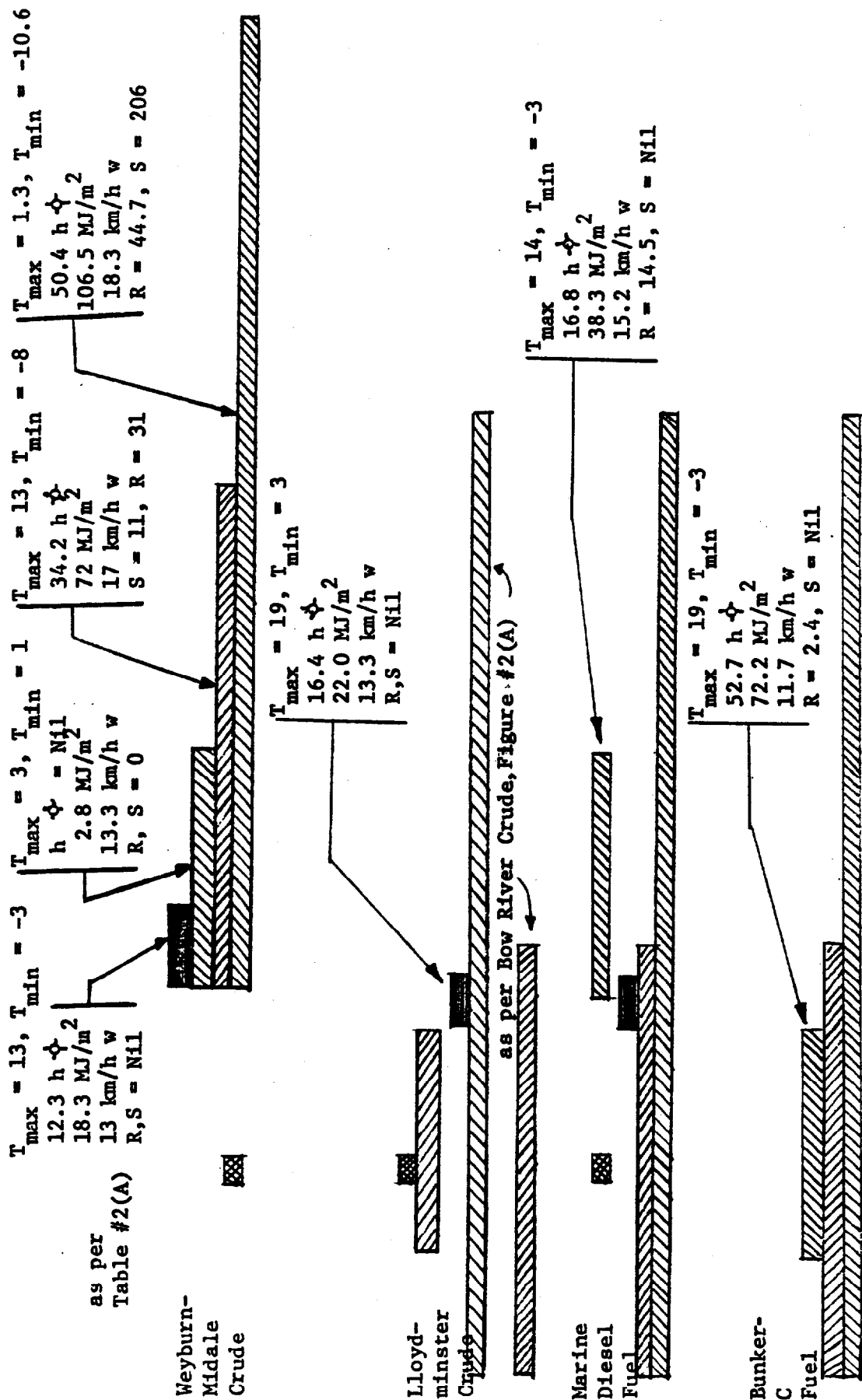


TABLE #2

VOLUMETRIC EVAPORATIVE LOSSES AND CUMULATIVE WEATHER DATA FOR OIL AGING INTERVALS

Aging Period and Time Interval	Oil Type	Volumetric Loss Due to Evaporation (% of original volume)	Daily Air Temperatures (°C)		Total Number of Bright Sunlight Hours (approx.)	Approx. Total of Solar Radiation (MJ/m ²)	Daily Wind Speed (km/h)		Total Precipitation (mm)
			Max.	Min.	Ave.		Ave.	Max.	Rain Snow
<u>6 Hours</u>									
Nov. 13	Norman W.	27.2							
	Swt. Bl.	16.0							
	Sour Bl.	16.2	4	-1	1.5	2.0	35.8*	36.3*	14.5 Nil
	Bow Riv.	11.3							
Nov. 15	Wey.-Mid.	16.0							
	Lloyd.M.	14.5							
	Marine D.	Nil	3	1	2	2.8	10	18	Nil Nil
	Bunker-C	N.T.							
<u>1 Day</u>									
Nov. 1-2	Norman W.	33.0							
	Swt. Bl.	25.0							
	Sour Bl.	27.6							
	Bow Riv.	19.5							
	Wey.-Mid.	17.5	14	-1	6.5	12.2	11.5	24	Nil Nil
	Lloyd.M.	16.8							
	Marine D.	Nil							
<u>2 Days</u>									
Nov. 4-6	Swt. Bl.	25.0							
	Sour Bl.	22.5	19	-2	8.8	14.5	12.3	31	0.2 Nil
	Bow Riv.	19.0							

TABLE #2 (Cont'd)

Aging Period and Time Interval	Oil Type	Volumetric Loss Due to Evaporation (% of original volume)	Daily Air Temperatures (°C)		Total Number of Bright Sunlight Hours (approx.)	Approx. Total of Solar Radiation (MJ/m ²)	Daily Wind Speed (km/h)		Total Precipitation (mm)
			Max.	Min.	Ave.		Ave.	Max.	Rain Snow
<u>2 Days (Cont'd)</u>									
Nov. 7-9	Norman W. Lloyd.M. Marine D.	36.0 20.0 Nil	13	-7	3.8	16.4	22.0	13.3	29 Nil Nil
Nov. 8-10	Wey.-Mid.	22.5	13	-7	4.8	12.3	18.3	13.0	29 Nil Nil
<u>1 Week</u>									
Oct. 30-Nov. 6	Lloyd.M. Bunker-C	23.5 Nil	19	-3	7.7	52.7	72.2	11.7	31 2.4 Nil
Nov. 1-8	Norman W. Swt. Bl. Sour Bl. Bow Riv.	29.0 21.0 27.0 10.0	19	-7	6.4	46.8	65.7	11.6	31 2.4 Nil
Nov. 8-15	Wey.-Mid. Marine D.	22.0 Nil	14	-7	4.2	16.8	38.3	15.2	35 Nil 14.5
<u>2 Weeks</u>									
Oct. 27-Nov. 10	Norman W. Bow Riv. Lloyd.M. Marine D. Bunker-C	54.0 34.0 45.0 7.0 N.T.	19	-7	6.2	95.8	136.7	12.1	31 2.4 Nil 30

(Cont'd)

TABLE #2 (Cont'd)

Aging Period and Time Interval	Oil Type	Volumetric Loss Due to Evaporation (% of original volume)	Daily Air Temperatures (°C)		Total Number of Bright Sunlight Hours (approx.)	Approx. Total of Solar Radiation (MJ/m ²)	Daily Wind Speed (km/h)		Total Precipitation (mm)	
			Max.	Min.			Ave.	Max.	Rain	Snow
2 Weeks										
Oct. 30-Nov. 13	Swt. Bl. Sour Bl.	47.5 46.0	19	-7	5.2	78.6	120.2	12.0	31	2.4 Nil
Nov. 8-22	Wey.-Mid.	38.0	13	-8	4.7	34.2	72.0	17.0	53	31 11
4 Weeks**										
Oct. 27-Nov. 24	Norman W. Bow Riv. Lloyd.M. Marine D. Bunker-C	58.8 44.0 44.0 8.0 N.T.	19	-8	4.1	118.1	193.0	15.0	53	48.5 2.3
Oct. 30-Nov. 27	Swt. Bl. Sour Bl.	43.3 48.9	19	-10.6	3.0	205.8	278.9	15.7	53	50.6 41
Nov. 8-Dec. 6	Wey.-Mid.	49.2	7	-9	-0.3	50.45	126.4	19.3	53	206 44.7

Notes:

N.T. - Value was not successfully established.

*Wind speed values obtained from weather data taken at the Waterloo-Wellington Airport, near Waterloo, Ont.

**Due to precipitation, water-in-oil emulsions had formed in the oil layers, thereby increasing the actual oil volume. The evaporative losses in this case were based upon the oil volume remaining after water and ice had been extracted from the collected oil.

TABLE #3

FLASH AND FIRE POINTS AS A FUNCTION OF WEATHERING PERIOD

		Norman Wells	Sweet Mixed	Sour Mixed	Bow River	Weyburn- Midale	Lloyd- minster	Marine Diesel	Bunker- C
0 Hours (fresh)	Flash Pt.	-	9 or less	-	12 or less	-	11	105	174
	Fire Pt.	13.5 or less	10	10.5 or less	22	14 or less	17	123	greater than 257
6 Hours	Flash Pt.	47	22 or less	16 or less	60	55	51	119	N.T.
	Fire Pt.	51	26	18	63	57	62	126	N.T.
1 Day	Flash Pt.	69	51	68	78	57	70	116	N.T.
	Fire Pt.	74	64	72	93	67.5	84	133	N.T.
2 Days	Flash Pt.	101	95	95	107	60	75	125	N.T.
	Fire Pt.	105	96.5	100	113	71	90	131	N.T.
1 Week	Flash Pt.	110	-	105	126	85	136	131	163
	Fire Pt.	112	124	110	151	106	150	150	greater than 213
2 Weeks	Flash Pt.	109	-	105.5	119	92	126	135	149
	Fire Pt.	124	120	109	134	95	142	136	203
1 Month	Flash Pt.	111	-	-	137	-	148	135	174
	Fire Pt.	125	131	135	151	105	159	138	212

N.T. - Value not taken, since the oil was not aged for such an interval.

TABLE #4A

VOLUMETRIC DISTILLATION DATA FOR NORMAN WELLS CRUDE OIL

Distillation Parameters	Aging Intervals				
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week
Initial Boiling Point (°C)	48	125	160	175	180
10% Distillation Range (°C)	85	150	189	208	240
20% "	120	185	224	239	265
30% "	165	220	260	270	300
40% "	215	270	288	302	335
50% "	270	305	338	337	398
60% "	330	350	340	340	360
70% "	360	375	340	356	370
80% "	370 (85%)	--	340	369	385
90% "	375	--	344	--	--
100% "	--	--	--	--	--
Loss (%)	19	29	61	30	18.2
Residue (% by weight)	16.8	30.5	60.2	28.5	38.6

TABLE #4B

VOLUMETRIC DISTILLATION DATA FOR SWEET BL. CRUDE OIL

Distillation Parameters	Aging Intervals						
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week	2 Weeks	4 Weeks
Initial Boiling Point (°C)	50	85	145	186	218	220	230
10% Distillation Range (°C)	95	135	175	225	252	254	255
20% "	130	175	222	256	289	291	285
30% "	185	220	260	290	315	296	320
40% "	230	310	301	325	320	323	345
50% "	280	355	340	356	325	356	370
60% "	335	370	370	378	380	380	385
70% "	370	380	363	385	383	380	385
80% "	380	390	367	386	390	--	403
90% "	385	395	--	--	--	--	--
100% "	--	--	--	--	--	--	--
Loss (%)	29	30	5	58	5	29	8
Residue (% by weight)	31.5	36.7	12.4	57.8	11.8	24	9.7

TABLE #4C

VOLUMETRIC DISTILLATION DATA FOR SOUR BL. CRUDE OIL

Distillation Parameters	Aging Intervals				
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week
Initial Boiling Point (°C)	45	70	153	176	170
10% Distillation Range (°C)	95	120	190	218	230
20% "	130	170	225	255	265
30% "	180	215	275	291	300
40% "	235	270	320	331	335
50% "	300	315	368 (44%)	368	385
60% "	345	345	--	375	393
70% "	380	375	--	380	410
80% "	385	--	--	--	--
90% "	(85%) 390	--	--	--	--
100% "	--	--	--	--	--
Loss (%)	30	29	56	39	28.3
Residue (% by weight)	32	35.3	23.7	9.7	25.5

TABLE #4D

VOLUMETRIC DISTILLATION DATA FOR BOW RIVER CRUDE OIL

Distillation Parameters	Aging Intervals						
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week	2 Weeks	4 Weeks
Initial Boiling Point (°C)	45.95	130	160	186	195	225	230
10% Distillation Range (°C)	115	220	223	231	257	270	280
20% "	185	280	285	284	300	315	325
30% "	265	320	330	325	325	335	335
40% "	310	330	335	336	355	345	336
50% "	350	350	355	340	360	360	360
60% "	370	355	360	345	365	375	380
70% "	385	360	386	345	370	--	--
80% "	390	--	--	345	381	--	--
90% "	--	--	--	--	--	--	--
100% "	--	--	--	--	--	--	--
Loss (%)	48	40	19	19	15	30	19
Residue (% by weight)	47.2	40.3	22.8	16.4	20	29.5	19.1

TABLE #4E

VOLUMETRIC DISTILLATION DATA FOR WEYBURN-MIDALE CRUDE OIL

Distillation Parameters	Aging Intervals						
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week	2 Weeks	4 Weeks
Initial Boiling Point (°C)	45	100	120	125	122	130	140
10% Distillation Range (°C)	90	180	175	185	225	230	235
20% "	130	225	230	240	265	278	285
30% "	190	272	275	280	312	320	325
40% "	230	326	305	310	330	340	365
50% "	265	330	330	340	335	340	380
60% "	275	335	335	365	350	345	385
70% "	335	340	335	385	--	--	390
80% "	385	--	385	385	--	--	390
90% "	--	--	--	--	--	--	--
100% "	--	--	--	--	--	--	--
Loss (%)	39	28	58	60	29	38.8	17
Residue (% by weight)	37	24.4	45.9	58	22.3	34.6	16.4

TABLE #4F

VOLUMETRIC DISTILLATION DATA FOR LLOYDMINSTER CRUDE OIL

Distillation Parameters	Aging Intervals						
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week	2 Weeks	4 Weeks
Initial Boiling Point (°C)	40	125	160	168	203	200	200
10% Distillation Range (°C)	110	200	210	203	269	280	270
20% "	190	260	272	267	295	320	299
30% "	260	288	285	317	334	345	350
40% "	290	295	310	357	345	360	365
50% "	335	350	330	376	352	375	370
60% "	345	360	380	379	360	390	395
70% "	356	--	400	380	362	405	400
80% "	371	--	--	381	363	--	--
90% "	380	--	--	--	--	--	--
100% "	--	--	--	--	--	--	--
Loss (%)	29	38	30	9	20	28	30
Residue (% by weight)	26.1	33.5	26.9	6.3	22.3	14.2	28.1

TABLE #4G

VOLUMETRIC DISTILLATION DATA FOR MARINE DIESEL FUEL OIL

Distillation Parameters	Aging Intervals					
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week	4 Weeks
Initial Boiling Point (°C)	100	219	210	200	210	220
10% Distillation Range (°C)	180	250	250	265	275	270
20% "	225	280	275	280	290	290
30% "	245	295	294	295	298	302
40% "	267	304	305	305	315	320
50% "	277	315	314	315	320	328
60% "	315	325	322	320	330	338
70% "	330	335	336	330	338	336
80% "	350	360	355 (76%)	342	348	354
90% "	355	380	--	--	357	360
100% "	--	--	--	--	--	--
Loss (%)	17	6	24	18	10	8
Residue (% by weight)	16.3	5.3	9.7	13.15	8.65	8.1

TABLE #4H

VOLUMETRIC DISTILLATION DATA FOR BUNKER-C FUEL OIL

Distillation Parameters	Aging Intervals					
	0 Hours (fresh)	6 Hours	1 Day	2 Days	1 Week	2 Weeks
Initial Boiling Point (°C)	115				300	325
10% Distillation Range (°C)	310	N.T.	N.T.	N.T.	314	350
20% "	335				330	356
30% "	345				350	360
40% "	350				358	368
50% "	355				358	374
60% "	367				365	375
70% "	370				--	376
80% "	(75%) 375				--	--
90% "	--				--	--
100% "	--				--	--
Loss (%)	49				40	30
Residue (% by weight)	42.7				35.5	27.6

N.T. - Oil samples not taken after such an aging interval.

TABLE #5

SPECIFIC GRAVITY VALUES

Aging Interval	Specific Gravity of Oil at Room Temperature							
	Oil Type							
	Norman Wells Crude	Sweet Bl. Crude	Sour Bl. Crude	Bow River Crude	Weyburn- Midale Crude	Lloyd- minster Crude	Marine Diesel Fuel	Bunker- C Fuel
0 Hours (fresh)	0.83	0.83	0.83	0.90	0.89	0.90	0.83	0.99
6 Hours	0.83	0.84	0.85	0.93	0.92	0.91	0.84	N.T.
1 Day	0.87	0.87	0.87	0.93	0.93	0.91	0.85	N.T.
2 Days	0.89	0.90	0.90	0.95	0.95	0.93	0.85	N.T.
1 Week	0.89	0.92	0.94	0.95	0.96	0.94	0.86	0.99
2 Weeks	0.90	0.93	0.94	0.95	0.99	0.95	0.85	N.E.
4 Weeks	0.93	0.94	0.94	0.99	0.99	0.98	0.87	0.99

N.T. - Value not taken, since the oil was not aged for such an interval.

N.E. - Value not established.

TABLE #6

OIL/AIR INTERFACIAL TENSION VALUES

Aging Interval	Surface Tension (Dynes/cm) at Room Temperature							
	Oil Type							
	Norman Wells Crude	Sweet Bl. Crude	Sour Bl. Crude	Bow River Crude	Weyburn-Midale Crude	Lloyd-minster Crude	Marine Diesel Fuel	Bunker. C Fuel
0 Hours (fresh)	22.7	24	24.1	15	24.1	25	22	27
6 Hours	16	26	23	13	20	23	16	N.T.
1 Day	20	18.5	22.2	25	23.2	24	15.5	N.T.
2 Days	18	18	21	23	23.5	19	15.9	N.T.
1 Week	14.8	17.6	21	20.3	23	19.6	7.1	28
2 Weeks	14.4	12.9	13.1	13	11.5	18	6.3	N.E.
4 Weeks	13.1	18.7	24	22.6	17	21.6	16.2	32

N.T. - Value not taken, since the oil was not aged for such an interval.

N.E. - Value not established.

TABLE #7OIL/WATER INTERFACIAL TENSION VALUES

Aging Interval	Oil/Water Interfacial Tension (Dynes/cm) at Room Temperature							
	Oil Type							
	Norman Wells Crude	Sweet Bl. Crude	Sour Bl. Crude	Bow River Crude	Weyburn-Midale Crude	Lloyd-minster Crude	Marine Diesel Fuel	Bunker-C Fuel
0 Hours (fresh)	26.8	27.3	27.5	28.95	29.7	31.2	36.4	39.82
6 Hours	28.3	28.3	28.9	30.4	30.5	31.5	30.7	N.T.
1 Day	29.6	30.6	32.0	31.3	32.0	33.1	31.65	N.T.
2 Days	30.6	31.2	32.1	33.3	32.15	33.4	32.1	N.T.
1 Week	31.8	31.7	32.25	33.5	32.25	33.7	31.2	41.7
2 Weeks	31.9	31.65	32.2	33.6	30.8	33.9	32.3	N.E.
4 Weeks	31.0	34	34.1	34.5	33	34.1	32.0	43.5

N.T. - Value not taken, since the oil was not aged for such an interval.

N.E. - Value not established.

TABLE #8
CALCULATED OIL SPREADING COEFFICIENTS

Aging Interval	Calculated Oil Spreading Coefficient at Room Temperature (Dynes/cm)							
	Oil Type							
	Norman Wells Crude	Sweet Bl. Crude	Sour Bl. Crude	Bow River Crude	Weyburn-Midale Crude	Lloyd-minster Crude	Marine Diesel Fuel	Bunker-C Fuel
0 Hours (fresh)	23.0	21.2	20.9	28.5	18.7	16.3	20.1	5.7
6 Hours	28.2	18.2	20.6	29.1	22.0	18.0	25.8	N.D.
1 Day	22.9	23.4	18.3	16.2	17.3	15.4	25.4	N.D.
2 Days	23.9	23.3	19.4	16.2	16.9	20.1	24.5	N.D.
1 Week	25.9	23.2	19.25	18.7	17.3	19.2	34.2	2.8
2 Weeks	26.2	28.0	27.2	25.9	30.2	20.6	33.9	N.E.
4 Weeks	28.4	19.4	14.4	15.4	22.5	16.8	24.3	-3.0

Values for oil spreading coefficients were determined by the following formula:

$$\text{Spreading coefficient} = \sigma_{WA} - \sigma_{OA} - \sigma_{OW}$$

(72.5
Dynes/
cm) (Table #5) (Table #6)

N.D. - Oil spreading coefficient values not determined, since the oil was not aged for such an interval.

N.E. - Value not established.

TABLE #9
OIL VISCOSITY VALUES

Oil Type	Aging Interval	Oil Viscosity (centipoise)		
		@ 0°C	@ 10°C	@ 20°C
Norman Wells Crude	0 Hours (fresh)	14.2	8.68	5.9
	6 Hours	39.4	16	11.3
	1 Day	164	65.6	21.4
	2 Days	440	90.6	29
	1 Week	560	121	46.1
	2 Weeks	680	125	42.3
	4 Weeks	862.5	240	89
Sweet Bl. Crude	0 Hours (fresh)	20.1	14.2	8.1
	6 Hours	42	24	10.7
	1 Day	145.1	50.8	23.5
	2 Days	520	142	60
	1 Week	3080	356	88
	2 Weeks	6200	420	108.4
	4 Weeks	22800	520	115
Sour Bl. Crude	0 Hours (fresh)	26.7	19.4	9.5
	6 Hours	123	30	12.1
	1 Day	461.5	150	51.6
	2 Days	8800	1380	80
	1 Week	27700	3400	87.6
	2 Weeks	35200	7400	91.6
	4 Weeks	36200	3000	75

(Cont'd)

TABLE #9 (Cont'd)

Oil Type	Aging Interval	Oil Viscosity (centipoise)		
		@ 0°C	@ 10°C	@ 20°C
Bow River Crude	0 Hours (fresh)	74	67	42.5
	6 Hours	400	130	80
	1 Day	760	440	202
	2 Days	1500	600	300
	1 Week	3700	760	430
	2 Weeks	8600	1090	480
	4 Weeks	21100	2150	665
Weyburn- Midale Crude	0 Hours (fresh)	88	29	18
	6 Hours	1300	123	40
	1 Day	5300	260	100
	2 Days	38500	560	140
	1 Week	77500	1260	205
	2 Weeks	18400	1430	180
	4 Weeks	35200	1250	97.5
Lloyd- minster Crude	0 Hours (fresh)	126	86.8	52.3
	6 Hours	440	156	93.4
	1 Day	773	454.3	205.7
	2 Days	2720	680	190
	1 Week	5840	1260	425
	2 Weeks	8400	1400	543
	4 Weeks	29000	2675	1425

(Cont'd)

TABLE #9 (Cont'd)

Oil Type	Aging Interval	Oil Viscosity (centipoise)		
		@ 0°C	@ 10°C	@ 20°C
Marine Diesel Fuel	0 Hours (fresh)	13.6	10.1	9.1
	6 Hours	14	11	9.6
	1 Day	15	11.2	10
	2 Days	15.7	11.2	10
	1 Week	32	12	9.5
	2 Weeks	20.4	11.7	10
	4 Weeks	31	17	12
Bunker- C Fuel	0 Hours (fresh)	7.35×10^7	2.87×10^7	5.98×10^6
	6 Hours	N.T.	N.T.	N.T.
	1 Day	N.T.	N.T.	N.T.
	2 Days	N.T.	N.T.	N.T.
	1 Week	7.44×10^7	2.96×10^7	6.6×10^6
	2 Weeks	N.E.	N.E.	N.E.
	4 Weeks	7.56×10^7	2.89×10^7	6.8×10^6

N.T. - Value not taken, since the oil was not aged for such an interval.

N.E. - Value not established.

TABLE #10

POUR POINT DATA (°C)

Oil Type	Aging Interval						
	Fresh	6 Hr	1 Day	2 Days	1 Week	2 Weeks	4 Weeks
Marine Diesel Fuel	-15	-14	-12.5	-9	-10	-11	-8
Norman Wells Crude	-85	-35	-36	-33	-9	-16	-8
Bunker-C Fuel	+7	N.T.	N.T.	N.T.	+8	+6	+12
Lloydminster Crude	-52	-36	-22	-11	-8	-16	-9
Sour Bl. Crude	-50	-30	N.T.	-15	-13	+2	+8
Sweet Bl. Crude	-35	-32	-27	-18	-5	-16	-12
Weyburn-Midale Crude	-28	-14	-10	-11	+3	+1	-3
Bow River Crude	-27	-20	-20	-10	-7	-7	0

N.T. - Value not taken, since the oil was not aged for such an interval.

TABLE #11WICKING TEST DATA

Aging Interval	Recoverable Oil Volume Absorbed by Sorbent Sheet (cm ³) at Room Temperature							
	Oil Type							
	Norman Wells Crude	Sweet Bl. Crude	Sour Bl. Crude	Bow River Crude	Weyburn- Midale Crude	Lloyd- minster Crude	Marine Diesel Fuel	Bunker- C Fuel
0 Hours (fresh)	440	460	440	430	N.T.	430	560	N.E.
6 Hours	450	450	415	375	140	250	500	N.T.
1 Day	365	450	470	370	205	390	435	N.T.
2 Days	490	425	85	385	150	265	500	N.T.
1 Week	250	145	120	250	100	120	465	N.T.
2 Weeks	400	100	120	300	140	160	470	N.E.
4 Weeks	230	90	130	90	190	90	480	N.T.

N.T. - Value not taken, since the oil was not aged for such an interval.

N.E. - Values not established.

TABLE #12

OIL SORPTION CAPACITIES FOR 3M BRAND OIL SORBENT

Oil Type	Aging Interval	Recovered Oil Weight from Sorbent (g)	Ave. Non-Recoverable Oil Weight in Sorbent (g)	Total Oil Weight in Sorbent (g)	Ave. Dry Sorbent Weight (g)	Ratio of Oil Absorbed to Sorbent Weight (g of Oil/g of Sorbent)	Reported in this Study	Reported by Robertson et al.
Bow River Crude	6 Hours	347.2	103.5	450.7	37.4	12.1	9, 10	
Sour Bl. Crude	6 Hours	361.9	103.5	465.4	37.4	12.4	9, 10	
Weyburn-Midale Crude	1 Day	191.3	103.5	294.8	37.4	7.9	9, 10	
Marine Diesel Fuel	1 Day	367.6	103.5	471.1	37.4	12.6	9, 10	
Lloydminster Crude	2 Days	246.4	103.5	349.9	37.4	9.4	9, 10	
Weyburn-Midale Crude	1 Week	93.8	103.5	197.3	37.4	5.3	9, 10	
Sweet Bl. Crude	1 Week	133.5	103.5	237.0	37.4	6.3	9, 10	
Norman Wells Crude	4 Weeks	204.7	103.5	308.2	37.4	8.2	9, 10	

TABLE #13A

IN SITU COMBUSTION DATA FOR NORMAN WELLS CRUDE OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Air Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)	10	10-12	--	0:22	1:58	0.68	-ignited by a match
6 Hours	5	-15 to -17	0:26	0:28	1:52	0.39	-intense flame with dense, black smoke
1 Day	5	10-12	0:45	0:40	1:50	0.85	-medium density, black smoke
2 Days	5		0:51	1:20	1:49	0.38	-intense flame with medium density, gray smoke
1 Week	5	2 to -2	0:55	1:50	1:51	0.65	
2 Weeks	5		0:55	1:55	1:41	0.85	-medium density smoke
4 Weeks	5		3:03	3:57	1:29	0.73	-weak, slow spreading flame -low density smoke

TABLE #13B

IN SITU COMBUSTION DATA FOR SWEET BL. CRUDE OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Air Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)	10	15	Nil	Nil	4:40	0.61	-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
6 Hours	5		0:09	0:33	2:32	0.4	-medium density, black smoke
1 Day	5	-15 to -17	0:50	1:05	1:55	0.5	-medium to low density, black smoke
		15	Nil	1:35	1:45	0.48	
2 Days	5	-15 to -17	2:05	1:20	1:30	0.53	-medium density, black smoke
1 Week	5	0 to -3	1:50	2:55	1:42	0.55	-medium to low density, gray smoke
2 Weeks	5	0 to -3	4:45	2:56	1:36	0.4	-low density, black smoke
4 Weeks	5		6:59	7:08	2:27	0.4	-intense flame, gray smoke

TABLE #13C

IN SITU COMBUSTION DATA FOR SOUR BL. CRUDE OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Air Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)	10	15	Nil	Nil	5:00	0.5	-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
6 Hours	5		0:12	0:29	2:03	0.55	-medium density, black smoke
1 Day	5		Nil	1:05	1:47	0.31	-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
2 Days	5		4:55	4:35	7:25	0.5	-very dense, black smoke
1 Week	5	-4 to -12	4:17	2:50		Not determined	-intense flame -black smoke
2 Weeks	5	0 to -3	4:38	4:05	1:43	Not determined	-intense flame -very dense, black smoke
4 Weeks	5	2 to -2	4:52	4:51	1:54	0.625	-intense flame -very dense, black smoke

TABLE #13D

IN SITU COMBUSTION DATA FOR BOW RIVER CRUDE OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Air Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)	10	15	Nil	Nil	4:50	0.61	-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
6 Hours	5	-15 to -17	0:26	0:35	1:44	0.5	-medium density, black smoke
1 Day	5		Nil	2:20	1:20	0.31	-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
2 Days	5		Not determined	1:15	1:45	0.45	-very dense, black smoke
1 Week	5	2 to -2	1:31	6:51	--	--	-flames did not cover entire surface
2 Weeks	5		1:20	8:50	1:34	0.66	-medium to high density, black smoke
4 Weeks	5		3:13	2:03	3:35	0.6	-very dense gray black smoke

TABLE #13E

IN SITU COMBUSTION DATA FOR LLOYDMINSTER CRUDE OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Air Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)	10	15	Nil	Nil	5:37	0.61	-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
6 Hours	5	-4 to -12	1:04	1:02	2:08	0.45	-intense flame -very dense, black smoke
1 Day	5		Nil	2:00	1:35	0.37	-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
2 Days	5	-15 to -17	0:40	0:47	1:27	0.63	-dense, black smoke
1 Week	5	-4 to -12	--	--	--	--	-oil layer did not ignite
2 Weeks	5	-4 to -12	2:15	2:30	1:05	0.47	
4 Weeks	5		7:37	6:26	1:37	0.7	-intense flame, dense black smoke

TABLE #13F

IN SITU COMBUSTION DATA FOR WEYBURN-MIDALE CRUDE OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Air Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)		15	Nil	0:58	2:42	0.74	-ignition achieved by piece of oil-soaked paper
6 Hours	5	2 to -2	0:22	0:55	2:30	0.74	-slick broken prior to ignition
1 Day	5	2 to -2	0:27	1:20	2:14	0.68	-intense flame -very dense, black smoke
2 Days	5	0 to -3	0:44	1:21	1:41	0.55	-medium density, black smoke
1 Week	5	0 to -3	1:17	2:11	2:43	0.7	-intense heat, black smoke
2 Weeks	5	-4 to -12	3:15	1:33	3:10	0.5	-very dense, black smoke
4 Weeks	5	2 to -2	1:25	1:34	1:50	0.3	-intense flame -grayish-black smoke

TABLE #13G

IN SITU COMBUSTION DATA FOR MARINE DIESEL FUEL OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Air Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)	10	15	Nil	2:30	4:40		-ignition achieved by pieces of oil-soaked paper and sorbent, which were lit and placed on the oil surface
6 Hours	5	-15 to -17	2:33	1:57	1:48	0.75	-low to medium density, black smoke
1 Day	5	15	2:35	4:10	2:04	Not determined	-low density smoke
2 Days	5		4:42	6:31	2:31	0.7	-intense flame, some water on surface boiled
1 Week	5	2 to -2	2:35	14:00	2:02	0.57	-intense flame -medium density, gray smoke
2 Weeks	5	2 to -2	2:10	7:01	2:22	Not determined	-intense flame -medium density smoke
4 Weeks	5	2 to -2	2:17	14:14	2:03	0.52	-very dense, black smoke

TABLE #13H

IN SITU COMBUSTION DATA FOR BUNKER-C FUEL OIL

Aging Interval	Initial Oil Layer Thickness (mm)	Ambient Temperature Range (°C)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
0 Hours (fresh)	10		4:09	1:53	2:56	2.63	-intense flame -very dense, black smoke
1 Week	10		40:35	1:03	1:34	2.25	-weak preignition flames -very dense, black smoke
2 Weeks	10		21:35	1:10	2:16	1.63	-very dense, black smoke
4 Weeks	10		4:21	2:46	2:06	1.92	-intense flame -very dense, black smoke

TABLE #14

COMBUSTION DATA CONCERNING THE MINIMUM IGNITABLE THICKNESS OF OIL LAYERS WITH SOLID FUEL IGNITERS

Oil Type	Aging Interval	Initial Oil Layer Thickness (mm)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
Norman Wells Crude	4 weeks	2	--	--	--	--	Ignition was unsuccessful
		3	N.D.	N.D.	1:47	0.575	Ignition was assisted by adding fresh crude
Sweet Bl. Crude	4 weeks	3	--	--	--	--	Ignition was unsuccessful
		4	N.D.	N.D.	1:46	0.585	Ignition assisted by adding fresh crude
Sour Bl. Crude	4 weeks	3	0:31	N.D.	3:05	N.D.	Entire slick surface was not ignited
Lloydminster Crude	1 day	3	--	--	--	--	Ignition was unsuccessful
		4	10:35	3:05	2:00	0.485	
	4 weeks	2	--	--	--	--	"
		3	N.D.	N.D.	1:46	0.64	Ignition was assisted by adding fresh crude
Weyburn-Midale Crude	4 weeks	2	--	--	--	--	Ignition was unsuccessful
		3	N.D.	N.D.	1:26	0.11	Ignition was assisted by adding fresh crude

(Cont'd)

TABLE #14 (Cont'd)

Oil Type	Aging Interval	Initial Oil Layer Thickness (mm)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
Marine Diesel Fuel	4 weeks	3	--	--	--	--	Ignition was unsuccessful
		4	N.D.	N.D.	2.33	0.46	Ignition was assisted by adding Marine diesel fuel
Bunker-C Fuel	4 weeks	4	--	--	--	--	Ignition was unsuccessful
		5.5	N.D.	N.D.	1:47	1.9	Ignition was assisted by adding fresh crude

N.D. - Not Determined.

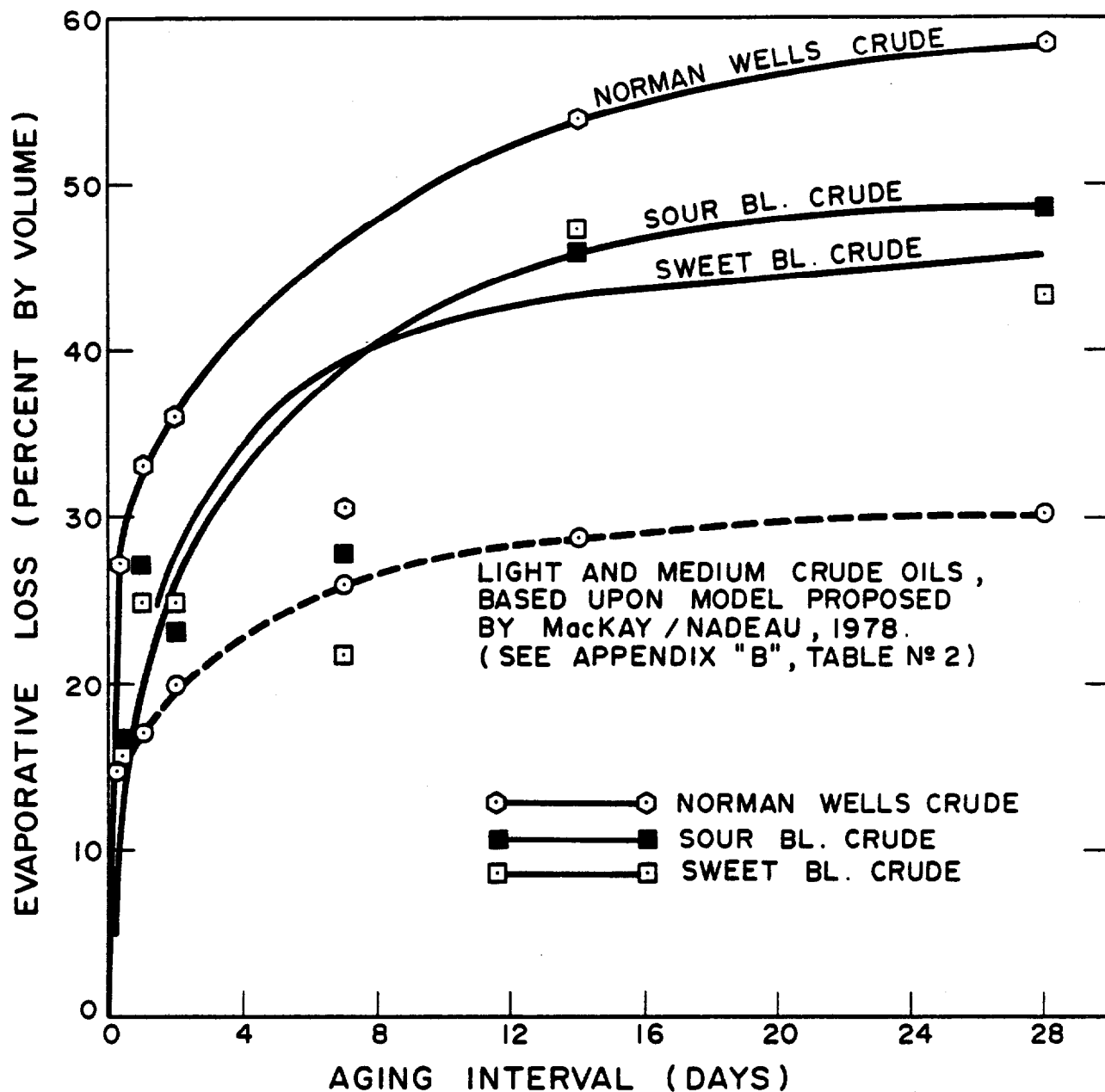


FIGURE 3A - EVAPORATIVE LOSS vs. AGING INTERVAL FOR NORMAN WELLS CRUDE, SWEET BL. CRUDE, AND SOUR BL. CRUDE (PLUS MODEL PREDICTIONS)

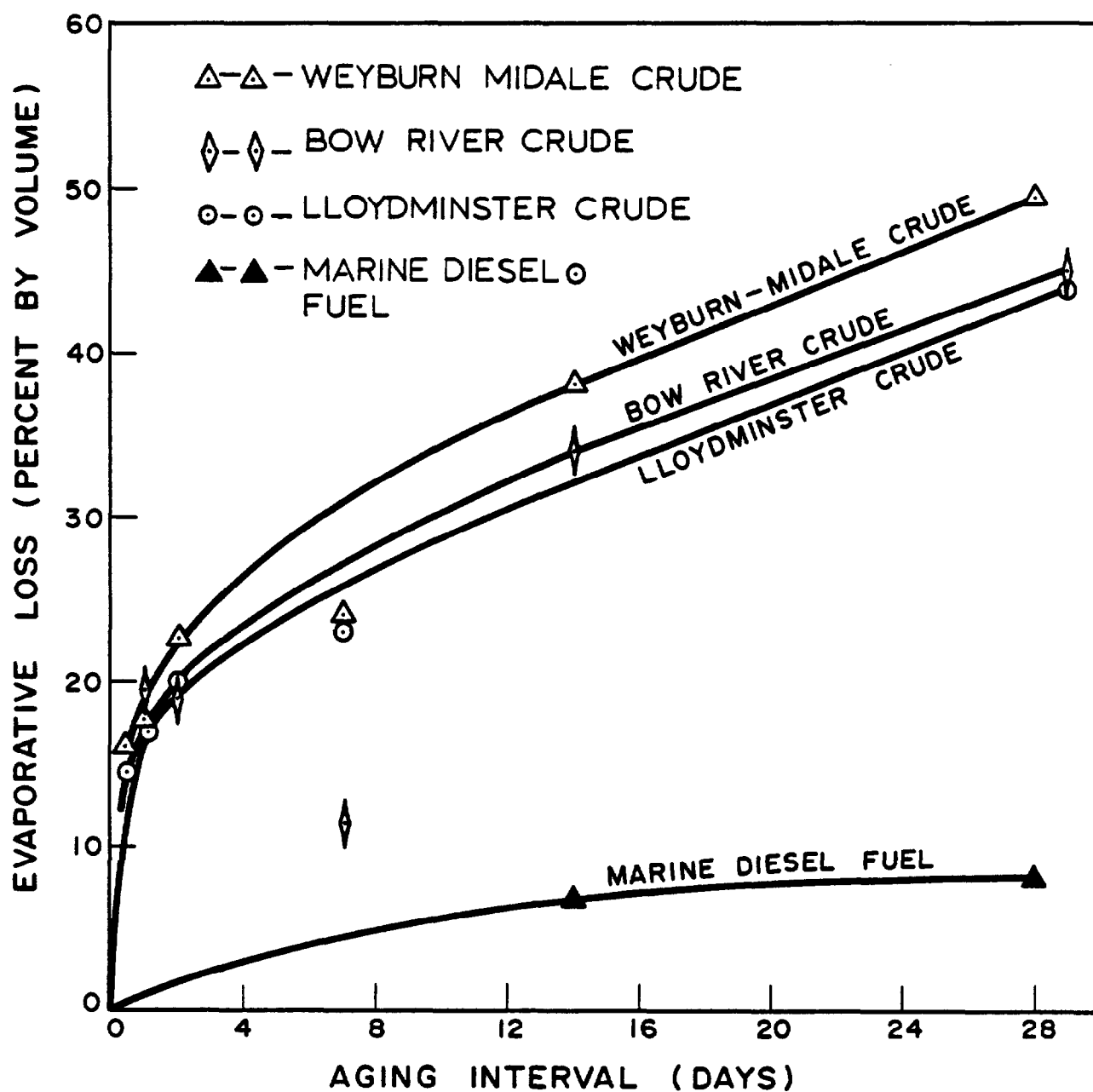


FIGURE 3B - EVAPORATIVE LOSS vs. AGING INTERVAL FOR BOW RIVER CRUDE, LLOYDMINSTER CRUDE, WEYBURN-MIDALE CRUDE, AND MARINE DIESEL FUEL

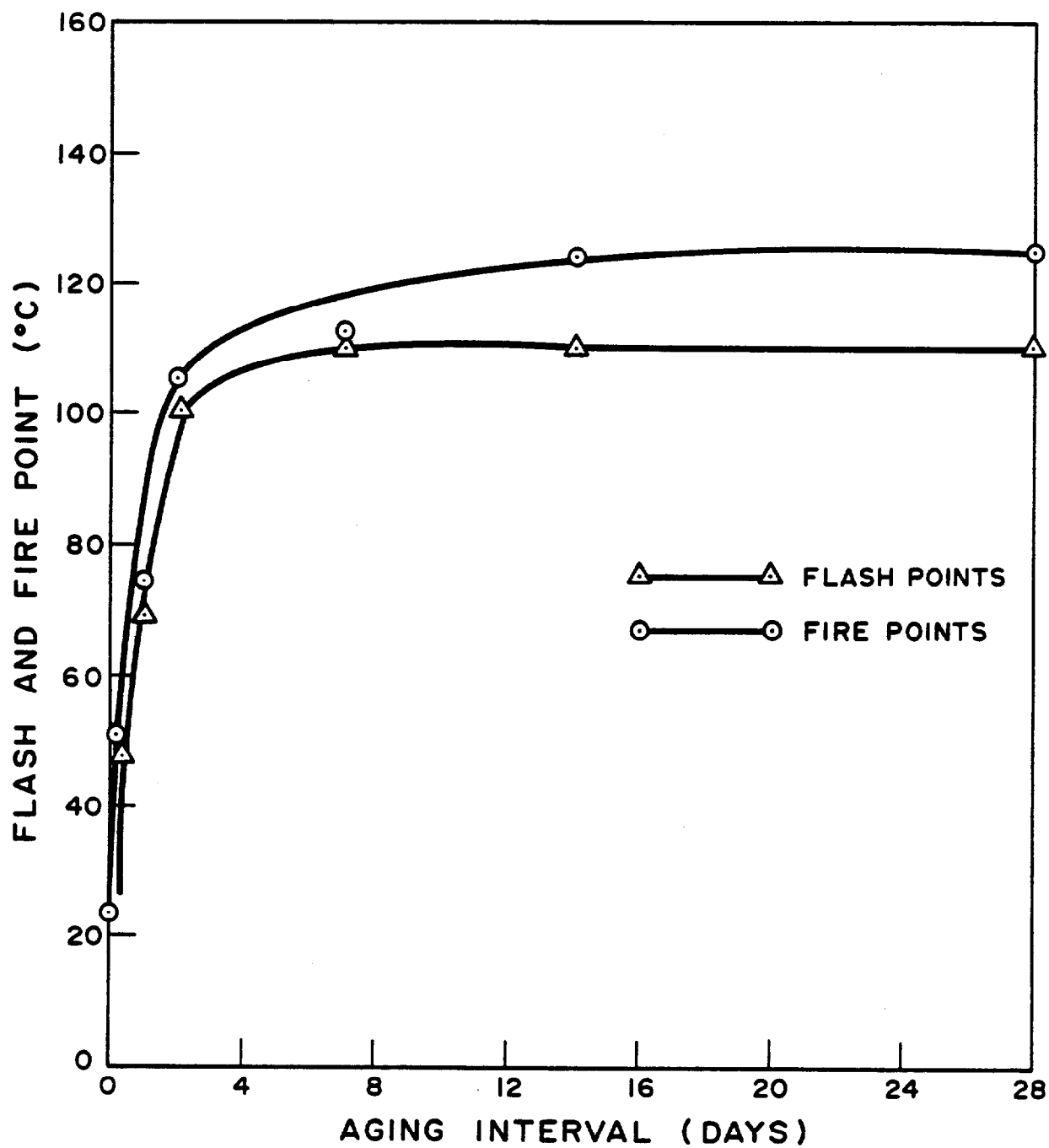


FIGURE 4A - FLASH/FIRE POINTS OF
NORMAN WELLS CRUDE
vs. AGING INTERVAL

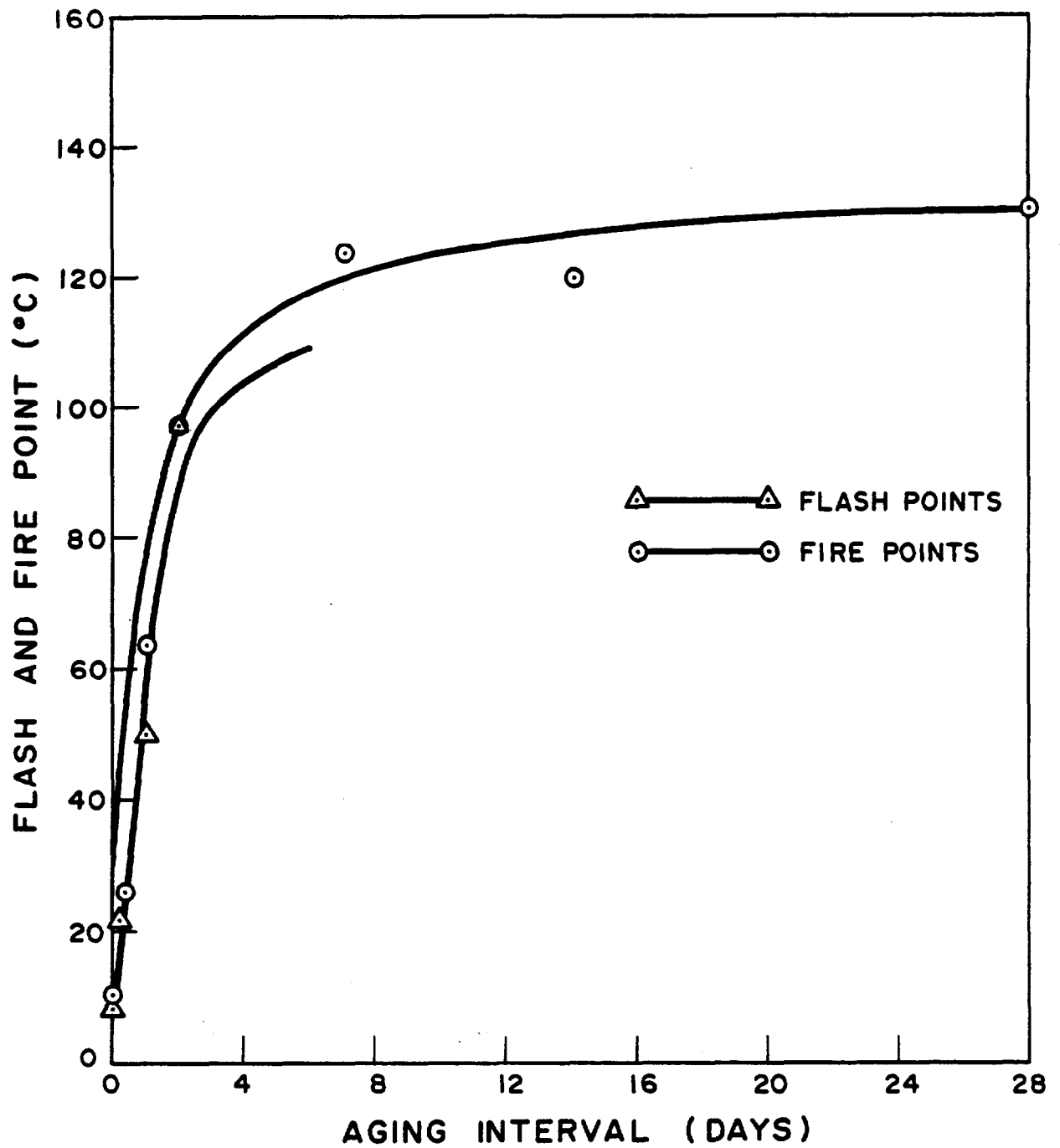


FIGURE 4B - FLASH/FIRE POINTS OF
SWEET BL. CRUDE
vs. AGING INTERVAL

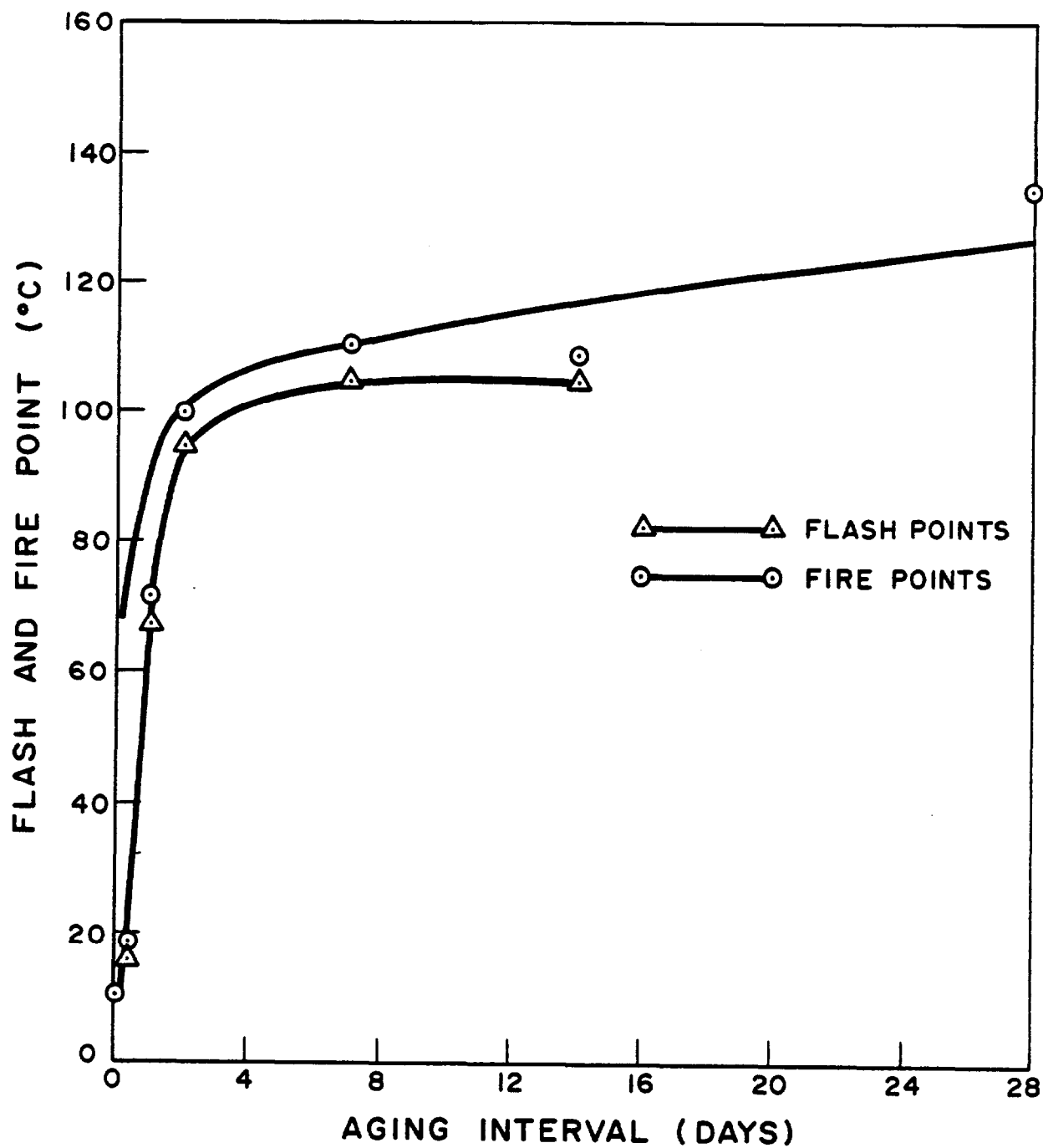


FIGURE 4C—FLASH/FIRE POINTS OF
SOUR BL. CRUDE
vs. AGING INTERVAL

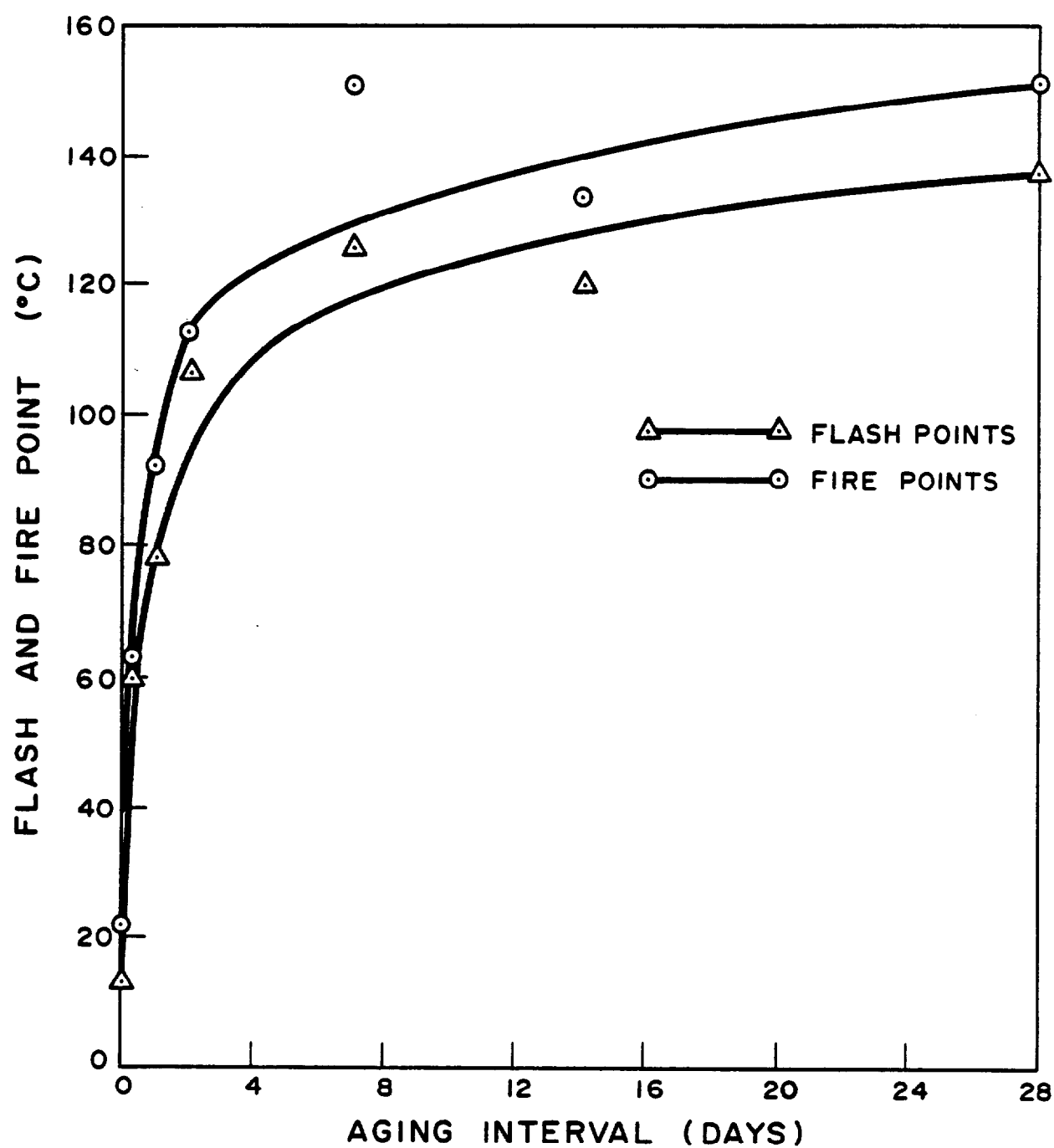


FIGURE 4D—FLASH/FIRE POINTS OF
BOW RIVER CRUDE
vs. AGING INTERVAL

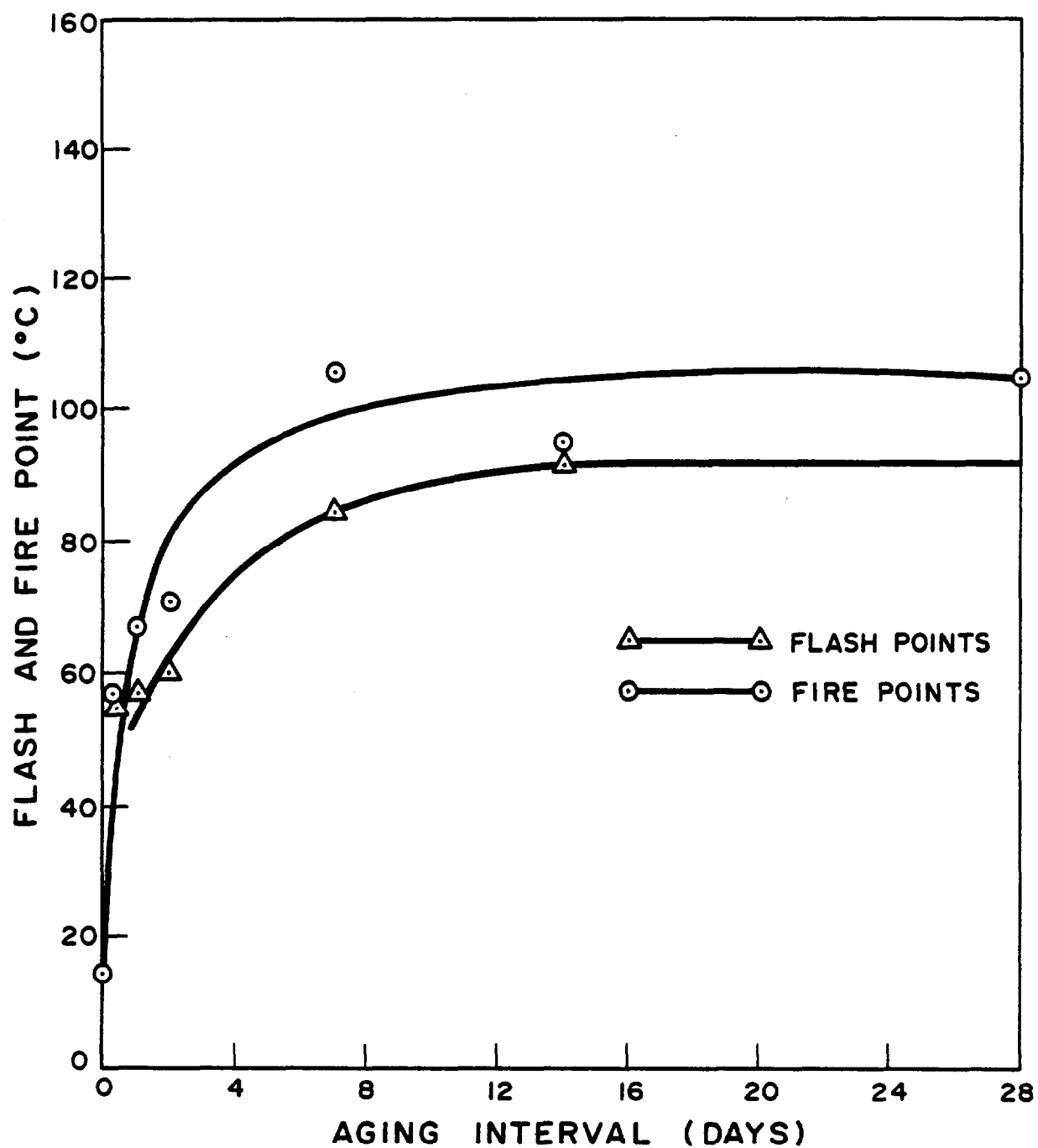


FIGURE 4E - FLASH/FIRE POINTS OF
WEYBURN-MIDALE CRUDE
vs. AGING INTERVAL

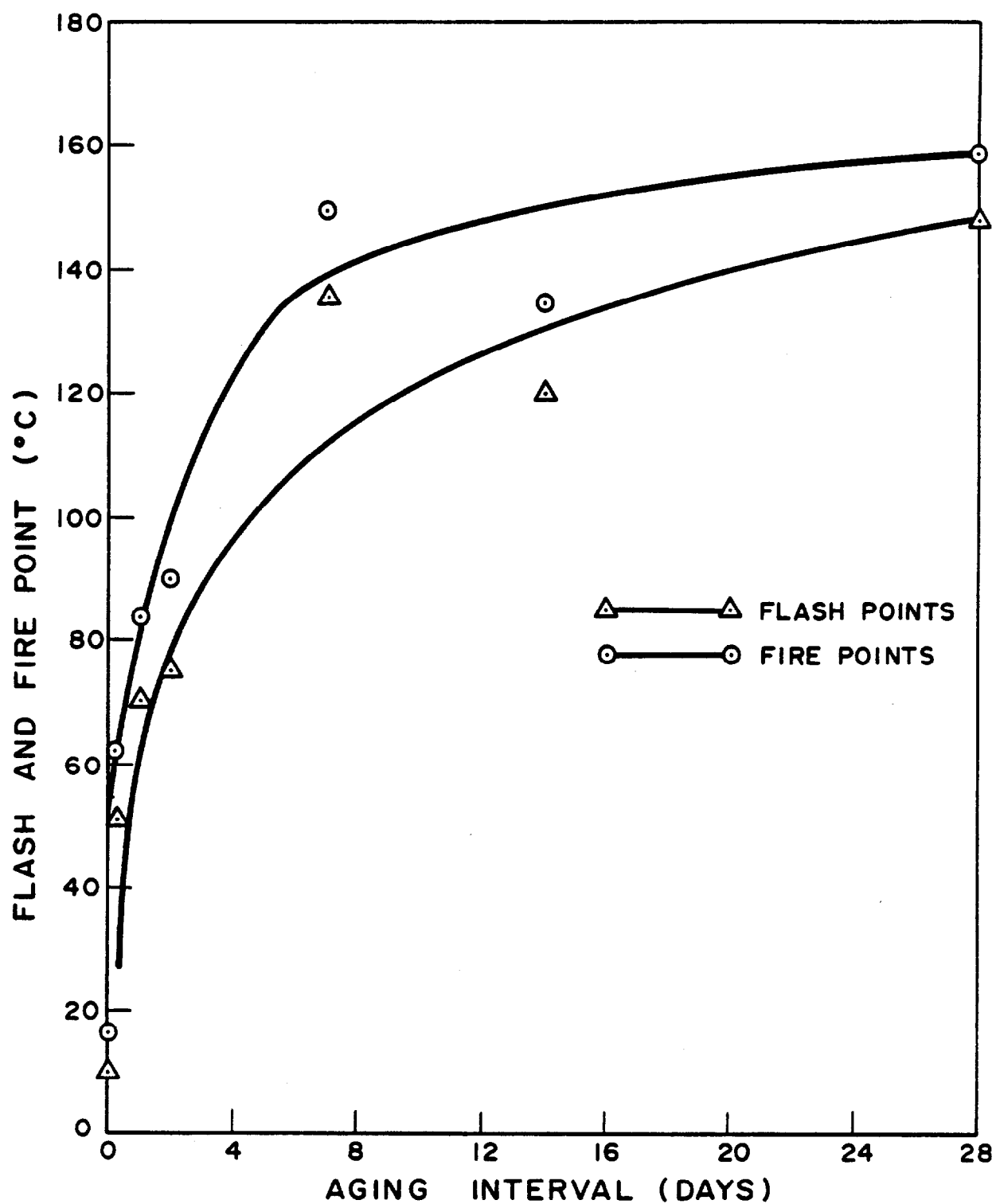


FIGURE 4F—FLASH/FIRE POINTS OF
LLOYDMINSTER CRUDE
vs. AGING INTERVAL

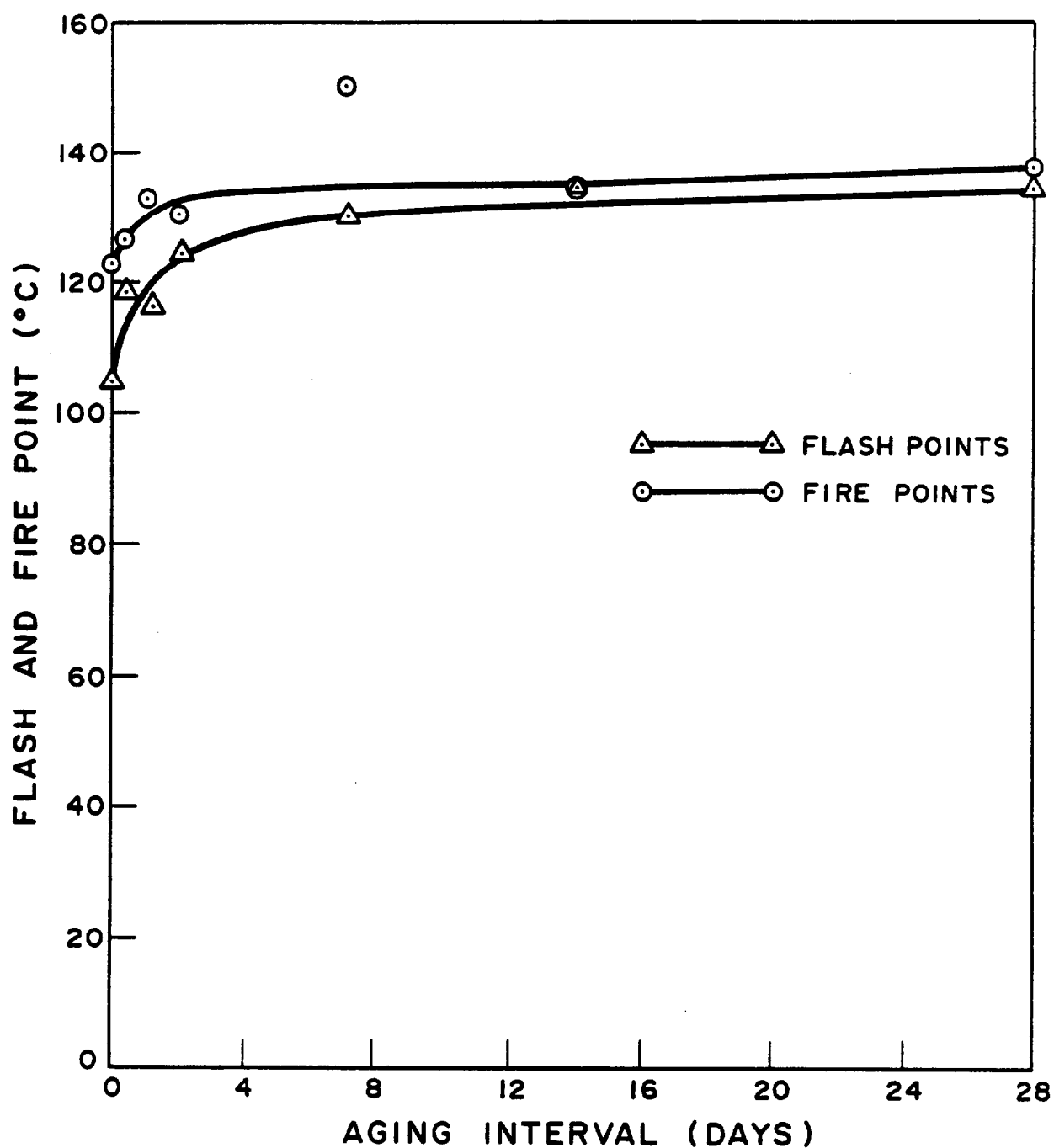


FIGURE 4G — FLASH/FIRE POINTS OF
MARINE DIESEL FUEL
vs. AGING INTERVAL

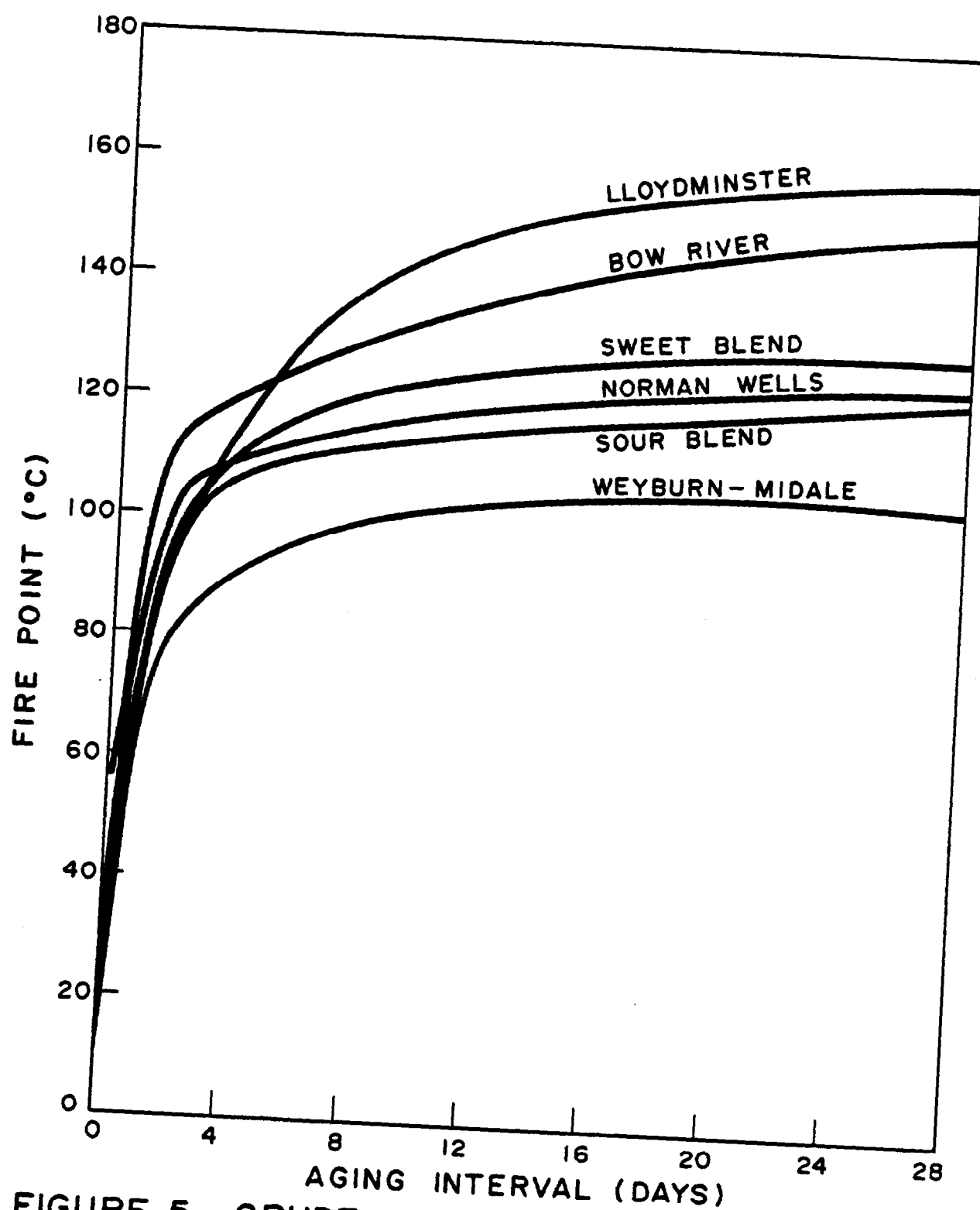


FIGURE 5—CRUDE OIL FIRE POINTS
vs. AGING INTERVAL

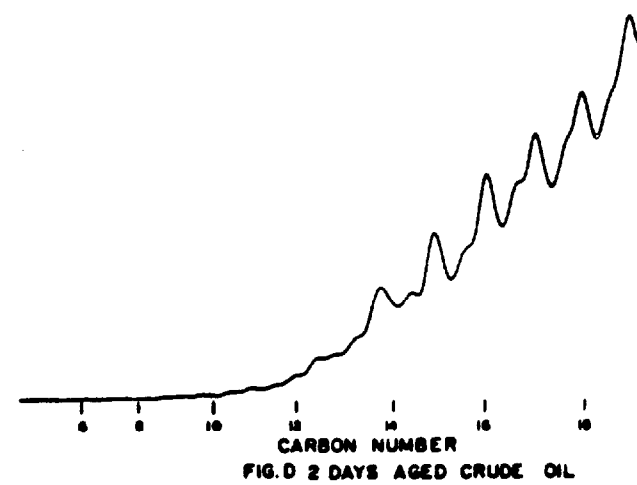
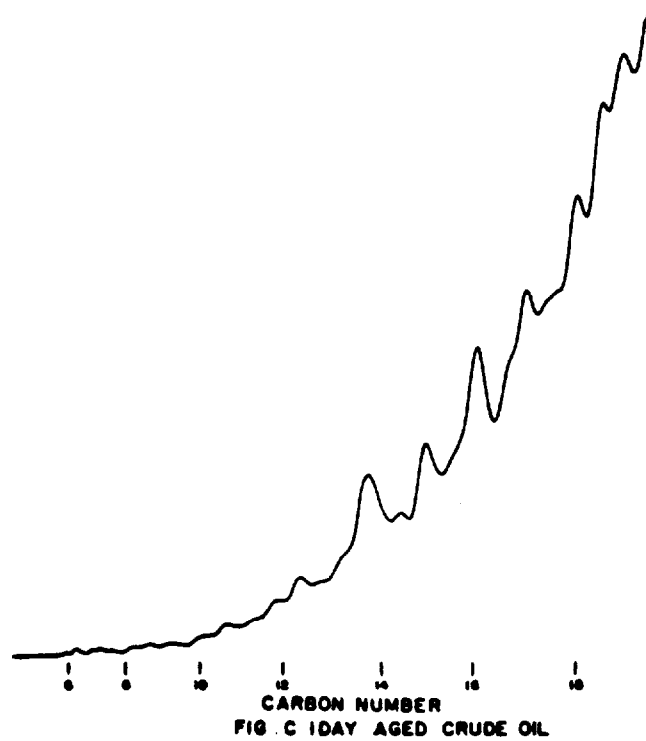
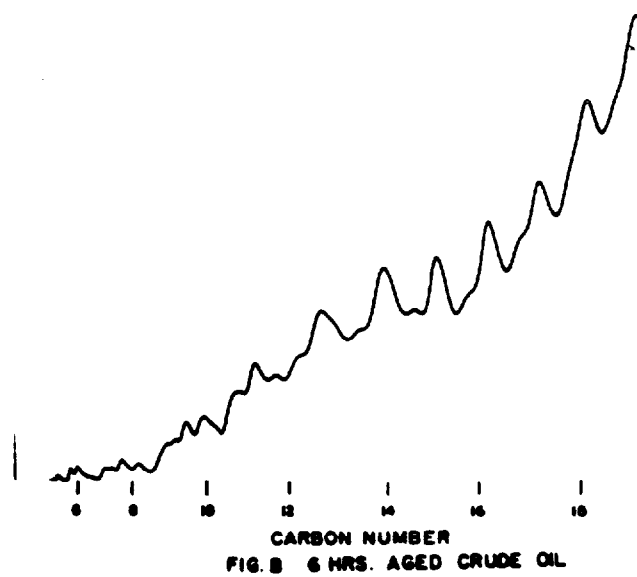
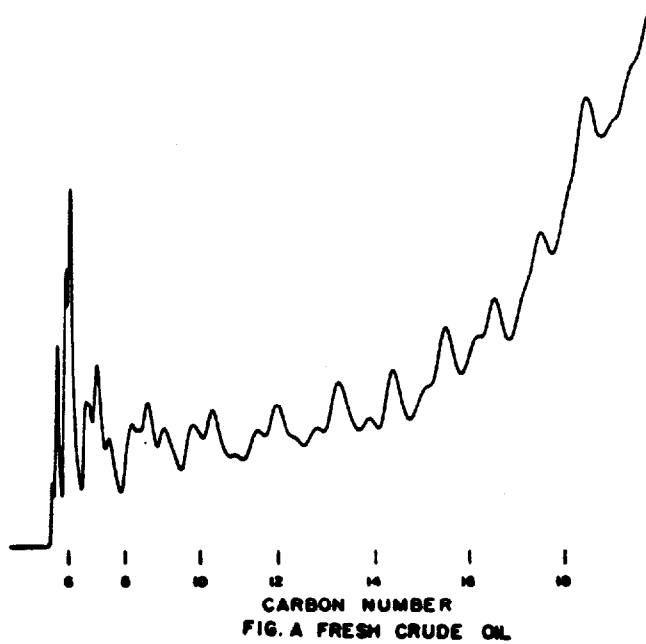


FIG 6-1A GAS CHROMATOGRAPHIC ANALYSIS OF BOW RIVER CRUDE OIL

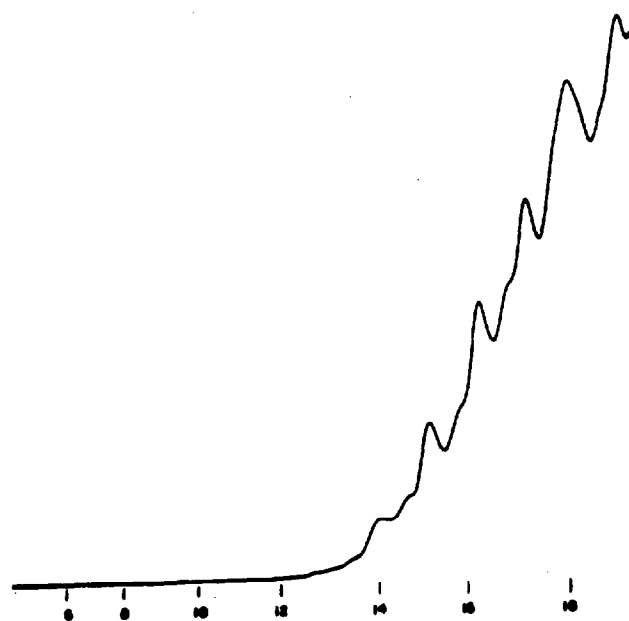


FIG. A 1 WEEK AGED CRUDE OIL

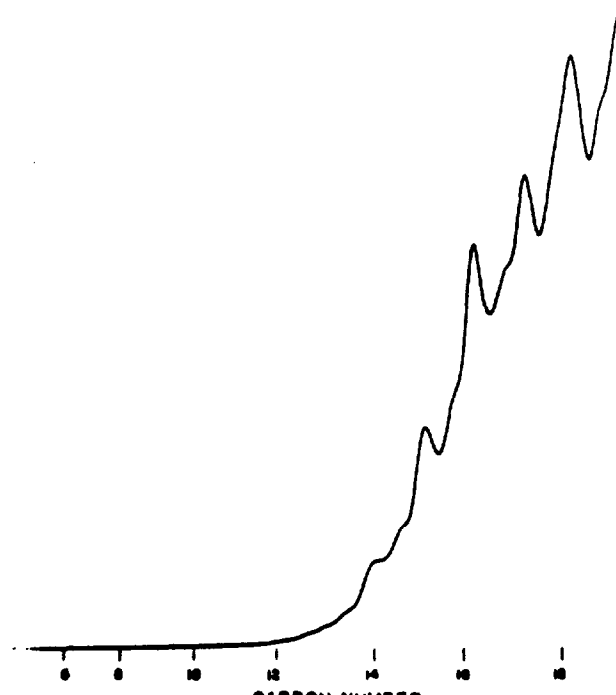


FIG. B 2 WEEKS AGED CRUDE OIL

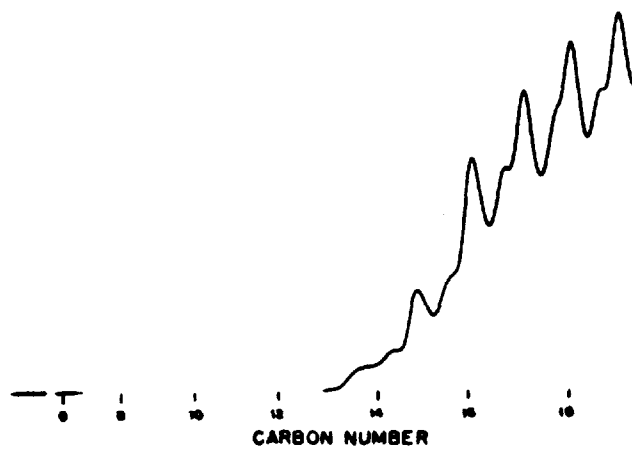


FIG. C 4 WEEKS AGED CRUDE OIL

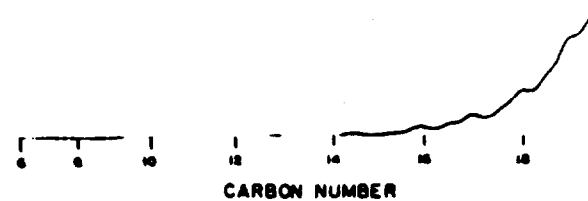


FIG. D CRUDE OIL RESIDUE (1 DAY AGED)

FIG. 6-1B GAS CHROMATOGRAPHIC ANALYSIS OF BOW RIVER CRUDE OIL

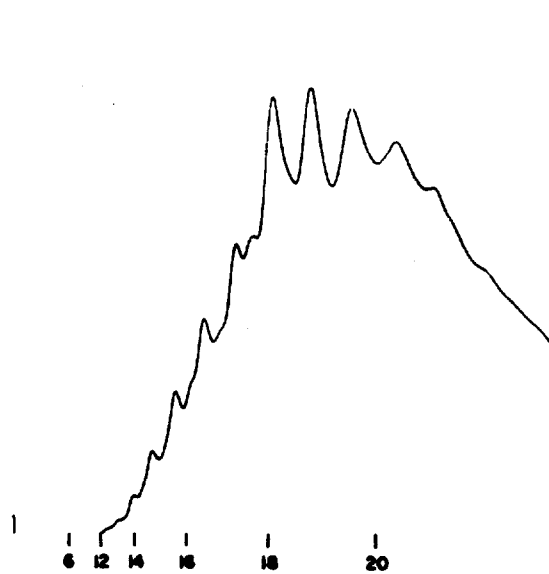


FIG.A RESIDUE OF FRESH FUEL OIL



FIG.B RESIDUE OF 6 HRS. AGED FUEL OIL

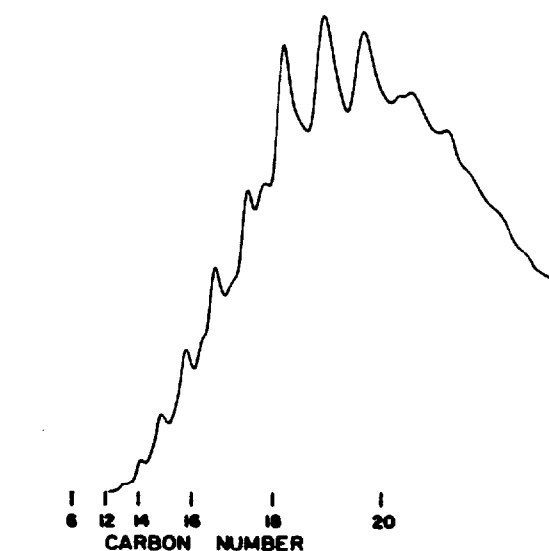


FIG.C RESIDUE OF 1 DAY AGED FUEL OIL

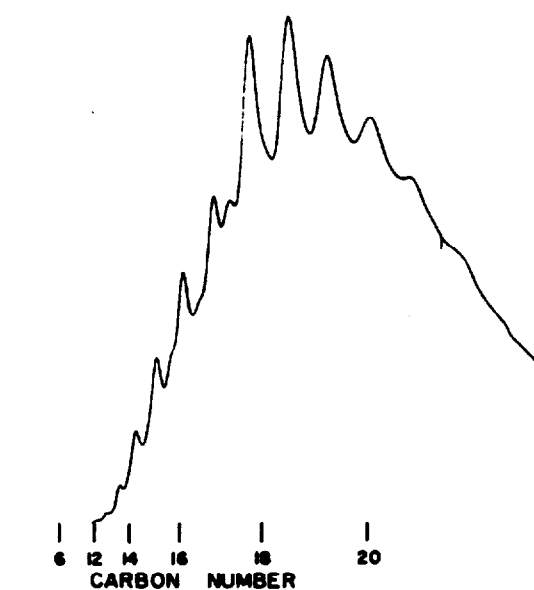


FIG.D RESIDUE OF 2 DAYS AGED FUEL OIL

FIG.6-2A GAS CHROMATOGRAPHIC ANALYSIS OF MARINE DIESEL FUEL OIL RESIDUE

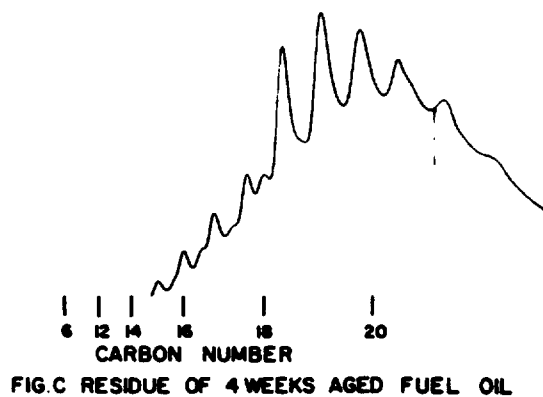
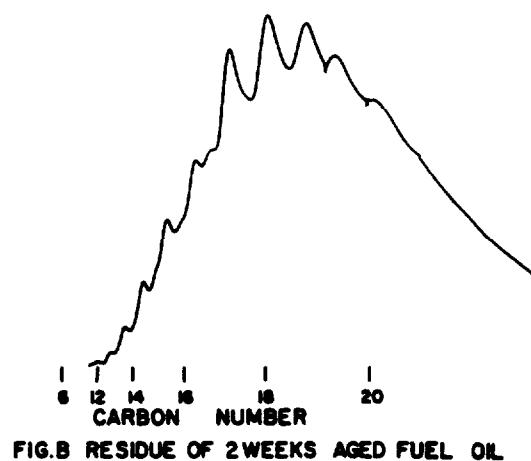
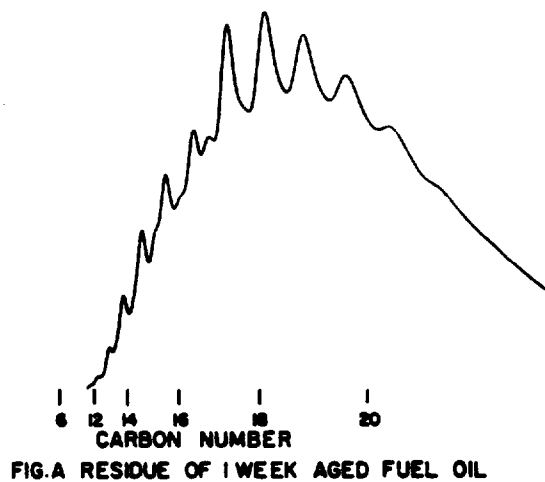


FIG.6-2B GAS CHROMATOGRAPHIC ANALYSIS OF MARINE DIESEL FUEL OIL RESIDUE

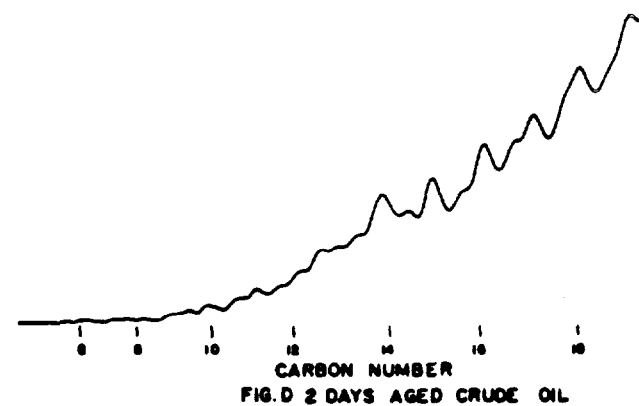
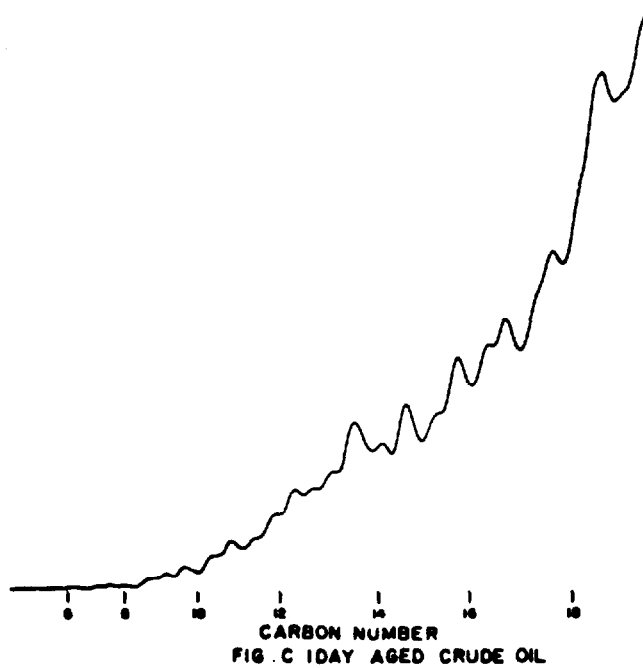
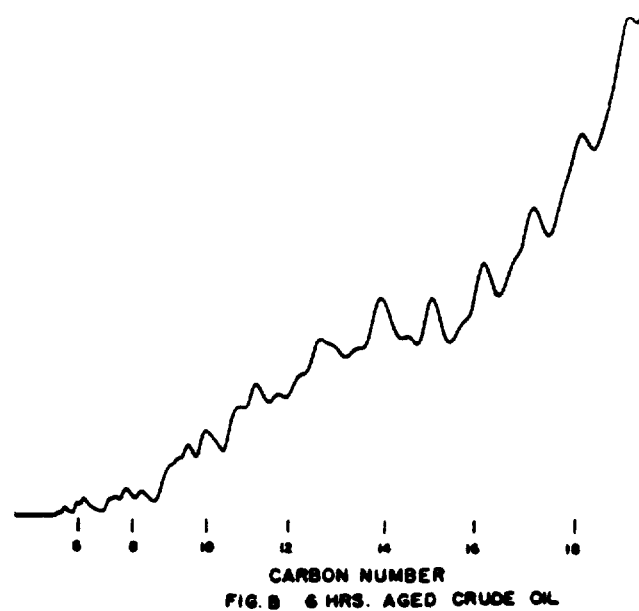
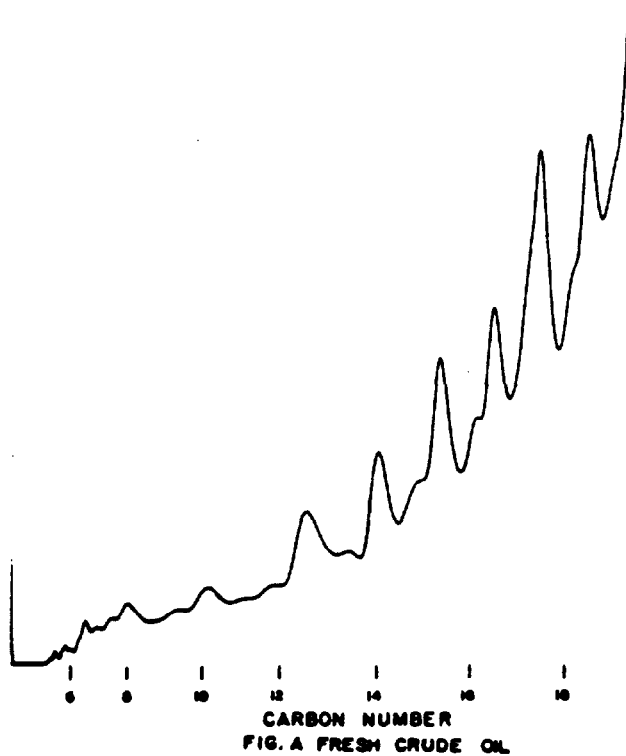


FIG 6-3A GAS CHROMATOGRAPHIC ANALYSIS OF LLOYDMINSTER CRUDE OIL

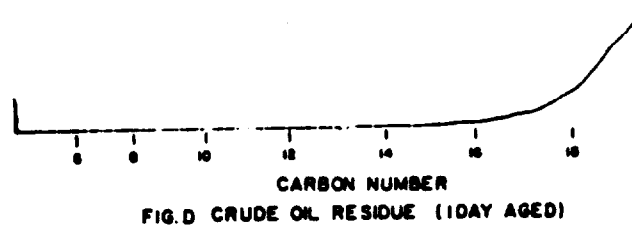
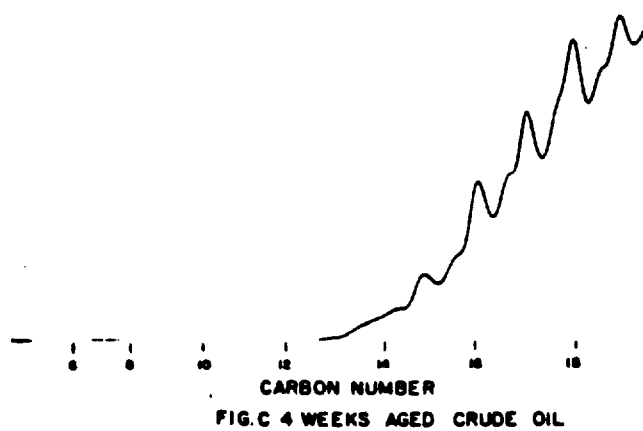
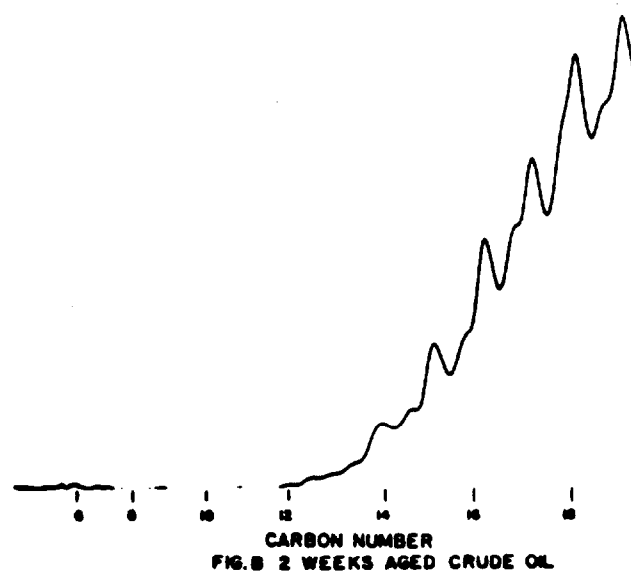
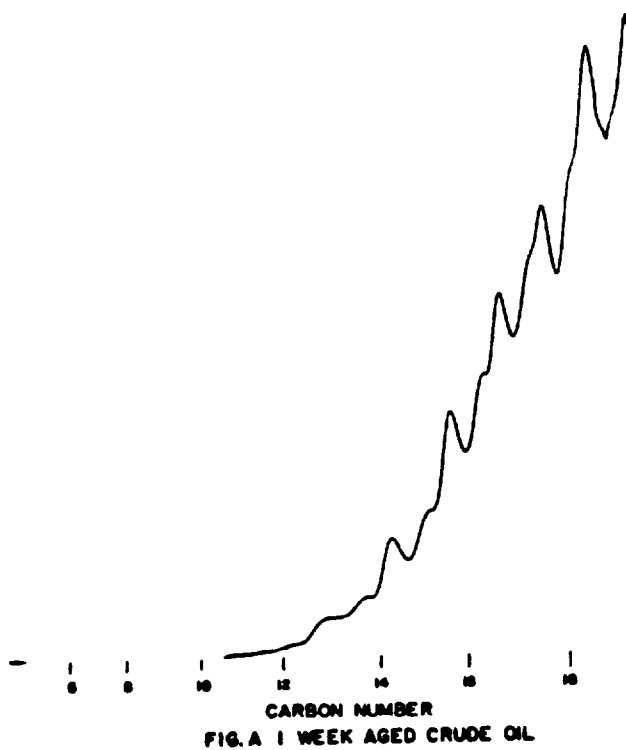


FIG. 6-3B GAS CHROMATOGRAPHIC ANALYSIS OF LLOYDMINSTER CRUDE OIL

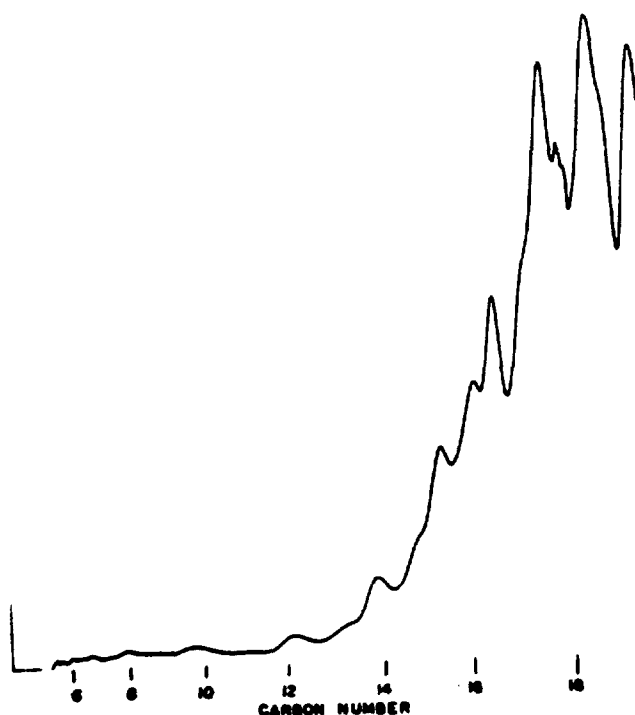


FIG. A FRESH FUEL OIL

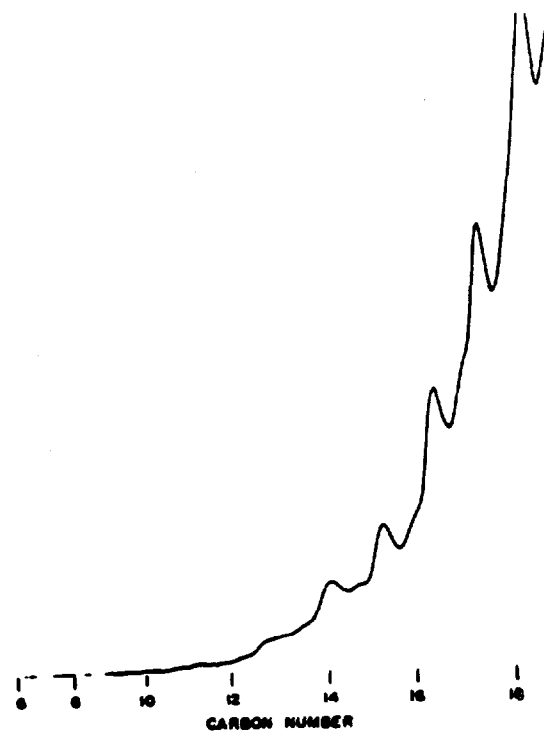


FIG. B 6 HRS. AGED FUEL OIL

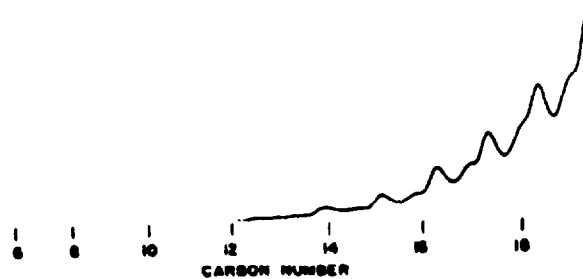


FIG. C 1 DAY AGED FUEL OIL

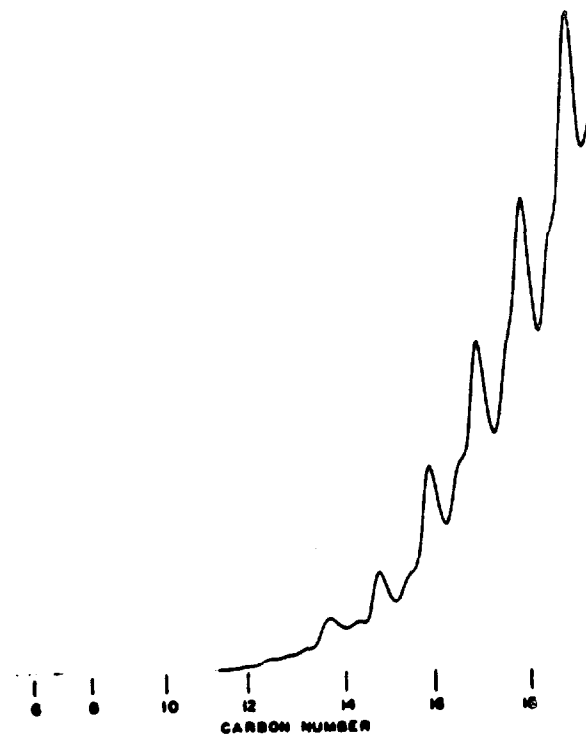


FIG. D 2 DAYS AGED FUEL OIL

FIG 6-4A GAS CHROMATOGRAPHIC ANALYSIS OF MARINE DIESEL FUEL OIL

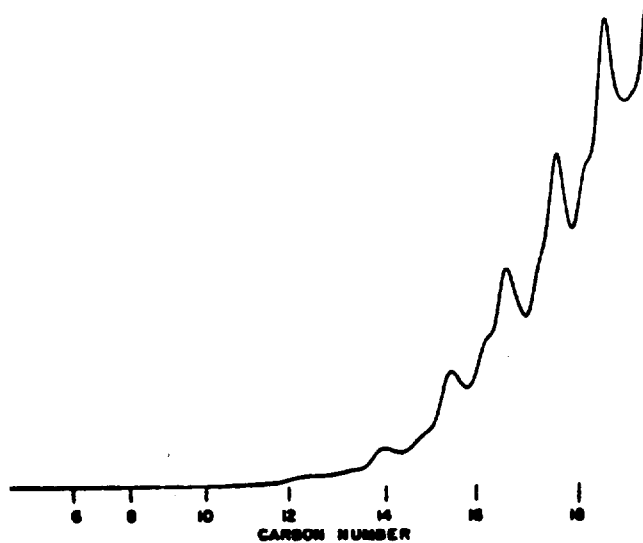


FIG. A 1 WEEK AGED FUEL OIL

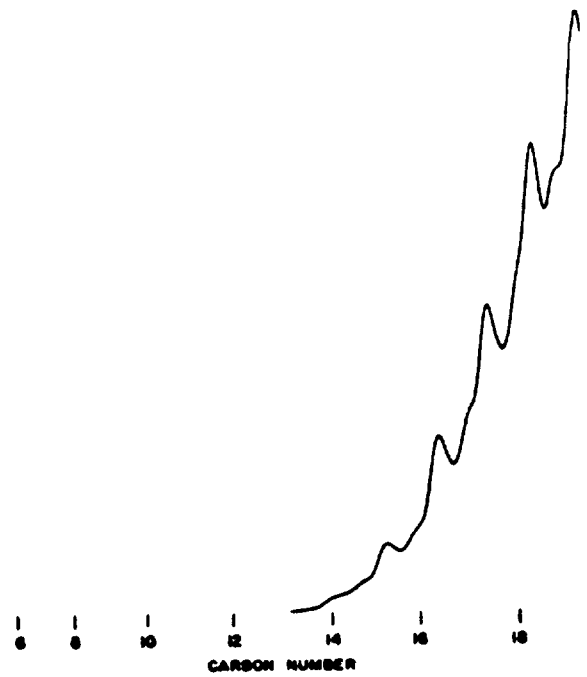


FIG. B 2 WEEKS AGED FUEL OIL

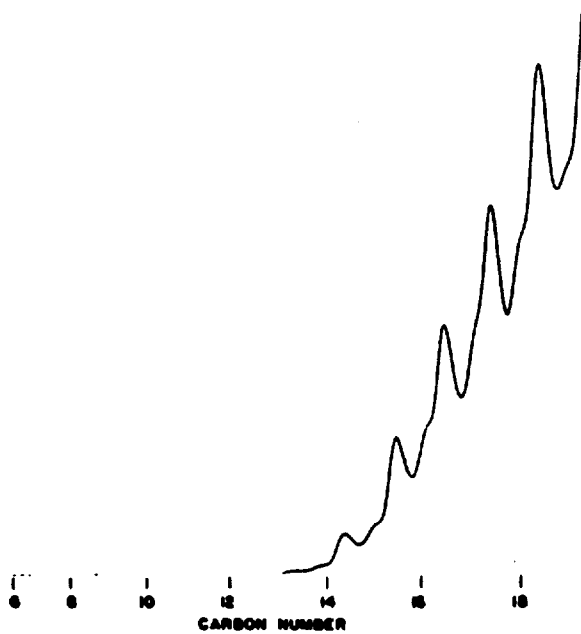


FIG. C 4 WEEKS AGED FUEL OIL

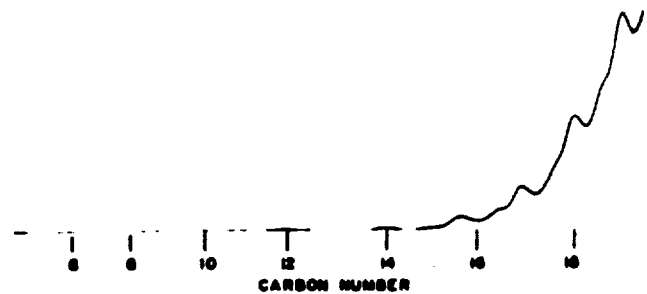


FIG. D FUEL OIL RESIDUE (FRESH)

FIG. 6-4B GAS CHROMATOGRAPHIC ANALYSIS OF MARINE DIESEL FUEL OIL

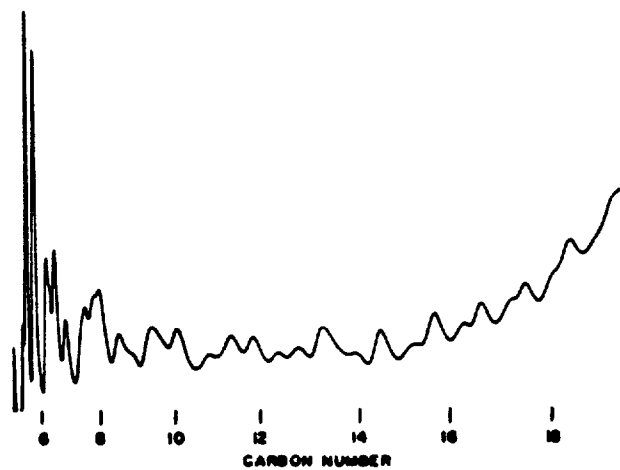


FIG. A FRESH CRUDE OIL

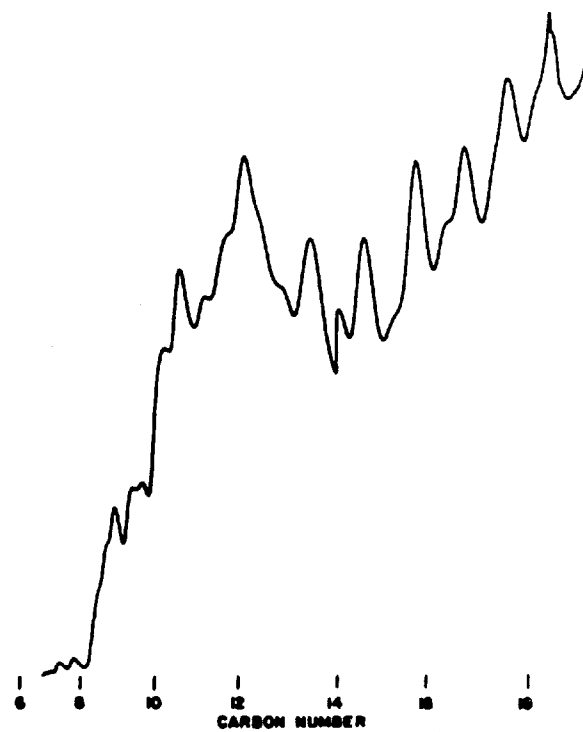


FIG. B 6 HRS. AGED CRUDE OIL

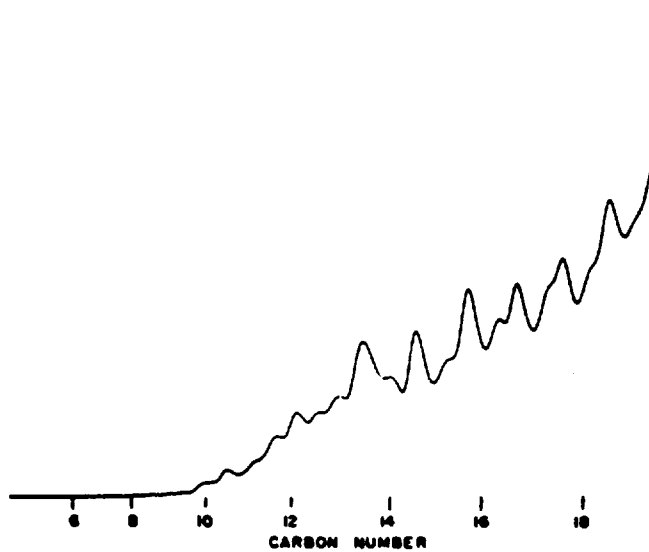


FIG. C 1 DAY AGED CRUDE OIL

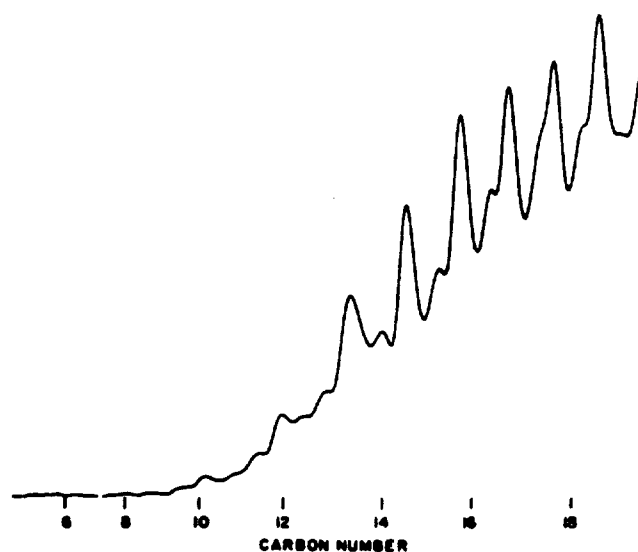


FIG. D 2 DAYS AGED CRUDE OIL

FIG. 6-5A GAS CHROMATOGRAPHIC ANALYSIS OF NORMAN WELLS CRUDE OIL

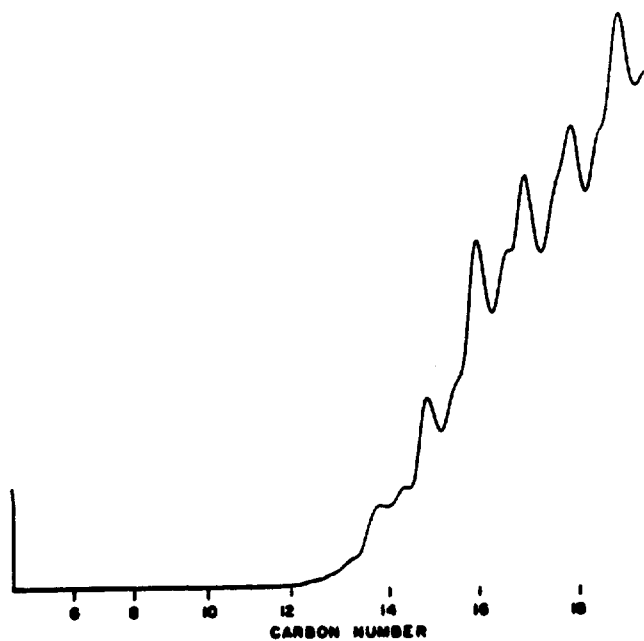


FIG. A 1 WEEK AGED CRUDE OIL

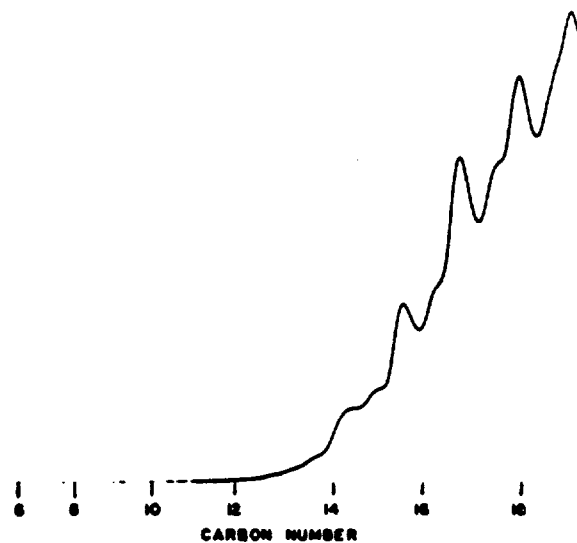


FIG. B 2 WEEKS AGED CRUDE OIL

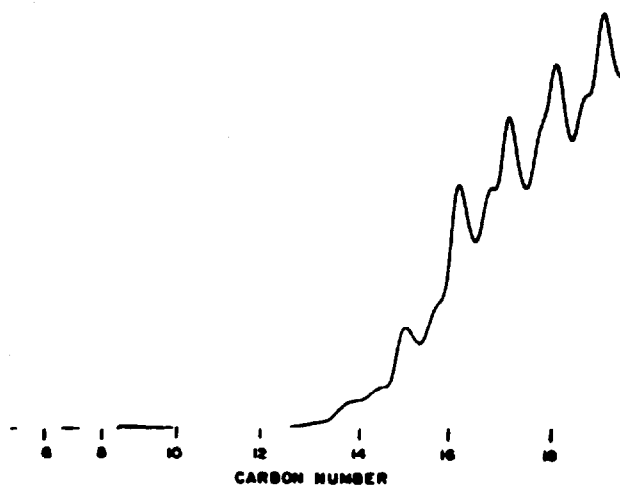


FIG. C 4 WEEKS AGED CRUDE OIL

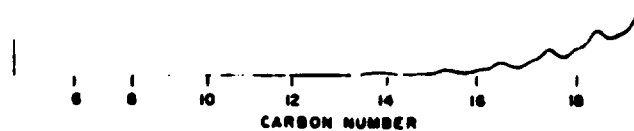


FIG. D CRUDE OIL RESIDUE (FRESH)

FIG 6-5B GAS CHROMATOGRAPHIC ANALYSIS OF NORMAN WELLS CRUDE OIL

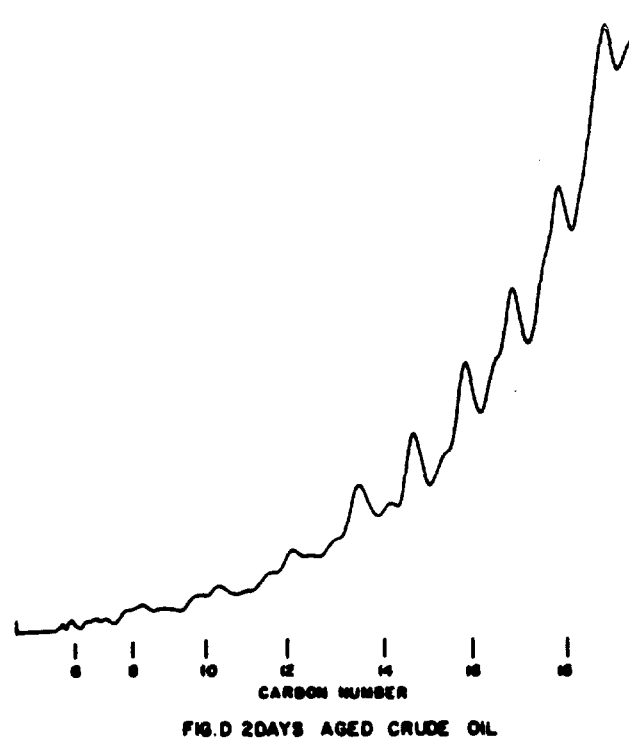
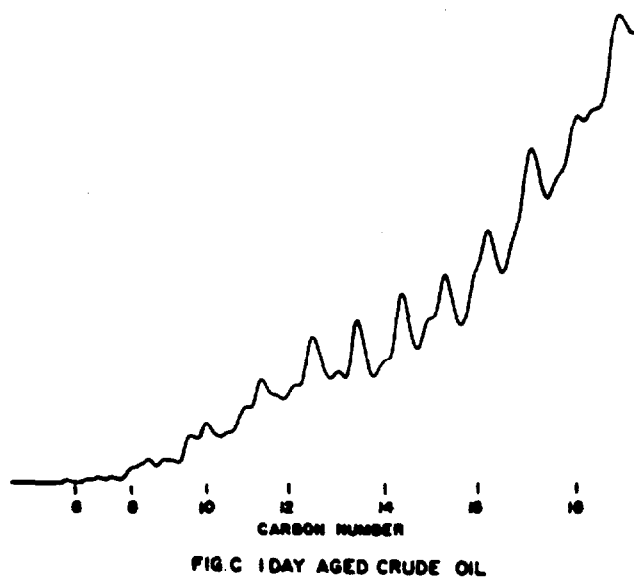
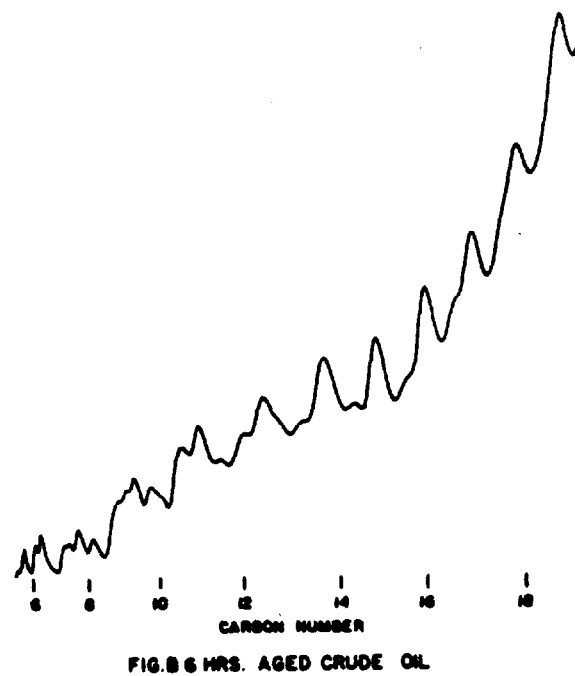
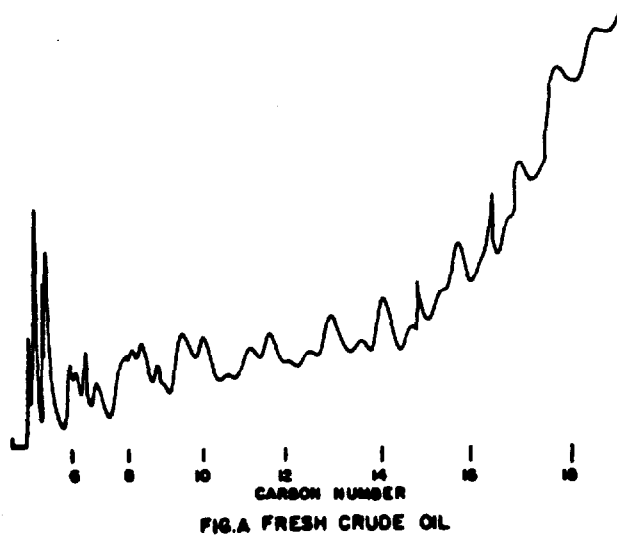


FIG.6-6A GAS CHROMATOGRAPHIC ANALYSIS OF WEYBURN-MIDALE CRUDE OIL

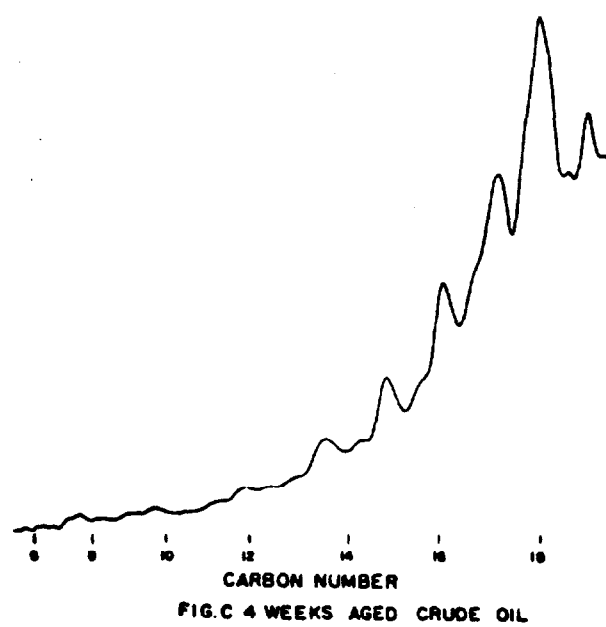
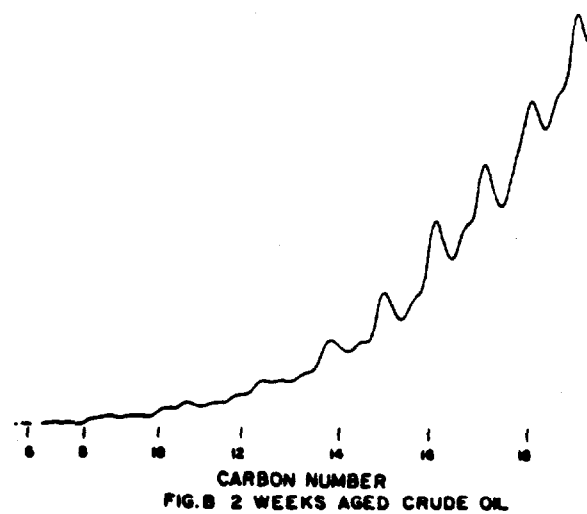
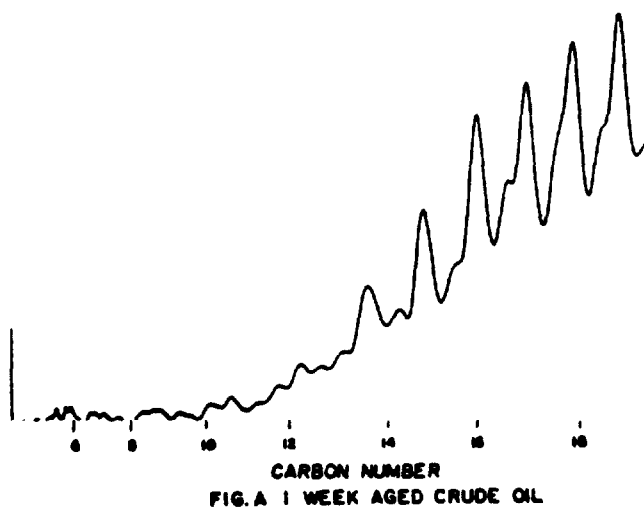


FIG 6-6B GAS CHROMATOGRAPHIC ANALYSIS OF WEYBURN-MIDALE CRUDE OIL

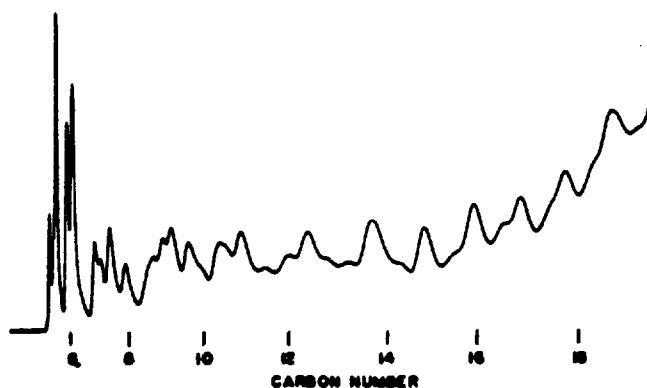


FIG. A FRESH CRUDE OIL

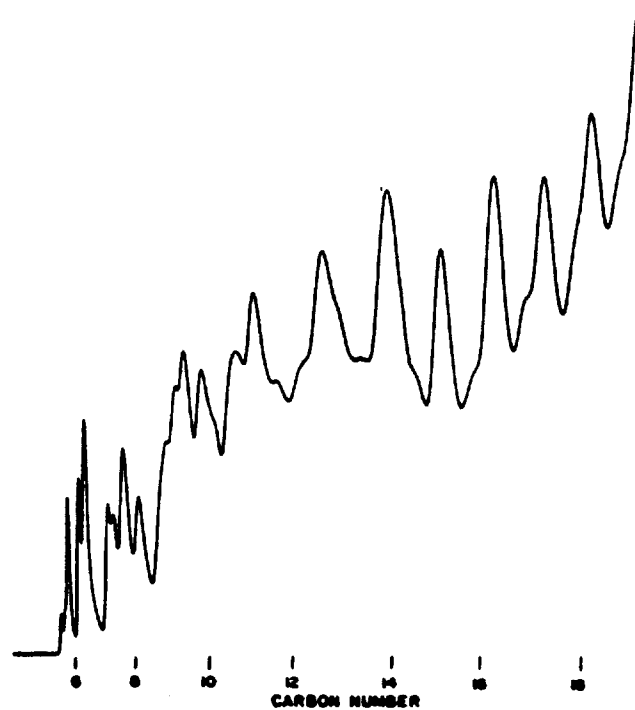


FIG. B 6 HRS. AGED CRUDE OIL

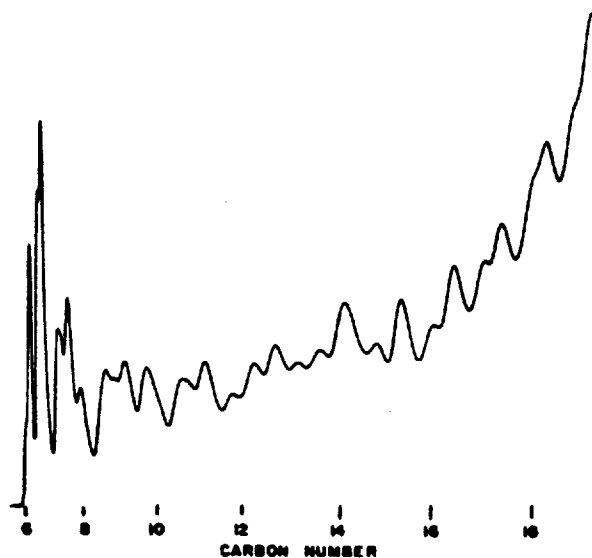


FIG. C 1 DAY AGED CRUDE OIL

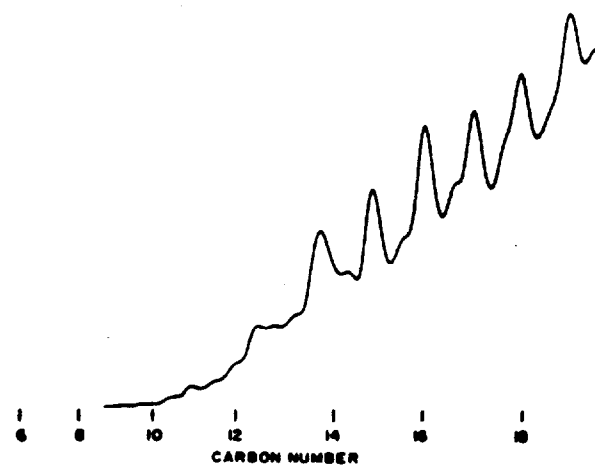


FIG. D 2 DAYS AGED CRUDE OIL

FIG. 6-7A GAS CHROMATOGRAPHIC ANALYSIS OF SOUR MIXED BLEND CRUDE OIL

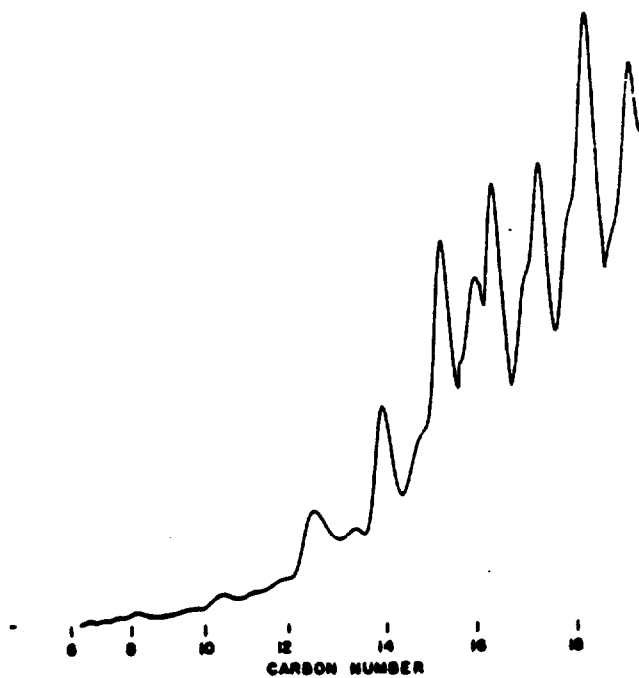


FIG. A 1 WEEK AGED CRUDE OIL

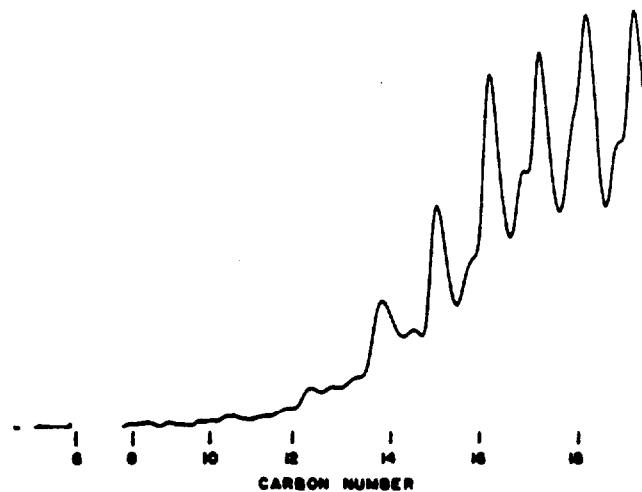


FIG. B 2 WEEKS AGED CRUDE OIL

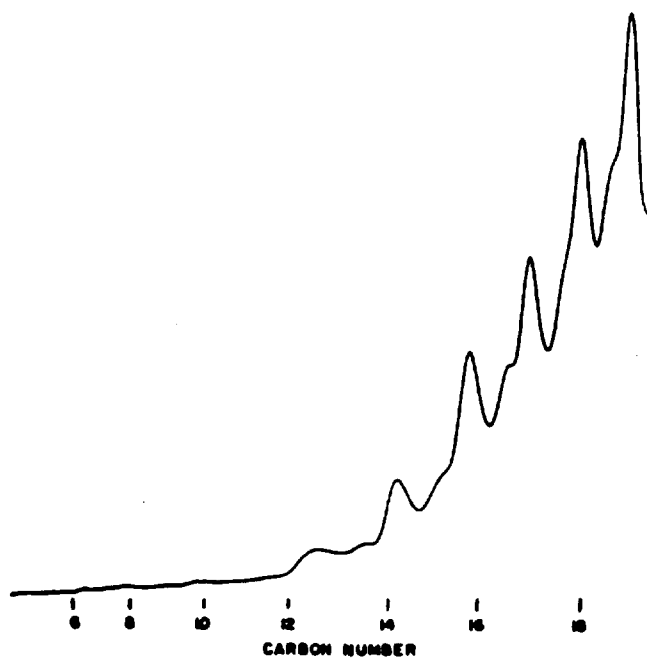


FIG. C 4 WEEKS AGED CRUDE OIL

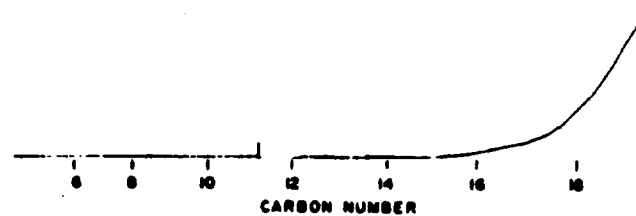


FIG. D CRUDE OIL RESIDUE (FRESH)

FIG 6-7B GAS CHROMATOGRAPHIC ANALYSIS OF SOUR MIXED BLEND CRUDE OIL

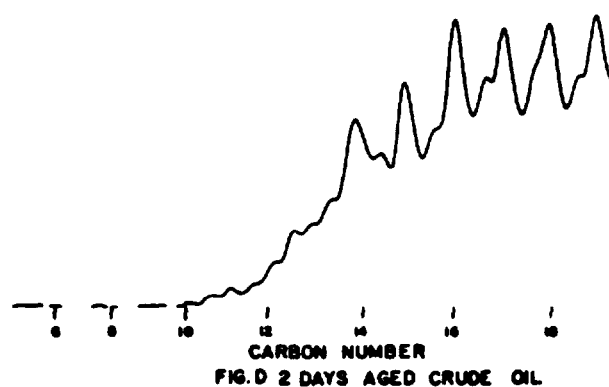
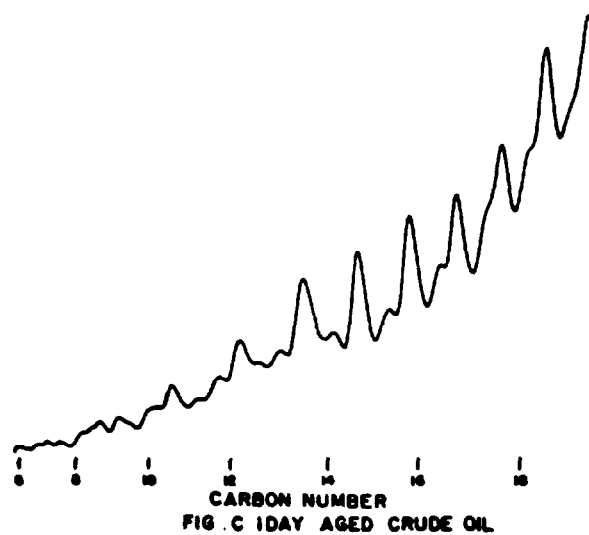
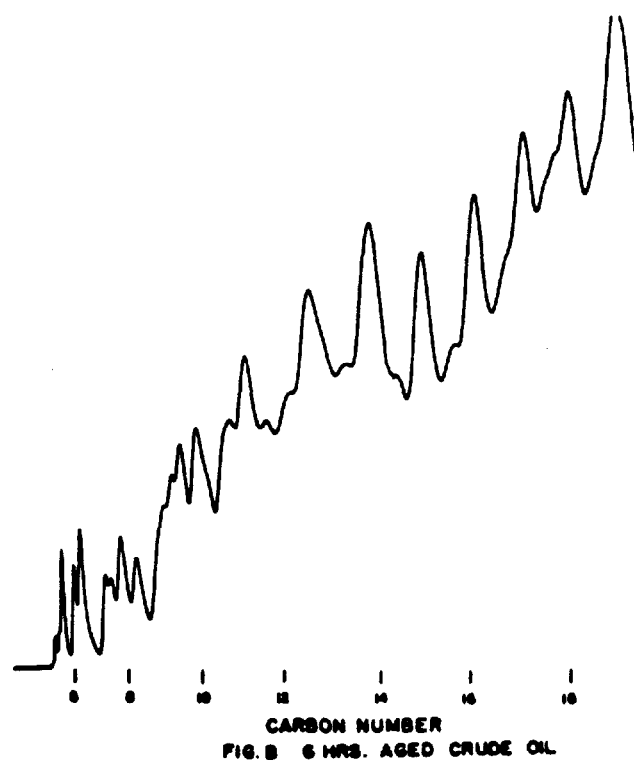
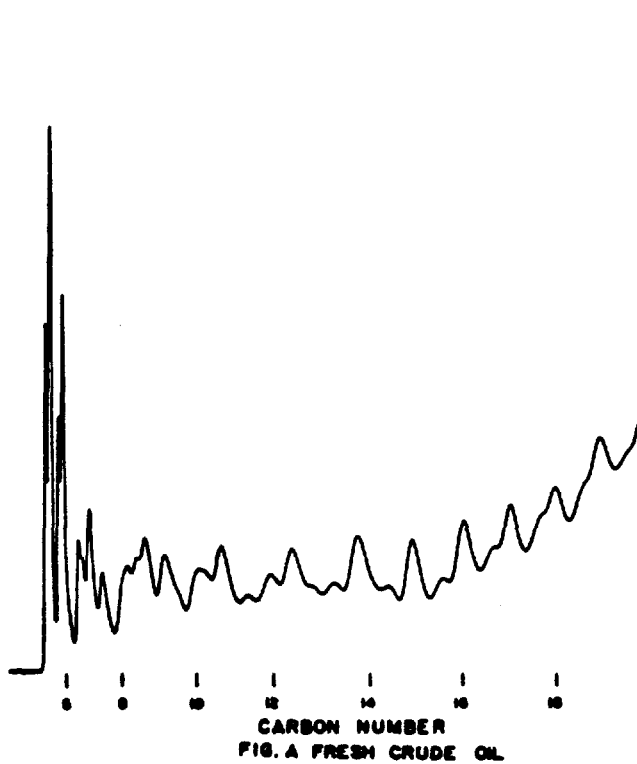


FIG.6-8A GAS CHROMATOGRAPHIC ANALYSIS OF SWEET MIXED BLEND CRUDE OIL

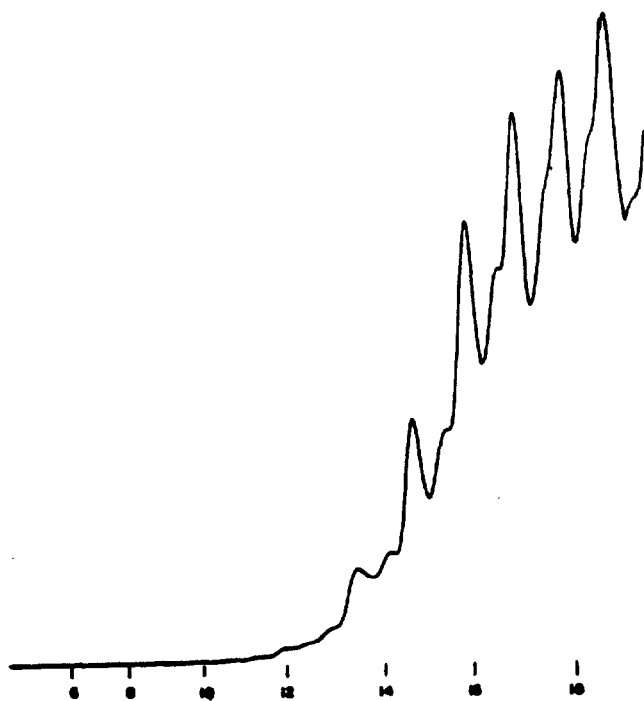


FIG. A 1 WEEK AGED CRUDE OIL

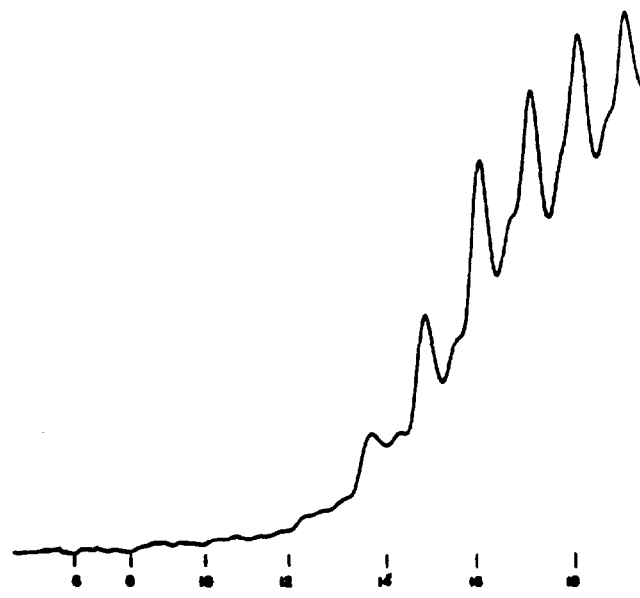


FIG. B 2 WEEKS AGED CRUDE OIL

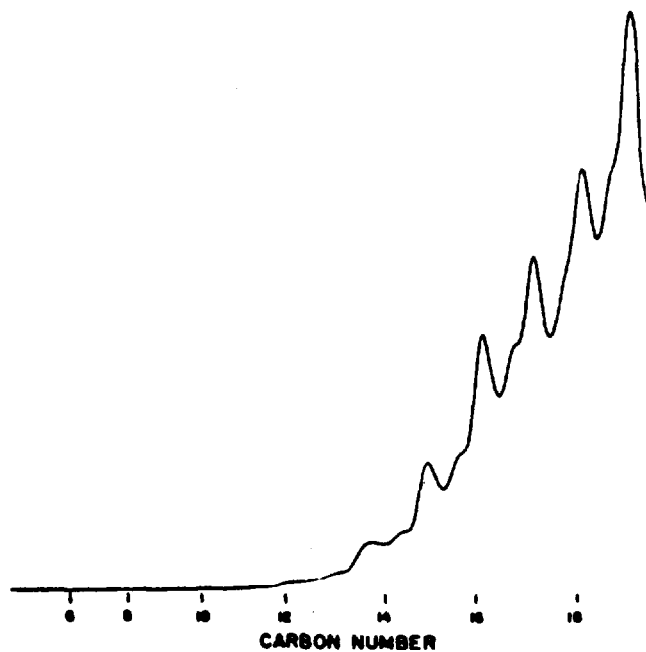


FIG. C 4 WEEKS AGED CRUDE OIL

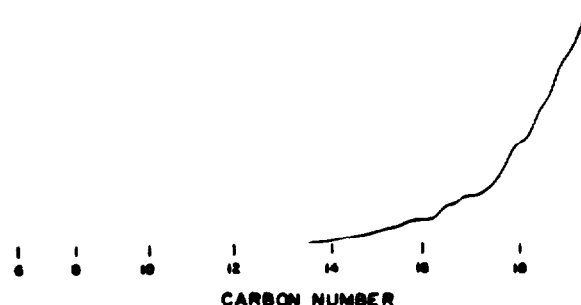


FIG. D CRUDE OIL RESIDUE (1 DAY AGED)

FIG. 6-8B GAS CHROMATOGRAPHIC ANALYSIS OF SWEET MIXED BLEND CRUDE OIL

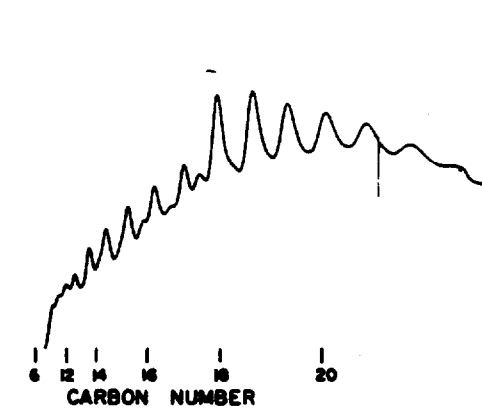


FIG.A RESIDUE OF FRESH CRUDE OIL

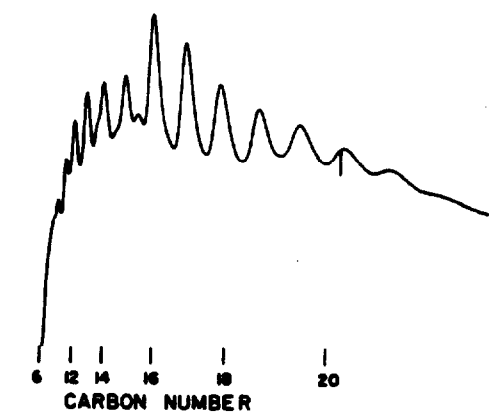


FIG.B RESIDUE OF 6 HRS. AGED CRUDE OIL

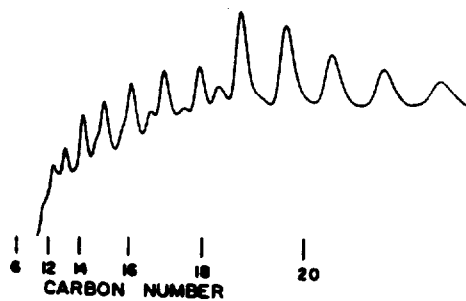


FIG.C RESIDUE OF 1 DAY AGED CRUDE OIL

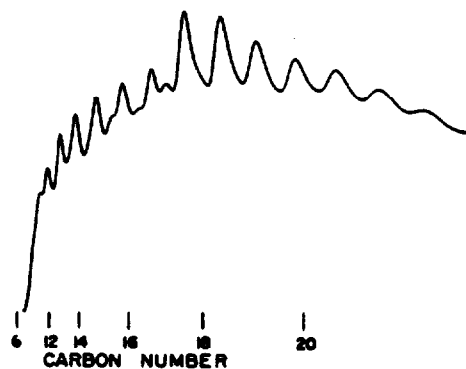


FIG.D RESIDUE OF 2 DAYS AGED CRUDE OIL

FIG 6-9A GAS CHROMATOGRAPHIC ANALYSIS OF SOUR MIXED BLEND CRUDE OIL RESIDUE

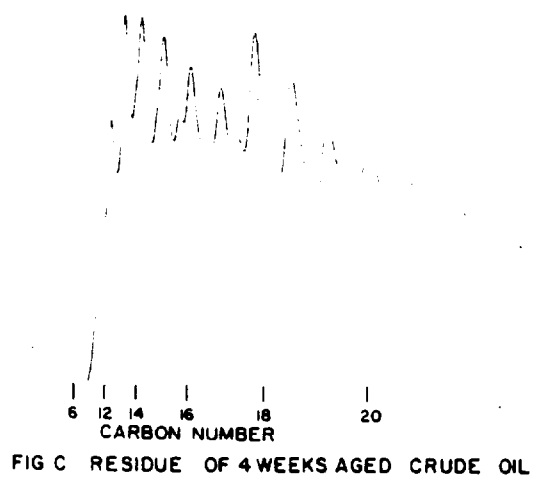
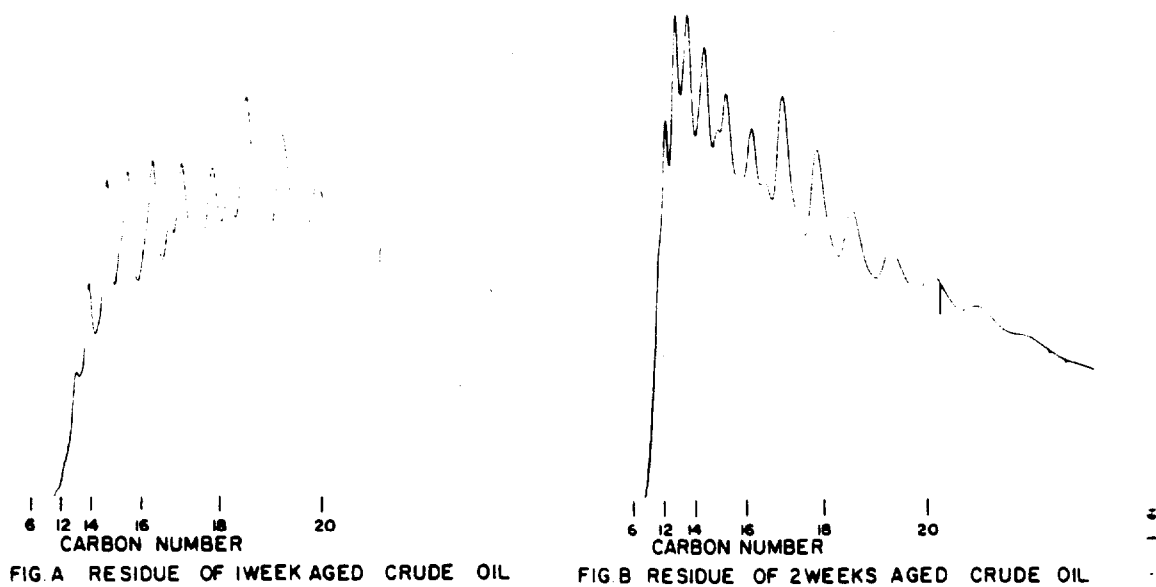


FIG.6-9B GAS CHROMATOGRAPHIC ANALYSIS OF SOUR MIXED BLEND CRUDE OIL RESIDUE

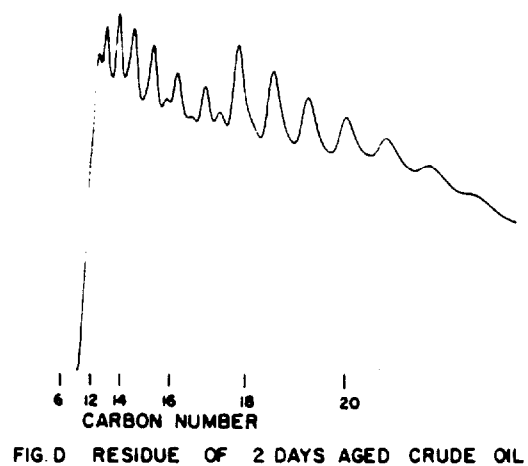
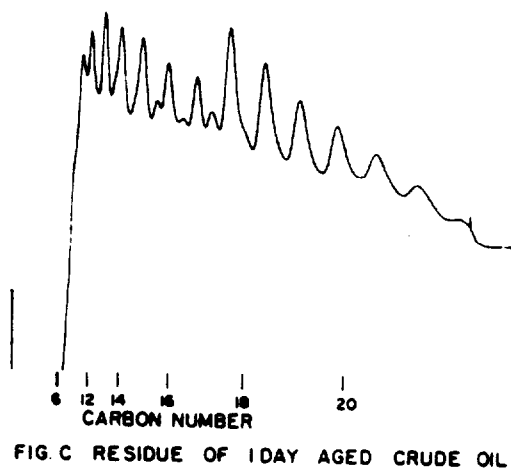
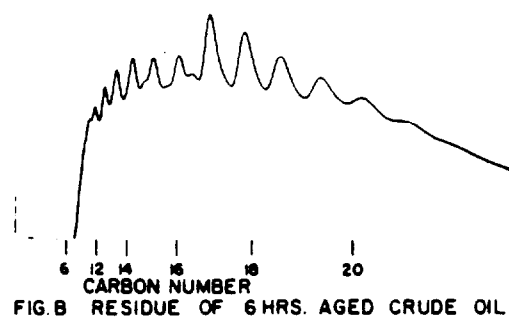
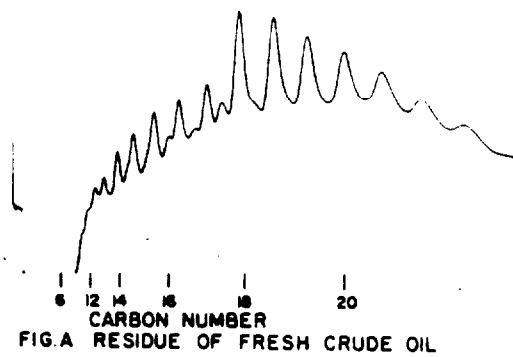


FIG. 6-IOA GAS CHROMATOGRAPHIC ANALYSIS OF SWEET MIXED BLEND CRUDE OIL RESIDUE

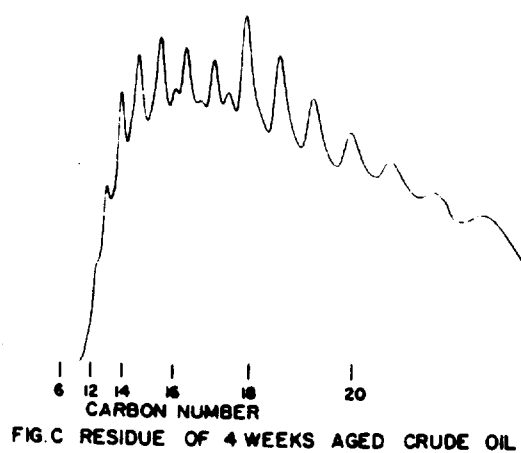
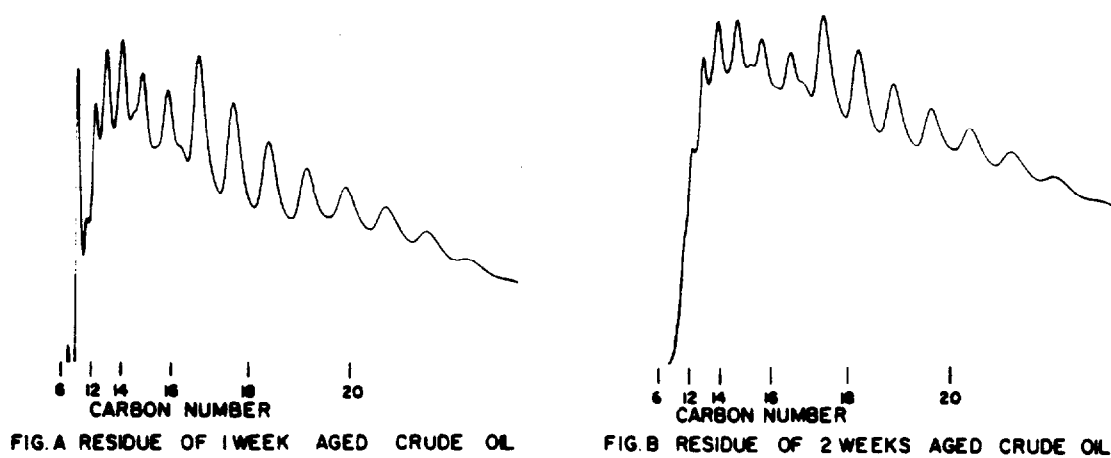


FIG. 6-10B GAS CHROMATOGRAPHIC ANALYSIS OF SWEET MIXED BLEND CRUDE OIL RESIDUE

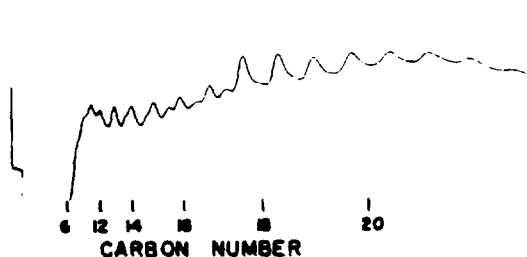


FIG. A RESIDUE OF FRESH CRUDE OIL

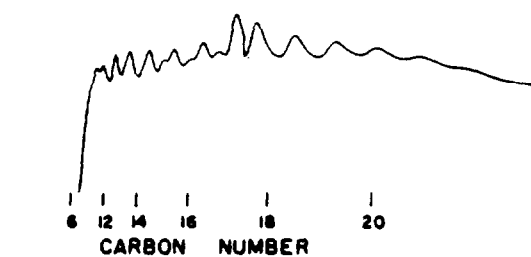


FIG. B RESIDUE OF 6 HRS. AGED CRUDE OIL

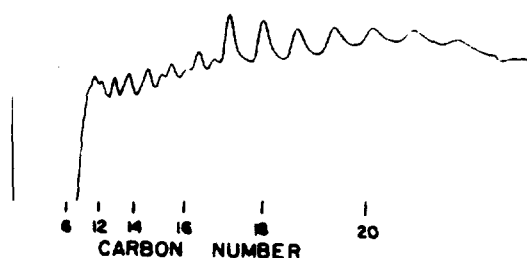


FIG. C RESIDUE OF 1 DAY AGED CRUDE OIL

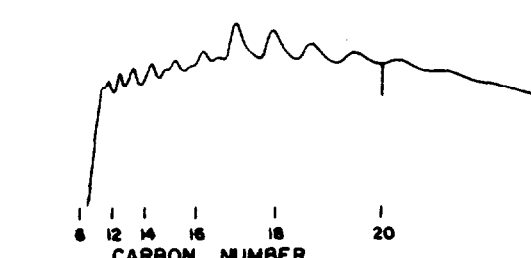


FIG. D RESIDUE OF 2 DAYS AGED CRUDE OIL

FIG. 6-HA GAS CHROMATOGRAPHIC ANALYSIS OF LLOYDMINSTER CRUDE OIL RESIDUE

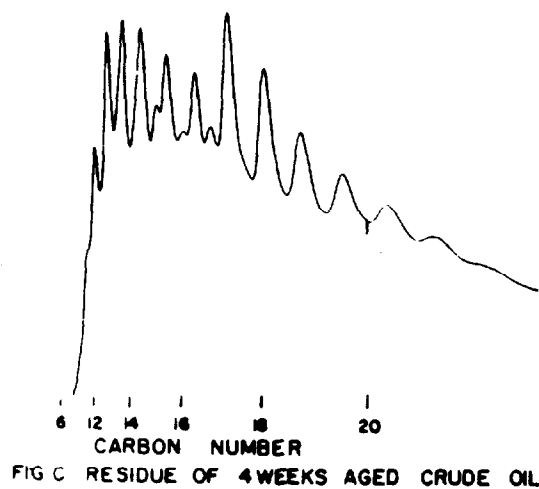
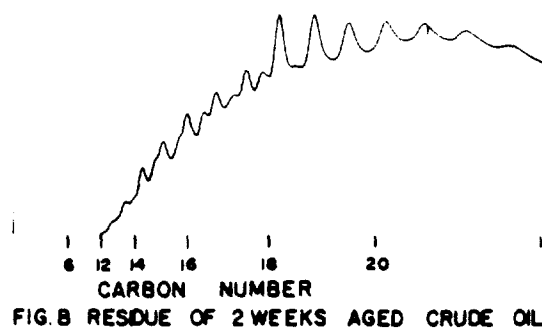
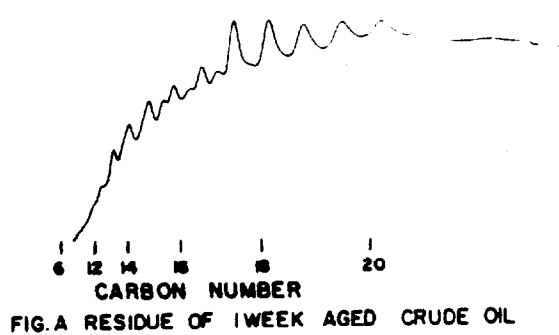


FIG.6-II B GAS CHROMATOGRAPHIC ANALYSIS OF LLOYDMINSTER CRUDE OIL RESIDUE

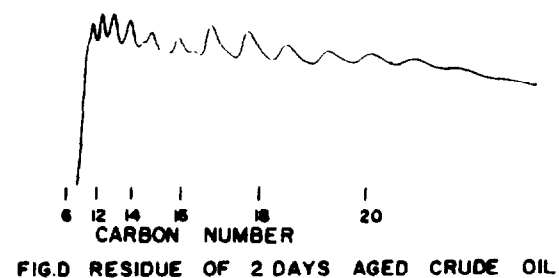
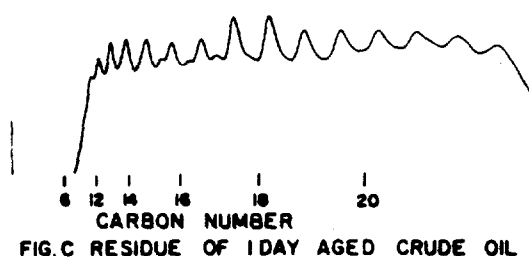
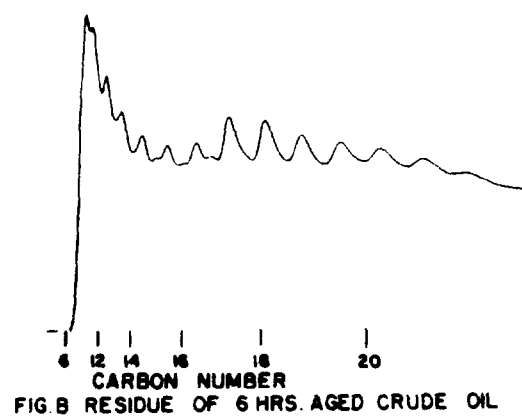
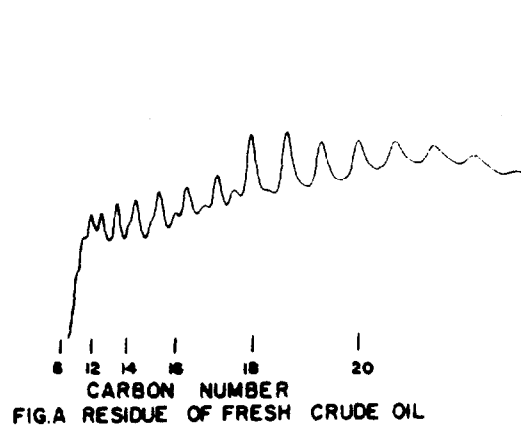


FIG. 6-12A GAS CHROMATOGRAPHIC ANALYSIS OF BOW RIVER CRUDE OIL RESIDUE

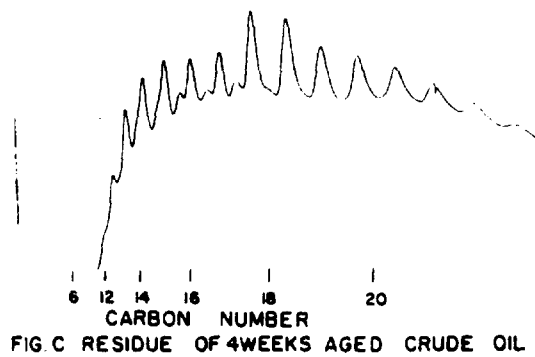
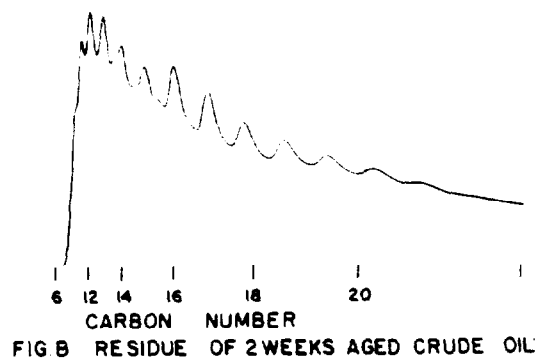
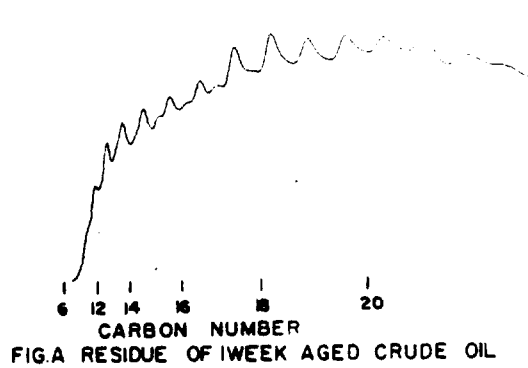


FIG 6-12B GAS CHROMATOGRAPHIC ANALYSIS OF BOW RIVER CRUDE OIL RESIDUE

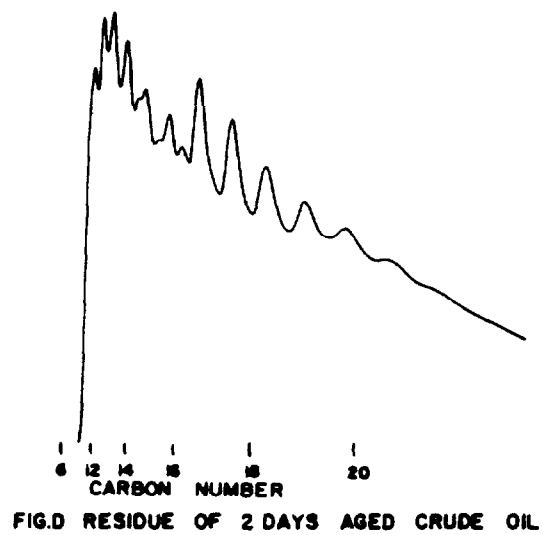
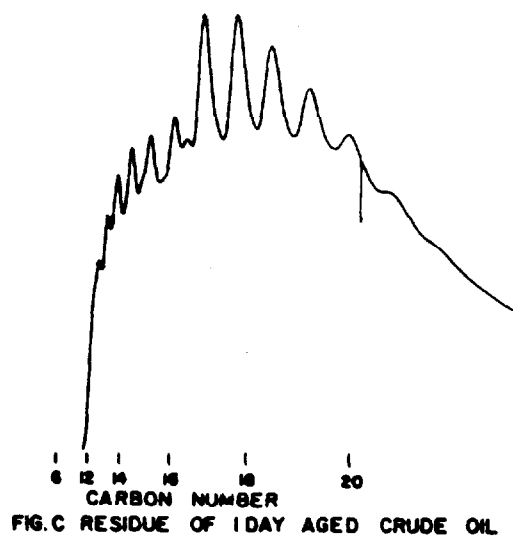
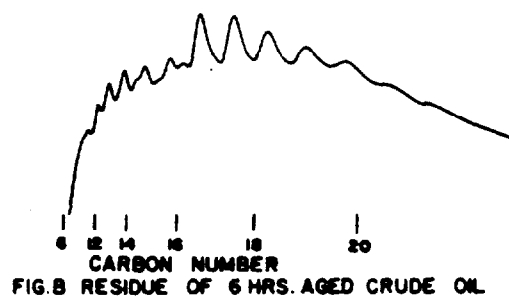
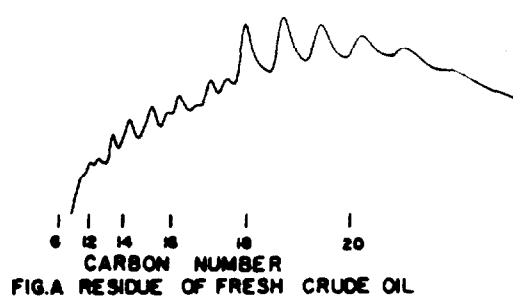


FIG.6-13A GAS CHROMATOGRAPHIC ANALYSIS OF NORMAN WELLS CRUDE OIL RESIDUE

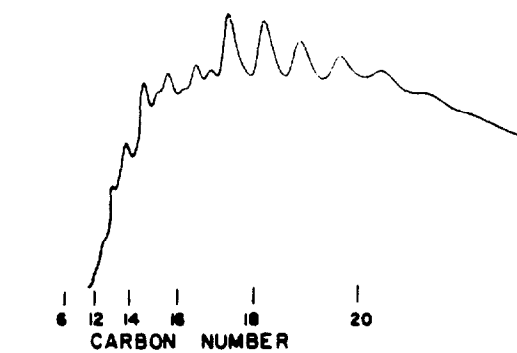


FIG. A RESIDUE OF 1 WEEK AGED CRUDE OIL

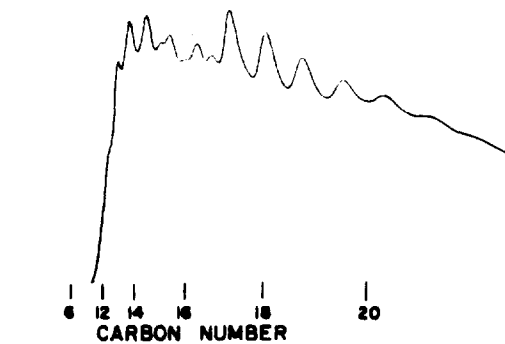


FIG. B RESIDUE OF 2 WEEKS AGED CRUDE OIL

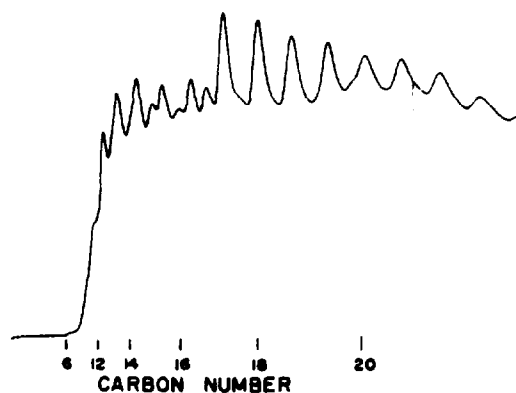


FIG. C RESIDUE OF 4 WEEKS AGED CRUDE OIL

FIG.6-13B GAS CHROMATOGRAPHIC ANALYSIS OF NORMAN WELLS CRUDE OIL RESIDUE

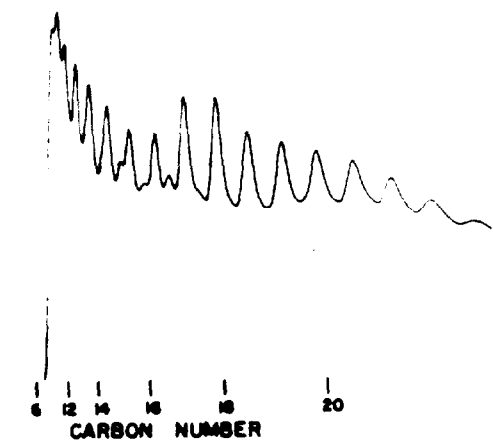


FIG.A RESIDUE OF FRESH CRUDE OIL

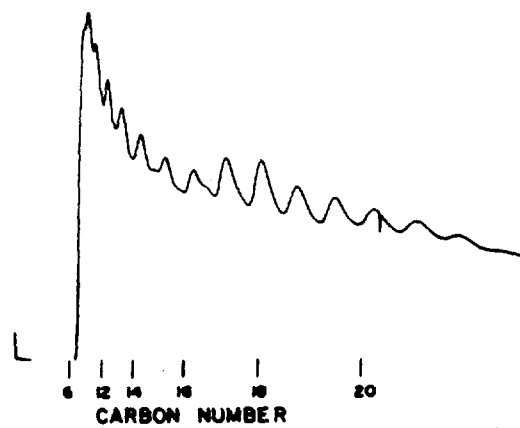


FIG.B RESIDUE OF 6 HRS. AGED CRUDE OIL

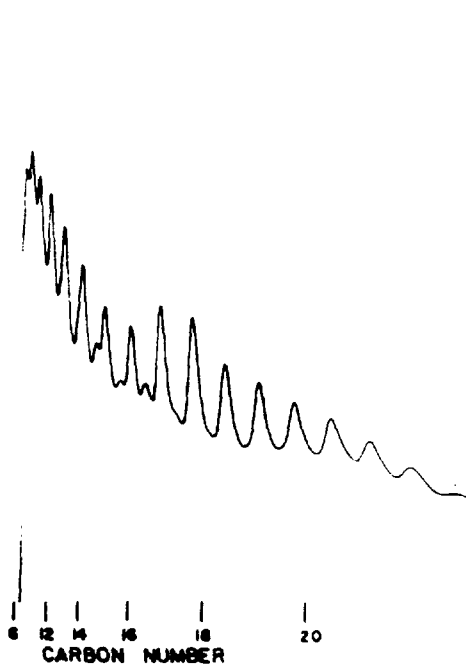


FIG.C RESIDUE OF 1 DAY AGED CRUDE OIL

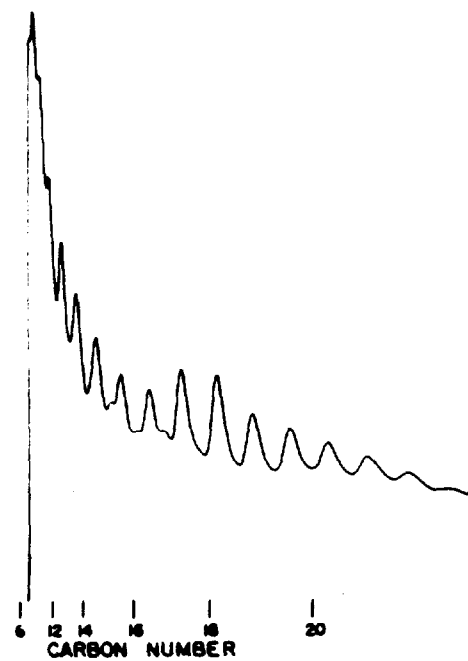


FIG.D RESIDUE OF 2 DAYS AGED CRUDE OIL

FIG.6-14A GAS CHROMATOGRAPHIC ANALYSIS OF WEYBURN-MIDALE CRUDE OIL RESIDUE

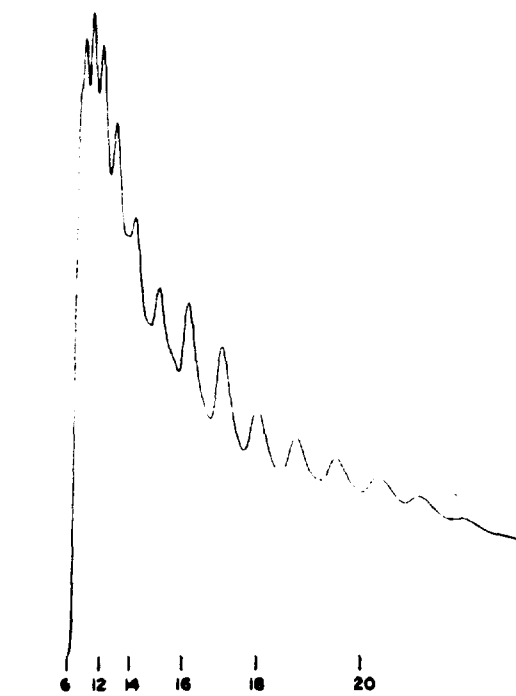


FIG. A RESIDUE OF 1WEEK AGED CRUDE OIL

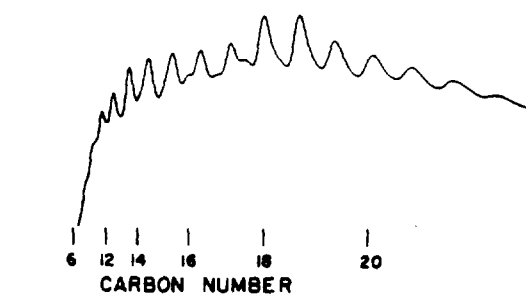


FIG. B RESIDUE OF 2WEEKS AGED CRUDE OIL

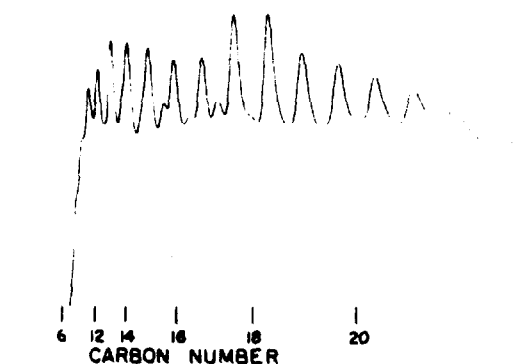


FIG. C RESIDUE OF 4WEEKS AGED CRUDE OIL

FIG.6-14B GAS CHROMATOGRAPHIC ANALYSIS OF WEYBURN-MIDALE CRUDE OIL RESIDUE

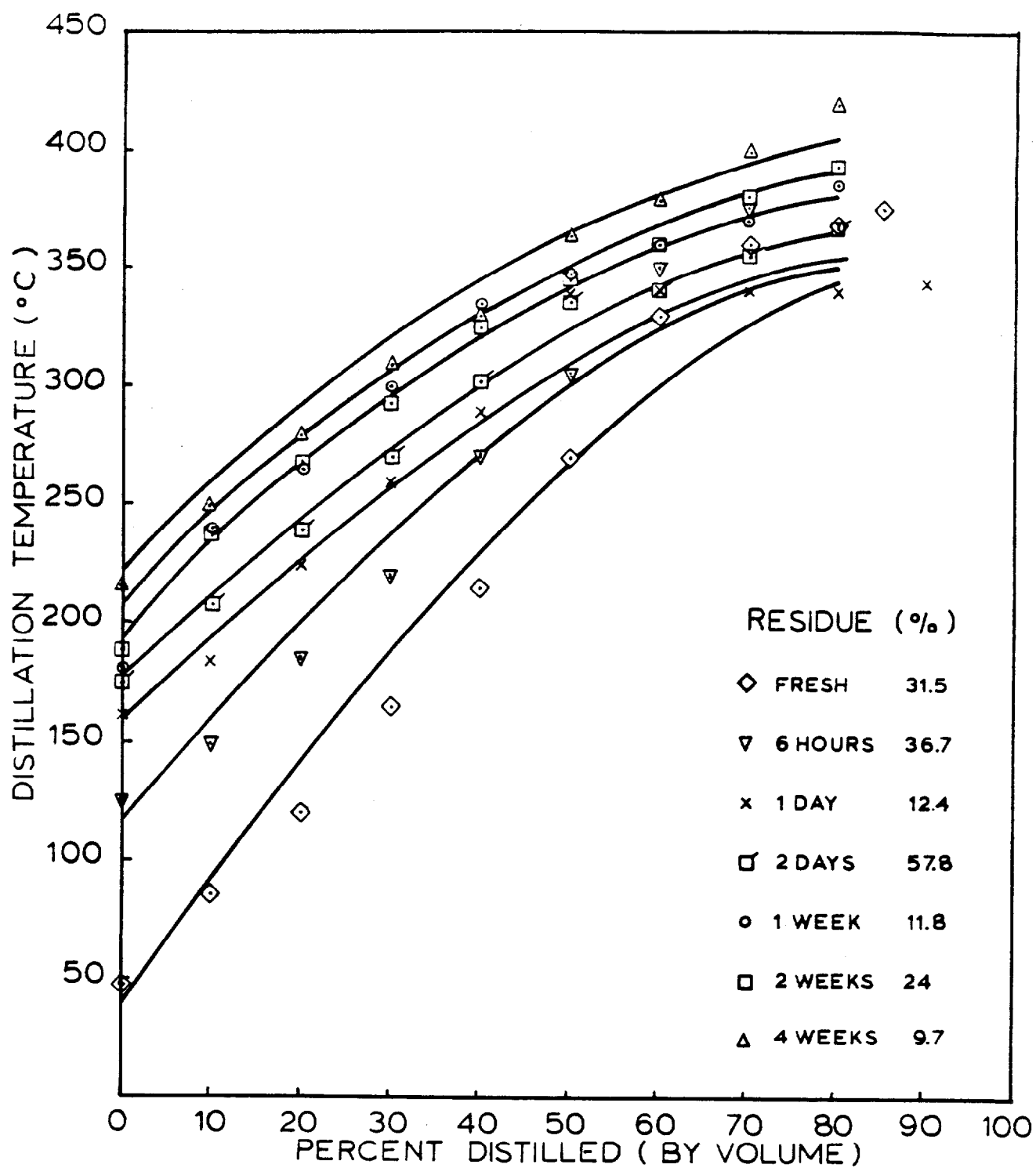


FIGURE 7A. DISTILLATION CURVES FOR NORMAN WELLS CRUDE

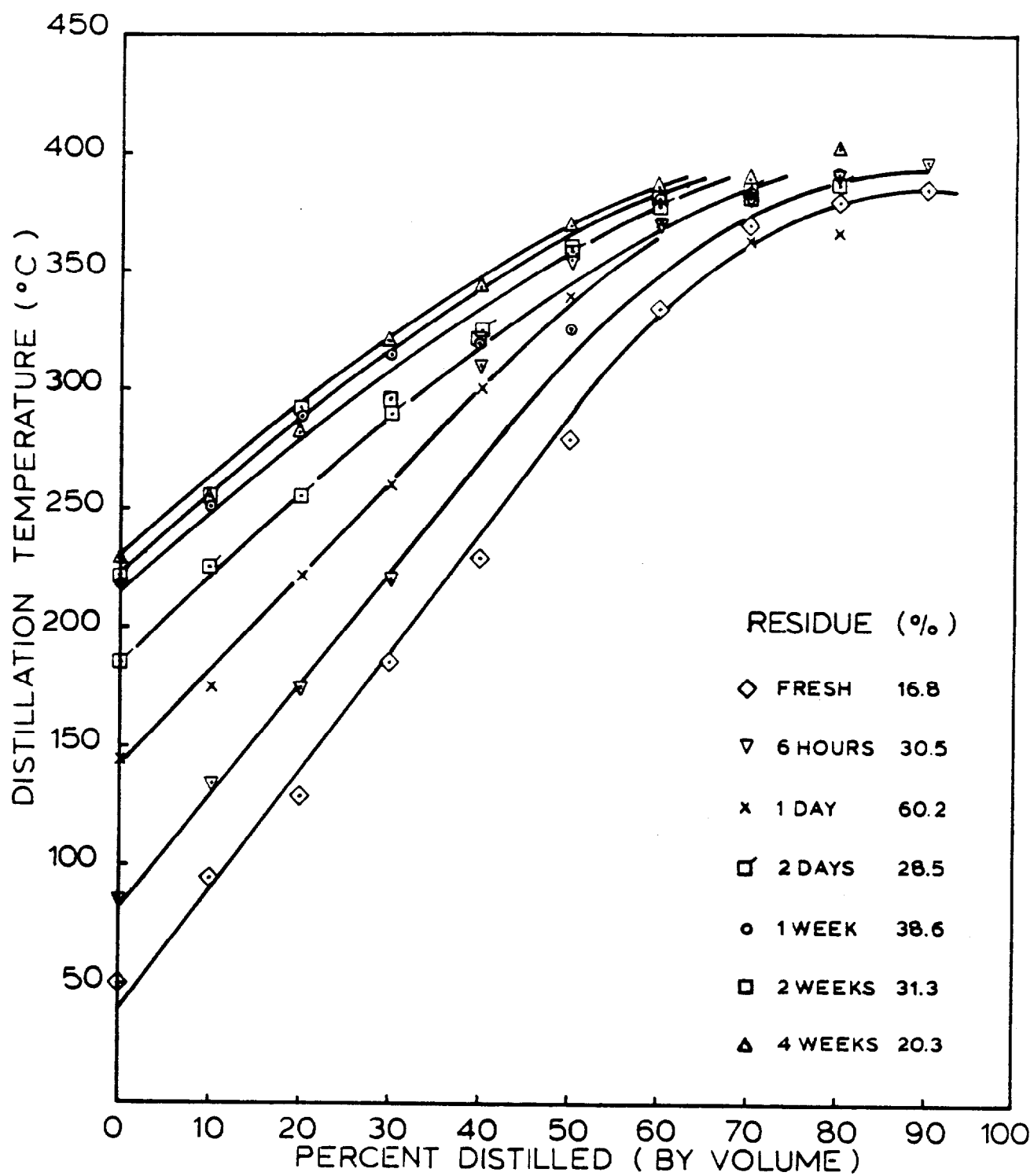


FIGURE 7 B. DISTILLATION CURVES FOR SWEET
BLEND CRUDE

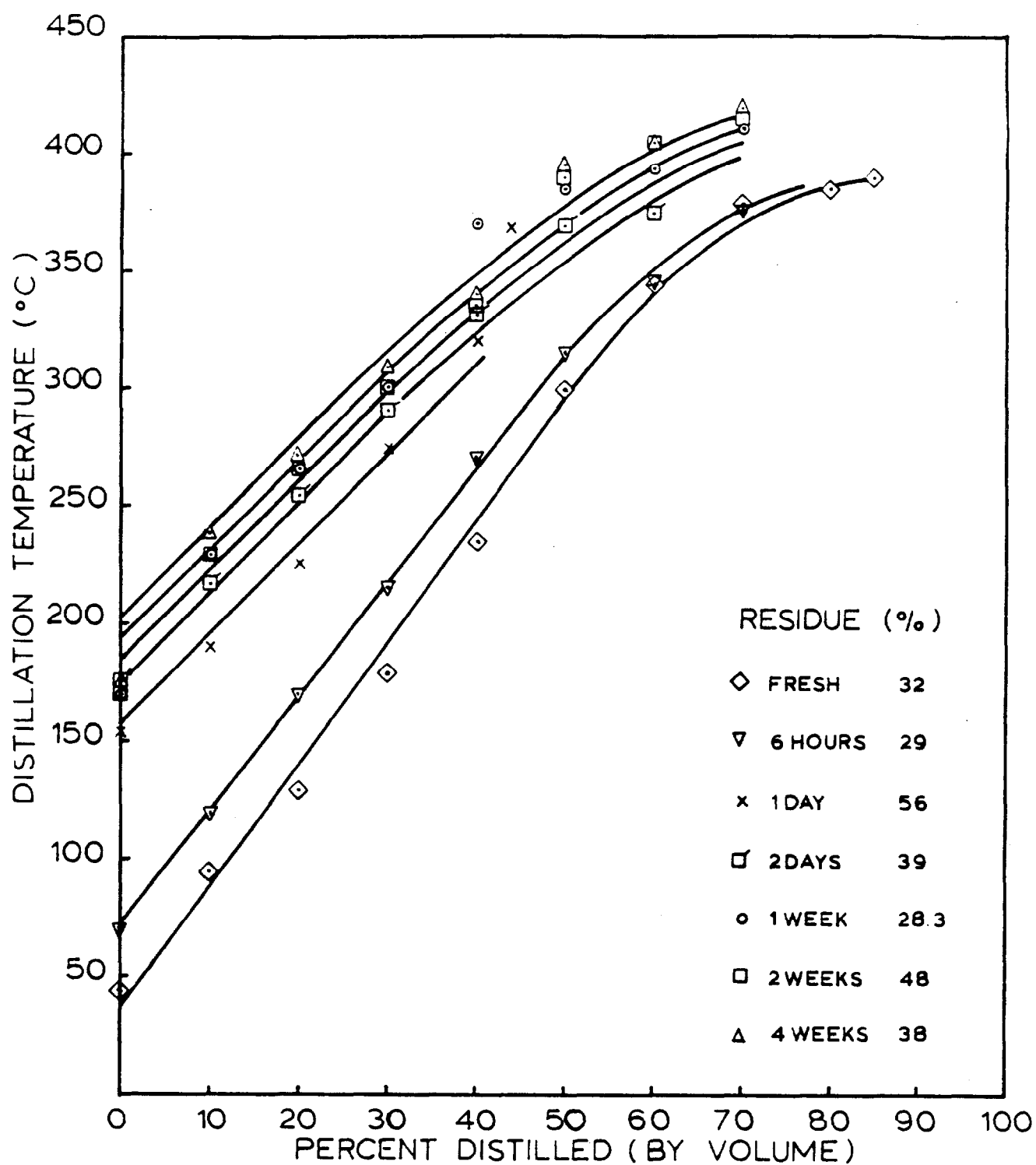


FIGURE 7C. DISTILLATION CURVES FOR SOUR BLEND
CRUDE

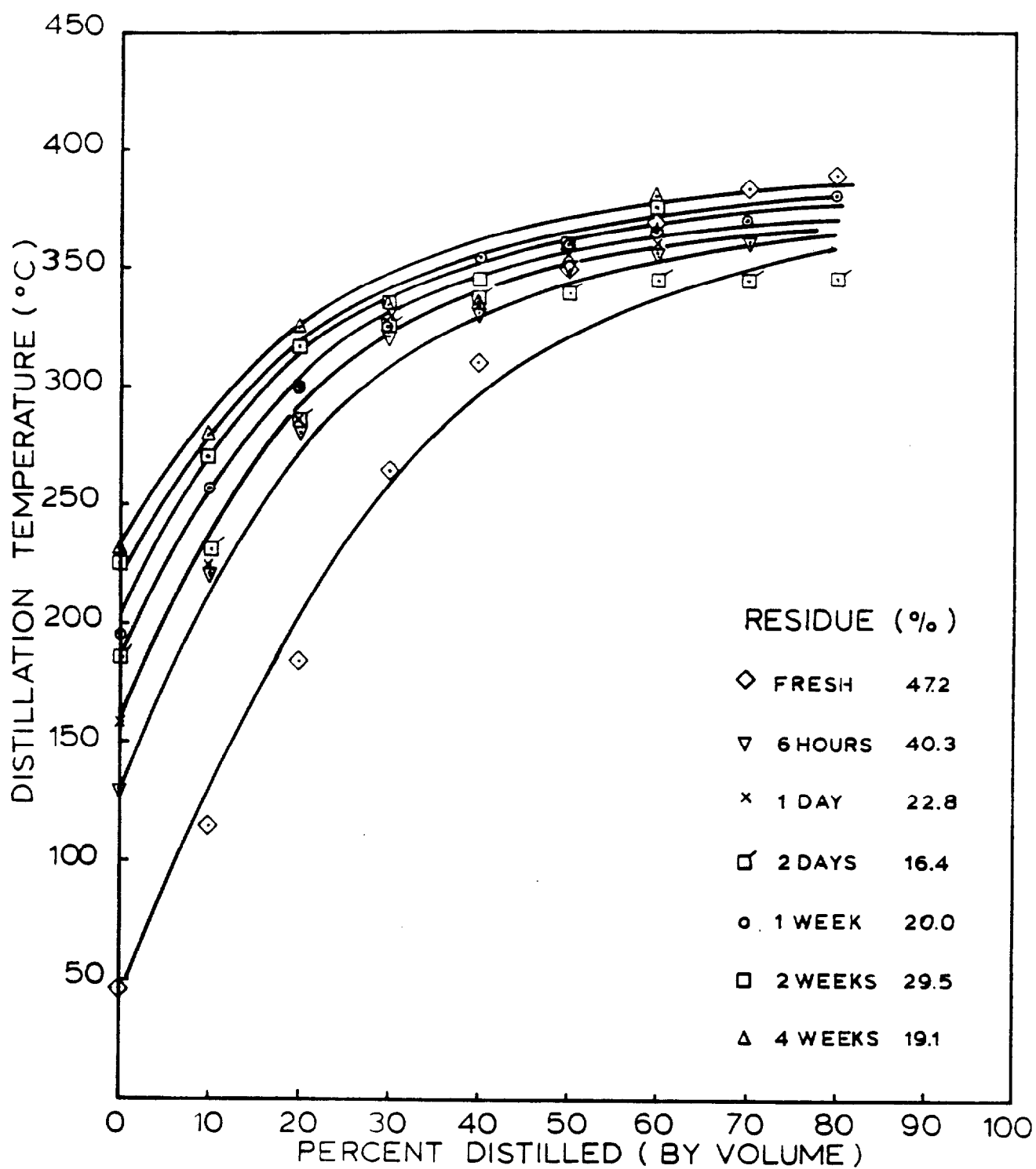


FIGURE 7 D. DISTILLATION CURVES FOR BOW
RIVER CRUDE

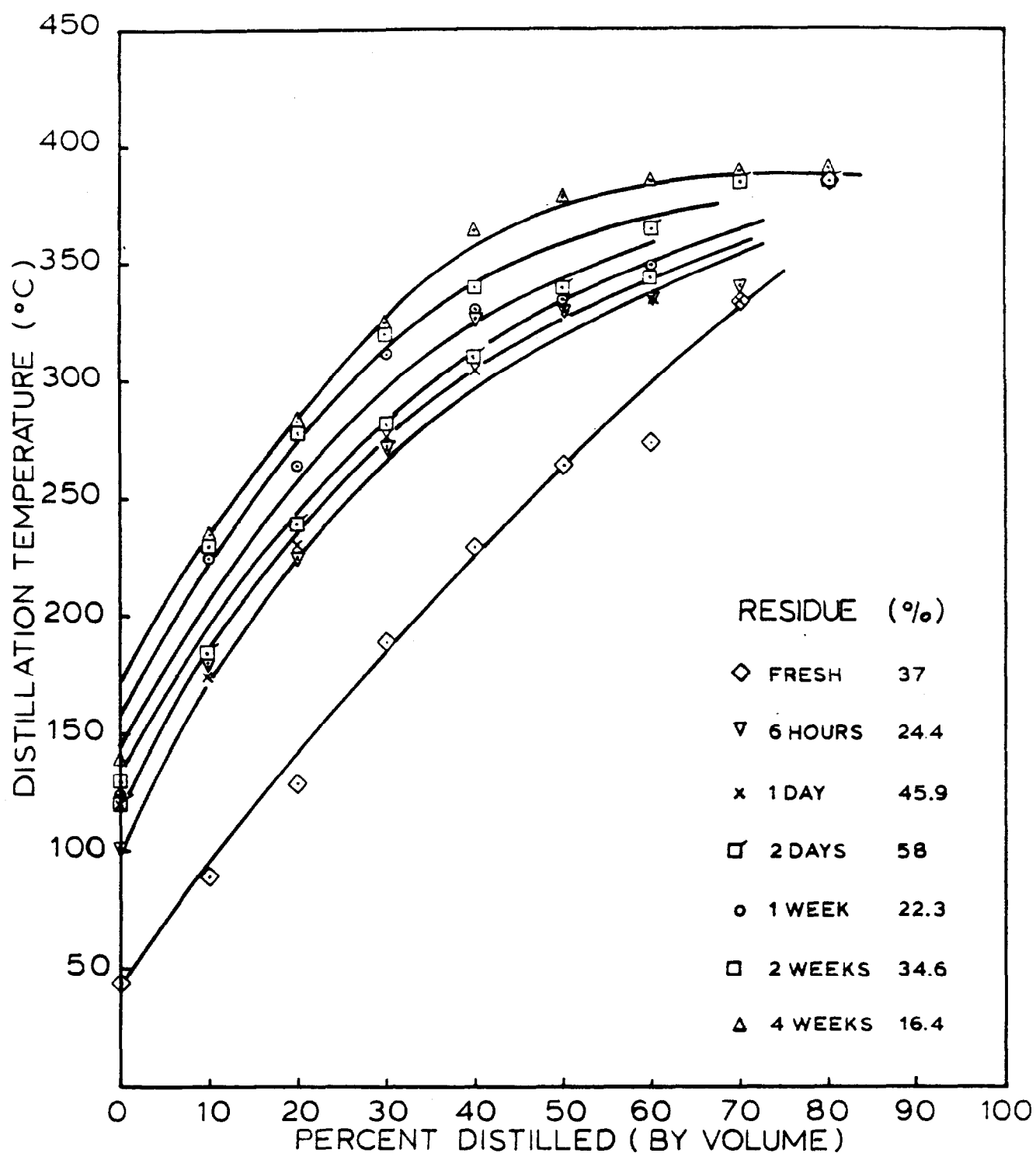


FIGURE 7 E. DISTILLATION CURVES FOR WEYBURN-MIDALE CRUDE

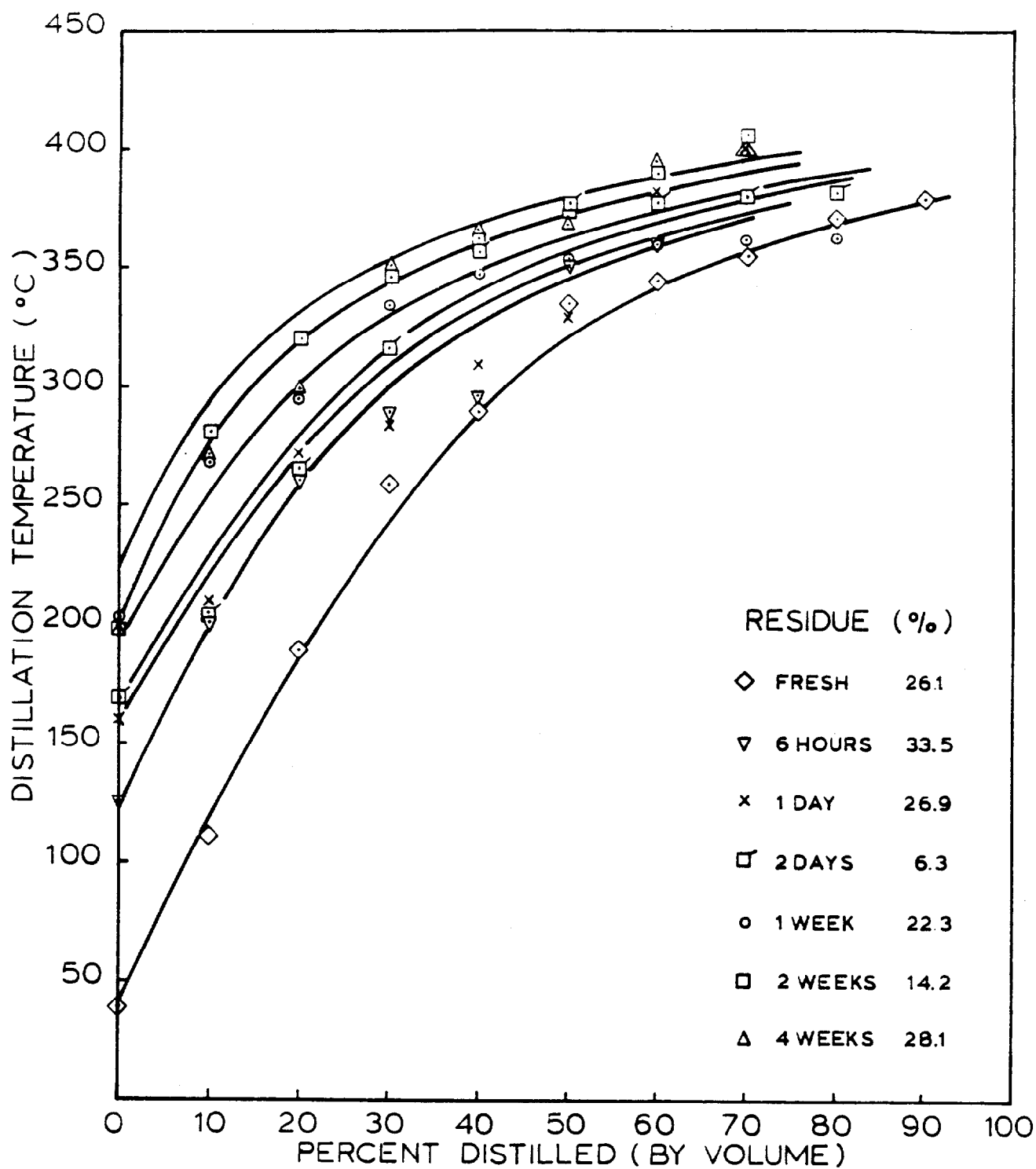


FIGURE 7 F. DISTILLATION CURVES FOR LLOYDMINSTER
CRUDE

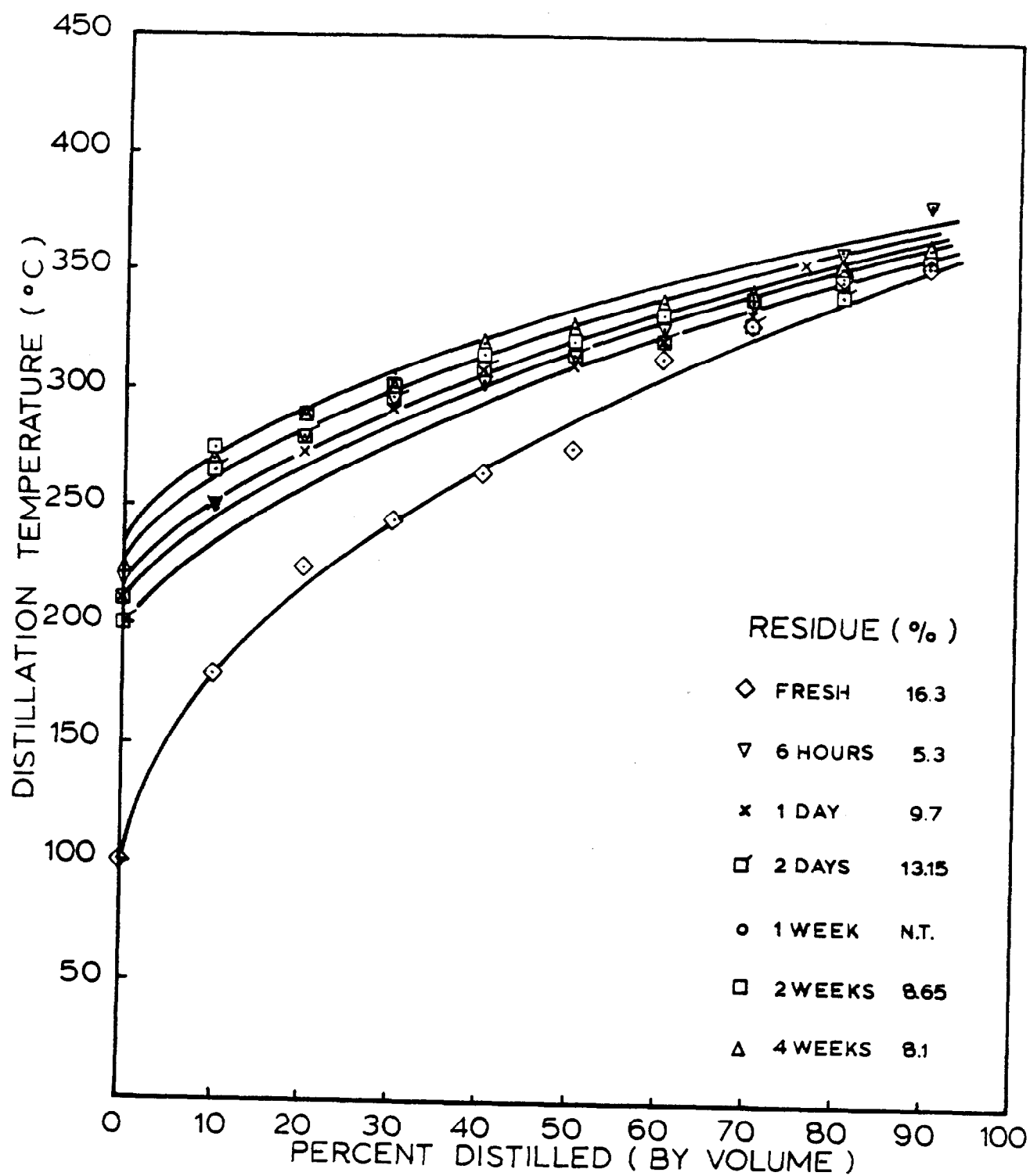


FIGURE 7 G. DISTILLATION CURVES FOR MARINE DIESEL FUEL

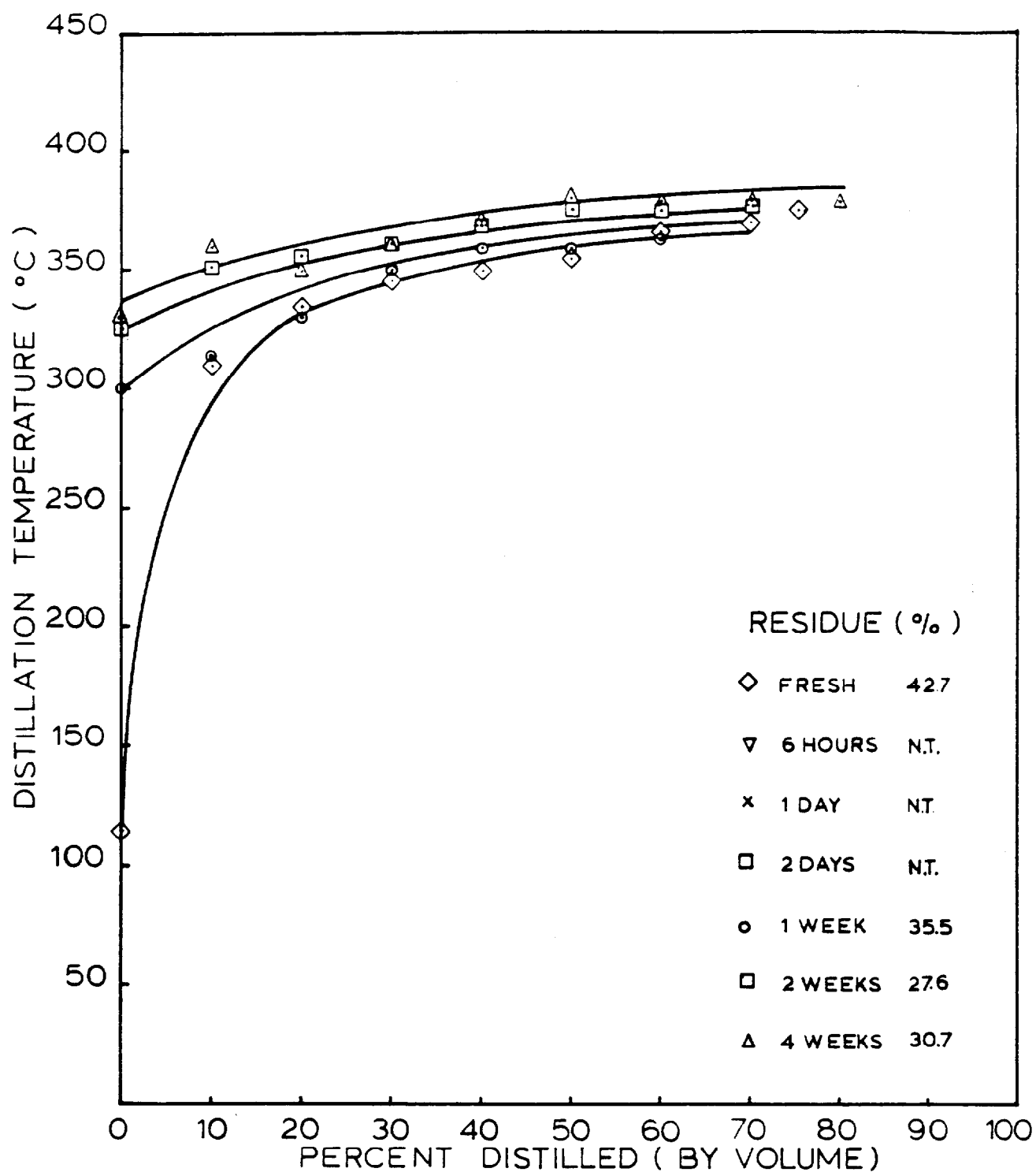


FIGURE 7H. DISTILLATION CURVES FOR BUNKER C FUEL OIL

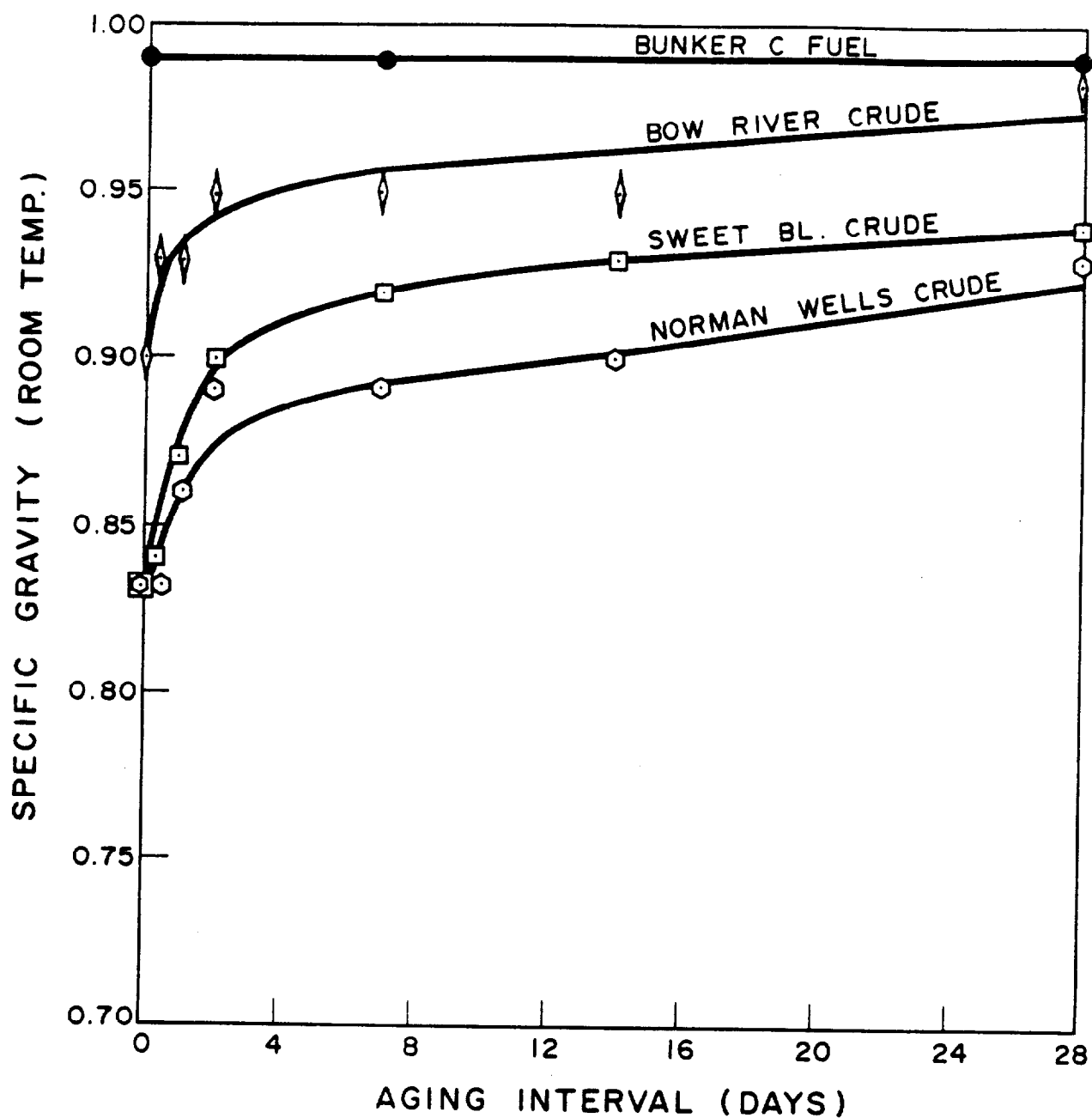


FIGURE 8A — SPECIFIC GRAVITY
vs. AGING INTERVAL

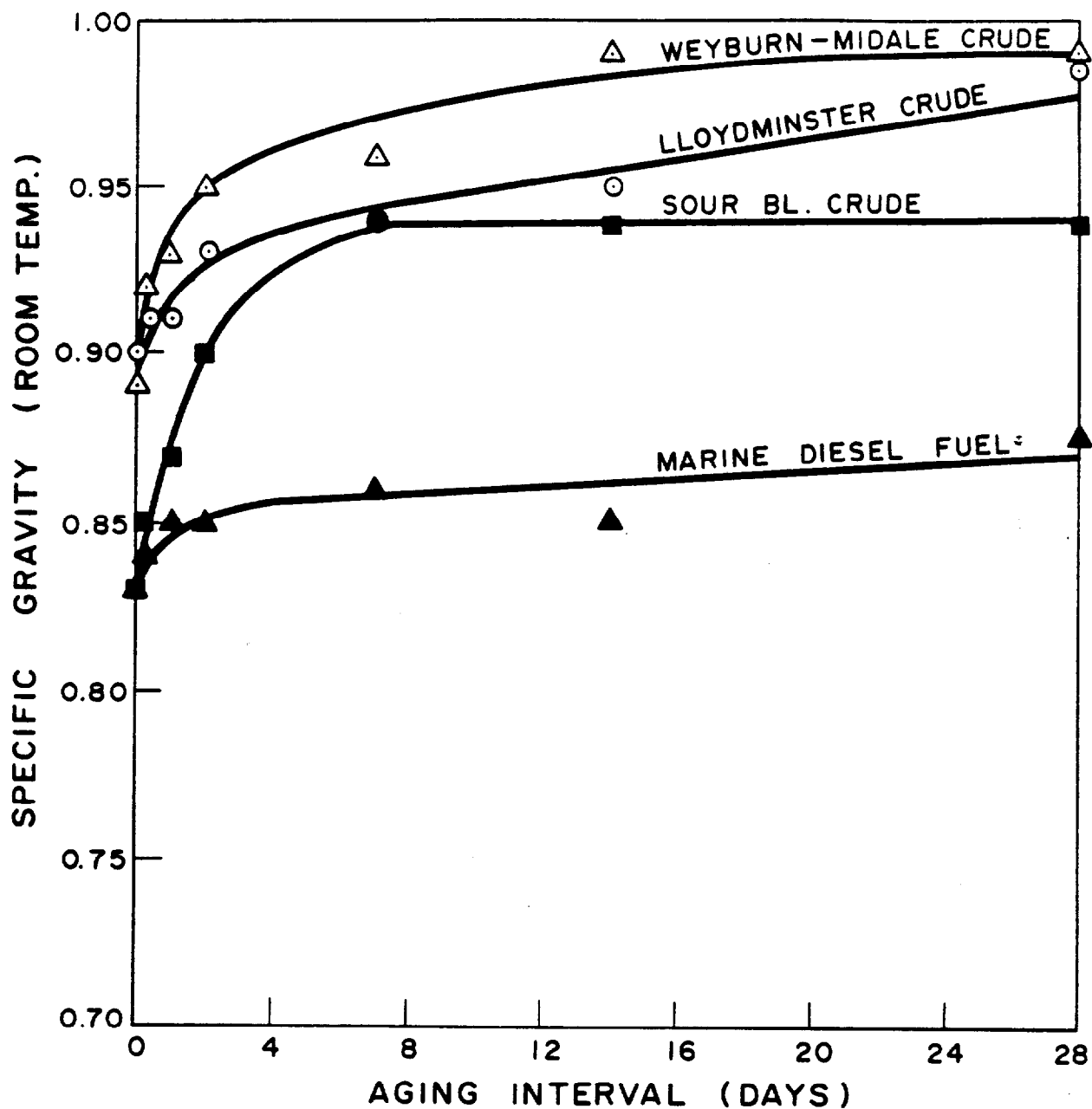


FIGURE 8B — SPECIFIC GRAVITY
vs. AGING INTERVAL

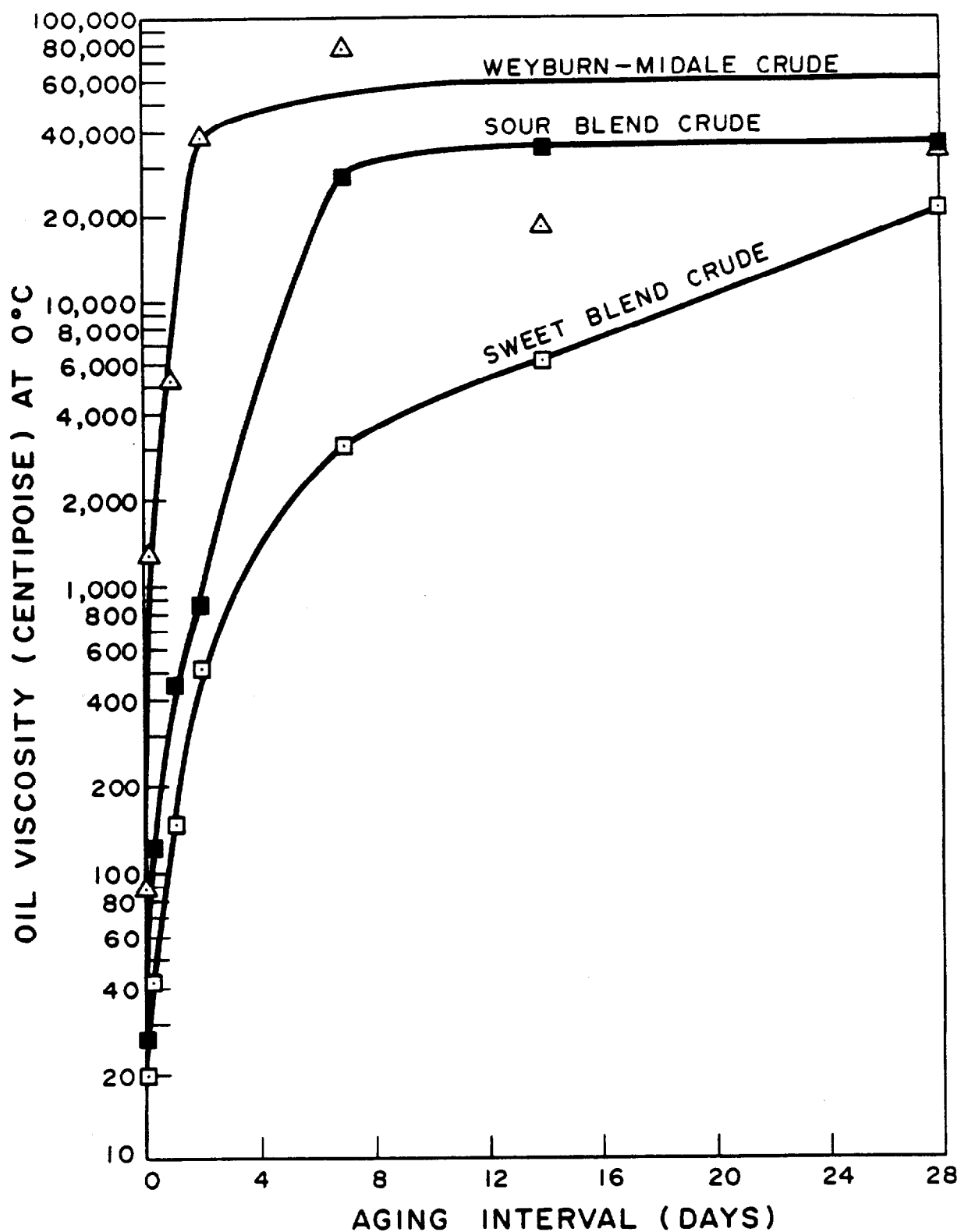


FIGURE 9A — OIL VISCOSITY (AT 0°C)
vs. AGING INTERVAL

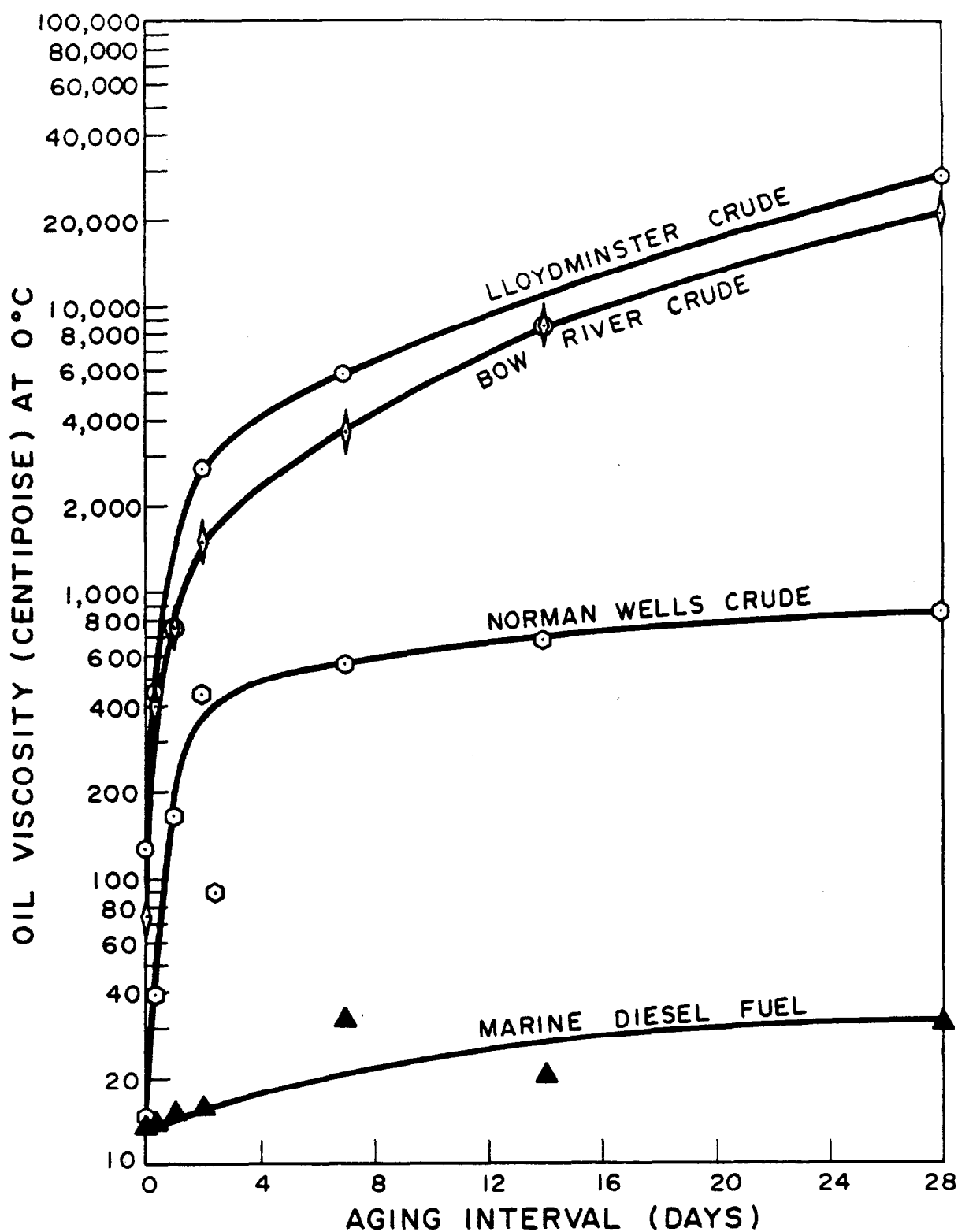


FIGURE 9B—OIL VISCOSITY (AT 0°C)
vs. AGING INTERVAL

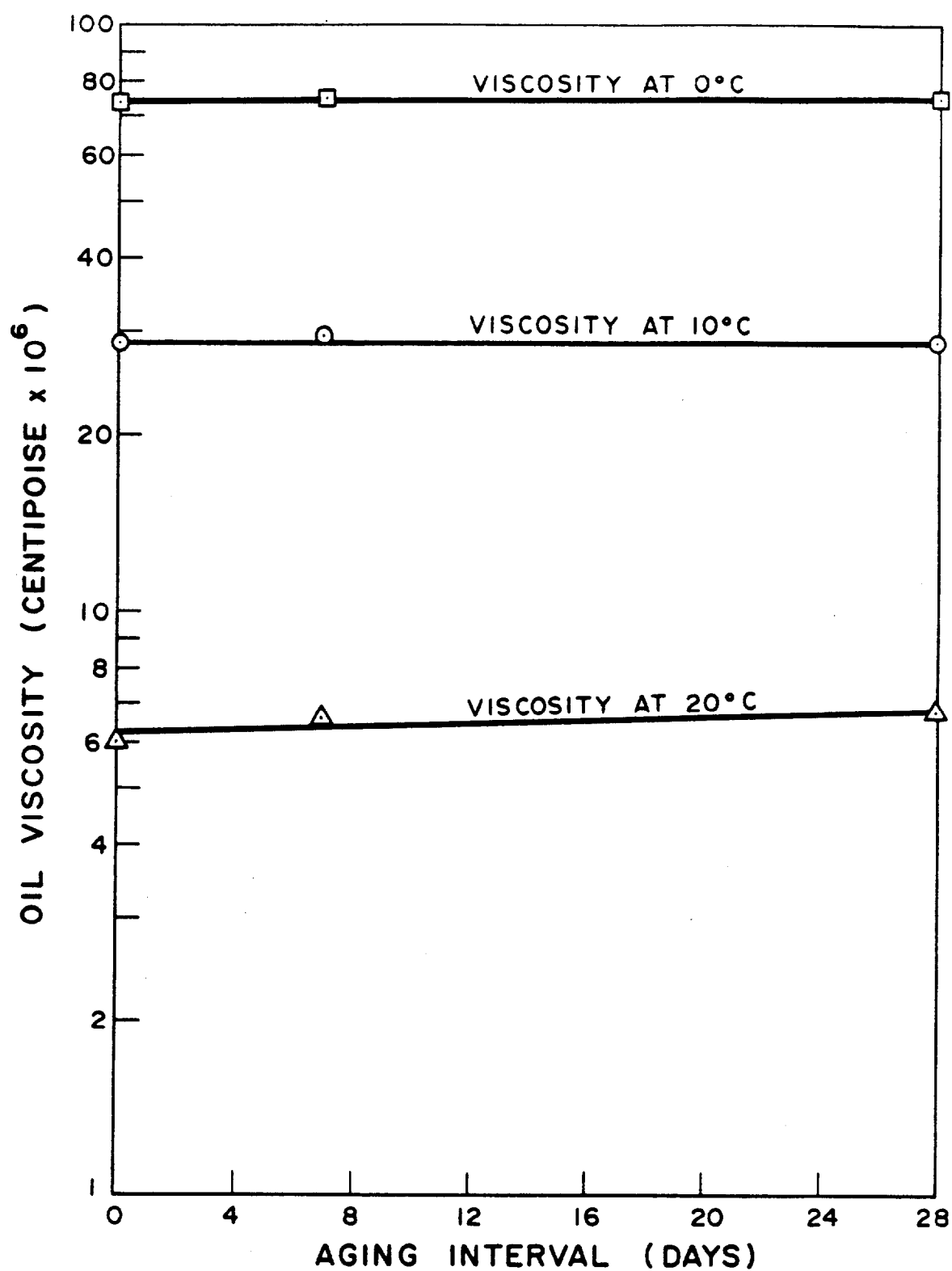


FIGURE 10—BUNKER C FUEL VISCOSITY
vs. AGING INTERVAL

4 CONCLUSIONS

1. Rain can be entrained into oil layers, and water entrained in this manner led to the formation of water-in-oil (W/O) emulsions with the crude oils and Bunker-C fuel oil.

2. The aging of oil slicks in the Arctic (or under climatic conditions similar to those encountered in the Arctic) occurs on a much different time scale than the aging of oil slicks in more southerly locations.

3. Under the weather conditions prevailing during this study, the evaporative loss of hydrocarbons (mostly within the C_4 to C_{14} range) from the crude oil layers was most significant during the aging intervals of 6 hours, 1 day, and 2 days. For longer aging intervals (1 week, 2 weeks, and 4 weeks), hydrocarbon evaporation from the crude oil layers occurred at much lower rates. Hydrocarbon evaporation from layers of marine diesel fuel oil and Bunker-C fuel oil was a relatively insignificant process under the prevailing weather conditions, due mainly to the low percentage of volatile hydrocarbons in these fuel oils.

4. Hydrocarbon evaporation during the aging intervals resulted in significant increases in the viscosity values and pour point values of the crude oils, and a notable reduction in the combustibility (i.e., higher flash and fire point values) of the crude oils. For marine diesel fuel oil and Bunker-C fuel oil, the properties of viscosity, pour point and combustibility (as observed by flash and fire point determinations) were not significantly altered over aging intervals of up to 4 weeks.

5. In general, the crude oils aged for intervals of 6 hours or longer were not as readily wicked (by 3M Brand Oil Sorbent) as the fresh crude oils. Marine diesel fuel oil was easily wicked by 3M Brand Oil Sorbent, and the amount of this oil that could be wicked by this sorbent was relatively independent of the intervals (ranging up to 4 weeks) over which the oil was aged.

6. In situ combustion was possible for confined slicks of the crude oils, marine diesel fuel oil, and Bunker-C fuel oil, even when these oils were aged for intervals of up to 4 weeks. For a given oil type, the minimum ignitable thickness of the oil layer is a function of the strength of the igniter (or ignition source) employed. The minimum ignitable thicknesses for layers of aged crude oils and marine diesel fuel oil ranged between 3 and 4 mm, when a solid fuel igniter was employed, and when fresh crude oil was added to assist slick ignition (the minimum ignitable thicknesses for these oils would probably be between 3 and 4 mm without a primer if a more powerful igniter was employed). Without assistance by the addition of fresh crude oil, it is felt that the minimum ignitable thickness for slicks of aged crude oils and marine diesel fuel oil is approximately 5 mm. The minimum ignitable thickness for layers of Bunker-C fuel oil range between 4 and 5.5 mm, when a solid fuel igniter was employed, and when slick ignition was assisted by adding fresh crude oil. Without the addition of fresh crude oil, it is estimated that the minimum ignitable thickness for layers of Bunker-C fuel oil would be approximately 10 mm, when a solid fuel

igniter was employed. The thicknesses of the residual oil layers remaining after the combustion of the crude oils and marine diesel fuel oil ranged between 0.3 and 0.85 mm. The thicknesses of the residual oil layers remaining after the combustion of Bunker-C fuel oil ranged between 1.63 and 2.63 mm.

5 SUGGESTIONS FOR FUTURE RESEARCH

1. Research should be directed towards establishing the effects of rainfall and snowfall upon the aging (or "weathering") of oil layers.

2. Quantitative work should be undertaken to study the aging (or "weathering") of marine oil slicks in rough weather conditions (i.e., in the presence of waves and white caps).

3. The aging (or "weathering") of oil layers under snow should be investigated quantitatively.

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PART II: A STUDY TO INVESTIGATE THE CHARACTERISTICS AND
COMBUSTION OF PETROLEUM (W/O) EMULSIONS

1 A REVIEW OF THE FORMATION AND PROPERTIES OF PETROLEUM EMULSIONS

1.1 General Aspects of Emulsions

The study of emulsions and emulsification represents a division of colloid science, which is consequently linked to the field of surface chemistry. An appropriate definition of an emulsion is a coarse dispersion of mutually immiscible liquids (Hatschek, 1925 and Becher, 1955). In an emulsion, droplets of one phase (the dispersed phase) are encapsulated within sheaths of another phase (known as the continuous phase). The dispersed phase can also be defined as the "internal phase", and the continuous phase defined as the "external phase" (Lissant, 1974). Two basic forms of emulsions are possible for oil-water mixtures:

- (1) oil-in-water (O/W) emulsions, in which oil droplets are encapsulated within sheaths of water
- (2) water-in-oil (W/O) emulsions, in which water droplets are encapsulated within sheaths of oil.

It has been generally concluded that three basic conditions must be met in order for a stable emulsion to form between two liquids:

- (a) the two liquids must be immiscible (or mutually insoluble with each other)
- (b) sufficient agitation (or mechanical energy) must be applied to disperse one liquid into the other
- (c) an emulsifying agent (or emulsifier) must be present.

One manner of examining the emulsification process is to consider the forces of interfacial tension between two immiscible liquids. Before emulsification (considering simply a layer of liquid A floating above a layer of liquid B), it can be said that the interfacial area between the two liquids is at a minimum. Here, the interfacial area is essentially determined by the surface tension values of the two liquids. Following emulsification, it shall be assumed that droplets of liquid A are dispersed into liquid B. If all droplets are considered, it can be seen that the interfacial area between liquids A and B is increased. Since liquids tend to keep their surfaces to a minimum, an emulsifying agent and work (or energy) are clearly required to allow emulsification to occur. In theory, the amount of work (ω) required to increase the surface area by an amount S can be given by the following formula (Becher, 1955):

$$\omega = \gamma \Delta S ,$$

where γ is the interfacial tension between the two liquids. The emulsifying agent may be a surface-active substance, which forms a thin interfacial film between liquid A and B in an emulsion, and maintains the emulsion by minimizing the contact and aggregation of liquid droplets of A. The emulsifying agent is therefore required to stabilize an emulsion, and has been noted to exhibit several important characteristics (Shawmont Newfoundland, 1978):

- reduce the interfacial tension between the liquids to approximately 5 dynes/cm for emulsions to be prepared with agitation, and to approximately 0.5 dyne/cm for emulsions to be prepared without intense agitation
- quickly absorb around the dispersed droplet as a condensed, non-adhered film
- have a specific molecular structure, in which the polar end is attracted to water, and the non-polar end is attracted to oil
- be relatively more soluble in the continuous (or external) phase, so that it can be readily available for adsorption around the dispersed (or internal) phase.
- impart an electrokinetic potential
- influence the viscosity of the emulsion formed
- usually enable emulsification while being present in relatively small quantities.

From a thermodynamic point of view, many emulsions are considered to be unstable (Wagner, 1976). The stability of emulsions is a significant factor that is not yet fully understood. Emulsion stability can be either increased or decreased by the addition of chemical substances (i.e., soaps containing monovalent ions can stabilize O/W emulsions, whereas soaps containing polyvalent ions can stabilize W/O emulsions). Emulsion stability can also be considered in terms of the packing density of dispersed droplets within the continuous phase, if one imagines the dispersed phase to consist of uniform rigid spheres. In experiments performed with benzene-in-water emulsions (Lissant, 1974), it is suggested that an increase in the packing density (ϕ) of the dispersed phase results in a destabilization of this emulsion. Phase changes (with respect to either the dispersed or the continuous phase) may greatly reduce emulsion stability. For example, it is common knowledge that emulsions are rendered unstable upon heating. Emulsions exposed to freeze/thaw cycles may also undergo phase changes that result in their destabilization. Becher has described three general destabilization processes that can occur with emulsions:

- (i) Creaming. In this process, an emulsion segregates into two separate emulsions, one richer in the dispersed

(or internal) phase than the original, and the other leaner in the dispersed phase than the original emulsion.

(ii) Inversion. In this process, an emulsion is suddenly transformed into an emulsion of the opposite type. The inversion process would transform an oil-in-water (O/W) emulsion into a water-in-oil (W/O) emulsion, or transform a W/O emulsion into a O/W emulsion.

(iii) Demulsification. This process results in the complete breaking of an emulsion. It has been noted that demulsification has been accompanied by the processes of creaming and inversion.

The creaming process can be considered analogous to Stokes Law, in which the sedimentation rate (μ) of a spherical particle in a viscous liquid is given by the following equation:

$$\mu = 2g r^2 \frac{(d_1 - d_2)}{9\eta}$$

where: g = the acceleration due to gravity

r = the particle radius

d_1 = the density of the particle

d_2 = the density of the liquid

η = the viscosity of the liquid.

Becher has considered the demulsification process in terms of two sequential stages, namely flocculation and coalescence. Flocculation was defined as a reversible stage, during which the droplets of the dispersed (or internal) phase aggregate. Coalescence was defined as an irreversible process, during which the aggregated droplets combine to form a single drop.

1.2 General Aspects of Petroleum Emulsions

As with the general study of emulsions, the scientific investigation of petroleum emulsions is in its initial stages, and has still left unanswered many questions concerning their formation, stability, properties, and ultimate methods for their disposal. Since these aspects of emulsions can vary significantly with environmental conditions and the type of petroleum concerned, the lack of solid quantitative data in this area is not surprising. Unfortunately, most of the work performed on petroleum emulsions has not been concerned with the Arctic environment. In this review, the term "petroleum" is used in reference to crude oils and fuel oils (such as diesel or Bunker C). Following an oil spill in a marine environment, it is generally accepted that both water-in-petroleum (W/O) and petroleum-in-water (O/W) emulsions can be formed. It has been claimed that both types of

emulsions are likely to form, unless the oil spill is close to the shore, or over extremely calm waters (Chen, 1973). Unrefined oils generally have a higher portion of W/O emulsifying agents than O/W emulsifying agents. For such oils spilled in a marine environment, the majority of the emulsions formed would be of the W/O type.

Petroleum-in-water emulsions arising from oil spills are reported to be rendered stable by various hydrophilic groups of molecules present in unrefined petroleum (Chen, 1973). In experiments performed with O/W emulsions prepared from 6 crude oils, Chen noted that the O/W emulsions prepared were fairly stable when sufficient mixing energy was applied. Chen also noted that the stabilized emulsions had dispersed oil concentrations ranging between 10^{-5} and 10^{-3} (by volume), and that the dispersed droplets had sizes less than 4 μm . With O/W emulsions prepared with California crude, the effects of shear rate, temperature, and oil concentration upon emulsion stability were studied (Mao/Marsden, 1977). From this work, it was observed that increases in temperature and/or oil concentration in an emulsion favoured the inversion of the O/W emulsions to W/O emulsions. Mao and Marsden also claim that increasing the shear stress (through pumping rates) also resulted in the inversion of O/W emulsions into W/O emulsions. It has been noted that petroleum-in-water emulsions would disperse readily in an oil spill situation (Shelton, 1969 and Frankenfeld, 1973). It is felt that these emulsions would not pose a significant problem in an oil spill cleanup operation.

Water-in-petroleum emulsions have been noted to be extremely stable. The asphaltene substances and porphyrin complexes present in unrefined oils have generally been considered as natural emulsifying agents for such emulsions (Berridge et al., 1968, Berridge et al., 1968a, Cairns et al., 1974, Canevari, 1969, and Frankenfeld, 1973). With respect to W/O emulsions obtained from oilfields, it has been mentioned (University of Texas, 1974) that carbon, various salts, organic acids, clays, and finely-divided solids may also serve as emulsifying agents. Water-in-petroleum emulsions are known to be extremely stable and persistent (such emulsions created after an oil spill have often been referred to as "chocolate mousses"). Since water-in-petroleum emulsions are considered to be the major type of emulsion to be formed during an oil spill, this review will be concerned primarily with this type of emulsion.

1.3 Significant Aspects of Water-in-Oil (Petroleum) Emulsion Formation

In the past, petroleum emulsions have been encountered in the following situations:

- (1) Petroleum production operations in oilfields.
- (2) Oil spill incidents in marine environments.

With respect to the first situation, it has been claimed (Blair, 1960) that the water content of naturally occurring petroleum emulsions commonly ranges between 5 and 40 percent, and that the dispersed water droplets can range

between 10 and 100 μ in diameter. From data obtained from recent oil spill incidents and experiments (shown in Tables #1 and #2, respectively), it can be seen that petroleum emulsions as a result of marine oil spills can have a considerable water content range, and can form in relatively short periods of time. With mechanical energy employed during oil spill cleanup operations (from the use of skimmers or pumps, for example), it is quite likely for recovered oil to become further emulsified with water. The maximum percentage of water that could be emulsified with a given petroleum under ideal conditions has not yet been established. According to an analogy based upon the closest packing of spheres (Lissant, 1974), the maximum volume that the dispersed water phase could achieve theoretically would be 74 percent of the total emulsion by volume, assuming that the water droplets are similar to rigid spheres. However, the density of dispersed water droplets in petroleum emulsions cannot serve as the only important parameter in determining the maximum water content of a stable emulsion. Although not quantitatively established, the concentration and effectiveness of the emulsifying agent present, the intensity and duration of mechanical energy applied, temperature, and the interfacial properties of the oil and water concerned are all definitely important parameters that would influence the formation of a petroleum emulsion.

1.3.1 Stability

It has been noted (University of Texas, 1974) that the stability of a petroleum emulsion is dependent upon a variety of parameters, which include the following:

- the emulsifying agent
- viscosity
- specific gravity
- water content
- emulsion age.

With respect to W/O petroleum emulsions, one could define emulsion stability as the resistance that the dispersed water droplets have against coalescing upon contact with each other. Such a definition is based upon the phenomenon of "Brownian movement", in which it is assumed that both oil and water molecules are constantly colliding with the dispersed water droplets and imparting a random motion to them. Thus, an emulsion having a relatively higher specific gravity and viscosity would be relatively more stable, since the movement of water droplets would be theoretically impaired in the emulsion. On the other hand, increase in temperature (or a reduction in the viscosity of a petroleum emulsion) or increases in the concentration of water droplets in the petroleum emulsion would increase the possibility of collision between the water droplets. The ability of an emulsifying agent to prevent the coalescence of the droplets upon contact is essentially dependent upon the durability of the interfacial film that it creates around the water droplets. It has been suggested (University of Texas, 1974)

TABLE #1PETROLEUM EMULSIONS FORMED FOLLOWING SELECTED OIL SPILL INCIDENTS

Date	Incident and Location	Type of Oil Spilled	Reported Water Content of Petroleum (W/O) Emulsion (%)	Reference
March, 1967	Grounding of the tanker TORREY CANYON at the Western entrance to the English Channel	Kuwait crude oil	50-80	Mackay et al., 1973 Stehle, 1970
February, 1970	Grounding of the tanker ARROW near Chedabuto Bay, Nova Scotia	Bunker-C fuel	40	Mackay et al., 1973
August, 1974	Grounding of the super-tanker METULA off the Chilean coast, near Isla Navarino	Bunker-C fuel and light Arabian crude oil	5-10 (dark brown emulsion) 25-30 (light brown emulsion)	Hann, 1977

TABLE #2

PETROLEUM EMULSIONS FORMED DURING SELECTED EXPERIMENTS

Test Location	Oil Type	Maximum Water Content of Petroleum (W/O) Emulsion (%)	Time Required for Maximum Water Content	Reference
Langstone Harbour, Portsmouth, U.K.	Kuwait crude oil residue	50	2 months (Sept.-Nov., 1971)	Davis and Gibbs, 1975
Warren Spring Laboratory (U.K.) on the North Sea	Ekofisk crude oil	83	7.4 hours	Cormack and Nichols, 1977
Fibreglass tank (in which the oil layer was exposed to wave action and radiation), maintained at 2°C within an environmental chamber	Guonipa (Venezuelin) crude oil	85 (falling to 75)	Several days (not specified)	MacGregor and McLean, 1977

that after extended periods of time, uncoalesced water remaining in an emulsion tends to stabilize a petroleum emulsion. Thus, aged petroleum emulsions may well be more stable than fresh ones. However, no experimental work concerning this phenomenon has yet been discovered.

The quality of the water present in petroleum emulsions may play a significant role in emulsion stability. Since salt water has a higher density than fresh water, it could be assumed that for a given W/O ratio, a petroleum emulsion formed with salt water would have a greater specific gravity than one formed with fresh water, and (as previously explained in this section) would be relatively more stable than a petroleum emulsion formed with fresh water. This conjecture, however, was not consistent with the results of a recent study (Cairns et al., 1974), in which 4:1 W/O emulsions of Zakum crude were prepared with fresh water, and aqueous solutions of CaCl_2 , NaCl , and MgCl_2 . In this work, it was found that the emulsion prepared with fresh water was more stable than those prepared with the aqueous solutions. From this work, it was claimed that the sodium and calcium ions altered the interfacial tension values. The effect of pH on the stability of W/O emulsions formed with Tia Juana medium and Zakum crude oils was also examined by Cairns et al. They have suggested that high values of pH in the aqueous phase lead to decreased emulsion stability.

1.3.2 Viscosity and Pour Point

The viscosity of petroleum emulsions formed during an oil spill is an important factor in the effectiveness of cleanup operations, especially when mechanical operations (such as pumping and skimming) are considered. For a given petroleum oil, it is generally realized that the W/O emulsion will have a relatively higher viscosity than the oil itself. The W/O emulsions of Bunker-C fuel resulting from the spill created by the ARROW incident were noted to have a viscosity of 30,000 poise at 32°F, whereas the viscosity of non-emulsified Bunker-C fuel was noted to be only 700 poise at the same temperature (Mackay et al., 1973). In experiments directed towards the evaluation of oil spill recovery devices (Solsberg et al., 1976) W/O emulsions were prepared with light Arabian crude oil. Emulsions having various water contents were prepared, and their viscosities are listed below:

<u>Water Content (percent)</u>	<u>Kinematic Viscosity (centistokes @ 20°C)</u>
53.2*	2,553
63.4*	2,227
69.7*	2,443
70.5	880
64.4	414
63.6	517

* Initially formed by a homogenizer, and consequently allowed to weather over water.

Only the last 3 emulsions were naturally formed during the weathering of the oil over a water layer. From this work, it can generally be seen that these emulsions had higher viscosities than light Arabian crude oil itself, which had a kinematic viscosity of only 6.04 centistokes at 37.8°C. With respect to pumping and skimming operations, it can be generally claimed that water-in-petroleum emulsions formed can achieve viscosities that could affect oil recovery, especially in cold temperatures prevailing in an arctic environment.

The pour point of a petroleum substance (defined by ASTM method D97-66) is an approximate indication of the lower temperature at which the substance can be handled or transferred as a liquid. At the present time, little quantitative information is available concerning the effect of water emulsification upon the pour point of a given petroleum.

1.3.3 Spreading and Weathering

The spreading and weathering (or "aging") of a marine oil spill are complex phenomena, in which oil spreading, water emulsification, and hydrocarbon evaporation can occur simultaneously. It has been noted (Stehle, 1970) that the following parameters can influence the spreading rate of a marine oil spill:

- viscosity
- pour point
- chemical composition
- density
- surface tension
- oil/water interfacial tension
- water current
- wind speed
- tides (or wave action).

If changes in the oil layer properties attributed to emulsification and hydrocarbon evaporation are considered, accurate quantitative modelling of the spreading of marine oil spills becomes an extremely difficult task. It has been claimed (Berridge et al., 1968, and Frankenfeld, 1973) that emulsification of water tends to decrease evaporation of hydrocarbons. However, no quantitative information has been presented.

For a circular oil spill, the Blokker equation (Blokker, 1964) has been developed. In this equation, the slick diameter (D) in meters at a given time (t) can be determined as follows:

$$D^3 = \frac{24}{\pi} K(d_w - d_o) \frac{d_o}{d_w} V_o t + D_o^3$$

where: D is the slick diameter

d_w and d_o are the density values for oil and water

V_o is the original oil volume, in meters

t is the time following the oil spill, in minutes

D_o is the immediate slick diameter from the oil spill
(or when $t = 0$)

K is a constant value, depending upon the oil type spilled.

From spreading experiments performed with various crude oils, Berridge et al. modified the Blokner equation to estimate the relationship between slick thickness and the time following an oil spill (Berridge et al., 1968 and Stehle, 1970). From this work, the slick thickness was calculated as follows:

$$\text{thickness (cm)} = \frac{K'}{t^{2/3}}$$

where t is the time, in seconds.

$$K' = \left(\frac{v}{\pi}\right)^{1/3} \left[\frac{D_w}{3D_o(D_w - D_o)k_r} \right]^{2/3}$$

where: v is the oil volume, in cm^3

D_o and D_w are the densities of oil and water, respectively,
in g/cm^3

k_r is a constant value, determined by the oil spilled.

Although neither of these models was designed to account for the emulsification process, one can generally estimate the change in spreading tendency created by the emulsification of oil and water. By substituting a higher value of oil density in both models (since W/O emulsions are denser than oil by itself), it can be seen that under the same conditions, emulsified petroleum will spread less readily, and not spread as thinly over water as non-emulsified petroleum. The increased viscosity of emulsified petroleum (discussed in Section 3.3) is another primary factor that reduces the rate of spreading of petroleum emulsions.

1.3.4 Separation Techniques

In general, a separating technique can be considered as a process that destabilizes an emulsion, thereby separating the dispersed (internal phase) from the continuous (external phase). The separation (or "demulsification") process can be carried out as a result of the following destabilization processes (described in Section 1.1):

- Creaming
- Inversion
- Flocculation and coalescence (collectively responsible for demulsification).

The W/O emulsions encountered during crude oil production operations have created significant difficulties in the past. Out of necessity, the oil industry has consequently investigated a variety of methods for breaking down (or separating) these emulsions. The most notable techniques involve (either singly or in combination) the following:

- Gravity separation (Centrifugal separation)
- Heat treatment
- Selective filtration
- Vacuum desorption
- Electrochemical flotation
- Chemical methods
- Electrical methods.

The major disadvantage with most of the above techniques is that they require equipment that would be large, heavy and awkward to transport and set up in a remote arctic environment. Once the water has been separated from the oil, there still remains the task of disposing of the oil, should the oil be of an unmarketable quality or quantity.

1.3.5 Disposal by Combustion

In a remote arctic location, the handling and transport of petroleum (W/O) emulsions recovered from a marine oil spill would be both difficult and expensive. The disposal of oil and W/O emulsions by combustion techniques would minimize handling operations, and may dispose of a significant percentage of their volumes at the spill site, should suitable conditions prevail. Three combustion techniques are considered here:

- Incineration

- Combustion by atomizing burners
- In situ combustion.

1.3.5 (a) Incineration

Incinerators are capable of disposing of W/O emulsions having large amounts of water or particulate matter, and have a definite advantage over atomizing burners for the disposal of such W/O emulsions. Incineration can allow for the effective combustion of emulsified oil (and oil-soaked debris) having varying compositions and with a wide range of feed rates. However, it should be noted that many incinerators on the market are relatively large (or of heavy construction), and consequently lack the important element of portability required for use in a remote Arctic location. A variety of incinerator designs have been developed in the recent past, which have been applied towards the disposal of municipal solid waste and towards the disposal of oily liquid waste. At least three basic incinerator designs have been considered for the disposal of recovered oil in an arctic location (Petersen et al., 1975):

- Rotary kilns
- Conventional, closed combustion incinerators
- Open-combustion, pit-type (open-pit) incinerators.

Although some of these incinerators would be capable of disposing of up to several thousand barrels of oil per day, it was also noted that the large size and heavy weight of most incinerator systems would render them unsuitable for use in remote arctic locations.

It is felt that the open-combustion, pit-type incinerator would be the most appropriate design for the disposal of oily waste (including W/O emulsions) in the Arctic. This type of incinerator is of simple construction, and would allow for the oily debris to be dumped directly into the firebox (and at varying feed rates) during incinerator operation. A portable open-pit incinerator has been designed by TRECAN Ltd. for the disposal of oily debris at the site of an oil spill cleanup operation (Trecan, 1978). Although not primarily intended for the disposal of W/O emulsions, it appears to be one of the first attempts in the development of small, portable incinerators for the disposal of oily waste in a remote Arctic location. It is felt that a new series of portable incinerators (constructed as a single unit, or consisting of a maximum of 2 major components) should be designed for this application. The incorporation of air-cooled or water-cooled fireboxes may eliminate the requirement for thick layers of refractory material, and could consequently allow for the construction of relatively lightweight incinerators.

1.3.5 (b) Atomizing Burners

For the disposal of oil and W/O emulsions, atomizing burners have one major advantage over incinerators, in that they are considerably lighter

than incinerators, and are capable of burning large amounts of fuel in relatively short periods of time (depending upon the size of the burner). An additional advantage with these burners is that smoke emissions would be less than those from incinerators. Due to their light weight, atomizing burners could be easily transported and deployed to a spill site, as required. The major drawbacks that would be encountered with the burners are as follows:

- feeding problems associated with high-viscosity oil or W/O emulsions (especially at low temperatures), and with oil or W/O emulsions containing sand, gravel, or solid organic matter
- the maximum water content of a W/O emulsion that can be handled by atomizing burners is approximately 50 percent
- a lower turn-down ratio would apply for atomizing burners, as compared to incinerators
- atomizing burners would be of more sophisticated construction than incinerators, and would require specifically trained personnel for their operation at the spill site.

In general, the minimum criteria for the disposal of W/O emulsions by an atomizing burner in the Arctic are listed as follows:

- (i) the burner must be able to accommodate foreign solids in the feed
- (ii) the burner must be capable of handling a high-viscosity liquid feed
- (iii) the burner must be capable of burning W/O emulsions with water contents of up to 50 percent
- (iv) the burner should operate with low smoke emissions
- (v) The burner should be easy to start up and operate.

It is felt that only the burners employing air-blast atomization techniques would be capable of satisfying the above criteria. A few burners employing air-blast atomization are available on the market, which are considered suitable for handling W/O emulsions. Burners developed by the National Airoil (NAO) Burner Company are capable of handling up to 12,000 barrels per day of unrefined crude oil (smokelessly), utilizing water injection techniques. Designed for offshore well-testing programs, these burners could handle oil feeds containing water, mud, drilling compounds and other impurities. The largest of these burners are certainly portable, weighing 1175 lbs. Smaller models can operate at feed rates of up to 4,000 barrels

per day, and are capable of handling oil containing up to 50 percent water (Petersen et al., 1975). The John Zink Company offers a similar burner design with a rated capacity of 10,000 barrels per day. The overall weight of this burner (including auxiliaries) is only 1288 lbs.

Burners incorporating air-blast atomization are attractive devices for the disposal of W/O emulsions, and have been proven effective in oil disposal operations. They meet the ideal size, capacity, and dirt-handling requirements, as well as the smoke suppression characteristics desired for this application. However, further study may have to be made concerning the effectiveness of these burners in Arctic operating conditions, and with weathered W/O emulsions (as opposed to oil pumped directly from the well). Also requiring further study is the design of a suitable auxiliary system required for the burner, which would allow the entire burner system to be portable. All of the burners would require an air compressor, high-pressure oil and water pumps, a pilot flame and ignition system, and hence, an overall power plant. In addition, burner operation in the Arctic would require a heating system to reduce the viscosity of the feed, so that proper atomization could take place.

1.3.5 (c) In Situ Combustion

In situ combustion of an emulsified marine oil spill (the burning of the oil layer directly over the water surface) is perhaps the most convenient method of combustion, since no handling or transport of oil would be required prior to its ignition. However, as in the case of non-emulsified oil slicks, the following conditions are required for effective in situ combustion:

- (i) the oil layer must be confined
- (ii) the oil layer must be of an ignitable thickness
- (iii) a calm water surface must prevail.

It has been noted (Energetex, 1978) during the in situ combustion of oil, heat radiated back from the flame is constantly required to vapourize the liquid hydrocarbons of the oil layer. During the process, a certain portion of this heat is constantly transferred through the oil layer to the water below (which serves as an infinite heat sink). As the oil layer burns down (or regresses) to a certain thickness, its thermal insulating value is considerably reduced, and an insufficient amount of heat is applied for the continued vapourization of the oil. It is at such a thickness that the combustion process is interrupted, and the flame is thermally quenched. As a result, a residual oil layer will always remain on the water surface following in situ combustion. Despite this fact, in situ combustion of W/O emulsions is a very attractive method for the disposal of W/O emulsions, especially at remote locations.

The in situ combustion of pure oil and W/O emulsions varies theoretically in a number of regards. Since oil emulsified with water has

reduced volatility, the vapourization and ignition of a W/O emulsion would take a longer period of time (or perhaps require a more powerful ignition source) than in a situation where the oil was not emulsified with water. In addition, a W/O emulsion layer would have (a) a lower thermal insulating value than an oil layer of the same thickness, (b) a higher value for minimum ignitable thickness, and (c) require the separation of water from the oil (by heat generated by flame) before effective combustion of oil can occur. It is reasonable to expect that the ignition of a W/O emulsion layer over water would require a more powerful ignition source (a larger flame from an igniter, for example) than for the ignition of an oil layer (of the same thickness) over water. It can also be expected that the ignition time (the time required for the flame to spread over the entire slick surface) would be longer for W/O emulsions than for unemulsified oil.

At the present, in situ combustion of W/O emulsions is a relatively unexplored area. In order to assess the feasibility of this technique for the disposal of W/O emulsion layers, in situ combustion tests were performed. The results of these tests are presented in Section 3.6.

2 EXPERIMENTAL APPROACH

The experimental work concerning the formation of W/O emulsions was performed in two separate phases. During both phases, the emulsions were prepared by means of impeller pumps, in which water and oil were drawn up and mixed together through a spray nozzle.

2.1 Phase #1

This phase was carried out at the North Campus Research Station during November and December of 1978. The W/O emulsions were formed with marine diesel fuel and the following six crude oils:

- Norman Wells
- Sweet Blended
- Sour Blended
- Bow River
- Lloydminster
- Weyburn-Midale.

The water contents for the emulsions formed are shown in Table #3.

Following their formation, the emulsions were poured into pans, so that they could be aged for periods of two weeks and four weeks.

2.2 Phase #2

This phase was carried out in the laboratory during January and February of 1979. The W/O emulsions were formed with four crude oils:

- Norman Wells
- Sweet Blended
- Lloydminster
- Weyburn-Midale.

The water contents for the emulsions formed are shown in Table #4.

Following their preparation, the emulsions were subjected to flash/fire point determinations, viscosity determinations, pour point determinations, wicking tests, and in situ combustion tests. The test procedures for these emulsions were identical to the procedures described in Part I of this report (Section 2).

3.5 Wicking Test Data for W/O Emulsions

The sorption capacities of 3M Brand Oil Sorbent with the emulsions prepared in phase #2 are shown in Table #7.

For W/O emulsions prepared with all four crude oils, it was observed that the emulsions containing 20 and 30 percent water were wicked to a greater extent by this sorbent than those emulsions containing 50 and 60 percent water. This trend was attributed to (a) the relatively higher viscosities of emulsions with higher water contents and (b) the hydrophobic (water-repelling) nature of 3M Brand Oil Sorbent. This sorbent was capable of wicking between 6.15 and 11.26 times its weight of W/O emulsions with water contents of 20 and 30 percent. The wicking capacity of this sorbent with these emulsions is similar to its wicking capacity for unemulsified crude oils (Table #12 of Part I of this report) that were fresh, or aged for intervals of up to 2 days. For the W/O emulsions having water contents of 50 and 60 percent, 3M Brand Oil Sorbent was capable of wicking between 3.53 and 8.81 times its weight of these emulsions.

It is therefore suggested that sorbent techniques and the use of sorbent-dependent skimmers would be less effective on oil slicks containing increasing amounts of emulsified water.

3.6 In Situ Combustion Data for W/O Emulsions

Test data obtained from the in situ combustion of the W/O emulsions is presented in Table #8. This data were compared to the in situ combustion data for the fresh crude oils (Tables #12A, #12B, #13E, and #12F), which is presented in Part I of this report. These tests were conducted with ambient air temperatures ranging between t and 15°C .

As anticipated, confined slicks of crude oils emulsified with water (10 mm in thickness) were considerably more difficult to ignite than confined slicks of the corresponding fresh crude oils (also of 10 mm thickness). The slicks of fresh Lloydminster and Sweet Bl. crude oils had negligible preheating and ignition times, and were easily ignited by a solid fuel igniter. The W/O emulsion layers with water contents of 20 percent (by volume) were easily ignited by such an igniter, but had preheating times ranging between 4 and 64 seconds, and ignition times ranging between 1 and 21 minutes (depending upon the oil type). A more powerful ignition source was required to ignite W/O emulsions of Lloydminster crude having water contents of 30 and 50 percent (one litre of fresh crude oil was added to assist the ignition process). The ignition and burning of Weyburn-Midale crude (W/O) emulsions with 20% water content is shown in Figure #3. Also the localized emulsion break-up due to the heat can be observed in Figure #3.

In general, "micro explosions" and foaming were observed during the ignition and in situ combustion of the W/O emulsion layers. This suggests that the emulsions required separation to allow for the ultimate combustion of the oil. During the combustion of Lloydminster crude having an emulsified water content of 50 percent, the foaming process was sufficiently intense to hinder the in situ combustion process.

It was noted that the residual oil layer thicknesses

from the in situ combustion of emulsions with water contents of 20 and 30 percent were similar to those values obtained from the in situ combustion of the unemulsified fresh crude oils.

W/O emulsions formed with Norman Wells and Sweet Bl. crude oils were successfully burned in situ, when they had water contents of up to 70 percent (by volume). W/O emulsions formed with Lloydminster and Weyburn-Midale crude oils were successfully burned in situ with water contents of 20 and 30 percent. W/O emulsions formed with Lloydminster and Weyburn-Midale crude oils were difficult to burn in situ with water contents of 50 percent, since the foam created during their combustion tended to extinguish the flames. However, with the addition of approximately 4 litres of fresh crude, it was possible to burn the emulsions of these two oils having 50 percent water and with 10 litres initial volume. Due to extensive foam generation during the combustion process, the combustion of emulsions (formed from Lloydminster and Weyburn-Midale crude oils) having water contents of 60 percent was not possible even though a fresh crude primer was added.

TABLE #3

CHARACTERISTICS OF W/O EMULSIONS FORMED DURING PHASE #1

Emulsion Composition (by volume)	Oil Type						
	Norman Wells Crude	Sweet Bl. Crude	Sour Bl. Crude	Bow River Crude	Lloyd- minster Crude	Weyburn- Midale Crude	Marine Diesel Fuel
80% oil 20% water	--	--	Stable for several days	Stable	Stable	Stable	Separated following formation
60% oil 40% water	Stable for several hours	--	--	Stable	Stable	Stable	Separated following formation
50% oil 50% water	Stable for several hours	Stable for several days	--	Stable	Stable	Stable	Separated following formation
40% oil 60% water	--	Stable for several days	--	Stable	Stable	Stable	Separated following formation
30% oil 70% water	--	Separated following formation	--	--	--	--	--
20% oil 80% water	--	No emulsion formed	No emulsion formed	--	Stable for several days	--	--

TABLE #4

CHARACTERISTICS OF W/O EMULSIONS FORMED DURING PHASE #2

Emulsion Composition (by volume)	Oil Type			
	Lloydminster Crude	Weyburn-Midale Crude	Sweet Bl. Crude	Norman Wells Crude
80% oil 20% water	Stable	Stable	Partially stable	Stable for several hours
70% oil 30% water	Stable	Stable	Partially stable	Stable for several hours
50% oil 50% water	Stable (extremely viscous)	Stable (extremely viscous)	Partially stable	Stable for several hours
40% oil 60% water	Stable (extremely viscous)	Stable (extremely viscous)	Partially stable	Stable for several hours
30% oil 70% water	N.P.	Stable (extremely viscous)	N.P.	N.P.

N.P. - Emulsion not prepared.

TABLE #5

FLASH AND FIRE POINTS (°C) FOR W/O EMULSIONS

		Oil Type			
Emulsion Composition (by volume)		Lloydminster Crude	Weyburn-Midale Crude	Sweet Bl. Crude	Norman Wells Crude
Flash Pt.	100% oil (fresh)	11	--	9 (or less)	--
Fire Pt.		17	14 (or less)	10	13.5 (or less)
Flash Pt.	80% oil 20% water	19.5	17 (or less)	19 (or less)	--
Fire Pt.		28	23	20.5	--
Flash Pt.	70% oil 30% water	23	18 (or less)	28.5	--
Fire Pt.		55	24	32	--
Flash Pt.	50% oil 50% water	45	32	28	--
Fire Pt.		78	71	33	--
Flash Pt.	40% oil 60% water	67	63	31.5	--
Fire Pt.		76	73	37.5	--
Flash Pt.	30% oil 70% water	--	50	--	--
Fire Pt.		--	58	--	--

TABLE #6

VISCOSITY AND POUR POINT VALUES FOR W/O EMULSIONS

Oil Type	Water Content (percent by volume)	Pour Point (°C)	Viscosity (centipoise)	
			@ 10°C	@ 20°C
Norman Wells Crude	20	-60	23	12
	30	-64	35	23
	50	-48	110	54
Sweet Bl. Crude	20	-41	80	27.5
	30	-27	155	67.5
	60		450	266
Weyburn- Midale Crude	20	-25	200	5.5
	30	-22	230	87.5
	50	-2.5	600	212.5
	60		4150	1450
Lloydminster Crude	20	-28	325	107.5
	50	-33	1275	250
	60		2800	1545

TABLE #7

SORPTION CAPACITIES* OF 3M BRAND OIL SORBENT WITH W/O EMULSIONS

Emulsion Composition (by volume)	Sorption Capacity (g of emulsion/g of dry sorbent)			
	Oil Type			
	Lloydminster Crude	Weyburn-Midale Crude	Sweet Bl. Crude	Norman Wells Crude
80% oil 20% water	9.86	6.25	9.77	10.96
70% oil 30% water	10.68	9.52	9.2	11.26
50% oil 50% water	8.81	3.53	5.91	6.46
40% oil 60% water	6.37	--	5.48	--
30% oil 70% water	--	--	--	--

*Sorbent capacity was evaluated as the ratio of the W/O emulsion weight wicked up (in grams) to the dry weight of the sorbent sheet (which had an average value of 37.57 grams). It is expressed in units of grams of emulsion per gram of dry sorbent.

TABLE #8A

IN-SITU COMBUSTION TEST DATA WITH W/O EMULSIONS FOR NORMAN WELLS CRUDE

Water Content (percent by volume)	Ambient Air Temperature Range (°C)	Initial Oil Layer Thickness (mm)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
20		10	0:04	1:20	2:24	0.40	Ignition by small piece of solid fuel, intense flame near the end, gray smoke, no foaming
30		10	0:00	1:53	2:54	0.49	Ignition by small piece of solid fuel, intense flame near the end, gray smoke, no foaming
50		10	0:21	4:34	2:12	0.725	Some creaming evident, ignition by solid fuel igniter, intense flame, very light smoke, no foaming
60		10	1:21	6:06	2:00	0.65	Some creaming evident, ignition by solid fuel igniter, intense flame, very light smoke, no foaming
70		10	2:01	10:51	2:48	0.65	More viscous, didn't spread over entire surface, flame propagation very slow, very light smoke

TABLE #8A (Cont'd)

Water Content (percent by volume)	Ambient Air Temperature Range (°C)	Initial Oil Layer Thickness (mm)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
70		10	2:09	10:51	2:48	0.65	More viscous, didn't spread over entire sur- face, flame propagation very slow

TABLE #8B

IN-SITU COMBUSTION TEST DATA WITH W/O EMULSIONS FOR SWEET BLEND CRUDE

Water Content (percent by volume)	Ambient Air Temperature Range (°C)	Initial Oil Layer Thickness (mm)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
20		10	0:20	5:06	2:56	0.625	Ignition by small piece of solid fuel, light smoke, intense micro explosions near the end, no foaming
30		10	1:04	20:47	3:04	1.50	Ignition by small piece of solid fuel, light smoke, intense micro explosions near the end, no foaming
50		10	1:15	5:30	2:30	1.0	Ignition by solid fuel igniter, intense flame, very light smoke, no foaming, intense micro explosions
60		10	2:00	7:30	2:00	1.25	Ignition by solid fuel igniter, intense flame, very light smoke, no foaming, intense micro explosions
70		10	4:30	18:00	1:30	1.5	Ignition by solid fuel igniter, weak flame, very light smoke, very slow flame propagation

TABLE #8C

IN-SITU COMBUSTION TEST DATA WITH W/O EMULSIONS FOR WEYBURN-MIDALE CRUDE

Water Content (percent by volume)	Ambient Air Temperature Range (°C)	Initial Oil Layer Thickness (mm)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
20		10	0:32	12:05	--	1.04	Ignited by cube of solid fuel, foaming occurred
30		10	N.D.	N.D.	≈9:00	0.94	Weak flame, slow propagation, intense flame for last 30 sec
40		10	N.D.	N.D.	≈15:00	0.95	Ignition was assisted by fresh crude, extremely intense flame for last 2 min of combustion, intense foaming
50		10	N.D.	N.D.	≈15:00	0.59	Ignition was assisted by fresh crude, flames were about 2' high during first 13 min of combustion time, 7' during last 2 min (intense heat radiation)

TABLE #8D

IN-SITU COMBUSTION TEST DATA WITH W/O EMULSIONS FOR LLOYDMINSTER CRUDE

Water Content (percent by volume)	Ambient Air Temperature Range (°C)	Initial Oil Layer Thickness (mm)	Preheating Time (min:sec)	Ignition Time (min:sec)	Combustion Time (min:sec)	Residual Oil Layer Thickness (mm)	Comments
		10	0:02	1:12	1:53	1.9	Ignited by match, light gray smoke, foaming occurred
30		10	1:00	27:00	4:30	1.0	Dark dense smoke, intense foaming and micro explosions
50							Ignition assisted by fresh crude oil, intense foaming which seemed to extinguish flames during ignition, several igni- tions were attempted but failed

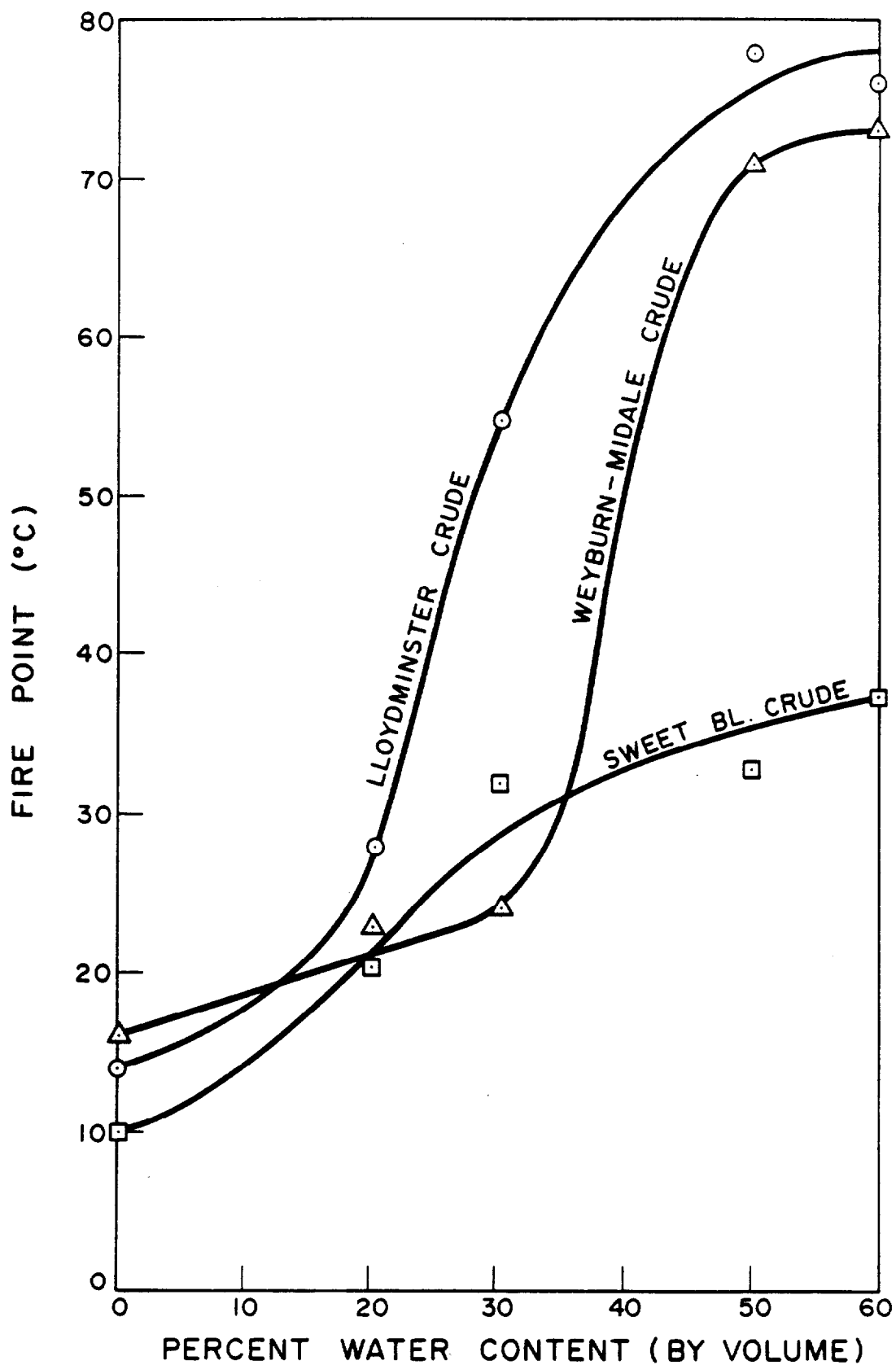


FIGURE 1—W/O EMULSION FIRE POINTS
vs. WATER CONTENT

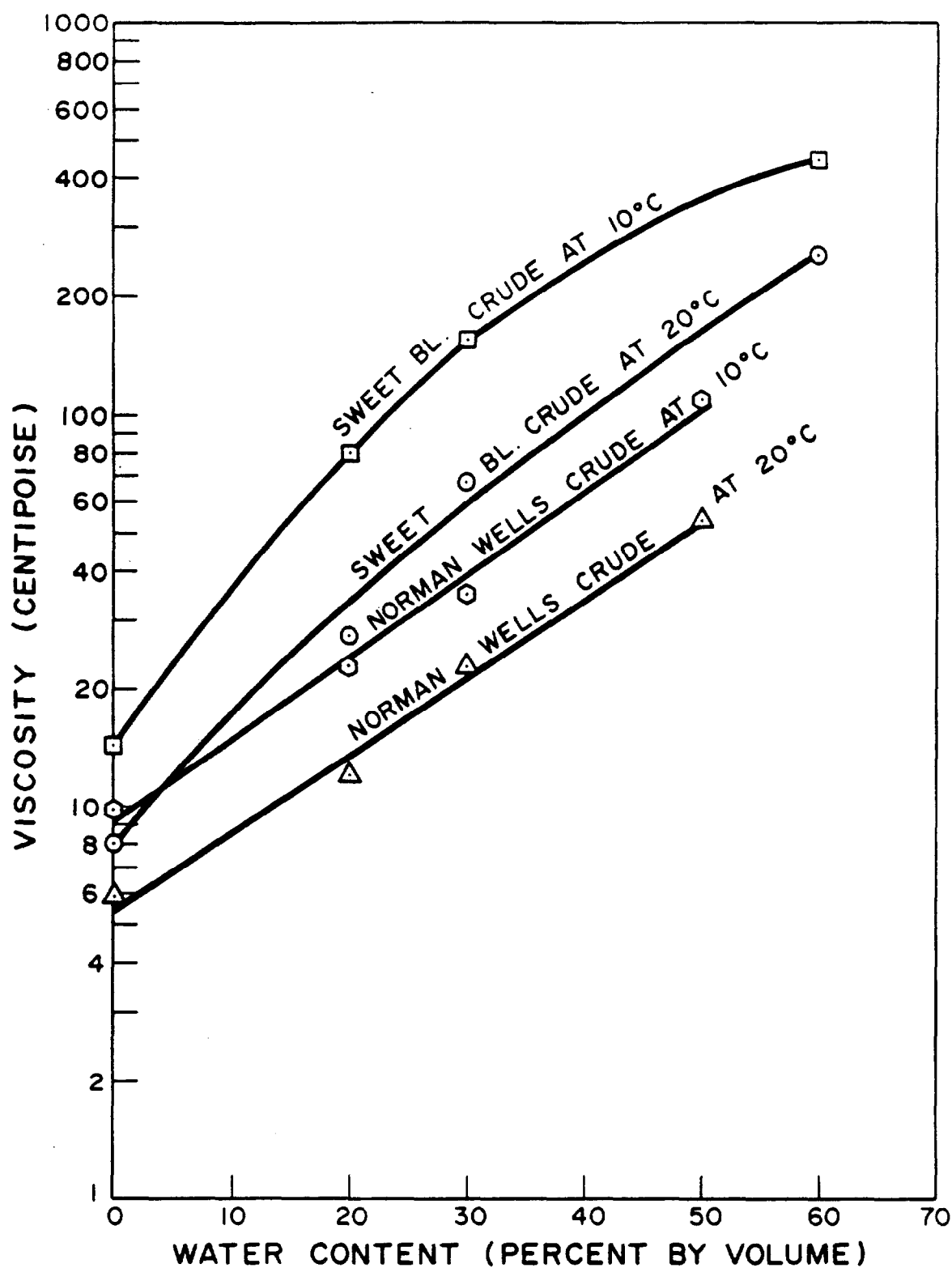


FIGURE 2A—W/O EMULSION VISCOSITY
vs. WATER CONTENT FOR
NORMAN WELLS AND
SWEET BL. CRUDE OILS

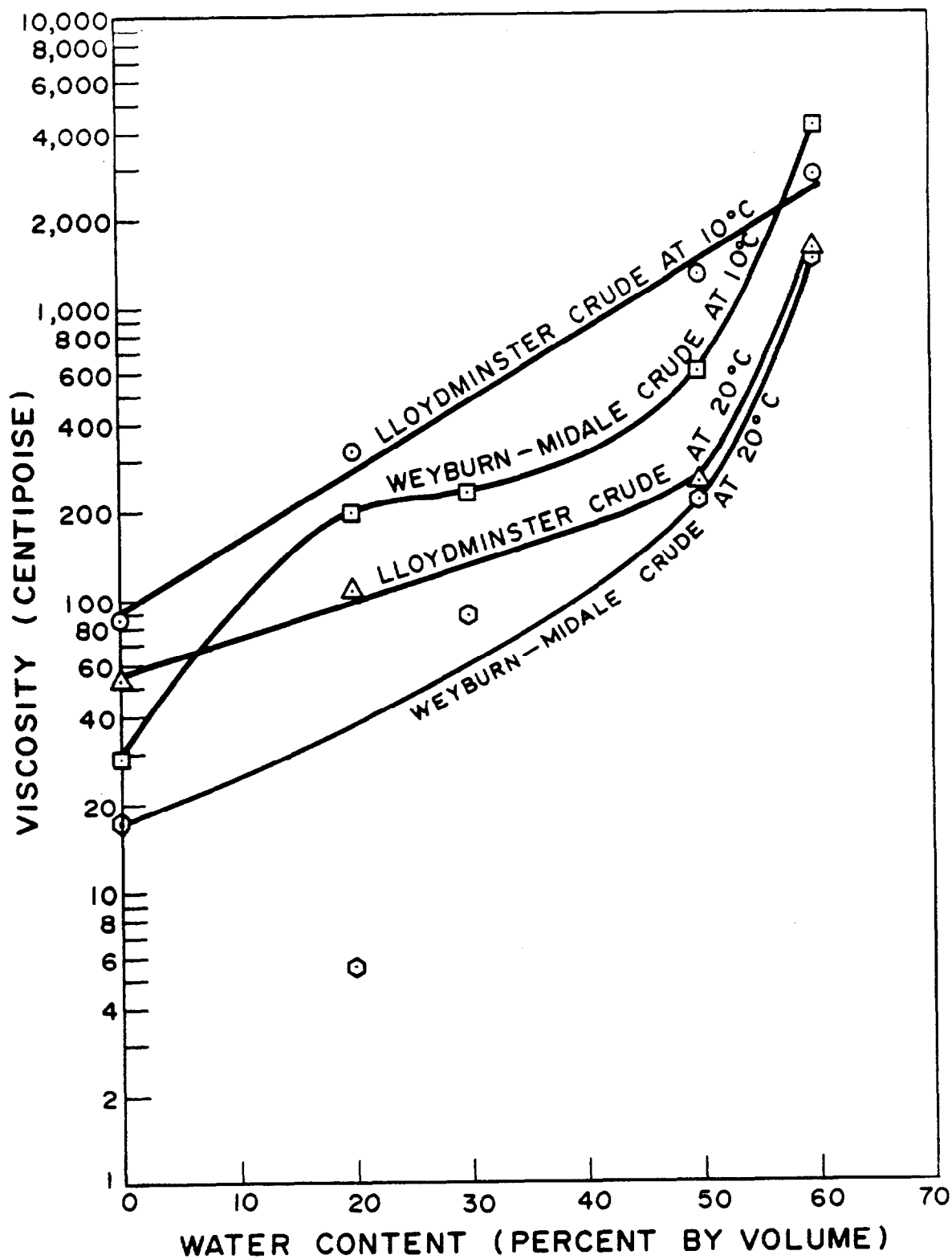


FIGURE 2B - W/O EMULSION VISCOSITY
vs. WATER CONTENT FOR
WEYBURN-MIDALE AND
LLOYDMINSTER CRUDE OILS

4 CONCLUSIONS

1. Compared to the fresh crude oils, the formation of water-in-oil (W/O) emulsions leads to an increase in the viscosity and pour point values, and an increase in flash and fire point values. In view of the low temperatures encountered in the Arctic, the increased viscosity and pour point values of W/O emulsions suggests that these emulsions would be much more difficult to handle and transport than fresh, unemulsified crude oils.

2. The wicking capability of 3M Brand Oil Sorbent for W/O emulsions having water contents of 20 and 30 percent (by volume) was generally similar to that for the fresh crude oils. However, the wicking capability of this sorbent for the W/O emulsions having water contents of 50 and 60 percent by volume was considerably reduced. This was attributed mainly to the increased viscosities of these emulsions, and also to the water repelling nature of the sorbent.

3. Water-in-oil emulsions formed with fresh crude oils were successfully burned in situ, when solid fuel igniters were employed to initiate the combustion process. The maximum water content for effective ignition of the emulsion layers was approximately 70 percent (by volume) for medium crude oils. For heavy crude oils the maximum water content was 30 percent.

4. The in situ combustion of the water-in-oil emulsions differs from the in situ combustion of unemulsified oil layers, in that the emulsions must separate before effective combustion can occur (this ultimately requires longer preheating and ignition times than in the case of unemulsified oil layers). Unlike the ignition of unemulsified oil slicks, the emulsified oil slicks required a definite size of flame before flame propagation over the entire oil surface could occur, especially for higher water contents and heavy crude oils.

5. 10 mm thick slicks of W/O emulsions formed with Norman Wells and Sweet Bl. crude oils (having water contents of up to 30 percent by volume) were easily ignited by solid fuel igniters. In fact, a 10 mm thick slick of Norman Wells crude oil emulsified with 70 percent water (by volume) was easily ignited with a solid fuel igniter. However, W/O emulsions of the same thickness that were formed with Lloydminster and Weyburn-Midale crude oils with water content above 30% were more difficult to ignite, and required the addition of fresh crude oil for their ignition. The main difficulty in igniting these emulsions was attributed to the foaming process, which tended to either impair flame propagation, or extinguish the flames altogether.

6. The residual oil layers remaining after the combustion of the W/O emulsions ranged between 0.4 and 1.9 mm in thickness. These values were similar to the residual oil layers remaining after the combustion of unemulsified oil layers of the corresponding crude oils.

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APPENDICES FOR PART I

APPENDIX "A": TABULATION OF WEATHER PARAMETERS

A.1 Data Procurement

The following data were determined on a daily basis, and supplied by the Agrometeorology Section, Department of Land Resource Science, University of Guelph:

- Total number of bright sunshine hours (obtained from a Campbell-Stokes instrument chart).
- Solar radiation (the incoming energy from the sun, measured on a horizontal surface by means of an Eppley Pyranometer), expressed in Megajoules per square meter.
- Wind speed (determined by an anemometer positioned 10 m above the ground, and expressed in km/h) measured between 0000 hrs and 23:59 hrs of the day concerned. Daily average and maximum daily wind speed values were observed.
- Water and snow precipitation (in millimeters) collected between 0800 hrs of the day concerned and 0800 hrs of the following day.

This data was obtained at the Elora Gorge Weather Station (approximately 20 km away from the test site), and was considered to be fairly representative of the conditions prevailing at the test site.

The following weather data was taken at the Waterloo-Wellington Airport (near Waterloo, Ontario), and supplied by the weather office at this airport:

- Daily temperatures (obtained by means of a thermograph) measured between 0000 hrs and 2400 hrs of the day concerned.
- Wind speeds measured hourly between 0000 and 2400 hrs of the day concerned. This information was used only when the wind speed data from the Elora Gorge Weather Station was unavailable for the day concerned.

Since the Waterloo-Wellington Airport was approximately 7 km from the test site, it was also felt that this data was representative of the conditions that prevailed at the test site.

Approximate values of the oil layer temperature were determined at the test site by means of a copper-constantan thermocouple, connected to a chart recorder. The tip of the thermocouple was initially immersed in a layer of Norman Wells (and later into Sweet Bl.) crude oil.

A.2 Estimation of Weather Parameters

For a given aging interval lasting 1 or more days, it should be noted that the aging interval began at a time between 0900 and 1700 hrs of the first day (when the oil was poured into the pan), and also ended between 0900 and 1700 hrs of the final day (when the oil was extracted from the pan). In general, it was not possible to alter the weather data to conform exactly to aging intervals which began and ended between these hours. Therefore, several generalizations were made in order to obtain approximate values of the weather parameters for aging intervals of 1 day or more. For aging intervals of 6 hours (in which oil samples were poured in pans and extracted from pans between 0900 and 1700 hrs of the same day), the weather data was essentially that obtained over the 24-hour period of the day concerned. The procedure by which the data was estimated is described below in detail. The estimated weather parameters are presented in conjunction with the evaporative losses for each aging interval in Table #1.

A.2.1 6-Hour Aging Intervals

Oil samples were aged for 6-hour intervals on November 13 and November 15. The weather parameters for 6-hour intervals were determined in the following manner:

Total Bright Sunshine (Hours) = the number of bright sunshine hours reported for the day concerned.

Total Solar Radiation (MJ/m^2) = the solar radiation reported for the day concerned.

Daily Mean Wind Speed (km/h) = the mean daily wind speed reported for the day concerned.

Maximum Wind Speed (km/h) = the maximum wind speed reported for the day concerned.

Total Rain Precipitation (mm) = the rainfall reported for the day concerned.

Total Snow Precipitation (mm) = the snowfall reported for the day concerned.

Minimum Daily Air Temperature ($^{\circ}\text{C}$) = the minimum air temperature between 0900 and 1700 hrs of the day concerned.

Maximum Daily Air Temperature ($^{\circ}\text{C}$) = the maximum air temperature between 0900 and 1700 hrs of the day concerned.

Average Daily Air Temperature ($^{\circ}\text{C}$) = The average value of the maximum and minimum temperatures reported between 0900 and 1700 hrs of the day concerned.

A.2.2 1-Day Aging Intervals

Oil samples were aged for 1-day intervals that began at a given time on November 1 and ended at approximately the same time on November 2. The weather parameters for the 1-day intervals were determined in the following manner:

Total Bright Sunshine (Hours)	=	$\frac{\text{Bright sunshine reported for first day} + \text{Bright sunshine reported for second day}}{2}$
Total Solar Radiation (MJ/m ²)	=	$\frac{\text{Solar radiation reported for first day} + \text{Solar radiation reported for second day}}{2}$
Daily Mean Wind Speed (km/h)	=	$\frac{\text{Daily mean wind speed reported for first day} + \text{Daily mean wind speed reported for second day}}{2}$
Maximum Wind Speed (km/h)	=	the maximum wind speed reported for either the first or second day.
Total Rain Precipitation (mm)	=	the rainfall reported for the first day.
Total Snow Precipitation (mm)	=	the snowfall reported for the first day.
Minimum Daily Air Temperature (°C)	=	the minimum air temperature between 0900 hrs of the first day and 1700 hrs of the second day.
Maximum Daily Air Temperature (°C)	=	the maximum air temperature between 0900 hrs of the first day and 1700 hrs of the second day.
Average Air Temperature (°C)	=	the average value of the maximum and minimum temperatures recorded between 0900 hrs of the first day and 1700 hrs of the second day.

A.2.3 Aging Intervals of 2 Days and Longer

For an aging interval consisting of two or more days, three types of days can be noted:

- The first day (on which the aging interval was started).
- The final day (on which the aging interval was ended).
- The intermediate days (the full days existing between the initial and final days).

It was generally considered that an aging interval of x days (where $x = 2, 7, 14$, or 28 days) would consist of $x - 1$ days, plus one-half of the first day, and one-half of the final day. The actual aging intervals for these situations are shown in Table #1. For such aging intervals, the weather parameters were determined in the following manner:

Total Bright Sunshine (Hours)	=	1/2 of bright sunshine reported for first day	+	1/2 of bright sunshine reported for final day	+	Sum of bright sunshine reported for all intermediate days
Total Solar Radiation (MJ/m^2)	=	1/2 of bright sunshine reported for first day	+	1/2 of bright sunshine reported for final day	+	Sum of solar radiation reported for all intermediate days
Mean Daily Wind Speed (km/h)	=	the average value of the mean daily wind speeds reported between the first and final days (inclusive).				
Maximum Wind Speed (km/h)	=	the maximum wind speed reported during the first, final, or intermediate days.				
Total Rain Precipitation (mm)	=	the total rainfall reported for the first and intermediate days.				
Total Snow Precipitation (mm)	=	the total snowfall reported for the first and intermediate days.				
Minimum Daily Air Temperature ($^{\circ}\text{C}$)	=	the minimum air temperature reported between the first day and the final day (inclusive).				
Maximum Daily Air Temperature ($^{\circ}\text{C}$)	=	the maximum air temperature reported between the first day and the final day (inclusive).				
Average Air Temperature ($^{\circ}\text{C}$)	=	the average value of the maximum and minimum temperatures reported between the first day and the final day (inclusive).				

TABLE #1
DAILY WEATHER PARAMETERS

Date	Air Temperatures (°C)		Bright Sunlight (Hours)	Daily Total of Solar Radiation (MJ/m ²)	Wind Speed (km/h)		Daily Precipitation (mm)	
	Maximum	Minimum			Mean Daily	Maximum in One Hour	Rain	Snow
Oct. 27	12	2	3.9	7.2	16	26	Nil	Nil
28	10	0	8.7	10.4	13	26	Nil	Nil
29	7.1*	-1.6*	3.4	8.3	9	11	Nil	Nil
30	14	-3	8.5	12.2	13	23	Nil	Nil
31	14	1	9.2	11.6	13	21	Nil	Nil
Nov. 1	11	-3	9.7	13.2	9	13	Nil	Nil
2	14	3	8.2	11.2	14	24	Nil	Nil
3	18	-1	8.9	10.9	8	18	Trace	Nil
4	19	0	5.6	9.4	7	18	Nil	Nil
5	19	-2	6.9	9.2	16	31	0.2	Nil
6	14	3	0.0	1.3	14	23	2.2	Nil
7	6	1	8.3	11.3	11	16	Nil	Nil
8	7	-7	8.1	11.5	14	29	Nil	Nil
9	13	3	8.2	9.8	15	27	Nil	Nil
10	13	0	0.2	5.6	10	16	Nil	Nil
11	10	2	1.1	4.1	-	-	Nil	Nil
12	1	-2	0.0	4.0	-	-	Nil	Nil
13	12	-1	0.0	2.0	-	-	14.5	Nil
14	14	2	3.3	5.7	27	35	Trace	Nil
15	3	-3	0.0	2.8	10	18	Nil	Nil
16	5	-4	7.5	9.9	10	23	Nil	Nil
17	13	2	0.0	0.7	31	48	Nil	Nil

(Cont'd)

TABLE #1 (Cont'd)

Date	Air Temperatures (°C)		Bright Sunlight (Hours)	Daily Total of Solar Radiation (MJ/m ²)	Wind Speed (km/h)		Daily Precipitation (mm)	
	Maximum	Minimum			Mean Daily	Maximum in One Hour	Rain	Snow
1	5	3	0.0	2.8	33	53	Nil	Nil
10	4	-1	4.9	6.5	21	31	Nil	Nil
20	-1	-8	0.0	3.3	14	21	Nil	11
21	-2	-8	5.0	7.9	9	11	Nil	Nil
22	0	-4	0.0	2.3	11	16	Nil	12
23	6	-1	0.0	0.5	20	34	15.1	Nil
24	2.4*	0.8*	0.0	1.0	22	31	2.1	4
25	-1.7*	-3.3*	0.5	4.6	18	27	Nil	Trace
26	-4.4*	-10.6*	5.9	8.8	14	23	Nil	14
27	-5.7*	-9.5*	0.0	2.8	24	31	Nil	45
28	-0.1*	-8.8*	0.0	3.7	16	27	Nil	6
29	2.0*	-9.6*	3.6	7.0	23	31	Nil	10
30	-2.5*	-6.0*	3.6	6.0	24	32	Nil	6
Dec. 1	0	-4	0.0	2.5	30	29	Nil	48
2	-2	-9	1.0	6.3	11	22.5	Nil	35
3	6	-9	0.0	1.7	19	29	10	Nil
4	7	-5	0.0	1.8	32	48	Nil	15
5	1	-4	1.0	4.9	29	34	3	Nil
6	1	-1	1.2	5.3	14	21	2.4	11

Notes:

*Temperature values were obtained from weather data taken at the Elora Gorge Research Station.

Wind speed values were not recorded at the Elora Gorge Research Station during November 11, 12, and 13, 1978. Data concerning wind speed and daily solar radiation at the Elora Gorge Research Station was not yet available.

APPENDIX "B": DETERMINATION OF EVAPORATIVE LOSSES FOR LIGHT/MEDIUM
CRUDE OILS, BASED UPON THE MODEL DEVELOPED BY MACKAY
AND NADEAU (1978)

A model had been developed (Mackay/Nadeau, 1978), in which the parameters of wind speed, slick area and thickness, specific gravity, ambient air temperature, and aging time were quantitatively employed to calculate the evaporative loss of various types of oils. This model (briefly described in Section 1.1) assumes that wind speed, temperature, and spill thickness remain constant over an aging interval, and that Raoult's Law and the Antoine vapour pressure-temperature relationships were applicable for the various mixtures of hydrocarbons. It was desired to compare the evaporative losses of the medium crude oils (Norman Wells, Sweet Bl., and Sour Bl.) with the evaporative losses of light and medium crude oils, as predicted by this model.

As can be seen from Table #14 in this report, the parameters of ambient air temperature and wind speed varied considerably for a given aging interval in this study. From Table #1, average wind speeds and the average ambient air temperatures (to the nearest 5°C), for a given aging interval were incorporated for this model. From the average wind speed, an approximate mass transfer coefficient K was determined (according to Figure #1 of Mackay/Nadeau, 1978). Using the following formula, a value of A was calculated:

$$A = \frac{\text{Spill area (m}^2\text{)}}{\text{Spill volume (m}^3\text{)} \times \text{Oil density (kg/m}^3\text{)}} .$$

The value of t was calculated by converting the aging intervals into time intervals of seconds. The product of KAt was then calculated, and (by referring to Figure #7 of Mackay/Nadeau, 1978) the fraction of oil remaining for such a KAt value was noted. Thus, the percentage of evaporative loss (by weight) for a given aging interval was determined. By dividing the percentage evaporative loss by weight of the oil by the specific gravity of Sweet Bl. crude oil for the corresponding aging interval, an approximate value for the percentage evaporative loss (by volume) was obtained for the oil, as a function of the aging interval. The calculation of the evaporative losses (by volume) for each aging interval is shown in Table #15. These values were used to plot a curve of evaporative loss vs. aging interval for light/medium crude oils, based upon this model (see Figure #4B).

TABLE #2

EVAPORATIVE LOSSES (BY VOLUME) FOR LIGHT/MEDIUM CRUDE OILS, BASED UPON THE MODEL DEVELOPED

BY MACKAY/NADEAU (1978)

Aging Interval	Average Wind Speed (km/h)	K (m/sec)	A (m^2/kg)	t (sec)	Kat* (m^3/kg)	Average Ambient Air Temperature (to the nearest 5°C)	Evaporative Loss (percent by weight) from Model	Specific Gravity of Oil	Evaporative Loss (percent by volume) based on Model
6 Hours	10	0.004	0.101	21,600	8.7	0	11	0.84	13.1
1 Day	11.5	0.0045	0.101	86,400	39.3	5	15	0.87	17.2
2 Days	13.3	0.005	0.101	172,800	87.3	5	18	0.90	20.0
1 Week	11.6	0.0045	0.101	604,800	274.9	5	24	0.92	26.1
2 Weeks	12.0	0.0045	0.101	1,209,600	549.8	5	27	0.93	29.0
4 Weeks	15.0	0.006	0.101	2,419,200	1466.0	5	29	0.94	30.9

(Cont'd)

TABLE #2 (Cont'd)

* Based upon the value of KAt, the fraction of oil (by weight) remaining could be determined for light/medium crude oil at a given temperature, by referring to Figure #7 of Mackay/Nadeau, 1978. The evaporative loss (by weight) was expressed as the percentage difference between unity and the fraction of oil remaining.

** The specific gravity values were based upon those for Sweet Bl. crude oil (see Table #5). The evaporative loss (percent by volume) was determined by dividing the percentage of evaporative loss by weight by the specific gravity of this crude oil.