

BRL MR 2076

AD 716578

BRL

AD

MEMORANDUM REPORT NO. 2076

IGNITION AND COMBUSTION OF UNCONFINED LIQUID FUEL ON WATER

by

Warren W. Hillstrom

November 1970

DDC
RECEIVED
JAN 14 1971
RECEIVED
C

This document has been approved for public release and sale;
its distribution is unlimited.

U.S. ARMY ABERDEEN RESEARCH AND DEVELOPMENT CENTER
BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MARYLAND

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
Springfield, Va. 22151

BALLISTIC RESEARCH LABORATORY

MEMORANDUM REPORT NO. 2076

NOVEMBER 1970

IGNITION AND COMBUSTION OF UNCONFINED LIQUID FUEL ON WATER

Warren W. Hillstrom

Terminal Ballistics Laboratory

This document has been approved for public release and sale;
its distribution is unlimited.

RDT&E Project No. 1T061101A91A

ABERDEEN PROVING GROUND, MARYLAND

BALLISTIC RESEARCH LABORATORY

MEMORANDUM REPORT NO. 2076

WHillstrom/meg
Aberdeen Proving Ground, Md.
November 1970

IGNITION AND COMBUSTION OF UNCONFINED LIQUID FUEL ON WATER

ABSTRACT

Burning of unconfined oil layers on water is an area from which techniques could be developed to improve flame weapons or to remove accidental oil spills. A method is presented by which most petroleum-based liquids can be burned to completion when spilled onto water.

TABLE OF CONTENTS

| | Page |
|--|------|
| ABSTRACT | 3 |
| LIST OF ILLUSTRATIONS | 7 |
| I. INTRODUCTION | 9 |
| II. THEORY | 10 |
| A. Fuel Lens Formation | 11 |
| B. Fuel Volatility | 15 |
| III. EXPERIMENTS AND RESULTS | 16 |
| A. Pan Fires | 17 |
| B. Fuel Lens Characteristics | 18 |
| C. Fuel Lens Modifications | 25 |
| D. Aggregate Lens Burning | 27 |
| IV. DISCUSSION | 36 |
| V. CONCLUSIONS | 37 |
| ACKNOWLEDGMENT | 38 |
| REFERENCES | 39 |
| DISTRIBUTION LIST | 40 |

LIST OF ILLUSTRATIONS

| Figure | Page |
|---|------|
| 1. Fuel Lens Cross Section | 12 |
| 2. Fuel Lens Thickness at 24°C | 19 |
| 3. Surface Aging Effect | 21 |
| 4. Effect of Temperature on Surface Tension | 22 |
| 5. Fuel Lens Burning | 24 |
| 6. Aggregated Lens Burning Representation | 29 |
| 7. Aggregate Lens Burning, After Ignition | 30 |
| 8. Aggregate Lens Burning, In Progress | 31 |
| 9. Aggregate Lens Burning, Residue | 32 |

I. INTRODUCTION

In connection with the study of the initiation and continued burning of military fuel fires, it was decided to apply the principles of liquid fuel burning to develop a method to promote burning of liquid fuels on water. This technique or method could be applied to improve weapon effectiveness against fuel containing targets and to remove accidental oil spills by burning.

Recently, there have been an increasing number of accidents where large quantities of petroleum-based fuels have spread over large ocean areas and eventually drifted into populated shores and recreational areas causing severe ecological damage. One of the most publicized oil spills was the wreck of the tanker Torrey Canyon in 1967. In this case about 118,000 tons of crude oil escaped from the tanker and formed an oil slick extending over many hundreds of square miles. This slick eventually drifted ashore and ruined many British and French beaches. One of the most costly spills for which exact figures are known^{1*} occurred when the tanker General Colocotronis sprang a leak off the Bahamas in 1968. The resulting oil slick cost some \$800,000 for clean up alone. Similar accidents happen continually with countless dollars spent to remove the oil. Personal, resort, and government areas are polluted at the same time.

An obvious way to remove these inherently combustible liquids is by burning. These materials are to be used eventually in one or another form of combustion. A significant amount of research in combustion, however, has been directed toward some particular commercial process, such as improved burning in the internal combustion

^{1*}References are found on page 39 of this report

engine. A gap exists between the knowledge available on the fundamentals of combustion and that resulting from research on specific processes or systems. This report attempts to elucidate some combustion phenomena associated with unconfined liquid fuel burning.

Burning of unconfined fuel layers on water has not been studied previously. The question of whether burning can occur involves processes taking place in the fuel liquid phase. Glassman and Hansel at Princeton pointed out² the importance of liquid phase processes in flame spreading over liquid fuels when the fuel had a flash point above ambient temperature. Glassman's work was devoted to confined liquid fuels and showed the role of convective currents in heating the fuel ahead of the flame front to the flash and fire points.

Unconfined fuels on the water move dramatically under the effects of a flame. Their equilibrium properties may be estimated, but the changes caused by the intense heat of a flame have not been studied previously. Observations of fuels burning both confined and unconfined on water are described in this report. Explanations to account for the observed phenomena are presented.

II. THEORY

The equilibrium behavior of unconfined fuel layers on aqueous substrates has been studied by several investigators.^{3,4,5} Application of these principles to burning fuel lenses also requires some knowledge of fuel volatility. The surface characteristics of liquid, hydrocarbon lenses and the volatility of hydrocarbon fuels are considered in this section with the aim of estimating their flammability.

A. Fuel Lens Formation

Hydrocarbons and petroleum fuels with high surface tensions such as decane or kerosene form a flattened lens when poured onto a water surface. A representative cross section is shown in Figure 1. The shape of the lens and its thickness are dependent on the surface properties and density of the particular lens material.

An expression to describe some of the properties of a lens may be derived as follows.⁶ In order to have physical equilibrium between a film of liquid 2 over liquid 1, it is necessary that the surface forces be balanced over the respective surface areas. Consider the fuel lens on water as shown in Figure 1. A_1 is the area of the air-liquid 1 interface; A_2 is the area of the air-liquid 2 interface; A_{12} is the area of the interface between the two liquids. The film is assumed to be thick enough to prevent either its upper or lower surfaces from influencing one another. At constant temperature and pressure a small change in the surface free energy G of the system is given by the total differential.

$$dG = \frac{\partial G}{\partial A_1} dA_1 + \frac{\partial G}{\partial A_{12}} dA_{12} + \frac{\partial G}{\partial A_2} dA_2 \quad (1)$$

$$\text{but} \quad dA_2 = dA_{12} = -dA_1$$

$$\text{and} \quad \left(\frac{\partial G}{\partial A_1} \right) = \gamma_1, \text{ etc.}$$

where γ is surface tension. The coefficient $\left(\frac{\partial G}{\partial A_2} \right)_{\text{area}}$ gives the

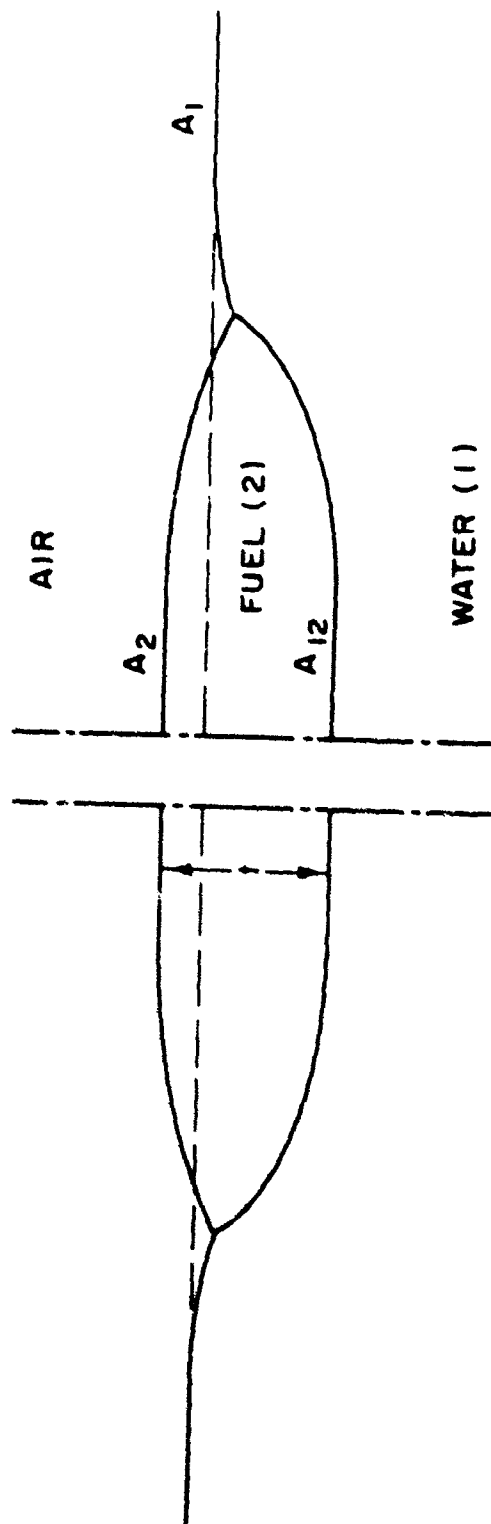


Figure 1. Fuel Lens Cross Section.

free energy change for the spreading of a film of liquid 2 over liquid 1. This coefficient is called the spreading coefficient, F_S .

$$F_S = \gamma_1 - \gamma_2 - \gamma_{12} \quad (2)$$

If $F_S > 0$ there is a decrease in free energy with spreading and the process is spontaneous. The fuel will spread over the water until it covers the entire surface or until the film becomes so nearly monomolecular that $\gamma_2 + \gamma_{12}$ increases to the value γ_1 .

If $F_S < 0$, the fuel gathers into one or more lenses with a thickness such that the forces of gravity are balanced with the surface forces. Thus, surface tension may be considered as a free energy per unit area as well as a force per unit length.

Spreading coefficients have been calculated⁶ for many substances on water. Some are shown in Table I.

Table I. Spreading Coefficients at 20°C for Liquids on Water

| <u>Liquid</u> | <u>F_S</u> | <u>Liquid</u> | <u>F_S</u> |
|-----------------|----------------------|--------------------|----------------------|
| isoamyl alcohol | 44.0 | nitrobenzene | 3.8 |
| n-octyl alcohol | 35.7 | hexane | 3.4 |
| heptaldehyde | 32.2 | heptane (30°C) | 0.2 |
| oleic acid | 24.6 | ethylene dibromide | -3.2 |
| ethyl nonylate | 20.9 | o-bromotoluene | -3.3 |
| p-cymene | 10.1 | carbon disulfide | -8.2 |
| benzene | 8.8 | iodobenzene | -8.7 |
| toluene | 6.8 | bromoform | -9.6 |
| isopentane | 9.4 | methylene iodide | -26.5 |

From this table it is expected that benzene and other compounds with positive F_S would spread on water while those with negative F_S should remain as a lens. However, this simple rule is complicated in cases where the two liquids are soluble in one another. In this case the surface tension of the mixture may be significantly different from that of the pure material. Even the relatively insoluble hydrocarbons are affected in some cases. For example, benzene has a solubility of only 0.07 g. per 100 g. in water.⁷ Yet, after addition to water, it consolidates into one or more lenses. Although this would not be expected due to its positive spreading coefficient, non-spreading in this case is due to reduction of the water surface tension by dissolved benzene. The higher molecular weight n-alkanes are less soluble in water and so their calculated spreading coefficients are presumably closer to true values. More accurate values for F_S would be obtained by using the surface tensions of the mutually saturated water and fuel.

The equilibrium shape of a large, free lens of oil on water was studied by Langmuir.³ He considered the total horizontal spreading force per unit length at the center of the lens to balance the spreading force in the water, remote from the lens boundary, down to the same depth. The limiting thickness with an infinite lens, is then given by³

$$t_{\infty}^2 = \frac{-2F_S \rho_1}{g \rho_2 \Delta \rho} \quad (3)$$

where ρ_1 and ρ_2 are the densities of water and the fuel, respectively, $\Delta \rho = \rho_1 - \rho_2$, and g is the acceleration due to gravity.

Thus, the lens thickness is a function of the fuel spreading coefficient, fuel density, and water density. The spreading coefficient, in turn, is a function of the fuel and water surface

tensions and their interfacial tension.

B. Fuel Volatility

In order to burn, a liquid fuel must vaporize in sufficient quantity to form a combustible vapor-air mixture. This mixture must be continuously replenished by air and fuel at a rate sufficient to maintain combustion.

One of the most widely used indications of fuel flammability is flash point.⁸ This is defined as the lowest fuel temperature at which a test flame causes the vapor above the liquid sample to ignite. The apparatus and method used for flash point determination are described in ASTM and Federal Test Method manuals.⁹ Another useful fuel flammability property is the fire point. This is the fuel temperature at which it begins to evaporate at a rate sufficient to maintain a continuous flame. Unfortunately, this temperature is very dependent on environmental conditions, and results are difficult to apply to other systems. Fire point data are rarely reported in the literature. Both the flash and fire points depend on the fuel vaporizing in order to burn.

The volatility of a fuel may be defined as its tendency to vaporize under given conditions.⁹ It is controlled for specification and manufacturing purposes by distillation test and vapor pressure test.⁹ The volatility or vapor pressure of a material may be greatly increased by the addition of only a small amount of highly volatile contaminants. For example, decane is not considered flammable at room temperature (20-25°C) because its flash point (46°C)¹⁰ is higher than room temperature. However, the addition of a very low flash point hydrocarbon such as

hexane (-23°C)¹⁰ can give a mixture with much higher volatility than the original decane. The amount needed to produce a combustible fuel-air mixture above the liquid may be estimated from the volatility of the liquid mixture and the flammability limits of the resulting fuel-air mixture.

Affens¹¹ has derived an equation combining Raoult's Law and LeChatelier's Rule of Mixtures which predicts the flash point of a two-component mixture of hydrocarbons.

$$\frac{N_A p_A}{L_A} + \frac{N_B p_B}{L_B} - 7.21 \times 10^{-6} t_f - 0.0102 = 0 \quad (4)$$

where N = mole fraction
 p = vapor pressure of the pure liquid, atm.
 L = lower flammability limit, vol.%
 t_f = flash point of the mixture, $^{\circ}\text{C}$

It can be seen that if one has a relatively non-volatile hydrocarbon, such as decane, with a high flash point, the flash point may be lowered to ambient temperature by addition of hexane. The amount calculated from Equation (4) was 0.061 mole fraction of hexane at 20°C . Affens' equation thus gives a quantitative method to modify a liquid hydrocarbon mixture to obtain a given flash point.

III. EXPERIMENTS AND RESULTS

The flash point of a binary, liquid, hydrocarbon mixture should be predictable using Equation (4). One should also be able to selectively modify the flammability of a fuel by changing its volatility. Simple experiments were carried out to test these principles with confined fuels, or fuels which were not allowed to spread freely over the substrate. The volatility of unconfined

fuel lenses on aqueous substrate were then modified to increase their flammability.

A. Pan Fires

The flash point of decane is above 25°C . Momentary application of an open flame to decane confined by the walls of a pan at 25°C will not ignite it. According to equation (4), the presence of only 0.061 mole fraction of hexane in decane will produce a combustible vapor-air mixture above the solution. This should flash when exposed to a sufficient ignition source. A mixture with 0.070 mole fraction hexane placed in a 50 ml beaker and covered. The cover was removed after a few minutes and an open flame was inserted into the beaker. The vapor-air mixture ignited, but burned only momentarily. However, when an identical hexane-decane mixture was poured into a shallow, open dish, an open flame did not ignite the vapors.

These simple experiments emphasize the importance of volatility in liquid fuel fires. First, a pool of decane will not ignite at room temperature. Addition of a small amount of hexane will produce a combustible fuel-air mixture above the liquid. This is equivalent to preparation of a mixture with its flash point at room temperature. However, in an open dish the highly volatile hexane is rapidly lost by diffusion to the surroundings. The hexane content of the mixture decreases as the hexane preferentially evaporates. The fuel will not flash when the hexane concentration is reduced.

Addition of volatile hydrocarbons to heavier hydrocarbons can thus produce solutions which have combustible mixtures above them. A series of experiments were carried out with several hydrocarbon materials in pans to produce sustained fires.

Table II. Pan Fires

| <u>Fuel</u> | <u>Flash Point</u> <u>°C</u> | <u>Hexane Mole</u> <u>Fraction Added</u> | <u>Established</u> <u>Fire</u> | <u>Remarks</u> |
|--------------|---------------------------------|---|-----------------------------------|----------------------|
| Decane | 10 46 | 0.14 | Yes | Burned to completion |
| Kerosene | 49 ¹² | 0.068 | Yes | Irregular burning |
| Paraffin Oil | 135 ¹² | 0.29 | Yes | Irregular burning |

In these experiments the hexane was poured onto the less volatile fuel without mixing. The fuel layer ranged from 5 to 11 mm. thick over a water substrate (ca. 2-3 cm. thick) in a circular, uncovered stainless steel pan of about 15 cm. diameter. Large excesses of hexane were used to give sustained fires. After burning a few minutes the kerosene and paraffin oil began to burn irregularly with hissing and ejection of small burning droplets. The agitation became very violent after a few more minutes. It is apparently due to water vaporizing at the fuel-water interface as the temperature of the fuel layer increases during burning. Addition of a mixture of hexane and decane to paraffin oil consistently led to a sustained fire while addition of only hexane did not.

B. Fuel Lens Characteristics

The properties of fuel lenses on water were studied experimentally to extend predicted behavior to systems of practical interest. Some basic characteristics of a lens which depend on its surface tension and spreading coefficient were measured first.

The lens thickness is dependent on the spreading coefficient, F_S according to Equation (3). A plot illustrating this dependence is shown in Figure 2 for several commercial grade hydrocarbons. The lens thicknesses were calculated from measurements of lens radius for a

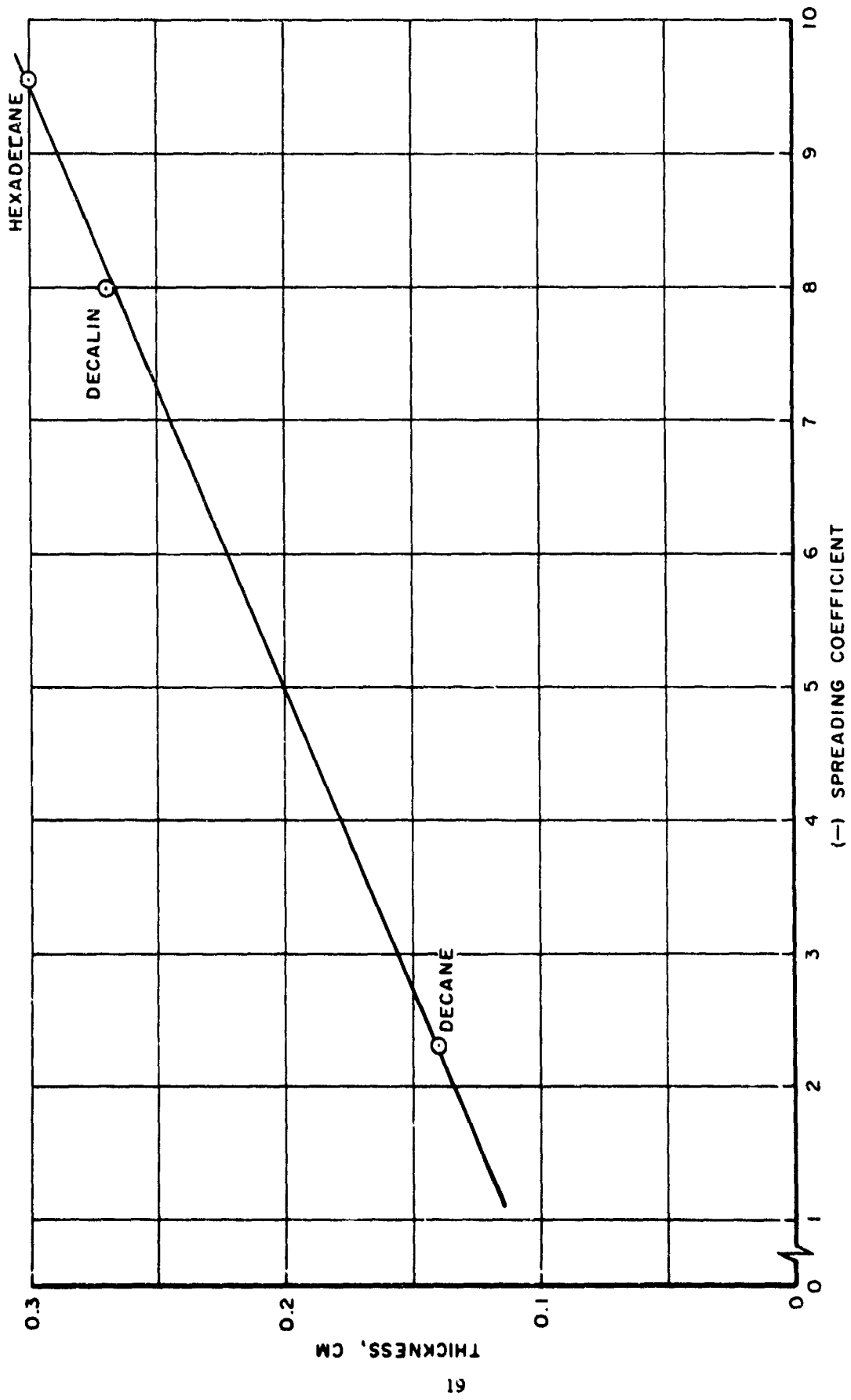


Figure 2. Fuel Lens Thicknesses vs Spreading Coefficient.

volume of 41 ml of each hydrocarbon at 24°C.

The lens radius for commercial grade hydrocarbons was also found to increase with time after lens formation. The effect is shown in Figure 3 for commercial grade decalin. It may be attributed to an aging effect where surface active substances diffuse to the newly formed lens surface and reduce the surface tension. The aging effect for lauryl sulfonic acid in the surface of its aqueous solution was studied by McBain and Wood.¹³ They measured the concentration of acid in the surface layer and found that its increase with time after the surface formation corresponded with the decrease in surface tension.

The decalin used in these experiments was purified by percolation through a column of activated charcoal. The percolated decalin formed a lens with a thickness much closer to t_{∞} . These lenses did not show the aging effect mentioned above for unpercolated decalin.

The surface tension of hydrocarbons is inversely proportional to temperature. Two examples of the effect of temperature on surface tension are shown in Figure 4.¹⁴ The spreading coefficient will also change but in a more complex fashion since it is also a function of the water surface tension and the interfacial tension at the fuel-water interface. For example, if the water substrate temperature remained essentially constant while the decane temperature rapidly increased, the fuel surface tension at which the spreading coefficient will go to zero can be calculated from Equation (2).

$$F_S = 0 = \gamma_1 - \gamma_2 - \gamma_{12}$$

$$\gamma_2 = 72.8 - 52.3$$

$$\gamma_2 = 20.5 \text{ dynes/cm.}$$

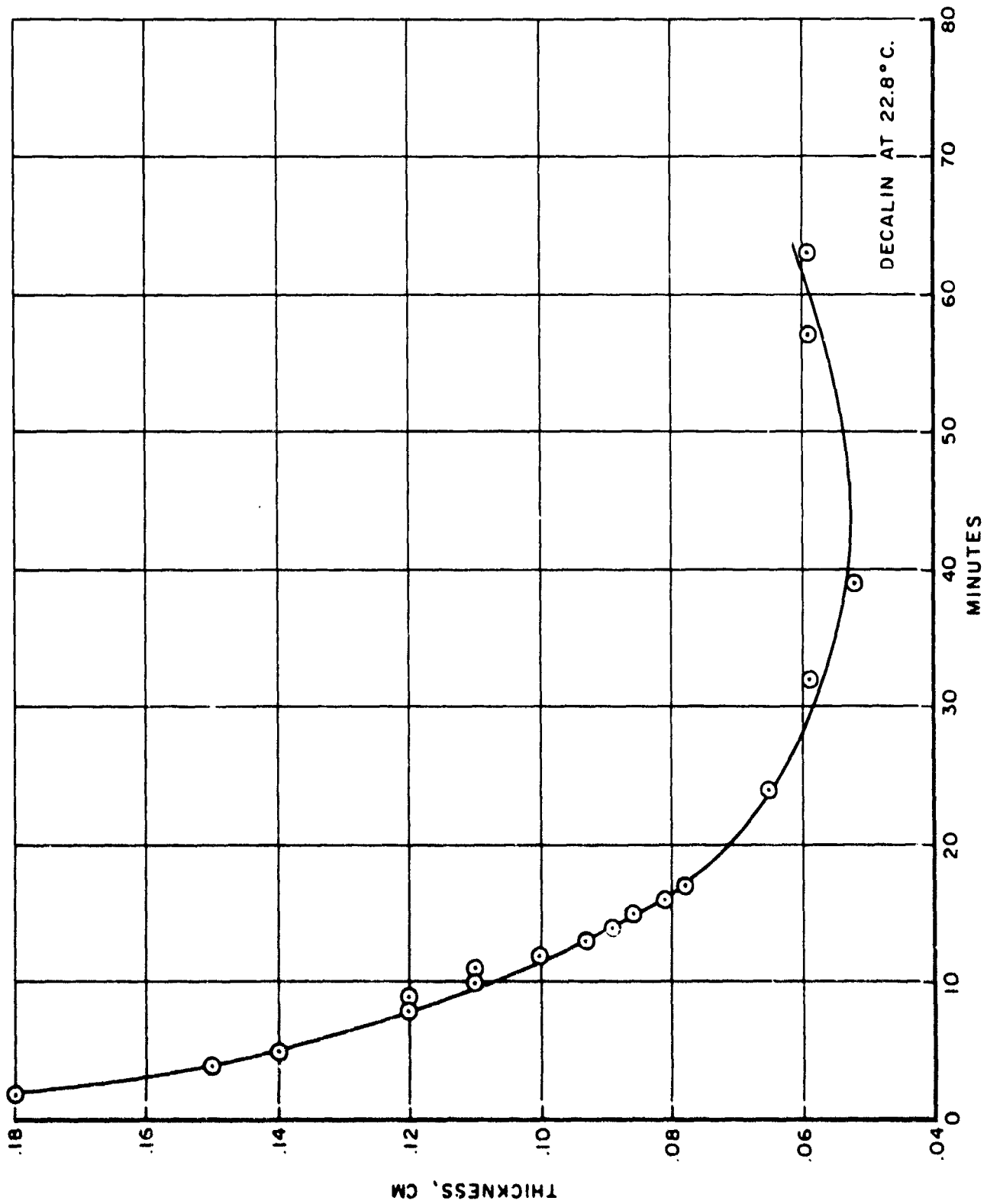


Figure 3. Surface Aging Effect.

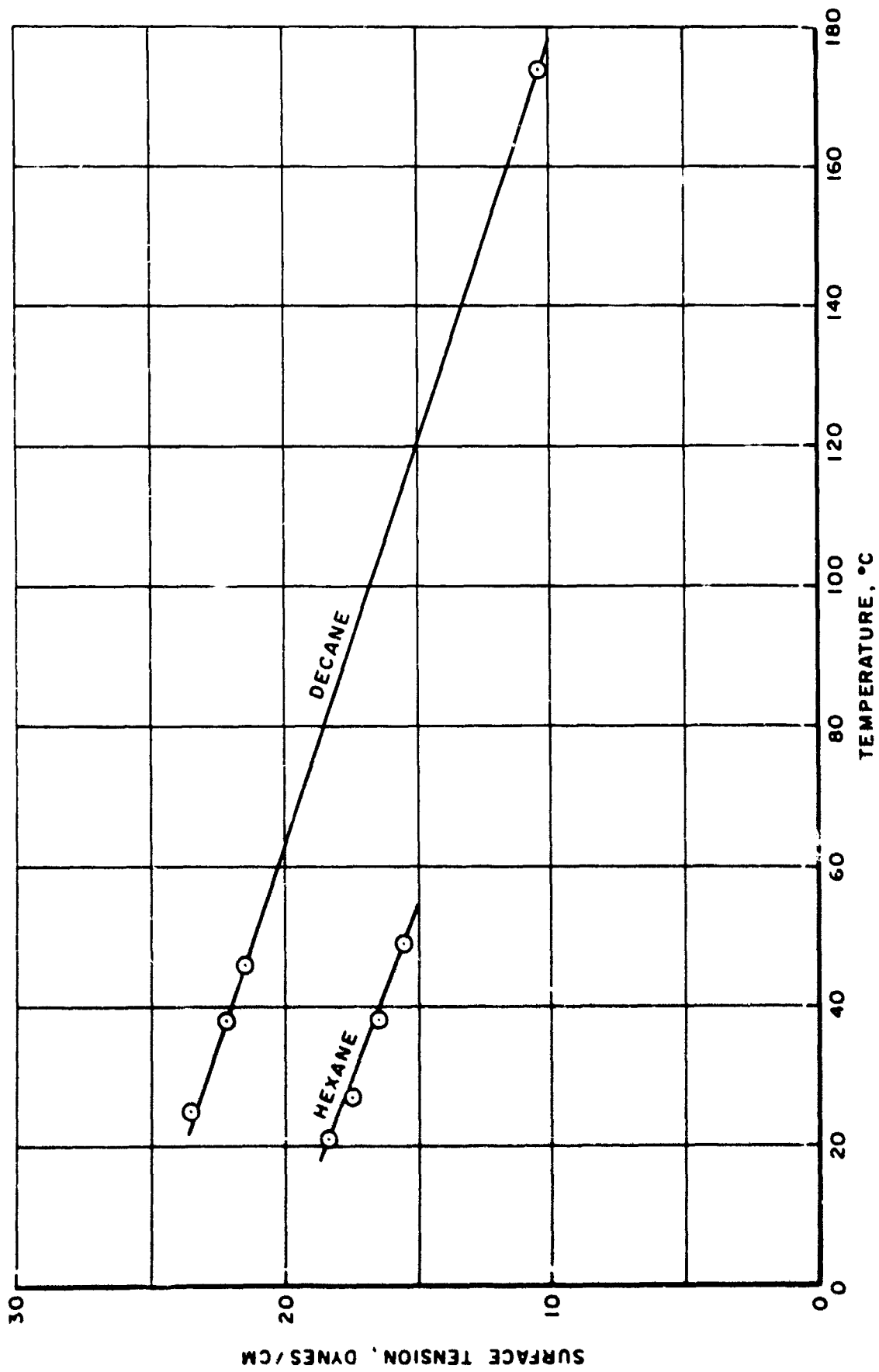


Figure 4. Effect of Temperature on Surface Tension.

Decane would have this surface tension at about 60°C. In this way, the temperature at which the lens would spread to a film can be calculated. Again, a more precise value would be obtained using mutually saturated values for the decane and water surface tensions.

A simple experiment was designed to burn a liquid fuel lens on an aqueous substrate by increasing the fuel volatility as in the previous section on pan fires. However, in this case the fuel was in the form of a lens unconfined by the walls of a pan. A small portion of kerosene was placed on water in a large pan. Some hexane was added to the kerosene lens. The lens diameter increased immediately and the lens became thinner. An open flame was used to ignite the vapors. As the fuel burned, the diameter of the lens increased. The fire shortly went out leaving most of the kerosene unburned. A diagram of an untreated, unconfined burning lens is shown in Figure 5.

Larger amounts of hexane were added to the kerosene to maintain burning for a longer time. However, the lens spread to a thin film covering the entire water surface within the pan. Although the mixture was easily ignited, the vapors burned only a short time.

The flame extinction may have been due to cooling of the thin fuel layer below its fire point by the water substrate. The fuel must be at a temperature above its fire point to continue burning. The substrate temperature was 20-25°C while the fire point of the fuel would have been greater than 50°C.

A comparison was made for a heavy oil burning in confined and unconfined modes to study this concept. In these experiments mixtures of 50 ml of Squibb's Mineral Oil, 20 ml of decane, and 10 ml of hexane were prepared. In one case the mixture was ignited by an open flame

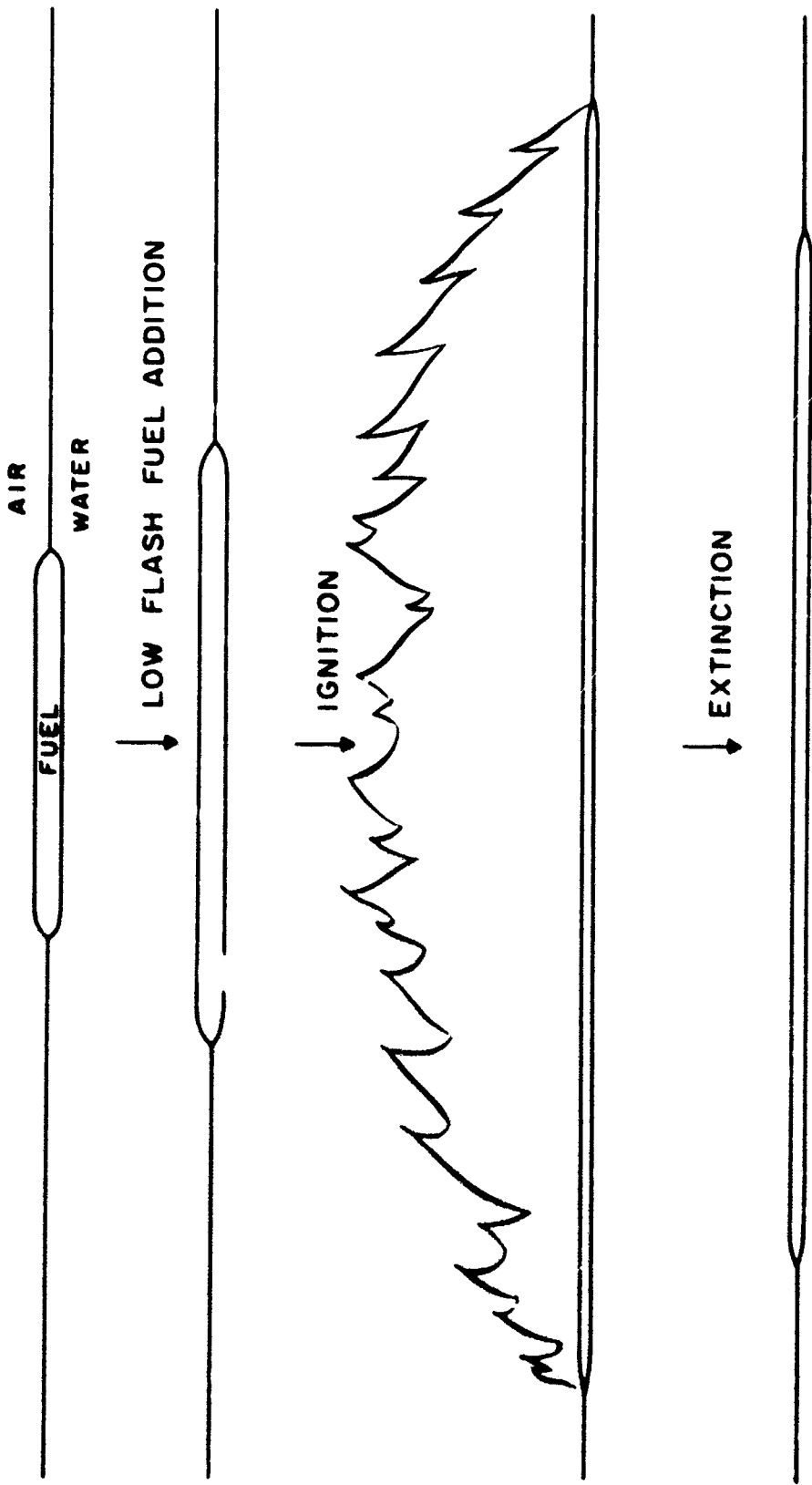


Figure 5. Fuel Lens Burning.

in a small beaker, and the burning mixture was poured into a small petri dish without water. The fire burned for 42 minutes leaving a small amount of tarry, dark residue.

An identical mixture was also ignited by an open flame immediately after preparation, but the burning mixture was poured onto water at 26°C in an open tray (12 x 18 in.). The mixture burned for less than 2 minutes as a thin film. This is about the length of time that the low flash point components would burn.

The thin oil layer on water from the second experiment must have cooled below its fire point while in close contact with the aqueous substrate. Once the fuel temperature fell below the fire point, the fire went out. The thick oil layer in the petri dish, however, maintains the fire point at its surface by its own insulating properties. Hydrocarbons have much lower thermal conductivities than water.

C. Lens Modification

Experiments in the previous section showed that thicker fuel layers of high flash fuels burned better than thin films of the same fuel on water. In order to maintain (or increase) lens thickness during burning, various materials were added to the fuel. Ignition of the fuel lenses on water and their subsequent burning were then observed. Thickeners were an obvious choice since viscous oils resist thinning under the influence of heat. Viscosity index improvers are used by the petroleum industry to minimize the decrease in oil viscosity at high temperatures.

A commercial viscosity index improver oil solution was tried first. A mixture of 50 ml of the oil solution with 10 ml of hexane and 20 ml of decane was poured on water and formed a lens.

The lens ignited easily with an open flame, but burned less than a minute. The thickener was not effective in maintaining lens thickness under the flame heat. A mixture with the same composition completely burned in a stainless steel pan.

The high molecular weight polymer, Vistanex, is commonly used as a viscosity index improver. About 1% of Vistanex was dissolved in kerosene by stirring. This solution was thick and had a much lower (more than 100°C) flash point than the lubricating or paraffin oils. About 5 ml of the solution formed a lens of 2.75 cm radius on water at 27.9°C. After adding 1.0 ml amount of hexane and lighting it, this mixture burned to completion on water. Only a thin film of polymeric material remained on the water surface.

The possibility of flame spreading from a thickened lens to unthickened fuel was also briefly studied. A few mls of Vistanex-kerosene solution were burned on water as above. Some additional unthickened kerosene was added adjacent to the burning lens. The fire did not spread to the unthickened kerosene. In fact, the unthickened fuel seems to be repelled by the burning lens. A depression formed in the unthickened fuel adjacent to the fire resulting in a very thin fuel film. This film should have been close to the substrate temperature (28°C) and thereby could not support a flame. As the fire subsided, the unthickened fuel did not show any tendency to flow into the burning area. The fire went out without burning the unthickened fuel.

The effect of some M-4 thickener (diacid aluminum soap of iso-octanoic acid) on the burning of an unconfined fuel lens on water was also examined. The thickener dispersed easily into the kerosene when sprinkled onto the lens. The lens was ignited by an open flame without

need for hexane. The lens swelled somewhat under the flame without changing the diameter. A thick, fuel-containing gel remained on the water after the flame went out. The fuel in the interior of the gel apparently could not move to the surface and vaporize fast enough to keep the fire going. Less thickener was used in other runs, but the lens broke up without burning to completion.

Some materials which would modify the surface characteristics of fuel lenses were also examined. Methylene iodide has a very low spreading coefficient (-26) compared with typical hydrocarbons (eg. hexadecane, -9). A mixture of methylene iodide and a hydrocarbon should form a thick lens according to Equation (3). The lens diameter of kerosene did not appear to be affected by saturation with methylene iodide. A silicon-based antifoam spray which reduces hydrocarbon surface tension was also examined. When sprayed onto a kerosene lens on water, it reduced the size of the lens. However, the lens would not ignite. In fact, a burning lens of thickened kerosene was extinguished by a slight spray of the antifoam. Apparently the antifoam agent inhibits combustion.

D. Aggregate Lens Burning

Finely powdered, activated charcoal has the dramatic ability to foster the burning of liquid fuel lenses on water when the ambient temperature is below the flash point of the fuel. The charcoal is preferentially wetted by the organic phase. The lens is then easily ignited by an open flame and burns to completion.

The mechanism of the ignition and burning is not completely understood, but it is tentatively described as follows. The charcoal apparently forms an internal, aggregated structure within the lens.

Fuel at the surface is easily vaporized and ignited by a glowing hot wire or open flame. After ignition, the fuel flows up through the aggregated structure by capillary action to the surface. It is rapidly vaporized in this zone of large thermal gradient and swept into the combustion zone. A representation of the process is shown in Figure 6.

The charcoal must be evenly distributed in the lens to form a continuous aggregate. During the burning the fuel flows away from areas where the aggregate structure is lacking or thinly distributed. The lens quickly breaks apart at these points. The breakup is probably due to a decrease in surface tension as the fuel surface temperature rises. The heated surface fuel has a tendency to flow away from the lens unless it is restrained or it vaporizes before flowing. This tendency may be called a flow potential. When a continuous charcoal aggregate is present in the lens only the fuel and charcoal near the surface are heated. This fuel vaporizes before it can flow. The charcoal serves both as an insulating medium to protect the lower layers of fuel from being heated and as a path by which fresh fuel flows to the surface for vaporization.

A wide range of hydrocarbons were easily burned as lenses with charcoal. Some of the fuels that were burned ranged from pure hydrocarbons such as decane and decalin to heavy, high boiling, high flash point materials such as mineral oil. Photographs of a typical decalin lens with 24 wt % added charcoal burning to completion on water are shown in Figures 7, 8 and 9. The residue is a dry powder which retains the original lens shape. The dry, charcoal residue eventually

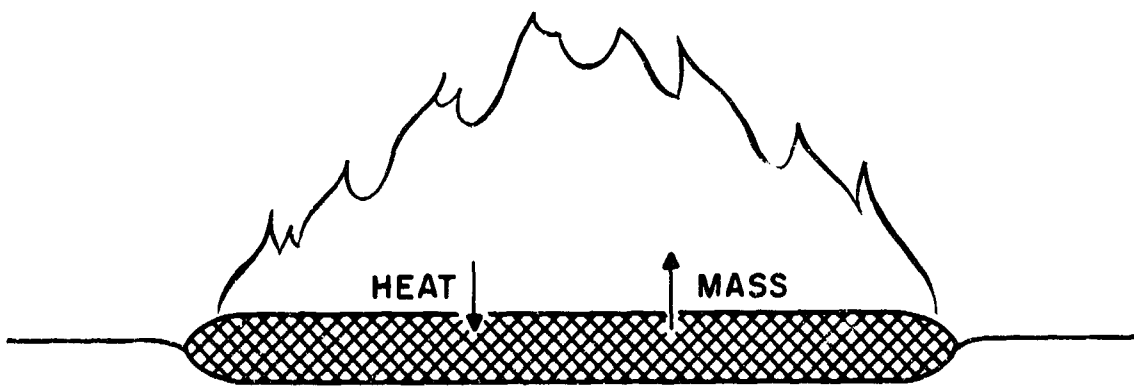


Figure 6. Aggregated Lens Burning Representation.

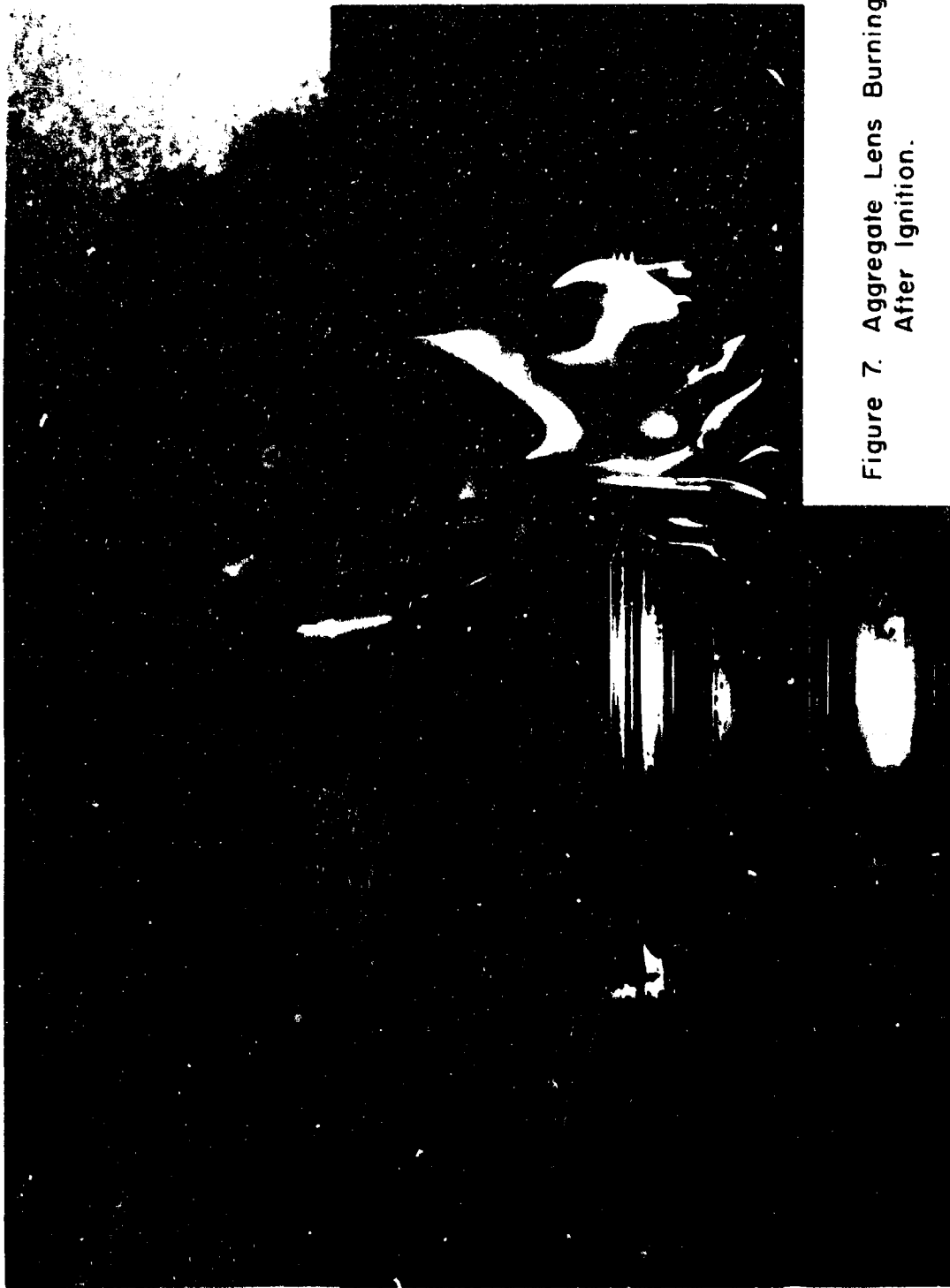


Figure 7. Aggregate Lens Burning
After Ignition.

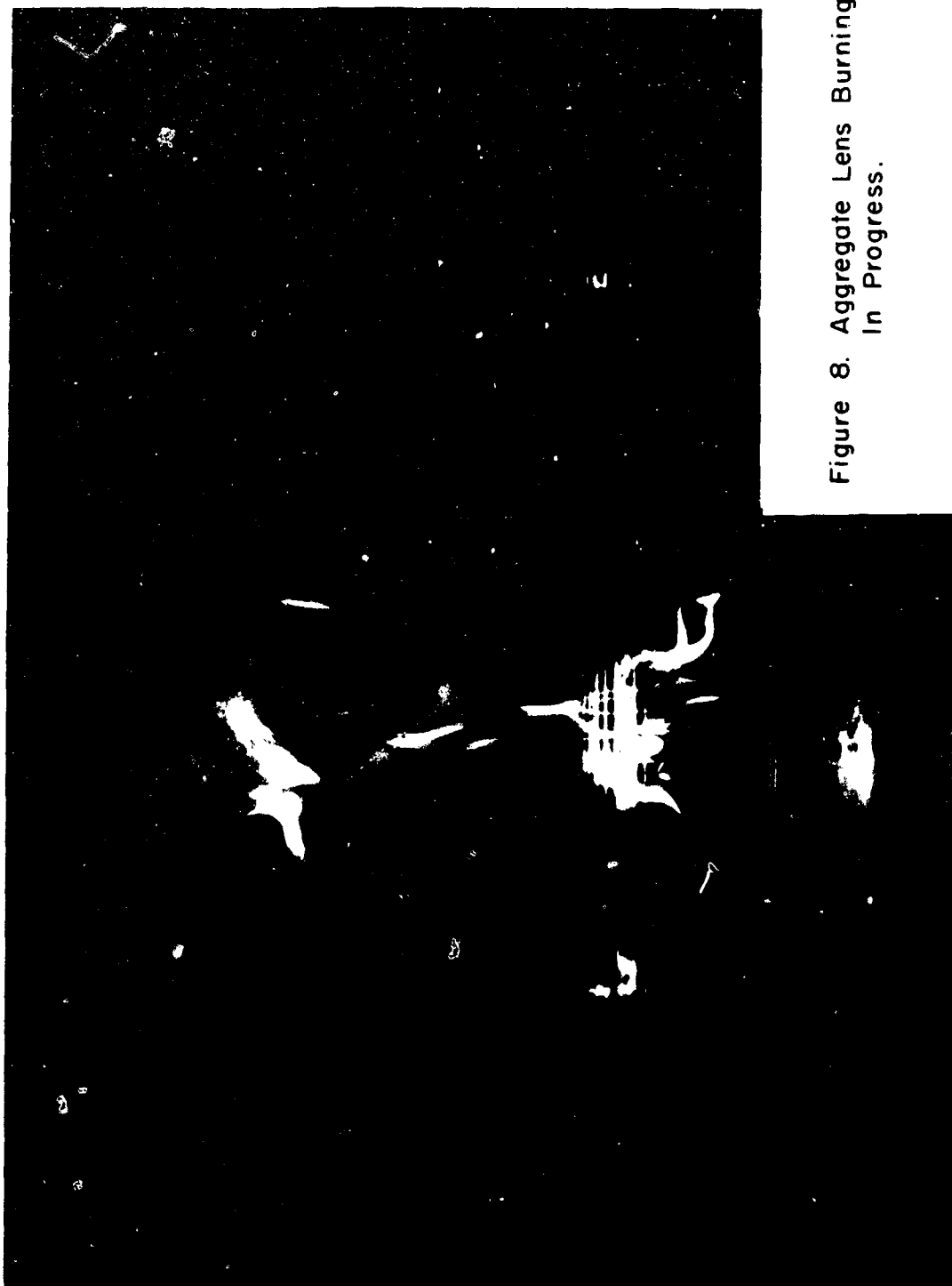


Figure 8. Aggregate Lens Burning
In Progress.

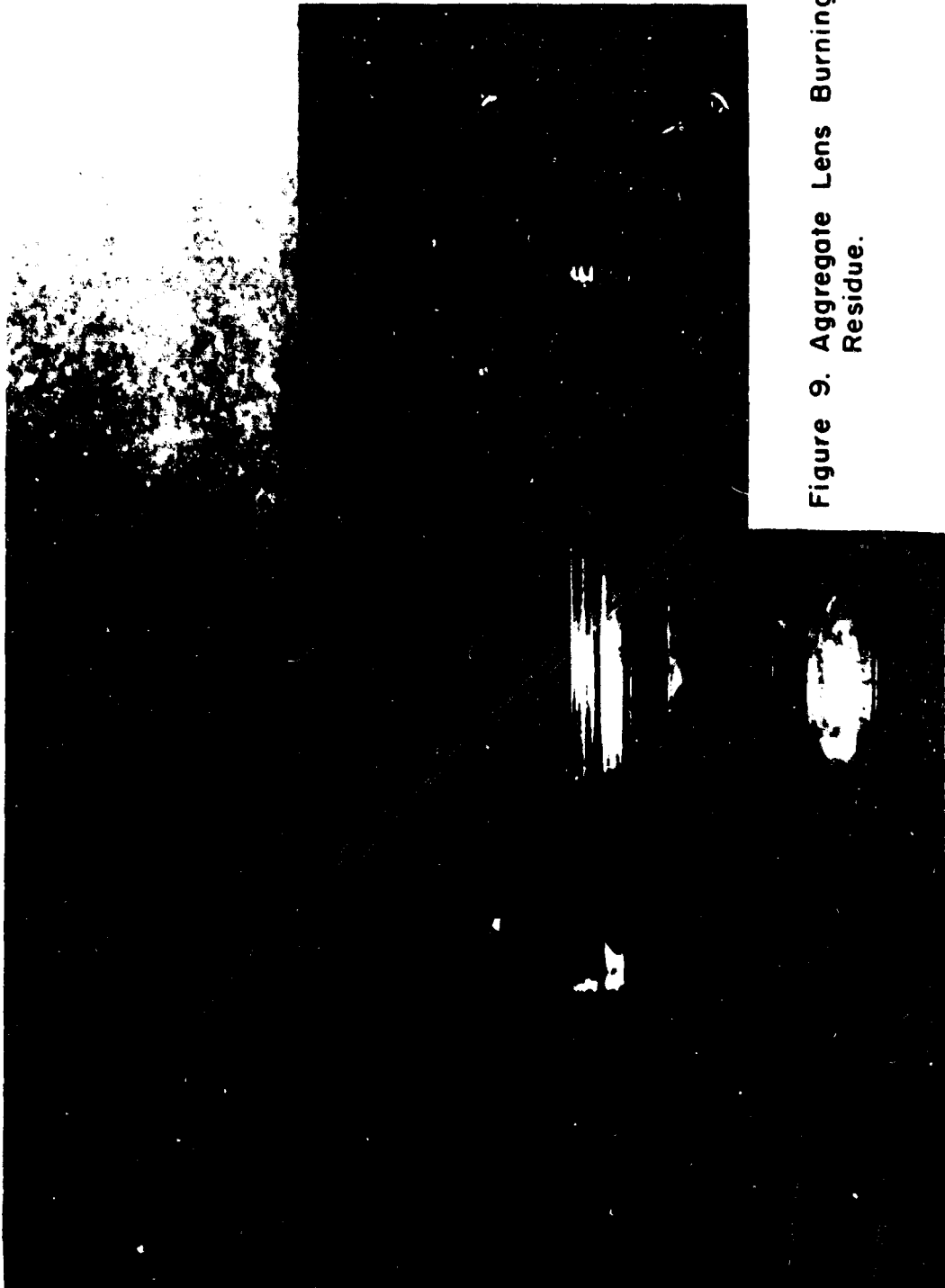


Figure 9. Aggregate Lens Burning Residue.

breaks up if exposed to waves. In this case the charcoal drops from the surface to the bottom of the dish in a loosely dispersed form.

In a series of experiments, various amounts of charcoal were added to lenses of decalin to study effect of added charcoal on the lens burning. The lenses were formed from 40.0 ml portions of decalin on water at 24.7°C. The lens radius was not measured for each case, but a typical size was 7.0 cm. Weighed amounts (3-25 wt.%) of Will Scientific, N.F. grade, activated charcoal were lightly sprinkled over the lenses. They were then ignited by means of a small flame. The lens burning characteristics are shown in Table III.

Some remarks can be made about the effects of varied amounts of charcoal on lens burning characteristics. With 3% added charcoal the lens would not ignite with a small open flame. With 11% added charcoal the lens was ignited but would not hold together. With 17% added charcoal, the lens was ignited and most of the decalin burned. With 25% added charcoal the lens remained intact and all of the decalin burned.

Impurities in the fuel play an important part in the case of burning of lenses on water. In one case, an old sample of hexadecane spread on water formed a thin film rather than the expected lens. A larger quantity of charcoal was required to burn this film.

The degree of difficulty involved in reaching sustained burning is highly dependent on the properties of the fuel. High flash point fuels such as heavy fuel oil or light-end depleted crude oil should require a greater amount of charcoal and may need longer contact with the ignition device. The ignition of charcoal thickened mineral oil was studied in this connection. It has a very high flash point.

Table III. Decalin Lens Burning Characteristics

| | <u>Charcoal Added</u> | | <u>Temperature</u> | | <u>Burning Characteristics</u> |
|----|-----------------------|--------------|--------------------|-----------------|--|
| | <u>Gms.</u> | <u>% Wt.</u> | <u>°C</u> | <u>Ignition</u> | |
| 1. | 1.00 | 3 | 24.6 | No | Could not ignite except for small mound. |
| 2. | 4.00 | 11 | 24.7 | Yes | Lens broke up and most of the fuel remained unburned. |
| 3. | 5.00 | 14 | 24.6 | Yes | Lens broke up. |
| 4. | 6.00 | 17 | 24.6 | Yes | Lens broke up, but most of the fuel burned off. |
| 5. | 7.00 | 19 | 24.6 | Yes | Small segments of main lens broke away, but most of the fuel burned off. |
| 6. | 8.00 | 22 | 24.6 | Yes | Small segments of main lens broke away, but most of the fuel burned off. |
| 7. | 9.00 | 25 | 24.8 | Yes | Lens remains intact and burned all fuel off. |

Twice the length of exposure to an open flame was needed to establish the flame on the charcoal-mineral oil lens as for similar charcoal-kerosene lenses. The lens was much thicker and was much less likely to break up by wave action.

The effect of different types of charcoal on the burning of fuel lenses was examined. Equal volumes of powdered wood charcoal, activated charcoal, and animal charcoal were added to kerosene lenses on water. The animal and activated charcoal did a better job of holding the lens together during burning. However, the bulk density of the animal charcoal (0.54 g/cc) is almost 3 times that for activated charcoal (0.20g/cc). The activated charcoal is three times as efficient by weight.

Several experiments were aimed at determining whether a flame would spread between fuel lenses. A 2 in. diameter aluminum dish filled solely with decalin was floated on water in a large tray. A doughnut shaped lens of decalin subsequently was formed concentrically around the exterior of the dish. Charcoal was added to the exterior lens. After a flame was established in the dish, it would not jump or spread one cm. from the dish to the outer doughnut-shaped lens.

A burning charcoal-decalin lens did not ignite an adjacent pure decalin lens. A burning charcoal-decalin lens ignited an adjacent charcoal-decalin lens only if it was brought into contact or if the flame plume drifted near the unburned surface. Large fires should spread more easily since a larger fire radiates much more heat to its surroundings.

Some larger scale tests have been carried out on open saline water. In a typical test, 200 ml of decalin was mixed with 200 ml of hexadecane. This mixture was poured onto the water at 10°C with

essentially no wind present. The fuel spread out over an area of about 2 ft. diameter. The lens broke up and some drifted onto the shore. Charcoal was sprinkled onto some of the smaller lens and the lens ignited by an open flame. The fire did not spread to the other lenses. About 10-20 ml of hexane was poured onto the area. The hexane vapors immediately burst into flame when they reached the burning lens and the flash ignited several of the other small charcoal-fuel lenses. The lenses which had been thickened with the charcoal burned to completion. Other irregular portions of fuel which had not received adequate charcoal were unburned.

IV. DISCUSSION

Application of this technique to burn large petroleum spills appears feasible. The charcoal could be quickly distributed onto the spill by air. The very fine particles distribute reasonably uniformly by their natural settling tendency if dropped from a sufficient height. Ignition of a liquid fuel below the flash point is a very complex process. The ignition device must heat the surface layer of fuel and aggregate to vaporize sufficient fuel to form a combustible mixture above the lens. Then, the device must ignite the vapors. A large number of ignition devices would furnish sufficient heat and/or energy for ignition. White phosphorus (WP) or napalm, for example, should easily ignite most charcoal-fuel combinations. Ignition would best be done at several locations since the flame spreads slowly over thickened fuel.

Environmental conditions such as waves, temperature and wind greatly affect the burning of a fuel lens on water. Waves tend to break up a lens and thereby diminish the intensity of burning. Waves

also tend to distribute the fuel in irregular patterns which are difficult to uniformly treat with charcoal. The temperature of the water affects the lens in several ways. At lower temperatures the fuel had to be heated a greater amount to vaporize the fuel. This is particularly important for high flash point fuels. However, at low temperatures the fuel consolidates into a thicker lens which should burn more efficiently after ignition.

Wind complicates the distribution of charcoal onto the fuel, hinders the ignition of the fuel, and tends to extinguish fires of low intensity. In short, wind is detrimental in almost all phases of the operation. It is of some value in bringing fresh air to a large, vigorously burning fire.

The principles of burning of unconfined liquid fuels on water have a number of applications. More efficient flame weapons may be developed for burning on water. Very volatile fuels such as gasoline burn easily on water but are quickly consumed due to their high volatility and high surface area to volume ratio. Lenses of lower volatility fuels such as kerosene form a much thicker layer on water. These thicker lenses burn for a much longer time and present a greater capacity for thermal damage.

V. CONCLUSIONS

Activated charcoal was shown to promote ignition and continued burning of lenses of high flash point fuels on water. The charcoal-fuel lens held its original shape during burning. The residue in most cases was a dry powder cake which could be easily collected and reused. Several model compounds and fuels were burned in laboratory experiments using this method. Large scale field tests have not been carried out, but there are not any foreseeable problems in application

of the method to burn off large oil spills in remote locations. The residue remaining after burning may be left to the elements to eventually sink to the sea bottom, or it may be collected for reuse.

ACKNOWLEDGMENT

The author would like to acknowledge many helpful discussions with Dr. J. Dehn and Dr. A. Finnerty during the course of this investigation.

REFERENCES

1. "Chemical and Engineering News," 47, 7, 26 (1969).
2. I. Glassman and J. G. Hansel, "Fire Res Abstracts and Reviews," 10, 217 (1968).
3. I. Langmuir, J. Chem. Phys., 1, 756 (1933).
4. N. F. Miller, J. Phys. Chem., 45, 1025 (1941).
5. D. J. Donahue and F. E. Bartell, J. Phys. Chem., 56, 489 (1952).
6. A. W. Adamson, "Physical Chemistry of Surfaces," 2nd ed. Interscience, New York, 1967.
7. N. A. Lange, "Handbook of Chemistry," 9th ed. Handbook Publishers, Inc., Sandusky, Ohio, (1956).
8. National Fire Codes, Vol. 1, National Fire Protection Association, Boston, (1963-4).
9. M. Popovich and C. Hering, "Fuels and Lubricants," John Wiley & Sons, Inc., New York, (1959).
10. W. A. Affens, "Flammability Properties of Hydrocarbon Fuels, Part I - Interrelations of Flammability Properties of n-Alkanes in Air," NRL Report 6270, (1965).
11. W. A. Affens, "Flammability Properties of Hydrocarbon Fuels, Part III, Flammability Properties of Hydrocarbon Solutions in Air," NRL Report 6617, (1967).
12. "Handbook of Industrial Loss Prevention," McGraw-Hill, New York, (1967).
13. J. W. McBain and L. A. Wood, Proc. Roy. Soc. A174, 286, (1940).
14. American Petroleum Institute, Technical Data Book - Petroleum Refining, American Petroleum Institute, New York, (1966).

Security Classification Unclassified

DOCUMENT CONTROL DATA - R & D

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

| | | | |
|---|------------------------------|---|--|
| 1. ORIGINATING ACTIVITY (Corporate author) USA ARDC Ballistic Research Laboratories Aberdeen Proving Ground, Maryland | | 2a. REPORT SECURITY CLASSIFICATION Unclassified | |
| | | 2b. GROUP | |
| 3. REPORT TITLE Ignition and Combustion of Unconfined Liquid Fuel on Water | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) | | | |
| 5. AUTHOR(S) (First name, middle initial, last name) Warren W. Hillstrom | | | |
| 6. REPORT DATE November 1970 | 7a. TOTAL NO. OF PAGES 43 | 7b. NO. OF REFS 14 | |
| 8a. CONTRACT OR GRANT NO. a. PROJECT NO. 1T061101A91A c. d. | | 8b. ORIGINATOR'S REPORT NUMBER(S) BRL Memorandum Report No. 2076 | |
| 8c. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | | | |
| 9. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited. | | | |
| 11. SUPPLEMENTARY NOTES | | 12. SPONSORING MILITARY ACTIVITY U. S. Army Materiel Command Washington, D.C. | |
| 13. ABSTRACT Burning of unconfined oil layers on water is an area from which techniques could be developed to improve flame weapons or to remove accidental oil spills. A method is presented by which most petroleum-based liquids can be burned to completion when spilled onto water. | | | |

DD FORM 1473
1 NOV 68

REPLACES DD FORM 1473, 1 JAN 54, WHICH IS OBSOLETE FOR ARMY USE.

U nclassified

Security Classification

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Diffusion flames, vaporization, hydrocarbon fuels, water surface pollution, surface chemistry, anti-material, antipersonnel | | | | | | |