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This report has been submitted in fulfillment of contract DOT-CG-01,381-A and is promulgated subject to the following qualifications:

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J. R. IVERSEN Captain, U. S. Coast Guard Chief, Applied Technology Division Office of Research and Development U. S. Coast Guard Headquarters Washington, D. C. 20591

FINAL REPORT

"Physical Processes in the Spread of Oil on a Water Surface"

Prepared for

The U.S. Coast Guard on Contract DOT-CG-01-381-A

by James A. Fay

9 April 1971

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David P. Hoult Principal Investigator

Abstract

Formulae are recommended for calculating the extent of the spread of oil slicks on water as a function of time. They are based on empirical measurements of spreading rates and analytical and theoretical studies of the physical processes which accelerate or retard the spread of a film. Both one-dimensional and two-dimensional (axisymmetric) slicks are treated. Comparisons of the recommended formulae are made with the limited number of field observations, both for the rate of spread and the maximum slick size.

I. Introduction

This paper reviews our current understanding of the physical processes which initially cause and ultimately terminate the spread of oil (or other immiscible fluids) on the surface of water. We are principally concerned with the spread of large volumes of oil, such as might be encountered in spills from ships or oil wells, and which cannot be reproduced easily in a laboratory at full scale. Our approach is to consider some simple cases of oil spread, which will not likely be duplicated precisely in practice, but for which a theoretical or semi-empirical description can be found, especially through use of properly designed laboratory experiments which simulate full scale spreading phenomena. Based on this understanding, a correlation of field observations is made as a test of the suitability and accuracy of these predictions, and empirical formulae for estimating spreading rates are recommended.

The physically most important assumption underlying our analysis, which is most likely to be violated in any real incident of a spill, is the absence of any effects of wind, tidal currents and waves. We would expect that the drifting motion caused by winds and tidal currents would simply be superimposed on the spreading motion to be experienced on calm, stationary water, since these latter motions are confined to a layer near the surface which is relatively thin compared with that subject to wind friction effects or tidal motion. It is more likely that wind and tidal current will produce relative shearing motion in the plane of the water surface, deforming the shape of the spreading slick from those simple shapes expected in calm water. Such distortion is commonly observed, and is most likely to limit the usefulness of the spreading laws which we propose. These effects are very difficult to predict or even describe, and there is little empirical evidence on which to base an estimate of their importance.

The first order effects of surface waves, on the other hand, can be shown to be negligible. Because of their periodic nature, waves produce oscillatory forces having zero mean value and which therefore do not affect the spreading motion which proceeds on a much longer time scale than the usual wave periods. Of course, there are non-linear effects of waves which are probably not separately distinguishable from those associated with winds and tidal currents, and are equally difficult to predict.

The use of laboratory scale experiments to establish empirical spreading laws and to check theoretical predictions has been discussed elsewhere. We shall make use of such experimental evidence to provide the best estimate of spreading rates, accepting the asserted validity of the scaling of these experiments to full size. The basis of such scaling is a well understood aspect of fluid mechanics, and will not be further discussed here. Accurate field observations of the spread of oil slicks are very rare. We have tried to include all measurements which have been published, but in most cases we have been forced to assume additional information, such as spreading coefficients, when comparing these observations with a theory. Given the inaccuracy of the observations, these assumptions are of no great significance, but only serve to emphasize the scarcity and crudity of the observations. A major goal of our proposed correlations is to permit the comparison with future (and hopefully more accurate) observations.

II. Spreading and Retarding Forces

Although the force of gravity acts downward, it causes a sidewise spreading motion of a floating oil film by creating an unbalanced pressure distribution in the pool of oil and the surrounding water. This force on an element of oil film acts in the direction of decreasing film thickness and is proportional to the thickness, its gradient, and the difference in density between oil and water. (See Fig. 1.) As the oil film spreads and becomes thinner, the gravity force diminishes.

At the front edge of the expanding slick an unbalance exists between the surface tension at the water-air interface and the sum of surface tensions at the oil-air and oil-water interfaces. The net difference, called the spreading coefficient, is a force which acts at the edge of the film, pulling it outwards. This spreading force does not depend upon the film thickness as does the gravity force, and will not decrease as the oil film thins out (unless the chemical properties change through aging). Eventually the surface tension force will predominate as the spreading force.

These spreading forces are counterbalanced by the inertia of the oil film and of the thin boundary layer of water below it which is dragged along by friction (see Fig. 1). The inertia of an element of the oil layer decreased with its thickness as time progresses and the film spreads, but the inertia of the viscous layer of water below the oil increases with time as its thickness grows. Consequently, the viscous retardation will eventually outweigh the inertial resistance of the oil layer itself.

It is also informative to consider these effects from the point of view of an energy balance. A pool of oil floating on water possesses a greater potential energy than the water it displaces, in proportion to its thickness. As it spreads and its thickness decreases, there is a loss of potential energy. Also, as air/water surface is replaced by an oil film, the surface energy per unit area (which has the same physical value as the interfacial tension) is reduced by an amount equal to the spreading coefficient. Thus both surface energy and potential energy are decreased as the slick spreads. This energy is converted either into heat by viscous dissipation in the water beneath the slick or into the energy of gravity surface waves which propagate away from the expanding oil pool. In other words, each spreading force is associated with an energy-producing process and each retarding force with an energy-

-3-

dissipating process.

It is thus clear that the spread of an oil film will pass through several stages as time progresses, in each of which one spreading force will be balanced by one retarding force². Although there are four such possible combinations, for large scale slicks only three regimes are important: (i) the gravity-inertia regime (called "inertial spread"), (ii) the gravity-viscous regime (called "viscous spread") and the surface tension-viscous regime (called "surface tension spread"). As time progresses, a large spill will pass through these three regimes in succession. A very small spill (a few liters, say) will almost form the start behave as a surface tension spread.

The spreading laws for each regime have been determined, to within an unknown constant, for each regime and for the cases of a one-dimensional and two-dimensional (axisymmetric) $slick^{1,2}$. These laws give the linear extent of the slick (length \pounds or radius r) as a function of the time t since the oil was released at the origin of the spread, the volume of the oil spill and the physical properties of the oil and water. These spreading laws are given in Table I, and the undetermined proportionality coefficients are denoted by the symbol k.

III. Evaluation of Spreading Laws

The proportionality constants k can be determined from laboratory experiments or from a suitable detailed hydrodynamic theory of the spreading motion in each regime. So far, only one-dimensional spreading experiments have been reported^{1,3}, and there have been advanced conflicting theories^{1,4} for the inertial spreading regime. We suggest below (and in Table II) best values for these coefficients, based upon published experimental data and our own (unpublished) theoretical analysis and extrapolation of the empirical data. We discuss below each entry separately.

<u>One-dimensional inertial spread</u>. Here we use the experimental value of $k_{11} = 1.5$ determined by Hoult and Suchon (see Fig. 2). Their theoretical value $(k_{11} = 3)$ is clearly in disagreement with the experiments. An alternative theoretical solution has been given by Fannelop and Waldman⁴, from which k_{11} is found to be $3/10^{1/3} = 1.39$. We believe that the correct theoretical value is $3/7^{1/3} = 1.57$, for reasons which we shall not elaborate on here. This latter theoretical estimate is certainly very close to the observed values in the laboratory experiments.

<u>One-dimensional viscous spread</u>. The empirical value of $k_{1v} = 1.5$ determined by Hoult and Suchon' (see Fig. 2) is recommended.

<u>One-dimensional surface tension spread</u>. The experiments of Garrett and Barger (see Fig. 3) and Lee (see Fig. 4) both support a value of $k_{1t} = 1.33$.

<u>Two-dimensional (axisymmetric) inertial spread</u>. Since there are no experimental results available, we recommend the theoretical value of $k_{21} = 2/(3\pi)^{1/4} = 1.14$ as determined by the same analysis leading to the one-dimensional value quoted above, and which agreed closely with the corresponding experiments. This value is also given by Fannelop and Waldman'.

<u>Two-dimensional viscous spread</u>. Again, no experiments have been reported. A boundary layer theory developed by Hoult and Suchon possesses no unique solutions and hence yields no definite values for k_{1v} or k_{2v} . It is our belief that the proper solution can only be determined theoretically by solving the complicated flow at the leading edge of the slick. However, we suggest that an estimate of k_{2v} can be made in the following manner. If we select the one-dimensional theoretical solution which leads to the observed value of k_{1v} , and then hypothesize that the two-dimensional solution should have the same boundary values, we can then determine the value of k_{2v} from this latter solution. Our justification for such a procedure is the supposition that the flow near the leading edge of the slick is the same for the two-dimensional as for the onedimensional case, and that the dimensionless boundary values of the theoretical solutions, which are determined by this flow, should also be identical. Using this procedure, we have found the value shown in Table II.

<u>Two-dimensional surface tension spread</u>. We have used the same procedure as that outlined in the preceding paragraph to estimate the value of k_{2t} , shown in Table II, since there are no experiments available. According to Fay, the maximum observed spread in field

observations would correspond to $k_2 = 10\sqrt{\pi} = 5.7$. While this is larger than the corresponding value recommended in Table II, it is most likely uncertain by a factor of two because of the difficulties of making observations and the imperfections of the field experiments. A comparisor of the theoretical spread area with observed values is shown in Fig. 5.

IV. The Termination of Spreading

It has already been noted that, after some time, slicks cease to spread^{2,7}. In almost all cases, the final film thickness is much greater than that of a monomolecular layer, being about 10^{-2} to 10^{-2} cm. Fay has suggested that the cessation of spread is caused by the evaporation of some oil fractions which reduces the spreading coefficient to zero. His estimate of slick size for which this evaporation (limited by diffusion through the oil layer) would be appreciable, was an order of magnitude smaller than the observed values.

We propose here a modified version of this theory. We believe that the spreading coefficient is reduced by an increase in the water-oil interfacial tension brought about by the dissolving of oil fractions in the water layer underneath the oil film. The volume of oil which can be dissolved in this layer (per unit area of oil/water interface) would then be $s(Dt)^{1/2}$, where s is the solubility of the significant oil fractions in water. As a consequence, the previous estimate of Fay would be increased by a factor of s^{-3/8}, or a factor of about ten for s = 10⁻³, a reasonable value. As a consequence, the maximum area A of the slick would be come,

$$A = k_{a} \left(\frac{\sigma^{2} v^{6}}{\rho^{2} v D^{3} s^{6}} \right)^{1/8}$$
(1)

in which k is an undetermined constant of order unity.

Because of the uncertainties in s and σ in the field observations, and the lack of laboratory data, it is proposed that the maximum slick area be related to the volume of the spill by the dimensional formula.

$$A(m^2) = 10^5 [V(m^3)]^{3/4}$$
(2)

This is compared in Fig. 6, with field observations recently summarized by Allen and Estes. Equation (1) yould have the value given by Eq. (2) if $\sigma = 10$ dyne/cm, D = 10 cm/sec, s = 10⁻³, and $k_a = 1$.

Table I

1

i.

Spreading Laws for Oil Slicks

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	One-dimensional	Axisymmetric
Inertial	$\ell = k_{11} (\Delta gAt^2)^{1/3}$	$r = k_{21} (\Delta g V t^2)^{1/4}$
Viscous	$l = k_{1v} (\Delta g A^2 t^{3/2} / v^{1/2})^{1/4}$	$\mathbf{r} = \mathbf{k}_{2v} (\Delta g v^2 t^{3/2} / v^{1/2})^{1/6}$
Surface tension	$\ell = k_{1t} (\sigma^2 t^3 / \rho^2 v)^{1/4}$	$r = k_{2t} (\sigma^2 t^3 / \sigma^2 v)^{1/4}$

Table II

Spreading Law Coefficients

	One-dimensional	Axisymmetric
Inertial	k _{li} = 1.5	1.14
Viscous	$k_{1v} = 1.5$	1.45
Surface tension	$k_{1t} = 1.33$	2.30

-7-

List of Symbols

A Volume of oil per unti length normal to x Acceleration of gravity 8 Thickness of oil film h Proportionality constant k l Length of one-dimensional oil slick r Maximum radius of axisymmetric oil slick t Time since initiation of spread Spreading velocity of oil film u V Volume of oil in axisymmetric spread Dimension in direction of one-dimensional spread х δ Thickness of viscous boundary layer in the water underneath the oil film Spreading coefficient or interfacial tension (with subscript) σ Kinematic viscosity of water ν μ Absolute viscosity of water Density of water ρ Δ Ratio of density difference between water and oil to density of water

Subscripts

- 1 One-dimensional spread
- 2 Two-dimensional (axisymmetric) spread
- a Maximum area
- i Inertialspread
- t Surface tension spread
- v Viscous spread
- ow Oil/water
- aw Air/water
- oa Oil/air

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List of Captions

Fig.	1	The four forces which act on an oil film (see list of symbols).
Fig.	2	Experiments showing the transition from inertial to viscous spread for a one-dimensional flow.
Fig.	3	Measurements of spreading velocity versus slick length for one-dimensional surface tension spreading experi- ments.
Fig.	4	Lee's experiments on one-dimensional surface tension spreading. Solid line corresponds to $k_{1,2} = 1.33$.
Fig.	5	A comparison of the theoretical axisymmetric slick area (for surface tension spread) with observed values ^{7,6} . Solid line corresponds to the value of k ₂ , shown in Table II and a spreading coefficient of 30 dyne/cm.
Fig.	6	Maximum slick area as a function of volume. Eq. (2) compared with observations taken from Ref. 7.

Physical Processes in the Spread of Oil on a Water Surface by James A. Fay

Fig. 1 The four forces which act on an oil film

 $\sigma \equiv \sigma_{wa} - (\sigma_{oa} + \sigma_{ow})$ ► gwg °0 °0 0 ¥0

 $\left|\frac{d\theta}{\chi \theta}\right|$ hgq Δ

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SURFACE TENSION

GRAVITY

J ph du

INERTIA

FRICTION 8=/1 • $\mu = \frac{U}{8} = \rho 8 \frac{\partial U}{\partial t} = \theta$

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. 2 Experiments showing the transition from inertial to viscous spread for a one-dimensional flow

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Fig. 3 Measurements of spreading velocity versus slick length for one-dimensional surface tension spreading experiments







Fig. 5 A comparison of the theoretical axisymmetric slick area (for surface tension spread) with observed values



