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The Spread of High- and Low-Viscosity Chemicals on Water

T.R. Sundaram*
T.S. Associates, Inc., Columbia, Md.

Introduction

WHEN hazardous liquid chemicals are transported over water, the possibility always exists for the accidental spill of these chemicals into the waterway. Initiation of appropriate response measures necessarily requires an understanding of the behavior of the chemicals once they are spilled. Many of the chemicals of concern have a specific gravity lower than that of water and are also either immiscible with water or have a very low solubility in water. Thus, the problem is essentially one of being able to predict the rates of spread of light, immiscible chemicals spilled onto water. While some of the hazardous chemicals (such as most oils) are more viscous than water, others (such as pentane, benzene, and allyl chloride) are less viscous than water. It will be shown in this Note that the rates of spread of these two classes of chemicals are controlled by somewhat different phenomena.

A number of analyses[1-4] exist in the literature on the spread of oil slicks on water. In a recent Note,[5] the present author has shown that simple power laws describing the growth of oil slicks can be derived by using order of magnitude analyses and simple phenomenological reasoning. In this Note it is shown that similar power laws can also be derived for the spread of low-viscosity chemicals, and the phenomenological differences between this case and the spread of oils (high-viscosity case) are pointed out.

Depending on whether the total duration over which the spill occurs is small or large compared to the characteristic time scales for spread, the spill can be considered to be either "instantaneous" or "continuous"; both of these limits of behavior are considered herein. Also considered are the effects on spread of any ambient currents that may be present in the waterbody.

In the remainder of this Note, the phenomenologies involved in the spread of low- and high-viscosity chemicals are first described. Power laws for spread on a quiescent body of water are then given, followed by the discussion of an asymptotic power law for the growth of the spill width in a uniform current at large distances downstream of the point of the spill. Finally, some conclusions and recommendations for further work are given.

Basic Phenomenology

The primary force causing the spilled chemical to spread is the gravimetric force due to its relative buoyancy. In his pioneering work on the spread of oil slicks on calm water, Fay[1] showed that two distinct and consecutive phases of spread can be identified. In the first phase, the buoyancy force is balanced by the inertia of the oil slick, while in the second phase of the spread it is balanced by the retarding viscous force exerted by the water layers underlying the slick. Fay also showed that in the final stages of spread, the net surface-tension force may be in balance with the viscous retarding force.

The shear stress τ_i at the interface between the spreading chemical pool and the underlying water layers can be expressed in the form

$$\tau_i = \mu_w \left.\frac{\partial u}{\partial y}\right|_w = \mu_c \left.\frac{\partial u}{\partial y}\right|_c \tag{1}$$

where μ_w and μ_c are, respectively, the viscosities of water and the spilled chemical, u is the local (radial) velocity, and the symbols $|_w$ and $|_c$ denote that the derivatives are evaluated on

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*President. Member AIAA.

the water and the chemical sides, respectively. Note that Eq. (1) follows from the requirement that the shear stress be continuous across the interface. By virtue of the "no-slip condition," the velocity u must also be continuous across the interface, although Eq. (1) shows that the velocity *gradient* cannot be continuous.

When considering the spread of a chemical whose viscosity is considerably higher than that of water, it is clear from Eq. (1) that the velocity gradient on the slick side must be considerably smaller than that on the water side, so that "the slick tends to move locally as a homogeneous slab relative to the water."[2] The foregoing feature, which has been termed the slug-flow assumption by Hoult,[4] has been used in most theoretical analyses of oil-slick spread since it enables the equations of motion to be integrated across the slick. The interfacial retarding stress τ_i on the slick is calculated by considering the developing boundary layer on the *water* side; see Fig. 1a.

Let R be the radius and h the thickness of the chemical pool at a time t after the spill. Then a measure of the slick-spread velocity is (R/t) and a measure[6] of the boundary-layer thickness is $(\nu_w t)^{1/2}$, where ν_w is the kinematic viscosity of water. Thus from Eq. (1) it can be seen that τ_i can be written as

$$\tau_i \sim \rho \nu_w^{1/2} R t^{-3/2} \tag{2}$$

Note that in the spirit of the Boussinesq approximation, it is not necessary to distinguish between the densities of the oil and water, and thus a single symbol ρ should suffice.

We next consider the case when the viscosity of the chemical is considerably less than that of water. The velocity profile can now be expected to be as shown in Fig. 1b, with the velocity gradient on the slick side being considerably larger than that on the water side, so that it is more appropriate to evaluate τ_i by considering the flow on the slick side. A measure of the velocity gradient on the slick side is merely u/h, so that

$$\tau_i \sim \rho \nu_c (R/th) \tag{3}$$

where ν_c is the kinematic viscosity of the spilled chemical.

It is interesting to note that in the high-viscosity case, only the viscosity of water appears in the expression for τ_i, while in the low-viscosity case the viscosity of the chemical appears explicitly.

Power Laws for Pool Spread on Calm Water

We first consider the case of a chemical spill onto calm water, so that the pool will spread out radially in an axisymmetric fashion. If G represents the reduced gravity, given by $g(\Delta\rho/\rho)$, where g is the acceleration due to gravity and $\Delta\rho$ is the density difference between the spilled chemical and the underlying water, then the buoyancy force B acting on a unit sector of the spill is given by

$$B \sim \rho G h^2 R \tag{4}$$

while the inertia force I is given by

$$I \sim \rho \frac{\partial u}{\partial t} R^2 h \sim \rho \frac{R^3 h}{t^2} \tag{5}$$

If the chemical is spilled "instantaneously," then the total volume of the spill must remain invariant during the spreading process, that is, $Q = \pi R^2 h = \text{const}$. On the other hand, if the chemical is spilled continuously and at a constant rate $\dot{Q}$, then $\pi R^2 h = \dot{Q} t$. Thus equating B and I for an instantaneous spill we obtain,

$$R \sim (GQ)^{1/4} t^{1/2} \tag{6}$$

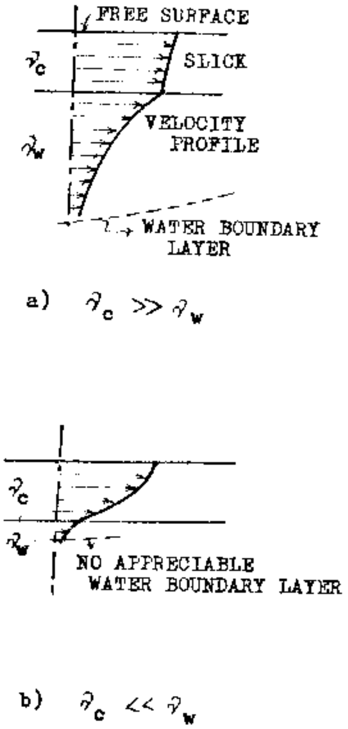

Fig. 1 Differences in velocity profiles when the slick viscosity is: a) much greater than, and b) much less than that of water.

whereas for a continuous spill,

$$R \sim (G\dot{Q})^{1/4} t^{3/4} \tag{7}$$

As is to be expected, the power laws for pool spread in the initial inertia-gravity regime are independent of the viscosity of the spilled chemical.

The power laws in the viscous-gravity regime are readily obtained by equating the buoyancy spreading force B to the viscous retarding force $\tau_i R^2$ acting on the pool, where τ_i is given by Eqs. (2) and (3) for the high- and low-viscosity cases, respectively. Specifically, we obtain the following formulas for the different cases:

Instantaneous spill of high-viscosity chemical

$$R \sim (GQ^2/\nu_w^{1/2})^{1/6} t^{1/4} \tag{8}$$

Continuous spill of high-viscosity chemical

$$R \sim (G\dot{Q}^2/\nu_w^{1/2})^{1/6} t^{7/12} \tag{9}$$

Instantaneous spill of a low-viscosity chemical

$$R \sim (GQ^3/\nu_c)^{1/8} t^{1/8} \tag{10}$$

Continuous spill of a low-viscosity chemical

$$R \sim (G\dot{Q}^3/\nu_c)^{1/8} t^{1/2} \tag{11}$$

The values of the numerical proportionality constants in the foregoing equations are, of course, not known a priori and cannot be determined from the order of magnitude analyses given herein—rather, their values have to be determined from experimental data. An equation similar to Eq. (10) has been derived in Ref. 7 using a relatively elaborate theory.

The critical time t^*, at which transition from the initial inertia-gravity regime to the subsequent viscous-gravity regime occurs, can be estimated by equating the inertia and viscous forces. Thus, for example, for the case of the instantane-

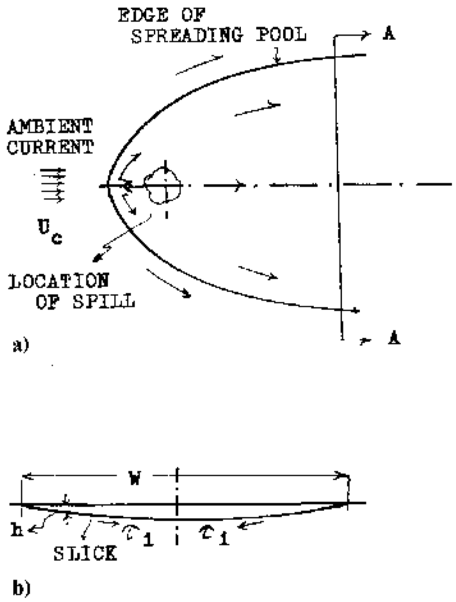

Fig. 2 Effect of ambient current on pool spread: a) plan view, b) section AA.

ous spill of high-viscosity chemical

$$t^* = (Q/G\nu_w)^{1/3} \tag{12}$$

Characteristic time scales such as t^* also enable the quantification of the terms "instantaneous" and "continuous" spills, since the former or latter can be considered to be the case depending on whether the total time over which the spill occurs is either small or large compared to t^*. For the spill of 10,000 gal of a chemical of specific gravity equal to 0.9, t^* is about 5 min.

Effect of an Ambient Current

When the spill occurs onto a waterbody in which an ambient current is present, the spilled (immiscible) liquid will be convected along with the current, with the gravity-induced spread occurring relative to the moving, underlying waters. For a continuous spill, the shape of the spreading pool will be as shown in Fig. 2, with some of the spilled chemical spreading *against* the current due to gravimetric effects. It is not the purpose of this Note to consider in detail the entire flowfield, but merely to point out that a simple asymptotic solution exists for the growth of the pool at distances sufficiently far downstream of the location of the spill.

As is evident from the power law relations noted earlier, the gravity-induced pool spread velocity (given by dR/dt) decreases with increasing distances from the point of the spill. Thus when a current is present, the axial velocity across any cross section (such as AA in Fig. 2) of the chemical pool will be nearly equal to that of the current velocity, with the gravity-induced spreading process in the lateral direction being analogous to that in a two-dimensional channel. Since the flux of the chemical through any lateral cross section must remain constant for a continuous spill, we have

$$\dot{Q}/U_c = Wh \tag{13}$$

where U_c is the current velocity and W the width of the pool.

Along any cross section of the pool, the lateral spreading force must be balanced by the frictional retarding force (in the lateral direction) exerted by the underlying water layers. That is, $\tau_i W \sim \rho G h^2$, or for the high-viscosity case

$$\rho \nu_w^{1/2} W^2 t^{-3/2} \sim \rho G h^2 \tag{14}$$

so that using Eq. (13) and the kinematic relation $x = U_c t$, we obtain

$$W \sim \left(\frac{G\dot{Q}^2}{U_c^{7/2} \nu_w^{1/2}} \right)^{1/4} x^{3/8} \tag{15}$$

Similarly for the low-viscosity case

$$W \sim \left(\frac{G\dot{Q}^3}{U_c^4 \nu_c} \right)^{1/5} x^{1/5} \tag{16}$$

Equations (15) and (16) represent the desired asymptotic solutions for the growth of the pool width.

Conclusion

In this Note we have shown that the power laws governing the spread of high- and low-viscosity chemicals spilled on water can be deduced by using relatively simple order of magnitude estimates, without the need for elaborate theoretical arguments. Careful laboratory experiments are necessary to evaluate the numerical constants appearing in the power laws, to assess whether the high- and low-viscosity cases do display the differences in the velocity profiles noted in Fig. 1, and to quantify the ranges of "high" and "low" viscosity.

In the foregoing analyses the boundary layer on the water side was assumed to be laminar; if it is turbulent, then the procedure noted in Ref. 5 can be used in place of Eq. (2) to specify the interfacial stress τ_i.

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