Experiments with Monomolecular Films on the Surface of the Open Sea

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ABSTRACT

Experiments with monomolecular films were conducted in the axis of the Gulf Stream, east of Miami, in June 1972, to examine the feasibility of spreading and maintaining a continuous partially-polymerized thin film on the ocean's surface under various wind conditions as part of an investigation directed toward hurricane abatement through evaporation suppression. Photographic documentation of the history and structure of the artificially produced sea slicks indicates that a clearly visible slick forms almost immediately upon deployment of the film-forming material from a ship, remains continuous and homogeneous for several hours, damps waves, and reforms after penetration by a ship. Initial results from laser profilometer measurements clearly document the wave damping characteristics of the slick; specifically, damping of gravity waves as well as capillary waves occurred. Relatively quiescent atmospheric and sea conditions prevailed, unlike those in a hurricane environment.

1. Introduction

Considerable research has been devoted to the retardation of water evaporation by monomolecular surface films formed artificially on the water's surface. Frenkiel (1965), La Mer (1962), Bean *et al.* (1969), and others, have formed monolayers on lakes and reservoirs that act as barriers to evaporation. Artificial slicks have been formed on the sea surface, using oleyl alcohol (Barger *et al.*, 1970) for example, that act to diminish the ripples and whitecaps which enhance evaporation, but which do not function as a molecular barrier to retard evaporation.

Air-sea exchange of sensible heat, moisture and momentum have long been considered important factors in developing and maintaining tropical storms. Numerical experiments (Rosenthal, 1971; Ooyama, 1969) that study the relative importance of these exchanges have provided support for initiation of evaporation suppression research with regard to hurricane abatement. For Rosenthal's control model storm with maximum surface winds of 50 m sec^{-1}, separate suppression of the fluxes of sensible heat, moisture and momentum resulted in maximum surface winds of 40, 8 and 29 m sec^{-1}, respectively.

A small-scale sea test was carried out in June 1972 as as an important step in evaporation suppression research. The purpose of this paper is to present the results of this experiment as revealed primarily by photographic documentation and initial results from laser profilometer measurements. Improvements that appear to be necessary before undertaking similar follow-on experiments are also discussed.

2. Monomolecular films and the mechanism of evaporation suppression

Under the sea conditions that would prevail on the water's surface in a hurricane environment, it seems unlikely that the monomolecular films used by other investigators on fresh and salt water surfaces would survive. The molecules of the monolayers are composed of a long hydrocarbon chain that is hydrophobic and a polar group that is hydrophilic. These molecules are largely water insoluble, adsorbing at the air-water interface with their hydrophilic group in the water and the hydrophobic segment oriented on or away from the sea surface. Monolayers that act as a barrier to evaporation are unable to retain their close-packed, hydrophobic-molecular form under severe wave action, and the hydrophilic portion does not provide enough anchorage to resist wind action. Some monolayers act on wave parameters (ripples and whitecaps) directly and do not function as a molecular barrier. Ideally, a monolayer that has characteristics of being tear resistant, that spreads easily onto the surface of the sea water, and that is compatible with the biological systems of the sea (i.e., biodegradable) would be the most desirable to use in a hurricane environment and the most likely to survive.

The effect of a monomolecular film on the water's surface is most perceptible in its ability to produce damping of short gravity waves and prevent the formation of capillary waves. Recently some investigators have considered wave suppression as perhaps the major mechanism at work in evaporation retardation by monolayers, in contrast to the chemical structure of the film as the major retarding mechanism as discussed by La Mer (1962).

a. Wave-damping effects of monolayers

Mangarella *et al.* (1971) have found that evaporation rates are significantly increased by the presence of small waves and by spray formation. Wave suppression acts to diminish the area of the water surface in contact with air (Garrett, 1971), which, in turn, affects the total evaporation. Also, studies on wind-wave interactions have demonstrated that the wind structure over a body of water is to a large extent governed by ripples, which constitute the dynamic roughness Z_0 of the wind-disturbed water surface (Wu, 1971). Barger *et al.* (1970) found that one effect of an artificial sea slick is the modification of the dynamic roughness length and a possible increase in mean wind speed. In one experiment, the mean roughness length Z_0 decreased 67% and the mean wind speed increased 13%, while in another, Z_0 decreased 85%, and the mean wind speed increased 33%. It is, however, interesting to note how this modified wind structure would affect the flux of moisture.

The flux of moisture can be determined from the equation derived in the bulk aerodynamic method; namely,

$$E=\rho C_a(\bar{q}_0-\bar{q}_a)\bar{U}_a, \qquad (1)$$

where E is the rate of evaporation per unit area and time, C_a the drag coefficient, $\bar{U}$ the mean wind velocity, and q the specific humidity. The subscript 0 refers to the surface and a to a level above the surface. In (1) we have made the usual assumption concerning a constant flux near neutral conditions, and also taken $\bar{U}_0=0$. Expressing C_a as a function of surface roughness (Roll, 1965, p. 153) and substituting into (1), we have

$$E=\rho(\bar{q}_0-\bar{q}_a)\frac{k^2\bar{U}_a}{[\ln(Z_a/Z_0)]^2}. \qquad (2)$$

Thus, the rate of evaporation will be reduced by a decrease in the moisture gradient, wind speed and surface roughness. It should be noted that (2) neglects the effect of spray, but is valid with and without the presence of a slick. However, the vertical moisture gradient $(\bar{q}_0-\bar{q}_a)$ is presumably affected (reduced) *only* by films that act as a barrier to molecular transfer. Consequently, for materials that modify wave parameters only, one may assume that $(\bar{q}_0-\bar{q}_a)$ can be taken as constant allowing the variation in wind speed and surface roughness to control the evaporation process.

Using as an example typical values of Z_0 and $\bar{U}_{10}$ (given in Table 1, from Barger *et al.* 1970, p. 398), and taking (q_0-q_a) as 5.0×10^{-3} and ρ as 1.3×10^{-3} gm cm^{-3}, one obtains values for $E(10^{-6})$ from Eq. (2) with and without the presence of a slick. With the passage of an oleyl alcohol slick through the test site, the rate of evaporation decreased from 8.26 to 7.46 in one case and from 6.00 to 5.35 in another or a calculated 10% reduction in moisture flux as a result of wave damping alone. Similarly, in applying Lake Hefner results to these same data, Mansfield (1972) attributed a 9% reduction in evaporation to wave damping effects, and a 55% reduction to molecular barrier effects for a total reduction in evaporation of 64%.

b. The energy barrier for monolayer penetration

The transport of water vapor through a monolayer is not an ordinary diffusion process which involves a small energy barrier. Rather, the process is one in which the water molecule must pass along a molecular pathway between hydrocarbon chains, thus requiring a substantially higher amount of energy (La Mer, 1962). Grundy (1962), Bean *et al.* (1969), and others, have firmly established the fact that a suitable monomolecular film reduces the rate of evaporation by about 50–60% under quiescent conditions. This reduction has been attributed to the chemical structure of the film that acts as a molecular barrier to evaporation. This same theory would be applicable to hurricane abatement provided the chemical structure of the film could be improved to resist disruption under turbulent conditions.

c. The effect of monomolecular films on the surface temperature of water

Reducing the rate of evaporation from a water surface by monolayers suggests an increase in surface water temperature. Normally, a great rate of evaporation would, in effect, produce a cool skin on the surface in the absence of mixing, convection and advection in the ocean. Presumably, "this reduction of evaporation and subsequent increase in temperature will give a small compensating increase in the rate of evaporation, but with a monolayer of high resistance to evaporation the net result will be a significant decrease in the amount of water loss through evaporation" (Jarvis *et al.*, 1962). And, in fact, Grossman *et al.* (1969) have shown that the surface water temperature was 0.3C warmer under the monolayer than in the surrounding open water, producing a percentage increase of evaporation of 3.3%. This is small when compared with the 60% reduction in evaporation commonly observed.

3. The sea slick experiments

IIT Research Institute (IITRI) has been under contract with the National Oceanic and Atmospheric Administration's (NOAA) National Hurricane Research Laboratory (NHRL) to investigate the feasibility of hurricane abatement employing thin polymer membranes. The material found in tank experiments to have desirable characteristics and to be most effective as an evaporation suppressant with slight polymerization, consisted of linoleic acid, polyvinyl alcohol, and derivatives of polyvinyl acetate (Stake, 1972).

Lake tests were conducted by IITRI in May 1972 to test the spreadability and wave damping capacity of this material (Stake, 1972). These tests indicated that the membrane could be dispensed from small containers to produce an acre of very calm surface (slick) in 20 min with a clearly visible and stable boundary.

These chemicals were determined to be of low toxicity and in amounts small enough to be nonharmful to aquatic life. Adverse affects to the induction intakes and cooling systems of ships from ingestion of the chemicals were not expected or experienced.

The primary goal of the monomolecular film experiments was to examine the feasibility of spreading and maintaining a continuous partially-polymerized thin film on the ocean's surface under various wind conditions. The major objectives were to determine the film's rate of spreading, formation and reformation characteristics, endurance on the ocean's surface, and the ability of the film to damp waves. The Naval Research Laboratory (NRL), with similar objectives in mind, participated in the experiment on 8 June and dispensed a fluid material composed of high-purity commercial oleyl alcohol. The test site area was located 15 n mi east of Miami, in the axis of the Gulf Stream, and is shown in Fig. 1. The test was conducted over a 3-day period from 7–9 June 1972.

a. Spreading and monitoring techniques

A research vessel, the *Virginia Key*, from NOAA's Atlantic Oceanographic and Meteorological Laboratories (AOML), was used as the dispensing platform on 7 and 8 June. The slightly polymerized material was poured from one-gallon bottles at the rate of 11.34 liters min^{-1}, and the oleyl alcohol was streamed from a garden sprayer at the rate of 0.35 liter min^{-1}. Both solutions were disseminated over the side and into the vessel's wake. A spray aircraft dispensed the IITRI material on 9 June from an altitude of 20–60 ft.

A rectangular spreading pattern, shown in Fig. 2, was followed by the research vessel and the spraying

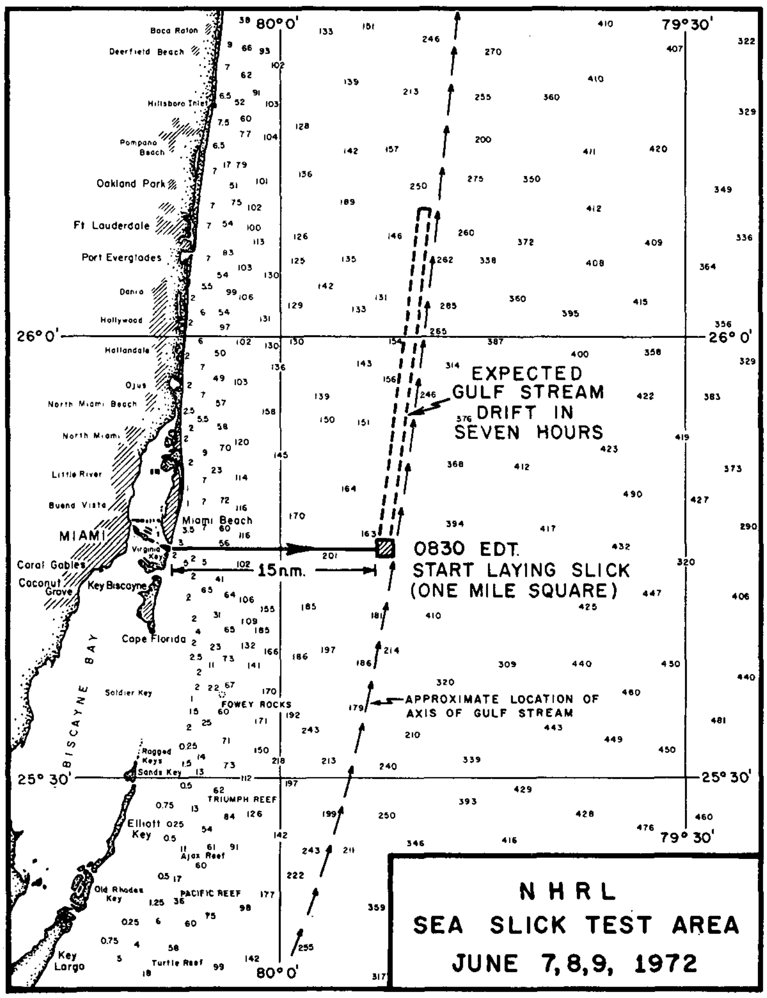


FIG. 1. The 1 mi² test site area for the sea slick experiment.

aircraft on the 7th and 9th of June. The north-south legs, beginning on the western reaches of the mile square, were chosen to take advantage of the sun angle for best observational results. An increasing spiral pattern, shown in Fig. 3, was used on 8 June for dispensing both the IITRI and NRL material in order to shorten the spreading time required for each material and keep the developing slicks in sight continuously for comparison purposes.

An instrumented DC-6 aircraft from NOAA's Research Flight Facility (RFF) and the AOML research vessel were used as monitoring platforms to document the life history of the artificial slicks. Hand-held photography from each platform provided frames with adequate contrast to document the salient features of the slicks. The photographs taken by cameras mounted on the aircraft and operating in time-lapse mode showed poor contrast due to presence of haze. Environmental sensors on board the aircraft were operated, but the slick size was too small to provide the long records required for analysis (Mallinger and Mickelson, 1973).

The aircraft monitoring patterns included legs parallel to the slick, looking into and away from the sun, across various portions of the slick, and photo boxes and circles. They were conducted at altitudes of 100, 500 and 2000 ft. The surface vessel moved in and out of the artificial slicks for the purpose of taking photographs and capillary wave-height measurements.

b. Photographic documentation of the 7 and 8 June experiments

Weather conditions were similar on both days. Scattered clouds were present with visibility restricted by haze. The winds diminished to less than 6 kt by mid morning with the sea surface noticeably rippled.

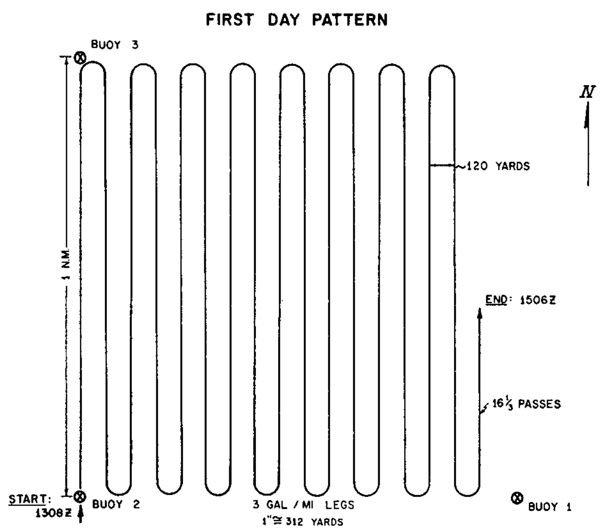


Fig. 2. The rectangular spreading pattern followed by the research surface vessel on 7 June 1972. The spraying aircraft used a similar pattern on 9 June.

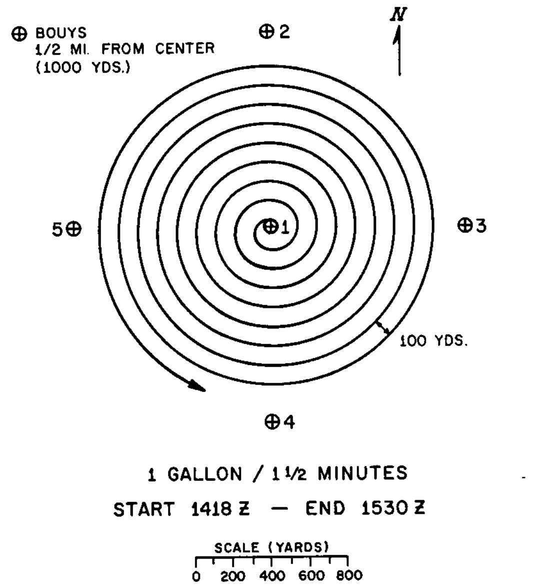
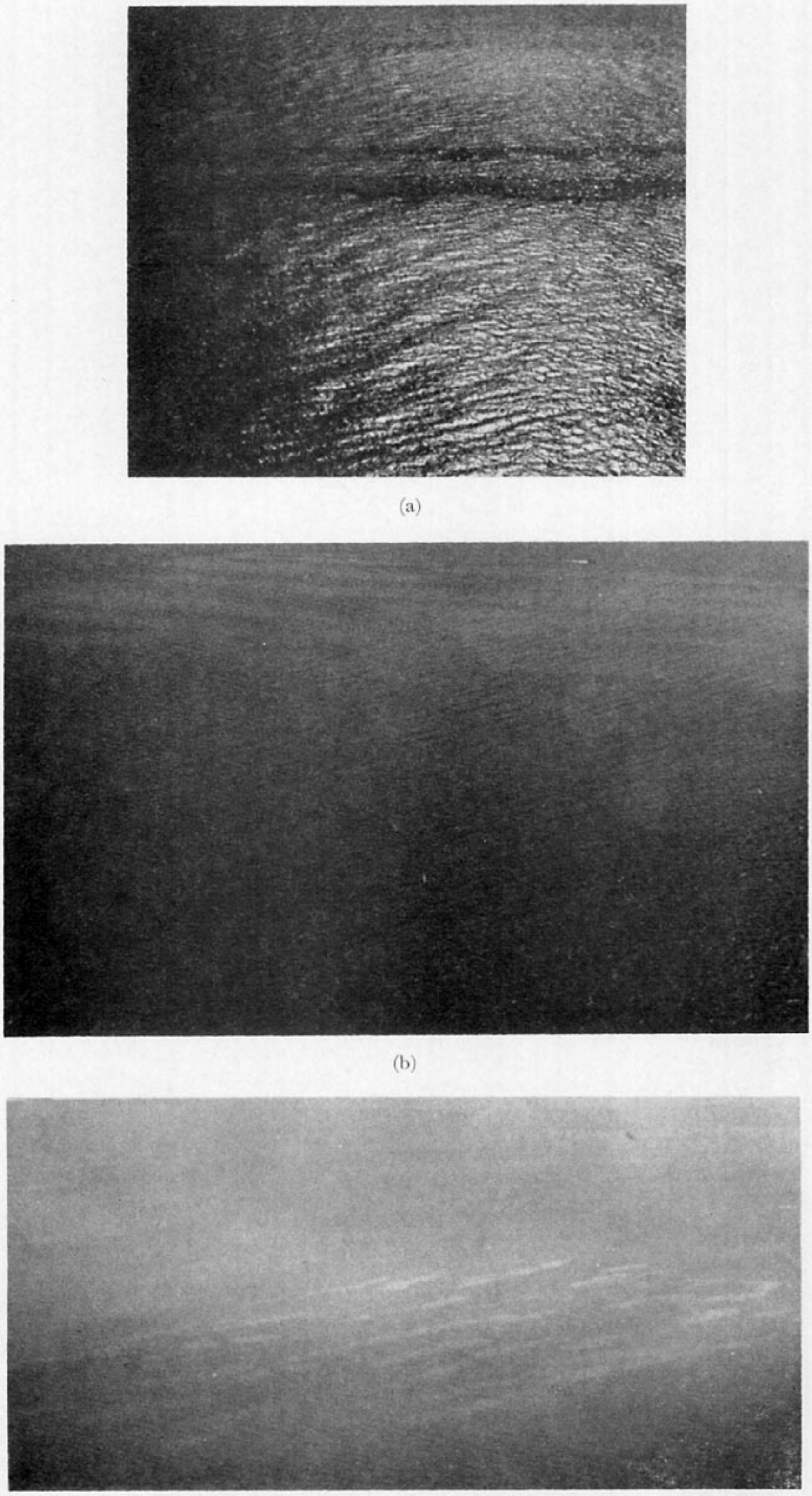


Fig. 3. The spiral spreading pattern used on 8 June for dispensing the IITRI material. A similar pattern was used in dispensing the NRL material.

Fig. 4 shows a series of photographs of the IITRI slick taken at approximately $\frac{1}{2}$, $1\frac{1}{2}$ and $3\frac{3}{4}$ hr after spreading began on 7 June. Two slick lanes (Fig. 4a) on the western portion of the square mile are evident in contrast to the sun's glitter pattern and the existing sea state. Each lane appeared 10–15 sec after pouring, and appeared to be continuous. The fact that they are distinguishable, one from another, is evidence that the lanes have not yet merged. There also appears to be a very striking suppression of waves in each continuous lane, since the sun's glitter pattern completely disappears in the lanes but is present on both sides of them. Outside the northern border (left edge) of the glitter pattern, wave suppression within the lanes is also evident in contrast to the existing sea state.

Continuous individual lanes are evident over the eastern reaches (background of Fig. 4b) of the mile square, whereas lane merging is apparent over the western portion (foreground). Good contrast between the slick boundary and the adjacent water is evident. A photograph of the IITRI slick, $1\frac{3}{4}$ hr after spreading ceased (Fig. 4c), shows a relatively ordered pattern with respect to the spreading pattern used on this day. Lane discontinuities (patches) without much lane merging are evident. The rate of application varied considerably with the "pour-from-a-gallon-jug" method, and probably accounts for many of the lane discontinuities.

Fig. 5 shows a series of photographs taken on 8 June of the NRL slick $\frac{1}{2}$ and $3\frac{1}{2}$ hr after spreading commenced (Figs. 5a and 5b). Also shown is the IITRI slick 2 hr after spreading began (Figs. 5c and 5d). Similar to the IITRI slick laid the previous day, the NRL slick boundary is easily discernible in contrast to the existing

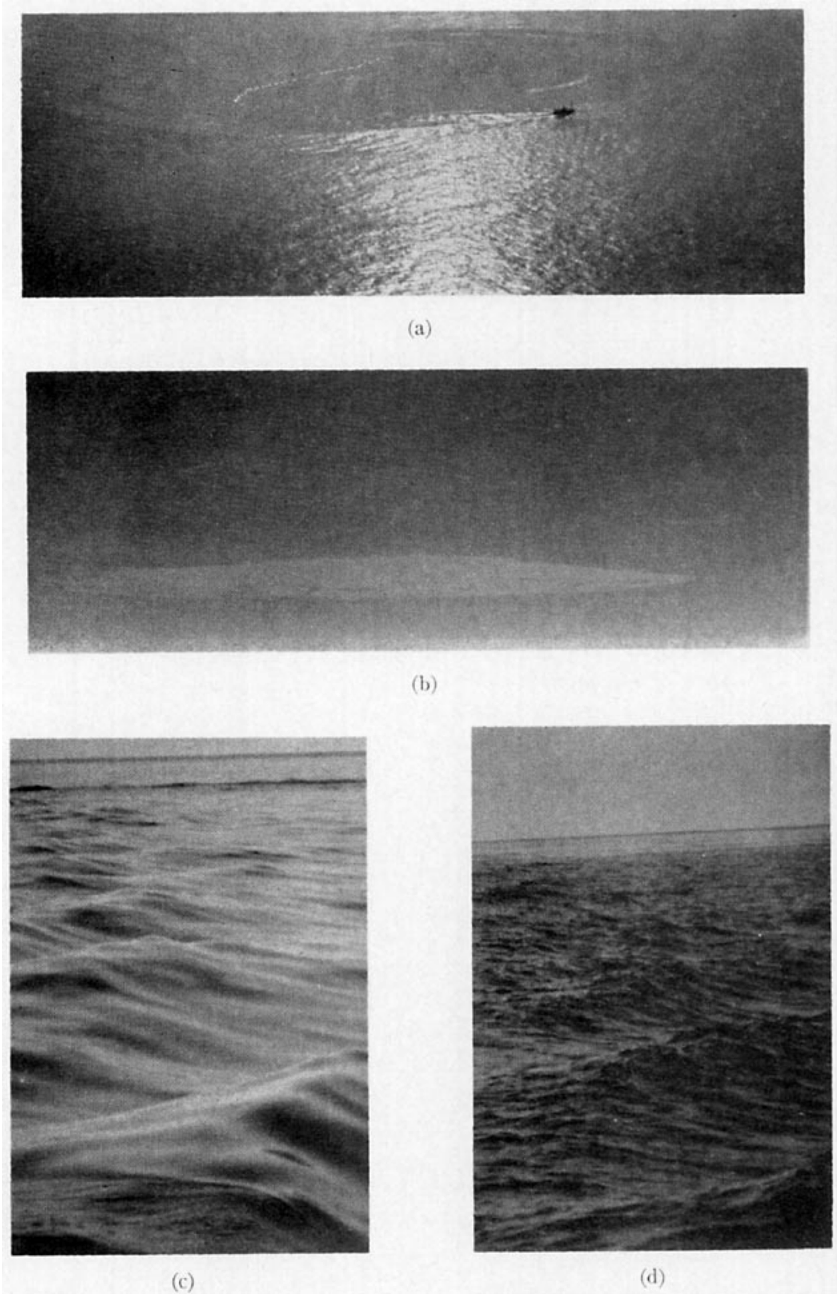


(a)

(b)

(c)

FIG. 4. Photos of the IITRI slick on 7 June 1972 within 1 mi² at (a) 1330, (b) 1430 and (c) 1646 GMT. See text for details.



(a) (b) (c) (d)

FIG. 5. Photos of the NRL slick on 8 June 1972 at (a) 1300 and (b) 1600 GMT, and the IITRI slick at (c) 1613 and (d) 1615 GMT. See text for details.

sea state and the sun's glitter pattern. Wave suppression is again evident within the artificial slicks. Lane merging has occurred throughout the slick (Fig. 5a), while the minor discontinuities (Fig. 5b) are due to the vessel's track which did not always compensate for the spreading of the slick caused by the ocean currents.

The IITRI slick exhibited characteristics similar to those of the NRL slick and to the slick laid the previous day (Mallinger and Mickelson, 1973). Figs. 5c and 5d, taken inside and outside the slick 2 hr after spreading began, show that the polymerized film had the effect of suppressing capillary waves superimposed on the bow wave of the ship.

The aircraft data indicated that at 1530 GMT the NRL and IITRI slicks covered 0.27 and 0.45 mi^2, respectively.

c. *Laser profilometer results*

A laser-wave profilometer (Ross *et al.*, 1970) was operated during low-level aircraft passes to document surface wave conditions. Figs. 6 and 7 present laser

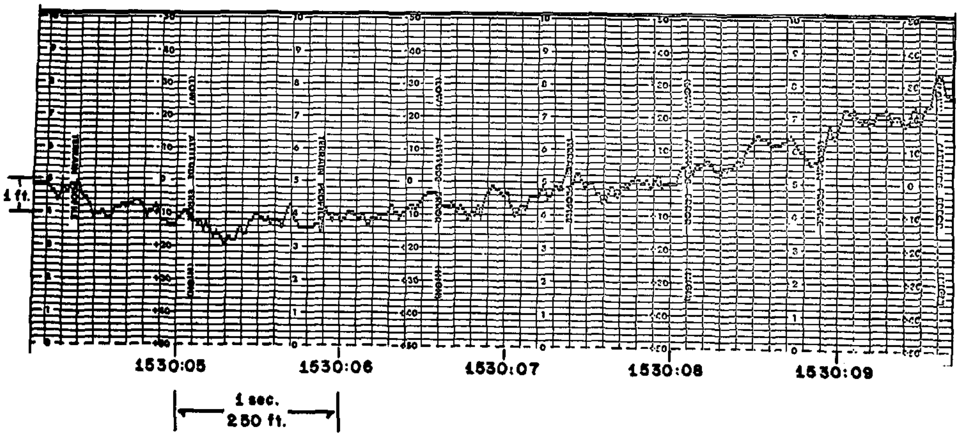


FIG. 6. Laser measurements of surface waves on 8 June 1972 between the IITRI and NRL slicks. The trend present is due to aircraft changes in altitude.

profilometer data obtained over the area between the IITRI and NRL slicks, and over the NRL slick. The trend shown in each sample is due to slow changes in aircraft altitude. The step function seen in Fig. 7 is produced as the phase difference passes through 360° in the phase comparison circuit and is routinely removed during analysis. Maximum wave heights are seen to be 1–2 ft with wavelengths $\leqslant$ 100 ft.

Fig. 6 is representative of conditions between the two slicks and shows the presence of high-frequency waves. In Fig. 7, a striking difference can be seen as the slick is crossed at 1530:45 GMT in that the shorter waves have virtually disappeared. Similar results were evident within the IITRI slick. The wave spectrum was computed by standard digital techniques for the high-frequency components of the waves, using the laser wave height data passed through a high-pass filter to remove aircraft motion. Fig. 8A represents the wave spectrum measured upwind of the NRL slick, Fig. 8B for waves within the NRL slick. At high frequencies (>0.29 Hz), it is apparent that the wave energy is reduced in the slick. It was found that the energy content within the slick was approximately 54% of that outside of the slick. Similar damping is evident during other low-level passes over the slick.

d. Aircraft dispensing experiment on 9 June

Weather conditions on this day were unfavorable with regard to visibility and winds. At the beginning of the spreading, a high overcast was present and visibilities were drastically reduced by haze. The winds were light and variable and the sea surface was slightly rippled with many natural slicks apparent.

The slick lines, formed by the spray aircraft flying at low altitude, appeared well after the aircraft passage and were perhaps 50 yards wide and very patchy. The lines were visible for 5–10 min, but were not similar in

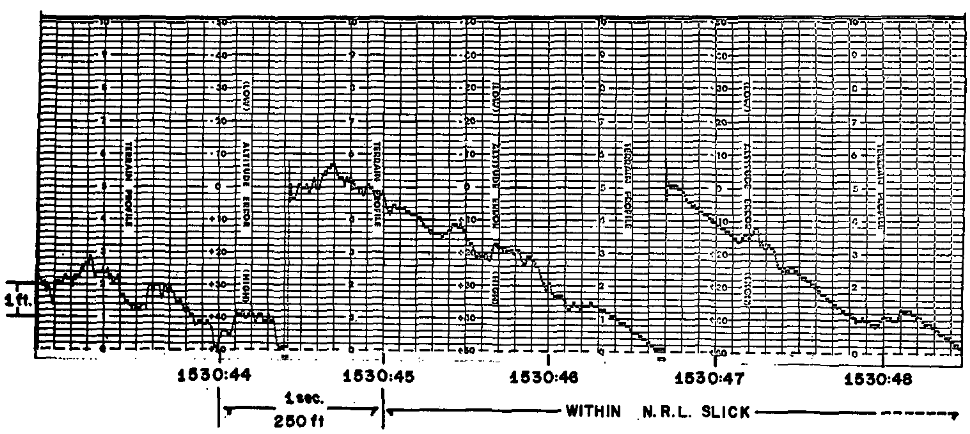


FIG. 7. Laser measurements of surface waves on 8 June 1972 near the edge and within the NRL slick. Measurements were similar within the IITRI slick. The trend present is to slow aircraft changes in altitude, and the spurious step functions are due to feedback from the phase lock failure warning circuit which triggers the automatic 180° phase insertion circuit. These are often present during measurements over slick waters and are associated with short duration signal dropouts.

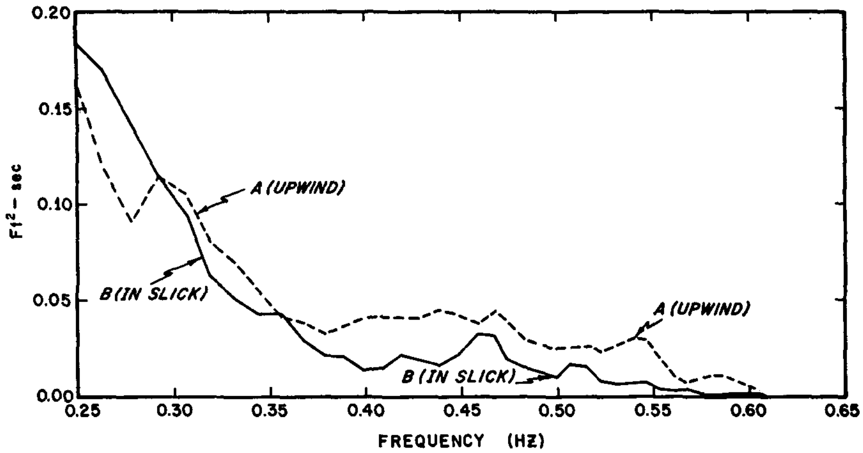


FIG. 8. Spectrum of high-frequency ocean wave energy computed upwind of the NRL slick (A) and within the same slick (B).

appearance to the slicks formed on the two previous days by the surface research vessel (Mallinger and Mickelson, 1973).

4. Conclusions

The individual lanes of film that composed the slicks and the shape and size of the slicks after the spreading period were easily seen in contrast with the surrounding area in the research vessel's wake, the existing sea conditions, the sun's glitter pattern, and conformed with the spreading pattern used for that day. It can be seen that:

1) A continuous film within a lane formed almost immediately after dispensing the film-forming material.

2) The film within a lane remained continuous for the entire spreading period.

3) Adjacent lanes began to merge half way through the spreading period in the case of the first day, and soon after dispensing on the second day, suggesting the film lanes also merged, *remaining* continuous between lanes.

4) A visible and stable boundary was apparent.

5) The film composing the slick began to look patchy 2 hr after spreading had ceased, suggesting that the film had become discontinuous.

6) The entire slick had a patchy appearance 4 hr after spreading ceased, but the spreading pattern used for that day was still discernible.

7) Before the film became patchy, reformation of the film occurred as the research vessel passed through the slick.

8) The existing sea state was relatively quiescent and the monitoring period not long enough to reveal the sustainability of the film under adverse surface conditions.

9) The rate of film spreading was observed to be roughly the same as that estimated for the lake test experiments.

10) The film successfully damped high-frequency waves.

These experiments have been a necessary step in research on hurricane abatement through sea-air evaporation suppression since the nature and persistence of the artificial slicks has been revealed. Future research should continue to concentrate on these aspects, but now under turbulent sea surface conditions and stronger winds, simultaneously documenting the effectiveness of these films in retarding water vapor transport. Since there may have been sufficient chemical coverage between visible slick patches to maintain a vapor barrier effect (Mallinger and Mickelson, 1973), surface tension measurements between patches using calibration oils would aid in verifying the existence of an organic surface film.

In addition, laboratory tests should be continued in an effort to develop a "hybrid" surface membrane with a chemical structure that continues to act as a high energy barrier to evaporation while at the same time makes the film longer-lived for application in hurricane abatement.

Increasing the size of the artificial slick to improve detection by airborne and surface environmental sensors is necessary and could be enhanced by developing improved methods of aircraft dispensing and marking the slick areas. Simultaneous dissemination of chemicals from both the surface and the air may be desirable, especially in hurricane abatement applications. We should be able to evaluate the effectiveness of these membranes in reducing the hurricane's energy after these problems have been solved and the necessary steps have been taken.

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