

Experimental Sea Slicks in the MARSEN (Maritime Remote Sensing) Exercise

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Abstract (Continued)

capillary and gravity waves. In addition, information was obtained on the influence of sea surface films on the interpretation of signals received by remote sensing systems.

Criteria for the selection of film-forming material for experimental slicks and various techniques for slick generation are discussed. Physical processes modified by natural and man-made surface films are reviewed, along with the resulting impacts of such modifications of the air-water interface on remotely sensed signals. The characteristics of the MARSEN surface films will be described as well as preliminary results from the remote systems which sensed the slicks.

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EXPERIMENTAL SEA SLICKS IN THE MARSEN (MARITIME REMOTE SENSING) EXERCISE

BACKGROUND

During the late summer and early fall of 1979, the Maritime Remote Sensing (MARSEN) experiment was conducted in the German Bight region of the North Sea. MARSEN was an international, multidisciplinary exercise involving numerous investigators and institutions from the United States and seven Western European countries. The Office of Naval Research coordinated the participation of the U.S. investigators. The project emphasized studies of the interactions of surface wind, waves, currents, and storm surge, using a wide variety of measurement methodologies including remote sensing. The ultimate goal of the experiment was to construct a storm surge/wind-wave prediction model which incorporates the interactions of various wind-wave fields and the variable bottom topography.

One aspect of the exercise involved the production of large monomolecular sea slicks to simulate natural organic surface films. Selected measurements were performed to determine the effects of the experimental slicks on air-sea interfacial processes and on remotely sensed surface phenomena. In coordinated experiments, these nontoxic surface films were generated upwind of the German research platform Nordsee, so that they drifted across the fields of view of microwave sensors and areas measured by wavestaffs mounted on the platform. In addition, the slick experiments were scheduled to coincide with flights of instrumented NASA aircraft.

The development of experimental slick technology has been reviewed in previous NRL reports [1,2]. These slicks are water-insoluble, organic films formed on the sea surface, which have been utilized for practical applications (seamarking, oil-spill control, *etc.*) as well as for fundamental studies of air-sea interactions [2]. In recent years experimental slicks have been used in a number of oceanic research projects to study their effects on wind-wave interactions [3,4], microwave backscatter [5], wave-wave interactions [6], and chemical and biological distributions at the air-water interface. The importance of experimental surface films for air-sea interaction research and remote sensing interpretation is discussed in the present report to illustrate their usefulness and future research potential. Selection criteria for slick-forming chemicals and film-generation techniques are included as part of the developmental research performed in preparation for the MARSEN exercise.

RATIONALE FOR RESEARCH WITH EXPERIMENTAL SLICKS

Surface-active organic material adsorbs at and spreads over the air-water interface. Natural slicks at sea associated with windrows, internal waves, calm water, and plankton

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blooms are thin films of biogenic polar organic matter at a sufficient surface concentration to modify physical interfacial properties. In general, sea surface films are monomolecular organic layers, which often exist at film pressures below those at which the film physically collapses and which may be thought of as two-dimensional gases or liquids. The film pressure *vs* area curve for a monolayer is analogous to the pressure *vs* volume curve for a gas. Surface tension is reduced by the organic film on water, and the degree of surface-tension reduction is the film pressure.

Small-scale hydrodynamic and physical processes at an air-water interface are modified by slicks at low film pressures, at a surface concentration where the film undergoes a transition from an expanded gas-like state to a state with liquid or solid properties. At this transition point the air-water interface is no longer "free," but is immobilized by the film. This effect has been clearly demonstrated by experiments on the capillary wave damping by water-insoluble organic surface films [7] and measurements of the influence of surface film pressure on water surface temperature and convective processes near the interface [8].

Adsorbed surface-active material not only attenuates existing waves but also inhibits wave formation [9,10]. According to Miles [11], the addition of a sufficient quantity of a soluble surface-active agent to produce an inextensible film at the air-sea interface can increase the minimum wind velocity necessary to produce waves by almost one order of magnitude. While natural sea slicks should in theory withstand winds of this order (12 m/sec), their constituents are dispersed at sustained wind speeds of from 5 to 7 m/sec and sometimes less. The concentration of surface-active material in the underlying seawater is usually insufficient to supply and maintain a coherent surface film under highly dispersive conditions.

On the other hand, artificially produced surface films of water-insoluble organic compounds may possess the wave-inhibiting properties against winds as high as 12 m/sec. On several occasions artificial slicks have been formed and maintained for a period of time when winds were as great as 10 m/sec. Even under these adverse conditions, coherent experimental surface films could be maintained as long as excess film forming material was present to repair ruptures in the man-made slick caused by dynamic processes at the air-water boundary.

The various effects of both natural and experimental surface films on air-sea interfacial properties and processes are reviewed in Table 1. In addition to the previously mentioned capillary-wave and surface-temperature effects, natural films modify bubble bursting characteristics and sea foam, alter electromagnetic wave reflection by attenuating capillary and small gravity waves, and act as an interfacial organic phase which accumulates oleophilic pollutants. Wave attenuation and ocean surface temperature effects have been studied using large experimental slicks at sea, while other film-induced modifications of interfacial properties have been demonstrated solely in the laboratory.

Most of the numerous effects of natural slicks (Table 1) may be duplicated by experimental surface films composed of selected pure compounds. These interfacial modifications may be caused by a wide variety of water-insoluble surface films which modify the micro-scale hydrodynamics and the rheology of the air-sea interface. It will be shown in ensuing sections that certain substances can be used to produce experimental sea slicks which are useful for fundamental studies of wave-wave and wind-wave interactions and for the evaluations of the effects of sea surface films on the interpretation of remotely sensed signals.

Table 1 — Impact of Natural and Man-Made Surface Films on Properties of the Air-Sea Interface

Surface Effect or Process Modification Studied	General Results and Literature References	
	Natural Surface Films	Experimental* Surface Films
Capillary Wave Attenuation	++ [12] [13] [17] [14]	++ [4] ++ [6]
Gravity Waves	- [12]	++ [4] ++ [6]
Breaking Wave Inhibition	? -	++ [4]
Gas Transport Reduction	? -	+ [8] ++ [15] + [16]
Oleophilic Pollutant Accumulation	++ [17] [18] [19]	? -
Foam Stability	+ [20]	+ [21]
Air Bubble Bursting	+ [22] [23]	+ [23] [24]
Surface Temperature	++ [25]	++ [26] + [8] + [27]
Electromagnetic Wave Reflection	++ [28] [29] [30]	++ [4] [5]

- significant influence of surface film unlikely; ? potential influence, but not proved by experiment; + demonstrated in laboratory, field studies if any were inconclusive; ++ effect demonstrated by laboratory and field research; * a continuous, monomolecular film added to water surface for research purposes.

The influences of natural organic sea surface films on remotely sensed signals are reviewed in Table 2. Since natural slicks attenuate and resist the formation of capillary waves, affected sea surface areas have different electromagnetic or light reflectance characteristics than those of surrounding nonslicked waters. When passive reflectance is sensed, the relative intensity of the signal is dependent upon the observation angle, the relative position of the sensor with respect to the sun, meteorological conditions, and other factors. With active sensors such as microwave radar, the power of the backscattered radiation is sharply reduced by the ripple-damped sea surface under the influence of the organic film.

In general, natural slicks appear slightly cooler than adjacent water surfaces when sensed by thermal infrared [25]. Although the emissivity of a planar water surface is not

Table 2 — Effects of Natural Organic Seasurface Films on Signals Received by Remote Sensing Systems

Seasurface Effect	Sensor Approach—Spectral Region	Influence on Signal
Capillary wave damping	Active reflectance—microwave radar Passive reflectance—UV, visible, near IR	Reduced backscatter power Modified light reflectance
Inhibition of convective overturn at surface	Passive emission—thermal IR	Slicks appear cooler
Inhibition of wave breaking Modified sea foam stability	Passive emission—microwave	Affects brightness temperature
Reduced seasurface roughness	Passive—microwave	Reduced brightness temperature

altered by the presence of a monomolecular layer of organic material [31], the cool-surface effect is produced by an immobilization of the near surface water by the relatively rigid surface film, thereby inhibiting convective overturn of the water cooled by evaporation in the surface microlayer [8]. Warm signatures of natural sea slicks have not been observed by thermal infrared sensors, since they are not expected to retard evaporation to a significant extent. When passive microwave radiometers are used to sense the sea surface, the observed signal depends upon emission and reflection from the structured air-water interface. Experimental oleyl alcohol slicks were sensed by airborne radiometers operated at 1.4 (K_u band), 8.35 (X band), and 14.5 (L band) GHz [32]. The monomolecular film on the sea surface affected the radiometric signals in the same way as would a decrease in surface roughness. The oleyl alcohol slick was manifested as a 2°K decrease in antenna temperature with X and K_u bands for both horizontal and vertical polarizations. No detectable effects were observed with L band. Since the slick damped the capillary wave spectra and was readily detected at the shorter wavelengths, it was concluded that small-scale roughness is an important parameter affecting emission from the sea surface.

Passive microwave sensors can also detect sea foam through a resulting increase of sea surface emissivity. Air bubbles and foam at the air-water interface are responsible for the passive microwave signals, while entrained air bubbles beneath the surface do not contribute to the effect. Surface-active material modifies sea foam through several mechanisms. Insoluble surface organic films may decrease wave breaking and also act to destabilize foams and bubbles once they reach the water surface. Water-soluble, surface-active materials, on the other hand, are foam stabilizers. The net effect of these opposing processes has not been determined experimentally at sea.

When petroleum spills or municipal effluents are present, thicker films are implicated in the production and modification of remotely sensed signals. The influences of petroleum films on remote sensing are similar to those of natural slicks, except for thermal IR sensors, to which a petroleum surface film may appear either cooler or warmer than adjacent clean water. The sensed IR signal may be due to a number of possible physical effects, the relative importance of which has not been demonstrated by sea-truth experiments.

Petroleum spills may be sensed across a broad spectral range by numerous sensor systems. Because oil spills vary greatly in thickness and in their physical and chemical characteristics, the portion of the spill sensed varies according to the sensing system used for observation. For example, microwave radar senses the entire area affected by the oil in which the capillary wave structure is attenuated, whereas dual-frequency, passive microwave radiometry senses only the thicker layers of the spill and can be used to determine spill thickness and volume. Both natural surface films and pollutants may be incorrectly identified as petroleum by many remote sensing devices. Under certain circumstances the use of multispectral sensing systems is required to avoid ambiguities.

In most instances sea truth must be determined if remotely sensed data are to be correctly interpreted. For example, reduced sea surface return of microwave radar signals may be due to the following sea-truth situations in which capillary waves are either diminished or absent; (1) zones of calm where no organic film is necessarily involved, (2) hydrodynamic damping in a ship's wake, (3) wind slicks, (4) natural sea slicks caused by organic films which attenuate and resist the formation of capillary waves, and (5) thicker layers of

wave-damping petroleum oils or other organic film forming pollutants. Other sensors used for the detection of oil on water also have a number of possible false alarms which require measurement and observation at the air-sea boundary to ascertain corresponding sea truth. The experimental slicks discussed in this report may be used to "calibrate" remote sensing systems to assist in the interpretation of sea surface events.

EXPERIMENTAL APPROACH

Criteria for the Selection of Slick-Forming Materials

Several physical and chemical criteria must be considered in the selection of a monolayer-forming material for the creation of a durable, continuous, and capillary-active experimental sea slick. The molecule of the slick-forming material should contain both polar and nonpolar functional groups; a hydrophilic group which adsorbs at the water surface and a hydrophobic hydrocarbon chain which is oriented away from the water surface when the film is under lateral pressure. The material must spread spontaneously over the water surface as a water-insoluble monomolecular film so that only small quantities are required to affect a large water surface area. The hydrocarbon portion of the molecule should contain at least 18 carbon atoms so that losses from the slick due to evaporation and dissolution will be small. A nonionic, film-forming chemical is required for use on saline water to obviate reaction with ionic species which would increase film solubility. Commercially available materials which satisfy these requirements include fatty alcohols and esters, glyceride esters of fatty acids (vegetable and fish oils), and several synthetic surface-active agents. Table 3 is a list of

Table 3 — Properties of Film-Forming Materials for the Production of Persistent, Highly Surface Active, Experimental Sea Slicks

Highly Surface Active—Strong capillary wave damping Resist generation of air-water interfacial disturbances
Liquid—Easily and rapidly spread onto water surface
Nonvolatile—Low evaporative loss rate
Nonionic—Little reaction with saline water to ensure film persistence
Low Water Solubility—Long film persistence
Fluid Monomolecular Film—Rapid, spontaneous spreading High respreading potential
Low Freezing Point—Effective fluid films in cold environments
Nontoxic—Ecologically acceptable

properties required for substances to be used for the production of persistent, highly surface-active, experimental slicks on the sea. Initial experiments were performed in the laboratory and on the Chesapeake Bay to determine (a) the feasibility of creating and sustaining a monomolecular film on the sea; (b) the resistance of various experimental surface films to natural dispersive forces of wind, waves, bursting bubbles, *etc.*; (c) the most effective monolayer-forming materials for the creation of a durable experimental slick for various applications and research purposes; and (d) the quantity of surface-active material required.

For comparison purposes a series of experimental slicks of different substances was produced simultaneously from point source applications. The slicks were made from the following film-forming materials:

oleyl alcohol (9-octadecen-1-ol, cis isomer) an 18-carbon, monounsaturated fatty alcohol, equilibrium spreading pressure = 31 mN/m.

cottonseed oil, glyceride esters, whose fatty acids are primarily palmitic C_{16} , oleic $C_{18:1}$, and linoleic $C_{18:2}$, equilibrium spreading pressure = 14 mN/m.

oleyl ether containing two oxyethylene groups, equilibrium spreading pressure = 42 mN/m.

isostearyl alcohol containing two oxyethylene groups, equilibrium spreading pressure = 44 mN/m.

oleic acid (9-octadecenoic acid, cis isomer), equilibrium spreading pressure = 30 mN/m.

sorbitan monooleate, equilibrium spreading pressure = 42 mN/m.

Since the slicks were deployed at approximately the same time, they were subjected to similar environmental stresses. These studies were performed several times with small quantities (25 to 150 ml) of film-forming substances so that the slicks could be observed and their dimensions measured during their lifetimes. The relative slick lifetimes and their capillary wave damping intensities were nearly identical for each series of simultaneously produced slicks. These studies were performed under conditions of steady winds (4 to 7 m/sec) with no natural or pollutant slicks in evidence.

During the first 20 to 30 min all of the slicks grew equally to a size determined primarily by wind-driven surface water flow. During this period excess film-forming material in equilibrium with the spread film was sufficient to overcome losses from the slick due to natural processes. After a period of about 30 min the more water soluble films, *e.g.* oleic acid, no longer increased in surface area. The less soluble films continued to increase in areas at about equal rates. At a slick lifetime of about 1 h, three of the moderately soluble slicks, sorbitan monooleate, isostearyl alcohol (2-oxyethylene groups), and oleyl ether (2 oxyethylene groups) disappeared rather suddenly over a short time period of from 5 to 10 min. Their constituents were no longer at a sufficiently high surface concentration to alter capillary waves and other small-scale interfacial dynamic processes. Since these effects modify light reflectance from a slick-covered water surface, the slicks in question were no longer visible. Oleyl alcohol and cottonseed oil are quite water insoluble even in monomolecular layers,

and their films persisted about three times as long as any of the others studied. Film lifetime is an important aspect when using experimental slicks for basic and applied purposes because of the difficulty in maintaining a one-molecule-thick organic layer against natural dispersive processes. Consequently, oleyl alcohol and cottonseed oil are examples of materials with relatively high and moderate film pressures which can be used effectively to produce persistent experimental slicks on bodies of water.

During the simultaneous observations of the adjacent slicks it was noticed that the capillary wave damping in the low-film-pressure slick of cottonseed oil was less intense than for the other experimental films whose film pressures were 30 mN/m or greater. More high-frequency wave structure was visible in the cottonseed oil slick, and its light reflectance effects were less pronounced, having the appearance of natural slicks with similarly low film pressures [7]. In the laboratory most surface films damp mechanically generated capillary waves to approximately the same degree when their film pressures are on the order of a few millinewtons per meter [7]. However, in the open-water studies the surface films were at their maximum spreading pressures in equilibrium with unspread droplets of film-forming material. The film pressure of the slicks with strong capillary wave effects (greater than 30 mN/m) was more than twice that of the less effective cottonseed oil film (14 mN/m). Thus the resistance of a slick to capillary wave formation is not solely related to its wave-damping characteristics as measured in the laboratory with mechanically generated ripples. It is not yet known which physical parameters of an organic surface film govern its influence on capillary waves at sea. It has been observed, however, that slicks with high film pressures damp water waves and small-scale turbulence more intensely than those of lower equilibrium film pressures.

Because of its long lifetime and strong surface effects, oleyl alcohol has been used for most experimental sea slick studies. In addition, this material meets the criteria listed in Table 2. On the basis of these criteria, cottonseed oil and methyl oleate are also suitable for the production of persistent slicks, except that with their lower film pressures they more closely simulate natural films in their physical effects on interfacial properties and processes.

Techniques for Generation of Experimental Slicks

A—Dispensing Film-Forming Material from a Surface Vessel

When organic surface-active material is placed on a clean water surface in the absence of wind, it spreads spontaneously in all directions. Its initial spreading velocity varies between 34 and 40 cm/sec for the types of film-forming materials discussed in this report. The spreading velocity is related in part to the equilibrium spreading pressure of the surface active material [33]. The spreading velocity decreases rapidly with distance from the source of the film-forming material, decreasing to 10 cm/sec or less when the leading edge of the film is 3 m from the point of application. Under the influence of wind, however, the film is moved along with the flow of the surface water (3 to 4% of the wind velocity), and the excess bulk material which exists as floating lenses also moves with the wind-driven surface water flow. The rate of motion of the downwind edge of the slicks is the sum of the surface water flow

and the film spreading velocity at that point. Thus, a point source addition of spreading oils under the influence of wind produces an elongated slick whose dimensions are primarily a function of wind velocity and surface current.

It is also possible to generate a slick by continuous dispensing from a vessel moving in a direction perpendicular to the wind. However, a stripe of slick does not grow uniformly, but eventually forms streaks along the downwind edge. Thus, in order to produce a large slick for experimental purposes which has a circular or rectangular shape, it is necessary to "paint" the slick-forming material onto the water surface. That is, it cannot be simply dispensed from a point source or a single stripe, but must be laid in adjacent bands or in an expanding spiral from either a surface vessel [3,4] or an aircraft [2,5].

B—Generation of Slicks by Aerial Dispensing of Frozen Oil Cubes

Several problems are associated with the production of experimental slicks from a surface vessel. The vessel may disturb the natural wave and turbulence fields and possibly emit interfering chemical pollution. In addition, there is a requirement for the production of large slicks several square kilometers in area in a relatively short time. Thus, an alternative method for the generation of experimental sea slicks has been developed, whereby frozen chunks (oil cubes) of the film-forming material are systematically distributed from a helicopter. During projects in 1974 [34] and 1975 [5], 80-g chunks of 96.5% oleyl alcohol (9-octadecen-1-ol, cis isomer) were prepared by freezing the material to 249°K in small paper cups. The frozen chunks were transported in large Dewar containers for dispensing from the helicopter.

If surface currents prevail during slick-forming operations, it is essential to drop several chunks to produce a sample slick prior to formation of the main experimental surface film. Thus, one can observe the spreading characteristics and direction of drift of the sample slick with respect to a fixed point, such as an anchored ship or instrumentation pile. This procedure is necessary to assure that the main experimental slick will drift through an array of wave-measuring and meteorological instruments or through the fields of view of sensors being used in conjunction with the slick research.

As mentioned previously, natural forces displace the slick-forming material from the air-sea interface. The rate at which this occurs is a function of the intensity of the dynamic processes operating on the interfacial film. To maintain a continuously slicked sea surface area, it is necessary to dispense an excess of film-forming material over that required to form a monomolecular film. The excess material does not increase the slick thickness above that of a monolayer, because the film-forming materials selected are autophobic, *i.e.*, they do not spread over their own monomolecular film. Thus, the excess material exists as unspread floating drops in equilibrium with the fully compressed slick. When a portion of the slick is dispersed by natural processes, the excess film-forming material represents a floating reservoir to rapidly replace the lost organic material and restore the equilibrium pressure of the surface film. The surface concentrations (liters-km⁻²) used successfully in various experimental sea slick studies are listed in Table 4. The quantities used can be compared with that required for a single molecular layer of oleyl alcohol, 1.75 l-km⁻².

Table 4 — Quantities of Oleyl Alcohol Used in the Production of Various Experimental Sea Slicks

Dispensing Mode	Slick Size (km ²)**	Oleyl Alcohol Volume (liter)	liters-km ⁻²	Reference
Boat*	0.50	13.0	26.0	[4]
Boat*	0.70	19.0	27.1	[3]
Fixed-wing Aircraft*	0.52	18.0	34.6	[2]
Point Source	0.005	0.1	20	[35]
Helicopter ⁺	1.5	30.0	20	[5]
Monolayer, theoretical	—	—	1.75	—

*Dispensed as a liquid stream from a pressured container

**Maximum area of slick during its lifetime

⁺Frozen, 80-g chunks dispensed periodically

EXPERIMENTAL SLICKS IN THE MARSEN EXERCISE

Three monomolecular, organic surface films were produced as part of the MARSEN exercise in the vicinity of the German research platform Nordsee (Fig. 1) located at 54° 42' 33" N, 7° 10' 7.4" E, in the North Sea. This location is about 72 km west of the southern end of Sylt Island and 72 km northwest of Helgoland Island. The upper deck of the research platform is about 28 m above mean water level and the water depth is 30 m. The experimental slicks were generated approximately 1.5 km upwind of the platform, so that they would drift across the footprints of various sensors mounted on the platform. In addition, the slicks were coordinated with overflights by instrumented NASA P-3 and CV-990 aircraft.

The experimental slicks were produced by dispensing frozen blocks of film-forming material from a helicopter flying at an altitude of 30 m above the sea surface. The blocks were dispensed at calculated intervals as the helicopter flew a series of parallel tracks perpendicular to the calculated surface drift in order to develop a continuous, approximately square surface film.

The initial center point of the dispensing pattern was calculated from tide tables and the ambient wind velocity and direction data obtained by radio from the platform. A test slick formed from several blocks of film-forming material was allowed to develop and move for several minutes to provide a final test of the direction of slick drift. These precautions were a necessary part of the slick-laying procedure to ensure that the experimental film would pass with its center near the platform and influence the wavestaffs and microwave sensors to the greatest extent possible.

The characteristics of the three slicks generated for the MARSEN exercise are reviewed in Table 5. Both slick-forming compounds were obtained from the Henkel Corporation, Dusseldorf, West Germany. The oleyl alcohol has a purity of 96.5%, and a freezing point of 4 to 6° C. The methyl oleate was a technical grade material (74.8%) with a freezing point at -6° C. Although the latter substance was not of high purity, its surface-chemical properties and capillary-wave damping characteristics were closely similar with those of high-purity methyl oleate (99%+) according to H. Hühnerfuss of the University of Hamburg, Hamburg,

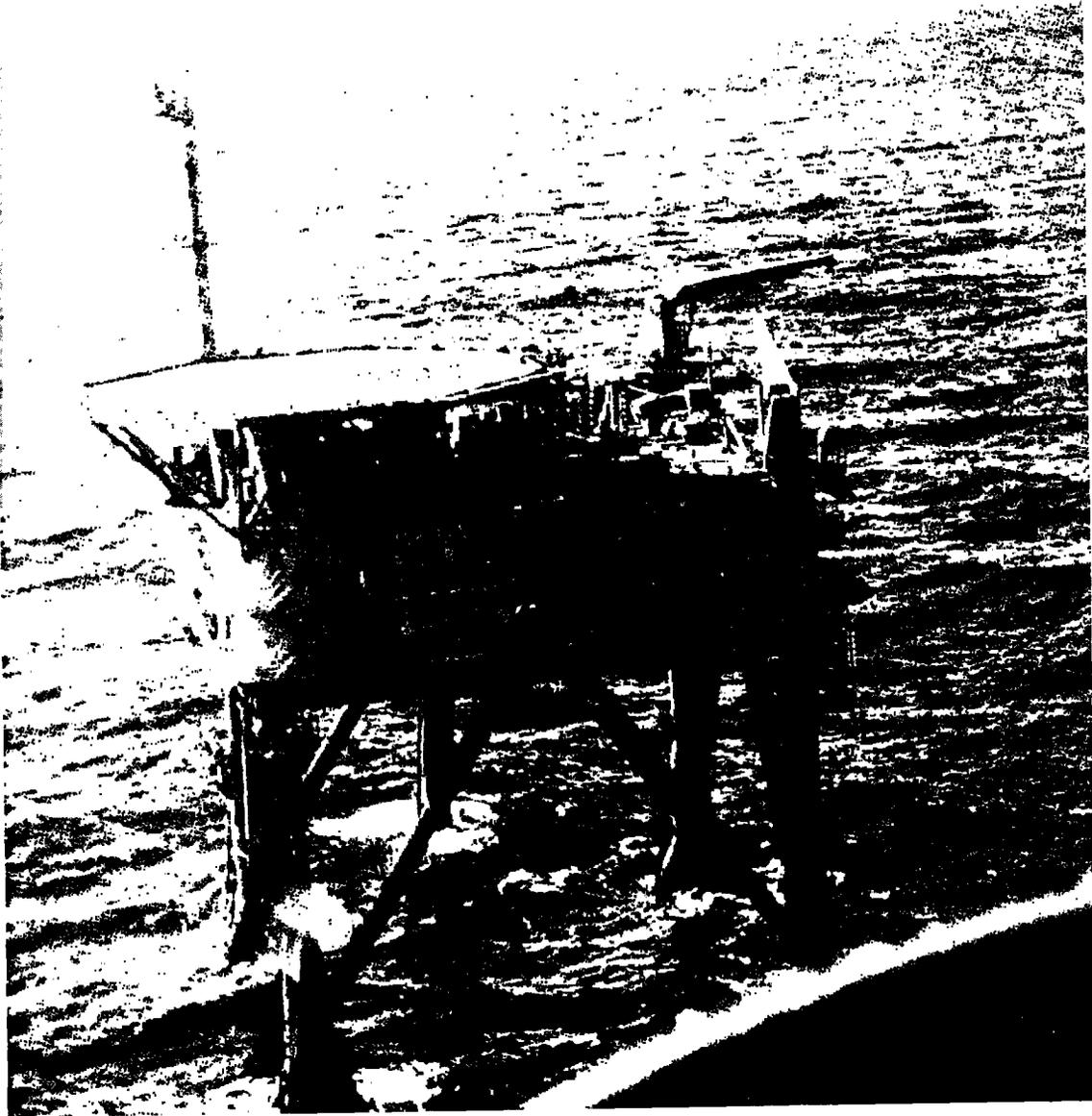


Fig. 1 — Research platform, Nordsee, located in the German Bight section of the North Sea ($54^{\circ} 42' 33''$ N, $7^{\circ} 10' 7.4''$ E) and used as focal point of MARSEN coordinated slick experiments. Helicopter pad is located at the southeast quadrant of the platform.

West Germany. During the slick experiments the wind was generally from the west at 10 to 16 knots, there were few whitecaps, and no natural slicks were evident. Film pressures measured by the calibrated spreading oil technique were essentially zero, indicating that no natural coherent surface films existed in the dynamic sea surface.

Slick number 2 depicted in Fig. 2 was formed from methyl oleate (9-octadecenoic acid, methyl ester, *cis*), a substance whose film pressure is about one-half that of the oleyl alcohol used in the other two experiments. The degree of wave damping in the methyl oleate film was somewhat less than that caused by the oleyl alcohol films. This wave damping difference was readily discerned from visual observations and was measured by differences in the power of backscattered radiation from X- and L-band radars mounted on the research platform. The backscattered X-band signal was reduced about fourfold over that from the nonslicked sea surface, while the backscattered L-band signal was about twofold reduced by the methyl oleate film. The reductions of the backscattered power of the microwave radar signals from the methyl oleate film was on the order of 5 to 7 times less than those from the oleyl alcohol slicks which attenuated capillary waves and short gravity waves more intensely. Furthermore, the methyl oleate spread more slowly than oleyl alcohol and took longer to form a continuous film over the water surface. The slower spreading of the methyl oleate was due to two factors. First, since the spreading velocity of a monomolecular film increases with film pressure [33], the methyl oleate would be expected to spread more slowly from its source, the bulk material floating on the sea surface. Furthermore, because of the lower freezing point of methyl oleate, it was necessary to solidify it with dry ice. Consequently, considerable time was required for the frozen blocks to melt in the cool sea (14°C) to form liquid lenses from which the surface film could readily spread. Spontaneous spreading of a monolayer is considerably slower from the solid phase than from the liquid phase.

Experimental slicks 1 and 3 (Table 5) were formed from oleyl alcohol (9-octadecen-1-ol, *cis* isomer). Slick number 1 was produced in close coordination with overflights by NASA P-3 aircraft equipped with an Airborne Oceanographic Lidar (AOL) as well as other remote sensing instrumentation. The AOL was operated in three modes to sense the monomolecular slick as well as some of the chemical parameters associated with and modified by organic surface films on water; specifically fluorescent organic substances and chlorophyll. The experimental slick was sensed by its attenuation of laser-induced, water-Raman backscattered radiation. As the aircraft crossed the slick, the Raman signal decreased rapidly to a constant value near the edge of the surface film and increased again to a value indicative of clean nonslicked water when the aircraft was no longer above the film-affected area. Thus, this measurement clearly defined the film-covered sea surface area, and the dimensions of the slick could be calculated from the transit time and speed of the aircraft. The fluorescence and chlorophyll measurements as well as results from S- and L-band passive radiometric sensing of slick number 1 from the P-3 will be presented elsewhere.

Experimental slick number 3, the largest formed, was 2.3 km^2 in surface coverage and measured 1520 by 1500 m (Figs. 3 and 4). This nearly square surface film passed directly across the center of the platform. The slick drift velocity of 0.71 m sec^{-1} was determined by measurement from the helicopter and from the entry and exit time for the slick at the western edge of the platform. This value agreed well with a drift velocity (0.69 m sec^{-1}) calculated as a resultant of wind and current vectors. The calculated slick drift velocity was determined in advance of the experiment by assuming that the drift component due to wind

Table 5 — Characteristics of MARSEN Experimental Slicks

Slick	Compound	Date	Dispensing Times*	Quantity (kg)	Size (km ²)	Film Pressure (mN/n)**	Drift Velocity (m/sec)
1	oleyl alcohol	22:9:79	0814-0837	32.0	1.5	31	0.59
2	methyl oleate	28:9:79	1050-1120	32.8	1.0	15	—
3	oleyl alcohol	28:9:79	1200-1235	48.0	2.3	31	0.71

*Universal time

**Laboratory measurement at 25°C



Fig. 2 — Aerial view of a 1.0 km² monomolecular film of methyl oleate passing the Nordsee platform. The photograph looks toward the wind direction at 290°.



Fig. 3 — Aerial photograph of slick 3, a monomolecular film of oleyl alcohol, 2.3 km² in area passing the Nordsee platform, 28 September 1979 at 1230 UT

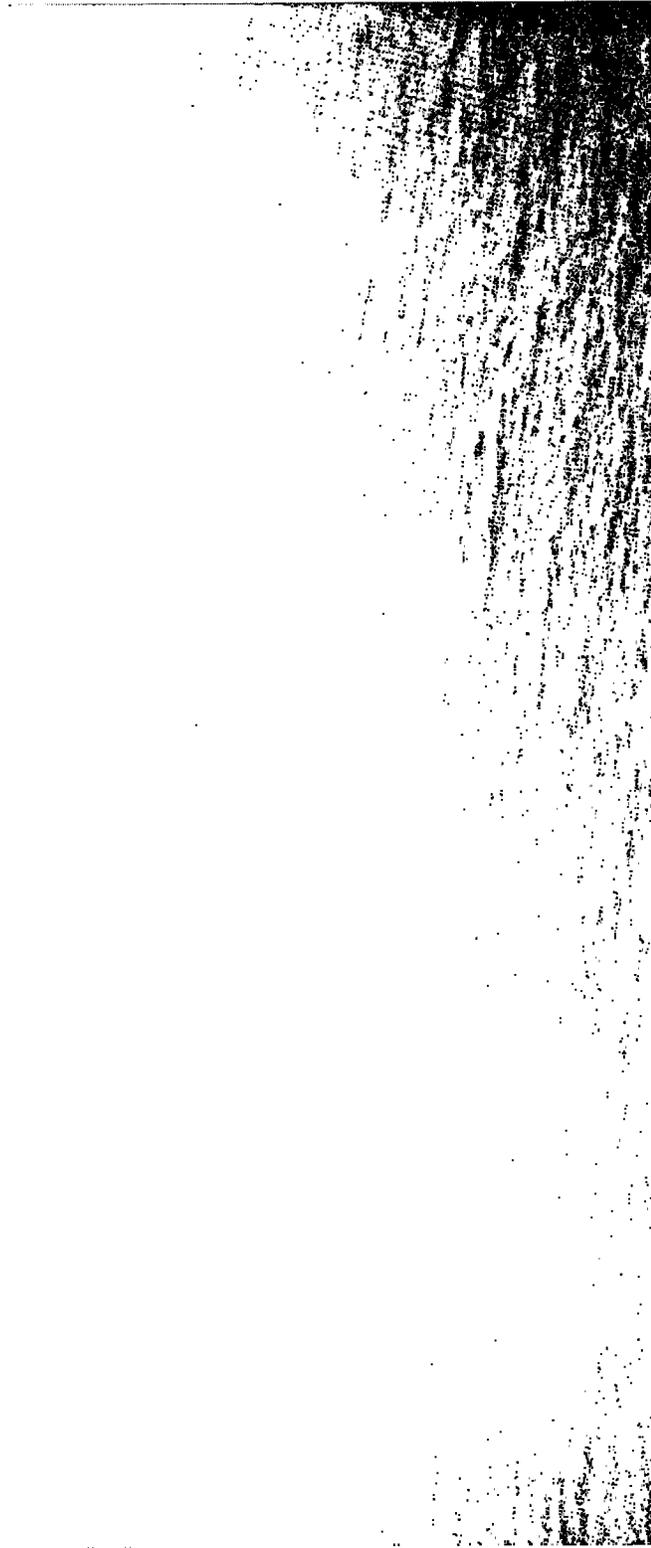


Fig. 4 — Aerial photograph of slick 3 looking west, 28 September 1979 at 1255 UT

was 3.5% of the wind speed. The transit time of slick 3 across any particular point of observation was about 35 min. This continuous slick was sensed by both X- and L-band radars and by wavestaffs capable of measuring the gravity wave spectra. Consequently, it is anticipated that the possible influence of the film on gravity waves and the role of capillary waves on the modulation of larger waves will be ascertained when the collected data have been analyzed by the MARSEN investigators involved in these measurements.

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REFERENCES

1. W. R. Barger and W. D. Garrett, "Modification of the Air/Sea Interface by Artificial Sea Slicks," NRL Report 6762, September 1968.
2. W. R. Barger and W. D. Garrett, "Artificial Sea Slicks: Their Practical Applications and Role in Fundamental Research," NRL Report 7751, June 1974.
3. W. D. Mallinger and T. P. Mickelson, "Experiments with Monomolecular Films on the Surface of the Open Sea," *J. Phys. Oceanogr.* **3**, 328-336 (1973).
4. W. R. Barger, W. D. Garrett, E. L. Mollo-Christensen, and K. W. Ruggles, "Effects of an Artificial Sea Slick upon the Atmosphere and the Ocean," *J. Appl. Meteorol.* **9**, 396-400 (1970).
5. H. Hühnerfuss, W. Alpers, and W. L. Jones, "Measurements at 13.9 GHz of the Radar Backscattering Cross Section of the North Sea Covered with an Artificial Surface Film," *Radio Sci.* **13**, 979-983 (1978).
6. H. Hühnerfuss, W. Alpers, W. L. Jones, P. A. Lange, and K. Richter, "The Damping of Ocean Surface Waves by a Monomolecular Film Measured by Wavestaffs and Microwave Scatterometers," accepted by *J. Geophys. Res.*
7. W. D. Garrett, "Damping of Capillary Waves at the Air-Sea Interface by Oceanic Surface-Active Material," *J. Mar. Res.* **25**, 279-291 (1967).
8. N. L. Jarvis, "The Effect of Monomolecular Films on Surface Temperature and Convective Motion at the Water/Air Interface," *J. Colloid Sci.* **17**, 512-522 (1962).
9. G. H. Keulegan, "Wind Tides in Small Closed Channels," *J. Res. Nat. Bur. Stand.* **46**, 358-381 (1951).

10. W. G. Van Dorn, "Wind Stress on an Artificial Pond," *J. Mar. Res.* **12**, 249-276 (1953).
11. J. W. Miles, "Surface-Wave Damping in Closed Basins," *Proc. Roy. Soc. A* **297**, 459-485 (1967).
12. J. T. Davies and E. K. Rideal, *Interfacial Phenomena*, 2nd ed. (Academic Press, New York, 1963), pp. 266-274.
13. G. Ewing, "Slicks, Surface Films and Internal Waves," *J. Mar. Res.* **9**, 161-187 (1950).
14. J. C. Scott, "The Influence of Surface-Active Contamination on the Initiation of Wind Waves," *J. Fluid Mech.* **56**, 591-606 (1972).
15. H.-Ch. Broecker, J. Petermann, and W. Siems, "The Influence of Wind on CO₂ Exchange in a Wind-Wave Tunnel, Including the Effects of Monolayers," *J. Mar. Res.* **36**, 595-610 (1978).
16. J. Petermann, "Der Einfluss der Oberflächenspannung wässriger Systeme auf die Kinetik der Gasabsorption," Dissertation, University of Hamburg, 276 pp., 1976.
17. R. Hartung and G. W. Klinger, "Concentration of DDT by Sedimental Pollutant Oils," *Env. Sci. Tech.* **4**, 407-409 (1970).
18. D. B. Seba and E. F. Corcoran, "Surface Slicks as Concentrators of Pesticides in the Marine Environment," *J. Pest. Monitor*, **3**, 190-193 (1969).
19. S. J. Eisenreich, A. W. Elzerman, and D. E. Armstrong, "Enrichment of Micronutrients, Heavy Metals and Chlorinated Hydrocarbons in Wind-Generated Lake Foam," *Env. Sci. Tech.* **12**, 413-417 (1978).
20. W. D. Garrett, "Impact of Natural and Man-Made Surface Films on the Properties of the Air-Sea Interface," in *The Changing Chemistry of the Oceans* (Almqvist and Wiksell, Stockholm, 1972), pp. 75-91.
21. W. D. Garrett, "Stabilization of Air Bubbles at the Air-Sea Interface by Surface-Active Material," *Deep-Sea Res.* **14**, 661-672 (1967).
22. D. C. Blanchard and E. J. Hoffman, "Control of Jet Drop Dynamics by Organic Material in Seawater," *J. Geophys. Res.* **83**, 6187-6191 (1978).
23. W. D. Garrett, "The Influence of Monomolecular Surface Films on the Production of Condensation Nuclei from Bubbled Seawater," *J. Geophys. Res.* **73**, 5145-5150 (1968).
24. M.P. Patterson and K. T. Spillane, "Surface Films and the Production of Sea-Salt Aerosol," *Quart. J. Roy. Met. Soc.* **95**, 526-534 (1969).
25. H. L. Clark, "Some Problems Associated with Airborne Radiometry of the Sea," *Appl. Opt.* **6**, 2151-2157 (1967).
26. R. L. Grossman, B. R. Bean, and W. E. Marlatt, "Airborne Infrared Radiometer Investigation of Water Surface Temperature With and Without an Evaporation-Retarding Monomolecular Layer," *J. Geophys. Res.* **74**, 2471-2476 (1969).
27. N. L. Jarvis, C. O. Timmons, and W. A. Zisman, "The Effect of Monomolecular Films on the Surface Temperature of Water," in *Retardation of Evaporation by Monolayers: Transport Processes* (Academic Press, New York, 1962), pp. 41-58.

28. J. T. Beard and J. L. Gainer, "Influence of Solar Radiation Reflectance on Water Evaporation," *J. Geophys. Res.* 83, 6187-6191 (1978).
29. W. E. Brown, Jr., C. Elachi, and T. W. Thompson, "Radar Imaging of Ocean Surface Patterns," *J. Geophys. Res.* 81, 2657-2667 (1976).
30. A. Maurer and A. T. Edgerton, "Flight Evaluation of U.S. Coast Guard Airborne Oil Surveillance System," in *Proc. Conf. Prevent and Control Oil Poll.* (American Petroleum Institute, Washington, D.C., 1975) pp. 129-141.
31. N. L. Jarvis and R. E. Kagarise, "Determination of the Surface Temperature of Water During Evaporation Studies," NRL Report 5727, December 1961.
32. B. D. Au, J. Kenney, L. U. Martin, and D. Ross, "Multi-Frequency Radiometric Measurements of Foam and a Monomolecular Slick," *Proc. 9th Symp. on Remote Sensing of Environ.*, Vol. III, pp. 1763-1773. Ann Arbor, Mich., 1974.
33. W. D. Garrett and W. R. Barger, "Factors Affecting the Use of Monomolecular Surface Films to Control Oil Pollution on Water," *Env. Sci. Tech.* 4, 123-127 (1970).
34. H. Hühnerfuss and P. Lange, "Modification of the Air-Sea Interaction Processes by Monomolecular Films, Part I: A New Method for Producing Artificial Sea Slicks," *Berichte des Sonderforschungsbereich 94* (University of Hamburg) 7, 1963-169 (1975).
35. W. R. Barger and W. D. Garrett, "Marking the Sea Surface with Artificial Sea Slicks and Fluorescent Dyes to Aid Search and Rescue or Ocean Dumping Surveillance Operations," United States Coast Guard Report No. CG-D-107-76, July 1976.