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RESEARCH AND LOGISTICAL SUPPORT
FOR THE OFFICE OF NAVAL RESEARCH
ACCELERATED RESEARCH INITIATIVE
ON MARINE MICROLAYER PROCESSES

Final Report

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Statement A per
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Logistical Coordination

ORINCON principal investigator, William D. Garrett, has many years of research involvement in sea surface microlayer processes, has been involved in many aspects of the present ONR program, and is cognizant of its research issues and program requirements. During the five years of the Marine Microlayer Processes Initiative (FY 87 through FY 91) he has coordinated logistics and assisted in planning numerous multidisciplinary field experiments in both coastal and open-ocean areas. In preparing for the field research it was necessary to arrange for ship services, land-based facilities, participant lodging accommodations, and numerous other logistical requirements. Information on these matters were communicated to program participants in a timely manner.

Liaison has been maintained with all program participants (14 principal investigators representing 11 different institutions), and periodic workshops were organized for planning and review of program activities and research results. The following list includes the field experiments, planning review sessions, and coordinated pre-experiment site visits coordinated by ORINCON.

**FY 87 THROUGH FY 91 ACTIVITIES PLANNED,
COORDINATED AND LOGISTICALLY SUPPORTED BY
ORINCON**

1. Initial planning meeting- San Francisco, 7 DEC 86 (during American Geophysical Union Meeting).
2. Site planning visit to University Maine Oceanographic Center, 19-20 Mar 87.
3. First Multidisciplinary Field Experiment, 3-16 May 87, Darling Oceanographic Center of Univ. Maine, Walpole, ME.
4. Interexperiment review/planning meeting, Scripps Institution of Oceanography, 14-15 JUL 87, La Jolla, CA.
5. Second Multidisciplinary Field Experiment, 8-19 SEP 87, Darling Oceanographic Center, Walpole, ME.
6. Meeting for review of FY 87 activities and planning for 1988, ORINCON Corporation, Arlington, VA 14-15 JAN 88.
7. Third Multidisciplinary Field Experiment, 8-26 May 88, Bermuda Biological Station for Research, Bermuda.
8. Pre-cruise planning meeting at Nimitz Marine Facility, San Diego, CA, 9-10 AUG 88.
9. Fourth Multidisciplinary Field Experiment, 13-27 SEP 88, Cruise aboard R/V Sproul (Scripps Institute Ocean.). 13-27 SEP 88.
10. Mid-term review planning meeting on Marine Microlayer Initiative, ORINCON Corporation., Arlington, VA, 17-18 NOV 88.

11. Planning meeting for 1989 field program, San Francisco, CA, 6 DEC 88 in conjunction with sessions on "Ocean Microlayer Multidisciplinary Processes" at American Geophysical Union meeting.
12. 27-29 MAR 89, NASA ER-2 remote sensing arrangements (NASA AMES Research Center, Moffett Field, CA) and planning meeting for 1989 activities and OCT 89 marine microlayer/remote sensing experiment, Oregon State University, Corvallis, OR.
13. 13 OCT 89, pre-cruise planning activities, San Diego, CA.
14. 13 OCT 89, pre-cruise planning meeting at Nimitz Marine Facility, San Diego, CA.
15. Fifth Multidisciplinary Field Experiment. 14-27 OCT 89, Marine microlayer cruise (SLIX-89) involving the R/V SPROUL (Scripps), R/V WECOMA (Oregon State) and NASA Ames ER-2 remote sensing flights.
16. 13-14 DEC 89, 1989-90 review/planning meeting on Marine Microlayer Processes Initiative, ORINCON Corporation, Arlington, VA.
17. 30 JAN 90, review of microlayer special cruise to Navy Group, John Hopkins University Applied Physics Laboratory, Laurel, MD.
18. 2 Mar 90, planning meeting for special microlayer cruise, Office of Naval Research, Arlington, VA.
19. 26-28 Apr 90, review and publication planning meeting of microlayer group, Oregon State University, Corvallis, OR.
20. Special Microlayer Cruise. 22 May-12 JUN 90, Bahama Islands.
21. 31 JUL 90, planning meeting, Office of Naval Research, Arlington, VA.

In FY 91 and CY 91 ORINCON continued to arrange subcontractor support of various marine microlayer activities as requested by the Office of Naval Research program office. William D. Garrett was requested to attend a workshop on High Resolution Remote Sensing in

support of the marine microlayer program. In addition, he acted as a guest editor for a special section of the oceans edition of the Journal of Geophysical Research published by the American Geophysical Union. He recommended reviewers for all special section manuscripts and reviewed a number of the papers in his scientific specialties. Although this special section included scientific papers outside of the Office of Naval Research program, it served to highlight this important geophysical boundary between the ocean and the atmosphere.

SUBCONTRACTOR SUPPORT FOR FIELD EXPERIMENT

ORINCON, through its contracts group, established subcontracts with the investigators' institutions to support travel expenses and per diem, experiment shipping, planning functions, and field equipment purchases. In addition, research vessels (ships and aircraft), field facilities, equipment for group use, etc. were supported through subcontracts with the oceanographic establishments hosting the multidisciplinary experiments. All subcontracting activities were performed with the prior approval of the Office of Naval Research Program Manager. William D. Garrett reviewed and approved all expense claims prior to payment.

RESEARCH SUPPORT FOR THE OFFICE OF NAVAL RESEARCH ACCELERATED RESEARCH INITIATIVE ON MARINE MICROLAYER PROCESSES

Organic sea-surface films are indicators of both surface and underwater processes which influence the physics of the sea surface. The modulation of air-sea interfacial processes by these organic films are in turn detectable in a wide variety of active and passive remotely sensed imagery, and these films serve to highlight oceanic events of larger scale. A long-term goal is the interpretation of remotely sensed imagery based on sea surface truth obtained in this program. Aerial photography is conducted during multidisciplinary field experiments to document the film-modulated condition of the sea surface and provide imagery (sun-glitter and other relevant viewing angles) for correlation with microlayer data provided by other program participants. In addition, in situ measurement of sea surface tension is performed simultaneously with the microlayer measurements to provide a surface-chemical basis for understanding mechanisms by which physical effects are modified by organic films.

Research studies pursued in support of the Marine Microlayer Processes Initiative include the measurement of water surface tension in situ and in real time with calibrated spreading oils. These measurements were made in the Damariscotta Estuary in conjunction with surface sampling and microlayer chemical measurements performed in the Maine field experiments during 1987. These data are reported in the enclosed technical report entitled "Involvement of Organic Sea Surface Films in the Highlighting of Surface and Underwater Oceanic Processes in Remotely Sensed Imagery" (Appendix A). This paper includes supporting aerial documentation of the condition of the sea surface. Aircraft flights were also used to guide other experiment participants to oceanic areas where important sea-surface microlayer events were taking place.

Surface tensions were also determined in ocean water near Bermuda in concert with the simultaneous measurement of the film-induced damping of short gravity waves with a microwave probe. Through these measurements it was possible to relate wave attenuation caused by films to the surface density and surface elasticity of the film-forming substances. The results of the Bermuda studies were published in the "Journal of Atmospheric and Oceanic Technology" in 1989 by the American Meteorological Society and is included as (Appendix B) to this report.

In one of the approaches to the objectives of this project aerial photography and multispectral imagery were obtained during multidisciplinary field experiments to document the film-modulated condition of the sea surface and to provide imagery for correlation with microlayer data provided by other program participants. In addition to sensor documentation of the sea surface, communications were established between the sensor aircraft and the research vessels, so that they can be directed to oceanic areas of scientific interest.

Low-altitude photographic flights were conducted in October of 1989 during the coastal portion of the SLIX-89 Marine Microlayer Experiment. High altitude remote sensing ER-2 flights were arranged with NASA in coordination with multidisciplinary marine microlayer research activities. Panoramic sun-glint and high-resolution nadir photography, and digitized multispectral color imagery was conducted in SLIX-89 in the Santa Cruz Island operating area. A protocol was written for flight initiation, and a flight line plan was prepared to optimize the remotely sensed information obtained from the experimental sites. Imagery was compiled and processed in conjunction with NASA Ames to provide information for correlation with marine microlayer research products.

A number of segments of the photographs taken with the Panoramic Camera were selected which contained surface features of the experiment sites. The surface effects were clearly delineated in the sun-glint photography and included (1) fields of natural surface films, (2) slicks at frontal boundaries, and (3) ship wakes. The surface ship wake signatures included Kelvin and turbulent wakes and transverse waves. The Airborne Ocean Color Imager (AOCI) produced image products which were broad in scope and covered most of the Santa Cruz Island experiment area. A mosaic of the sun-glint photographs was made to cover a similar area. A comparison of the photographic mosaic with the thermal infrared imagery for the AOCI suggests that surface temperature structure can be detected by differences in optical scattering in sun-glint photography. The specifics of the ER-2 activities arranged by ORINCON follow.

ER-2 DATA ACQUISITION AND DATA PRODUCTS (SLIX-89)

Two ER-2 flights were operated by the NASA High Altitude Missions Group, Moffett Field, CA, following flight specifications developed by SLIX-89 investigators in consultation with NASA pilots. The aircraft was flown at 65,000 feet over the experimental site and operated three imagers; two photographic and a multispectral ocean color imager. All sensors

are nonsteerable and nadir looking. Flights were on station taking imagery between 1200 and 1300 on 26 OCT 89, and between 0930 and 1030 on 27 OCT 89. The ER-2 aircraft data blocks for the flights have been received and include LAT.-LON., time, altitude, true heading, air and ground speed, etc., data essential for the interpretation of the remotely sensed imagery. Based on flight-time limitations and the requirement to utilize sun-glint photography to enhance sea-surface features, the following five flight lines were flown; (1) normal to the sun glint and over the experimental site, (2) perpendicular to flight line one in line with and away from the sun, (3) normal to sun glint as in line one, but offset to the north, such that the experimental site was included in the glint pattern, (4) similar to flight line three, but in opposite direction, and (5) repeat of flight line one.

An ITEK IRIS Panoramic Camera (high resolution) was flown in the belly mounting of the aircraft using black and white film with a blue haze filter. The panoramic camera viewed 70 degrees on either side of the nadir. Flight headings normal to the sun direction enabled the inclusion of the sun glint within the field view of the panoramic lens. At 65,000 feet the 140-degree lens has a ground coverage (footprint of 2 x 58.7 nautical miles and a nominal resolution of from 0.3 to 4 meters. In addition to the panoramic camera, a 9 x 9 inch metric, mapping camera (RC-10) was flown using natural color film. With a 12-inch lens the ground coverage of the camera was 8 x 8 nautical miles with a nominal resolution of 1.5 to 4 meters. The aerial photography was utilized for technical comparisons with sea surface measurements. The research vessels and adjacent land masses (islands) were included in the panoramic photography for scaling and location determination.

An Airborne Ocean Color Imager (AOCI, Daedalus Enterprises) was operated simultaneously with the aerial photography aboard the ER-2. The AOCI provides 10-bit digitization of eight bands of the visible spectrum and two bands of 8-bit digitization in the near and thermal infrared. The ground resolution is 50 meters and the scan width is 33.3 km with 716 pixels per scanline, when flown at 65,000 feet and 390 knots. This multispectral imagery was processed to yield sea surface temperature and ocean color maps of the SLIX-89 experimental sites.

ER-2 DATA PRODUCTS: VOLUME AND QUALITY

Mapping Camera

The RC-10 mapping camera produced a strip of color negatives. Only sixteen of were printed, as most of the exposures contained blue ocean without any scientifically interesting features. There was little sun glint in any of the images, and subsurface features, even the 12.8 km-wake of a large ship, as difficult to differentiate by eye.

Panoramic Camera

Panoramic camera b/w negatives measured 4.5 x 72 inches and were connected in long rolls. Specific segments of these negatives containing sun-glint highlighted features were developed; 18 segments for the flight of 26 OCT 89, and 35 segments for 27 OCT 89. Clearly defined surface features, some of which involved slicks, included; (1) fields of slicks, (2) slicks at boundaries (fronts), and (c) ship wakes (Kelvin, turbulent, and transverse). There is weak photographic evidence of internal waves and slicked edge bands on ship's turbulent wakes. Photographic quality is high and in the sun-glint pattern surface features are well delineated.

Airborne Ocean Color Imager

The NASA Aircraft Data Facility processed various combinations of the AOI digitized spectral bands to produce imagery products. These included; (1) thermal infrared imagery in both gray scale and pseudo color (temperature resolution 0.4 degrees C), (2) natural color, and (3) yellow spectral bands selected to indicate oceanic sediments. The AOI imagery from 65,000 ft are very broad in scope and cover most of the northern experiment area (Santa Cruz Island).

Additive Sea Surface Films

When natural sea surface films are not present as a result of high wind-wave organics and/or low biological productivity, it is useful to apply additive "slicks" to the sea surface in order to approximate the physical effects of a natural film-covered surface. A compilation of information on slick-simulating materials, their essential properties and various methodologies for their deployments was prepared in March of 1991 and is included as Appendix C to this final report. The document, prepared under the Marine Microlayer Processes ARI, relates to sea surface microlayer research and to an ongoing Office of Naval Research ARI on High Resolution Remote Sensing.

APPENDIX A

Involvement of Organic Sea Surface Films in the Highlighting of Surface and Underwater Oceanic Processes in Remotely Sensed Imagery

Report Prepared for Review Meeting of the Marine Microlayer Processes
Program
January, 1988

INVOLVEMENT OF ORGANIC SEA SURFACE FILMS IN THE HIGHLIGHTING OF SURFACE AND UNDERWATER OCEANIC PROCESSES IN REMOTELY SENSED IMAGERY

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Organic sea surface films can modify the following hydrodynamic and air-sea interfacial processes.

- capillary and short gravity waves
- wave-wave interactions
- wind-wave interactions
- surface microlayer stability - temperature
- wave breaking
- bubble and foam stability
- gas and particle exchange

As a result of these surface film effects, a number of ocean phenomena can be highlighted in remotely sensed imagery. These include:

- internal waves
- Langmuir circulation, windrows
- frontal boundaries
- convergent zones over bathymetric features
- ship wakes
- eddies
- upwelling
- biological activity

Many of these oceanic processes originate beneath the surface and cause surface convergences or currents. These subsurface processes are manifested in remote imagery when organic films are formed or organized by the sea surface straining. For example, ship wakes, eddies, fronts, internal waves, current shears, and organic slicks (both natural and anthropogenic) have been imaged by space-borne synthetic aperture radar (SAR) and photography. Any or all of these oceanic processes may be evident in the imagery, depending upon environmental conditions, the type of sensor, and the sensor look angle and travel direction relative to the target. SEASAT SAR imagery of sea surface features have been reviewed by Fu and Holt (1982), Vesecky and Stewart (1982), and by Kasischke et al. (1984).

Petroleum oil slicks and pollutant oils spilled into the turbulent wakes of ships have also been imaged by the SEASAT SAR and described in the foregoing literature. Natural organic sea slicks have been identified in space-based photography (Soules, 1970; Maul et al., 1974; and Maul, 1978). Kaltenbach et al. (1984) presents SIR-A (Shuttle imaging L-band SAR) and sun-glint photography of spiral eddies, whose surface flow patterns are probably highlighted by natural organic films which modulate the reflective characteristics of the sea surface through their ability to attenuate and resist the formation of capillary waves. Numerous examples of spiral eddies in fields of natural surface films also appear in sun-glint photography taken from the Shuttle Mission 41-G of October, 1984 (Scully-Power, 1986). In addition, the turbulent wakes of ships are clearly highlighted for distances as great as 50-80 kilometers by the extensive filigree pattern of sea surface films. These sun-glint photographs represent an example of the involvement of organic films in the remote detection of sea surface features.

Figure 1 is a representative example of the numerous Shuttle sun-glint photographs which show spiral eddies, ship wakes, shear current boundaries etc. These sea surface events are highlighted by light reflectance patterns due to extensive fields of noncontinuous slick-like features. The coordinates of the center point of this photograph is 36.5° N and 1.5° W located in the Mediterranean Sea between Spain and Algeria. The hand-held photographs were made with a NASA-modified Hasselblad 500 EL/M, 70-mm camera using a 250-mm CF Sonar 5.1 lens. Using graphs developed at NASA, it can be estimated from the Shuttle altitude, the focal length of the lens, and the look angle that the distance across the images is approximately 45 kilometers.

The sun-glint pattern is observed when the angle of view equals the angle of incidence of the sun's rays on the sea surface. When the sea is roughened by waves, especially those in the capillary wave spectrum, a broad sun glitter pattern is produced with a diminishing brightness outward from the sub-solar point on the sea surface (Soules, 1970). According to Cox and Munk (1954), the farther a wave face is from the specular point, the larger its slope must be to reflect the sun's rays toward the observer. Thus, the brightness distribution in the glitter pattern is related to the distribution of wave slopes.

Within the sun glitter pattern the slick-like features are brighter than the ambient sea surface, suggesting that the surface is more specular due to a smaller average wave slope caused by capillary wave suppression by organic sea surface films. Outside the glitter pattern the opposite reflectance contrast is observed; the slicks appearing darker than the surrounding water surface. In this latter instance, less skylight is reflected toward the observer from the less roughened sea surface zones.

Within and adjacent to the sun glitter pattern the turbulent ship wakes are highlighted by the filamentous and "cloud like" slicks for distances as great as 80 kilometers. Within the sun-glint for a distance of several ship lengths behind the ship, the turbulent wake is as specular as the surrounding slick due to intensive turbulent damping of surface scatterers. Further behind the ship the turbulent wake has roughened somewhat and appears as a darker narrow track through the slick field. When no pollutant oils are present in the turbulent wakes, as is usually the case, a slick-like band sometimes forms on either side of the wake. When no slicks are present (a "clean" sea surface), the turbulent wake is either not visible or is detectable for a few ship lengths.



1. Shuttle mission 41-G sun-glnt photograph of western Mediterranean Sea showing slick highlighted eddies, ship wakes and current shear boundaries. Photograph taken 8 OCT 1984 at 13:12:57 GMT; altitude 125 nautical miles.

The observations in the foregoing paragraph are consistent with the presumption that the turbulent wakes are rendered visible in space-based photography by their influences on the field of organic sea surface films. In this regard a review of the physiochemical effects of organic films at the sea surface and their role in the interpretation of remotely sensed imagery has been recently published by Garrett (1986). Figure 2 is presented in support of the argument that organic surface films are instrumental in the highlighting of turbulent ship wakes in sun-glint, space-based imagery. This photograph is of a ship of opportunity in coastal waters west of San Diego, CA, and were taken from an altitude of 1000 feet. When a ship passes through a field of slicks its turbulent wake disperses the organic film-forming material from the sea surface leaving a more choppy, slick-free path. A double surface convergence on either side of the turbulent wake increases the level of organic surface-active material in the sea surface to the point that two slick lines are formed at the outer edges of the wake. Wake surface convergencies of this kind as a consequence of wake hydrodynamics in a stably stratified ocean were described and demonstrated with airborne thermal IR imagery of ship wakes by Garrett and Smith (1984).

The ship wake photograph (fig. 2) shows a strong similarity to the turbulent wake signatures in the Shuttle sun-glint photography. There is a film-free path produced by the turbulent wake through a field of natural slicks, a convergence-generated double slick band on either side of the wake, and an extension of the two convergence slicks into nonslicked water. The extension of the convergence-generated slicks is due to the increase of the concentration of slick-forming material to a critical level where surface scatterers are damped and suppressed, and visible films are formed. This evidence strongly argues for organic film involvement in the highlighting of turbulent surface ship wakes in sun-glint photography from space. It is difficult to imagine that current modulation of capillary scatterers or that fields of different atmospheric stability would be responsible for ship-wake highlighting in the sun-glint imagery.

An experiment was conducted in 1986 (Kaiser et al.) which generated definitive evidence that organic surface films were involved in the "railroad track" signatures of turbulent ship wakes in remotely sensed optical imagery. Large freight ships produced the characteristic double convergence slick bands in an otherwise slick-free area of the Chesapeake Bay. The surface tension was measured across these turbulent wakes numerous times using the calibrated spreading oil technique (Adam, 1937; Zisman, 1941). Surface tensions within the slicked bands were 3-5 mN/m less than the tension value for the ambient "clean" surface. Between the convergence-generated slick bands behind the ship the surface tension was substantially the same as the ambient surface, since subsurface water is carried into the surface by the vortices generated by the ship's displacement hull. Thus, organic films are involved in highlighting ship wakes in sun-glint images from space and may also be implicated in outlining other events such as eddies, fronts, upwelling, etc.

The relationship between organic sea surface films and remotely sensed information on ocean dynamics is part of the rationale for the Marine Microlayer Processes Program. Consequently, aerial photography (35mm) was used to document visible surface film distributions in specific program experimental areas and to provide an overview of surface-chemical effects at the adjacent coastal and open ocean surface near the Damariscotta River mouth in Maine. Flights were made on May 8, 9, 11, and 13, and September 15 and 16, after consideration of existing meteorological conditions and the NOAA-weather prognosis. In both the May and September experiment periods there was a series of weak to moderate cold fronts which passed through the area every two



2. Ship of opportunity passing through a field of natural, organic, sea-surface films between the California coast and San Clemente Island. Features of the ship's turbulent wake are delineated by the slick field responses. Photograph taken on 27 FEB 1986 from an altitude of 1000 feet.

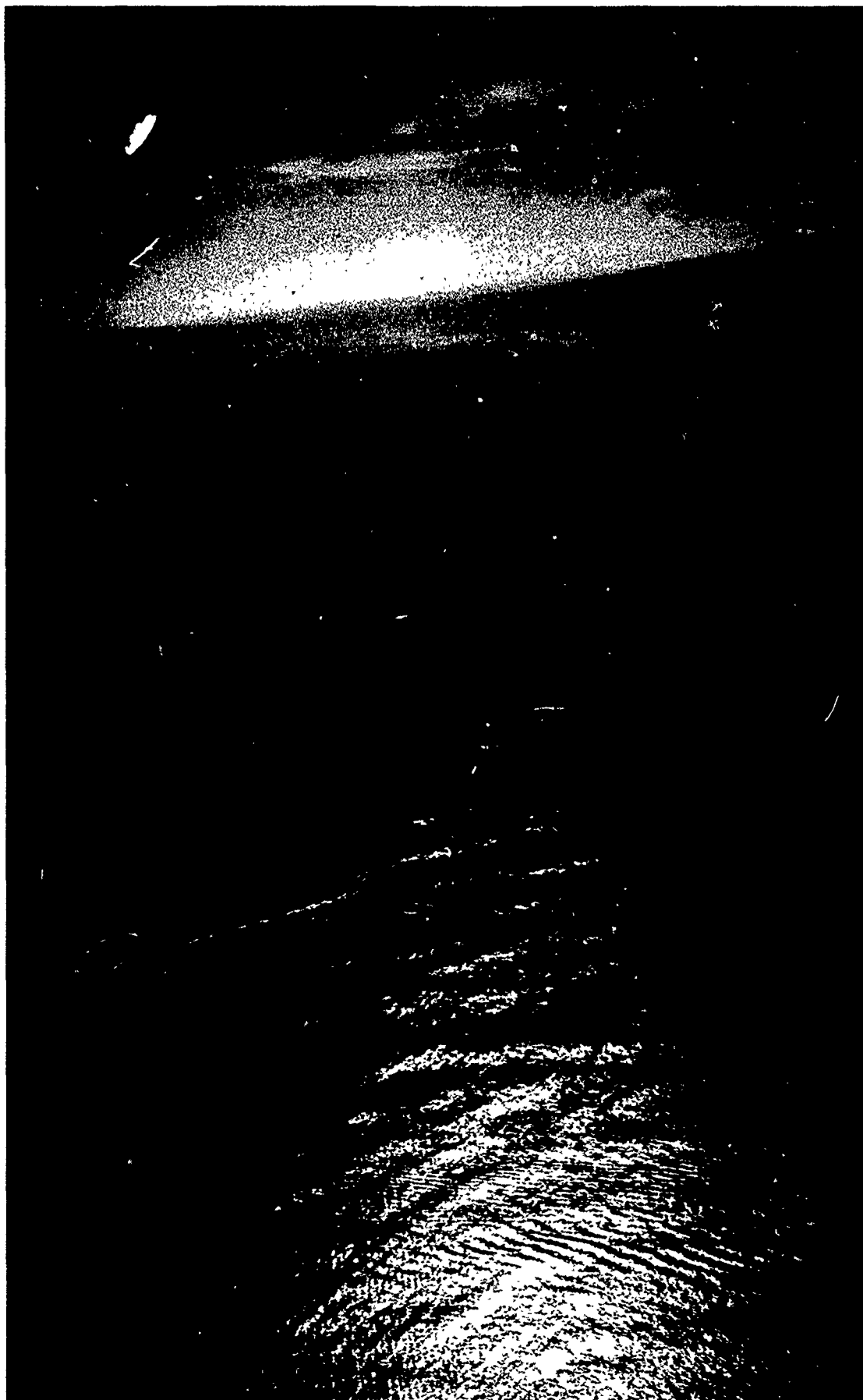
to four days. Episodes of extensive surface film coverage of the experiment area coincided with the relatively calm periods following frontal passage when the region was under the influence of high pressure within the cold air mass. On each flight day winds were light, 10 kts or less, and natural sea slicks were prevalent. On May 11 and Sept 15, surface films were widespread in all riverine, coastal and open-ocean zones and existed in numerous configurations, including small patches, large completely covered areas, and various types of elongated bands.

Although it did not appear that surface film manifestations of internal waves existed, the fields of organized films clearly highlighted physical processes such as wind-driven currents and boat wakes. On several occasions the sea surface was reminiscent of sun-glint photography taken from the 41-G shuttle mission, even though our photography was taken between 500 and 5000-foot altitudes in contrast to the shuttle altitude of 128 miles. There is a contrast between the appearances of slicks from shuttle and those from aircraft altitudes. Within the sun glint slicked or calm sea surface areas are more specular from shuttle, and appear brighter than more rippled water, whereas when aircraft observations were made into the sun's reflection, slicks were darker than the surrounding rippled water. In the latter case, elimination of the capillary waves allows less light to be scattered forward toward the observer. Outside of the sun glint slicked areas appear darker from shuttle and lighter from our aircraft altitudes when contrasted with the surrounding rippled sea surface. The sun glint and viewing angle tonal effects can be noted by comparing the shuttle photograph (figure 1) with figure 3, a photograph of slicks over the Atlantic Ocean, 4 mi south of the mouth of the Damariscotta river at 1106 on 11 May 1987. The aircraft altitude was 1000 feet and the view is toward the southeast.

NATURAL SLICKS: ORGANIC FILMS VS. PHYSICAL CAUSATION

Slick-like features on the sea surface are rendered visible because the capillary and short gravity wave spectra are less developed than the surrounding sea surface. As indicated in an earlier section, the slicks may appear as either a brighter or darker reflectance anomaly depending upon the observer's angle of view relative to the sun and to the sea surface. These relatively calmer areas may be due to natural biogenic organic surface films which attenuate and resist the formation of capillary waves, or they may be surface zones where the scatterers are diminished by surface turbulence/currents generated by physical processes such as wind slicks, turbulent ship wakes, internal waves, or current anomalies above subsurface topographic elevations.

In areas of calm, capillary ripples are absent and little wave-slope scattering of light or microwave radar results. In such quiescent cases, however, the surface tension is usually depressed, because surface-active organic molecules absorb readily at the air-sea interface to form films, and there are few processes acting to disturb the interfacial boundary. There are oceanic situations where physical modulations of Bragg and light scatterers may yield zones of tonal differences in SAR imagery and space-derived photographs. Scatterers may be influenced by local winds, currents, bottom topography, and also by unstable conditions of the atmosphere and the near surface water when the air is cold relative to that of the sea. These effects are manifested in remotely sensed imagery as outlines of bottom topographic features or as broad areas where the capillary waves have been modulated by physical processes. However, the slick-like filamentous patterns such as those in the sun-glint photographs which highlight spiral eddies and the turbulent wakes of surface vessels are due to biogenic organic films. Since no



3. Coastal Atlantic Ocean, 2 miles south of the mouth of the Damariscotta River, ME. Photograph taken at 11:54 on 15 SEP 1987 from an altitude of 1400 feet with view toward SE.

surface film measurements have as yet been obtained in conjunction with the space-derived imagery, it is essential to perform appropriate multidisciplinary remote sensing/sea truth experiments to ascertain the sea surface parameters which are responsible for the modulations of the capillary scatterers.

There have been several studies of these oceanographic processes which presumably create slick-like features through the physical modulation of the visible or microwave radar scatterers. Few of these experiments included the measurement of surface chemical effects in order to prove or discount the involvement of organic films in the observed effects. Valenzuela et al. (1983) attribute the sensing of bathymetric features by the L-band Seasat synthetic aperture radar (SAR) to hydrodynamic processes coupled to the bottom topography that modulate the amplitude of the short Bragg resonant waves, the main contributors to the power of the backscattered radar signal. The SAR imagery included surface manifestations of underwater shoals and sand ridges which were delineated by zones of calmer and rougher water.

X- and L-band SAR and photographic imagery of the surface manifestations of internal waves (IW) have been examined by Kasischke et al. 1984. They concluded that surface currents driven by zones of convergence and divergence above the internal waves produced areas of relatively rough and calm water which outlined the IW surface effects in the remote imagery. Surface chemical influences were not considered. On the other hand, Barger et al. (1974) measured the surface tensions of banded sea slicks associated with incoming internal waves in the coastal Pacific Ocean west of San Diego. In all instances, surface tensions in the slick bands caused by the IW convergences were less than tensions in the ambient nonslicked surface, indicating that organic films were involved in these visible slicks. It is important to learn whether organic films are a necessary ingredient in the remote detection and imagery of all internal waves. The definitive experiment has yet to be conducted.

Finally, there is one clear case where intense surface currents and turbulence produce calmer surface water without the involvement of organic films. On several occasions this investigator has measured the sea surface tension of the turbulent wake from the stern of ships under way. Although the waves in the turbulent wake behind the ship were intensely damped, there was no surface tension depression and no evidence of organic film involvement. However, in my experience all other in situ surface tension measurements made at sea indicated that organic films were responsible for the visible slicks measured.

In order to address the issue of organic film vs. physical causative factors responsible for slicks, surface tensions were measured of slicks and clean water during two transects of the Damariscotta River. These measurements were made several hundred yards behind the SCUMS surface sampler operated by D.J. Carlson, who also measured UV absorbance, temperature, and salinity. The surface tensions were measured using a set of calibrated spreading oils prepared by W.R. Barger, using a refinement of a method for the measurement of the tension of a dynamic water surface first described by Adam (1937). A series of 22 spreading oils were prepared and calibrated to ± 0.6 mN/m, so that surface tension could be determined in approximately 1 mN/m increments between 75 and 68 mN/m and every 2 to 4 mN/m for lower values of the surface tension. Calibration was performed on a hydrophil balance by the piston monolayer technique described by Zisman (1941).

Transects of the river were made on 10 and 14 September 1987 from Fort Island northward to Wentworth Point. Tables 1 and 2 list time, location, surface tension, and the visible condition of the water surface. The location symbol corresponds to the numbered grid on the chart of the Damariscotta River (fig. 4). Surface tensions are given to the nearest tenth of a mN/m when a spreading oil for that value was nearly at equilibrium with the water surface tension, i.e., alternating dilations and contractions of the surface due to passing waves caused the oil to oscillate between a spread film and unspread lens due to small surface tension variations. Otherwise the surface tension is given to the nearest mN/m based on the values assigned to the oils which bracket the spread-nonspread condition. A range of surface tension values represents more than one determination.

The surface tension of clean river water can be calculated from the following empirically derived expression. Surface Tension = $75.65 - 0.144T + 0.02215 S$, where T is in degrees C and Salinity (S) is in parts per thousand. Using an average water surface temperature of 15°C and average salinity of 31.5 ppt, the surface tension of the clean river surface was about 74.2 mN/m.

Surface tensions of highly rippled "clean" water (Tables 1,2) agreed closely with that calculated from the empirical equation. Occasionally, there was a condition where the surface contained some ripples, but shorter capillary waves (wavelengths less than 1 cm.) were absent. In this instance the surface tension was about 73 mN/m, suggesting that the concentration of film-forming material was near but below that for full slick formation, i.e., near the point in the film-pressure vs. area curve where the film compressibility is beginning to increase. Most slicks, whatever their size, were characterized by film pressures of 10 mN/m or greater. Intense slicks which were very flat in appearance and sometimes contained stabilized bubbles and foam had film pressures as high as 40 mN/m. In conclusion, the slicked zones were characterized by significant surface tension decreases caused by organic films. Between slicks the water surface was rippled with surface tensions near that calculated for clean water.

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TABLE 1
SURFACE TENSION MEASUREMENTS
DAMARISCOTTA RIVER TRANSECT: FORT ISLAND TO WENTWORTH POINT

10 SEPTEMBER 1987

<u>TIME</u>	<u>LOCATION</u>	<u>SURFACE TENSION</u>	<u>SURFACE CONDITION</u>
1259	1, WEST	73.0	INTENSE SLICK
1301	1, WEST	35-55	INTENSE SLICK, IN FOAM PATCHES
1312	4-5, CENTER	72.7	RIPPLED, NO SMALL CAPILLARIES
1314	4-5, CENTER	74.4	CLEAN, FULL RANGE OF CAPILLARY WAVES
1321	7, CENTER	52	OBVIOUS SLICKS, NO BUBBLES
1323	7, CENTER	74.4	CLEAN, FULL RANGE OF CAPILLARIES
1327	10, WEST	52	INTENSE SLICK BE- TWEEN CLEAN AREAS
1335	12, CENTER	34	INTENSE SLICK, SEA WEED
1342	14-15, CENTER	74.4	CLEAN, FULL RANGE OF CAPILLARIES
1344	15-16, CENTER	72.4	LIGHT, SMALL SLICK
1346	16, CENTER	35-39	SMALL INTENSE SLICK
1355	18, WEST	74.4	CLEAN, ALL CAPIL- LARIES

TABLE 2
SURFACE TENSION MEASUREMENTS
DAMARISCOTTA RIVER TRANSECTS: FORT ISLAND TO WENTWORTH POINT

14 SEPTEMBER 1987

<u>TIME</u>	<u>LOCATION</u>	<u>SURFACE TENSION</u>	<u>SURFACE CONDITION</u>
1235	1, WEST	74.4	CLEAN, ALL CAPILLARIES
1240	2, WEST	64-73	MEDIUM INTENSITY AND SIZE SLICK, TENSION DECREASED FROM DOWNWIND TO UPWIND
1243	3, WEST	56	SMALL SLICK
1247	3, WEST	73.5	RIPPLED, NO SMALL CAPILLARIES
1250	4-5, WEST	74.4	CLEAN, ALL CAPILLARIES
1255	6, WEST	74.0	RIPPLED, CLEAN
1301	8, WEST	74.0	RIPPLED, CLEAN
1308	10, WEST	54-64	SMALL SLICK
1314	11, WEST	50	SMALL, INTENSE SLICK
1317	11, WEST	74.0	RIPPLED SURFACE JUST OUTSIDE 1314 SLICK
1319	12-13, WEST	54	MEDIUM SIZED SLICK
1325	14, CENTER	74.4	CLEAN, ALL CAPILLARIES
1331	14-15, CENTER	54	ELONGATED SLICK ORIENTED APPROXIMATELY WITH WIND
1336	16, EAST	<33.6	INTENSE SMALL, SLICK, BUBBLES, SEAWEED

FIGURE TITLES

1. Shuttle mission 41-G sun-glnt photograph of western Mediteranean Sea showing slick highlighted eddies, ship wakes and current shear boundaries. Photograph taken 8 OCT 1984 at 13:12:57 GMT; altitude 125 nautical miles.
2. Ship of opportunity passing through a field of natural, organic, sea-surface films between the California coast and San Clemente Island. Features of the ship's turbulent wake are delineated by the slick field responses. Photograph taken on 27 FEB 1986 from an altitude of 1000 feet.
3. Coastal Atlantic Ocean, 2 miles south of the mouth of the Damariscotta River, ME. Photograph taken at 1154 on 15 SEP 1987 from an altitude of 1400 feet with view toward SE.
4. Chart of a portion of the Damariscotta River with numbered grid to identify surface tension measurement sites between Fort Island and Wentworth Point.

APPENDIX B

Modulation of the Spectra of Short Gravity Waves by Sea Surface Films: Slick Detection and Characterization with a Microwave Probe

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**Modulation of the Spectra of Short Gravity Waves by Sea Surface Films:
Slick Detection and Characterization with a Microwave Probe**

P. P. LOMBARDINI, B. FISCELLA, P. TRIVERO AND C. CAPPÀ

W. D. GARRETT

Modulation of the Spectra of Short Gravity Waves by Sea Surface Films: Slick Detection and Characterization with a Microwave Probe

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ABSTRACT

Organic sea surface films are often indicators of surface and subsurface processes that influence their formation and their spatial and temporal distribution. The films modify the physics of the sea surface and influence remotely sensed optical and microwave imagery.

Natural sea surface films have been detected, charted, and characterized by measurements of the short-gravity spectra of wind waves during three experimental periods, one in the Sicilian Channel, and two in the Gulf of Maine. Wind wave spectra with and without organic films were measured in situ with a microwave probe. These spectra were analyzed to characterize the elasticity moduli of the wave modulating films using a recently developed theory. Theory and experiment are in good agreement.

It has been demonstrated that the microwave probe can detect the presence of sea surface films and their visco-elastic properties by the measurement of their wave-modulating effects. The data collected by this system can possibly be further interpreted to deduce film weathering, concentration, and homogeneity.

1. Introduction

Sea surface phenomena influence both active and passive signals detected by remote sensing systems. For example, capillary and short-gravity-wave reflectance determines the backscattered EM characteristics of real and synthetic aperture radars. By modulating a wide range of air-sea interfacial parameters, organic surface films (slicks) are manifested in remotely sensed imagery (Garrett 1986). One of the most visible and sensible film-induced effects is the attenuation of capillary and short gravity waves.

The modulation of wave by organic films at the sea surface alters EM reflectance and renders the slicks detectable by both optical and microwave radar systems. This paper deals with the in-situ measurement of the spectra of short gravity waves with a microwave probe, with emphasis on the modulation of sea surface waves by organic slicks.

Natural sea slicks are composed of polar, organic, surface-active material adsorbed at the air-sea interface. These organic substances are usually present on natural water surfaces as monomolecular films. When the surface concentration of the surface-active material attains

a value of $\sim 1 \text{ mg m}^{-2}$, the resulting film becomes relatively incompressible, a thin layer of water at the air-sea interface is immobilized, and the sea surface can no longer be considered as "free." This occurs at low film tension of from 1 to 2 mN m^{-1} , and it is at this point that the film begins appreciably to modify physical processes at the air-sea interface (Garrett 1986).

The constituents of natural films are products of the marine biosphere and include lipids, proteins and carbohydrates (Williams et al. 1985). It should be noted that these three chemical classes accounted for only 40% of the total carbon in analyses of natural films, the remaining 60% being as yet uncharacterized. A slick contains constituents with varying degrees of water solubility. The insoluble substances are the most permanent residents of the air-sea interface. As the surface film ages, photocatalytic oxidation and surface compressions due to wave actions cause water soluble substances to be displaced from the sea surface. Consequently, an aged film should contain more water insoluble species.

The numerous effects of organic surface films on air-sea interfacial parameters and exchange processes have been reviewed by Garrett (1986). One of the most obvious and sensible film-induced effects is the attenuation of capillary and short gravity waves. This paper deals with the modulation of the spectra of these waves

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by sea surface films as measured with a microwave probe.

Theoretical considerations and experiments (Cini et al. 1983; Loglio et al. 1986; Lombardini 1986) have shown that, for pure film components, dilational and rheological properties of adsorbed films can be inferred from the thermodynamic surface parameters of said surfaces. In this research we use the method of measuring in-situ damping of short-gravity waves to determine the rheological properties of sea surface films.

2. Maximum of damping ratio in presence of films

The theory of rheology of water-air interfaces predicts a maximum in the frequency response of the ratio of the damping coefficient of waves on a pure water surface to that for a water covered by a monolayer

(Cini and Lombardini 1978). This maximum occurs in the 2–10 Hz band, and may be interpreted in terms of coupling of Marangoni and Laplace waves (Cini et al. 1987). In particular, we have extended the concept of tensio-elasticity developed by Lucassen Reynders and Lucassen (1969) and we have obtained complex solutions of the characteristic equation of Levich (1962) derived from Navier-Stokes equation for the case of small ripples at the air-water interface in presence of both soluble and insoluble films.

The analytical form which describes the ratio between real parts of the complex radian frequencies on a pure water to that for a water covered by slick (damping ratio) is given by:

$$\gamma(f) = \frac{1 \pm 2\tau + 2\tau^2 - X + Y(X + \tau)}{1 \pm 2\tau + 2\tau^2 - 2X + 2X^2}, \quad (1)$$

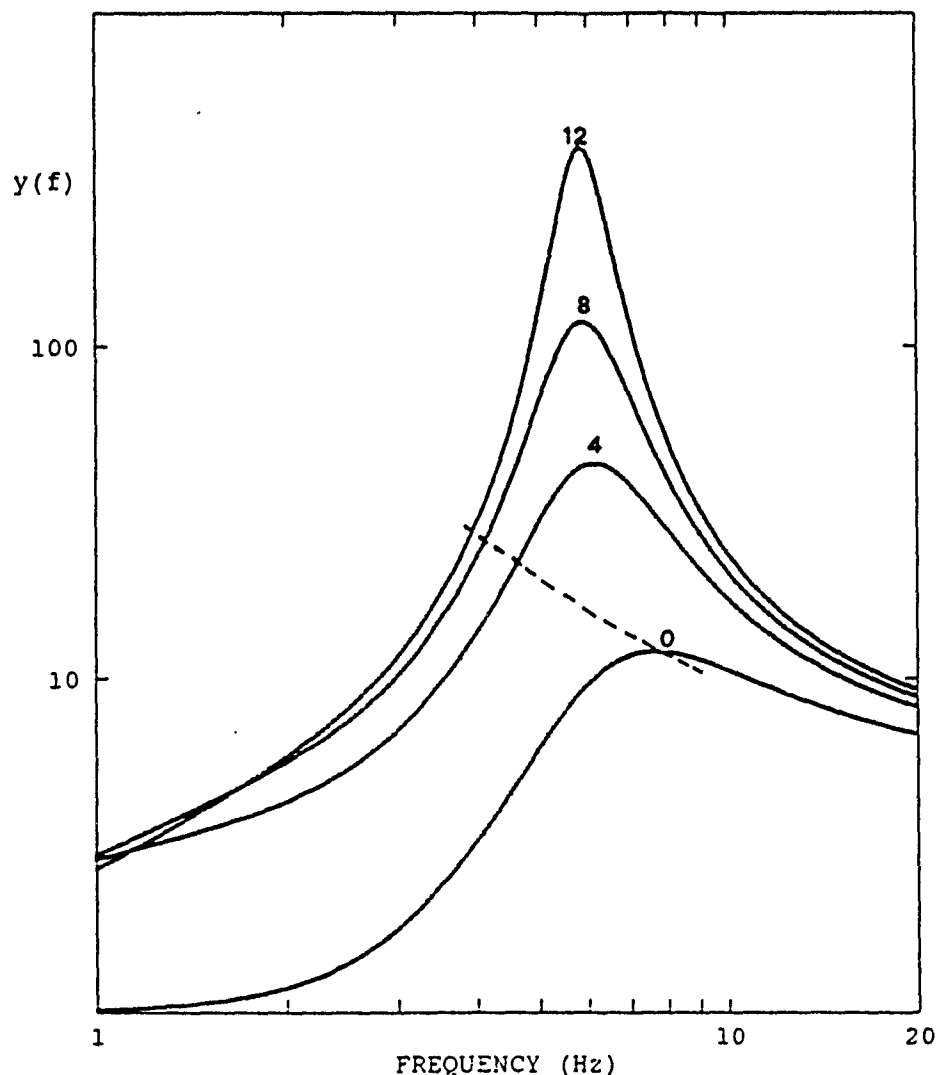


FIG. 1. Frequency dependence of damping ratio for constant $\epsilon_0 = 10 \text{ mN m}^{-1}$ and different values of $\omega_D = 2, 8, 4, 0 \text{ rad s}^{-1}$. The dashed line marks a segment of the locus of maxima for $\omega_D = 0 \text{ rad s}^{-1}$, and $8 \text{ mN m}^{-1} < \epsilon_0 < 42 \text{ mN m}^{-1}$.

where:

$$\tau = (\omega_D / 2\omega)^{1/2}, \quad X' = \frac{\epsilon_0 k^2}{(2\eta\omega^3)^{1/2}}, \quad Y' = \frac{\epsilon_0 k}{4\eta\rho\omega}$$

are adimensional quantities and

$$f = \omega / 2\pi = (\sigma k^3 / \rho + gk)^{1/2} / 2\pi$$

the dispersion law, σ surface tension, ρ water density, g acceleration of gravity, k wavenumber, η kinematic viscosity; furthermore, the constant characteristic parameters of the film used are: elasticity modulus $\epsilon_0 = d\sigma/d(\ln\Gamma)$ where Γ is the surface concentration, and characteristic frequency ω_D which, for soluble films, depends upon the diffusional relaxation, and for insoluble films, depends upon structural relaxation between intermolecular forces. In (1) a plus sign refers to soluble films, while a minus sign indicates insoluble films. Cini et al. (1987) reports a complete account of the distinction between soluble and insoluble films.

Graphically, for each choice of the parameters ϵ_0 and ω_D the damping ratio $y(f)$ plots versus frequency as a cuspidate curve. The frequency where the peak occurs is essentially controlled by the value of the elasticity modulus ϵ_0 , while the height of the peak is determined by ω_D .

In Fig. 1 we display four cases for which $\epsilon_0 = 10 \text{ mN m}^{-1}$ and $\omega_D = 12, 8, 4, 0 \text{ rad s}^{-1}$. The dashed line

marks the condition $\omega_D = 0 \text{ rad s}^{-1}$, and $8 < \epsilon_0 < 42 \text{ mN m}^{-1}$. Insoluble films have their maxima above that line, soluble films have their maxima just below that line. A measurement of the pattern $y(f)$ may describe the solubility characteristics of the film.

3. Spectra of wind waves in presence of films

The spectra of wind waves have been extensively studied (Pierson and Stacy 1973; Fung and Lee 1982; Durden and Vesecky 1985). Recently, Donelan and Pierson (1987) have published a comprehensive account of the subject.

In our experiments we have limited ourselves to winds having intensities between wave threshold and breaking speeds, since it is in this region that natural slicks persist long enough for study. Parameterized spectra have been taken as the reference for "clean water". Later we will show that in the slick-free cases observed spectra are in good coincidence with the reference spectra. When a film is present the spectrum observed exhibits a depression in the 2–10 Hz region. In the domain of short gravity waves, the dissipative portion of the spectrum of the clean water, $S_c(f)$, is mainly due to the viscous loss.

Clearly, considering areas small in terms of wind energy exchange and duration small in terms of cross spectral transfer time, the spectrum of slicky water,

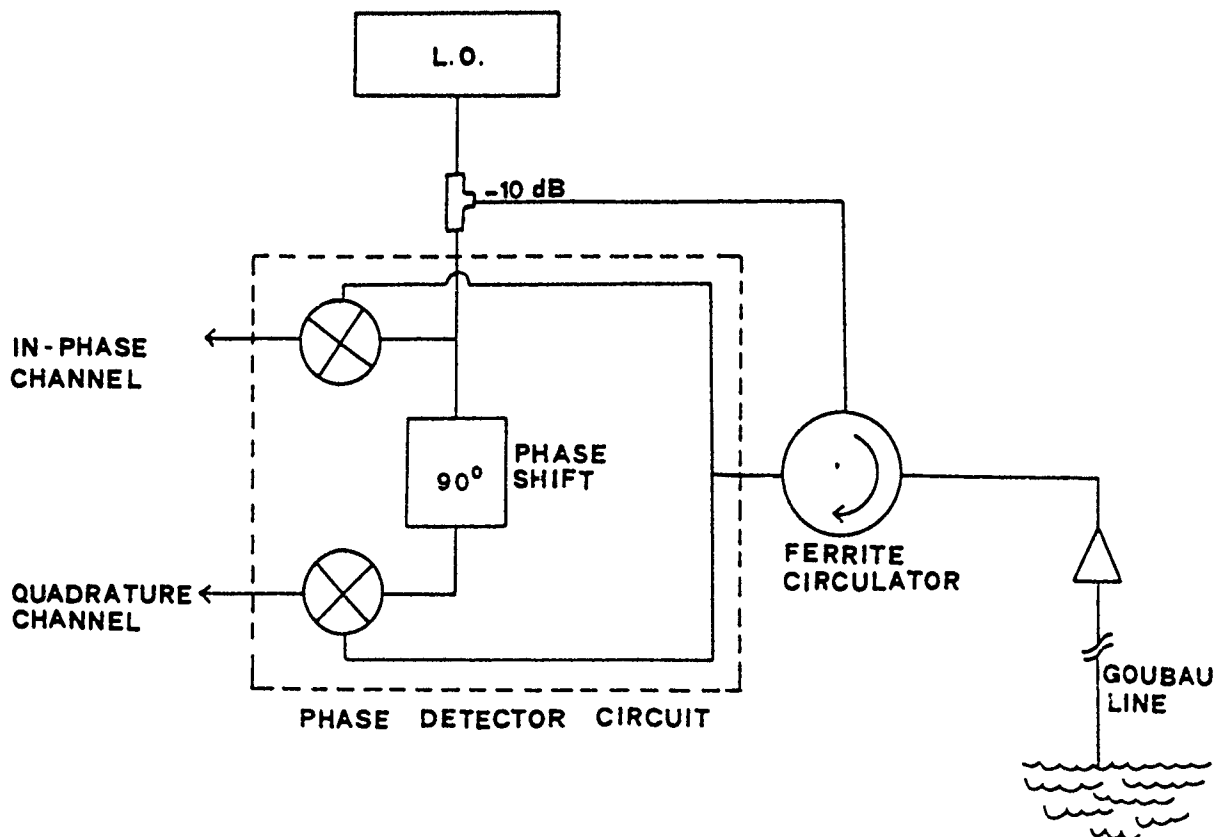


FIG. 2. Block diagram of the Goubau line.

$S_d(f)$, is related to the clean water spectrum by the damping ratio

$$y_s(f) = S_c(f)/S_d(f). \quad (2)$$

In general the damping ratio $y_s(f)$ should not be directly interpreted as corresponding to (1). It would be so if the film was uniformly distributed over the surface. During the time of measurement, however, the film may be partially dispersed by wind and waves, so that the surface investigated results only partially covered by the film. In this case we shall introduce (Lombardini 1986) a fractional filling factor, F , i.e., the ratio of the area covered by film with respect to the

total area considered, and write for the damping ratio (2) the expression

$$y_s(f) = \frac{1}{1 - F + F/y(f)}, \quad (3)$$

where $y(f)$ is given by expression (1).

4. Instrumentation

Wind spectra have been measured with a microwave probe which measures wave heights on an absolute, self-calibrating scale (Fiscella et al. 1982). The basic concept of this probe is a teflon coated wire. The lower

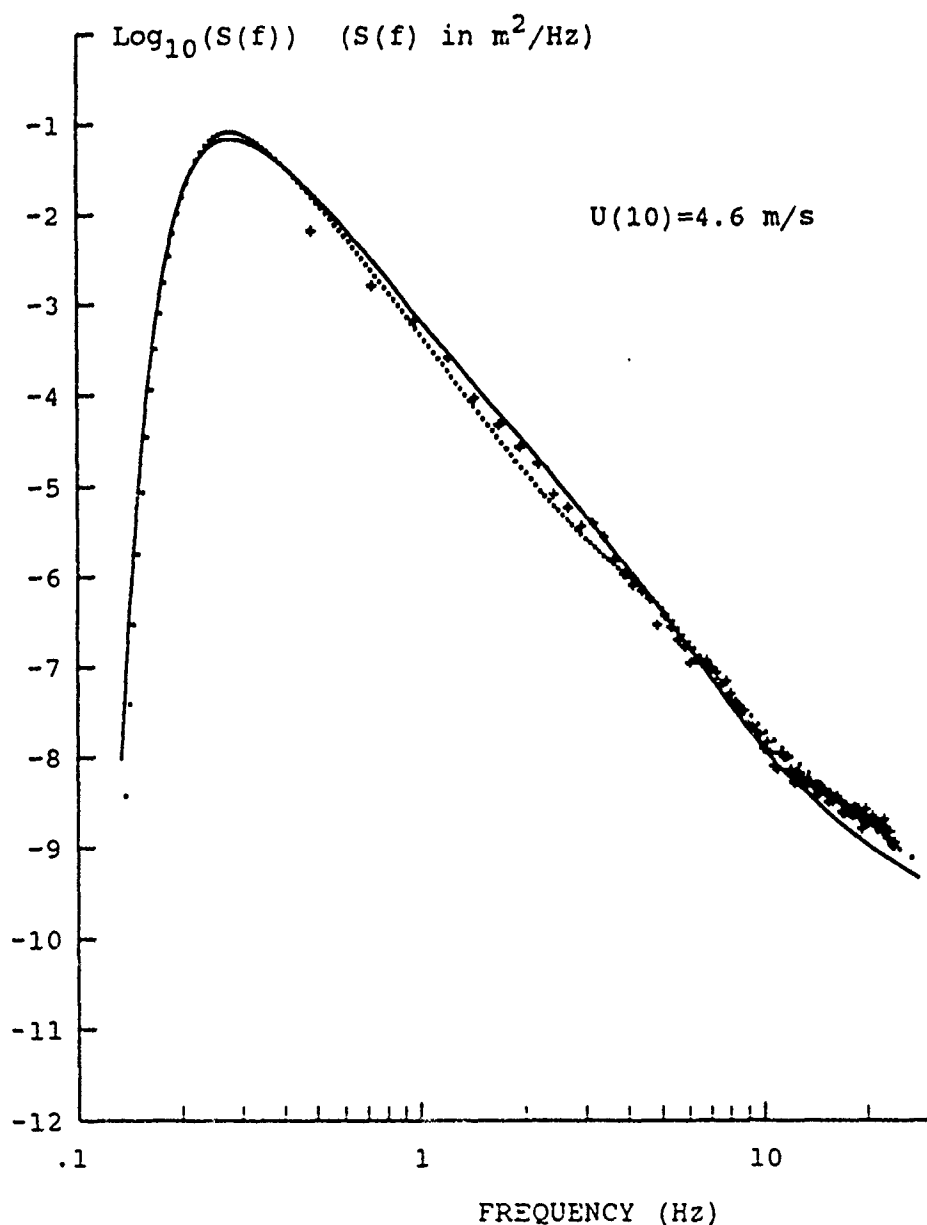


FIG. 3. Data observed in absence of slicks (crosses) and the parameterized spectra calculated for the wind speed of observation (solid line: Donelan and Pierson 1987; dotted line: Pierson and Stary 1973).

end of this wire is held straight vertical and dipped in water, while the other end is fed by a microwave source. The microwave energy travels downward, confined to a close proximity of the coated wire (Goubau line). The contact with the water acts as a short circuit, giving origin to a reflected wave. In condition of good matching of the microwave system the field in the transmission line has a standing wave pattern which is uniquely determined by the location of the water contact with the coated wire.

The apparatus employed in our measurements is an improved version of that described by Fiscella et al.

(1982). The adopted circuit, shown in Fig. 2, includes the microwave source (10 mW, 10 GHz Gunn oscillator), which feeds the Goubau line via a 10 dB directional coupler and a ferrite circulator. A standard phase detector circuit (dashed box in the figure), composed by a ring hybrid and a 90° coupler, is used. The outputs of the two mixers are low-pass filtered (bandwidth 110 Hz) and are sine voltages in quadrature, namely V'_x and V'_y . Displayed on an $x - y$ scope, they will give origin to a point moving on a circle and having a phase:

$$\Phi = n\pi + \arctan(V'_y/V'_x). \quad (4)$$

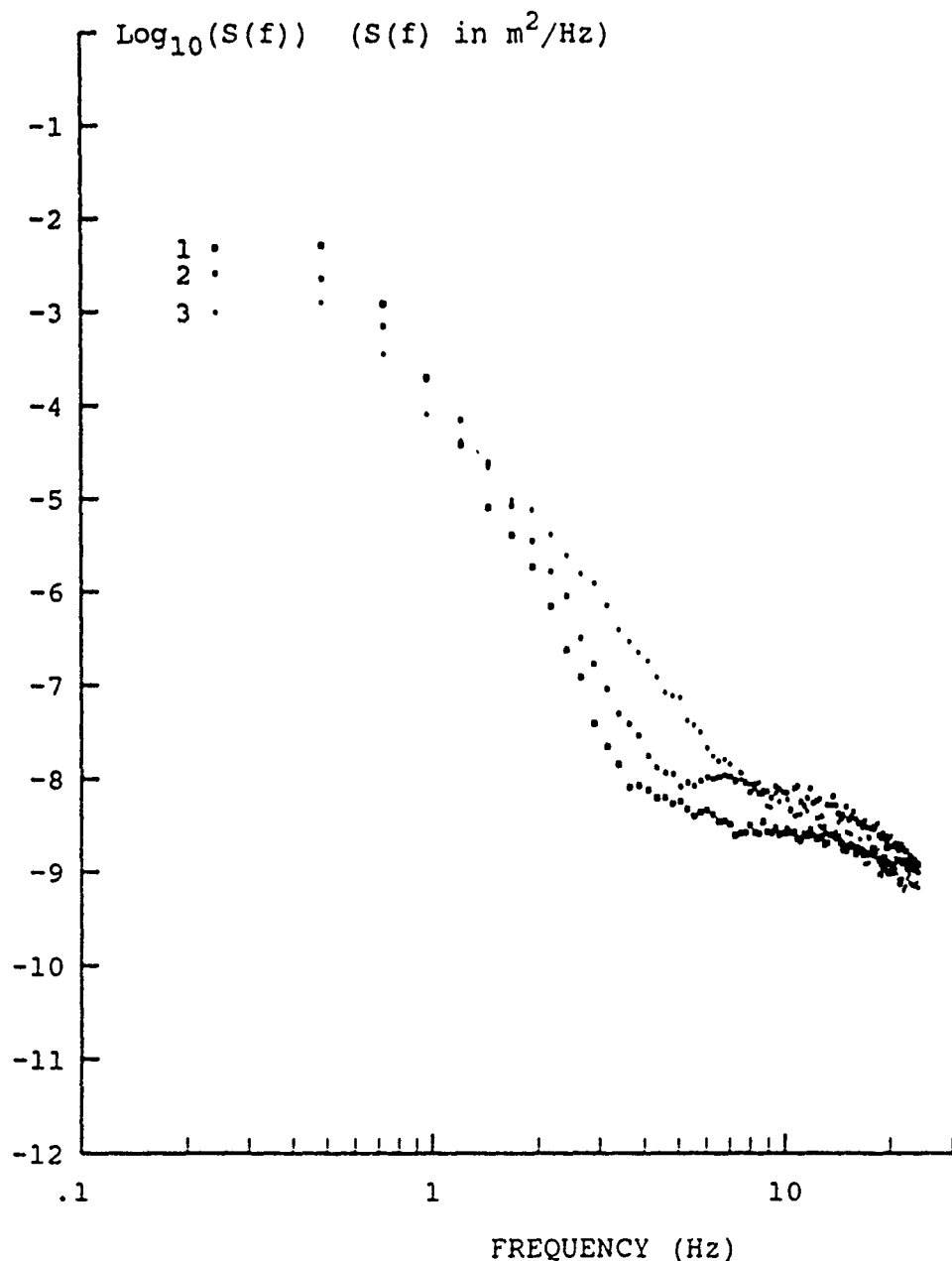


FIG. 4. Spectra measured in Maine in presence of film: cases (1), (2) and (3) described in the text.

Changes in height of the water surface correspond to changes in phase angle. The relationship between phase Φ and water height z is given by the formula

$$\Phi = 4\pi z / \lambda, \quad (5)$$

where λ is the radio wavelength.

Two amplifiers provide independent amplification, and zero offset of the output signals V_x and V_y , so both channels have same amplitude and zero mean value. During the acquisition the phase is updated adding $\pm\pi$, as V_y undergoes a zero crossing. Each datum consists of V_x , V_y and n ; storage is made every 50 data acquisitions in three 2-byte locations. Data reduction starts by data decoding according to formulas (4) and (5). Power spectra are obtained by data segmentation, Hanning windowing, FFT operation and subsequent power spectra meaning. Typically, 10^4 data are gathered with an acquisition time of 161 s, but sampling of

V_x , V_y , and phase updating are accomplished at a rate 50 times higher.

In a Goubau line with a copper wire radius of 0.6 mm and coating thickness of 0.3 mm, (assumed relative dielectric constant $\epsilon_r = 2.1$), the radius of the area in which 50% of the propagated power is concentrated is: $\rho_0 = 2.4$ mm. This area includes the meniscus (for clean water) and implies a Voltage Standing Wave Ratio ≥ 2 . In this case the liquid wavelength $4\rho_0$, i.e., 26 Hz, may be considered the upper frequency limit of the probe (Fiscella et al. 1982).

It has been found that within this maximum the contact angle hysteresis of teflon does not limit perceptibly the high frequency response of the device, as long as the coating is kept clean. The measurement of z can thus be accomplished with an accuracy of the order of few micrometers. Under favorable conditions the accuracy was proved to be $\pm 3 \mu\text{m}$.

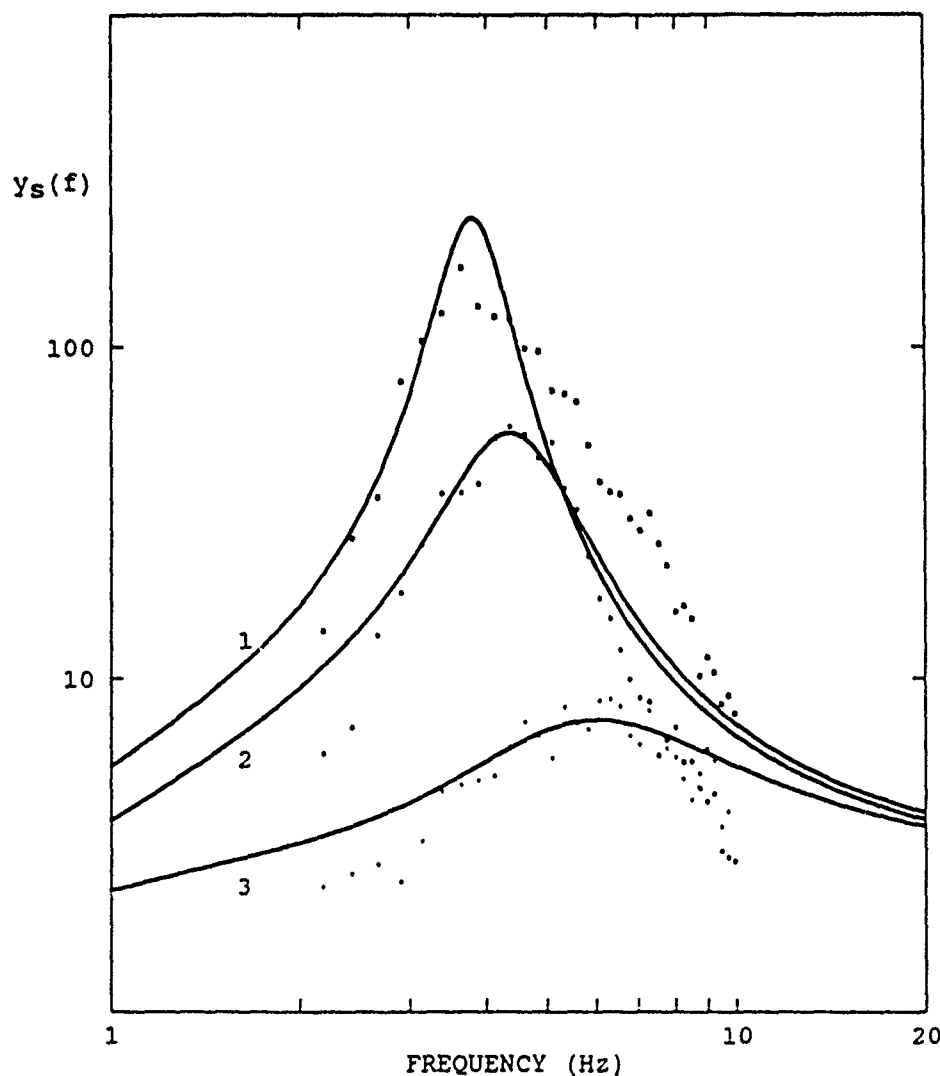


FIG. 5. Measured damping ratios for cases (1), (2) and (3) the same of Fig. 4. The continuous lines are best-fit curves according to formula (3).

TABLE 1. Parameter specifications

Case	ϵ_0 (mN m ⁻¹)	ω_D (rad s ⁻¹)	F (%)
1	25.0	11.0	99.6
2	18.0	13.0	98.2
3	9.0	6.0	88.0

5. Measurements of natural microlayers

Natural sea surface films have been measured in the Sicilian Channel and in the Gulf of Maine. During the Sicilian Channel experiment, the Goubau probe was mounted on a rotating riser fixed to the sea floor at a depth of 96 m. This riser was the mooring point of the tanker "Agip-Milano" belonging to the Italian Oil Company Agip. The ship, fastened to the riser and

could rotate with wind and current. The ship was equipped with a set of meteorological instruments capable of measuring the wind vector at two heights, 16 m and 28 m, respectively.

The test site (latitude 37°31'.2 N, 11°53'.6 E) is about 60 km away from the nearest coast of Sicily. The adjacent coast is barren and scantily inhabited. Sixty observations have been performed from 22–28 June 1986.

During the Maine experiments, the data were collected offshore of the Damariscotta River in sites free from contamination by shipping, but rich in natural organic material from forest and marine sources. At this location the average tide excursion is about 4.5 m.

The Goubau probe was installed on the bow of R/L Lee, Darling Center, University of Maine, a 35-foot-long vessel, and linked to a personal computer for the on-board acquisition, processing and recording of observed data. The methodology of observation was to

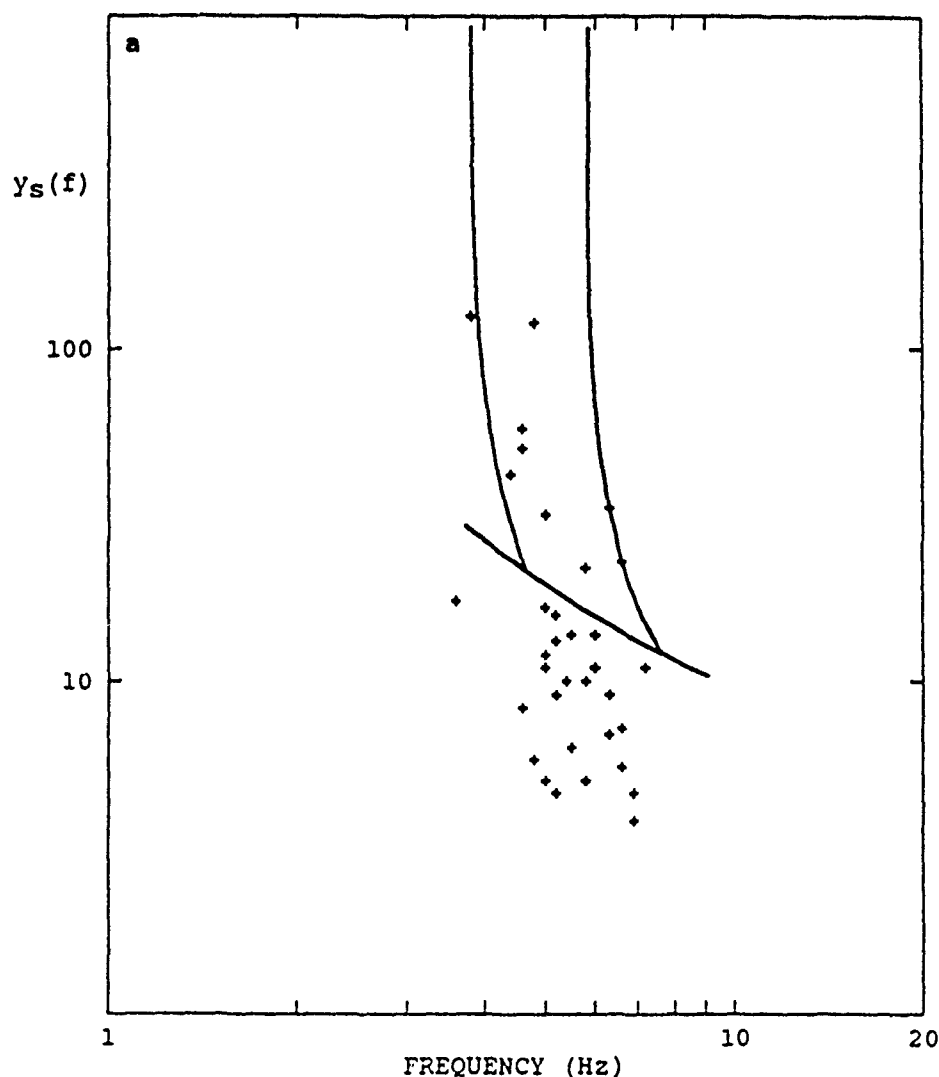


FIG. 6. Maxima of damping ratios (+) observed in Maine: (a) May. (b) September. Vertical lines indicate from left to right $\epsilon_0 = 25$ and $\epsilon_0 = 10$ mN m⁻¹. Horizontal line marks $\omega_D = 0$ rad s⁻¹.

identify optically a slicky spot, sail the boat in the center of that spot, cut the boat's engine, start the data acquisition being sure that the probe remains in the spot throughout the acquisition time, measure the local wind strength with a portable anemometer. During 18 days (5-14 May 1987) (10-17 September 1987) 83 observations were performed.

6. Analysis of data

The 143 observations in the three campaigns were performed following a common technique:

- measurement of wind speed at a given height;
- measurements of air and sea surface temperatures;
- reduction of the wind speed at 10 m height;
- calculation of the parameterized spectrum of clean water in the frequency domain, $S_c(f)$, relative to the measured wind speed;

- measurement of the sea spectrum, $S_d(f)$, by means of the Goubau line.

The analysis of the data started with the computation of the ratio: $y_s(f) = S_c(f)/S_d(f)$ obtained with a computer program. Clean water condition corresponds to $y_s = 1$: i.e., absence of film. In the Sicilian Campaign 85% of cases revealed clean water. Figure 3 shows data observed in absence of slicks (crosses) and the parameterized spectra calculated for the wind speed of observation (solid line: Donelan and Pierson 1987; dotted line: Pierson and Stacy 1973).

The two formulas are in good agreement with our spectra in the region of interest. On the basis of Fig. 3, we use parameterized spectra as reference of "clean water" in our computations.

Frequencies below 1 Hz, which may include rolling and pitching of the boat, have not been considered in our studies. In the presence of a surface film, the ex-

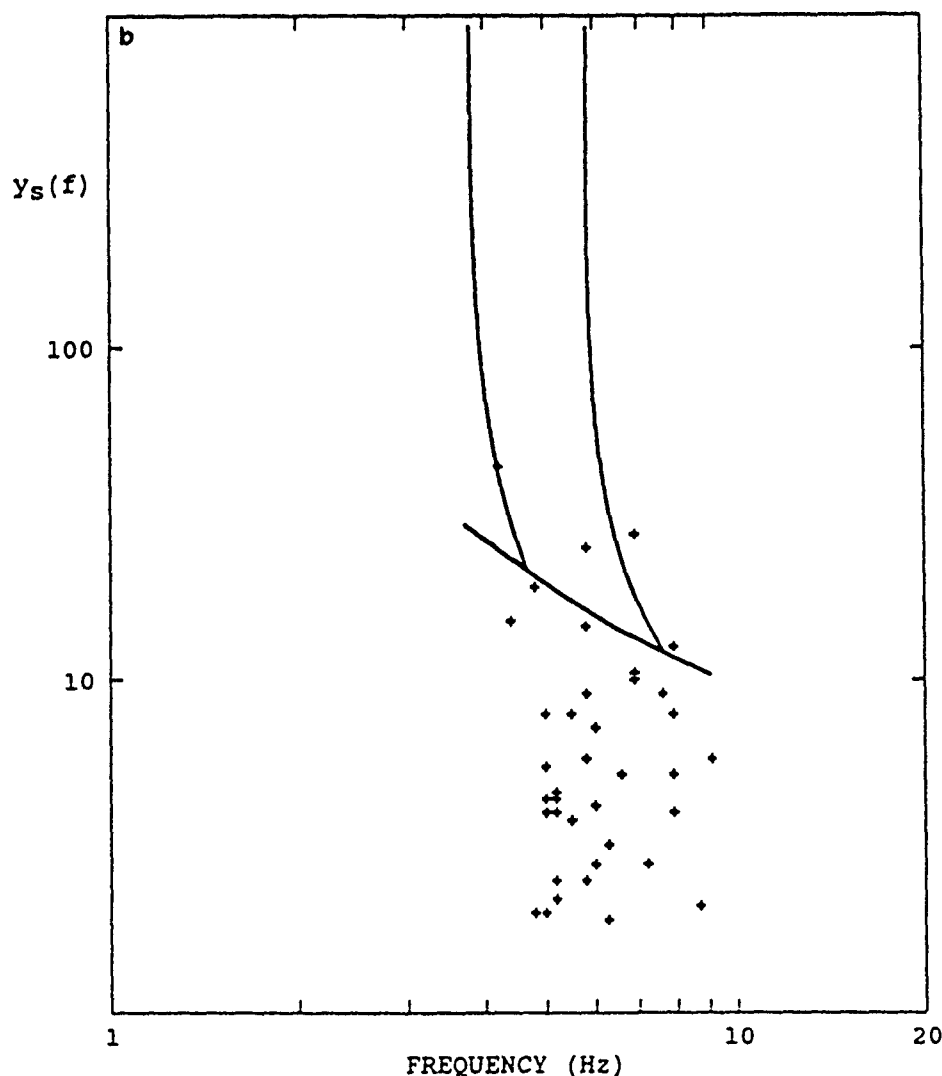


FIG. 6. (Continued)

perimental ratio γ_s is plotted in the frequency domain by a curve which presents a region of maximum. In Fig. 4 are shown the spectra measured for three typical cases: the corresponding $\gamma_s(f)$ are displayed in Fig. 5. For each of the clusters of data presented in Fig. 5, a theoretical curve is drawn according to expression (3), with a proper choice of the parameters ϵ_0 , ω_D and F . This choice is based upon a best-fit method applied mainly in the region of maximum. For the three cases, the parameters obtained by this methodology are presented in Table 1.

The 72 sea surface observations of slicks performed in Maine are displayed in Fig. 6a and 6b corresponding to measurements made in May and September, respectively. In the figures, the abscissae are the frequencies f_M of the damping maxima, and the ordinates are the values of maxima, $\gamma_s(f_M)$, while each cross denotes one observation. The two running vertical lines indicate loci of constant ϵ_0 (25 and 10 mN m⁻¹), while the quasi-horizontal line marks the condition $\omega_D = 0$.

Both Fig. 6a and 6b show films having elasticity moduli in the same bounded domain, suggesting that the films measured in both May and September contain a limited number of prevailing substances with similar solubility characteristics. In the May data (Fig. 6a) 26% of the points lie above the $\omega_D = 0$ line, implying films whose constituents are essentially water insoluble. The fact that in September (Fig. 6b) 90% of the data lie below that line, suggests that in May the average of the measured films were more weathered, and as a result contained less water-soluble species. This result may be explained by considering that in September the wind was higher and the wave-spectral probing was performed further from shore, conditions conducive to less persistent, less aged films which have not had the opportunity to lose their more soluble constituents.

7. Concluding remarks

The three experimental campaigns have demonstrated that natural organic surface films on the sea can be detected, charted and their dilational properties characterized by measurements of short-gravity spectra of wind waves.

A complete interpretation of the information gathered in order to deduce aging, concentration, homogeneity and chemical constitution of films requires further studies both in-situ and in the laboratory. The intrinsic merit of this method consists in measuring an

attenuation of waves which depends solely upon the visco-elastic characteristics of the sea surface.

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APPENDIX C

Additive Sea Surface Films

Compilation of Information in Maturity and Methods

Prepared in the Marine Microlayer Processes Program for the High
Resolution Remote Sensing ARI

ADDITIVE SEA SURFACE FILMS

for

**OFFICE OF NAVAL RESEARCH ARI
HIGH RESOLUTION REMOTE SENSING**

**Compilation of Information on
Materials and Methods**

Prepared By

**WILLIAM D. GARRETT
ORINCON CORPORATION**

March, 1991



ADDITIVE MONOMOLECULAR FILMS AS INDICATORS OF SEA SURFACE AND UNDERWATER PROCESSES

It is possible to generate artificial organic films on the sea surface or to introduce sub-critical levels of film-forming substances to act as remotely sensible indicators of surface and underwater oceanic processes. This approach is especially valuable when the sea surface concentration of natural film-forming materials is low and no natural sea slicks exist, or when air-sea dynamics preclude the existence of natural films. Certain additive surface films have been shown to be persistent and readily detectable in winds as great as 10 meters per second. Relevant publications and supporting graphics are included in this document. Such films can be used to determine currents across shear boundaries, surface flow (a resultant of wind drift and current vectors), and as an approximate model to mimic natural films for research purposes.

Sub-critical concentrations (less than approximately 1 mg per square meter) are levels of film-forming material below which no coherent film will form. At these low surface concentration levels remotely sensible air-sea interfacial processes are not altered. However, if the sea surface has been seeded with surface-active organic material to levels just below that where a detectable film will form,

convergences due to Langmuir circulation, internal waves, upwellings etc., could increase the surface concentration of the additive surfactant to a point where a sensible sea surface film would result. The quantities of surface-active material required to seed the sea surface are readily calculated from hydrophil balance data (film pressure or wave damping vs film area curves). Air and ship dispensing procedures are available, and there are potential controlled-release techniques which can be developed for the production of a controlled surface concentration of indicator-film material.

Applications of additive surface films at various surface concentration levels are summarized in the accompanying graphics. When natural films do not exist, the artificial slicks may be used to (1) highlight sea surface processes, (2) simulate surface film effects for studies of film influences on remotely sensed imagery, and (3) indicate surface manifestations of underwater processes. All active and passive remotely sensed signals are influenced by sea surface films. The processes modified by the films affect the sensor signal. The character of the film-effect/sensor-response relationship is determined by the sensor type and spectral range. Consequently, additive indicator films have application to a broad range of sensors, including SAR, RAR, thermal IR, and microwave radiometry [Garrett and Barger, 1980].

SELECTION CRITERIA FOR SEA-SURFACE FILM-FORMING MATERIAL

Criteria for the selection of materials for the generation of a sea surface film depends upon the particular Naval or civilian application involved. Considerations include:

1. desired film persistence
2. interfacial parameters to be modified; e.g. capillary waves, surface bubble and foam stability, surface temperature, etc.
3. optimum film geometries
4. deployment requirements
5. environmental conditions in area of application; winds, sea state, air-sea stability, sea temperature, etc.

Once these requirements have been identified, film-forming substances can be selected on the basis of a suite of chemical and physical properties which will satisfy the particular application. The properties of both the bulk chemical and its spread film must be considered. The physical and chemical properties are determined by the structural and chemical characteristics of the film-forming molecule, its chemical functional groups, and even its geometric shape.

Film-forming agents are surface-active, composed of polar organic molecules which adsorb at a phase boundary, reduce its surface free energy, and modify its viscoelastic properties. Oceanic phase boundaries of interest include the air-sea interface, the air-water interfaces of air bubbles and foam at the sea surface, and the surfaces of bubbles and particulate matter in the bulk ocean. Within

the chemical industry there are thousands of off-the-shelf surface-active chemicals exhibiting a broad range of physicochemical properties. Many of these can be used to form spread or adsorbed films at interfaces in the marine environment.

SELECTION CRITERIA FOR A REMOTE SENSING STUDY

An example of criteria for selection of a persistent and continuous sea surface film are described in the enclosed publications [Garrett and Barger, 1980; Hühnerfuss and Garrett, 1981]. Simulated sea slicks were utilized in the MARSEN (Marine Remote Sensing) Experiment to demonstrate slick effects on both active and passive remote sensors. Table 1 lists property requirements for both the film-forming agent and its spread film.

Table 1

PROPERTIES REQUIRED FOR THE PRODUCTION OF SIMULATED SEA SLICKS IN THE MARSEN EXPERIMENT
MONOMOLECULAR - SMALL QUANTITIES COVER LARGE AREA AUTOPHOBIC - FILM IN EQUILIBRIUM WITH BULK LIQUID STRONG SURFACE EFFECTS - SIGNIFICANT WAVE ATTENUATION - RESISTS WAVE FORMATION - IMMOBILIZES SEA SURFACE NONVOLATILE - LOW EVAPORATIVE LOSS RATE NONIONIC - LITTLE REACTION WITH SALINE WATER LOW SOLUBILITY - FILM PERSISTENCE FLUID FILM - RAPID, SPONTANEOUS SPREADING - HIGH RESPREADING POTENTIAL LOW FREEZING PT. - EFFECTIVE FLUID FILM IN COLD SEAS NONTXIC - ECOLOGICALLY ACCEPTABLE

To achieve this suite of properties it is necessary to consider the molecular constitution of the film-forming material and its relation to the physicochemical properties of the agent and its spread film. The molecule of the slick-forming material should contain 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 surface pressure. The agent 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 16-18 carbon atoms or more, so that losses from the slick due to evaporation and dissolution will be small. A nonionic, film-forming chemical is required for use on sea water to obviate reaction with ionic species which would increase film solubility.

Compounds of the type described in this section, if relatively pure, spread spontaneously across the sea surface into monomolecular films. Because there are losses from the film due to peripheral spreading at the slick edges and dispersion of the film material out of the surface by air-sea dynamics, an excess of film-forming material is dispensed to replace lost film and maintain its lifetime. These film-forming chemicals possess a property called

"autophobicity", i.e. the excess liquid does not spread over its own monomolecular film, but remains on the surface as bulk droplets in equilibrium with the film. Thus, the excess droplets represent a reservoir of material to spread and replace losses of the additive film caused by environmental dispersive processes. Since the film spreading process occurs at the sea surface, it is also essential that the film-forming liquid have a specific gravity that is less than that of seawater. It must remain at the sea surface in equilibrium with its film.

Molecular geometry plays an important role in the selection process. It is desirable to disperse fluids and to produce films that are fluid in character. Film-forming materials which are fluid at room temperature and the surface films which they produce have rapid spontaneous spreading. In addition, the films have a high respreading potential into surface areas where the film has been displaced by air-sea interfacial disturbances. It should be noted that the spreading of solid surface-active substances is orders of magnitude slower than for liquid agents.

A nonlinear or bent molecular structure leads to a fluid condition, both in the bulk material and in the spread film. Linear molecules have strong intermolecular forces, are more solid in character for a particular molecular weight, produce films that are slow to spread, and do not respond

readily to surface perturbations. This problem is overcome by selecting molecules with hydrocarbon chains which are permanently bent or are branched, a condition which prevents the close packing of the hydrocarbon chains in the spread film and allows for fluidity. Alkyl groups which interfere with hydrocarbon chain adlineation include those with a point of chemical unsaturation (cis geometric isomers) yielding a permanently bent chain (e.g. oleyl alcohol), or those with chain branching such as is found in isostearyl alcohol. A relatively new product line of commercially available beta-branched alkanols has become available. These liquids have freezing points well below that of seawater, and may have potential utility in oceanographic programs and applications. However, at present there is little at-sea experience with this class of compounds.

Two liquids were selected to meet the surface film requirements of the MARSEN Experiment, oleyl alcohol (9-octadecen-1-ol, cis isomer) and methyl oleate, the methyl ester of oleic acid. The former is a highly surface-active material which was selected because of its intense damping of microwave scatterers. The methyl oleate has a moderate spreading pressure of 15 mN/m, and was studied because its film pressure was lower and more like that of natural slicks. Butyl stearate (octadecanoic acid, n-butyl ester), with a film pressure of approximately 11 mN/m may, be an even more realistic simulant for natural slicks. However,

little information is available on its surface chemistry, and experience in spreading it as a film onto the sea is essential before it can be recommended

This report addresses the use of additive organic films in remote sensing exercises such as MARSEN and HIGH RES ONE, where persistent film are desired. There are several other Navy applications for intentionally added organic films at sea which require a different set of properties (foam destabilization, short persistence, etc.) These applications are noted in the presentation graphic entitled "Marine Applications of Artificial Slicks". A discussion of the selection criteria applicable to these other applications will be detailed in future reports to appropriate agencies.

HIGH RES REMOTE SENSING ADDITIVE ORGANIC SURFACE FILMS

WHEN NATURAL FILMS ARE NOT ABUNDANT

- (1) DEPLOYED AS VISIBLE SLICKS IN VARIOUS GEOMETRIES
- (2) FILM CONSTITUENTS DISPENSED IN SUB-CRITICAL CONCENTRATIONS

TO ELUCIDATE:

SURFACE FLOW
CONVERGENCE PATTERNS
FILM INFLUENCE ON REMOTELY SENSIBLE SEA
SURFACE PARAMETERS

MARINE APPLICATIONS OF ARTIFICIAL SLICKS

SEA SURFACE MODIFYING ORGANIC FILMS

- SURFACE FILM INVOLVEMENT IN REMOTELY SENSED IMAGERY
 - ATTENUATION OF RADAR/VISUAL SURFACE SCATTERERS
 - SUPPRESSION OF WHITE WATER
 - SEA SURFACE TEMPERATURE EFFECTS
- INDICATOR OF SURFACE FLOW
- RADAR/VISUAL DETECTABLE SEAMARKER (SEARCH/RESCUE)
- MODIFICATION OF ENTRAINED AIR BUBBLE DISTRIBUTIONS
- SUPPRESSION OF AMBIENT SEA-SURFACE NOISE SOURCES
- OIL SPILL CONTROL
- PERISCOPE WAKE SUPPRESSION

SEA SLICK SIMULATION

AUTOPHOBIC ORGANIC FILMS

- OLEYL ALCOHOL 31 mN/m
- METHYL OLEATE 15 mN/m
- BUTYL STEARATE 11 mN/m

$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}$ (CIS ISOMER)
OLEYL ALCOHOL



METHYL OLEATE



BUTYL STEARATE

$$\text{mg/m}^2 = \frac{\text{MW}(\text{mg/mole}) \times 10^{20} (\text{\AA}^2/\text{m}^2)}{\text{\AA}^2/\text{molecule} \times 6.023 \times 10^{23} (\text{molecules/mole})}$$

Surface concentration of monomolecular film constituents (mg/m^2) as a function of molecular weight (MW) and the area occupied ($\text{\AA}^2$) per molecule.

Experimental Sea Slicks: Their Practical Applications and Utilization for Basic Studies of Air-Sea Interactions

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INTRODUCTION

Practical applications of organic surface films added to the sea surface date back to ancient times. Aristotle, Plutarch, and Pliny the Elder describe the seaman's practice of calming waves in a storm by pouring oil onto the sea [Scott, 1977]. It was also noted that divers released oil beneath the water surface so that it could rise and spread over the sea surface, thereby suppressing the irritating flicker associated with the passage of light through a rippled surface.

From a scientific point of view, Benjamin Franklin was the first to perform experiments with oils on natural waters. His experiment with a 'teaspoonful of oil' on Clapham pond in 1773 inspired many investigators to consider sea surface phenomena or to conduct experiments with oil films. This early research has been reviewed by Giles [1969], Giles and Forrester [1970], and Scott [1977]. Franklin's studies with experimental slicks can be regarded as the beginning of surface film chemistry. His speculations on the wave damping influence of oil induced him to perform the first qualitative experiment with artificial sea slicks at Portsmouth (England) in October of 1773. Although the sea was calmed and very few white caps appeared in the oil-covered area, the swell continued through the oiled area to Franklin's great disappointment.

Giles [1969] reviewed the literature published after Franklin's paper and found 17 authors discussing wave damping by oil prior to 1951. But apart from some experiments on wave quelling by John Shields at Peterhead Harbor (Scotland) in 1882, 70 years passed before surface films again became of interest as a tool for the practical modification of air-water interaction processes, when Mansfield and several other authors started their investigations on the retardation of evaporation by monomolecular films (reviewed by La Mer [1962]).

The mechanisms of the wave calming phenomenon are not well understood, especially with regard to gravity wave damping. However, some pioneering quantitative research on the open sea has been performed since 1968, which has led to an improved understanding of some of the effects of organic surface films on air-sea interaction processes [Barger *et al.*, 1970; Mallinger and Mickelson, 1973; Hühnerfuss *et al.*, 1980]. Furthermore, slick experiments are useful for studies of the drift response of the ocean surface [Lange and Hühnerfuss, 1978], the formation of Langmuir cells, the backscattering of radar signals from the ocean surface [Hühnerfuss *et al.*, 1978; Hühnerfuss *et al.*, 1980], and the gas exchange processes across the water surface [Brockmann *et al.*, 1980]. Thus continued re-

search with experimental sea slicks will be necessary in future years to address such problems.

RATIONALE FOR RESEARCH WITH EXPERIMENTAL SLICKS

Surface-active organic material adsorbs at and spreads over the air-water interface. Slicks at sea associated with windrows, internal waves, calm water, and plankton blooms are surface films of polar organic matter at a sufficient concentration to modify physical interfacial properties. In general, sea surface films are monomolecular organic layers, which often exist at surface pressures below those at which the film physically collapses.

Small-scale hydrodynamic and physical processes are modified at low film pressures, at a point in the area compression plot for the film where it undergoes a transition from an expanded gas-like state to a state where it possesses liquid or solid properties. At this transition point, the air-water interface is no longer 'free' but is immobilized by the incompressible film. This effect has been clearly demonstrated by experiments on the capillary wave damping by water-insoluble organic surface films [Garrett, 1967a] and measurements of the influence of surface film pressure on water surface temperature and convective processes near the interface [Jarvis, 1962].

Adsorbed surface-active material not only attenuates existing capillary waves but also inhibits wave formation [Keulegan, 1951; Van Dorn, 1953]. According to Miles [1967] 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 1 order of magnitude. While natural sea slicks should in theory withstand winds of this order (12 m/s), their constituents are dispersed at sustained wind speeds of from 5 to 7 m/s and sometimes less. The concentration of surface-active material in the underlying seawater is insufficient to supply and to 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/s. On several occasions, artificial slicks have been formed and maintained for a period of time when winds were as great as 10 m/s. 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

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

Surface Effect or Process Modification	Type of Organic Surface Film	
	Natural	Experimental ^a
Capillary wave attenuation	<i>Davies and Rideal</i> [1963] ^b <i>Ewing</i> [1950] ^b <i>Garrett</i> [1967a] ^b <i>Scott</i> [1972] ^b	<i>Barger et al.</i> [1970] ^b <i>Hühnerfuss et al.</i> [1980] ^b
Gravity waves	<i>Davies and Rideal</i> [1963] ^c	<i>Barger et al.</i> [1970] ^b <i>Hühnerfuss et al.</i> [1980] ^b
Breaking wave inhibition	... ^d	<i>Barger et al.</i> [1970] ^b
Gas transport reduction	... ^d	<i>Jarvis et al.</i> [1962] ^e <i>Brockmann et al.</i> [1980] ^b <i>Petermann</i> [1976] ^e
Oleophilic pollutant accumulation	<i>Hartung and Klinger</i> [1970] ^b <i>Seba and Corcoran</i> [1969] ^b <i>Eisenreich et al.</i> [1978] ^b	... ^d
Foam stability	<i>Garrett</i> [1972] ^e	<i>Garrett</i> [1967b] ^e
Air bubble bursting	<i>Blanchard and Hoffman</i> [1978] ^e <i>Garrett</i> [1968] ^e	<i>Garrett</i> [1968] ^e
Surface temperature	<i>Clark</i> [1967] ^b	<i>Patterson and Spillane</i> [1969] ^e <i>Grossman et al.</i> [1969] ^b <i>Jarvis</i> [1962] ^e <i>Jarvis et al.</i> [1962] ^e
Electromagnetic wave reflection	<i>Beard and Gainer</i> [1970] ^b <i>Brown et al.</i> [1976] ^b <i>Maurer and Edgerton</i> [1975] ^b	<i>Barger et al.</i> [1970] ^b <i>Hühnerfuss et al.</i> [1978] ^b <i>Hühnerfuss et al.</i> [1980] ^b

^aA continuous, monomolecular film added to water surface for research purposes.

^bEffect demonstrated by laboratory and field research.

^cSignificant influence of surface film unlikely.

^dPotential influence, but not proved by experiment.

^eDemonstrated in laboratory; field studies if any were inconclusive.

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 by 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 microscale hydrodynamics and the rheology of the air-sea interface. It will be shown in ensuing sections that experimental sea slicks 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. In addition, several practical applications of surface films in the marine environment have been developed in recent years.

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 surface-active experimental sea slick. The molecular structure 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 orients away from the water surface when the film is under pressure.

The material must spread spontaneously into 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 in order that losses from the slick caused by evaporation and by dissolution will be small. A nonionic film-forming chemical is required for use on saline water to obviate reaction with ionic species which increase the solubility rate. 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 2 is a sample list of properties required for substances which could 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 (1) the feasibility of creating and of sustaining a monomolecular film on the sea,

TABLE 2. Properties of Film Forming Materials for the Production of Persistent, Highly Surface Active Experimental Sea Slicks

Properties	
Highly surface active	strong capillary wave damping; resists 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	

(2) the resistance of various monolayer-forming materials to natural dispersive forces of wind, waves, bursting bubbles, etc., (3) the most effective monolayer-forming materials for the creation of a durable experimental slick for various applications and research purposes, and (4) the quantities of surface-active material required.

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

1. Oleyl alcohol (9-octadecen-1-ol, cis isomer) an 18-carbon, monounsaturated fatty alcohol, equilibrium spreading pressure = 31 dynes/cm.
2. Cottonseed oil, glyceride esters, primarily palmitic C_{16} , oleic $C_{18:1}$, and linoleic $C_{18:2}$, equilibrium spreading pressure = 14 dynes/cm.
3. Oleyl ether, containing two oxyethylene groups, equilibrium spreading pressure = 42 dynes/cm.
4. Isostearyl alcohol containing two oxyethylene groups, equilibrium spreading pressure = 44 dynes/cm.
5. Oleic acid (9-octadecenoic acid, cis isomer), equilibrium spreading pressure = 30 dynes/cm.
6. Sorbitan monooleate, equilibrium spreading pressure = 42 dynes/cm.

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 (25–150 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 (4–7 m/s) with no natural or pollutant slicks in evidence.

During the first 20–30 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 owing 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 area at about equal rates. At a slick lifetime of about 1 hour, three of the moderately soluble slicks, sorbitan monooleate, isostearyl alcohol (2-OE), and oleyl ether (2-OE) 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 3 times as long as any of the other films studied. Film lifetime is an important aspect when using experimental slicks for basic and for 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 dynes/cm 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 [Garrett, 1967a].

In the laboratory, using mechanically generated waves, most surface films damp capillary waves to approximately the same degree when their film pressures are on the order of a few dynes cm^{-1} [Garrett, 1967a]. 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 dynes cm^{-1}) was more than twice that of the less effective cottonseed oil film (14 dynes cm^{-1}). 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 pressure.

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, cotton seed oil and methyl oleate are suitable for the production of persistent slicks with lower film pressures which more closely simulate natural films in their physical effects on interfacial properties and processes.

Techniques for Generation of Experimental Slicks

Method 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 intrinsic spreading velocity varies between 34 and 40 cm/s 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 [Garrett and Barger, 1970]. The spreading velocity decreases rapidly with distance from the source of the film-forming material, decreasing to 10 cm/s 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 (3–4% 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 slick 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, probably owing to convergence zones caused by wind-generated cellular water motions. Langmuir cells and internal waves may also produce surface zones of convergence and divergence which will prevent continuous coverage by the experimental slicks.

Thus to produce a large slick for experimental purposes

TABLE 3. Quantities of Oleyl Alcohol Used in the Production of Various Experimental Sea Slicks

Dispensing Mode	Slick Size, km ^{2a}	Oleyl Alcohol Volume (l)	1 km ⁻²	Reference
Boat ^b	0.50	13.0	26.0	<i>Barger et al.</i> [1970]
Boat ^b	0.70	19.0	27.1	<i>Mallinger and Mickelson</i> [1973]
Fixed-wing aircraft ^b	0.52	18.0	34.6	<i>Barger and Garrett</i> [1974]
Point Source	0.005	0.1	20	<i>Barger and Garrett</i> [1976]
Helicopter ^c	1.5	30.0	20	<i>Hühnerfuss et al.</i> [1978]
Monolayer, theoretical	...	...	1.75	...

^aMaximum area of slick during its lifetime.

^bDispensed as a liquid stream from a pressurized container.

^cFrozen, 80 g chunks dispensed periodically.

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 [*Barger et al.*, 1970; *Mallinger and Mickelson*, 1973] or an aircraft [*Barger and Garrett*, 1974; *Hühnerfuss et al.*, 1978].

Method 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 surface film-forming material are systematically distributed from a helicopter [*Hühnerfuss and Lange*, 1975]. During project Koff 1974 (Kombiniertes Oberflächenfilm projekt) and Jonswap 1975 (Joint North Sea Wave Analysis Project) 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 changing tidal 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 and meteorological instruments or through the footprints of sensors being used in conjunction with the slick research.

The procedure for the generation of a typical experimental slick by helicopter dispensing of frozen oil cubes is summarized as follows:

1. Dispensing pattern: 10 parallel rows perpendicular to the wind (about 50 m apart), 80 g chunks of frozen oleyl alcohol every 4 s, total of 320 oil cubes dispensed.
2. Flight altitude: 30 m (minimum altitude to avoid rotor downwash, depends upon helicopter type).
3. Flight speed: 93 km/h.
4. Wind velocity: 3.5 m/s for this example.
5. Area of developed slick: 1.5 km².
6. Total dispensing time: 30 min (includes time required for the individual frozen oil cubes to melt and to spread).

As was 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 replace rapidly the lost organic material and to restore the equilibrium pressure of the surface film. The surface concentration (1 km⁻²) used successfully in various experimental sea slick studies are listed in Table 3. The quantities used can be compared with that required for a single molecular layer of oleyl alcohol, 1.75 l/km².

Figure 1 is an aerial photograph taken from an altitude of 450 m of a 2.3-km² oleyl alcohol experimental slick recently generated for research purposes during the Marsen (maritime remote sensing) exercise, September 1979. The surface film was formed by dispensing 600 80 g blocks of frozen film-forming material from a helicopter. The slick was positioned such that it would pass directly across the Nordseeforschungsplattform (54°42'33"N, 7°10'7.4"E) in the German Bight. The slick moved at a velocity of 0.7 m s⁻¹ under a 13 kn wind ($u_{10} = 6.7$ m s⁻¹) from 290°.

REVIEW OF RECENT BASIC RESEARCH USING EXPERIMENTAL SLICKS

During Jonswap 75, several monomolecular oleyl alcohol films of about 1.5 to 3 km² in area were produced by helicopter dispensing of the frozen film-forming material. The influence of the film on wave spectra was measured under moderate wind conditions ($u_{10} = 3.5$ to 7.7 m s⁻¹) by conventional wave staffs, a coherent X band microwave scatterometer mounted on a sea-based platform, and in one case the slick area was overflown by a NASA C-130 aircraft carrying a 13.9-GHz pencil-beam scatterometer (AAFE RADSCAT).

A typical example of the wave attenuation characteristics measured by wavestaffs is depicted in Figure 2. Between 3.2 and 16 Hz, the observed wave attenuation was in the range of about 40–60%, with only a slight increase in damping with frequency. In addition, because of the large size of the slick, it was possible to make a preliminary judgment on the influence of a surface film on long gravity waves. The data seem to indicate that waves in the frequency range between 0.12 and 0.7 Hz are subject to some damping by an oleyl alcohol surface

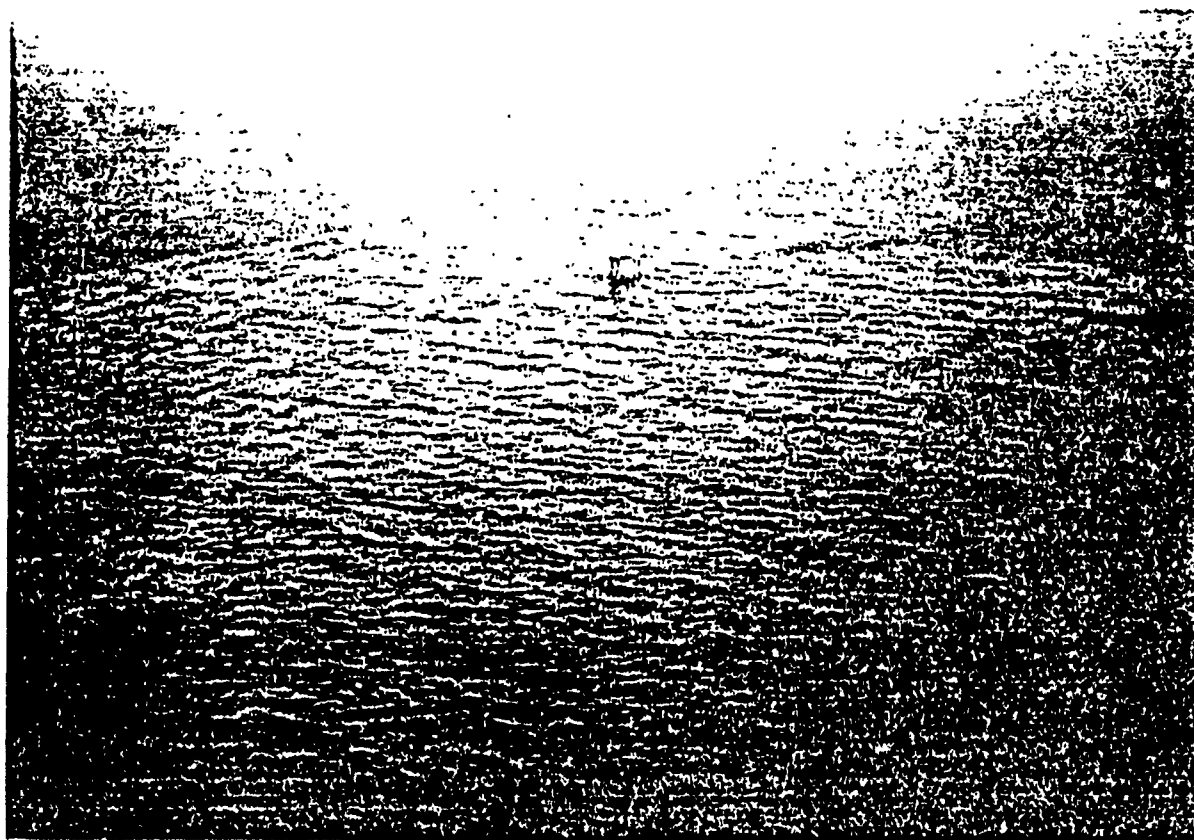


Fig. 1. Aerial photograph taken from an altitude of 450 m of a 2.3 km² oily alcohol experimental slick (Marsen experiment, September 1979).

film. This may be accounted for if it is assumed that the surface film influences wave-wave interactions and/or the wind coupling [Barger *et al.*, 1970], because a direct effect of such surface films on wave damping is confined to frequencies greater than 2 Hz, as has been shown by wave tank experiments [Hühnerfuss *et al.*, 1980].

The question of the direction of energy transfer between short and long waves has been the subject of considerable debate in recent years. The observed wave damping (Figure 2) is compatible with the assumption that an energy transfer from short to long waves occurs. In the presence of the surface film, about 40–60% of the energy in the short wave spectrum is dissipated. This implies that less energy is available for transfer to the longer waves.

The wave attenuation value measured by the tower scatterometer is also included in Figure 2 and seems to be higher than that measured by the wavestaff at the same water wavelength. However, because of the overlapping error bars, it is

not yet clear if this is a real effect owing to a modification of the anisotropy of the wave spectrum in the presence of a slick [Hühnerfuss *et al.*, 1980]. If such is the case, wave attenuation values would be different when measured by a wavestaff (no directional dependence) vis-a-vis a scatterometer with unidirectional dependence, and flight direction dependence of the observed wave attenuation values measured by airborne scatterometers would be expected. This has in fact been observed by Hühnerfuss *et al.* [1978], but large error bars associated with these measurements indicate the need for additional experimental verification.

Wave attenuation values owing to oily alcohol films have also been determined by evaluation of Doppler shift spectra measured by a tower-based radar [Hühnerfuss *et al.*, 1980]. Again, a stronger wave damping is shown by these radar data in comparison with conventional wavestaff measurements, but owing to the large error bars, the authors would only tentatively conclude that the Doppler shift data show a directional

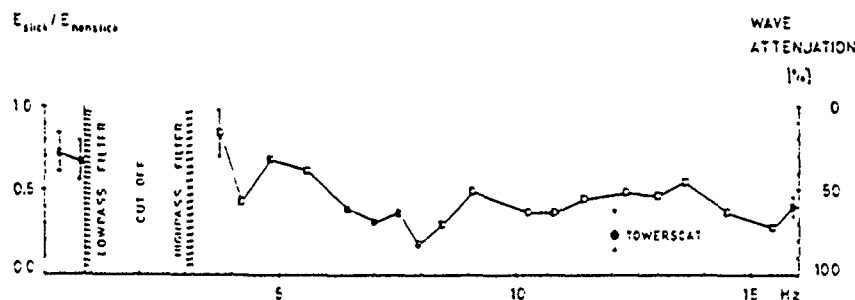


Fig. 2. The ratio of wave energy (slick/non-slick area) versus frequency measured by the vertical wavestaff. The scale on the right-hand side shows the corresponding values for the wave attenuation in per cent. Circled cross marks the value measured by the tower scatterometer [from Hühnerfuss *et al.*, 1980].

dependency which is different in the presence of a sea slick.

During the Koff 74 experiment, oleyl alcohol surface films of smaller size were produced by method B, using a spiral flight pattern. The experiments were designed to study the chemical and the biological effects of artificial surface films and the modification of air-sea gas exchange caused by such films [Brockmann *et al.*, 1980]. Natural and experimental surface film samples were collected with a rotating drum skimmer [Harvey, 1966] several times during the 6-hour experiment. The samples were analyzed by gas chromatography for oleyl alcohol and for fatty acids, the latter serving as a tracer for the natural surface films. The data indicated that oleyl alcohol pushed aside the natural fatty acids in the sea surface during the spreading process. A slight increase of the fatty acid concentration in the samples taken from the experimental slick during the last 4 hours of the experiment was observed. This might have been due to natural surface active substances slowly entering the experimental slick from subsurface water, since relatively calm weather conditions prevailed and natural slicks existed around the periphery of the experimental surface film [Hühnerfuss *et al.*, 1977].

The surface 'cleaning effect' of the spreading oleyl alcohol suggested by the fatty acid data was confirmed by independent measurements of colony forming units (CFU) of heterotrophic bacteria [Brockmann *et al.*, 1980]. A strong reduction of CFU in surface samples occurred immediately after formation of the experimental slick. A slight additional decrease of CFU in the slick was observed after the slick had fully developed, which suggested that the oleyl alcohol surface film inhibited repopulation of the air-sea interface by the organisms.

Some of the slicks produced during the Koff 74 and Jonswap 75 experiments have been used to determine the drift responses of the slicks to wave and to wind action [Lange and Hühnerfuss, 1978]. The relative position of the slicks was determined by logging the direction and the distance from a fixed instrumentation pile to the slick's center with the helicopter. The helicopter's speedometer readings were corrected with the appropriate wind component. In connection with additional wind wavetank experiments, it could be shown that the tidal currents, wind, and gravity wave-induced Stokes drift obviously contribute to slick drift on the sea surface. A comparison of laboratory and field results indicated that the pure gravity wave drift component composes 25–30% of the total surface drift (without tidal current). Furthermore, monomolecular surface films proved to be a good tool for studying the surface drift because of their extreme thinness. Conventional surface floats generally indicate different drifts depending on their depth of immersion.

PRACTICAL APPLICATIONS OF SURFACE FILMS AT SEA

In recent years, several practical applications of organic surface films have been developed which are based upon small-scale modifications of the physical properties of the air-sea interface. One of the most notable manifestations of a slick, a consequence of its effects on capillary waves, is its high visibility under most conditions. The decreased average wave slope within a slick produces a light reflectance anomaly so that the affected area may appear either lighter or darker than the surrounding rippled water surface, depending upon the angle of view with respect to the sun. It was the high visibility of slicks produced by small quantities of certain organic substances that was the basis for the development of a novel sea

marker package for rescue and recovery operations at sea [Garrett and Barger, 1972].

This application of organic surface films is depicted in Figure 3, an aerial photograph of three seamarks taken from an altitude of 200 m. The upper surface mark is a wave-damped zone elongated in the direction of the wind. This chemical sea marker was generated by a floating package composed of oleyl alcohol and sodium fluorescein (uranine) dye mixed with chemicals that generate carbon dioxide gas bubbles upon contact with water and gradually dispense the slick. The center mark (barely visible) is a narrow band produced by a standard search-and-rescue dye marker package composed primarily of sodium fluorescein, a water soluble fluorescent chemical. The lower slick patch in the figure was formed by the release of 27 g of oleyl alcohol from a subsurface, seltzer-type, slow-release dispenser. At this viewing angle, the slicks appear dark, because the sun glitter pattern that reflects light toward the observer is weak where capillary waves are absent. The dye-only pattern (center) is barely visible under these viewing conditions. At certain other viewing angles, on the other hand, the slick detectability is poor, and the dye marker is more apparent. Consequently, both dye and surface film sea markers are used together to assure visibility at all angles and to increase the distance at which a mark on the sea surface can be detected. Furthermore, it has been demonstrated that oleyl alcohol surface slicks are detectable by X band radar, making them sensible from aircraft under many weather conditions and at night as well as by day.

Another application of artificial sea slicks that has been proposed is the enhancement of underwater visibility through the use of organic surface films. In folklore as well as in modern practice, fish oils have been used to calm the sea surface and to clarify the underwater scene. For example, divers sometimes carried and released such surface-active oils to mollify the sea surface and to reduce underwater shadows and bright spots caused by wave-induced refractions of light. To test the validity of this notion, 0.085 km² artificial slicks were generated in July 1970 above the Tektite II habitat, which rested in 17 m of water in Lameshur Bay, St. John Island, U.S. Virgin Islands. On the basis of previous research [Barger and Garrett, 1968], oleyl alcohol was selected for this application because it would produce a calmer, more intensely damped sea surface than either fish or vegetable oils. Photographic and visual observations were obtained by divers in the water beneath the surface film. Similar observations of underwater objects were made from vantage points above the sea surface before and after slick passage. Relative irradiance data and sun angles were measured for these experimental situations. A number of experiments were performed in the neighborhood of the Tektite II habitat in 17 m of water and in shallower water elsewhere in Lameshur Bay. In this series of underwater observations, there were no visual, photographic, or irradiance data that indicated significant visibility enhancement within the underwater environment because of the modification of the water surface by the artificial slicks and the attendant decreases in wave slope.

On the other hand, the visibility of underwater objects observed from above the air-water interface was greatly increased by the glassy water surface condition produced by the additive slick. The multiple reflected images of the sky caused by the numerous small waves were eliminated, and the water surface approached that of a glass plate on which there were only minor perturbations caused by gravity waves. Details of



Fig. 3. Aerial photograph of three seamounts taken from an altitude of 200 m. Upper mark: Oleyl alcohol and sodium fluorescein (uranine) dye; center mark: standard search-and-rescue dye marker package (primarily sodium fluorescein); lower mark: experimental slick formed by the release of 27 g oleyl alcohol.

underwater objects that had been obscured by the multiple reflection pattern of a rippled surface could be seen clearly through the smoothed air-water interface when the slick was present. This effect was demonstrated by photographs and by observations of the undersea habitat whose uppermost portion was about 7 m below the surface of the water. When viewed through a rippled surface in the absence of a wave-damping organic film, only the blurred outline of the habitat could be discerned while objects with smaller dimensions could not be visually resolved. Viewing downward through a ripple-free film-covered surface, one could clearly see the major segments of the habitat and smaller features such as flanges and bolts could be identified, whereas they could not be seen without the surface film.

A third application of water-insoluble film-forming agents is directed at environmental protection. Organic chemical films that reduce the surface tension of water have been developed to confine and to control spills of petroleum products on water [Garrett and Barger, 1972; Garrett, 1969]. The application of suitable film-forming agents to the water around the edge of an oil spill reduces the water surface tension, one of the principal forces causing oil to spread into thin layers. The unmodified surface tension of the oil and the oil-water inter-

facial tension can then draw the oil layer into a significantly smaller area of greatly increased thickness. Decreasing the area of the oil film with surface-active chemicals does not cause emulsification or dispersal of the oil into the water but confines it on the water surface. Because oil-collection devices perform with greater efficiency on thicker oil layers, the use of chemical film to control oil on water has been adopted as a viable oil-spill control technique.

FUTURE RESEARCH

Organic Film Sea Truth for the Interpretation of Remotely Sensed Signals

It is evident from the wave attenuation values measured by wavestaffs during Jonswap 75 (Figure 2) that the decrease of L band (15–30 cm wavelength) radar cross section is expected to be almost as large as for K_u band (1.7–2.4 cm wavelength), since the wave damping was not strongly dependent on water wave frequency in the range from 3.2 to 16 Hz. Thus many ocean surface features which are discernible on L band SEASAT SAR images and which possibly indicate the presence of internal waves, oceanic fronts, current boundaries (e.g., Gulf Stream), and Langmuir cells, might be explained by a nonuni-

form distribution of monomolecular organic surface films. Consequently, simultaneous wave measurements by wavestaffs and L band radars of nonslick and slick-covered ocean areas would provide some of the 'sea truth' needed for the proper interpretation of remotely sensed signals.

Wave attenuation rates measured by K_u radars in the presence of an oleyl alcohol surface film seem to be higher than those measured by conventional wavestaffs [Hühnerfuss *et al.*, 1980]. It is presumed that wave damping caused by surface films shows a directional dependence which is resolved differently by wavestaffs (omnidirectional) than by the relative back-scattered power received by a K_u band radar (unidirectional) or by the directionally dependent resolution shown by the spectra of the Doppler shift. To confirm this hypothesis and to improve the evaluation of radar data in the presence of natural slicks, measurements of the wave attenuation rates with both wavestaffs and radars (with different directions of observation) should be performed on slicked and nonslicked sea surfaces.

Natural surface films consist of a wide variety of different surface active compounds which may interfere with the wind-wave field in various ways. Therefore, several compounds characteristic of natural slicks should be used for generating experimental surface films for the studies proposed in the preceding paragraphs.

Wind-Wave Coupling

The wave attenuation due to surface films can result from (1) direct influence of the film, (2) modification of short-wave-long-wave interactions, and (3) modification of the wind energy input. Whereas basic studies of the first and the third can be performed in wind-wave tanks by using different organic chemical films, wave-wave interactions must be investigated in situ with very large slicks, which for statistical reasons should permit a 30-min period of measurement. Open sea experiments should be conducted to provide additional information on the modification of wind-wave interactions by surface films for comparison with the experiments of Barger *et al.* [1970]. These studies should include air turbulence measurements directly above the waves with a wave follower and the use of surface films formed from chemical compounds with different interfacial properties.

Wave-Wave Interactions

The Jonswap 75 data [Hühnerfuss *et al.*, 1980] seem to indicate some damping of longer gravity waves in the frequency range 0.12–0.7 Hz by oleyl alcohol films. This influence should be confirmed by experiments with a slick of several square kilometers in area, one which would allow a long period of wave measurement for quantitative calculations of wave-wave interaction processes. Studies of experimental slicks formed from chemical compounds with varying influence on the capillary wave spectra are recommended as a means of gaining further insight into the coupling mechanisms between short and long waves.

Air-Sea Exchange of Organic Material

In recent years, several authors have stressed the importance of the transport of organic materials from the ocean to the atmosphere [Barger and Garrett, 1976; Hoffman and Duce, 1974]. Furthermore, organic surface films accumulate organic and inorganic materials as well as biological entities, so that fractionation occurs during air bubble bursting processes, and

the relative concentrations of the chemical and the biological species in the ejected drops are different from those in the sea. Quantitative calculations concerning fractionation processes could be improved by in situ studies of experimental surface films with specified physicochemical characteristics. Atmospheric samples would be taken directly above the slick area and upwind of the slick for subsequent chemical and biological analyses, and appropriate wind and wave measurements would be made.

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

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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 overtum 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 convectional 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 sensible 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 ($\text{liters}\cdot\text{km}^{-2}$) 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, $1.75 \text{ l}\cdot\text{km}^{-2}$.

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,

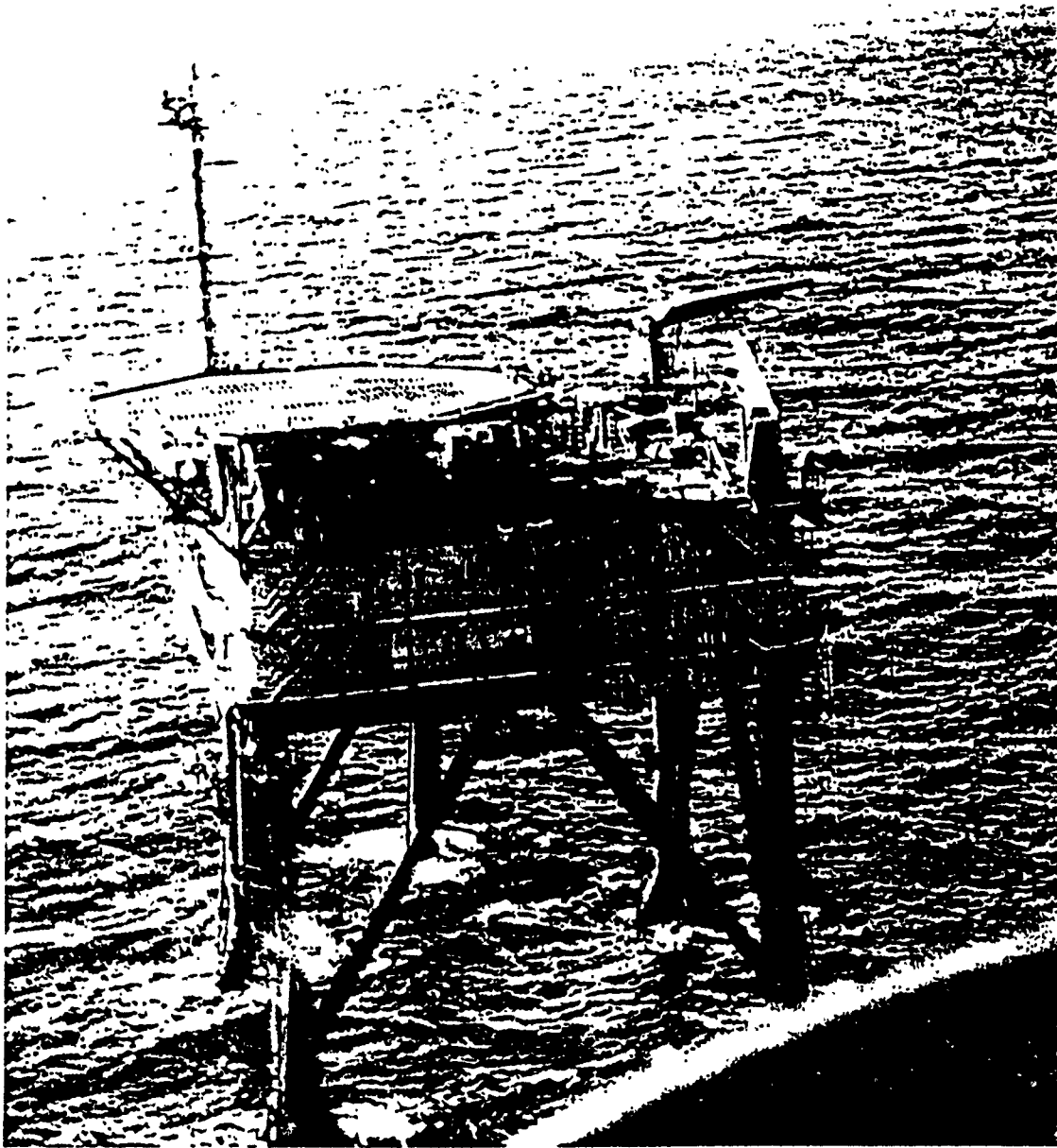


Fig. 1 — Research platform, Nordsee, located in the German Bight section of the North Sea ($54^{\circ} 42' 33''\text{N}$, $7^{\circ} 10' 7.4''\text{E}$) and used as focal point of MARSEN coordinated slick experiments. Helicopter pad is located at the southeast quadrant of the platform.

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°.

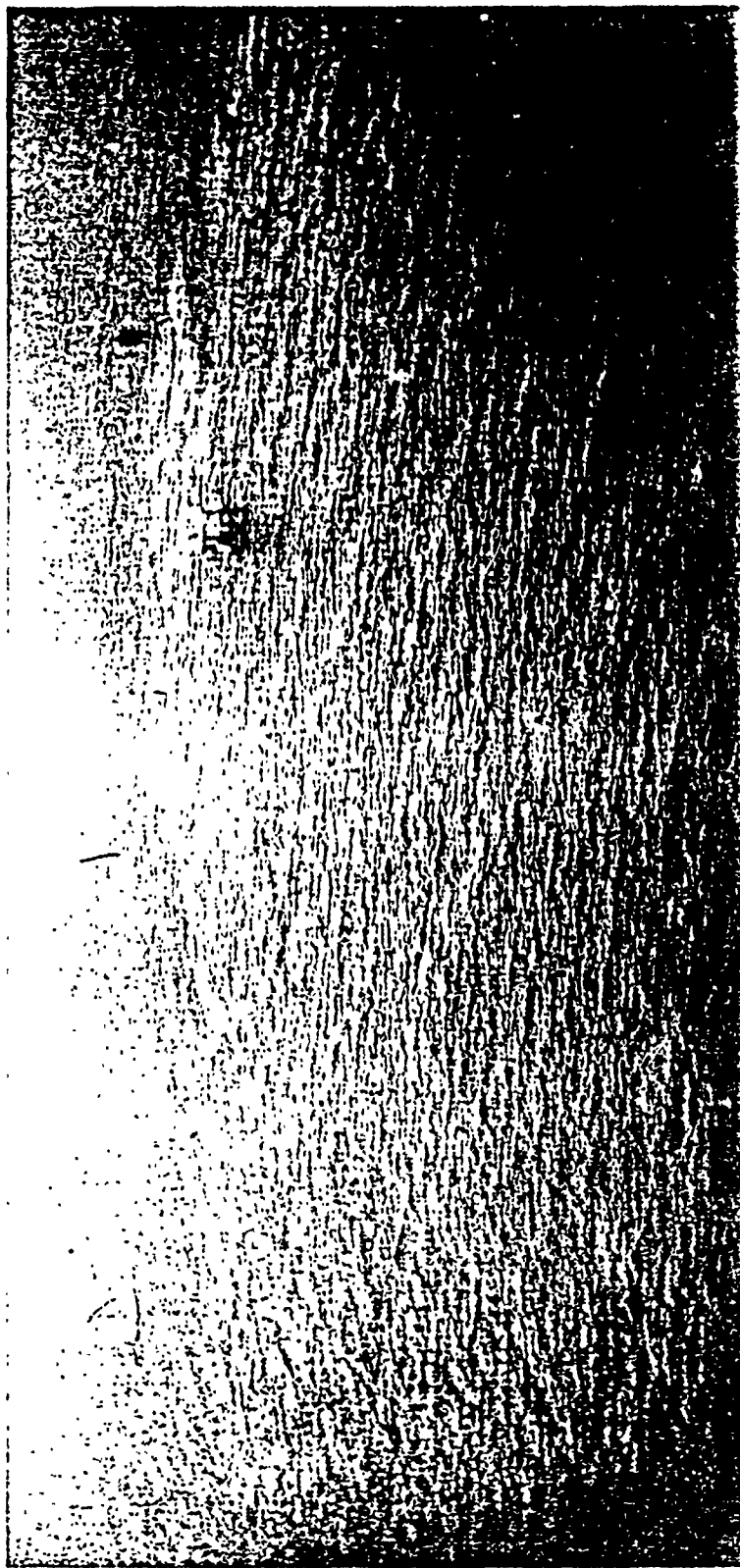


Fig. 3 -- Aerial photograph of slick 3, a monomolecular film of oleyl alcohol, 2.3 km^2 in area passing the Nordsee platform, 28 September 1979 at 1230 UT

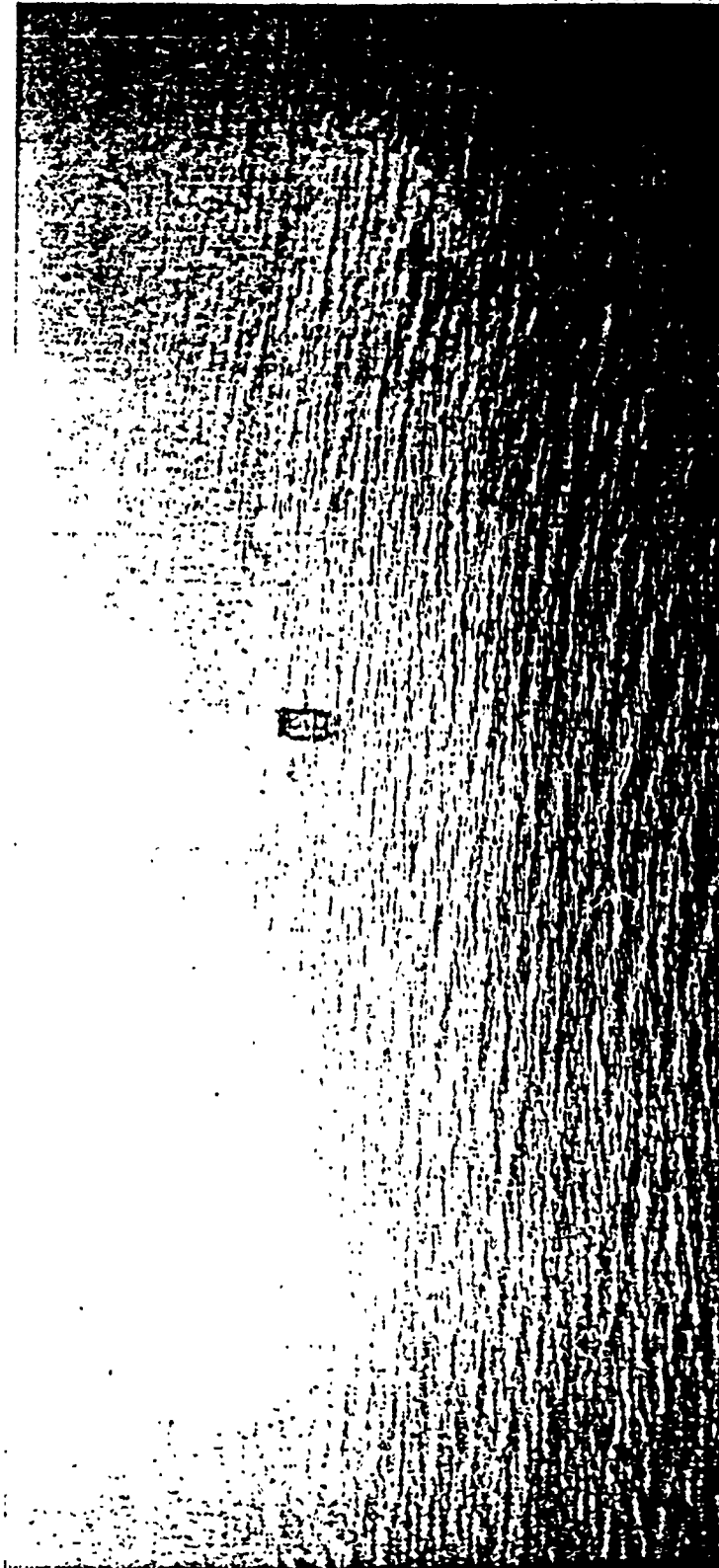


Fig. 4 — Aerial photograph of slick 3 looking west, 28 September 1979 at 1255 UT

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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