J. Fluid Mech. (1972), *vol.* 56, *part* 3, *pp.* 591–606
Printed in Great Britain

The influence of surface-active contamination on the initiation of wind waves

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(Received 22 March 1972)

A small-scale apparatus was used to examine the effects of surface materials on the initiation of waves on water by the action of wind. Rigorous procedures were followed to ensure freedom from contamination of the initial water surface, and the effect of various forms of subsequent contamination were investigated, using a sensitive moiré fringe wave slope observation technique. Provision was made in the design of the water container for insoluble films to circulate, avoiding the downwind buildup of contamination.

In measurements on pure water surfaces, no evidence of a 'critical wind velocity' was found, although slightly contaminated water was found to be appreciably less responsive to the wind excitation at wind speeds up to $4\,\mathrm{m\,s^{-1}}$. Measurements on monolayer-covered surfaces showed that, at these wind speeds, a compressed monolayer of relatively high surface tension and low dilational elasticity can have a greater stilling effect than one of low surface tension and high dilational elasticity. Measurements on a series of solutions of surface-active material, covering a range of surface tensions from 63 to $26\,\mathrm{mN\,m^{-1}}$ at a concentration expected to reduce dilational elasticity by bulk-to-surface diffusion, indicated that the damping effect becomes steadily greater as the surface tension decreases.

1. Introduction

The addition of surface-active materials to the surface of pure water has been found to have a very marked effect on the wave propagation characteristics of the surface. This effect is observed both in the damping of free waves, particularly those of short wavelength (less than about 50 mm), and also in the calming of the wind-excited surfaces of exposed areas of water.

Considerable success has been reported in the explanation of the effect of surface films on capillary ripples (wavelength less than 9 mm) using linearized hydrodynamic theory with surface chemical concepts such as that of the dilational elastic modulus (Lucassen-Reynders & Lucassen 1969). This elasticity arises from the variation of surface free energy (and hence surface tension) with the degree of compression of the film: stretching a film of organic material usually increases the surface tension, generating a force which opposes the

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stretching action (Marangoni 1872; Gaines 1966). This concept has allowed the explanation of certain sharp peaks which have been observed in measurements of the spatial damping of ripples as the film is steadily compressed (Scott & Stephens 1972). An important aspect of experimental observations on free surface waves has been found to be the degree of cleanliness which must be maintained in order to achieve consistent results (Davies & Vose 1965), and therefore an investigation into the influence of added materials on the wind-excited system must begin with a surface free from the accidental contamination which is the bane of the colloid scientist.

The earliest reported work which attempted to compare the relative efficiency of different oils is due to Aitken (1883), who with apparently clean conditions showed that, for a range of oils, the damping effect of the superposed layer appeared to increase as the surface tension of the oil-covered water decreased. The thickness, or surface concentration of the applied layers, is not deducible from this work. Davies, Qidwai & Hameed (1968) presented measurements of the amplitudes of waves generated with fetches around 3 m by winds in the low velocity range, between 1·6 and 3·1 m s^{-1}, using scrupulously clean conditions. At the highest wind velocity examined, the amplitudes of waves on clean water of 30–100 mm wavelength were observed to reach 7 mm, while the presence of a compressed monolayer reduced amplitudes to as little as 7 % of this height, as well as increasing the range of observed wavelengths to between 70 and 180 mm.

Hino, Kataoka & Kaneko (1969) measured the damping effect of dissolved surface-active material, and observed a maximum damping at surface tensions between 55 mN m^{-1} and 45 mN m^{-1}. One possible explanation of this maximum is that, since the reduction in surface tension was produced by increasing the surfactant concentration, the effect of decreasing surface tension was diminished by the dilational elastic properties of the surface being modified by increased diffusional interchange of the active material between surface and bulk.

The present investigation is concerned with the effect of surface-active material, both soluble and insoluble, on the initiation of waves with a short fetch. The choice of a short fetch was determined by the need to distinguish between the effect of the surface activity on the suppression (or prevention) of wave activity and its effects on the attenuation of pre-existing wind-generated disturbances travelling in the wind direction.

In the investigation of insoluble films, an attempt was made to prevent the downwind accumulation of active material by providing a means of surface circulation. The effects of soluble material were examined by choosing a range of surface-active materials which give a wide range of surface tensions when present at the same bulk concentration, so that the effects of varying diffusional interchange might be minimized.

2. Experimental techniques

2.1. *The wind tunnel*

A schematic diagram of the apparatus is shown in figure 1. The tunnel section was 178 mm wide and 103 mm high, air being drawn through the working section

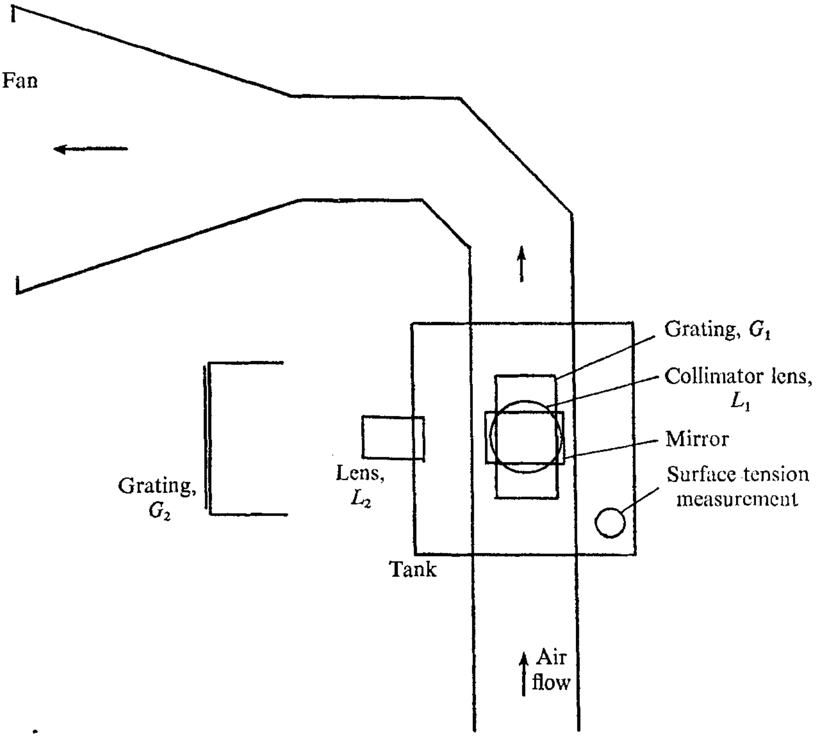

FIGURE 1. Layout of the wind tunnel, showing the disposition of the optical components.

via a 310 mm entry length by a Dayton $\frac{1}{8}$ h.p. fan with three blades sweeping a 225 mm radius. The entry section drew on nominally still air and contained no turbulence-smoothing screens. The transition from this section into the water-containing working section was made as smooth as possible, although 2 mm strips were necessary at the water's edge to avoid wind- and wave-induced overflow. Wind speed was measured on the centre-line of the working section of the tunnel using a flattened 1·5 mm bore hypodermic tube (vertical aperture about 0·3 mm) with an inclined water manometer containing wetting agent and calibrated *in situ*. Variation in wind speed was by means of a variable-voltage transformer feeding the fan motor.

2.2. *The wave tank*

The tank, designed to contain a 25 mm depth of water, was constructed entirely from $\frac{1}{2}$ inch sheet Plexiglas (polymethylmethacrylate), chosen for its relative ease of use in investigations of surface activity. This material is not always found to be acceptable by surface chemists, since there is a possibility that low molecular weight components of the polymer might gradually be leached away to contaminate the water. Since, on this occasion, prolonged contact of water with the tank failed to give detectable contamination, it was considered adequate. Internal cleaning was very thorough, using commercial liquid detergent and intensive rinsing with pure contamination-free water. The water used for the investigation was distilled in an all-silica glass apparatus from dilute alkaline

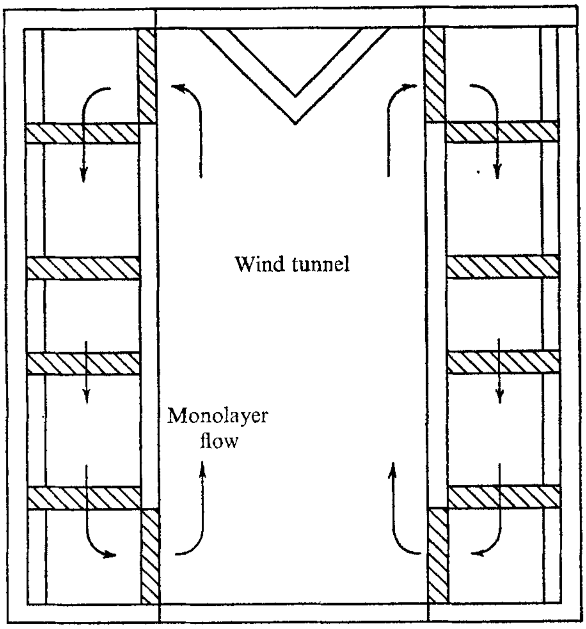

FIGURE 2. Layout of the wind/wave tank, showing the monolayer circulation. The shaded areas represent partitions ending 2 mm above the water surface. The 45° wave deflector at the downwind end rests on the bottom of the tank, and stands just clear of the surface.

potassium permanganate solution, its freedom from surface-active contamination being verified by both its surface tension measurement and by the rapid disappearance of surface bubbles after shaking (Kitchener 1964).

Provision was made in the tank for *in situ* surface tension measurement via a 54 mm diameter Plexiglas cylinder passing through a hole in the top of the enclosed tank at one corner. This cylinder, normally in contact with the water, could be raised quickly after a period of tunnel operation, allowing measurement of the surface tension force on a platinum 'Wilhelmy blade', by means of a null point moving coil electric balance (after Padday 1957).

The design of the tank, shown in figure 2, was such that the 178 x 103 mm cross-section of the tunnel was formed by the roof, which totally enclosed the tank, and two parallel sides, which hung from the roof at the necessary separation, only making contact with the water when this was of sufficient depth in the tank to allow the requisite tunnel height. At each end of the tunnel, these sides were designed not to touch the water, but to leave gaps 70 mm long and 3 mm high, through which the surface film was allowed to pass. This device provided a relatively sheltered path for surface-active material to return upwind, replenishing the film being continuously blown downwind.

2.3. *The observation technique*

The wind-induced wave disturbance of the surface was observed using a sensitive moiré fringe optical technique (Scott 1969; Scott & Stephens 1972) which translates small slope variations of the surface into lateral displacements of a set of

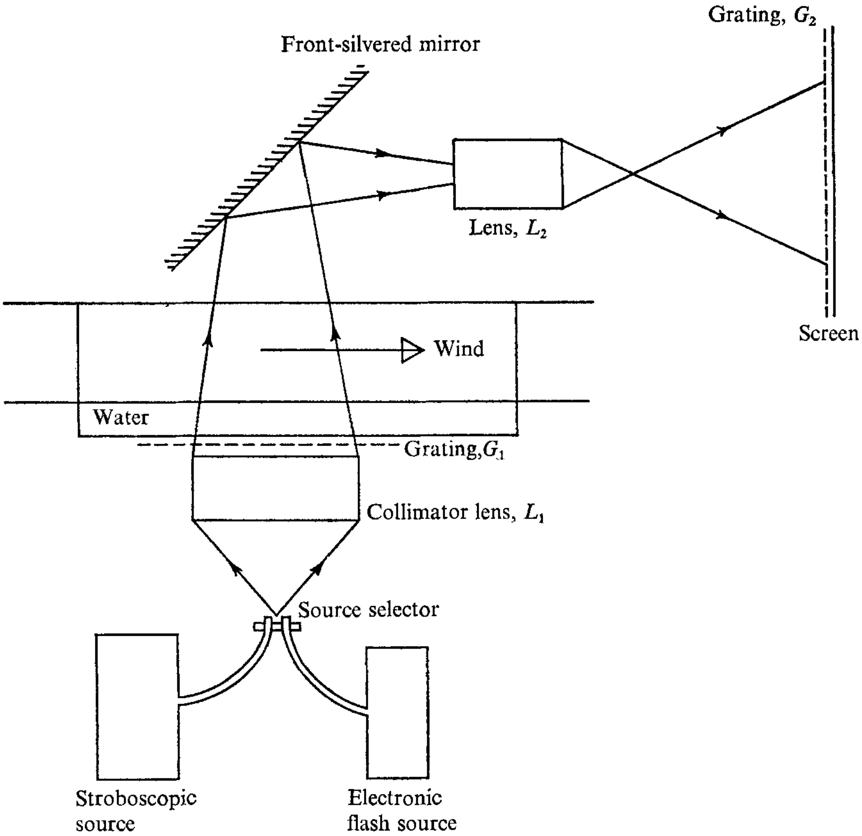

FIGURE 3. Schematic diagram of the ripple observation apparatus.

straight parallel moiré fringes running parallel to the wind direction (figure 3). The moiré fringes occur in the plane of the second (G_2) of a pair of identical parallel line gratings (2·56 lines per mm), light from the first grating (G_1) passing through the water surface before being focused by a 228 mm, f/5·6 copy lens (Edmund Scientific Co.). The essence of the technique is that the slope component of the surface in a direction perpendicular to the G_1 rulings (and therefore parallel to the wind direction) refracts light coming from G_1 so that the near-unity-magnification image in the G_2 plane is distorted, grating rulings being displaced along the wind direction by a distance proportional to the surface slope at the point where the light traversed the surface. This line displacement is translated into a fringe movement perpendicular to the direction of the displacement and also perpendicular to the original fringe direction; the displacement of the fringe is much greater than that of the line, the magnification being inherent in the nature of moiré fringes.

Thus, an original picture of straight, parallel, equispaced moiré fringes which appear to run along the wind direction over the whole of the observed area of the surface becomes distorted by the fringes deviating laterally from their original positions by amounts proportional to the slope disturbance of the part of the water surface represented by the original position of the fringe. A surface slope of 10^{-2} would produce a fringe displacement of 2 mm in the arrangement used for the present experiments, although there is considerable scope for increasing the fringe displacement should the need arise. The sensitivity may be increased by increasing the optical distance between G_1 and the water surface, or by using gratings composed of finer lines. The maximum measurable wave slope in the present arrangement was approximately 0·2, being limited by the light being deflected away from the aperture of the lens by the surface, the result being a complete lack of image in areas of greater slope. This is a form of schlieren effect, which, in a suitably refined form, is often used for the visualization of the flow of compressible fluids. The effect could be used to study the shape of the wind-disturbed water surface, but it would not give detailed information about the magnitude of surface distortions.

Either of two light sources, stroboscopic and single-flash, could be used for observation of the surface, the flash source being used to produce negative single photographs of the fringes directly onto sheets of photographic paper (Kodak Linagraph 553) held in contact with G_2. Stroboscopic illumination was found useful for the general observation of the surface distortion, a flash rate of up to 10 per second being found to give a much clearer impression of the irregularly moving distortion than did continuous illumination.

2.4. *Picture measurement*

As was explained in the previous section, a picture taken using single-flash illumination displays a set of nominally straight, parallel fringes delineating the wind direction. The deviation of these fringes from their original positions is a measure of the wave slope distortion of the surface. Since the large distortion of one fringe at a given point might carry that fringe past the original positions of adjacent fringes, the spacing of the fringes across the field must be arranged so that the change in distortion between adjacent fringes is unlikely to be as great as the distance between fringes. It is a property of fringe systems of the type used here that the fringes can be moved closer by increasing the angle between the G_1 and G_2 rulings in the G_1 image plane. Although the displacement of the fringes for a given slope distortion is reduced by this procedure (in the same proportion as the reduction of fringe spacing), the measurability of the fringes remains almost constant, since the fringe itself becomes narrower and better defined. It was found in the present experiments that a fringe spacing of 3·9 mm adequately sampled the observed field.

The information contained in a single-flash fringe picture of the distorted surface is considerable, there being about 24 fringes of length approximately 90 mm. However, at the lower wind speeds, pictures often showed only a few areas where distortion was appreciable, and since these few distortions were invariably small, simple averaging of the displacement over the complete length of observable fringe would have been inordinately influenced by the uncertainty in estimation of the distortion of the much greater proportion which was below the limit of detection. It was found, however, that the peak displacement found on a picture was reasonably consistent throughout a series of pictures with identical wind and surface conditions. Thus, in the results presented here, three

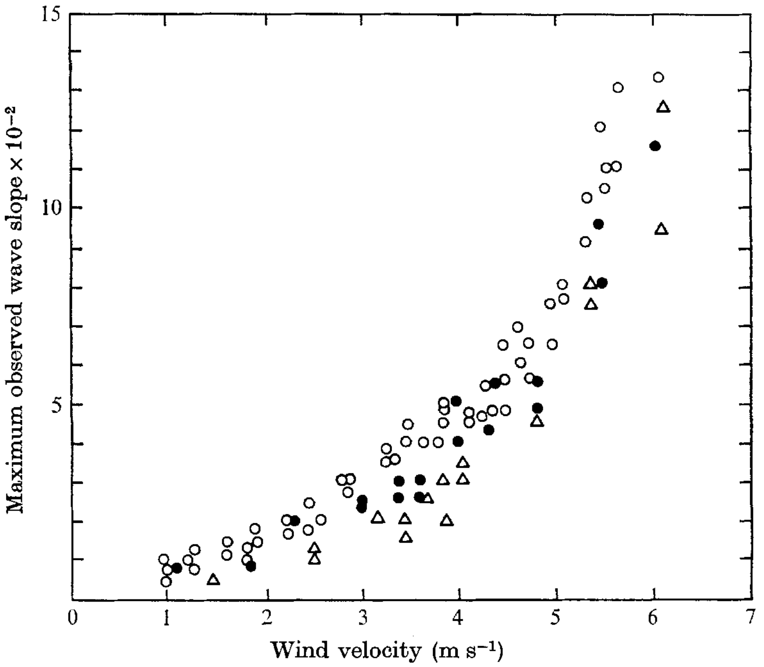

FIGURE 4. Wind-induced surface disturbance of various water surfaces. ○, clean water; ●, tap water; △, dirty water.

pictures were made for each set of conditions, and the peak displacement was measured on each picture, the mean of the three peaks being taken as representative of the surface.

Surface distortions were rarely observed to be truly wavelike, except in some pictures of heavily contaminated surfaces. This observation was equally applicable to the whole range of wind velocities measured in these experiments. Disturbances on pure water surfaces tended to have typical 'wavelengths' in the range 10 to 25 mm, although an identifiable wavelike disturbance never appeared to occupy a distance greater than two wavelengths in the downwind direction, and perhaps less in the cross-wind direction. On the addition of surface-active substances, the disturbance, apart from being more heavily damped and of a rather greater wavelength, is considerably more regular, and a wavelike ordering may persist for several wavelengths in both directions. It is possible that this greater apparent regularity follows from the preferential damping of the shorter wavelength disturbances which might prevent visual appreciation of any longer wavelength regularity, but it is also a strong possibility that the surfactant-loaded surface is preferentially resisting the initiation of short wavelength disturbances.

3. Results

3.1. *Measurements on clean water surfaces*

Moiré fringe pictures were made of the water surface distortion using centre-line wind speeds between 1 and 8 m s^{-1}, the purity of the water surface being monitored occasionally by the use of the surface tension balance and by checking the persistence of surface bubbles. Measurements from these pictures of the maximum observed slope, with a fetch of between 170 and 270 mm (this being the length of the observed area), are presented in figure 4. The results of four separate runs using clean water are combined on this graph, to show the likely variation in this measurement of the greatest slope occurring at any instant. The slope is observed to increase continuously, as the wind velocity increases, the rate of increase becoming extremely rapid at the higher wind speeds as the slope approaches the limit of measurement of the moiré fringe apparatus.

The only quantitative results with which these results may be compared are those of Davies *et al.* (1968), who measured wave amplitudes on very clean surfaces with a considerably greater fetch, around 3 m. A similar increase of wave activity with wind speed was observed, up to the highest wind velocity of 3·1 m s^{-1}. The more rapid increase observed by Davies *et al.* may be explained by the much greater fetch examined in their work. The results are in apparent contrast with the work of Cox (1958), who found that the disturbance required a 'critical wind velocity' of 3 m s^{-1}, although rigorous cleanliness procedures were not followed in his investigation. Cox observed a visible contaminant film continuously forming on his tank, and he allowed this to overflow at the lee end in an attempt to minimize its effect.

3.2. *The effects of common contamination*

The above experiment was repeated with distilled water which had momentarily been touched by clean human skin which had recently been washed with soap and water and adequately dried. The results, also shown on figure 4, show an appreciably smaller surface disturbance at the lower wind speeds, below 4 m s^{-1}, the effect tending to be less important at higher wind speeds. The key to this reduction in the surface damping effect at high wind speeds may lie in the observation that the surface tension of the water, which had fallen appreciably as a result of the contamination (from 73 to about 68 mN m^{-1}), showed a substantial recovery towards the pure-water value after a wind of velocity 6 m s^{-1} had excited the water surface for a period of ten minutes. Over a period of 6 h following this experiment, the surface tension was observed slowly to fall again, although it did not reach the initial low value in this period.

The effect of high wind velocities appears, therefore, to be in the destruction of the adsorbed surface layer, causing the removal of active material from the surface, presumably mixing it into the bulk water, in a dispersed or a 'dissolved' state. That the 'insoluble' layer becomes stirred into the bulk is indicated by the facts that: (i) no water was allowed to leave the channel during the excitation, (ii) there was no foaming which could have caused expulsion of active material into the fast moving wind (Blanchard 1963) and (iii) the wind-induced surface tension recovery began eventually to be lost, probably by the diffusion of the active molecules back to adsorbed sites at the surface.

Tap water was examined in the same way as the clean water, and it was noticed that in pouring the water into the tank several bubbles took 2 or 3 s to burst.

The surface did not have the lively response to external vibration which is a striking characteristic of surface-clean water. The measurements of surface disturbance, plotted in figure 4 with the other results described so far, show the same type of increased stability as the 'contaminated-water' measurements, although to a lesser degree. Again, it could be proposed that the effect became rather less significant for wind speeds greater than 4 m s^{-1}. The contaminating agency may be similar to that in the deliberately contaminated sample, perhaps being some grease from a tap or valve, or even natural organic material originating at the water source.

It may be concluded from the above-described experiments on different samples of water that there is a definite ripple stilling effect when the water is not scrupulously surface-clean. Below about 4 m s^{-1}, the effect is most important, substantially decreasing the roughness of the surface. This is likely to have an effect on the rate of growth of 'significant' waves at these low wind velocities either by retarding the development of initial ripples into longer waves, or by reducing the wind stress, the surface being aerodynamically more smooth.

Above 4 m s^{-1}, and certainly at 5 or 6 m s^{-1}, there is little observable effect of such minor contamination on the surface disturbance. At these high wind speeds, slight contamination would not be expected to have a significant effect on the rate of development of the wave field, or on the characteristics of the field itself.

3.3. *The effect of surface-active materials*

In these experiments, the initially clean surface was loaded with known amounts of contaminants whose surface activity was relatively well known. The first contaminant to be used was oleic acid, a highly surface-active fatty acid; with the oleic acid monolayer, the surface tension decreases very rapidly as the surface concentration increases from 1 to 2×10^{-3} g m^{-2}, a phenomenon common to pure surface-active materials of this type.

In order to achieve a measurable disturbance for all degrees of contamination, a wind speed of 5 m s^{-1} was used, at which a certain amount of monolayer destruction was to be expected. Measurements were therefore made as soon as possible after the start of the wind.

Figure 5 shows the variation of mean maximum wave slope with the surface pressure of the oleic acid monolayer (the difference in tension between that of the layer and pure water at the same temperature (Davies & Rideal 1963)). The mean values shown each represent three separate pictures, and the actual variation is indicated for each mean. Although the results show appreciable scatter, probably due to the slow destruction of the monolayer at the wind speed used, it is apparent that there may be a slight damping effect at very low surface pressures (around 1 mN m^{-1}).

The damping appears to decrease between 3 and 5 mN m^{-1}, eventually increasing again until, between 10 and 15 mN m^{-1}, the damping is approximately that of a highly compressed monolayer.

The possible maximum in the damping effect at low surface pressures could be connected with the very large similar effect observed with free ripples

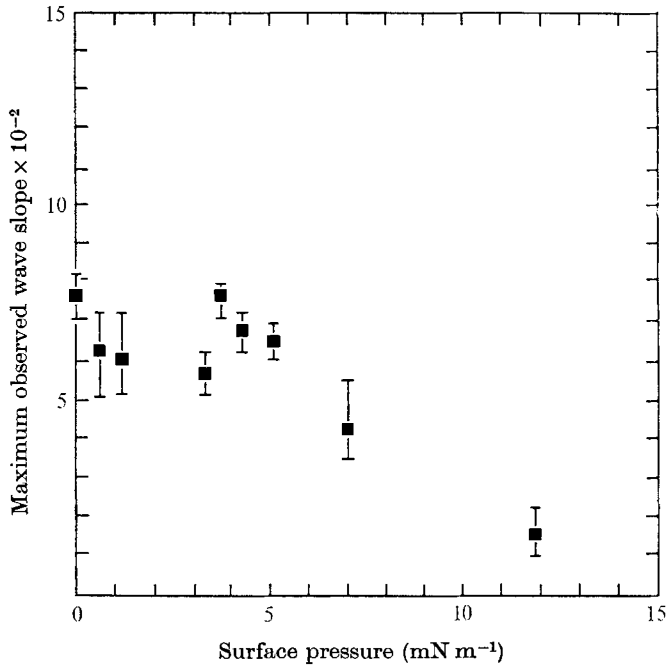

FIGURE 5. The damping effect of oleic acid monolayers of varying surface pressure. Water temperature = 20 °C, wind speed = 5 m s^{-1}.

(Lucassen-Reynders & Lucassen 1969). The fact that the effect is much smaller in the present case may be due to the monolayer loss mechanism described above, but it is most likely to be due to the dissimilarity between the present ripple initiation situation and free ripple damping. It is also possible that the observed increase in damping is more closely related to the residual effect in the observed area of existing ripples, generated upwind and travelling into the field, although by using a short fetch it was intended to reduce this possibility as much as possible.

Figure 6 shows the variation of slope with wind velocity for a dense monolayer of oleic acid, of surface tension 36·0 mN m^{-1}. The difference between this variation and the pure-water variation is shown by the 'clean surface' curve, drawn through the points given in figure 4. The low wind velocity damping is considerably in excess of both the contaminated-water and tap-water results of figure 4, which is understandable in view of the extreme contamination present. Of greater interest is the sustained high damping at wind velocities in excess of 5 m s^{-1}, and the rapid increase in observed wave slope which occurs between 6 and 7 m s^{-1}. In extending the picture described in § 3.2, it appears necessary to specify a given surface disturbance at which the monolayer influence diminishes, rather than a 'critical' wind velocity for the effect. For the slightly contaminated systems shown in figure 4, the velocity after which the monolayer began to lose its effect was between 4 and 5 m s^{-1}, the maximum wave slopes produced being around 5×10^{-2}. It is interesting to note that the dense oleic acid monolayer begins to lose its effect sharply after the wave slope reaches a similar value.

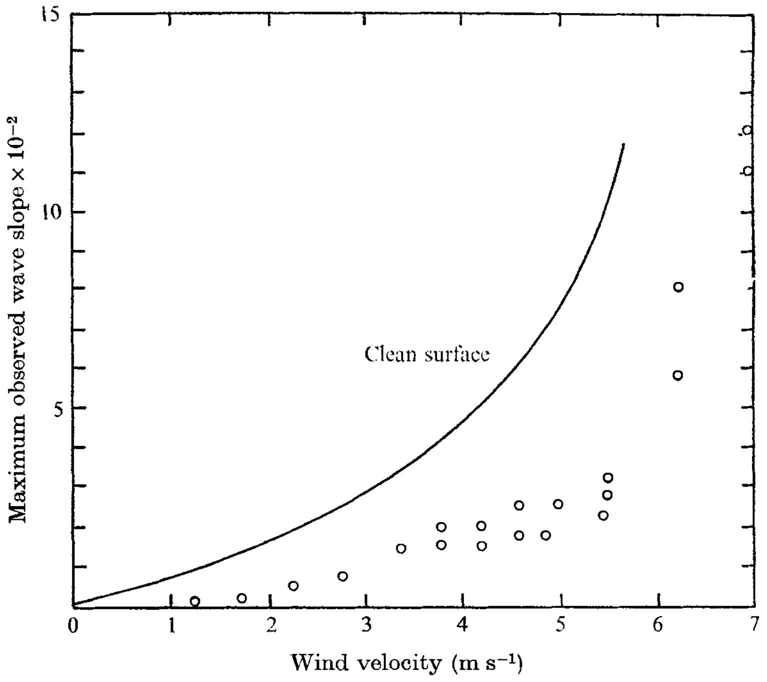

FIGURE 6. Surface disturbance of a dense oleic acid monolayer, surface tension = 36·0 mN m^{-1}, compared with the clean surface variation.

The results described so far indicate that an adsorbed monolayer on the surface of water has a damping effect on the initiation of ripples which in general increases as the contamination increases. At a level of wind excitation sufficient to generate maximum wave slopes around 5×10^{-2}, the interface is sufficiently disturbed to reduce the effect of the monolayer; unfortunately the range of surface slopes measurable with the present apparatus is not sufficient to determine whether at higher wind speeds the monolayer eventually has no effect. However, since it has been shown that an interfacial mixing process does exist, any surface effect at a wind speed adequate for thorough mixing will be small, more dependent on the bulk concentration of the dispersed insoluble material than on the initial surface concentration.

In an attempt to elucidate the role of mean surface tension in the behaviour of spread monolayers, a dense monolayer of relatively high surface tension was produced, the material being poly(ethylene oxide) WSR N10 (kindly supplied by Union Carbide Co.). This material is a polymer of mean molecular weight about 10^5, and although it is highly water-soluble, it has been found that it will spread at the air/water surface as though it were insoluble, and thereafter remain at the surface in a stable form (Scott & Stephens 1972). The spread material will even tend to return to the surface after forcible dispersion in the bulk water. It is believed that this tendency is due to the low probability that enough of the weakly adsorbed identical monomer segments of a long polymer chain can be simultaneously desorbed to effect complete desorption of the whole molecule. The molecules are apparently very flexible, since when a dense monolayer is

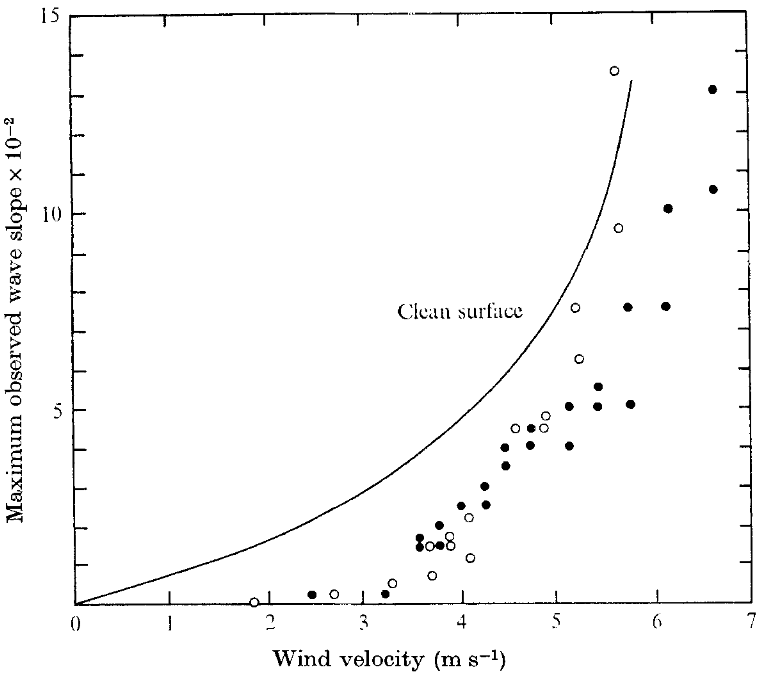

FIGURE 7. Surface disturbance of poly(ethylene oxide) WSR N10 monolayers. ○, spread; ●, from solution. Surface tension = 63 mN m^{-1}.

compressed, its dilational elasticity is very small, the surface tension being almost independent of surface concentration. This fact has been ascertained both by static surface tension measurements and by free ripple damping measurements (Shuler & Zisman 1970; Scott & Stephens 1972), and shows a contrast between this material and the majority of surface-active materials, whose monolayers show a steadily increasing elasticity as they are compressed to their minimum extent. The surface tension of a dense monolayer of WSR N10 is approximately 63 mN m^{-1}.

The results of the surface slope measurement on this spread monolayer are presented in figure 7, together with a further set of measurements on a solution of the same polymer, which will be considered in § 3.4. The spread layer is seen to damp the low wind velocity disturbance very heavily compared with clean water, more heavily, in fact, than the dense oleic acid monolayer, of much lower surface tension. This suggests that low-speed stability is not a simple function of surface tension. Beyond 4 m s^{-1}, however, the slope rapidly increases, approaching the clean-water values in the manner observed with other monolayers.

The fact that the damping is greater below 4 m s^{-1} for this 63 mN m^{-1} monolayer than for the oleic acid 36 mN m^{-1} monolayer is not easily explained. Apart from having a much higher surface tension, the elasticity of the WSR N 10 monolayer should be much smaller than that of the oleic acid monolayer, and Scott & Stephens (1972) found that the dense WSR N10 monolayer caused surprisingly little free wave damping compared with other dense monolayers. Scott & Stephens showed that as the surface pressure of a WSR N10 monolayer is increased from zero to its maximum value, the spatial damping of 30 Hz free ripples is observed to pass through two sharp peaks, each greater than the damping on a pure water surface by a factor greater than five. As the maximum surface pressure is approached, however, the free ripple damping decreases to a value well below the peaks. This behaviour was found to correlate very well with static measurements of surface tension and dilational elasticity using the theory of Lucassen & Hansen (1966).

3.4. *Effects of surfactant solutions*

The difference between a solution of surface-active material and a dense monolayer of the same material on pure water is that diffusional interchange is possible with the former, maintaining a dynamic equilibrium with active material on the surface. Thus the low wind speed properties of the WSR N10 monolayer described in § 3.3 (figure 7) are not expected to be changed by the presence of a relatively high (10^{-3} or 0·1 %) concentration of the same material in the substrate. As was mentioned above, the dilational elasticity of this particular monolayer has been shown to be small even in the absence of diffusional interchange. Measurements on the 10^{-3} solution presented in figure 7 are indeed very little different from the monolayer measurements, at velocities below $5\,\mathrm{m\,s^{-1}}$. Above that velocity, however, where the monolayer results tend towards the clean-water values, the solution values remain substantially more damped, even above $6\,\mathrm{m\,s^{-1}}$. The effect is not great, however, and the damping at these high wind velocities is less than for a dense oleic acid monolayer, in contrast to the behaviour at lower wind velocities.

In order to see whether the observed behaviour of poly(ethylene oxide) WSR N10 was connected in some way with the strange adsorption behaviour described in § 3.3, a second experiment was made, using another surface-active material, polyvinyl pyrrolidone (PVP), with almost identical surface tension. The reason for the choice of another polymer is simply that aqueous solutions of most available surface-active materials have very low surface tensions at concentrations of 10^{-3} (chosen to promote considerable diffusional interchange). Water-soluble polymers, although definitely surface-active, tend to have much less effect on the surface tension of the solution than other surfactants. The measured surface tension of the PVP used (PVP K-15, kindly supplied by GAF Co.) was $63\,\mathrm{mN\,m^{-1}}$ at concentration 10^{-3}, approximately the same as for the WSR N10 sample. The maximum slope measurements of the two polymer solutions are compared in figure 8. They have approximately the same effect on the wave initiation, implying that, in the supposed absence of low frequency dilational elastic effects, the wave stilling properties may be determined principally by surface tension. Although all water-soluble polymers are observed to increase the bulk liquid shear viscosity at high concentrations, the 10^{-3} concentration used here is not sufficient to produce an important increase for these particular samples.

Two other soluble surfactants were investigated, using similarly high concentrations. One of them was another polymer, Pluronic F38 (kindly supplied by Wyandotte Chemicals Co.), a copolymer of poly(ethylene oxide) and

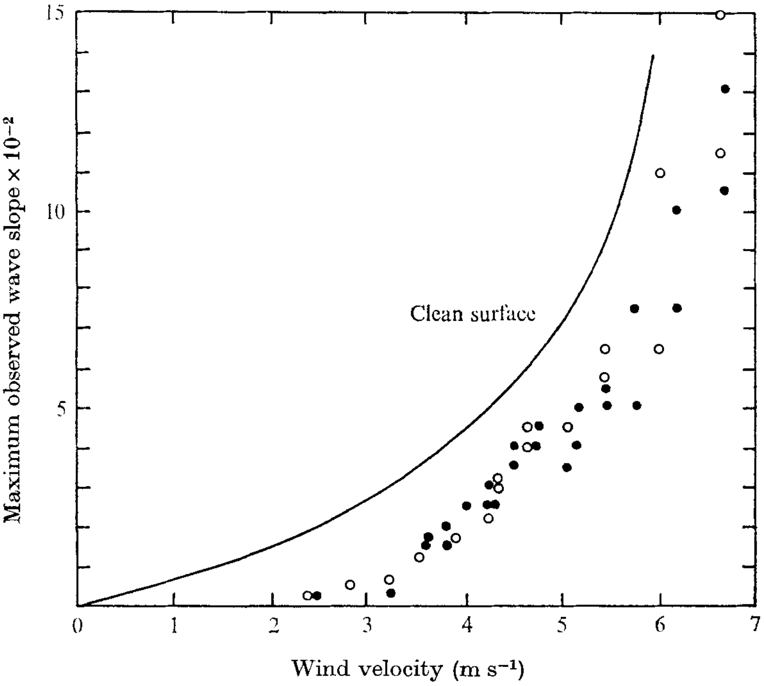

FIGURE 8. Surface disturbance of two solutions of the same equilibrium surface tension, 63 mN m^{-1}. ○, 10^{-3} concentration WSR N10; ●, 10^{-3} concentration PVP K15.

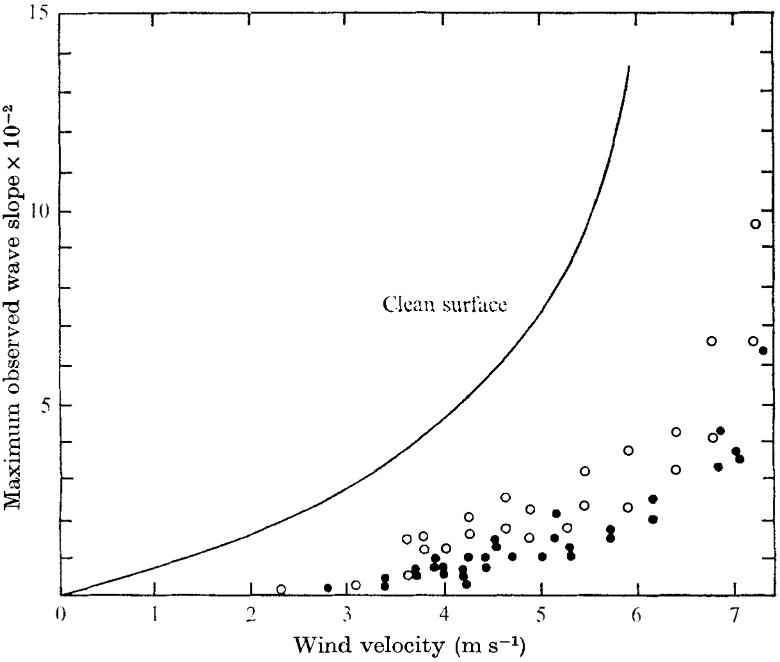

FIGURE 9. Surface disturbance of two surfactant solutions. ○, 10^{-3} concentration Pluronic F38, surface tension = 54·5 mN m^{-1}; ●, 10^{-4} concentration Tergitol 15-S-3, surface tension = 26 mN m^{-1}.

poly(propylene oxide) which had a surface tension of $54{\cdot}5\,\mathrm{mN\,m^{-1}}$ at 10^{-3} concentration. The second surfactant examined was Tergitol 15-S-3 (kindly supplied by Union Carbide Co.), a non-ionic ethoxylated linear alcohol. This material is not as freely soluble as the other chemicals examined; at the greatest possible concentration (about 10^{-4}) the surface tension of the solution was $26\,\mathrm{mN\,m^{-1}}$.

The measurements made on these two materials are presented in figure 9. The damping produced by both is considerably greater than that of all the other materials considered here, the solution with the lower surface tension, 15-S-3, having the greater effect. It is apparent that for such high concentrations of detergent, at which diffusional interchange between surface and bulk is expected to modify the elastic properties of the surface to a large extent, the wave initiation properties of the surface are strongly dependent on equilibrium surface tension.

4. Conclusions

By observing the effect of wind on a clean, pure water surface with a short fetch, it was found that a measurable surface disturbance is generated at wind speeds in excess of $1\,\mathrm{m\,s^{-1}}$, which becomes steadily greater as the wind speed increases. No evidence of a 'critical wind speed' was found, below which the disturbance is negligible. When the surface was allowed to be contaminated in a way not uncommon in large-scale experiments, by touching the water with human skin, the surface disturbance was significantly decreased at wind speeds below $4\,\mathrm{m\,s^{-1}}$. Similar results were found when tap water replaced the pure water, and also when controlled quantities of oleic acid, a pure surface-active insoluble contaminant, were present.

The occurrence of greater damping in the presence of small amounts of contaminating material indicates that, in wind/wave experiments at low wind speeds, extreme precautions must be taken to ensure that contamination is absent. In investigations of the wind/wave effect where films were definitely proved to be present, by means such as the observation of the damping of free ripples (e.g. Gupta, Landahl & Mollo-Christensen 1968), results for low wind speeds must be treated with caution.

The degree of contamination present may not be enough to affect the propagation of free gravity waves to a significant extent, but the observed reduction in the surface response in the short wavelength region suggests that the subsequent development of longer waves further downwind may be retarded. Another effect of this reduced surface response could be in the reduction of wind-generated roughness on the surface of pre-existing gravity waves. Wu (1968) concluded that the capillary wave content of a surface determined its aerodynamic roughness.

The surface damping effect of contaminating insoluble films was observed to decrease sharply when the maximum surface slope exceeded a value in the region of 5×10^{-2}. For 'slightly contaminated' systems such as were observed in § 3.2, this stage was reached between 4 and $5\,\mathrm{m\,s^{-1}}$, and it appeared that the contaminating film was being broken up, its material being dispersed in the bulk water. This mixing of the monolayer material into the deeper layers of the water may be related to the transition of the surface layers to turbulent flow. The existence of the mixing process suggests that wind/wave experiments conducted at wind velocities well beyond the 4–5 m s^{-1} 'transition region' may be free from the effects of slight contamination. The measurements on relatively high bulk concentrations of surface-active substances imply that, as 'accidental' water contamination increases, there will eventually be significant contamination near the surface even with some turbulent mixing, and the 'transition region' would be expected to move to increasingly higher wind velocities. However, for commonly used liquid depths, there is a wide range of surface concentrations of contaminant which would be expected to affect the surface only as a coherent layer, resulting in a very low bulk concentration when thoroughly mixed. The extent of the contamination can only be assessed by accurate *in situ* surface tension measurement, both before and after a very high velocity wind is allowed to destroy the coherence of the layer. Complete recovery of the pure-water surface tension value after the wind action implies that a particular surface may give valid results in the higher wind speed range, if not at low velocities.

The author wishes to thank the Office of Naval Research for their financial support of this work. The encouragement of Dr R. W. B. Stephens is also gratefully acknowledged.

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