III. *The Spreading of Fluids on Glass.**By W. B. HARDY*.*

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THE phenomena which accompany the spreading of an immiscible fluid over the surface of water under the influence of surface forces have been known for a long time and studied in great detail. The salient facts are these—when a small drop of some, not all, fluids is placed on a clean surface of water on which a few dust particles rest, a film of insensible thickness rapidly spreads from it in all directions, driving the dust particles before it. Sometimes, indeed usually, the drop itself also expands to a plate of sensible thickness which is in tensile equilibrium with the invisible film. This plate usually is not in equilibrium. It thins in places and, after certain changes, settles down to an irregular or regular pattern, the spaces of which are occupied by an invisible film, the counterpart of that which surrounds the expanded drop.

There are thus two distinct processes, the spreading to form the invisible film, and the spreading of the drop to form a layer. Some confusion has crept into the literature of the subject by the use of the same word to describe these two dissimilar processes. I propose therefore to distinguish the first as primary spreading and the surface formed by it as a “primary composite surface,” and the second as secondary spreading which forms a “secondary composite surface.” A primary surface is covered by a film of the order of 1 micron in thickness, whilst a secondary surface is covered by a layer from 50 to 500 microns in depth.

By employing pure chemical substances I was able to verify Lord Rayleigh’s suggestion, that the complicated secondary changes in a secondary composite surface are due to the chemical heterogeneity of the surface layer, and to prove further that when a drop of a rigorously pure chemical substance is placed on a clean surface of water, a primary composite surface is formed by the spreading from it of an invisible film, and there the matter ends, since the equilibrium state for a single pure chemical substance spread on water is such a surface in tensile equilibrium with a lens-shaped drop into which the excess of the substance is gathered†.

The existence of the invisible film is made manifest by the

* Communicated by the Author.

† *Proc. Roy. Soc. A.* lxxxviii. p. 314 (1913).

fall in surface tension occasioned by its presence, by the sweeping away of motes of dust on the surface as it spreads, and by the fact that it can be scraped off the surface, the surface tension being thereby raised to the full value of clean water. The movement of motes during the process of scraping shows that the invisible film confers on the surface the property of tangential elasticity or contractibility. This is an exceeding delicate test for its presence. The film is at an electrical potential different from that of the water; there is a contact difference of potential between it and the water*.

In the paper already referred to I described how drops of certain fluids of low chemical reactivity, *and whose vapour-pressure was negligible*, such as a paraffin of high boiling-point, could be placed on a clean surface of water without either displacing motes on the surface or lowering its tension, or making the surface "contractile."

Some fluids therefore will not spread on water *at all*, and that despite the fact that they are capable of lowering the tension of water. Saturated paraffins of low boiling-point will form a film, but that only by condensation of the vapour, and not by direct spreading of the drop, for reasons given in the earlier paper.

The point of interest and, so far as I know, of novelty, is that all these relations hold quite simply for a clean solid face. From a drop of certain fluids primary spreading occurs, if the fluid in question is not rigorously pure secondary spreading follows, and certain fluids will not spread at all.

A drop of acetic acid which has been purified by recrystallization when placed upon a surface of glass which has become contaminated by exposure to the atmosphere does not spread. On clean glass the drop flattens out rapidly, dust particles or drops of water being swept away. It was found, however, that the flattening was due to the water vapour present in the air. The remarkable character of the action as an instance of the operation of small quantities of matter upon surface energy cannot be exaggerated.

Attention was drawn to it by the following observation. A clean plate of glass was placed in a chamber through which a rapid current of dry air was flowing. After the plate had been in the chamber for 30 minutes, the cover was lifted slightly for a moment to allow of a drop of acid being placed on the plate from a fine capillary tube. The drop at once spread to an even layer, thin but distinctly visible. After being for some minutes in the dry air the layer altered.

* Proc. Roy. Soc. B. lxxxiv. p. 220 (1911); A. lxxxvi. p. 608 (1912).

It thinned in places, and the thicker parts contracted into a number of bead-like drops which then slowly moved towards one another and fused until finally one or a few drops remained, the rest of the plate being apparently but not really free from acid. On lifting the cover even for a moment the drops at once expanded again, and the layer again proceeded to contract when the cover was replaced.

The question therefore arose whether acetic acid would spread if water vapour were rigorously excluded. By a simple device drops were placed on the glass plate without lifting the cover, and no flattening occurred. But though the drop remained where it was placed without visible change, there had in fact spread from it over the plate an invisible film. In other words, the single pure chemical substance acetic acid behaves on glass as does a single chemical substance on water; from it a film spreads to form a primary composite surface, and if any secondary spreading of the drop itself occurs it is due to an impurity—in this case water.

It is not possible to measure the surface tension of a solid in the simple way applicable to fluids, but the existence of an invisible film of acid covering the surface can be proved by the fall in static friction which it produces.

The static friction of a clean glass plate measured in the way described in the last paper was found to be 0.92 gramme per gramme weight of the watch-glass. A small drop of acetic acid was placed on the plate near one corner. It remained apparently unchanged, but the friction of the general surface was found to have fallen to 0.47 gramme per gramme weight. The surface was therefore covered by an invisible film of acid. In the complete absence of aqueous vapour, pure acetic acid forms a primary composite surface on glass with the excess acid gathered into a lens just as, for instance, oleic acid or benzene will form a primary surface in tensile equilibrium with a lens on clean water.

Tripropylamine, just distilled to a constant boiling-point, exhibits precisely similar phenomena. A drop placed near a corner of a plate lowered the static friction over the whole surface to 0.25 gramme per gramme weight of the watch-glass.

When water is present in the acetic acid itself, or as vapour, the acid behaves on glass just as does an impure chemical substance on water. A drop spreads to form a secondary composite surface. The concentration of water needed to upset the equilibrium of a drop of pure acid and induce secondary spreading must be incredibly small. A drop of

acid standing quietly on the surface at once spreads if the cover to the chamber be slightly lifted for a moment *whilst the current of dry air is pouring in*.

For reasons to be given presently, it is important to note that these observations on the behaviour of acetic acid were made at 18°C .

Not all fluids will spread to form a primary composite surface on water, and this is true for glass. At 18°C . neither castor oil nor B.P. "paraffin" formed such a surface when drops were placed on a plate.

When more than one drop of acetic acid is present on a plate at 18°C ., the existence of an invisible film about them is manifested in a curious way. Drops which are not more than one or two centimetres apart attract one another. They become oval in outline, the long axes being directed towards one another, and slowly move across the plate until they meet and fuse. The edge of the plate acts like another drop, a single drop tends to move to the edge and cling there, but the edge does not attract it so strongly as does another drop. The experiment is a simple one, but very striking. The invisible film is nowhere greater than 1 micron in thickness, yet it is capable of pulling large drops of fluid along. The stress per unit area of transverse section must be enormous.

The reason for the movement of the drops is probably to be found in the evaporation due to the current of dry air. The film everywhere is thinned by this, and the tension of the composite surface therefore greater than what it would be if the space above were saturated with the vapour of acetic acid. The evaporation is continually made good by the drops which are as continually feeding the film. The surface tension in a line joining two drops will therefore always be *lower* than elsewhere. Why are the drops not pulled away instead of towards each other? The answer can only be that on the general surface of the plate the layer is so thin and so closely applied to the solid face as to have lost fluidity. It is practically a non-contractile solid. Between the drops it is thick enough to preserve some degree of fluidity and it contracts, pulling the drops together. This explains the fact that drops more than 1 to 2 centimetres apart do not attract each other at 18°C .

There is much of interest in considering how the water vapour acts when it causes the drop of acetic acid to spread over the primary composite surface. The most obvious suggestion is that it is condensed on to the composite surface where, by diluting the film of acetic acid, it raises the

tension and the drop of acid is pulled out to a plate. Of course, the same result would be produced if it diluted the drop of acid and lowered the tension of one or both faces, but the quantity of water operating would seem to be too small to produce a sensible change in a large drop of acid.

The suggestion that the water vapour condenses on to the primary composite involves a paradox, namely that a vapour can condense on to a surface whilst raising its surface tension. At first sight this looks like a spontaneous increase in free energy. A parallel case can, however, be found. When the area of a primary composite surface of pure oleic acid spread on water is contracted, by narrowing the boundaries, it is possible sometimes to force the surface tension down to a very low level. The surface is then supersaturated with the acid, and it not infrequently changes, apparently spontaneously, the excess acid gathering itself into lenses, and this change is accompanied by a *rise* in the tension*.

Returning to the case of acetic acid, the fact that a drop which has spread rapidly contracts when in dry air, points to the aqueous vapour being condensed on to the composite surface and not on to the lens; for in the latter case the acid is present in mass, and water would not readily distil off from a very concentrated solution of acetic acid. If the water distils off the primary composite surface more readily than the primary acid, we may conclude that it lowers the surface energy of glass less than does the acid; and this is in agreement with the fact that water does not, and acetic acid does, lower the static friction of glass.

When a layer of sensible thickness of a pure fluid such as benzene is formed on water and allowed to thin by evaporation, it becomes unstable when the thickness falls to a certain point. The layer then thins in places so as to form primary composite surfaces, and the excess benzene is gathered into a lens-shaped drop or drops. The surface energy is a function of the depth of the layer of benzene, but it is a discontinuous function. At the edge of a drop of a pure fluid which is on water and in tensile equilibrium with a composite surface, a peculiar state must therefore obtain, for at the junction of the drop with the film the instable thicknesses must be somehow bridged over, just as are the instable thicknesses at the junction between the black or grey areas with the rest of a soap-bubble. There is then this difference between the formation of a primary and a secondary composite surface by spreading from a drop: in

* Proc. Roy. Soc. A. lxxxviii. p. 326 (1913).

the latter the edge state moves bodily over the surface, and in the former the substance of the drop has to be, as it were, dragged through the instable thickness. It is this latter fact which I think accounts for the remarkable phenomena exhibited by a drop of ethyl hydrocinnamate on water*.

The importance of the vapour in jumping the barrier at the edge of a drop must not be overlooked. Experience of the formation of primary composite surfaces on water by many pure chemical substances leads me to conclude that the surface is formed by actual spreading of the substance of the drop itself only when the sum of the tensions of the upper and lower surfaces of the lens-shaped drop is considerably less than that of water, or, using Gibbs's notation, in which the vapour phase is indicated by the numeral 1, the water by 3, and the substance which is to form the composite surface by 2, when $T_{12} + T_{23}$ is considerably greater than T_{13} .

Taking oleic acid and ethyl hydrocinnamate as examples:—

	$T_{12} + T_{23}$	T_{13}
Oleic acid	$31 + 15 = 46$	< 74
Ethyl hydrocinnamate ...	$33 + 24 = 57$	< 74

When the sum of the tensions is only slightly less than that of water, the drop does not flash over the surface, it remains apparently unaltered, but it is the vapour phase which condenses to form the primary composite surface, *e. g.*:

Octane	$20.6 + 53 = 73.6$	< 74
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These relations are clearly indicated by Gibbs†, but for the purposes of some part of his argument the surface 13 is the primary composite surface, and not the water-air surface.

No fluid amongst those which I examined was found to flash over glass. Judged by the fall in static friction, a film takes some seconds to spread a few centimetres from a drop of acetic acid.

Whether primary or secondary spreading does or does not occur on a fluid face depends mainly upon the relative value of the surface tensions, but on a clean solid face it must depend wholly upon the vapour tension. For consider a drop of any fluid placed upon a clean solid surface. The tension of the latter (T_{13}) may be much greater than $T_{12} + T_{23}$: but, since the 13 surface is not contractile owing to its solidity, the disparity of force acting at the edge of the drop is inoperative.

* Proc. Roy. Soc. A. lxxxviii. p. 324 (1913).

† Trans. Conn. Acad. vol. iii. p. 422.

If vapour is given off from the drop it will condense to form a primary composite surface, and this *being contractile* may pull the drop itself out to form a secondary surface. The fact that B.P. "paraffin" and castor oil do not spread at all on clean glass is due to their low vapour pressure, and is no evidence as to the tension of the glass-oil interface.

I confess I should not have expected that a film of fluid of the order of 1 micron in thickness on a solid face would be spontaneously contractile, but the migration of the drops of acetic acid appears to afford conclusive evidence on this point. Any primary composite surface will contract only if a further thickening of the film lowers the surface tension. A fully formed primary surface, that is to say one in which the film has thickened to the point at which the function $\frac{dT}{dx}$ (where T is the tension, and x the thickness of the film) changes its sign, would have no tendency to contract; indeed it would resist further contraction. The fact that primary surfaces saturated with fluid actually do contract spontaneously when exposed to air, is due frequently to the thinning of the surface film by evaporation. This is readily demonstrable with pure benzene on water. Substances such as benzene on water and acetic acid on glass behave in fact as though the film on a primary composite surface varied in thickness with variations in the vapour pressure of the fluid of which it is composed. If this be so the film on a composite surface cannot be always and of necessity one molecule thick as some writers suppose.

IV. *On the Discovery of Four Transition Points in the Spectrum and the Primary Colour Sensations.* By FRANK ALLEN, Ph.D., F.R.S.C., Professor of Physics, University of Manitoba, Winnipeg*.

THE researches in colour-vision which I have made from time to time have had for their secondary object the extension of our knowledge of the persistence of vision, and for their primary object the determination in an incontrovertible manner, if possible, of the number of fundamental colour-sensations, and the precise waves of light by which they are excited, concerning which there has been and still is much controversy.

In this communication I have gathered together some

* Communicated by the Author.