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II. *Note on Static Friction and on the Lubricating Properties of certain Chemical Substances.* By W. B. HARDY and Flight Lieutenant J. K. HARDY, R.A.F.*

(From the Goldsmith Metallurgical Laboratory, Cambridge.)

IN the Philosophical Magazine for February 1918, Lord Rayleigh describes experiments which were undertaken to examine more particularly the well-known fact that a few drops of water wetting the parts in contact will prevent a cup of tea from slipping about in a saucer. A glass carriage with three legs terminating in three feet of hemispherical form was made to slide over a plate of glass or copper. The horizontal pull needed to cause movement was found to be 42 grams where the surface was covered by a film of oil estimated as being of the order of 1 micron in thickness. The superposition of a layer of water on the film of oil decreased the lubrication, the threshold value of the force rising to 126 grams, that is a threefold increase, and the effect was the same when the water layer was a film deposited by the breath as it was when the plate was completely flooded.

Paraffin (lamp) oil gave a similar result, the force needed to bring about slipping being least when the layer of oil was of insensible thickness. Therefore, in Lord Rayleigh's words, the "friction is greater with a large dose than with a minute quantity of the *same* oil, and this is what is hard to explain."

We started with the object of clearing up if possible this paradoxical phenomenon, and in a certain sense this limited aim has been attained. The two cases, namely, water on a grease film, and lamp oil used alone, are similar in that the phenomena in both cases are due to chemical heterogeneity. Lamp oil appears to consist of substances of high lubricating power dissolved in a more volatile fluid with little or no lubricating power. In the process of forming a thin film the former are concentrated on the surface by evaporation of the latter.

It was felt at the outset that no progress would be made unless individual chemical substances were used. Ethyl ether, ethyl alcohol, and benzene were tested, the specimens in each case being supposed to be pure. Each fluid was found to act to some degree as a lubricant, but no consistent figures could be obtained. This suggested the presence of

* Communicated by the Authors.

impurities. By following up this clue it was found that none of the three substances mentioned above had when chemically pure any power of lessening the pull needed to cause the one glass face to slip over the other. Chemical substances in fact fall into two classes according to whether they are active or inactive in this respect under the conditions of the experiments. Water is an inactive substance, and this is the basis of the tea-cup experiment.

In our observations watch-glasses weighted with lead run into them whilst hot were used. A small arm projecting from the lead was attached to a silk thread which passed over a pulley to a pan which held the weights. We were at some pains to procure a glass plate for the watch-glasses to slide upon having an "optical" face. But it was found that ordinary plate glass gave the same value as the plate with an accurately plane surface. Measurements were carried out on a levelling table.

Plates and glasses were cleaned by washing with soap-powder and then rubbing under a vigorous flow of tap-water with the finger-tips, previously washed, until the peculiar clinging stage was reached which sets a finger-bowl vibrating when the wet finger-tip is rubbed round the edge. Both plates and glasses were drained and dried in air. Contamination will creep over the clean surfaces from solids touching them, therefore contact during the drying process must be reduced to a minimum*.

A solid surface dried in air will retain a layer of water in equilibrium with the aqueous vapour, and some of the fluids used, such as acetic and sulphuric acids, absorb water. For these reasons it was necessary to carry out the measurements in air free from aqueous vapour. This was done by using a chamber through which a rapid stream of dry and dust-free air could be passed. The results recorded below will not be obtained unless this precaution be taken. In such a chamber a cleaned surface retains its purity for hours, the substances used to dry the air seeming completely to remove the lubricating matter which condenses to form the "grease" film on surfaces exposed in the ordinary way.

According to the accepted view a "clean" surface as defined above would differ from the "raw" surface produced by splitting a solid in a vacuum by the presence of a layer

* In using a Pockell's trough to measure the surface tension of water under various conditions, in order to obtain really steady readings, one of us found it necessary to reduce contact between the trough and the table by interposing a couple of glass rods.

of condensed gas. There does not, however, appear to be conclusive proof of the existence on all solid faces of such a layer. It would seem therefore that we can assert nothing as to the presence of a layer of foreign matter on a "clean" surface of glass in contact with dry air.

The tangential force was applied gradually about 1 cm. above the centre of gravity of the watch-glass by slowly withdrawing support from the pan. The effect was to cause the watch-glass to rock forward until equilibrium was reached, when the static friction balanced the tractive force. If the latter were increased beyond a certain quantity determined by the nature and state of the surfaces static equilibrium was not reached, but the cohesion gave and the watch-glass moved bodily forward. The limit of static friction is the force which just fails to bring about this movement forwards. It is called the "threshold value."

The watch-glasses were of the same pattern and make, but differently weighted. The threshold values in grammes were :—

Watch-glass.	Weight.	Pull.	Pull per gr. wt.
1	54·25 grms.	46 grms.	0·85
2	58·5 „	50 „	0·85
3	57·79 „	51 „	0·85
4	170·2 „	143 „	0·84

For plates of a rather greenish glass—

5	14·58 grms.	13·5 grms.	0·93
	„ „	16·2 „	1·1
6	58·25 „	54·2 „	0·93
7	46·95 „	45·0 „	0·96

Over a considerable range therefore and for clean surfaces the threshold value is, as a first approximation, equal to the total weight multiplied by a constant which is different for different kinds of glass.

The effect of temperature was tested by altering the temperature of the stream of dry dust-free air passing through the chamber, the actual temperature of the surfaces being taken to be that of a thermometer whose bulb was inside the chamber. Over the narrow range available no effect of importance was detected.

Glass 2.....	15.5° C.	Pull 49.5 grms.
	19.	„ 49.5 „
	23.	„ 50. „
	23.7	„ 51. „

In order to be certain that the watch-glass and plate were actually at the temperature of the air in the chamber, each stage occupied about an hour. The experiment therefore affords striking testimony to the steadiness of the state of clean surfaces for over four hours in clean dry air.

These observations were undertaken merely to satisfy ourselves that small fluctuations of temperature did not introduce sensible error.

The forward movement is always accompanied by an actual tearing of *both* glass faces. The length of the tear on the plate is of course determined by the distance forward the watch-glass travels. The length of the tear on the watch-glass is much the same, and is caused by the glass rocking backwards when the seized faces give.

The appearance to the naked eye or hand-lens is that of a fine scratch pointed at one end. A high magnification (1000 to 2000 diameters), however, shows that there is no regular continuous cutting of the faces. On both watch-glass and plate the scratched line is composed of an irregular collection of very shallow pits and very thin plates which have been torn from the opposite face. The track begins at the pointed end, it rapidly widens, and the sides, which are more or less clearly defined, become parallel. It ends abruptly with a square or bluntly rounded end. At the pointed end where the movement starts, it consists of delicate flakes or pits of the order $1\ \mu$ across.

These features prove that cleaned faces cannot slide over one another. The forces of cohesion come into play and they seize. Once seized, the substance of the glass fractures before the seized faces will give. Very slight normal pressure is needed to cause seizing. An unweighted watch-glass cannot be moved on a plate even quite slowly without producing these characteristic torn tracks, if both faces are really clean.

The breadth of the track may be as much as $50\ \mu$. Why does it broaden? Why does it not continue as it begins at a breadth of about $1\ \mu$? The widening cannot be due to the abrasion of the curved surface since the contact is continually changing owing to the rocking backwards of the watch-glass.

The appearances suggest that it is owing to minute and very rapid vibrations or oscillations of the watch-glass at right angles to the direction of pull. When the glass tears the "give" is not directly in the line of the pull, the watch-glass is thus thrown out of its balance to one side or the other with the result that it chatters forward vibrating rapidly from side to side. The breadth of the track is determined by the amplitude of these vibrations. When a watch-glass is moved by hand, owing to the unsteadiness of the motion the track commonly begins in more than one (five or six) fine lines which keep separate for say 40μ and then blend into one wide track.

The appearance under the microscope is consistent with the view that the faces are seized before movement starts, and the thesis developed in these pages is that static friction both of clean and lubricated faces is due to cohesion which, in the case of clean faces, causes the glass itself to seize and in the case of lubricated faces causes the film of lubricant on the one face to seize to that on the other face.

We can find no justification for the view commonly held that static friction is due to inequalities of the surfaces. Actual measurements proved that the threshold value for glass with an "optical" face is the same as that for ordinary plate glass, whilst the value for ground glass is lower probably because it is impossible to clean it. If static friction be due to inequalities these must be of insensible magnitude, and "inequalities" of this order are indistinguishable from the attractions of individual molecules* across the interface.

The weight of the watch-glass will form a depression in the plate, and it might be supposed that resistance to slip is due to this fact, the surface of the plate being heaped up into a crest which ruptures and so starts the tear when the stress exceeds a certain limit. This amounts to supposing that the watch-glass acts as a cutting tool. Deformation of both surfaces must occur, but the action cannot be of the kind just described since *both* faces are torn, and always in such a way as to detach very thin flakes. The microscope reveals no sign of a burst through.

The resistance offered to slip is large. If it be due to cohesion, why should there be no sensible resistance to displacement of the surfaces along the normal?

Two answers may tentatively be given to this very difficult question. The first is that, in movement along the normal,

* This word is used merely to denote the units out of which the matter is built.

the curved is as it were peeled off the flat surface, so that the force required for an infinitely small displacement is infinitely small.

This answer is more general than would appear at first sight. The range of the force of cohesion is so small that all surfaces, no matter how carefully trued, may be considered to touch only at the summits of elevation. The play of Newtonian colours between glass plates affords pretty testimony to this.

The second answer is, that at the surface of any solid or liquid the molecules are orientated by the normal component of the forces of attraction, and that this contributes specially to resistance to slip.

It is not easy to see why cohesion should resist slip since the potential energy of the forces of attraction will be the same wherever contact is made.

If both faces were formed of continuous solids there would be no initial force to resist slipping, though there would be dissipation of energy in compression waves *during movement* if the bodies were elastic.

Resistance to slip must be due to the discontinuity of matter. When the applied faces are at rest the molecules on either side of the interface take up the position in which the potential of the attractive forces is minimal. Consider a single molecule: it will "seize" in a position of least potential and a tangential force applied to it produces a displacement until the internal and external forces on it balance one another. If the molecules of a solid were able to change partners freely, as they can do in a fluid, slipping would occur, as it of course does occur in a fluid. The fact that solid faces will not slip past one another when external force is applied, means that the uncompensated force on the molecules at the surface increases rapidly for displacements from the equilibrium position which are small in comparison with the distances between their centres. Why, then, is there not resistance to slip, that is to say, initial resistance as distinct from the dissipation of kinetic energy during relative motion, in a fluid? The answer is to be found in the fact, which van der Waals emphasized, that the problem is dynamical and not statical. Increase in the heat energy decreases the damping of the heat vibrations of a solid until a point is reached at which the molecules are able to change partners freely.

Resistance to slip is, however, not due merely to the short range of the forces acting on the molecules, but to their orientation. In 1913 one of us showed that the work done

by the forces of cohesion in the formation of an interface is determined by the chemical nature of the substances concerned, and that it is greatest when the molecules of these substances are of a salt type such as esters, acids, or alcohols. It was then pointed out that such molecules are readily polarizable, and that they would be oriented by the forces acting across the interface* and that this orientation is the cause of contact difference of potential. From this it was inferred that "The surface film (of fluid or solid) must therefore have a characteristic molecular architecture and the condition of minimal potential involves two terms, one relating to the variation of density, the other to the orientation of the fields of force" of the molecules †.

The theory of surface forces has since been developed along these lines in a very striking and beautiful way by Harkins ‡ and Langmuir §.

Any polarization of the molecules at the surface must introduce a factor in the resistance to slip which is absent from any resistance there may be to displacement along the normal, for the former includes the resistance which the molecules may offer to disturbance of their orientation, and this might be as great as or even greater than the resistance to displacement of the molecule as a whole along the axis of the normal to the interface.

If this view be correct, the effect of a tangential force would be to produce a fresh orientation of the molecules at the interface, and this would, amongst other things, alter the contact electrical potential between the faces. In the case of fluids, the new orientation would disappear when the external force was removed, but in the case of solids the new orientation would be irreversible if it exceeded a certain small amount ||, and the work done in causing slip would

* Proc. Roy. Soc. A. lxxxvi. p. 610 (1912); *ibid.* A. lxxxviii. p. 312 (1913).

† *Ibid.* A. lxxxviii. p. 330 (1913).

‡ Journal of the American Chem. Soc. xxxix. p. 354 & p. 541 (1917).

§ *Ibid.* xxxix. p. 1848 (1917).

|| Since the above was written we have come across two lectures by Sir Alfred Ewing, in which he suggests that friction may be due to the attraction between molecules. ("The Molecular Process in Magnetic Induction," Royal Institution of Great Britain, May 1891: "The Inner Structure of Simple Metals," Journal of the Institute of Metals, viii. 1912.) When one face is made to slide past the other "the polar forces continue to act across the plane of sliding, causing first a quasi-elastic turning (of the molecules); but when a certain very limited range of movement is exceeded there is dissipation of energy through the original bonds being broken and new bonds established with oscillation of the particles."

be in part consumed in producing this new setting of the molecules.

There is fortunately direct evidence available to prove that irreversible changes in molecular configuration are produced when clean glass faces are forced over one another. The original interface is preserved at the junction of the thin flakes, torn off one solid, with the other solid, and these flakes are found to be doubly refractive.

Lubricated Faces.

The effect of the depth of the layer of lubricant must be taken account of. No attempt was made to measure this, but three stages were distinguished—the film, the smear, and complete flooding. A film is a layer completely invisible, of depth insufficient to give Newtonian colours and almost certainly of the order of $1\ \mu\mu$. A smear is a visible but thin layer. In complete flooding the watch-glass moves in a pool.

The difference between the film and the two other states of the surface is more than one of mere depth of the layer. We know from experiments with fluids that when a layer of one fluid spreads upon another, the surface energy is at first a function of the depth of the layer. Thus, when olive oil spreads on clean water, the surface tension is a function of the quantity of oil per unit area until this exceeds a certain limit at which two independent interfaces are formed, that of oil-air and that of oil-water. Over the range of varying tension the properties of the surface, such as its chemical potentialities, its electric charge, and its mechanical tension, are a function of the thickness of the film on the surface, the chemical composition of the material composing the film and the fluid on which it lies, and the temperature. Surfaces of this kind, whose properties depend upon the interaction of two kinds of states of matter, have been called by one of us "composite surfaces" *.

The experiments described in this and the following paper prove that in the "film" stage of lubrication we are dealing with a composite surface.

The feature of a composite surface which is of most importance in lubrication, is that the energy per unit of mass of the film is a function of position on the axis of the normal. Two consequences follow—the film resists tangential displacement, and therefore has tenacity, and, since

* A soap-bubble is composed of two composite faces placed back to back, *cf.* Proc. Roy. Soc. A. lxxxvi. p. 609 (1912).

the potential energy of the molecules composing it is a function of their position, the film is not completely fluid even though it be formed from material which is a fluid when in mass at the same temperature and pressure. This is true of composite surfaces of fluids as well as of solids.

Owing to this defect in fluidity composite surfaces are capable of seizing, and the static friction of such surfaces is, in our opinion, due to this fact.

By seizing is meant the capacity for offering resistance to slip when both faces are at rest. Though it is due to the operation of the same forces of attraction as bring about cohesion, resistance to slip and cohesion are not identical. Any internal surface of a fluid may be considered to be formed by bringing together two fluid faces which cohere, but there is no resistance to slip gained thereby. Composite faces resist slip because of their defect in fluidity.

If the matter stopped here, if, that is to say, the defect in fluidity were due solely to the surface energy being a function of the thickness of the film, static friction between composite plane faces would be purely an edge phenomenon and would vanish if the area of the faces was infinite. The way in which the energy of an interface depends upon chemical constitution, the fact, already noted, that it is closely related to the polarizability of the molecules, proves that the surface energy is a function of the orientation of the molecules as well as of their position on the axis of the normal, and it is to this that we may look for the source of the static friction of composite surfaces as well as of clean faces. There is, indeed, no final distinction between composite faces as defined and clean faces, for there is an orientation of the molecules at the surfaces of any fluid or solid, and this skin, which has its own peculiar configuration, constitutes, as Gibbs pointed out, a separate phase.

The distinction between the film and the smear or flooded states of a surface is now seen to be not merely one of degree but one of kind. This follows not only from what has been just said, but also from the way in which the surface energy varies with the thickness of the film. The well-known phenomenon of the grey and black area of soap-bubbles, and the fact that a layer of fluid of small but sensible depth when spread on another fluid or on a solid, is not in equilibrium, but breaks under the influence of surface forces into a film and thick sheets or lenses which are in tensile equilibrium with the film, proves that the surface energy is a

discontinuous function of the thickness. When the layer is about 1 micron thick the function changes its sign. There is thus a region of instability, or regions of instability, which definitely mark off the composite surface from the true double surface.

In static lubrication a layer of fluid is interposed between two solid faces. Now, though we know that the energy of a composite surface is a discontinuous function of the depth of the layer of fluid when the surface is bounded on the one side by air or vapour, we know nothing directly of the form of the function when it is bounded by another solid. Let us assume that it is discontinuous also in this case, and consider what must happen when the two solid faces are forced together by a normal pressure. The fluid will be squeezed out the less rapidly the greater its viscosity until a certain critical thickness is reached at which the layer becomes unstable. It will then collapse until the thickness is reached at which the surface energy begins to increase as the thickness decreases. The film now has gained tenacity and lost fluidity. For a certain normal pressure therefore a certain critical thickness of film will persist, and therefore a certain definite resistance to slip. The critical thickness may be expected to vary very little over a wide range of pressure since the energy of thin films is a rapidly varying function of their depth.

The layer of fluid must have some tenacity to be able to maintain itself, and as increase in tenacity and loss of fluidity go together, a limit will be set to the lubrication. The resistance to slip will never wholly vanish as it should do if the surfaces were separated by true fluid. Thus, what Osborne Reynolds calls "boundary conditions" must always operate in static friction, whereas they may be absent in kinetic friction. The existence of a discontinuity in the variation of energy with the thickness of the layer of lubricant would tend to confine this maximum of lubrication within narrow limits, and observation shows this to be the case.

As the facility for slipping increases the character of the movement changes. When the surfaces are clean the pull is 0.85 or 0.93 gramme per gramme normal pressure, and steady slow sliding motion cannot occur owing to the violent seizing. As the facility for slipping increases seizing decreases, and the motion assumes more and more a gliding character. When the threshold value has fallen to

0.1 gramme per gramme weight true gliding is completely established. Any small increase in the tangential force beyond the threshold value now causes a slow glide without noticeable acceleration. In other words, the state of the surfaces is such as to dissipate any small increments of energy as heat as fast as they are gained.

No fluid was found which would increase the facility for slipping beyond this point. It appears to be a true maximum for the kind of surfaces employed. Between this maximum and the minimum of clean surfaces there is a greater or less degree of seizing which must be broken away. The force necessary to effect the break away is too great to be absorbed as heat, and the movement therefore, instead of being a steady glide, is characterized by more or less marked acceleration.

Films of lubricant can be deposited on the surfaces in many ways, such as by bubbling the air which comes to the chamber through the fluid (ethyl alcohol, ethyl ether, benzene, water, ammonia fortiss., acetic acid); by flooding the surface and evaporating off the excess with dry pure air until nothing visible remains (acetic acid, tripropylamine, and triethylamine); by flooding the surface, washing off excess with a vigorous stream of tap-water, and draining and drying the plate and watch-glass in the way described earlier (acetic acid, oleic acid, sulphuric acid, castor oil, and paraffin); or by flooding the surface with a very dilute solution in pure dry ether and evaporating off the ether with dry air (oleic acid, castor oil).

Technically, the most beautiful method of forming a film is by taking advantage of the fact, dealt with more fully in the next paper, that a totally invisible film is formed about a drop of some fluids when placed upon a clean glass plate, provided water-vapour is completely excluded. With a substance such as tripropylamine, in order completely to alter the state of the whole surface of the plate it is sufficient to place near one corner a small drop of the fluid.

It is not permissible to form a film by polishing off excess with "clean" linen since such linen for these purposes is not clean. Simply polishing the surface with clean linen effectively lubricates it by leaving behind an invisible film.

If the static friction of lubricated surfaces is determined by the variation of the surface energy, we should expect to find it closely dependent upon the chemical constitution of the lubricant. This is the case, and the most unexpected

fact is that certain fluids have no power of lowering the friction.

The *inactive fluids* discovered were :—Ethyl alcohol, ethyl ether, benzene, water, and ammonia fortiss. sp. gr. ·880. Films of insensible thickness and visible layers were without any influence upon the friction, as also was light and heavy flooding. Finally, these fluids when dried off left the surfaces uncontaminated and the cohesion unchanged.

It is of course obvious that when a layer of any fluid in mass is maintained between solid faces, the friction will be fluid friction and the facility for slipping infinite. Thus, when two glass plates are flooded with water or ammonia and placed face to face, the one plate can be readily slipped past the other since a layer of fluid is maintained between them by capillarity. But a very slight normal pressure suffices to displace such a layer, and the faces then seize. Inactive fluids therefore are lubricants only in this limited sense. *They are inactive in the sense that they have little or no power of so altering the solid surfaces as to facilitate slipping.*

This statement may be put in another way. The available energy of a composite surface is a function of the thickness of the layer of fluid. If the energy increases as the thickness is reduced the layer will resist displacement. In the case of inactive fluids the variation of the available energy must be such as to confer little or no capacity for resisting displacement. The behaviour of ordinary commercial glycerine is interesting in this connexion.

Glycerine is remarkable in that it can increase the facility for slipping nearly if not quite to the maximum, but only when the surfaces are heavily flooded, when, owing to its viscosity, and in consequence of the rocking forward of the watch-glass, a thick layer of fluid is maintained between the solid faces. A film of glycerine had no effect whatever, thus :—

Glass 2. Clean : Threshold value 51 grammes.

	Films*.	Smear.	Plate flooded and drained.	Heavily flooded.
Threshold value ...	51	43	30	6
Per gr. pressure ...	·87	·73	·51	·10

* Deposited from a ·002 per cent. solution in alcohol, the plate being flooded with the solution and dried off without draining four successive times without change in the threshold value.

Glycerine therefore belongs to the class of inactive fluids as defined above.

By looking for the Newtonian colours one can form some conception of the depth of an inactive fluid which must be maintained between the plates to permit freedom of movement. With strong ammonia ($\cdot 880$) most violent seizing occurred so soon as these colours began to appear. With water, seizing was perhaps less violent and Newtonian colours well seen before it took place.

Active Fluids are those which facilitate slipping when present on the surfaces in layers of any thickness. They operate when the layer is of insensible thickness and of the order of 1 micron in depth. It may be claimed therefore that it is not *quâ* fluid that they act, but because they react with the solid face to form a composite surface having a lower available energy and therefore a lower capacity for seizing.

The active substances differ amongst themselves, as might be expected, in the extent to which they reduce friction; some only are capable of reducing it to the limit, noticed in a previous section, at which a slow steady glide is possible. Threshold value in grammes per gramme normal pressure :—

	Film.	Smear.	Flooded.
Acetic acid	$\cdot 62$	$\cdot 73$	$\cdot 73$
Butyric acid	$\cdot 5$	$\cdot 5$	—
Oleic acid	$\cdot 1$	$\cdot 1$	$\cdot 17$
Sulphuric acid	$\cdot 58$	—	$\cdot 75$
Strong Hydrochloric acid	—	—	$\cdot 63$
Trimethylamine, strong solution ...	—	—	$\cdot 6$
Triethylamine	$\cdot 39$	—	$\cdot 32$
Tripropylamine ..	$\cdot 26$	—	$\cdot 27$
Pyridine (impure sample).....	—	$\cdot 46$	—
Castor Oil	$\cdot 1$	$\cdot 1$	$\cdot 1$
"Paraffin"	$\cdot 29$	$\cdot 15$	$\cdot 22$

The influence of chemical constitution is seen in the sharply contrasted action of acetic acid and ammonia, the former is active the latter inactive; in the alkaline series, ammonia, trimethylamine, triethylamine, and tripropylamine. It will be noticed, too, that friction slightly increases as the quantity of an acid present on the plate increases, and decreases slightly as the quantity of an alkali present

increases. In both acids and alkalies the activity of the fluid increases as the molecular weight increases.

If these several relations are confirmed by more extended investigations, the case "hard to explain" of lubrication diminishing as the quantity of lubricant increases will arise, but, when the bulk of the measurements given above were made, the extreme sensitiveness of the faces to minute traces of water was not appreciated by us (see the next paper). The figures given in the table were obtained under comparable conditions, but they are not free from the suspicion of the influence of water. The sample of butyric acid almost certainly contained a trace of water. Acetic acid in the complete absence of water-vapour gave the values :—

Weight of watch-glass.	Film.	Flooded.
46.95 grammes.	0.47	0.36
170.2 ,,	0.64	0.58

The film, however, is subject to intense evaporation, due to the rapid current of dry air. The maximum of lubrication was therefore probably not reached. Acetic acid frozen on the plates gave the values :—

Weight of watch-glass.	Film.	Flooded (<i>i. e.</i> sensible layer of ice).
65.25 grammes.	0.23	0.23

The sample of tripropylamine was specially purified, and the values given in the table were obtained in the complete absence of water. The vapour-pressure of this substance is low, and the values therefore are probably close to its maximum of lubrication.

The evidence, so far as it goes at present, is against the conclusion that lubrication is a function of the quantity of lubricant on the plate when the lubricant is a single pure chemical substance, and when its viscosity is not very great.

The fluid called "paraffin" is the rectified "paraffin" of the British Pharmacopœia. It was somewhat uncertain in its effects, behaving as though it were a mixture of active and inactive substances.

The basis of the original observation on the tea-cup is revealed by these results. The sticking of the cup is not due to the fact that a thick layer of homogeneous fluid lubricates less than a thin layer, but to the fact that an inactive fluid, in this case water, diminishes the effect of an active fluid. There is much of scientific interest in the way the water acts. It does not remove or even temporarily detach the film of lubricant, for the full influence of the latter is restored when the water is dried off. On the other hand, it would seem to lessen the grip of the film on the glass, for the latter can be detached by lightly rubbing the surface *under the water*.

Glass 2. Paraffin. Film polished with linen : Threshold value 10.5 grammes. 17° C.

Flooded with water	18 grammes.
Rubbed lightly under water with the finger-tip, which had been freed from grease by washing	36 ,,
Rubbed more vigorously	41 ,,

Glass 3. Castor Oil. Polished film : Threshold value 11 grammes. 19° C.

Flooded with water	Pull 18 grammes.
Rubbed under water with cleaned finger-tips	,, 43 ,,

That the water should act by reducing the tenacity of the film is quite in accord with the classical theory of capillarity. When the film is formed of a *solid*, flooding the surfaces with water has no effect, the solidity of the film apparently enabling it to resist the tangential stress. A solid film was formed by coating a clean surface of glass with melted solid paraffin. The excess was then polished off with linen until nothing visible remained. The threshold value was found to be 0.1 gramme per gramme weight. Flooding the surface with water did not alter this value.

Attention has already been drawn to the fact that ordinary "pure" ether and benzene contain a lubricant in solution and leave behind a lubricating film on evaporation. Rectified spirit also contains an impurity which causes it to behave

in an interesting way. Friction was lowered when the plate was flooded with the spirit, but rose to the "clean" value when the fluid was completely dried off. The point of interest is that the full value was not restored until the layer of fluid had been reduced by evaporation to well past the Newtonian colour stage.

Actual values in grammes are :—

Clean 49; flooded 43; Newtonian colours seen about 45; colours vanished 46; and one hour later 49.

The question now arises whether the difference between active and inactive substances is one of degree or one of kind. The final answer must be left to further investigation with more refined apparatus. All that can be said now is that the inactive fluids were inactive for the lightest as well as for the heaviest watch-glass used. On the other hand, an insensible film of an active fluid lubricates the surface for the heaviest watch-glass used, and in the case of tripropylamine, oleic acid, castor oil, and paraffin just as effectively as for the lightest glass. The insensible film formed by spreading from a drop of tripropylamine under the influence of surface forces gave for instance the following values :—

	Weight of watch-glass.	Threshold value per gramme weight.
Flooded ...	46·95 grammes.	0·24 gramme.
Film	46·95 "	0·25 "
	170·21 "	0·26 "

Temperature 10° C.

SUMMARY.

One of us has shown that the variation of the surface energy at an interface between two fluids, and of a composite surface is closely related to the chemical constitution of the substances concerned. The inference to be drawn is that the work done in forming the interface or the composite surface is done by chemical forces. In the theory of capillarity as developed by Young and Laplace cohesive forces are taken to be, like gravity, incapable of saturation, and unlike gravity only in being of very short range. If cohesive forces are chemical they are capable of saturation, or, as a chemist would put it, of neutralization, and the film of matter on a composite surface may be said to reduce the

surface energy by neutralizing to a greater or less extent the forces at the surface of a solid or fluid. The function of a lubricant is to reduce the energy of the surface, and thereby to reduce the capacity for cohesion and the resistance to slip when two composite surfaces are applied the one to the other. The function of a lubricant therefore is the opposite to that of a flux. A good deal is to be gained, in our opinion, by recognizing lubrication as a special case of that incomplete chemical reaction characteristic of surfaces in which the law of multiple and definite proportions does not hold.

Evidence for the orientation of the molecules at an interface or on a composite surface which we take to be the source of static friction, is to be found in the fact that chemical substances whose molecules are by their nature readily polarizable such as those of acids, bases, and esters, produce the greatest changes in surface energy*, and that there is contact difference of potential between the film of a composite surface and the matter on which it lies†. This holds even when no part of the matter concerned can with certainty be said to be pre-ent in mass as in soap bubbles. In these "free films" the films on each face are at an electrical potential different from that of the middle portion‡.

The theory of static friction which seems best to accord with the facts is that it is due to cohesion between the faces. When a lubricant is present we may consider the friction as operating at an imaginary surface situated in the lubricant parallel to and midway between the solid faces. This surface is an interface between two composite surfaces, and may be considered as being formed by bringing these two composite surfaces together. Work is done by the forces of cohesion when the film of lubricant is applied to the solid face to form each composite surface, and the surface energy is decreased by this quantity. A further quantity of work is done when the two composite surfaces are applied to one another with a further change in the surface energy. The static friction is an unknown function of the total change in surface energy.

* Proc. Roy. Soc. A. lxxxviii. p. 303 (1913).

† Proc. Roy. Soc. B. lxxxiv. p. 220 (1911).

‡ Proc. Roy. Soc. A. lxxxvi. p. 608 (1912).