#### THE FRICTION OF LUBRICATED METALS

## By F. P. BOWDEN AND L. LEBEN

Laboratory of Physical Chemistry, Cambridge

(Communicated by G. I. Taylor, F.R.S.—Received 11 August 1939)

[Plates 1-5]

#### ABSTRACT

An analysis has been made of the kinetic friction between metals sliding under conditions of boundary lubrication. With mineral oils and many other lubricants an intermittent clutching and breaking away of the surfaces still occurs through the oil film. The friction, the surface temperature and the area of contact all show violent fluctuations and the behaviour may be essentially the same as with unlubricated metals. Certain substances, however, are able to prevent this "stick-slip" motion and allow continuous sliding to take place. With short-chain fatty acids, for example, the motion is "stick-slip", but when the chain reaches a certain length continuous sliding occurs. Alcohols and saturated hydrocarbons of the same, or longer, chain length do not cause continuous sliding. Even with the best lubricant the film breaks down to some extent during sliding and some wear of the surfaces takes place. The metal is torn to a depth which is large compared with the dimensions of a molecule. The frictional force between lubricated metals must therefore be greatly influenced by the bulk properties of the metals concerned.

The frictional behaviour of metallic surfaces covered with successive monolayers of lubricant has also been investigated. A single layer can cause a large reduction in the friction but the film is soon worn away. With multilayers the rate at which the film wears off is markedly dependent on its molecular thickness and methods are described for measuring the rate of wear of lubricant films. A single film of long-chain fatty acid molecules is more effective than a single film of the flat leaf-shaped cholesterol molecule.

It is clear that a primary film is not sufficient, but that for effective boundary lubrication it is necessary to have present a layer of lubricant several molecules thick. The experiments show that boundary lubrication cannot be regarded as a purely surface phenomenon.

On the basis of these experiments a theory has been put forward to explain boundary lubrication. In general it appears that even with lubricated surfaces the local pressures in the region of contact are very high, so that the lubricant film between the surfaces is partly broken down. If the sliding speeds are appreciable this breakdown is aided by the local high temperatures. Metallic junctions, the size of which is large compared with the dimensions of a molecule, are formed between the surfaces. There will, of course, be some resistance due to the interaction of the surface films themselves, but under many conditions of sliding the resistance to motion is due mainly to the force necessary to break the junctions. The frictional behaviour of boundary lubricated surfaces is therefore largely governed by the extent to which the lubricant film breaks down during sliding.

It has been known for a long time that many substances reduce the friction between sliding solids, and several theories have been put forward to account for this. The most comprehensive and systematic work is due to Sir William Hardy and his collaborators (1919–34). This work has shown the great importance of the "boundary" layer and the influence of the length of the adsorbed molecule on its lubricating properties. Hardy's measurements were confined to static friction, that is, to a measurement of the force required to start the motion between the stationary solids. The results are

Vol. 239. A 799 (Price 8s. 6d.)

[Published 27 June 1940

explained on the assumption that the adsorbed films of lubricant on each surface remain intact and that the frictional resistance is due entirely to molecular interaction between the outside surfaces of the two adsorbed films. A more detailed examination of kinetic friction shows that the physical processes that occur during sliding are more complex, solid contact occurs through the lubricant film, the solids are distorted and torn to a considerable depth, and it is clear that kinetic friction cannot be regarded as a surface phenomenon (Beare and Bowden 1935).

A recent analysis of the kinetic friction between unlubricated metals (Bowden and Leben 1937, 1939) has shown that the motion may not be continuous: an intermittent clutching and breaking away of the surfaces takes place during sliding. Since the surfaces touch only locally at the summits of the surface irregularities, the area of contact is small and the local pressures are sufficiently great at these points to cause plastic flow of the metal. When the surfaces move the area of contact changes and there is a well-marked correlation between these changes and the frictional fluctuations (Bowden and Tabor 1939). It was suggested that the friction between the unlubricated metals was due to the formation and subsequent breaking of metallic junctions between them.

This paper describes the results of an analysis of the frictional behaviour of lubricated metals. The metals were carefully cleaned, but the experiments were carried out in air so that oxide and other films were present. These surface films have a very important influence on the friction (Bowden and Hughes 1938, 1939). Two methods of adding the lubricant were used.

In the first method a comparatively large amount of the lubricant was applied to the surface, either directly or from solution. Excess was then wiped off, leaving behind a film many thousands of molecules in thickness. With the high loads and low speeds used in these experiments the conditions were those of boundary lubrication. Experiments with metals lubricated with mineral oils and many other lubricants showed that the frictional behaviour is very similar to that observed with unlubricated metals. The friction fluctuates and the motion again proceeds by a process of "stick and slip". At the same time considerable wear of the surfaces takes place. It is clear that an intermittent clutching and breaking away of the surfaces is occurring through the oil film. The influence of the length of the molecule was investigated for a number of pure straight-chain acids, alcohols, and hydrocarbons. With the short-chain fatty acids stick-slip occurs, but as the chain length increases the stick-slips become smaller and finally disappear so that continuous sliding occurs. At the same time there is a considerable reduction in the wear between the surfaces.

The second method of adding the lubricant was based on the Langmuir and Blodgett technique for the deposition of multilayers on solids. By this method single layers could be added to the metal and the film built up to any required thickness. It was found that a film one molecule thick may have a profound effect on the friction and may change the motion from stick-slip to continuous sliding. When sliding occurs

the film is worn off. The influence of film thickness on the friction and wear was investigated, and a comparison was made between the behaviour of single and multiple films of a flat leaf-shaped molecule, such as cholesterol, with that of a long rod-shaped molecule such as a fatty acid. The bearing of these observations on the theory of lubrication is discussed.

#### EXPERIMENTAL

The apparatus has been described elsewhere (Bowden and Leben 1939). The lower surface was a flat steel plate which was driven at a uniform rate by a water piston. The upper surface which rested on the plate was a small curved steel slider which was attached to a high-frequency device for measuring the frictional force. This force could be recorded photographically in a moving-film camera, so that any rapid fluctuations that occurred in it could be measured. The surfaces were prepared by fine grinding and lapping on lead laps with 320 carborundum and were carefully cleaned. The speed of the lower surface in these experiments was usually ca. 0.003 cm./sec., and the applied load varied from 400 to 5000 g. Two forms of the apparatus were available, the smaller for use at low loads and the larger for use at high loads. The frictional behaviour was essentially the same at all the loads and speeds used.

The lubricants which were liquid at room temperatures were applied to the surface either directly or with a piece of specially purified cloth. Except where otherwise stated, excess lubricant was then wiped off until only a comparatively thin film remained on the surface. This film was, however, still many thousands of molecules in thickness. Lubricants solid at room temperatures were usually deposited on the surface from a dilute solution in pure acetone. If necessary the surface could be warmed by an electric heater and the solid lubricant film thus melted.

Immediately after each experiment the lubricant was cleaned off the lower steel surface with acetone and a photomicrograph taken of the track. In the following figures the tracks obtained under a load of 400 g. are shown; this enables comparison to be made with the results shown in the previous paper for unlubricated surfaces.

#### RESULTS

#### Mineral oils

The frictional behaviour of a medicinal paraffin oil, of a white oil which was principally naphthenic but contained 2-3% of aromatic compounds, and of another commercial oil is shown in figure 1 (plate 1). In these traces the passage of time is from right to left. The tangential force between the surfaces is recorded by the trace. This tangential force divided by the normal load gives the coefficient of friction, and the value of this is marked on the ordinates. Each trace therefore represents the fluctuations of the friction with time. These fluctuations all consist of a period AB, during which the tangential force is increasing steadily, followed by a very rapid fall

BC. A measurement of the slope of the line AB shows that the top surface is moving forward with the same velocity as the bottom one, i.e. there is no relative motion of the surfaces; they are sticking together. Suddenly at B a very rapid slip of the upper surface occurs. When the tangential force has fallen to C the surfaces again stick and the process is repeated indefinitely. In each case therefore the motion proceeded by a process of stick and slip. Even if a large excess of lubricant was placed on the surface so that the slider was moving through a pool of liquid it was found that stick-slips still occurred. Figure 1 also shows that the average value for the coefficient of friction for each oil lay between 0.1 and 0.2.

A photomicrograph of the track formed with paraffin oil as lubricant is shown by the arrow in figure 1 d. The magnification is 50. With the other oils essentially similar tracks were obtained. It will be seen that with paraffin oil a well-marked track is cut in the lower surface. This track is similar to, but somewhat smaller than, that observed with unlubricated metals.

The fluctuations in the frictional force between the surfaces would be expected to give rise to corresponding fluctuations in the surface temperature. To test this experimentally the surface temperature was measured by the thermoelectric method, as described in earlier papers. Figure 1e shows the results obtained for constantan sliding on steel with paraffin oil as lubricant. It will be seen that the surface temperature as well as the frictional force is in fact fluctuating violently during sliding. During the stick the surface temperature remains sensibly constant, but at the instant a slip occurs there is a sudden rise and fall in the surface temperature. The whole temperature flash may be over in less than a thousandth of a second. Similar results were also obtained in the presence of other lubricants.

## Fatty acids

The friction and wear of a series of saturated fatty acids of increasing molecular weight were examined, and the results are shown in figures 2 and 3 (plate 2).

It was found that with the lower members of the series—acetic, propionic, and butyric acids—motion proceeded by stick-slips and the behaviour was similar in many ways to that shown by mineral oils. Typical traces for acetic acid and propionic acid are shown in figure 2a, b. As the molecular weight was increased, however, a marked change in the frictional behaviour was observed. The stick-slips gradually diminished in size and eventually, at caproic acid, they disappeared. All the long-chain acids above caproic acid prevented stick-slip and allowed continuous sliding to take place between the surfaces instead. The friction in every case was low  $(\mu=0.1)$ , and very little change occurred in the frictional force during sliding. The traces for caproic acid and pelargonic acid are shown in figure 2d, e. The higher fatty acids are solid at room temperatures, but this change of state did not affect the frictional behaviour. Furthermore, if the lubricant were melted on the surface continuous sliding still occurred. The results of the experiments with cerotic acid are shown in figure 3a, b.

The first of these traces shows the behaviour of the friction when the acid was present on the surface in the solid state at room temperature, while the second shows the results after heating the steel plate to a temperature sufficiently high to melt the cerotic acid. It is clear that continuous sliding occurs whatever the state of the lubricant. A similar behaviour has been found with capric, lauric and myristic acids, all of which are solid at room temperatures.

Valeric acid was intermediate in behaviour and showed both types of sliding; sometimes stick-slips would take place, while at other times continuous sliding occurred. An actual change from one type of sliding to the other during one run is shown in figure 2c.

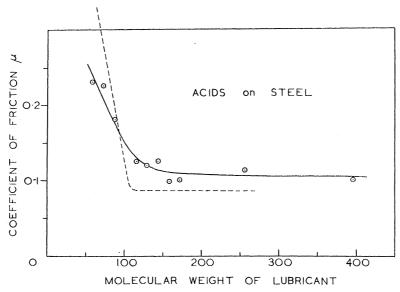


Figure 4. The dotted curve shows the results obtained by Beare and Bowden (1935) for sliding speeds of 600 to 60 cm./sec.

Interesting changes in the mean value of the frictional force were also observed, and the average coefficient of friction for each fatty acid is plotted against the molecular weight in figure 4 (continuous curve). The coefficients given are those obtained with the acids in the liquid state and with the surfaces moving at a higher speed of 3.0 cm./sec. It will be seen that for the lower members of the series  $\mu$  has a comparatively high value. However, the value of  $\mu$  decreases with increasing molecular weight, and from caproic acid onwards  $\mu$  remains constant at the low value of 0.1. This curve is in very good agreement with the results obtained by Beare and Bowden (1935) for the kinetic friction between surfaces sliding at speeds of 600 to 60 cm./sec. (figure 4, dotted curve).

Photomicrographs of the tracks were also taken after each run, and it was found that when the stick-slips disappeared there was a corresponding reduction in the wear between the surfaces. With the lower fatty acids extensive tearing was observed; a photomicrograph of the track formed with propionic acid is shown in figure 3c. The

higher fatty acids, however, gave very little wear, and figure 3d shows a typical trace obtained with caprylic acid as lubricant. A broad band (indicated by arrows) can be seen marking the region over which the upper slider had passed. An occasional scratch is visible within this band showing that some seizure of the surfaces had occurred, but the wear is obviously much less than that shown for propionic acid. (The comparatively great width of these tracks is due to the fact that a small flat was initially present on the upper slider during these two runs.)

A marked corrosion of the surfaces occurred with the shortest fatty acids, but this decreased in extent as the molecular weight increased. A little corrosion was observed with caproic and heptylic acids and none at all with the acids of greater molecular weight.

#### Primary alcohols

The friction of the homologous series of saturated primary alcohols was investigated. It was found that, provided the lubricant was present on the surface in the liquid state, the motion always proceeded by stick-slips, and there was no sign of any change-over

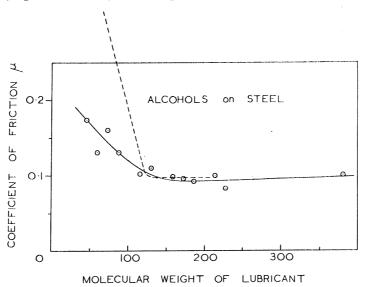


FIGURE 6. The dotted curve shows the results obtained by Beare and Bowden (1935) for sliding speeds of 600 to 60 cm./sec.

in the frictional behaviour with increasing molecular weight such as that shown by the fatty acids. For illustration, the traces obtained with butyl alcohol and octyl alcohol are shown in figure 5a, b (plate 2). With all the alcohols considerable wear occurred between the surfaces during the sliding, and figure 5e shows a photomicrograph of the track formed with octyl alcohol as the lubricant. This track is very similar to those obtained with the other members of the series.

The relation between the molecular weight of the alcohol and the mean coefficient of friction is shown in figure 6, and it will be seen that  $\mu$  falls to a minimum value with increasing number of carbon atoms. The behaviour is essentially similar to that shown

by the fatty acids and is in agreement with the results obtained at higher speeds by Beare and Bowden.

When the lubricant was present on the surface in the solid state a different behaviour was always observed and continuous sliding was found to take place. Cetyl alcohol is a solid at room temperatures and was deposited on the surface from a solution in acetone. Immediately after deposition stick-slips were observed and the average friction was high  $(\mu = ca. \ 0.3)$ , but soon a gradual change in behaviour became evident. The friction slowly fell, the stick-slips became smaller, until eventually continuous sliding set in and the friction remained steady at the low value of  $\mu = 0.1$ . The final frictional behaviour is shown in figure 5c. This change of friction with time might have been due to some latent period phenomenon (see Hardy), but it is more probably to be explained by the evaporation of the last traces of acetone from the surface. Only when a solid coherent film of cetyl alcohol had finally formed on the surface was continuous sliding possible. This hypothesis was confirmed by a subsidiary experiment in which cetyl alcohol was deposited directly on the surface from the molten state and the friction of the solidified film measured. Continuous sliding was found to occur from the very start, and there was no sign of any subsequent change in the behaviour. If the temperature of the steel surface was then raised so that the film of alcohol melted, the motion changed over to stick-slips (figure 5d). On again solidifying the alcohol the continuous sliding was resumed.

## Hydrocarbons

It has been shown that in the presence of mineral oils motion proceeds by stick-slips. Since these oils are mixtures of various hydrocarbons, it was expected that the pure hydrocarbons themselves would show a similar type of behaviour. The friction of several straight-chain paraffins has been examined and it has been found that, provided the lubricant was liquid, stick-slips did always occur. Typical examples of such behaviour, obtained with nonane and hexadecane, are shown in figure 7a, b (plate 1). However, when the lubricant was present on the surface as a solid a different behaviour was observed and continuous sliding was found to take place. The results of experiments with the paraffin  $C_{22}H_{46}$  are given in figure 7c, d, and the influence of the change of state on the nature of the sliding is clearly seen. It is evident that the paraffins are essentially similar in their frictional behaviour to the saturated straight-chain alcohols. Figure 8 shows the relationship between the average friction and the molecular weight, and it is seen that  $\mu$  again falls to a constant minimum value with increasing chain length. This behaviour is essentially the same as that found with acids and alcohols, the main difference being that with the paraffins a greater number of carbon atoms is necessary before the minimum value of  $\mu$  is attained.

## Mixtures of lubricants

Several workers have observed that the addition of a trace of a fatty acid to a mineral oil can bring about a considerable reduction in the friction and wear. It was considered of interest to determine whether a change in the nature of the sliding also occurred as a result of such an addition.

Experiments were first tried with a medicinal paraffin oil as the base. When in the pure state this oil gave stick-slips as shown in figure 9a (plate 3). A photomicrograph of the track formed has already been given in figure 1d. The frictional behaviour of a 1% solution of caprylic acid in this oil was then measured and the results obtained are shown in figure 9c. It will be seen that the stick-slips had disappeared and that continuous sliding was taking place between the surfaces. The mean coefficient of friction

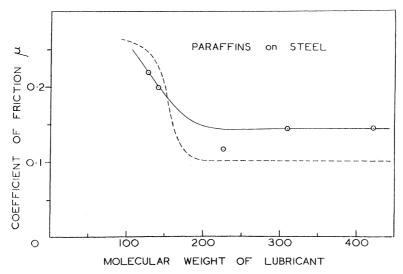


Figure 8. The dotted curve shows the results obtained by Beare and Bowden (1935) for sliding speeds of 600 to 60 cm./sec.

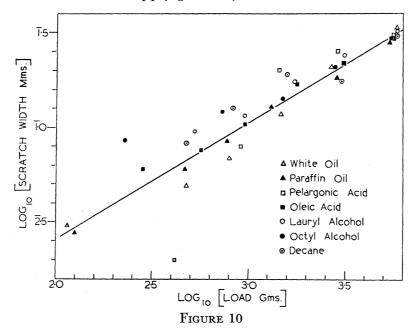
was equal to 0.13 and was therefore slightly less than that found for the pure paraffin oil. A photomicrograph of the track formed under these conditions is given in figure 9g. The track lies between the arrows and is barely visible on the photograph. It is clear that the wear had been considerably reduced by the addition of the fatty acid.

The experiment was repeated with a commercial mineral oil and similar results were obtained. The frictional behaviour of the pure oil is shown in figure 9b, and it is seen that the usual stick-slips were taking place. The track formed was very similar in appearance to that obtained with paraffin oil as lubricant (figure 1d). Figure 9d shows that addition of a trace of palmitic acid to the oil eliminated the stick-slips, and observation of the track showed that the wear was also reduced. The same result was obtained by adding a small amount of a commercial dope (A7, Asiatic Petroleum Co.) to the pure mineral oil (see figures 9e, h). In another experiment the friction of a

solution of cetyl alcohol in the same mineral oil was examined, and the results obtained are shown in figure 9f. It will be seen that motion still proceeded by stick-slips, and it is clear that the addition of this substance did not bring about any change in the frictional behaviour.

## The effect of load on the friction

The dependence of the frictional behaviour on the load was investigated for the following substances: paraffin oil, white oil, pelargonic acid, oleic acid, octyl alcohol, lauryl alcohol and decane. For all these substances it was found that variations of the load caused no essential change in the frictional behaviour. With all the lubricants except pelargonic acid and oleic acid motion occurred by stick-slips throughout the range of load 1000–5000 g. With the acids, however, no sign of stick-slip motion was observed at any load—continuous sliding always occurred. The results described in the previous sections therefore apply generally.



The main effect of increasing the load was to increase the magnitude of both the average friction and the fluctuations. In general it can be stated that both the average friction and the magnitude of the fluctuations are approximately proportional to the load.

The tracks formed at various loads were also examined microscopically, and for each lubricant no noticeable change in the appearance of the track was observed with different loads. It was frequently found that the track was not uniform in appearance. Under the microscope the track appeared as a broad band, part of which seemed to be extensively cut and deformed while the remainder showed a much smaller deformation. Furthermore, the general appearance of the track varied for different lubricants. Thus a good lubricant, such as a long-chain fatty acid, showed only a few tear marks

within the broad band over which contact had occurred. On the other hand, with a bad lubricant, such as a mineral oil, the track was extensively torn over most of its width. The sum of the widths of both these deformed parts was taken as the real width of the track, and this quantity was measured for each load. The width increased with increasing load, and the relationship between these quantities for all the lubricants tested is shown in figure 10. It will be seen that the points on the graph tend to fall together on one straight line. That is to say, the width of the track formed at any given load during sliding is approximately the same whatever the lubricant present between the surfaces. This agreement is most marked at the higher loads; in particular, the track widths at the highest load of 5000 g. are almost identical. At the lower loads the agreement is less satisfactory, but in view of the difficulty of accurate measurement of the small track widths it can be considered to be sufficient.

#### THE FRICTION OF MULTIMOLECULAR FILMS

The results already described have shown that during sliding continual breakdown of the lubricant film and seizure of the surfaces takes place. However, in these experiments a comparatively large quantity of lubricant had been placed on the steel plate, so that it is probable that even though the lubricant film was partly destroyed during the moment of contact the film was repaired again immediately after the surfaces separated from one another. For a fuller understanding of lubrication we need more detailed knowledge of the conditions governing the breakdown process and the rate at which destruction of the film takes place. A detailed study has therefore been made of the frictional behaviour of surfaces covered with thin films of molecular dimensions.

There are several methods by which a film whose thickness is only of the molecular order of dimensions can be deposited on a surface. When a drop of a suitable liquid is placed on a solid surface a film spreads out from the drop and, according to Hardy, this film is only one molecule thick. Condensation from the vapour phase has also been made the basis of a method for the formation of films on surfaces and, by suitable variation of the concentration of the vapour, Hardy was able to control the thickness of the film so formed. In another method, recently described by Claypoole (1939), the oil is converted into a highly dispersed fog of positively charged particles and the fog then allowed to deposit itself on to a negatively charged metal surface. By this means films of the order of  $10^{-7}$  cm. can be obtained, the final thickness depending on the length of time during which deposition is allowed to take place.

The most convenient method for the deposition of very thin films is, however, that devised by Langmuir and Blodgett (Blodgett 1935), and it was a very slightly modified version of this technique that was used in the present series of experiments.

### Method of deposition of films

A unimolecular film of the substance to be used as lubricant was first spread from petro-ether solution on to the surface of ordinary tap water contained in a glass trough. Successive films were then transferred to the steel surface by the usual dipping process; oleic acid was used as piston oil. The transference of the film from the water to the steel was followed by closely observing the movement of the waxed silk barrier separating the lubricant film from the piston oil, and the dipping process was repeated until the required number of films had been built up. It was found that during the first few dippings the surface was hydrophilic, so that it was necessary to allow the films to dry on between each immersion. After a few dippings, however, the surface became hydrophobic and films could then be deposited in rapid succession.

The steel plate on which the previous experiments had been carried out was found to corrode in the presence of water, and in order to avoid this happening a similarly shaped plate of stainless steel was used in its place. The upper slider was also of stainless steel and possessed a considerably larger radius of curvature and a greater area than the mild steel slider previously employed.

Two substances were used as lubricants in the course of these experiments. In the first part of this work a solution of stearic acid was spread on the water, but, from the results of other workers, it is known that the films deposited on the metal consisted, not of stearic acid, but of a mixture of stearic acid and calcium stearate. For the second part of the work cholesterol was used as the lubricating substance. This material forms very stable condensed films, and it was thought possible that it might function as a very efficient lubricant. The stearic acid films were usually found to deposit during both the up and the down movement of the steel plate (Y deposition), but the cholesterol film during only the downward part of each dipping (X deposition).

The recent work of Bikerman (1939) has shown that recrystallization occurs in the film, so that the surface becomes covered with a layer of microcrystals. Nevertheless, the method is a very convenient one for the deposition of films of known and controllable thickness, in spite of some uncertainty as to their exact structure.

### Experimental procedure

The larger form of friction apparatus was used and two main series of experiments were carried out with each lubricant.

In the first set of experiments the small upper curved slider was covered with a known number of films while the lower surface was unlubricated. The surfaces were very carefully placed in contact under a load of 5000 g., and the lower surface was then started moving at a speed of 1.0 cm./sec. The behaviour of the kinetic friction from the very beginning of the sliding was recorded in the camera. After the run the track was photographed and special care was taken to include in the photomicrograph

the part corresponding to the beginning of sliding. The experiment was repeated several times with different thicknesses of film on the upper surface.

In the second set of experiments a known number of films were deposited on the lower plate while the upper surface in most cases was kept unlubricated. The surfaces were allowed to slide together under a load of 5000 g. and the friction recorded at intervals. The upper slider was then run repeatedly over the same track on the lower surface and the friction during each run observed. The process was continued for 100 runs, or until the friction had risen to a very high value and the surfaces were being badly torn. A small portion of the original track was preserved so that the wear after one run could be compared with the wear at the end of the experiment. The experiment was then repeated with different numbers of films on the lower surface.

A few experiments were also carried out in which films were deposited on both surfaces; the latter type of experimental procedure was employed.

#### RESULTS

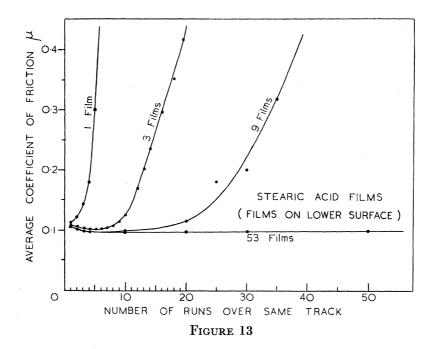
## Stearic acid films

(1) Films on upper surface only. Figure 11 (plate 3) shows the photographs obtained with various numbers of unimolecular films on the upper surface. The instant at which sliding began is indicated by the letter A on each photograph. It will be seen that in every case immediately after motion began the friction was low and was equivalent to a coefficient of 0.1. The friction, however, remained at this low value only for an instant and soon began to show a gradual rise. The photographs show that the fewer the number of films on the upper slider the greater was the rate of this rise. In these experiments the wear on the upper surface was concentrated on one small area on the surface, and it is clear that this gradual rise in friction is associated with the removal of the protective film from this region.

The photomicrographs of the track obtained in these experiments are reproduced in figure 12 (plate 4). As the magnification is different in each case, a suitable distance scale has been superimposed on each photomicrograph. The track and the direction of sliding are indicated by an arrow in each case, the point at which sliding began being shown by the letter B on each photomicrograph. These photographs all show a gradual change in the appearance of the track during sliding, although the actual width of the track remained constant. It is clear that at the beginning of the sliding comparatively little tearing of the lower surface occurred, but that as motion proceeded the tearing became more and more pronounced. Measurement showed that this increase in wear corresponded to the rise in friction during sliding. It will also be seen that the fewer the number of films on the slider, the more rapidly does the track change in appearance.

With one film on the upper surface, a subsidiary experiment was carried out in which the speed of the lower surface was reduced to 0.001 cm./sec. and the friction observed at known intervals of time after the start of sliding. The results will be described and discussed later.

(2) Films on lower surface. When two surfaces slide together under these conditions fresh portions of the film are continually coming under the upper slider, and consequently during any particular run over the surface no change in the friction could be observed. However, a marked change in the behaviour often took place as the slider was run repeatedly over the same track, and the results obtained for various thicknesses of film are shown in figure 13. It will be seen that even when only one



film was present on the surface the coefficient of friction during the first run was low and equal to 0·1. The actual trace obtained during this first run is shown reproduced in figure 14a (plate 4) and a photomicrograph of the track formed on the lower surface is given in figure 14c. Continuous sliding was taking place between the surfaces and there was very little wear; the behaviour was, in fact, very similar to that found when excess stearic acid was present on the surface. However, on repeated running over the same track, the friction soon began to rise and eventually attained the high value characteristic of unlubricated surfaces. At the same time the wear betweeen the surfaces was increased enormously, and the appearance of the track after twenty runs is shown in figure 14d. It is clear that as a result of the repeated sliding the protective film is rapidly worn off the lower surface, and that as this film is removed the seizure between the surfaces increases, the friction rises, and a marked tearing of the lower surface begins to take place.

Similar results were obtained in the presence of other initial thicknesses of film, but the curves given in figure 13 show that as the thickness of the film was increased there was a gradual decrease in the rate at which the friction and wear rose on repeated sliding. Eventually, when a sufficiently large number of films were present, no rise in friction was observed even after 100 runs over the lower surface. The frictional behaviour during the first run on a film 53 mol. thick is given in figure 14b and the corresponding track is shown in figure 14e. It is important to note that these results are not very different from those obtained during the first run on only one film. The track formed after 100 runs on the fifty-three films is illustrated in figure 14f, and it will be seen that there was very little tearing of the surfaces. This result stands in marked contrast to the extensive wear observed after only twenty runs on the *single* film (figure 14d). An interesting colour change was also observed in the film during the experiment with fifty-three films on the lower surface. Viewed at normal incidence in ordinary daylight the colour of the undeformed film was blue, but the regions over which the slider had passed showed a definite yellow. This change in colour offers direct evidence that the thickness of the film is reduced as a result of sliding.

A few experiments were also carried out with films on both the top and bottom surfaces. In general the results showed that for a given number of films on the lower surface the friction and wear throughout the experiment were independent of the thickness of film on the upper surface. In fact the results were the same as those obtained with no films at all on the upper slider. Since the film at the point of contact on the upper surface is always worn away rapidly during the very first run, this result is to be expected.

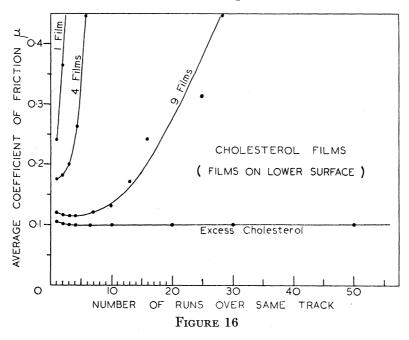
#### Cholesterol films

The experiments were repeated with cholesterol films, and the results obtained are shown in figures 15 (plate 5), 16 and 17 (plate 5). It will be seen that in many ways the behaviour was similar to that observed with "stearic acid" films. With films on the upper surface only, a rapid rise in the friction and wear was observed during the sliding, and the rate of this rise was dependent on the number of films present. When the films were placed on the lower surface the friction and wear remained unchanged during each run but, as before, showed an increase during subsequent runs. The rate at which the lubricating layer wore off again depended on the number of molecular films of which it was composed.

One important difference in the behaviour of these two lubricants will be seen however. We have seen that with "stearic acid" a unimolecular film was able to reduce the friction almost to the same value as that observed when many films were present. With cholesterol this was not the case. Figure 16 shows that when only one film was present on the surface the friction during the first run was comparatively high  $(\mu=0.25)$ , and the lower value  $(\mu=0.1)$  which is observed in the presence of excess cholesterol was only attained when several films had been deposited on the

surface. It thus appears that these films of cholesterol afford less protection to the surfaces than do thin films of "stearic acid".

In agreement with this we find that, although the general behaviour was the same, the films of cholesterol were worn off the surface more rapidly than were those of "stearic acid". Thus comparison of figures 15 and 11 shows that for equal numbers of films on the upper surface the rate of rise of friction during sliding was approximately twice as great for cholesterol as for "stearic acid". Similarly, it is seen from figures 16, 17, 13 and 14 that for a given number of films on the lower surface the friction and wear rose more rapidly during repeated sliding when the film was composed of cholesterol than when it was composed of "stearic acid".



#### DISCUSSION

In a previous paper it was shown that the sliding of two unlubricated metals is discontinuous and that an intermittent clutching and breaking away of the surfaces occurs during the sliding. It is clear from the results described above that even in the presence of a lubricant the same processes may occur. The oil film at the surface is unable to prevent local metallic contact and seizure from occurring. The fact that an e.m.f. can be developed between the surfaces, even in the presence of lubricants, has already been given as evidence that metal to metal contact is taking place under these conditions (Bowden and Ridler 1936). During the subsequent motion the metallic junctions are broken and extensive distortion and tearing of the metal occurs. Typical examples of such behaviour are given by mineral oils. Figure 1 shows that with these substances motion takes place by stick-slips and a well-marked track is formed on the lower steel surface. It has long been known that mineral oils are bad lubricants from

the point of view of "oiliness". These observations show that this lack of oiliness arises from the weak attachment of the oil film to the surface and its consequent inability to prevent extensive metal to metal contact from taking place between the surfaces during sliding.

The experiments described above show that when a certain chain length is exceeded, long-chain fatty acids, in both the solid and liquid state, are able to prevent this intermittent clutching and breaking away of the surfaces. Instead, a continuous sliding takes place and at the same time the wear is much reduced. Increased protection is therefore afforded to the surfaces and this effect is due, no doubt, to the adsorbed layer of fatty acid which is present on the surface. As is well known, the COOH group is strongly polar so that the molecules of which it forms the end-group are orientated with this group in contact with the metal. The molecules of fatty acid adhere firmly to the surface and the film is not ruptured so easily by the applied load. The orientated layers on the two surfaces glide more smoothly over one another; there is less seizure and the wear is reduced. Nevertheless, it is important to note that even in the presence of a good lubricant some tearing of the surfaces is observed, showing that some breakdown of the film must have occurred.

The experiments with mixtures of lubricants afford confirmatory evidence for this hypothesis. It has been shown that the addition of only a trace of a fatty acid to a mineral oil is sufficient to change the frictional behaviour from the stick-slips characteristic of the oil to the continuous sliding characteristic of the fatty acid. The polar properties of the fatty acid molecules are much greater than those of the mineral oil molecules, and the presence of a very small amount of the former in the oil is enough to cause the displacement of all the mineral oil from the surface with the formation of an adsorbed layer of fatty acid. The frictional behaviour observed with the mixture will therefore be that typical of the fatty acid and not that of the mineral oil.

With the short-chain fatty acids a different behaviour was observed and stick-slips and extensive tearing were found to occur. This result suggests that a certain minimum length is necessary for the lubricant molecule before the adsorbed lubricating layer can afford appreciable protection to the surfaces. This condition seems to be attained at caproic acid (C<sub>5</sub>H<sub>11</sub>COOH). At this point continuous sliding sets in and at the same time the minimum value of the friction is reached. The corrosive properties were found to diminish as the chain length increases and also become very small above caproic acid.

It has been shown that, in the liquid state, alcohols and hydrocarbons are unable to prevent stick-slips and do not afford much protection to the surfaces. Their behaviour is, in fact, essentially similar to that shown by mineral oils. The molecules of these substances must therefore be attached to the surface comparatively weakly so that the film of lubricant is easily broken down by the applied load. This view is supported by the fact that the addition of a trace of cetyl alcohol was ineffective in changing the nature of the sliding of a mineral oil. In contrast to the behaviour of a

fatty acid, this substance is unable to form a very protective adsorbed layer on the surface.

When an alcohol or a hydrocarbon is present on the surface in the solid state, however, continuous sliding does occur. This effect is probably mechanical and is due to the comparatively thick films of solid present on the two surfaces gliding over one another.

In connexion with these observations it is interesting to recall some results recently obtained by Suge (1938) during an investigation of the structure of lubricant films by the electron diffraction method. For fatty acids he found orientation only when the number of carbon atoms in the acid exceeded sixteen, while in the case of alcohols eighteen carbon atoms were found to be necessary. Apart from a few exceptions, which he ascribed to the presence of waxy impurities, mineral oils did not show any orientation.

## The relationship between friction and load

Figure 10 (p. 9) shows that for a given load the track width is roughly independent of the composition of the lubricant present, and that when the track width and the load are plotted logarithmically a straight line with a slope of about 0.5 is obtained. Furthermore, other experiments have shown that almost the identical curve is obtained for unlubricated steel surfaces. The width of the track is related to the area of contact between the surfaces, and it is reasonable to assume that this area is a circle whose diameter is equal to the width of the track. The area of contact would then be directly proportional to the load and, by similar reasoning to that employed by Bowden and Tabor (1939), we can deduce that the metal at the point of contact is undergoing plastic deformation during sliding. This observation that the area of contact is proportional to the applied load offers an explanation of Amontons' Law.

Since adhesion occurs and metallic junctions are formed between the surfaces, it is not clear at first sight why the frictional force should decrease when the load is diminished. If actual movement of the slider occurs the original junctions will be broken and junctions corresponding to the smaller load will be formed afresh; in this case therefore there is no difficulty. In the case of stationary surfaces it is not so obvious. It has been pointed out however (Bowden and Tabor 1939), that, although the very points of the surface irregularities may flow plastically, the metal beyond this is elastically deformed by the applied load. If the load is reduced this elastic strain will be released and the old junctions will be torn away. Moreover, the act of pulling the slider to measure the "static" friction will itself break the junctions. Under most conditions of measurement the strain cannot be applied so that it is taken equally by all the scattered junctions. The old junctions will be broken easily one by one. The number and strength of the junctions, and hence the friction, will be determined by the load which is actually applied during the measurement. For similar reasons the

normal force necessary to lift the surfaces apart will be small once the load has been removed. This point has been discussed by Hardy. This explanation of the effect of decreasing the load will, of course, apply to the case of unlubricated as well as lubricated surfaces.

## Testing of a lubricant

It is clear that an analysis of the frictional behaviour may give more information about the properties of a lubricant than is obtained from a measurement of the average coefficient of friction. The experiments show that when stick-slip occurs the metal surfaces are worn and torn, but when the motion changes over to continuous sliding the wear is greatly reduced. If a substance causes continuous sliding it is usually a better lubricant than one which does not, even though the average value of the coefficient of friction may be higher. It is a matter of considerable experimental difficulty to devise a laboratory method of testing a lubricant which can give any real information about its behaviour. Most of the standard methods at present in use depend upon a measurement of the average friction, or upon a measurement of the load at which seizure occurs, or upon a crude measurement of wear. It is now generally agreed that these methods give little agreement with one another or with the performance of the lubricant in practice. It is probable that this analysis, particularly the simultaneous analysis of the changes in the friction, the surface temperature and the area of contact during sliding can give information of more real value. This analysis shows in much greater detail the part played by the lubricant molecule and the influence it has on the physical processes that occur during sliding.

It is clear that the conditions of the test should approach as closely as possible the conditions under which the lubricant is to be used in practice. It has been pointed out in an earlier paper (Bowden and Leben 1939) that the nature of sliding and the effect of the lubricant are very dependent upon the particular combinations of metals used. A lubricant which is suitable for one pair of metals is not necessarily suitable for another. The temperature is, of course, particularly important. The results described in this paper would suggest that a long-chain fatty acid is an excellent lubricant and that the addition of a trace of it to a mineral oil should lead to a considerable improvement. This is probably true on cold steel surfaces which are sliding comparatively slowly. At high temperatures, however, the behaviour is quite different. Thus experiments described elsewhere (Bowden, Leben and Tabor 1939 a) have shown that on hot steel surfaces fatty acids cause stick-slips and heavy wear. On the other hand, at high temperatures a mineral oil may develop oxidation products which improve its lubricating properties and allow continuous sliding. This analytical method of measuring friction was thus used to follow the changes which occur when a mineral oil is heated and to determine with greater precision the temperature and conditions under which they take place. Other laboratory experiments have also shown that on hot surfaces a mineral oil containing fatty acid may be a worse lubricant than

an undoped oil.\* The present apparatus is so constructed that the nature and surface finish of the metals, the temperature, the load, the speed, and the atmosphere, can be separately controlled.

In the experiments described in this paper one of the surfaces (the upper slider) was attached to a high-frequency elastic measuring device and the restraint was such that a momentary arrest could occur. Under many practical conditions, for example, in most parts of an engine, any appreciable arrest in the moving parts is difficult because one surface is held rigidly while the other is driven steadily on. However, the experiments of Bowden and Tabor (1939) have already shown that when two rigidly held surfaces slide against one another very rapid fluctuations in the contact resistance can still occur. This suggests that an intermittent clutching and breaking away of the surface regions is still taking place although, as calculation shows, the relative movement corresponds to a distance of only a few atoms. The size and frequency of the fluctuations are determined by the elastic properties of the restraining system and in the limiting case by the elasticity of the surface irregularities themselves. Lubrication will not necessarily produce smooth motion since, as we have already seen, with many lubricants the clutching and breaking away of the surfaces still occurs through the oil film. We would expect that lubricants such as long-chain fatty acids which show continuous sliding in the usual friction tests would also produce a smoother motion under practical conditions.† The importance of these conclusions on engineering

\* The various effects that are mentioned here are all observed at high temperatures of the order of 200–300° C. These changes are not reversible on cooling and are all due to chemical changes in the oils themselves. More recent experiments (Tabor 1940) have shown that at much lower temperatures a very different type of frictional change can occur. For example, when a commercial oil which gives smooth sliding on steel surfaces at room temperature is warmed to a certain temperature (usually between 40 and 80° C) the motion changes from continuous sliding to stick-slips; on raising the temperature further the stick-slips gradually increase in size. Provided the heating has not been sufficient to cause appreciable oxidation of the lubricant, these changes are completely reversible on cooling and are probably due to a desorption or disorientation of the lubricant film as a result of the increasing temperature. It is important to note that these results indicate that a lubricant which behaves well at room temperatures (that is, which gives smooth sliding) may have poor boundary lubricating properties at quite moderate temperatures of the running parts.

Experiments have also been carried out with pure fatty acids and similar effects have been observed, though the temperature at which stick-slips commence is appreciably higher than the values given above and increases with the chain length of the acid. The temperature at which this reversible effect occurs is in fact a characteristic of the particular oil used and, as Tabor has suggested, it probably provides a measure of the strength with which the lubricant film adheres to the metal surface; the higher the transition temperature, the more strongly is the film adsorbed on the surface. It would thus be possible by such means to compare different lubricants in this respect. This opens up a new field of investigation.

† A preliminary investigation of the detailed physical processes that occur during the sliding of rigidly-held lubricated metallic surfaces has recently been carried out using a cathode ray oscillograph. In the presence of a mineral oil very rapid and violent fluctuations in both the surface temperature and the contact resistance were observed, often in periods of less than 1/30,000 sec.; with oleic acid some fluctuations again occurred, but to a less marked extent. These are, in fact, the results that would be expected if the motion were smoother with oleic acid than with the mineral oil.

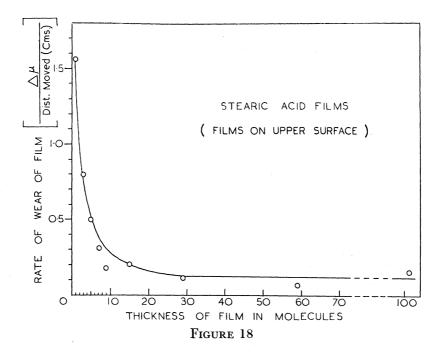
practice has been fully discussed elsewhere (Bowden et al. 1939 b). It was shown that any minute stick-slips that take place during sliding may set up vibrations in the moving parts. The amplitude and frequency of these vibrations will depend on the mechanical properties and the restraints of the moving parts. The resultant motion between the surfaces will be complex and will be determined by the nature of the stick-slips, the natural frequency of the system, and the speed of the forward motion. It is this resultant motion which governs the friction and wear.

## The influence of monolayers

The experiments described in the latter part of this paper show that the presence of a unimolecular film on the surface may have a marked effect on the friction and wear during the first moments of sliding. A single layer of molecules may be able to keep the metal surfaces partly separated over the area of contact, so that the seizure which occurs is less than for unlubricated surfaces. In consequence the friction and wear are much reduced. With stearic acid the reduction is nearly as great when the layer is only one molecule thick as when excess lubricant is present on the surface. This is however not always the case. With cholesterol, one film is insufficient to reduce the friction to its minimum value for that particular substance; a layer of lubricant several molecules thick is necessary.

Although the precise number of molecular films initially present may not have much effect on the friction and tearing which are observed at the beginning of sliding, it is clear that it has a profound influence on the frictional behaviour during subsequent sliding. In the first type of experiment when the film was present on the small slider the wear was concentrated at one small area on the surface and the film was rapidly worn off from that area. In consequence as sliding proceeded the metallic surfaces seized together to a continually increasing extent, the friction rose, and the wear became continually greater. As a measure of the rate at which the film wears off we may take the rate of rise of the coefficient of friction with distance moved on the lower surface. We may for convenience define the rate of wear as equal to  $\Delta\mu/(\text{distance slid in cm.})$ . For the trace shown in figure 11a calculation gives a rate of wear equal to 1.56 in the appropriate units. This experiment had been carried out at a sliding speed of 1.0 cm./sec. with one film of "stearic acid" on the surface. A subsidiary experiment was also carried out with one film again on the upper surface but with the lower surface moving at the slower speed of 0.0011 cm./sec.; the results obtained gave a rate of wear of the film equal to 1.67 in the same units. It is clear that, considered in this way, the rate of wear of the film is roughly independent of the speed of sliding. The rise in friction depends only on the relative distance moved by the surfaces and not on the time during which they have been sliding together. The rise in friction during sliding has also been measured for a large number of films of different thicknesses and some of the traces obtained have been shown in figure 11. The calculation has been repeated for these cases and the values so obtained for the rate of wear are shown plotted against the

film thickness in figure 18. This graph shows clearly that the rate at which the film wears off the surface during sliding is markedly dependent on its thickness. With increasing thickness of film the rate decreases and it seems possible that at sufficiently great thicknesses the rate of wear attains a constant value. The curve suggests that under these conditions this occurs when there are approximately 30 films on the surface. A similar effect was observed with cholesterol films although for any given molecular thickness the rate of wear of the film was greater than for stearic acid. Thus on a film a single molecule thick the rate of wear was equal to  $2 \cdot 2$  (in the above units), while on a film 30 molecules thick the rate of wear was reduced to 0.32.



The results obtained with lubricant on the lower surface lead to an essentially similar conclusion. We have seen that on repeated running over the same track the friction rises and the wear between the surfaces increases. This result must be due to the progressive removal of the protective film as a result of the sliding. In consequence the metallic surfaces are able to come more and more into direct contact, the friction rises steadily, and there is a corresponding increase in the wear. Figures 13 and 16 show the results for different thicknesses of film and it is clear that as the thickness of the film increases there is a gradual decrease in the rate at which this film wears off the surface.

Working with films deposited by the method previously described, Claypoole (1939) found a similar effect. Thus he states that a film thickness of  $4 \times 10^{-6}$  mm. affords a greatly increased protection as compared with one only 25% thinner. In the experiments of Langmuir and Schaefer (Langmuir 1934) a hemisphere of glass rested upon a glass slide covered by a monomolecular film of stearic acid, and the point of contact

between the hemisphere and the slide could be made to move accurately back and forth along a given line. The experiments showed that it took about 700 strokes before the coefficient of friction rose from 0·11 to 0·13, while in another 200 strokes the friction rose to 0·24 and soon afterwards seizing occurred. With a film seven layers thick the coefficient of friction did not increase perceptibly even after 4000 strokes.

The experiments described in this paper show that substances which give the same coefficient of friction are not necessarily equally efficient as lubricants. The extent to which they are able to reduce the wear between the sliding surfaces may be very different. This experimental method enables an estimate to be made of the rate at which the lubricant film wears off the surface during sliding. This gives further information about the capacity of the lubricant to maintain surfaces in the state of boundary lubrication and enables different lubricants to be compared in this respect. Thus it has been shown that with cholesterol the lubricant film wears off more rapidly than with stearic acid, so that it appears that stearic acid is a better lubricant than cholesterol under these conditions. This method of investigation can be extended to other substances.

It is of interest to consider the possible reasons for the greater lubricating properties of a stearic acid film as compared with a cholesterol film of equal molecular thickness. It is well known that on water the molecules of both these substances are orientated with the longest axis of the molecule vertical and with the polar group (i.e. the COOH group in stearic acid and the OH group in cholesterol) in the water. When multilayers of these films are formed on a metal surface the first molecular layer is orientated with the polar group adhering to the metal. We would expect that the COOH group, which can form salts with the metal, will stick more tightly to the metal than the OH group. This may account for the greater resistance to wear of the fatty acid film. Other factors may, however, be of importance. Thus the surface density in molecules per sq. cm. of a cholesterol film is approximately half that of a stearic acid film. Again, as Adam has pointed out in a private communication, the molecules of the fatty acid film are probably flexible while the skeleton part of the sterol molecule is not. These may all be possible causes of the difference between the lubricating properties of the two substances.

#### The mechanism of boundary lubrication

The mechanism by which a lubricant in the boundary condition is able to reduce the friction and wear between sliding surfaces has been much studied in the past. Since at sufficiently large rates of motion the hydrodynamic properties of the lubricant may cause the surfaces to become separated by a more or less thick film, most of the investigations of boundary lubrication have been of the static friction coefficients. As a result of such measurements several theories of boundary lubrication have been put forward in the past. According to the earliest workers the effect of a lubricant was to form a film so thick that the roughnesses of the surfaces could not come into contact with one another, interlock, and so cause friction.

The more modern theories of boundary lubrication assume that the resistance to motion is due to intermolecular forces at the points of contact. Experiments showed that the friction was influenced not only by the chemical nature of the lubricant but also by the nature of the underlying surface. The most direct evidence that friction is intimately connected with the chemical fields of molecules was obtained by Sir William Hardy and his co-workers who measured static friction, using homologous series of paraffins, alcohols and acids as lubricants. The relationships obtained were unexpectedly simple and the friction was found to be a function of separate contributions by the solid surfaces, the chemical series to which the lubricant belonged and the number of carbon atoms in its chain. To interpret these data he assumed that the molecules of the lubricant are orientated at each metallic surface to form a monomolecular adsorbed film. The solids sink through the lubricant layer until the surfaces are separated only by the unimolecular films of lubricant adsorbed on each surface. Slip can then occur between these adsorbed films. Since the polar groups adhere to the metal, contact between the surfaces takes place, not between the metals themselves, but between the non-polar groups at the other end of the lubricant molecules. The force necessary to bring about sliding is therefore diminished. Hardy also assumed that the extent of the reduction of the surface fields of force, which determines the force of adhesion between the non-polar end-groups, is a function of the length of the molecule. In this way he explained the linear relationship observed between the friction and the molecular weight for different members of a homologous series.

The existence of orientated films at the surface of a metal has been confirmed directly by the X-ray experiments of Trillat (1925), Bragg (1925) and Muller (1923). The orientation of many compounds has also been investigated by Clark, Sterrett and Lincoln (1936); for purposes of comparison the film strength of each substance was determined in a Timken machine. From their results the authors concluded that orientation is important but that it is not the only factor determining the lubricating properties. More recently the electron diffraction technique has been used to study the structure of films, and by this means Finch and Zahoorbux (1937) have been able to show that the degree of orientation depends greatly on the degree of perfection of the surface (i.e. the absence of crystalline projections). Andrew (1936) has also used the electron diffraction method to investigate the orientation of a large number of oils, and he has made a detailed study of the changes that can be brought about by oxidation of the oils. On the supposition that a good lubricant should possess a high degree of orientation he found good agreement with the results of engineering practice.

Most of the theories of boundary lubrication have been put forward as a result of experiments on static friction. It is by no means true, however, that the conditions defining the static friction between two lubricated bodies are the same as those

governing the kinetic friction. Many complications can arise during motion on account of the complex and varying nature of the surfaces in contact. The local pressure will be continually changing as the surface asperities approach and recede from one another. If the pressure becomes too great the oil film may be broken down, followed by seizure between the surfaces. An important factor which has been overlooked in the past is the surface temperature of the sliding solids. Using the thermoelectric method Bowden and Ridler (1936) showed that even in the presence of lubricants the surface temperature may be very high (500° C or more). This will cause volatilization and decomposition of most lubricants and is an important cause of the breakdown of the lubricant film. If either the load or the speed is too great, a welding together of the "hot spots" on a large scale may occur with consequent damage or seizure of the surfaces. The fact that an electromotive force is developed shows that some metal to metal contact is occurring through the lubricant film. This is in harmony with some earlier work (Beare and Bowden 1935) which showed that the boundary film of lubricant was unable to afford complete protection to the sliding surfaces. Some wear and abrasion of the surfaces always occurred. Corrosion and wear through a lubricant film has also been reported recently by Tomlinson, Thorpe and Gough (1939).

The experiments described in this paper have an important bearing on the theory of boundary lubrication. The earlier theories all assumed that the sliding between two lubricated bodies was always continuous. It is clear, however, that this is not the case; with many lubricants sliding is discontinuous and motion proceeds by a process of stick and slip. The earlier theories, and in particular that put forward by Hardy, also suggested that the surfaces were completely separated by the unimolecular films of lubricant adsorbed on each surface and that slip occurred between these adsorbed films. It was assumed that under these conditions no actual wear of the solid surfaces could take place. Boundary lubrication was therefore regarded as a purely surface phenomenon. From the results of these and earlier experiments it has been shown, however, that when two lubricated bodies slide together the lubricant film is partly broken down, the metals come into direct contact, and some wear of the surfaces always occurs.

It was shown earlier in this paper that for a given load the track width is roughly independent of the lubricant present. Furthermore, from the observed slope of the load-track width curve it was deduced that the metal at the point of contact is undergoing plastic deformation during sliding. On the basis of these observations we can now form a simple picture of the processes that occur at the points of contact between lubricated surfaces sliding at low speeds. It seems probable that the metal is deformed plastically and flows until a joint is formed that is capable of supporting the load. The fact that the track width (and hence the area of contact) is independent of the lubricant and is the same whether lubricant is present or absent agrees with this hypothesis. As a result of the deformation a film of the lubricant will be trapped between the two metal surfaces and there subjected to very high pressures. The pres-

sure will, however, not be uniform in the region of contact but will be at a maximum at the centre of this region and will fall off towards the perimeter. It is reasonable to suppose that under a sufficiently high pressure the lubricant film can be broken down, allowing the metal surfaces to come into contact and weld together. Only a portion of the lubricant film in the region of contact (the most compressed portion) will be broken down and the extent of breakdown and subsequent seizure will vary for different lubricants. The formation of these metallic joints will greatly increase the resistance to motion, and the extent to which breakdown of the film occurs will therefore largely determine the nature and magnitude of the frictional force necessary to maintain sliding. Differences in the nature of the sliding would therefore be expected for different lubricants and it has been shown earlier in this paper that such differences do in fact exist. Similarly the amount of tearing that occurs between the surfaces will largely depend on the extent to which the lubricant film has broken down during sliding, and as has already been mentioned, marked differences are observed in the appearance of the track for different lubricants. According to this view the frictional behaviour and the wear between the lubricated surfaces are largely determined by the ability of the lubricant film to prevent metallic contact.

Further experiments with different combinations of metals should afford confirmation of this theory. The more plastic the metals, the smaller will be the pressures in the region of contact and hence the less the extent of breakdown of the lubricant film. The position is complicated by the fact that the strength of the adsorbed film will vary for different metals, and also by the fact that at the points where the film breaks down three distinct types of metallic junction may occur, depending on the nature of the metals. Nevertheless, in general, we might expect that as metals of greater plasticity are employed the protection afforded by any lubricant would become greater, the frictional behaviour tending more and more to resemble that shown by long-chain fatty acids on steel.

It has been shown that the extent of the wear varies for different substances but that even with the best lubricants some tearing of the surfaces is observed. The sliding effects are therefore not confined to the adsorbed layers of the lubricant but penetrate deeper and cause abrasion and distortion of the underlying metal. In addition, elastic interaction of the surface irregularities must be taking place continually during sliding and this may be an important factor determining the frictional force. As in the case of unlubricated friction, therefore, a complete interpretation of the phenomena must take into account, not only the surface properties, but also the bulk properties of the sliding solids.

The fact that friction is not a purely surface effect is also brought out by the experiments on multilayers described in this paper. This work shows that although a single molecular layer may be capable of reducing the friction and wear, the protective layer is rapidly worn off during sliding with consequent increase in the friction and wear between the surfaces. A layer many molecules thick wears off much more

slowly and therefore affords much better protection to the surfaces. A primary film is therefore not enough, and for effective protection of the surfaces it is necessary to have present between the surfaces a layer of lubricant several molecules thick.

In this connexion it is interesting to consider some recent work by Bowden and Hughes (1938, 1939) on the effect of fatty acid vapours on the friction of clean degassed metals. In the absence of all surface films the friction between the clean metals was very great. When the vapour was first admitted so that a monomolecular film was present on the surface there was an immediate reduction in the friction. This reduction was, however, comparatively small and the friction did not fall to the low values normally observed until a relatively thick layer was present on the surface. This supports the above observations that in order to afford adequate protection to the surfaces a comparatively thick layer of lubricant must be present. The experiments described in this paper also show, however, that even a comparatively thick layer will eventually be broken down, and thus for complete protection it is important that the film be capable of repair. A suitable reserve of lubricant must therefore be present between the surfaces and must be readily available to the points of contact at which wear of the film has occurred.

We wish to express our thanks to the Goldsmiths' Company and the Electors to the Amy Mary Preston Read Scholarship for maintenance grants to one of us (L. L.), and to the Department of Scientific and Industrial Research, to the Royal Society and to the Chemical Society for grants for apparatus.

#### REFERENCES

```
Andrew 1936 Trans. Faraday Soc. 32, 607.
Beare and Bowden 1935 Phil. Trans. A, 234, 329.
Bikerman 1939 Proc. Roy. Soc. A, 170, 130.
```

Blodgett 1935 J. Amer. Chem. Soc. 57, 1007.

Bowden and Hughes 1938 Nature, Lond., 142, 1039.

— 1939 Proc. Roy. Soc. A, 172, 263.

Bowden and Leben 1937 Institution of Mechanical Engineers. Proc. of the General Discussion on Lubrication and Lubricants, 2. Group IV, Properties and Testing, p. 236.

— 1939 Proc. Roy. Soc. A, 169, 371.

Bowden, Leben and Tabor 1939 a Trans. Faraday Soc. 35, 900.

——— 1939 b Engineer, 168, 214.

Bowden and Ridler 1935 Proc. Camb. Phil. Soc. 31, 431.

— — 1936 Proc. Roy. Soc. A, **154**, 640.

Bowden and Tabor 1939 Proc. Roy. Soc. A, 169, 391. (See also Tabor 1939 Dissertation. Cambridge.)

Bragg 1925 Proc. Roy. Inst. 24, 481.

Clark, Sterrett and Lincoln 1936 Industr. Engng Chem. 28, 1318.

Claypoole 1939 Trans. Amer. Soc. Mech. Engrs, 61, 323.

Finch and Zahoorbux 1937 Institution of Mechanical Engineers. Proc. of the General Discussion on Lubrication and Lubricants, 2. Group IV, Properties and Testing, p. 295.

Hardy, Sir W. B. 1936 Collected Works. Camb. Univ. Press.

Langmuir 1934 J. Franklin Inst. 218, 143.

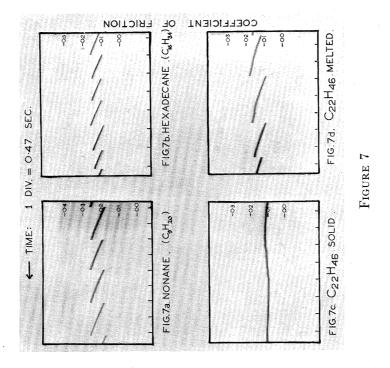
Muller 1923 J. Chem. Soc. 123, 2043.

Suge 1938 Sci. Pap. Inst. Phys. Chem. Res., Tokyo, 34, 1244.

Tabor 1940 Nature, Lond., 145, 308.

Tomlinson, Thorpe and Gough 1939 Proc. Inst. Mech. Engrs, 141, 223.

Trillat 1925 C.R. Acad. Sci., Paris, 180, 280.



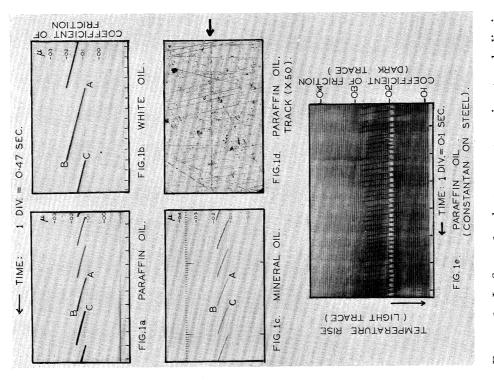
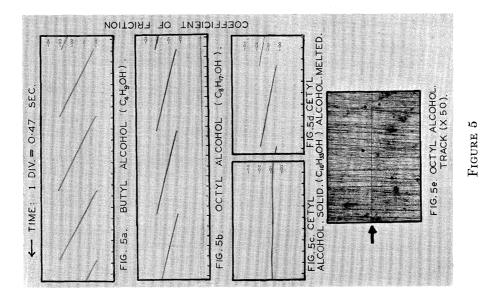
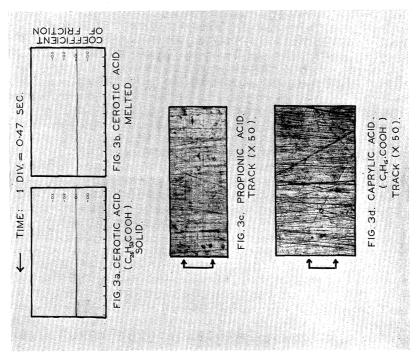


FIGURE 1. In figure 1e, the temperature rise at each slip is shown by the downward movement of the white trace. It appears only faintly on the photograph. The more obvious upward trace beyond the zero is instrumental and may be ignored.





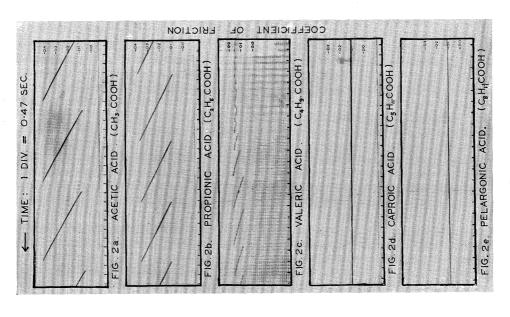


FIGURE 2

FIGURE 3

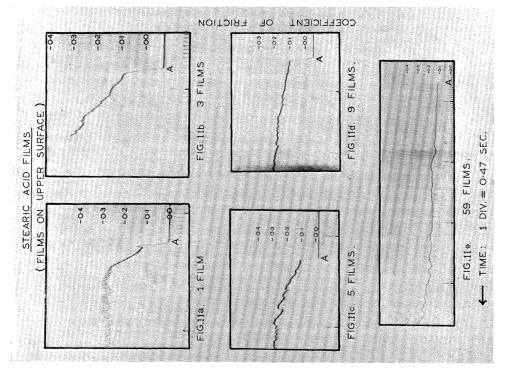
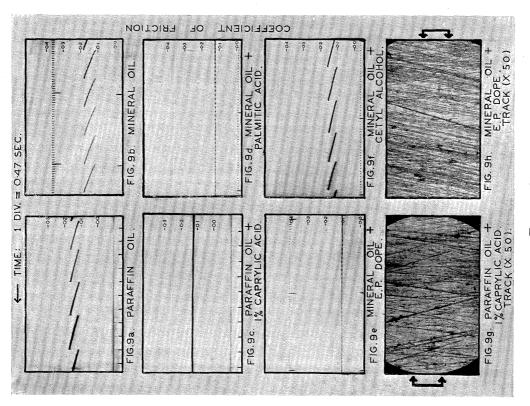
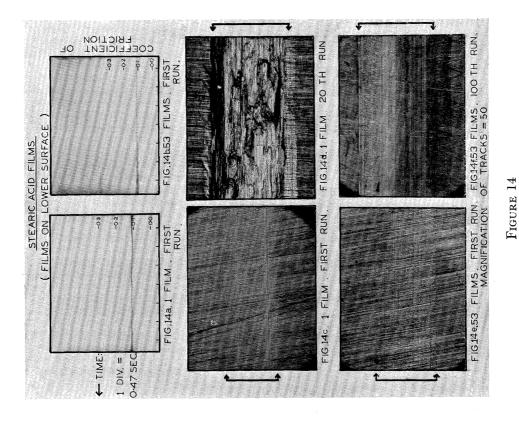


Figure 11. The photographs show the frictional behaviour during sliding. The instant at which sliding began is indicated by the letter A on each photograph. Note the gradual rise in friction as the film wears off the surface. Sliding speed = 1.0 cm./sec.



FIGURE



5-FILMS

F16.12c.

3 FILMS

F16.12b.

FIG.12a. 1 FILM.

F-20

2021

a

0

Ŋ

mm.

E E

( FILMS ON UPPER SURFACE ) STEARIC ACID FILMS

case. The point at which sliding began is shown by the letter B on each photomicrograph. Note the gradual increase in the tearing of the lower surface. Sliding speed = 1·0 cm./sec. sponding to the friction photographs of figure 11. The track and the direction of sliding are indicated by an arrow in each

FIGURE 12. The photomicrographs show the tracks corre-

FIG.12e 59 FILMS.

9 FILMS.

F16,12d.

<u>0</u> Juidu

لىنىلسىلس<u>ا</u>

Ф

COEFFICIENT FRICTION

FIG.15b. 30 FILMS.

ŏ

1 DIV. = 0.47 SEC.

FIG.15a. 1 FILM.

5 0 0

FILMS ON UPPER SURFACE )

CHOLESTEROL FILMS

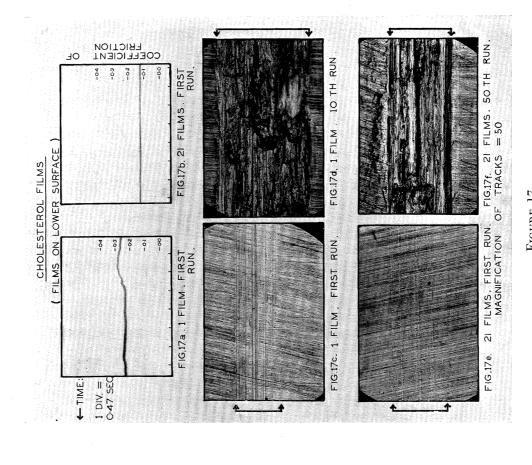


Figure 15. a and b show the frictional behaviour. The instant at which sliding began is indicated by the letter A on each photograph. Note the gradual rise in friction as the film wears off the surface. c and d show the corresponding tracks. The track and the direction of sliding are indicated by an arrow in each case. The point at which sliding began is shown by the letter B on each photomicrograph. Note the gradual increase in the tearing of the lower surface. Sliding speed = 1.0 cm./sec.

FIG.15d. 30 FILMS,

FIG.15c. I FILM.

0

mm.

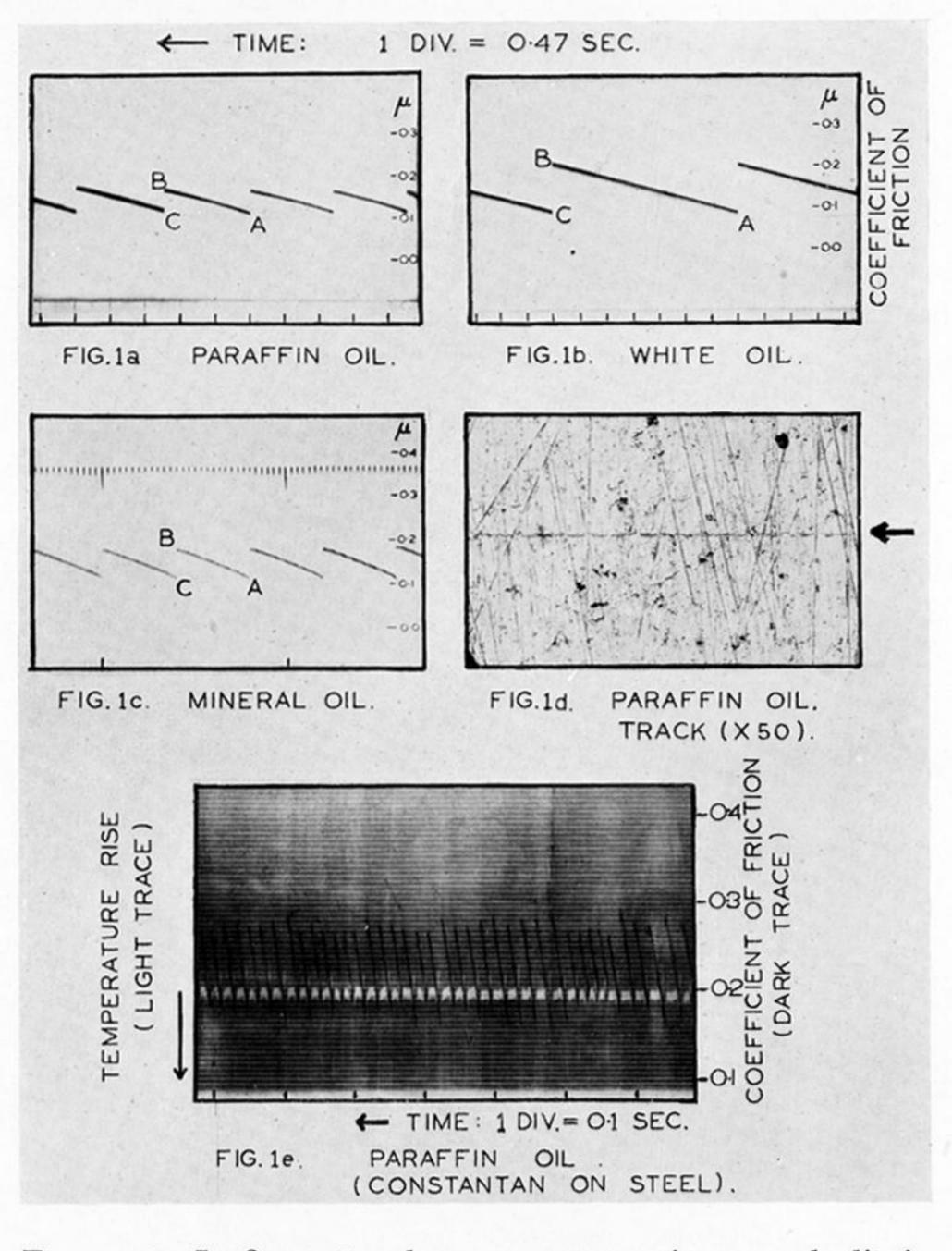


FIGURE 1. In figure 1e, the temperature rise at each slip is shown by the downward movement of the white trace. It appears only faintly on the photograph. The more obvious upward trace beyond the zero is instrumental and may be ignored.

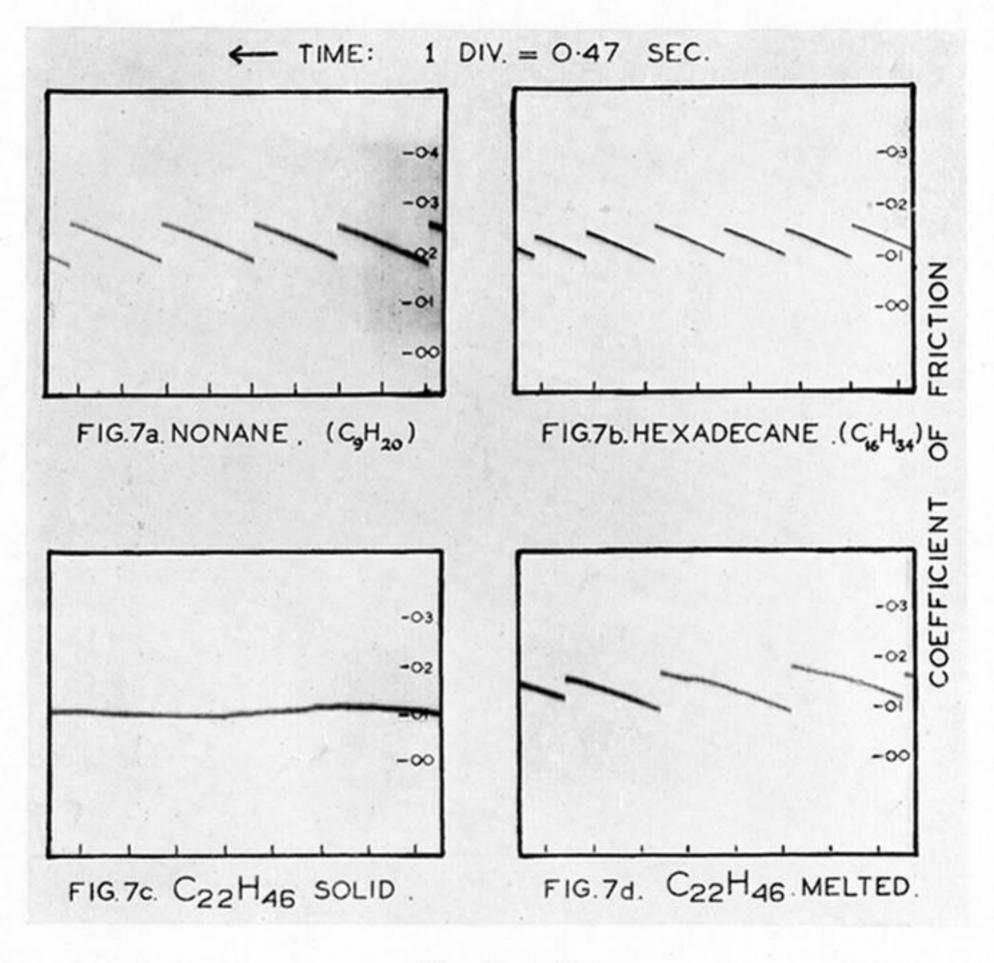


FIGURE 7

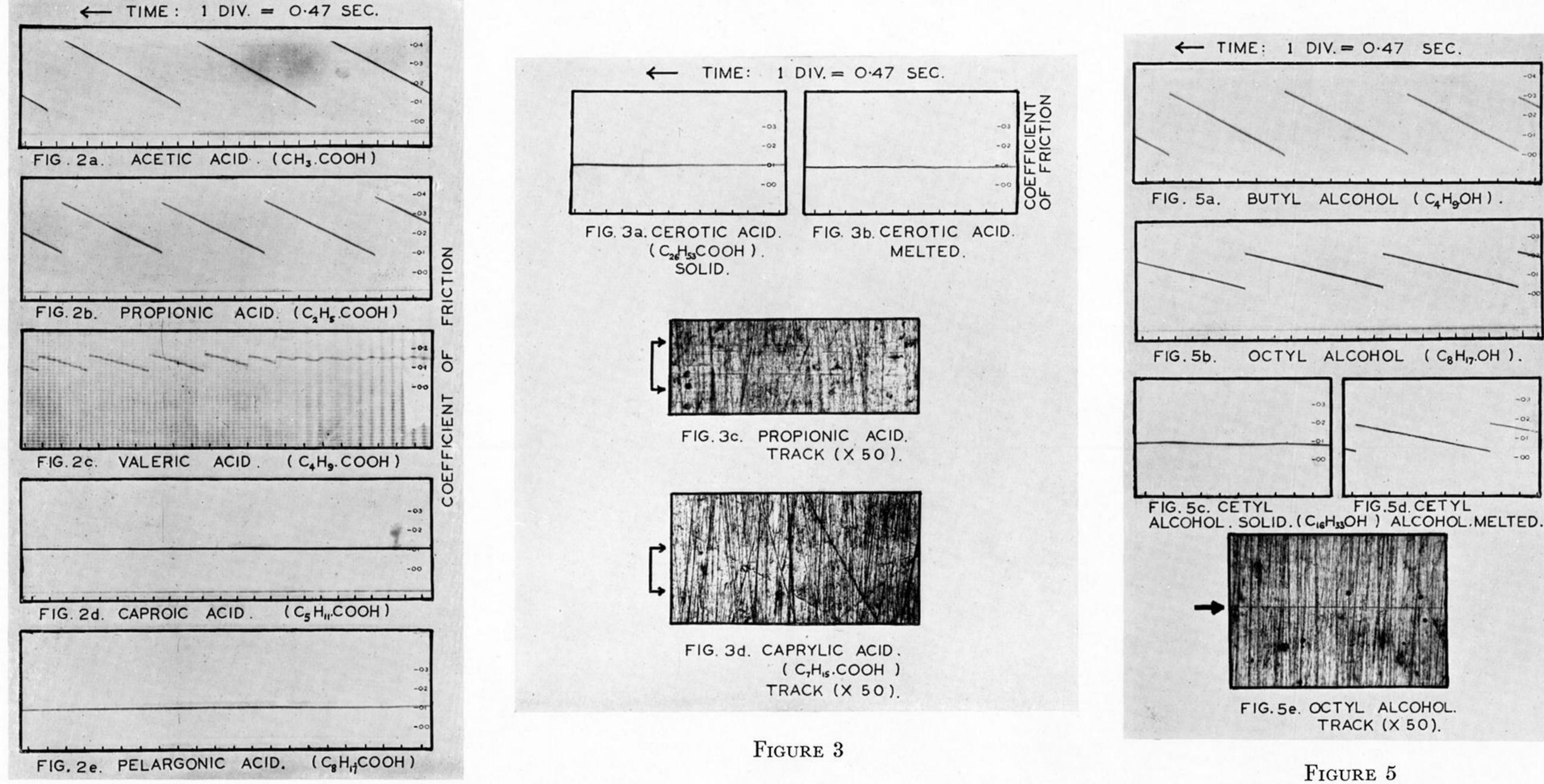


FIGURE 2

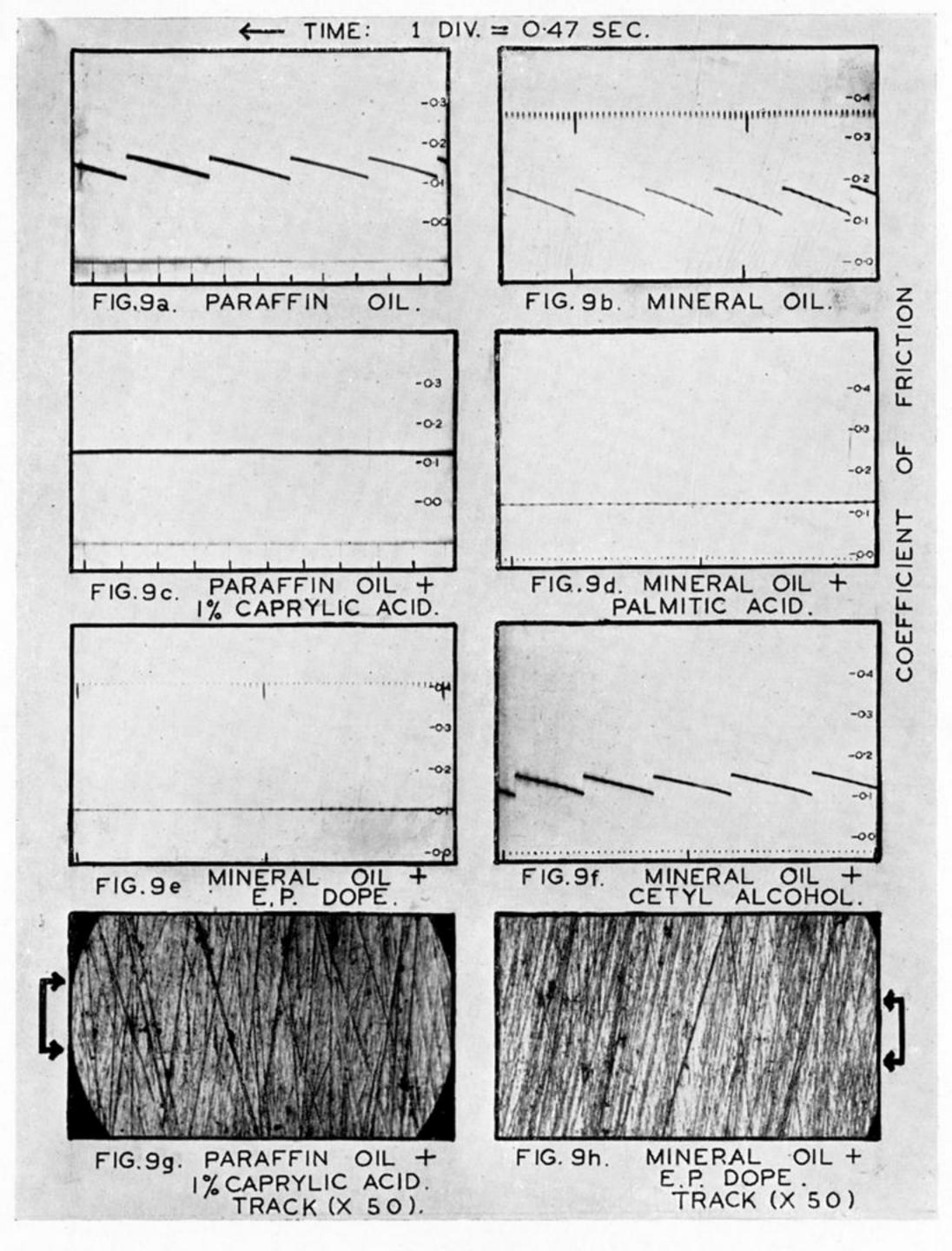


FIGURE 9

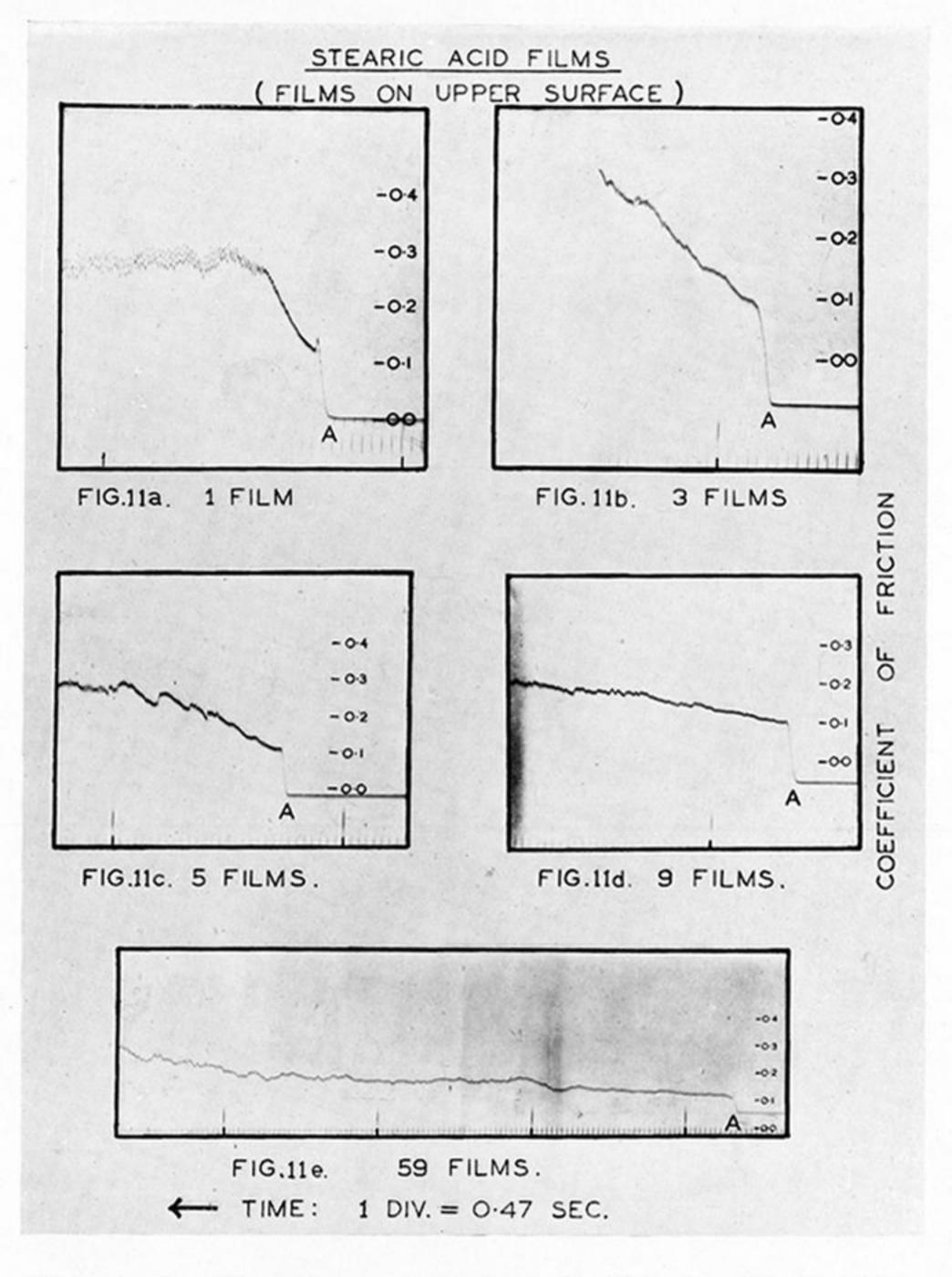


FIGURE 11. The photographs show the frictional behaviour during sliding. The instant at which sliding began is indicated by the letter A on each photograph. Note the gradual rise in friction as the film wears off the surface. Sliding speed = 1.0 cm./sec.

# STEARIC ACID FILMS

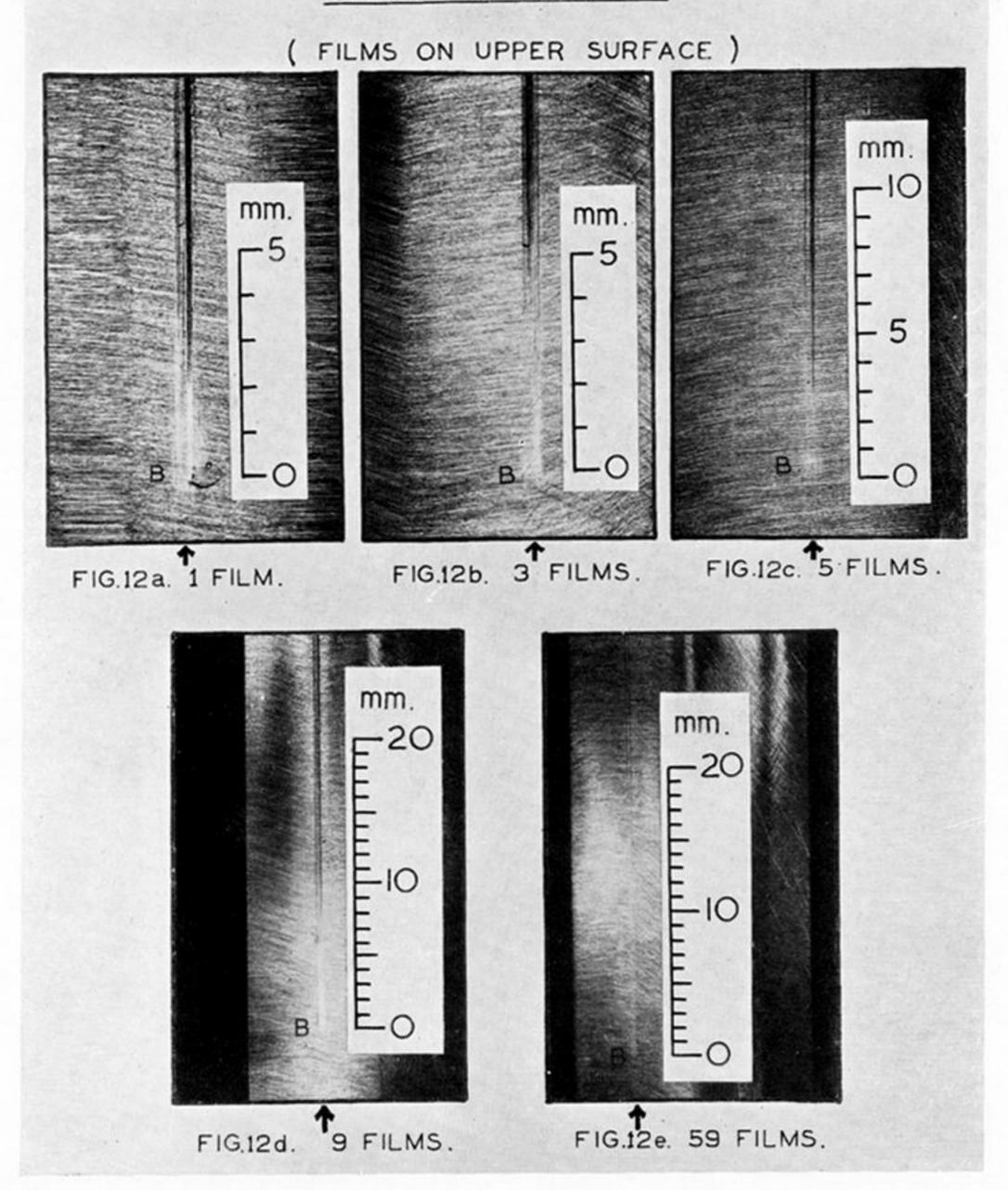


FIGURE 12. The photomicrographs show the tracks corresponding to the friction photographs of figure 11. The track and the direction of sliding are indicated by an arrow in each case. The point at which sliding began is shown by the letter B on each photomicrograph. Note the gradual increase in the tearing of the lower surface. Sliding speed = 1.0 cm./sec.

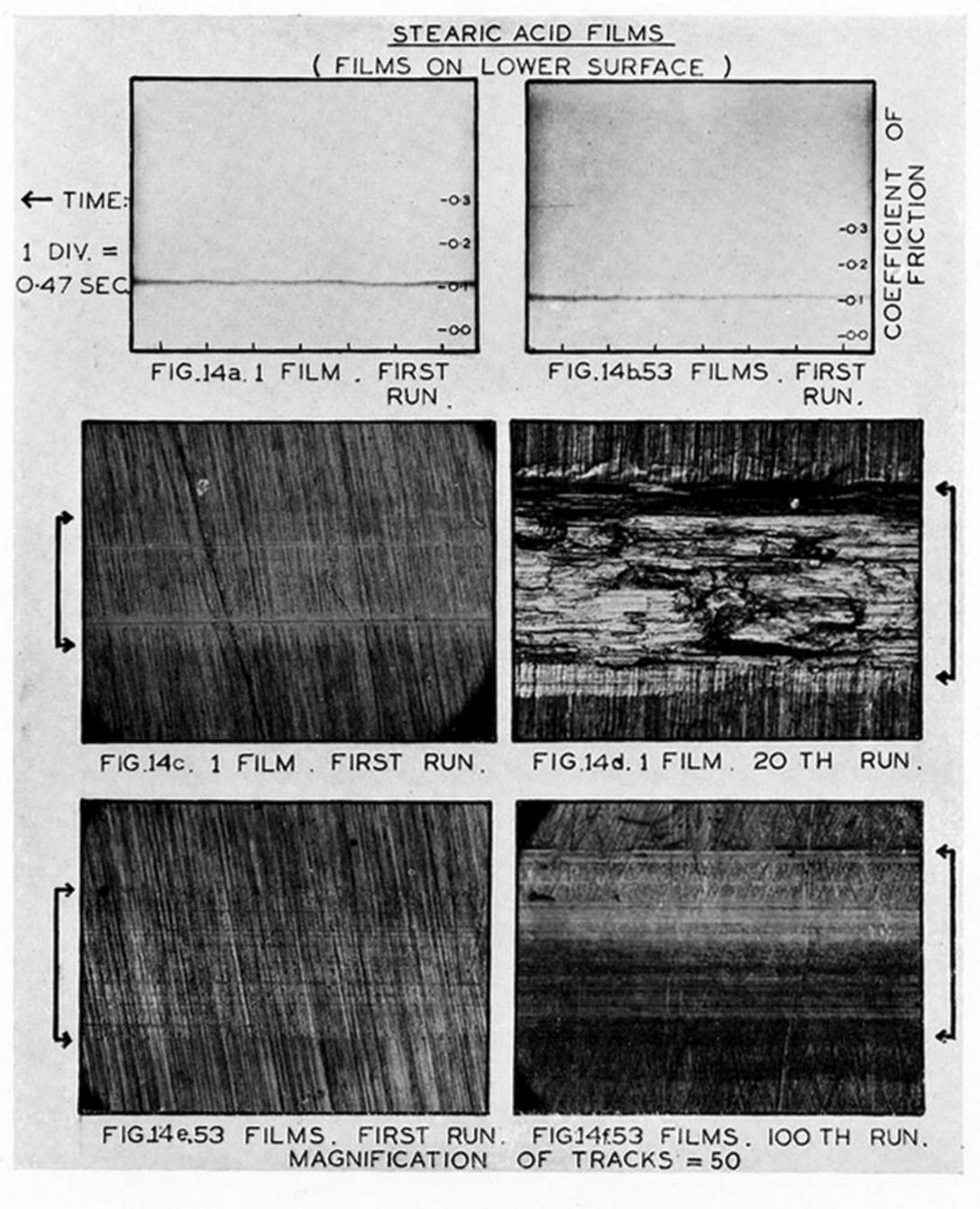


FIGURE 14

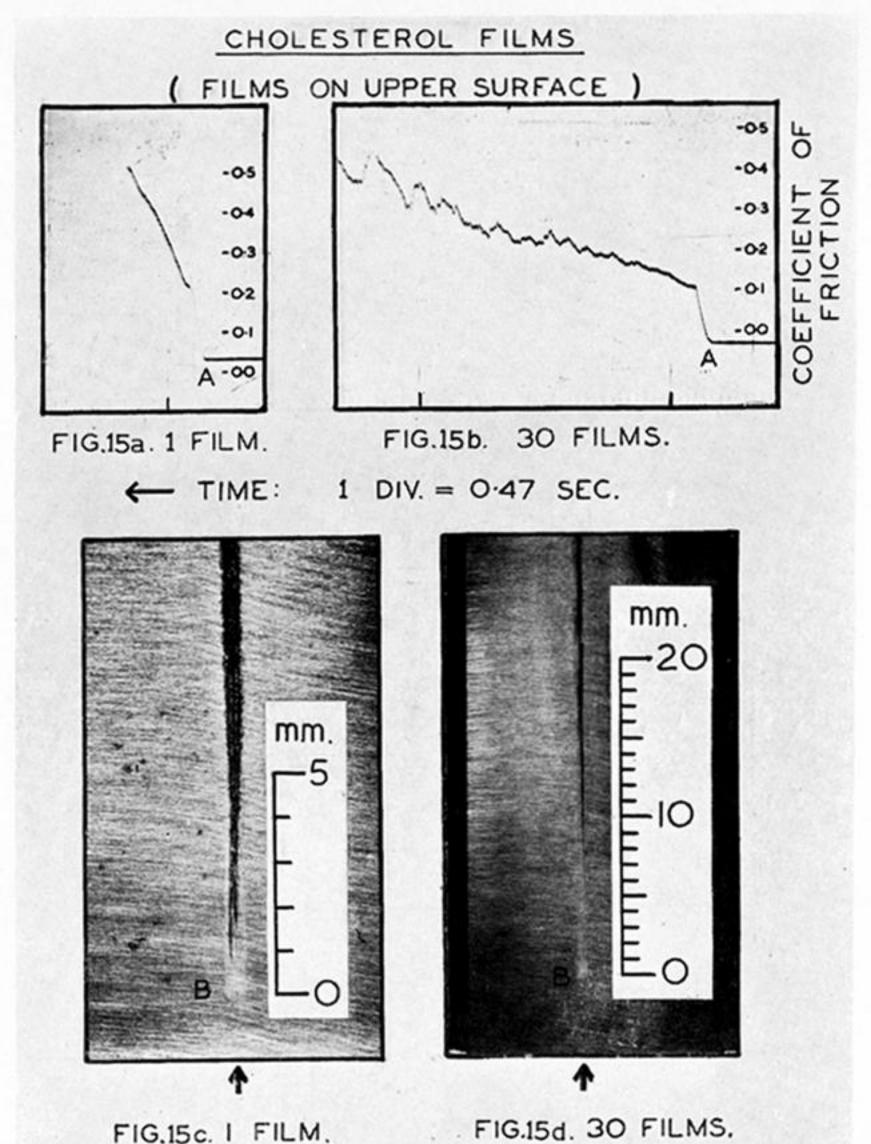


FIGURE 15. a and b show the frictional behaviour. The instant at which sliding began is indicated by the letter A on each photograph. Note the gradual rise in friction as the film wears off the surface. c and d show the corresponding tracks. The track and the direction of sliding are indicated by an arrow in each case. The point at which sliding began is shown by the letter B on each photomicrograph. Note the gradual increase in the tearing of the lower surface. Sliding speed = 1.0 cm./sec.

# CHOLESTEROL" FILMS

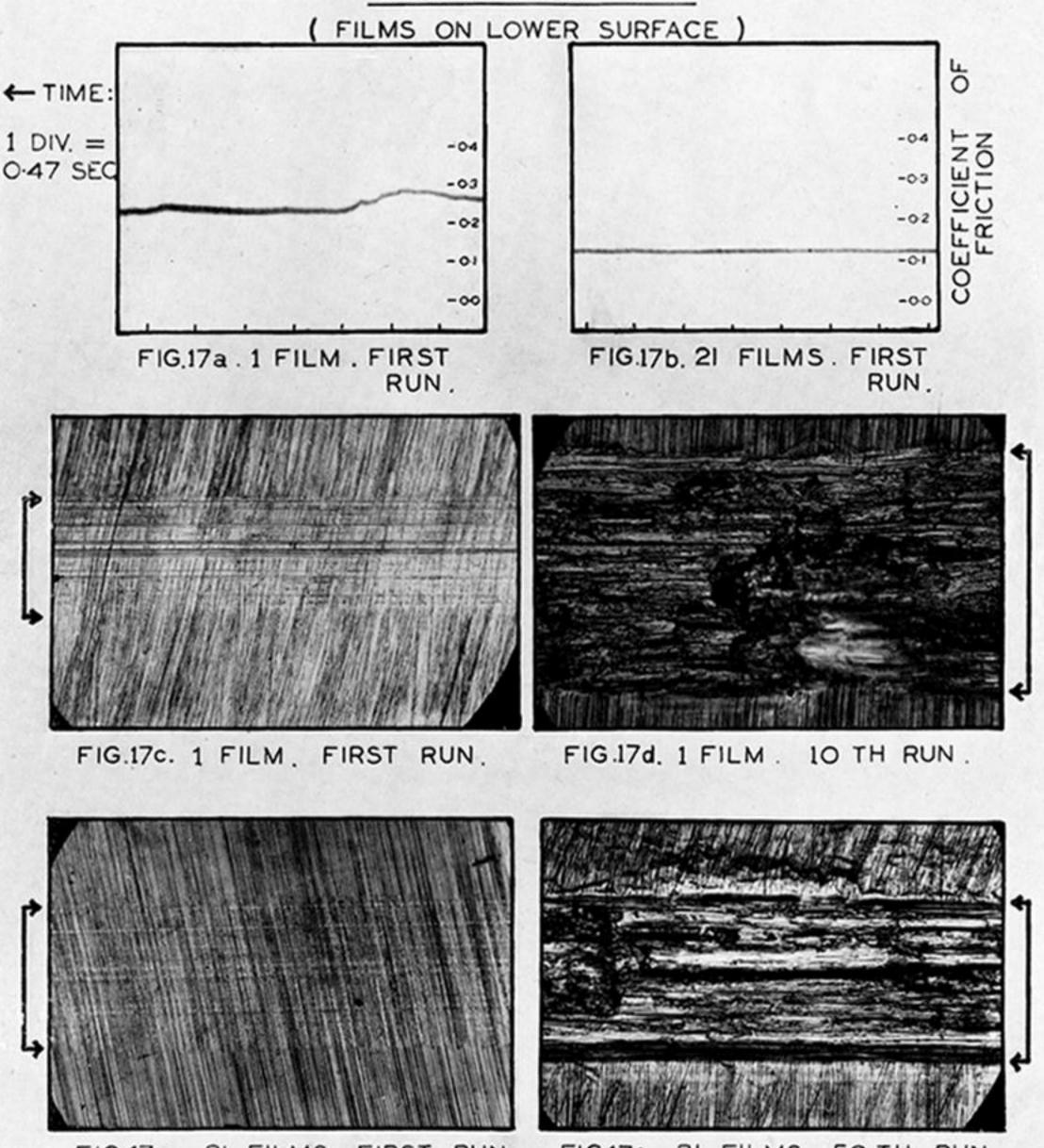


FIG.17e. 21 FILMS. FIRST RUN. FIG.17f. 21 FILMS. 50 TH RUN. MAGNIFICATION OF TRACKS = 50