Kinetic boundary friction

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(Communicated by Sir Charles Darwin, F.R.S.—Received 10 October 1945—Read 28 February 1946)

[Plate 3]

It is shown that the exhibition of smooth sliding and relaxation oscillations, or 'stick-slips', under conditions of boundary lubrication, when frictional forces are measured by the deflexion of an elastic system, may be explained as due to the dependence of kinetic friction on velocity. In the cases giving smooth sliding, kinetic friction decreases as velocity decreases, at very low speeds; for the cases giving relaxation oscillations kinetic friction increases as velocity decreases. That is, sliding under boundary conditions is not inherently discontinuous, any discontinuous motion being due to the dynamics of the measuring instrument, and is the result of kinetic friction increasing as velocity decreases. Curves of boundary friction against velocity, using various sliding surfaces, have been determined for a number of lubricants, which show both the above-mentioned types of friction-velocity relationship; and the dependence is shown of kinetic boundary friction on molecular weight for a series of esters of the fatty acids, on percentage of fatty oil in a compounded lubricant (actually oleic acid in mineral oil) and on temperature for a pure substance and a mineral oil. The measurements with the series of esters show some agreement with results given by Fogg (1940). The mixtures of oleic acid with mineral oil give decreasing kinetic friction with increasing percentage of oleic acid right up to 100% oleic acid. The effect of temperature on the dependence of friction in velocity shows that the temperature at which relaxation oscillations first occur depends on the speed of sliding, from which it appears that measurements of the temperature at which relaxation oscillations start at constant sliding speed (Frewing 1942) are not a measure of the temperature at which there is a discontinuity in the properties of the boundary layer.

Introduction

Although numerous investigations into the nature of boundary friction, and friction in general, have been made over a period of some 250 years, it is only during the present century that any real advance has been made towards some slight understanding of the phenomenon of boundary lubrication and the nature of boundary lubricating layers.

Now, of necessity, investigations into the nature of friction under conditions of boundary lubrication consist mainly of measuring coefficients of friction. Examinations of boundary layers by electron diffraction, etc., are only of a subsidiary nature. Hence the investigator of boundary-friction phenomena is in the somewhat difficult position of trying to obtain fundamental information by means of something (friction) the mechanism of which is not understood. All the investigator can hope to do is to interpret the values of coefficients of friction obtained in the light of information available on the physical and chemical properties of thin films of organic substances (lubricants are almost invariably organic) on solid, usually metal, surfaces. That useful literature of the desired nature is almost non-existent is well
Figure 3
known. However, the nature of thin films of organic substances on water has been very fully investigated since Langmuir's paper on the subject in 1917 (see Adam 1938), and this knowledge was drawn on by Hardy (1936) to interpret his friction measurements. To explain the continuous change in frictional properties with chain length for series of long-chain compounds, fatty acids, alcohols, etc., Hardy assumed that the power to act as a boundary lubricant is due to an adsorbed layer which is monomolecular and orientated, as are films of the same substances as condensed films on water. Orientation of lubricant layers on metal surfaces has been confirmed by X-ray and electron-diffraction experiments by many investigators including Trillat (1925), Bragg (1925) and Clark, Sterret & Lincoln (1936). An attempt to take the analogy between films on water and film on metal surfaces still further has been made by Frewing (1942). It is presumed by Frewing that his friction measurements determine the temperature at which the orientated boundary layer becomes disordered and that surface films may change from condensed to expanded types; but it is thought that the experimental evidence is insufficient to warrant all the conclusions drawn.

However, full use of the available variables, which might reasonably be expected to affect boundary friction, has not been made until quite recently; in particular, the effects of speed and temperature. For example, the greatest number of friction measurements made is probably of values of 'static' friction. In all Hardy's work values of the coefficient of 'static' friction were determined, the static value being that at which motion is first apparent with slowly increasing tangential load. It was, however, shown, as long ago as 1877, by Kimball that kinetic friction \( (F_k) \) may decrease with decreasing velocity at very low speeds, and Kaufmann (1910) and Jacobs (1912) suggested that kinetic friction tends to zero as the speed falls to zero and that at high speed the friction approaches an asymptotic value \( (F_a) \) (see figure 1c). Hence, for any value of tangential force applied less than \( F_a \) uniform motion will ensue. This is as Hardy found for the longest chain compounds he used, e.g. palmitic acid, but he failed to appreciate that 'static' friction \( (F_s) \) might in fact not exist, for clearly the value of \( F_s \) will depend on the sensitivity of the method used to ascertain when motion has started, unless \( F_s > F_k \), when it would seem that no ambiguity could occur. It will be seen later, however, that even if \( F_s \) is apparently greater than \( F_k \) unambiguous determinations of 'static' friction are not necessarily possible.

If the frictional force is measured with an elastic system, which carries one friction surface and presses it against a moving surface, the elastic system may perform relaxation oscillations, called in the literature 'stick-slips' (see Bowden & Leben 1939, 1940; and Muskat, Morgan & Reed 1941). The term relaxation oscillation is preferred to 'stick-slip', since 'stick-slip' appears to be associated with 'fluctuations in friction' rather than with the motion of an elastic system. At first an explanation of these relaxation oscillations—and also of the cases where no oscillations occur—was sought in the difference between 'static' and kinetic friction and the dependence of kinetic friction on velocity. In actual fact the relation of
static' friction (if it exists) to the work discussed later proves to be obscure, and simple considerations of the dynamics of the apparatus used and examination of the results obtained indicates that, if relaxation oscillations occur, it is sufficient that kinetic friction increases with decreasing velocity, at low speeds (see figure 1b), and, if no relaxation oscillations occur, that kinetic friction decreases with decreasing velocity, at very low speeds (figure 1c). The presence or absence of 'stick-slips' at any particular temperature is therefore dependent on the speed of sliding, the dynamics of the instrument and the nature of the dependence of kinetic friction on velocity. The work of Bowden & Leben (1939, 1940) and Muskat et al. (1941), and the work of Frewing (1942) on the effect of temperature on boundary lubrication all suffer from the failure to consider the dynamics of the instrument used.

In the following pages elementary considerations of the behaviour of the friction measuring instrument used, and several representative examples of kinetic boundary-friction determinations are given. The discussion also covers the apparatus used by Muskat et al. (1941), Bowden & Leben (1939, 1940) and Frewing (1942). It is considered that as yet knowledge of the phenomena exhibited under boundary conditions is not sufficient to make it possible to deduce from the results obtained a reasonable theory of either kinetic boundary friction or the nature of the molecular layers responsible for boundary lubrication. Hence the results are given quite separately and discussed in connexion with comparable results of other workers and not in relation to one another.

Elementary theory of the behaviour of an elastic system deflected by boundary-friction forces at a moving surface, and pertinent experiments

The considerations put forward here concern the motions of an elastically restrained upper surface which are produced by the frictional forces at its point of contact with a lower moving surface against which it is pressed. The simple assumptions made in the first instance are that static friction ($F_s$) is greater than kinetic friction ($F_k$), and that kinetic friction is independent of velocity (see figure 1a). This case has been considered in some detail by Thomas (1930), and it is easy to show that the elastic system exhibits relaxation oscillations for slow sliding speeds.

Consider the upper friction surface to be in its undeflected position; then, as the lower surface moves it carries the upper with it until the spring force ($F$) (plus a small force due to viscous damping) exceeds the static friction force and slip takes place. The system will now perform oscillations according to the equation, with suitable choice of units,

\[ \ddot{x} + k\dot{x} + x = \pm F_k. \]

If $F_k$ is not much less than $F_s$ only one swing is made about $+F_k$ before the system comes to rest relative to the moving surface in such a position that $F$ lies between $+F_k$ and $-F_k$ and oscillations must cease. Then the upper surface is carried forward again by the lower until $F_s$ is again exceeded and the cycle repeated.
This is illustrated in figure 2 for various amounts of damping. If the damping is such as to make the system aperiodic, after the first deflexion and slip, the deflexion will become constant at \( F_K \).

\[ F_K = F_s \]

\[ F_K = F_s \]

If \( F_K \geq F_s \) clearly no oscillations occur, the deflexion being stable at \( F_K \).

If the system is virtually undamped, the natural period of the elastic system short and the velocity of the moving surface low, the relaxation oscillation will be 'sawtoothed' in shape, as are the 'stick-slip' figures given by Bowden & Leben (1939). That the motion during slip is approximately sinusoidal has been shown by Bristow (1942) and Muskat et al. (1941).* If the velocity during 'slip' is sufficiently high a noticeable temperature 'flash' may be produced by the work done against the frictional force. Calculations of the rise of temperature to be expected on the lines

* A case shown by Muskat et al. (1941) (figure 7, their paper) where \( F_K \) is small compared with \( F_s \) shows two 'swings' between each slip about first \(+ F_K\) and then about \(- F_K\), indicating that \( F_s \) does not come into play immediately because the relative velocity between the surfaces is zero, and that the condition of 'stick' is that \( F \) falls between \(+ F_K\) and \(- F_K\).
given by Blok (1937) and Jaeger (1942) give values of the same order of magnitude as those measured by using sliding contacts of dissimilar metals as thermocouples. The highest temperature flash that has been recorded on an instrument identical with that of Bowden & Leben is about 30° C. It would appear that the observations published by Bowden & Leben (1939) are sufficiently explained by the above considerations.

However, further observations of the motions of such an elastic system indicated that the above simple assumptions regarding boundary friction were only a first approximation.

The important observations were: (a) if the system is damped to be aperiodic, oscillations did not cease; (b) with a virtually undamped system the size of the relaxation oscillations decreases as the speed of the moving surface increases, eventually becoming vanishingly small; at still greater speeds quasi-sinusoidal oscillations may be maintained in the system; and (c) the total movement of the elastic system during 'stick' was less than the movement of the lower surface in the same time, and decreased with increase of lower surface speed to become necessarily zero when oscillations ceased. From these experimental observations it is clear that $F_K$ is not independent of velocity, and it appears that, in fact, $F_K$ decreases rapidly as velocity increases, quickly becoming sensibly constant (see full-line figure 1 b). It may readily be shown that if $F_K$ varies as in figure 1 b, the elastic system may exhibit relaxation oscillations depending on the amount of viscous damping.

Let the frictional force be $F(v)$, where $v$ is the relative velocity between the two surfaces. Then the equation of motion, when the lower surface is moving with velocity $V$, with suitable choice of units, is

$$\ddot{x} + k\dot{x} + x = F(V - \dot{x}). \quad (1)$$

Suppose the motion is steady, then $x$ is constant, i.e. $x = F(V)$. This condition may be unstable. Suppose a small perturbation given by $x = F(V) + y$, then substituting in (1)

$$\ddot{y} + k\dot{y} + F(V) + y = F(V - \dot{y}).$$

Expanding the right-hand side by Taylor's theorem

$$\ddot{y} + k\dot{y} + y = -F'(V) + [F(V) - \dot{F}(V) + ...],$$

neglecting terms in the expansion after the second

$$\ddot{y} + (k + F'(V))\dot{y} + y = 0.$$

For $F_K$ varying with velocity as in figure 1 b, $F'(V) < 0$. Hence if $k$ is negligible the motion is certainly unstable, but stability may be produced if the value of $k$ is sufficiently great. If $F_K$ varies as in figure 1 c obviously the motion is always stable. (Case of Jacobs 1912 and Kaufmann 1910.)

These considerations and experimental observations agree with the work of Papenhuyzen (1938) on the sliding of rubber on glass and other surfaces. Papenhuyzen was also able to show, however, that on reducing the speed of the lower
friction surface sufficiently, oscillations ceased and smooth sliding ensued at values of friction \((F_K)\) which decreased with speed. This is indicated by the dotted extensions to the curves in figure 1 b.

In concluding this section it may be emphasized that on the foregoing analysis relaxation oscillations (or ‘stick-slips’) are fundamental to the type of instrument, having regard to the dependence of friction on velocity and the dynamics of the elastic system, and not that ‘these discontinuities are inherent in the sliding of metals’ (Bowden & Leben 1939). Hence it is not possible to deduce from the papers of Bowden & Leben (1939) or others describing work with similar apparatus any information regarding kinetic friction other than that \(F_K < F_s\), if ‘stick-slips’ occur.

**Experimental**

The friction-measuring apparatus was designed to determine curves of boundary friction against velocity at low speeds on the basis of the foregoing analysis, which indicates that to determine \(F_K\) the period of the elastic measuring system is not of primary importance but that high damping is required to make the system stable.

A general view of the instrument is shown in figure 3, plate 3, and the essential part of the system diagrammatically in figure 4. The tangential forces due to friction are measured between the upper spherically ended surface, \(A\), and the lower flat surface, \(B\). The use of a spherically ended surface on a flat in order to obtain boundary conditions is as described by Hardy (1925). The flat surface is carried on a trolley, \(T\), driven at various constant speeds by hydraulic ram designed to impart as smooth a motion as possible to the trolley. The driving rod, \(R\), of the ram, is just visible in figure 3. The speed is controlled by the rate of flow of the hydraulic fluid into the system. In order to work at temperatures above normal room temperatures, a heater, \(H\), is built into the trolley; the cooling system, \(C\), beneath the heater is to keep the heat localized to the friction surface. The trolley wheels run on horizontal rails, one of which is a V-groove to define the direction of motion. The speed of the lower surface is measured by timing over a fixed distance by a stop-watch electrically operated by the trolley. The top spherically ended surface is carried on the rigid frame, \(F\), attached to the four wires \(W, X, Y\) and \(Z\), which are arranged to be in equal tension in pairs (i.e. \(T_W = T_X, T_Y = T_Z\)) and are tensioned by the spindles, \(V\). Then, with the top surface fixed on the centre line of the frame, \(F\), it will be deflected parallel to the direction of motion of the trolley by the forces at its point of contact with the lower surface. This arrangement was adopted, as it was at one time thought that twisting of the surfaces relative to each other might produce increased adhesion between the surfaces (Bristow 1942). This was later found to be an unnecessary refinement. The elastic system is heavily damped by the arrangements \(D, D\), each of which consists of a piston attached to the carriage and moving in a cylinder, carried on the body of the apparatus. There is a small clearance between piston and cylinder which is filled with oil. Deflexions of this elastic system are measured by a mirror-lamp system \(M\), and are observed visually on a scale (not shown). The
deflexions are calibrated in terms of force by pulling the system forwards by a string attached to the upper friction surface which runs over a pulley (not shown) to a scale pan. Load is applied through the cantilever, $L$, by turning the screw, $S$, which bears on the frame, $F$. The load is determined by measuring the force necessary to lift the top surface out of contact with the lower by means of the weigh beam, $E$. The observations taken are deflexion and time to travel a certain distance, from which the coefficient of friction and velocity can be determined, and curves of friction against velocity constructed. In some cases, with the heaviest convenient damping, small oscillations occur at the very lowest speeds. For such cases the curves through the experimental points are drawn through the mean of the points obtained from the maximum and minimum deflexions during the oscillations. This does not produce any great uncertainty in the curves, as in such cases the coefficient of friction is always rising very rapidly as velocity decreases.

Two methods of cleaning the friction surfaces have been used: (1) polishing with 0000 emery paper, scrubbing in strong caustic soda solution with cotton-wool until the entire surface is completely wetted with water, washing in water and drying with acetone; and (2) cutting the surface with a clean tool as described by Ernst & Merchant (1940). In general the first method has been used on steel surfaces and the second on soft materials. All the results given were obtained under conditions of constant load and with excess lubricant present.

**Results**

A selection of curves of coefficient of friction against velocity are given here which are directly comparable with other published work on boundary friction, and which illustrate the discussion already given. It will be seen that these results do not conflict with those given by other workers, but do add information which is not in agreement with the interpretations given by previous investigators.
Results are given for:

(i) A series of ethyl esters of saturated fatty acids for two pairs of sliding surfaces, (1) hard steel on hard steel, and (2) phosphor bronze on hard steel, at room temperature.

(ii) A mineral oil containing additions of various percentages of oleic acid, with sliding surfaces of (1) steel on steel, and (2) brass on hard steel, at room temperature.

(iii) For (1) ethyl palmitate lubricating the sliding of tin on hard steel and for (2) a mineral oil used as lubricant for steel sliding on hard steel, at various temperatures.

(i) The kinetic boundary friction of a series of esters

The series of esters used is given in table 1, and the measurements were made at room temperature. The results of the determinations are given in figures 5 and 6, the curves being numbered for the corresponding lubricants as in table 1. The nature of the results may perhaps be seen better in the plot of coefficient of friction against molecular weight given in figures 7 and 8.

### Table 1. Esters used

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<th>number</th>
<th>ester</th>
<th>formula</th>
<th>molecular weight</th>
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</thead>
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<tr>
<td>1</td>
<td>ethyl formate</td>
<td>C₂H₅·CO·O·C₃H₇</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>ethyl acetate</td>
<td>CH₃·CO·O·C₃H₇</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>ethyl propionate</td>
<td>C₄H₇·CO·O·C₃H₇</td>
<td>102</td>
</tr>
<tr>
<td>4</td>
<td>ethyl valerate</td>
<td>C₅H₉·CO·O·C₃H₇</td>
<td>130</td>
</tr>
<tr>
<td>5</td>
<td>ethyl oenanthate</td>
<td>C₆H₁₃·CO·O·C₃H₇</td>
<td>158</td>
</tr>
<tr>
<td>6</td>
<td>ethyl caprylate</td>
<td>C₇H₁₅·CO·O·C₃H₇</td>
<td>172</td>
</tr>
<tr>
<td>7</td>
<td>ethyl pelargenate</td>
<td>C₈H₁₇·CO·O·C₃H₇</td>
<td>186</td>
</tr>
<tr>
<td>8</td>
<td>ethyl laurate</td>
<td>C₉H₁₉·CO·O·C₃H₇</td>
<td>228</td>
</tr>
<tr>
<td>9</td>
<td>ethyl palmitate</td>
<td>C₁₀H₂₁·CO·O·C₃H₇</td>
<td>284</td>
</tr>
</tbody>
</table>
Figure 6. Phosphor bronze sliding on hard steel lubricated with ethyl esters of saturated fatty acids at room temperature.

Figure 7. Hard steel sliding on hard steel lubricated with ethyl esters of saturated fatty acids at room temperature.

Figure 8. Phosphor bronze sliding on hard steel lubricated with ethyl esters of saturated fatty acids at room temperature.
The results given in figure 7 for hard steel on hard steel are comparable with those of Fogg (1940) for 'static' friction measurements on the same series of esters, using a modified Deeley machine. Fogg's measurements gave a curve of coefficient of 'static' friction against molecular weight similar to the one given for a constant velocity of 0.01 cm./sec., with the maximum of the curve between ethyl propionate (3) and ethyl valerate (4). Roughly the explanation given, on the assumption that the coefficient of friction is inversely proportional to the distance between the two friction surfaces as determined by a monomolecular adsorbed layer on each surface, was that the esters are attached to the surface by the double-bond oxygen atom in the molecule with the two branches (oxygen atom and ethyl group, and varying fatty acid chain) standing at angles determined by their relative weights, the greater the difference in branch size the more perpendicular the longer branch stands to the surface. Hence a minimum thickness of adsorbed film may be expected between ethyl propionate (3) and ethyl valerate (4), at which the maximum friction of the series was found.

However, for the determinations of kinetic boundary friction a maximum is only found at slow speeds for hard steel on hard steel. At high speeds, the friction falls continuously with increasing molecular weight for hard steel sliding on hard steel, and for phosphor bronze on hard steel no maximum is shown even at very low speeds (in this latter case the points are somewhat scattered).

It is apparent that the explanation given by Fogg is insufficient to explain all of the above results.

(ii) The kinetic boundary friction of a mineral oil containing additions of oleic acid

The results are given in figures 9 and 10. It will be seen that the coefficients of kinetic boundary friction are continuously reduced by increasing additions of oleic acid to the mineral oil, the oleic acid having good properties as a boundary lubricant, and the mineral oil poor properties. The effect of additions of fatty oil is greatest at low concentrations, and it will be noted that at high concentrations of fatty substance the friction-velocity curve changes in type from that shown in figure 16 to that shown in figure 1c, for brass on steel, but not for steel on steel. It is clear that compounding a mineral oil with a fatty oil produces considerable improvements in boundary lubricating properties even for small additions, say up to 5% fatty oil, but that the friction still continues to decrease slowly right up to 100% of the fatty constituent. At high speeds the effect of additions of the fatty substance tends to decrease.

Such a result is to be expected, since the boundary layer will probably always contain a greater percentage of the more 'active' constituent than the solution. But apparently even at high concentrations of the 'active' substance (oleic acid) the boundary layer still contains an appreciable amount of the less active substance (mineral oil). The effects to be expected will, of course, depend on the relative surface 'activities' of the constituents of any particular mixture.

In figures 11 and 12 coefficients of friction are plotted against concentration of oleic acid in mineral oil at certain constant speeds, and show very clearly how small
amounts of oleic acid reduce the friction very considerably. These graphs may be compared with those given by Fogg & Hunwicks (1940) for additions of rape oil to mineral oil and oleic acid to B.P. paraffin, for determination of 'static' friction with a modified Deeley machine. The curves given by Fogg & Hunwicks are the same shape, and show the same facts as those given in this paper for low velocity.

Figure 9. Brass sliding on steel lubricated with mineral oil—oleic acid mixtures at room temperature.

Figure 10. Steel sliding on steel lubricated with mineral oil—oleic acid mixtures at room temperature.
The effect shown of the decreasing effect of additions of oleic acid at higher speeds has not so far been satisfactorily explained.

**Figure 11.** Brass sliding on steel lubricated with mineral oil—oleic acid mixtures at room temperature.

**Figure 12.** Steel sliding on steel lubricated with mineral oil—oleic acid mixtures at room temperature.
The effect of temperature on kinetic boundary friction for various surfaces and lubricants appears to be somewhat complicated, and the discussion here is confined

**Figure 13.** Tin sliding on hard steel lubricated with ethyl palmitate at various temperatures.

**Figure 14.** Steel sliding on hard steel lubricated with a mineral oil at various temperatures.
to two of the simpler cases investigated, namely, (1) tin sliding on hard steel lubricated
with ethyl palmitate, and (2) steel sliding on hard steel lubricated with a thin mineral
oil. The friction velocity curves for several temperatures are given in figures 13a
and b and 14a and b. Figures 13b and 14b give the low-velocity ends of figures
13a and 14a in greater detail by plotting velocity on a larger scale.

(1) Ethyl palmitate lubricating tin on hard steel. This case is of particular interest
in relation to the work published by Tabor (1940, 1941), Frewing (1942) and Hughes
& Whittingham (1941).

At the higher velocities the coefficient of kinetic friction decreases with increase
of temperature; at the lower velocities, however, the coefficient of kinetic friction
increases, the increase extending to greater speeds as the surfaces get hotter. The
change of shape of the curves of friction against velocity shown at very low velocities
necessarily means that the tendency to give relaxation oscillations increases as the
temperature is raised. The crosses on the graphs of figure 13 indicate approximately
the highest velocity at which relaxation oscillations are first apparent. The velocity
at which the oscillations vanish is, of course, dependent on the amount of damping
employed. It is clear, therefore, that if the lower surface velocity in the apparatus is
constant at, say, 0.01 cm./sec., no relaxation oscillations will occur even if the
temperature is raised to 170° C. On the other hand, if the surface velocity is less
than about 0.002 cm./sec., relaxation oscillations will occur at room temperature.
It is clear that over this range of temperature ‘stick-slips’ can start at any desired
temperature as the surface temperature is raised by choosing the correct velocity
of the lower surface. Using steel on steel lubricated with ethyl palmitate the change
in shape of the curves at very low velocity is essentially the same as for the above
case.

That some change is taking place, as the temperature is raised, which is connected
with the nature of the molecule of the lubricant and surfaces concerned, cannot be
doubted. But that this change is necessarily connected with the sudden disorienta-
tion or desorption of an adsorbed film, and that the temperature is characteristic
of the lubricant (i.e. that there is some sudden change at this temperature) as
suggested by Tabor (1940, 1941) and supported by Frewing (1942), cannot be
maintained. In this connexion it may be noted that the values given by Hughes
& Whittingham for the temperature at which ‘stick-slips’ start, with fatty
acids as lubricants, are between 20 and 50° C higher than the values given by
Frewing.

(2) A mineral oil lubricating steel on hard steel. For this case the coefficient of
friction increases with rise of temperature over the whole of the velocity range used
(except for 170° C at very low speed). Here again, however, the tendency to give
relaxation oscillations (‘stick-slips’) increases as the temperature rises. As in (1)
above it is possible to make the temperature at which relaxation oscillations start
any desired value by fixing correctly the velocity of sliding.

At this stage, it is not possible to give a satisfactory explanation of these pheno-
mena.
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