LUBRICANT ACTIVITY IN
SLOW SPEED FRICTION TESTS

by

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ABSTRACT

This thesis investigates lubricant activity in slow speed friction tests. A novel modification to a Bowden-Leben machine has been used to allow multiple passes to be made over the same track. This has enabled the action of an E.P. additive to be thoroughly investigated, both by friction tests, and some subsequent chemical analysis.

A literature survey is presented, giving a basis for the subject from previous research. The apparatus is described and a comparison made between single and multiple pass friction testing. Initial tests are presented, which provide an insight into the frictional process. They involved the production of sequential photomicrographs and certain metallurgical investigations.

A great number of mechanical factors were varied in a series of tests, so that the effect of each on the friction - temperature graph might be demonstrated. An E.P. additive was employed, which caused the friction to be reduced at elevated temperatures (termed, a friction drop). The temperature of this drop was found to be insensitive to almost all mechanical factors apart from sliding speed. This effect has not been observed, as such, before.

An investigation into the effect of varying certain chemical factors is also given. The process governing the friction drop was deduced to be a bulk chemical reaction, probably oxidation of the E.P. additive. The friction drop could be 'delayed' by the addition of an oxidation inhibitor, or 'advanced' by preoxidising the lubricant.

Confirmatory tests were conducted to analyse some chemical aspects of the friction tests. The use of I.R.Spectroscopy, X-ray Photo-electron Spectroscopy and Electron Probe Micro Analysis is described. The previously deduced hypothesis concerning oxidation of the lubricant is confirmed.

ACKNOWLEDGEMENTS

My thanks go to Prof. A. Cameron for his supervision. They are also due to all the members of the Lubrication Laboratory, for their cheerful assistance, most especially Reg Dobson. I would also like to mention Dr. H. Spikes, Dr.R. Hiley and Mr. A. Bowyer, whose constant advice and encouragement made it possible to complete this project (even if we did not always see eye to eye).

I am very grateful to the S.R.C. for the provision of a grant.

Finally my gratitude to Ann, both for her typing and patient support.

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MAIN SYMBOLS AND ABBREVIATIONS

C	Concentration
...C	Temperature in degrees Celsius
...°C	Temperature interval in degrees Celsius
DBDS	Dibenzyl disulphide
E.P.	Extreme pressure
Hz	Hertz
I.R.	Infra-red
kg	Kilogramme
min	Minute
mm	Millimetre
µm	Micrometre
nm	Nanometre
O.C.T.	Out of contact time
s	Second
T	Absolute temperature
T.L.C.	Thin layer chromatography
V.p.n.	Vicker's hardness (pyramid) number

CHAPTER 1

INTRODUCTION TO FRICTION TESTING AND LUBRICANT ACTIVITY

1.1. FRICTION

The problems created by friction, and ways of overcoming them, have been of great concern to man since earliest times. Davison (1) describes how the Egyptians used oil to reduce the sliding friction developed whilst moving colassae, and how they used grease to reduce the wear in their chariot axles. However the scientific analysis of friction phenomena has had to wait until relatively recently. Amonton is usually credited with the discovery of the classical laws of friction, but it has been suggested by Bowden and Tabor (2) that these were understood by Leonardo da Vinci. These basic laws have served well up to the present century, but with our ever widening variety of engineering systems, the need has arisen for a quantified understanding of the frictional process. For example static and kinetic friction were long known to differ in value and may even have been considered qualitatively different; Much more recently, Sargent (3) has argued that static friction cannot even be said to exist, because friction always involves movement, however small, and no force can be measured (or detected) without some displacement.

Often this "desire for numbers" with which to describe the friction that exists between two surfaces has led to confusion in the search for fundamental understanding of the processes involved. It is now known that observed friction will depend on a multitude of factors, and that comparison between two different experiments, even employing nominally the same surfaces, must be made with great care. If the fundamental mechanism of the frictional process is not appreciated then the only result from experimental study will be a morass of empirical concepts. This thesis sets out to give an understanding of this mechanism, and although it may not complete the task, it is to that end that it was written.

1.2. EARLY FRICTION TESTS

Hardy (4) in the 1920's performed elementary experiments in which he determined the static coefficient of friction for different materials. He concluded that friction arose from elastic forces existing between surface layers. It should be noted that only the friction experienced between nominally solid bodies is being considered in this thesis. Any friction that results from fluid films between solid surfaces, as in hydrodynamic or elastohydrodynamic conditions is outside the scope of this work. Bowden and his co-workers continued to grapple with Hardy's ideas about surface layers, applying them more realistically to the conditions known to exist within the contact region. Bowden and Leben(5) describe an apparatus that is basic to this research, and is known as the Bowden- eben machine. They coined the phrase "stick-slip" to describe oscillations of the slider resulting from the elastic nature of its restraint. Concluding that sliding will almost always take place intermittantly, they demonstrated that large temperatures can be generated during the short "slip" period.

Bowden and Leben explain the "stick-slip" process by the following considerations. The load is supported by the tips of the asperities, which are only a small fraction of the apparent contact area. The high local pressures at these points will rupture any intervening film, and so form metallic junctions. As the carriage moves, the elastic restraint of the slider imposes an increasing tangential force, which will reach a limit when it is sufficient to shear all the metallic junctions. Then the elastic restraint will push the slider forward relatively fast, and the process repeats itself. Bowden and Tabor (6) published parallel work and used conductance measurements to verify these ideas. They showed that the real area of contact is small and varies considerably during a "stick-slip" cycle. These researchers worked mainly with unlubricated contacts, and found that there was less tendency to "stick-slip" with lubricated surfaces. Having concluded that "stick-slip" was a result of metal to metal contact (and presumably indicated poor lubrication performance) they reported the apparently significant implications to engineers (7) concerned with lubricant activity.

1.3. LUBRICANT ACTIVITY

Once the equipment had been established for friction testing, many workers proposed their own theories of lubricant activity, backed up with some simple test results. Hardy had shown the major influence of a single layer of organic molecules on a metal surface as regards friction. Frewing (8), following some work of Tabor (9), heated simple lubricants whilst continuously monitoring the friction on a Bowden-Leben machine. He found that at a particular temperature, appropriately called the transition temperature, "stick-slip" would begin and he concluded that the lubricant film had broken down at this point, allowing metal to metal contact. The reversibility of the transition suggested that it was caused by a reversible physical process, and the fact that both a monolayer and excess lubricant gave the same friction, caused Frewing to deduce that it was an adsorbed monolayer acting in the contact, excess molecules having been squeezed out by the large pressures involved. Further work (10) with lubricant additive solutions of different strengths in white oil (liquid paraffin), revealed a variation in the transition temperature with concentration. Frewing proposed an adsorption theory to govern the system. By assuming a particular critical surface coverage below which the transition occurred, he could apply simple thermodynamics to the adsorption equilibrium. This enabled him to predict a relationship between the concentration of active lubricant and the temperature at which this critical surface coverage would occur. His analysis produces a logarithmic relationship between concentration and the inverse of the absolute temperature, irrespective of the value of the critical coverage. His experimental results proved to fit into just such a relationship and Frewing derived a heat adsorption from the slope of the graph he obtained.

A few years later, however, Bristow (11) showed that "stick-slip" could be an oscillation predictable from the mechanics of the system if the friction varies with sliding speed. He performed experiments similar to those of Frewing, but was careful to mechanically damp out any "stick-slip" oscillations, and by varying the speed he obtained friction velocity curves at different temperatures. He found an increasing tendency to "stick-slip" for a number of lubricants when heated. Bristow discussed how the onset of "stick-slip", in an inadequately damped system such as Frewing's, could be arranged to develop at any temperature, by adjusting the sliding speed. He also indicated how the mechanical factors such as stiffness and inertia, as well as damping, will affect the "stick-slip" oscillations. Unfortunately Bristow could suggest no cause for this change of friction with velocity. Although Bristow's work undermined the assumption Frewing made, that "stick-slip" indicated lubricant breakdown, Frewing's conclusion regarding an adsorbed film has remained. Indeed no better hypothesis has since been advanced. For the type of compounds so far considered low friction conditions are a result of a reversibly adsorbed layer of molecules from the lubricant on the surface.

1.4. HEAT OF ADSORPTION

The application of thermodynamics to a frictional system, has been of continual interest since Frewing (10). Many have followed his analysis, but a more general approach may be found in Spikes (12). Spikes was the first to measure a heat of adsorption directly and then compare it with results from a frictional system. For equilibrium conditions, it can be shown from thermodynamic principles that:

where C is the Concentration of adsorbate in solvent

$\Delta H^{\circ}_{\theta}$ is the isosteric Heat of Adsorption, at the coverage θ

T is the absolute Temperature

R is the universal gas content

Assuming (i) a reversible system

(ii) very small concentrations

Spikes measured the extent of adsorption of an amine on stainless steel at different temperatures and concentrations. From this data he plotted the variation of temperature and concentration which produced a particular coverage. He also performed friction tests similar to those of Frewing, but giving each test 15 minutes in which to reach equilibrium before sliding was commenced. Both this and the question of reversibility he considered most important. Finally he plotted in C against $\frac{1}{T}$ (at transition) as Frewing had, and compared this with the adsorption plots from his earlier experiments. Fig. 1.1. is taken from this work. The best coverage to choose was 40% of a monolayer, and the extent of correlation may be assessed from the graph.

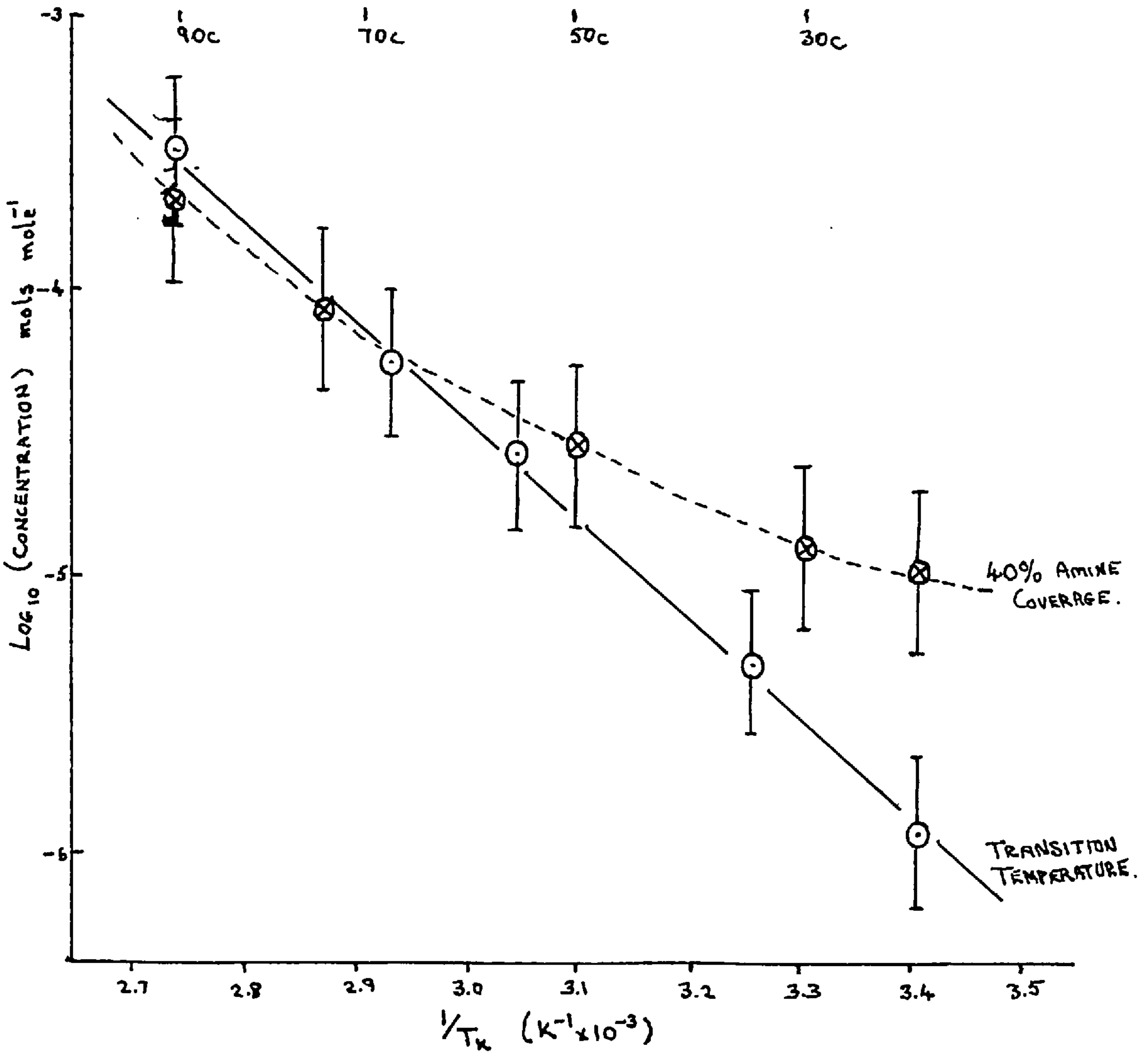


Fig. 1.1. ref. (12)

It is of course important that the two lines have the same slope and lateral position to satisfy the theory (that transitions occur when some definable surface coverage is reached). Now that Spike's work provides good evidence in support of the theory, it is worth considering the implications and validity of the concepts used initially in these friction tests.

1) The process governing the transition is confirmed as reversible. This does not mean that all the adsorption is reversible, but that around the critical coverage the adsorption is truly reversible. In fact Spikes found that about one third of the amine was adsorbed irreversibly onto the stainless steel.

2) The slope of a ln C against $\frac{1}{T}$ plot may be associated with the heat of adsorption of the additive at the particular surface coverage below which a transition would occur. No further assumptions need be made, except that the system is at equilibrium.

3) Direct determinations of heats of adsorption can provide data, from which the actual surface coverage at transition may be deduced. It would seem that half a monolayer is a reasonable estimate of this coverage. There is no other practicable way of determining the actual value. The fact that nearly all workers obtain a straight line from a ln C against $\frac{1}{T}$ plot is merely good evidence that the transitions do occur at some constant coverage, because a constant $\Delta H^{\circ}_{\theta}$ implies a constant θ also.

4) It must be remembered that the results of slow speed friction tests are being analysed here. Transitions do occur in high speed tests but they are not caused by the same process. This is because the above ideas imply that failure results from the excessive desorption of an adsorbed layer on the track ahead of the slider, allowing damage to develop as the slider meets the "exposed" track. Thus the

bulk temperature of the system is important, on the other hand in high speed tests the "flash" temperatures generated by frictional heating in the contact are reckoned to cause the failure, when it occurs. Therefore no longer do equilibrium conditions exist, nor can the effects of pressure or material properties be ignored. The application of the ideas gained from slow speed tests to a high speed system is very complex. Good discussions of this point are made by Tabor (13) and Hirst and Stafford (14).

5) Lastly, the value of deducing a heat of adsorption, however valid, from transition temperatures is not clear. It is not a complete measure of the lubricants activity, the transition temperatures themselves are a better measure. Further work, such as the comparison of the performance of a range of additives in both high and slow speed tests with their heats of adsorption directly measured, would provide useful insight into this question. Forbes and Reid (15) have done some of this, but without the slow speed friction tests, and their work is discussed later in section 1.14. Otherwise it is of minimal value to determine the slope of a graph (ln C against $\frac{1}{T}$), so long as its lateral position remains unspecified.

1.5. CHEMICAL ASPECTS OF AN ADSORBED FILM

Chemical reactions have long been known to play a part in lubricant activity. Long chain fatty acids were shown to react with metal surfaces by Bowden and Moore (16), presumably with the metal oxides to produce a "metal soap". This soap was presumed to remain attached to the metal surface and provide the effective lubrication that is effected by this oiliness agent. The observed transition temperatures of a sliding system lubricated by fatty acids were close to the softening point of the soap, i.e. the temperature at which molecular disorder significantly increases. In contrast the fatty acids themselves melted some 70°C below the transition temperature. This was shown earlier by Tabor (17) and so although the transitions were reversible, an essentially irreversible chemical reaction is postulated to explain the observed frictional behaviour. It may be seen that chemical reactions are only to be expected within a practical lubricant, especially when metal surfaces are present, whether or not these reactions are necessary to the action of the lubricant. Also any oxidation of the lubricant will affect its performance, as Tabor (18) has pointed out. This complication arises in many friction tests, especially at high temperatures, and the subject will recur in this thesis.

1.6. PHYSICAL ASPECTS OF AN ADSORBED FILM

The properties of an adsorbed film, even if of known chemical composition, are not well understood. Normal rheological concepts will not apply to a mono-molecular layer on a metal surface. Bailey and Courtney-Pratt (19) sheared two mono-molecular layers of calcium stearate between mica sheets and produced a shear strength for the film well below those found in frictional junctions. Inevitably however, their experiments were carried out at low pressures and as has been pointed out by Tabor (13), little is known of the behaviour of monolayers at pressures high enough to cause yielding in metals. Further work by Israelachvili and Tabor (20) along similar lines to that of Bailey and Courtney-Pratt, but employing higher pressures, revealed marginally higher shear strengths. Wilson (21) has suggested that although a monolayer would be expected to be stable with all the molecular chains normal to the surface, when a tangential stress is applied the chains may be bent over (like the flattening of wheat by a storm) and sliding occur more easily. He bases his ideas on results from contact resistance measurements, which are a little tenuous. Israelachvili and Tabor found that the molecular chains between the mica sheets in their experiments were not bent by more than 20° from the normal, when sliding occurred. Nevertheless the process Wilson describes may be involved, even if only locally. Cameron (22) has discussed the possibility that realistic friction coefficients may be predicted from the inter-molecular forces (Van der Waals etc.) known to exist in boundary lubricant variations in friction with sliding speed, as observed by Bristow (10), might then be caused by orientation effects of the type already mentioned. Unfortunately Cameron had to assume flat surfaces and uniform films for his analysis, which may be realistic in static conditions but this has yet to be demonstrated experimentally.

1.7. STICK - SLIP

The phenomenon of"stick-slip" has not yet been fully explained. Certain time dependent functions have been postulated, particularly that static friction will vary with the time of contact e.g. Bowden and Tabor (23). Recently Johannes, Green and Brockley (24) have demonstrated that the effective parameter is the rate of application of shear stress (i.e. for an elastically restrained system, stiffness times sliding speed). It is also known that vertical oscillations affect the "stick-slip" process. Antoniou(25) considers the effect of these "triggering oscillations" on the relaxation oscillation process, whilst on a larger scale vibrations are commonly used to aid pile driving, flow of particles and the like. Godfrey (26) has reported a reduction in the effective load and therefore the apparent coefficient of friction, although this was only when the vertical acceleration of the forced surface exceeded that of gravity, for some period. Gaylord and Sho (27) measured "static" coefficients of friction, using statically and dynamically applied loads and several material combinations. They found for steel on steel that the friction was lower when the load was applied dynamically.

It may be seen, then, that variations are inevitable in the friction developed between slowly moving surfaces, especially when the restraints operating are elastic and insufficiently damped. Indeed, if the damping in the system were large enough, certain changes in the coefficient of friction which were of interest might be unwittingly suppressed. Thus it must always be remembered, most of all in slow speed friction tests, that the mechanical properties of the experimental arrangement will affect the value of friction measured, since friction is itself a mechanical property of the contact. It is also worth making a distinction between regular frictional oscillations of a lubricated contact (that is with a coefficient of friction around 0.1) as observed by Frewing (8) and the gross irregularities in the friction when two badly lubricated metals slide over one another as observed by Bowden and Leben (5). The former may best be understood to result from a change in friction with velocity; the latter by the formation of metal junctions and their subsequent shearing. It is this adhesional process, which will be considered in the next section.

1.8. ADHESION

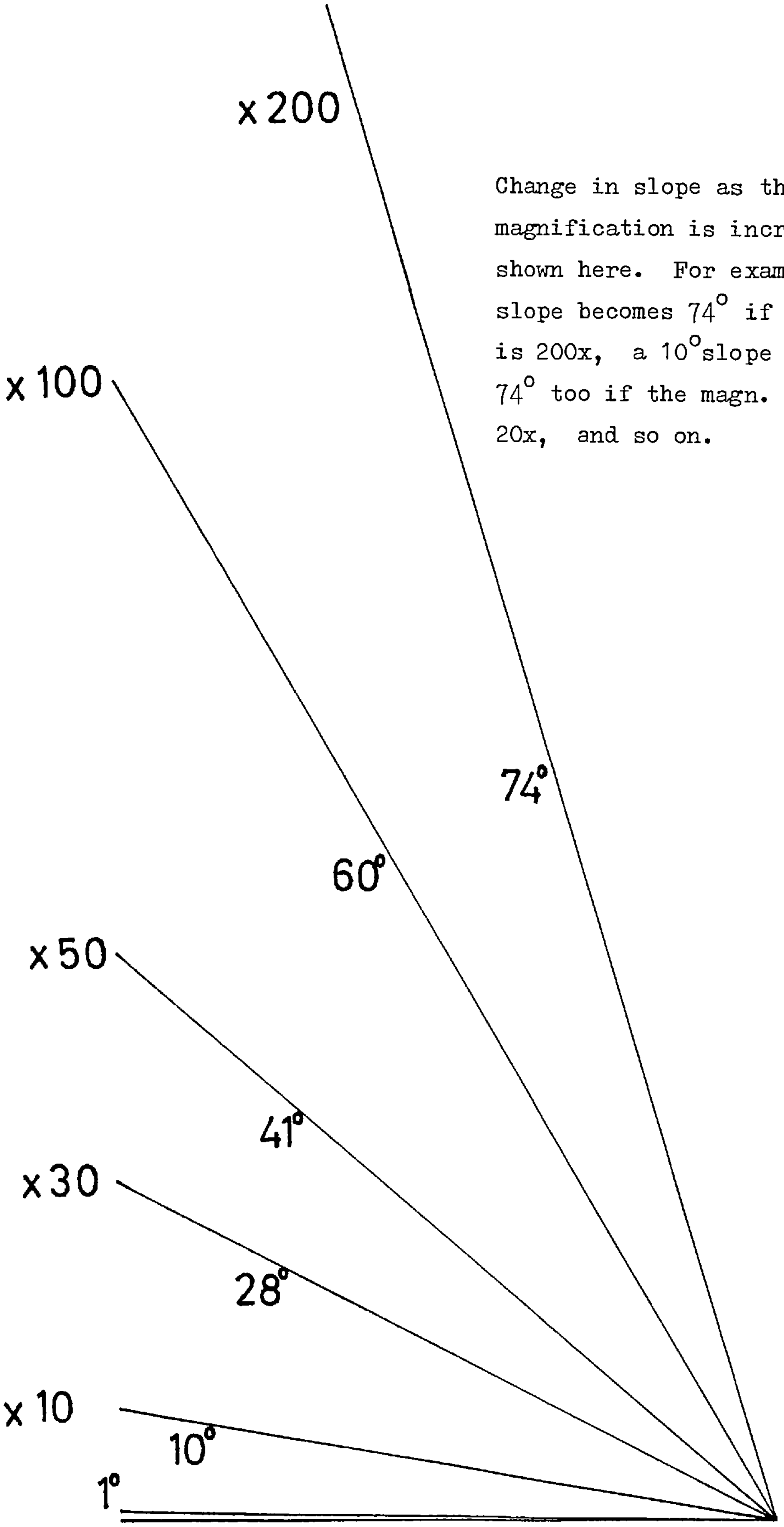
So far the friction between surfaces, separated by a boundary layer, has been discussed. When such a layer breaks down, considerable surface damage ensues and the friction rises to high values because of the adhesion of one surface to the other. Confirmation that small amounts of metal transfer occurred in their friction tests, was reported by Bowden and Moore (28). They used chemical tests, and so proved that adhesion was taking place. A very sensitive determination of transfer can be obtained by using a radioactive slider. The position of the transferred material may be ascertained by employing photographic emulsions, as is described by Gregory (29). These techniques have been applied to a wide variety of rubbing contacts, to check for the occurr of transfer. It is to be noted, from the results of such tests, that adhesion also occurs in lubricated contacts, although on a vastly reduced scale and only on the high spots. This evidence raises two questions as to the specific conditions to be found in the contact region of two metal surfaces. What is the real area of contact and what is the pressure acting within that area?

1.9. REAL AREA OF CONTACT

This subject has long been of interest, for the true scale of the roughness of an engineering surface has long been appreciated. Coulomb's (2) early theories of friction saw its cause in the interlocking of the asperities, and an understanding of the factors which result in the validity of Amonton's laws must include a knowledge of the real area of contact. The simplest conceivable explanation would be if the real area of contact were proportional to the normal load, thus implying a constant pressure within that contact area. Amonton's laws would then be expected to hold true, for with constant conditions within the actual contacts, the shear stresses required would be constant and the total friction proportional only to the area or load. Likewise the overall area of th slider would have no effect on the friction. Considerable effort has therefore been expended to demonstrate the likelihood of this relationship applying to practical situations.

One tool, often used, is the surface profilometer, which provides a trace of vertical displacement, magnified many times, against horizontal displacement, which is also magnified. The effect of having vertical displacements magnified relative to horizontal ones can be very misleading to the observer. This can arise not only with profilometer traces, but with micrographs, where shadowing at low angles is used to indicate the height of asperities, or with taper sections. This relative magnification, often up to 50:1, alters the slopes of asperities, making interpretation very difficult. This alteration is illustrated in Fig. 1.2., which demonstrates why the surfaces described must not be imagined too literally from the information presented.

Further analysis of the output from a surface profilometer may be made using the digital computer. Effective mapping techniques are also becoming possible for the first time, and real, or imaginary, surfaces can be "pressed together" and theoretical considerations applied to determine the area of contact which would result, using a system developed by Thomas (30). Dyson and Hirst (31) used an optical technique to observe the growth in the contact area between a steel surface and a coated glass disk with the imposition of increasing load. They found that the contact was spread over many small areas, depending on the degree of polishing employed and they challenged earlier work which had used electrical resistance measurements to deduce the contact area. Archard (32) followed up their suggestion that there may be several different scales of



Change in slope as the vertical magnification is increased is shown here. For example a 1° slope becomes 74° if the magn. is 200x, a 10° slope becomes 74° too if the magn. is only 20x, and so on.

Fig. 1.2.

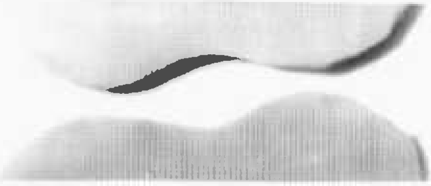
roughness on any surface. From a theoretical basis he showed that elastic considerations would indicate that the area of contact should be proportional to load, if the range of roughness is sufficiently great. Of course, the size of asperities must remain low in any real metal, to prevent the elastic limit being exceeded, but as Archard pointed out a well run-in engineering surface might easily fulfill the conditions required.

On the other hand, experiments by Courtney-Pratt and Eisner (33) demonstrated that plastic flow occurred within the asperities of normally loaded surfaces when a tangential load is also applied. This was indicated by a non-recoverable tangential movement. Furthermore electrical resistance measurements revealed an increase in the contact area which also did not recover on removal of the tangential stress. Although not reliable quantitativily, especially if oxides are present, electrical resistance measurements are of qualitative value. Thus it is the combined stress, from both normal and tangential loads, which governs the conditions in the contact. Whilst in many metals elastic deformations occur, and indeed cause the reappearance of surface features even after plastic damage has been effected it is clear that if frictional forces are developed, all but the smallest loads will result in plastic flow in the asperities. If plastic flow is general then the direct proportionality of contact area with load, is expected, governed by the yield pressure of the metal.

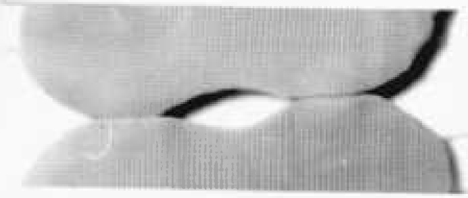
1.10. ADHESIONAL FRICTION MODEL

The work described above provides insight into the mechanism of friction, when there is adhesion between two metals. Tabor (34) extended the model to explain convincingly the unexpected consistency in measured friction of various clean metal pairs. Earlier work, described by Bowden and Tabor (35), had shown that extremely high friction was generated by surfaces which had been cleaned and kept in a vacuum. In fact welding took place immediately on contact. If the metals had been thoroughly outgassed, the apparent friction coefficient was extremely high, when an attempt was made to shear the specimens. An explanation of this becomes clear when the increase in real area of contact is appreciated, as reported by Courtney-Pratt and Eisner (33). As any tangential force (that is the force used to determine the friction) is applied the contact area grows, and on clean surfaces with no oxide or other layer to impede growth this will continue until the two specimens have effectively become one. Tabor analyses the effect of contaminant films of different effective surface coverage on the ultimate shear strength of the junction, as the tangential force is increased. Thus he assessed the degree to which junction growth would occur before shearing breaks the junctions - how much "stick" will occur before "slip" so to speak. Fig.1.3. illustrates this process in a plasticine model.

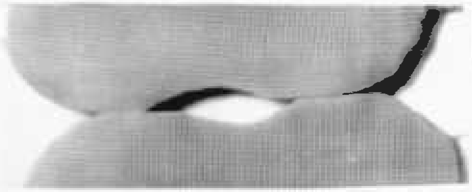
Having derived an equation for junction growth, Tabor fixes the ultimate shear strength of the contaminant film as some fraction, k, of the bulk metal shear strength. When k is unity i.e. the surfaces are perfectly clean, Tabor's equation predicts infinite junction growth, but if k is only slightly smaller (about 0.95) the coefficient of friction would be reduced from this "infinite" value to about unity. As k becomes progressively smaller so junction growth reduces to negligible values and the coefficient of friction to typical boundary values, e.g. if k is



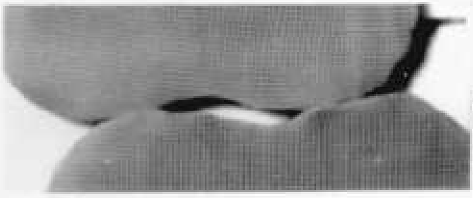
(a) original surfaces.



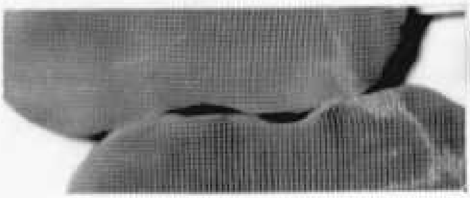
(b) normal load only.



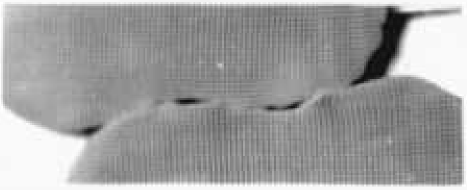
(c) shear strain begun...



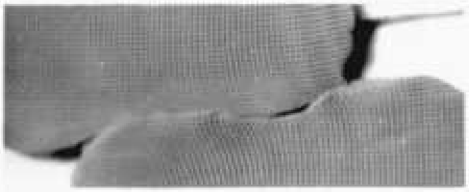
(d) ...continued...



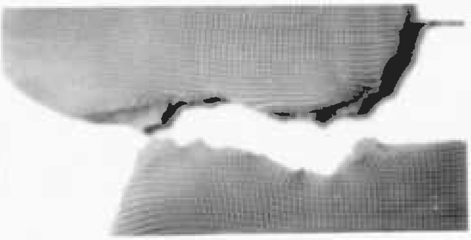
(e) ...further...



(f) ...and...

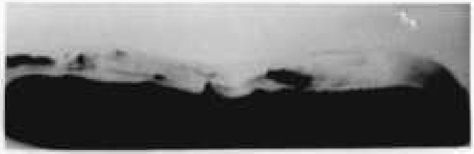


(g) ...further



(h) surfaces forcibly separated...
...large area of adhesion revealed.

(i)



(j)

edge views of model show damage from plastic flow & tearing.

Fig 1.3

about 0.2. the coefficient of friction would be around 0.1. and junction growth less than 2%. Despite some simplifying assumptions, for example the ignoring of work hardening effects, these ideas accord well with the observations of slow speed and poorly lubricated conditions during which gross surface damage occurs. These are, in fact, the conditions found in most of the tests described in Chapters 4,5 and 6 of this thesis.

Tabor discusses the obvious ways by which friction may be reduced, the interpositioning of a softer layer between the metals, or the reduction of the available area for adhesion by some contaminant such as an oxide film.

1.11. ROLE OF OXYGEN AND OXIDE LAYER

The presence of an oxide film on the surface of most metals is worth noting, for it certainly complicates the picture when analysis of the conditions in the contact is attempted. Many oxides are relatively brittle compared with the metal, and so are easily cracked when plastic flow is induced on the metal itself - a process which could encourage adhesion. Steel appears to exhibit such an effect. Courtney-Pratt and Eisner (33) obtained a dramatic drop in contact resistance when plastic flow was induced in the steel specimens they were testing. This accords well with the postulations of Hirst and his co-workers, who since 1952 (36) have suggested this mechanism. More recent work, Hirst and Stafford (37) and Hirst and Hollander (38) has produced more experimental evidence and the application of topographical manipulations to enable a better appreciation of the scale of the asperities involved. Most interestingly they find that it is plastic flow in the bulk, not merely in the small scale asperities which causes the serious damage.

Not only the oxide layer, but also oxygen directly has been part of the suggested hypothesis in friction research. Oxygen dissolved in a lubricant will affect its properties as warned by Tabor (39) as early as 1941. Arguments as to the beneficial or adverse affects of oxygen have continued ever since, with many experimenters comparing results from experiments conducted in normal atmospheres with those where attempts were made to remove oxygen. In practice it is only possible to reduce the oxygen concentrations and often no checks were carried out on the relative concentrations in the two lubricants. Evidence has also been produced from analysis of wear debris and oxidation products left in the lubricant. The formation of any of these substances is known to be very complex, and is poorly understood. Furthermore the analysis of these wear products, at the end of a test, can only provide circumstantial evidence unless all the conditions during the test are known to have been constant. This is an almost impossible requirement to meet in a wear test, and the problem that arises all too commonly is one of "chicken and egg". An illustration of the kind of problem encountered may help. Suppose that two comparative sets of tests are performed with two levels of oxygen concentration, and the first tests with higher oxygen levels show a higher wear rate and the debris consists of metal oxides containing more oxygen than the second set of tests. It may be concluded that the higher oxygen activity in the first tests created higher oxides on the rubbed surfaces which displayed more severe wear patterns. That is, the increased oxidation of the metal caused more severe wear to occur. On the other hand it is equally plausible that the oxygen in the lubricant, in the first tests, may have upset its lubricating effect and caused the increased wear rate. The wear debris produced would then be oxidised by the oxygen in the lubricant to a greater extent than in the second tests as the analysis revealed. A similar difficulty arises with analysis of the used lubricant. Thus whatever the results, analysis performed after a test cannot always assist because the observations may relate either to the cause of the overall results or to the products of the actual causal process.

The answer to the question of "which came first"? may be best gained from studies of the course of oxidations involved. In boundary friction studies Rowe, Fein and Kreuz (40) completed some early work with model lubricants in a high speed wear machine and also carried out some seperate experiments (41) on the origins of the oxidation products. They found an increase in wear rate (and friction) with degree of oxidation and concluded that the oxidation products formed interfered with the boundary film produced during "running-in" of the surfaces. This "polymer" layer, which has often been advanced to explain test results, has never been satisfactorily defined, although the experimental evidence remains intact.

On the other hand many workers have reported the beneficial effects of oxygen (at least the detrimental effects of its removal), such as Ming Feng and Chalk (42) who found a massive increase in the wear rates of steel and cast iron balls in a four ball machine when oxygen was removed from the paraffinic base oil. They concluded that the oxygen was necessary to protect freshly exposed metal from severe adhesion, an idea common to much thinking concerning E.P. additives (see section 1.18). Needless to say, wear tests are never conducted at low speeds and comparison between the conditions in low and high speed tests is not straightforward. However an understanding of wear processes can only help in comprehending the forces at work in friction tests.

Although results from wear tests can often be very sensitive to conditions, such as load, and have often been said to show either "mild" or "severe" wear regimes, these cannot be equated with "low" and "high" friction conditions. Particularly dubious is the assumption that severe wear is due to adhesional forces, such as those described in section 1.10. literally tearing the surfaces apart. Modern ideas about severe wear expressed in the delamination theory of Suh (43), focus attention on dislocation propagations within the metal due to repeated traverses over the same track (these ideas arose from very close examination of wear fragments). A good review of these concepts appears in a book by Cameron (44). It is now accepted that the mechanism of "mild" and "corrosive" wear are one and the same and occur in the following way. If a surface layer is formed after rubbing has taken place, because of reaction with the lubricant (as is suggested for cast iron and oxygen by Ming Feng and Chalk above), then inevitably on further rubbing the first to wear will be this "corroded" layer exposing more metal for reaction. Thus the corrosion of the metal goes hand in hand with the process of wear. Often the corroded layer is hard and wears well (as with iron oxide and cast iron) and the wear observed is in the mild regime, and of course anything which interfered with the corrosion process might increase the wear. In other instances the corroded layer is very weak and easily removed, then the wear rate may be very high, but the wear mechanism remains the same.

1.12. EXTREME PRESSURE ADDITIVES, INTRODUCTION

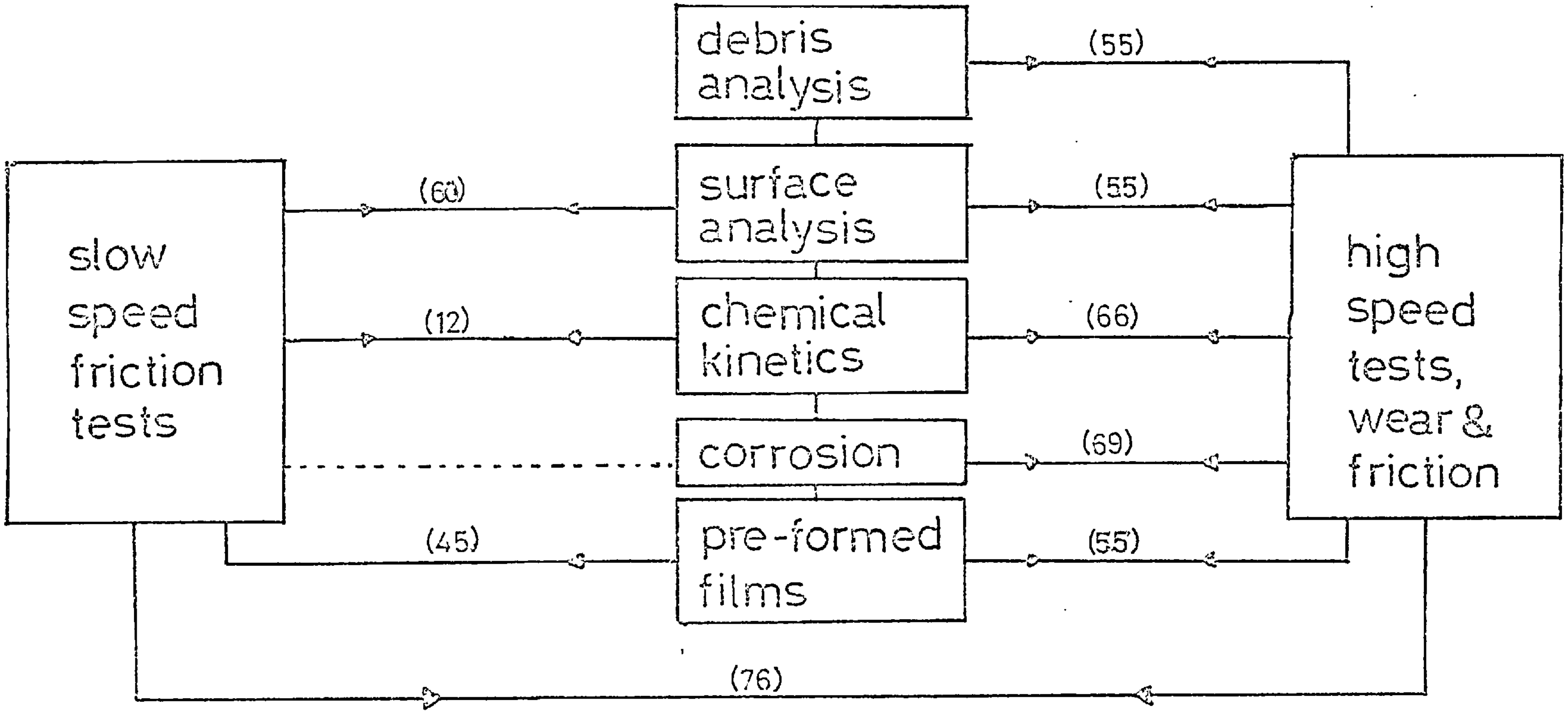
Oxygen is not the only substance which may behave in the manner discussed above. Fully formulated oils contain many chemicals that may behave similarly, and the factor which is of greatest importance is the temperature involved, because it will dictate which reactions occur fastest and which bulk reactions within the lubricant will create new agents. High temperatures will affect the strength of the surface layers and the underlying metal, and in some cases cause them to melt. In certain high speed tests, when large flash temperatures are experienced, asperities may be seen to have melted and sometimes the specimens are welded together. This extreme of "scuffing" results in a total failure of the bearing surfaces, but can be prevented, in all but the most arduous conditions, by the use of modern lubricant additives - extreme pressure (E.P.) additives.

The domain of the E.P. additive is the prevention of failure between sliding surfaces subjected to high temperatures and loads, classically the hypoid, crown wheel and pinion, in an automotive rear axle. These additives are organic compounds containing Sulphur, Phosphorus, Lead or a Halide and have in the past been considered to react with metal surfaces, forming an inert inorganic film, and protecting against scuffing up high temperatures. The organic part ot the additive was to assist solubility in the base oil, but was not reckoned to play a significant part in protecting the surfaces.

Greenhill (45) performed some early experiments, using a Bowden-Leben machine, and measured the friction coefficient (that is "observed peak static friction") for a variety of preformed sulphide films on metal strips. He found that copper strips gave a minimum friction (of about 0.5) when covered with a sulphur film, which he estimated (by interference colours) to be 0.15 µm thick. This means his optimum conditions developed friction which was high in engineering terms from a film which was chemically very thick. With steel specimens he obtained similar frictional results and achieved a further reduction in friction, to very acceptable values even up to 200C, by the addition of a fatty acid to the lubricant. However he fails to give the effect of the acid additive on steel without the sulphide film. Greenhill concludes that reaction with the metal must be the basis of all E.P. additive action and he used the term "controlled corrosion" to describe the compromise that must be found between high reaction rates, where failure may be caused by excessive corrosion, and low rates where insufficient protection may be given to sliding parts.

These ideas may be accurate enough for some additives, such as certain organic chlorides, but it has become increasingly clear over the years that the action of sulphur additives is much more complicated. This thesis will concentrate on sulphur additives, dibenzyl disulphide in particular, and before going into further details of the research that has been carried out in this field, it is important to grasp the overall pattern of these studies. Each piece of experimental data needs to be interpreted in the proper context of all the various studies that have been made. Fig.1.4. shows the interrelations between these various types of test that have been conducted. Although slow speed testing is the basis of this thesis, a simple discussion of the other types of test is necessary, so that a clear idea of how it fits into a

E.P additive action - pattern of research.



(nos. given are appropriate refs.)

Fig 1.4.

general picture of lubricant activity may be gained. Indeed much of the best work carried out to determine the mechanisms operating in lubrication, has correlated the results from two types of test, correctly identifying the causal chains. Without the proper interrelations, speculations and hypotheses would multiply, because the relevant links between types of test would not be defined. It is intended to emphasis these links in the following sections.

1.13. HIGH SPEED TESTS

(Here it will be considered that high speed tests are those in which sliding speeds are of the order of 1 $m\ s^{-1}$ or higher, where as slow speed tests employ speeds less than 0.1 $m\ s^{-1}$.)

There are a great number of tests of this type, because many companies have devised their own aimed at simulating most closely the conditions of the real situation in which they are interested. Pin - on - disk machines and four - ball machines are most commonly used especially by research workers. Both tests create conditions of pure sliding and can be used to measure both the friction developed and the wear rate. The four - ball machine is probably more popular for experiments on lubricant activity, because it uses a small quantity of lubricant, offers three wear scars for each run and can be used in a variety of ways. Unfortunately it suffers from two disadvantages, the apparent load per unit area changes as the wear scar diameter grows, and the portion of the load carried hydrodynamically is indeterminate and varies with the base oil used. Since it originated in 1933 (Boerlage (46)), it has been used to determine "orders of performance" for different groups of additives such as in the work of Allum and his co-workers (47,48). They have been careful to distinguish two regimes within the four - ball test, the anti-wear (A.W.) or mixed lubrication regime and the extreme pressure (E.P.) or anti-scuffing regime. These may best be understood from a typical plot of results from a four - ball test. Fig.1.5. shows a graph of "mean wear scar diameter" against load taken from A.S.T.M. procedure on the test (49), although it may be taken that the friction against load graph is similar.

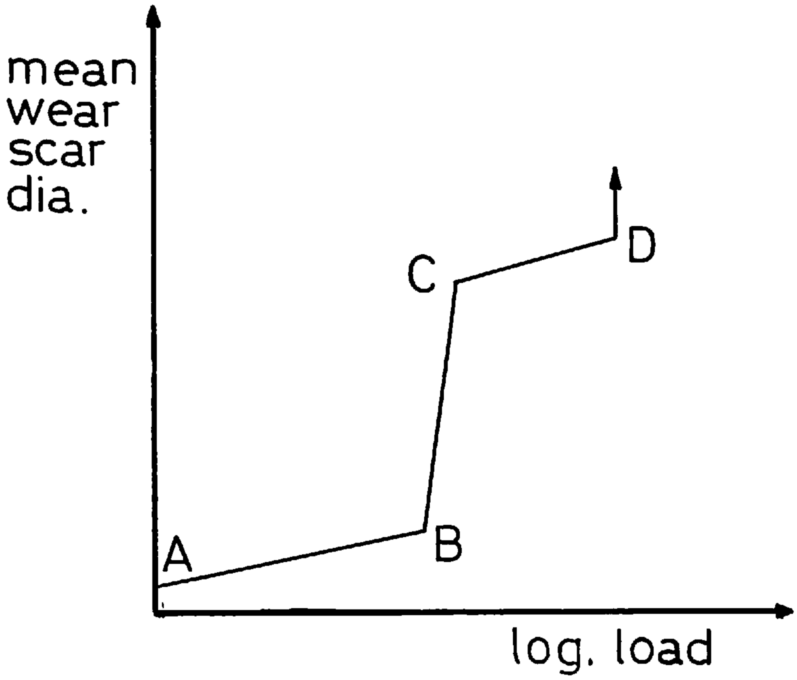


Fig. 1.5.

Tests performed in the regime marked A - B, that is before seizure occurs, are in the A. W. regime. The wear scars are of the order of the Hertzian diameter, and so it is assumed the lubrication is mixed elastohydrodynamic and boundary and therefore the additive is functioning to reduce friction and wear during occasional asperity interaction. Above the seizure load, in the E.P. regime marked C - D, considerable metal to metal contact occurs, friction is high and flash temperatures (as well as bulk heating) large. The additive must function to protect the metal surfaces from one another, reduce friction as much as possible and delay the total failure or weld, shown at point D.

Allum and Forbes (50) describe results in which there is a change in the order of performance of a set of additives between tests conducted in the A. W. and in the E.P. regimes. The explanation for this may not be clear, but it may provide some insight into the lack of comparability between high speed test results obtained from machines of different designs. This lack of comparability complicates the task of the research worker, but cannot be avoided.

The differences between the two regimes probably result from the differing frictional energy inputs, which cause the temperatures in the E.P. regime to be much higher. Allum and Forbes (50) have suggested that an iron mercaptide (an iron-sulphur organic soap) layer is formed and acts in the anti-wear regime, whilst in the more arduous extreme pressure regime this film would reform into a simple iron sulphide layer. Although commonly accepted, this hypothesis has been made untenable by further work of theirs (see section 1.14.). Dorinson (52) has shown the sensitivity of the four - ball test to operating procedure, again emphasising the problems of comparability. Fein (53) has made similar observations, from a pin-on-disk machine. Thus it is worth summarising the differences between high and slow speed tests, in terms of what is known and what is not.

FACTOR	HIGH SPEED TESTS	SLOW SPEED TESTS
LOAD	PORTION CARRIED BY BOUNDARY FILM USUALLY INDERMINATE	KNOWN
FRICTION	KNOWN, BUT COEFFICIENT OF FRICTION ONLY KNOWN AS WELL AS LOAD	KNOWN
BULK TEMPERATURE	KNOWN - TRANSIENTS CAN BE ESTIMATED	KNOWN
FLASH TEMPERATURES IN CONTACT	UNKNOWN - CAN BE CALCULATED APPROXIMATELY	NONE
WEAR RATE	MEASURABLE	NOT MEASURABLE
SIMULATION OF REAL CONDITIONS IN PRACTICAL MACHINE	REALISTIC	UNREALISTIC

It is clear that in order to comprehend events taking place within the rubbing contact, slow speed tests must be used,for only then are such basic essentials as load, coefficient of friction and temperature known. In contrast high speed tests realistically simulate conditions in real engineering systems. This topic will be discussed further in section 1. 17, but one way of discovering the processes occuring in an actual rubbing contact is to employ the variety of surface analytical techniques available. Once the surfaces can be accurately specified, the conditions that had been acting in the contact may be deduced.

1.14. SURFACE ANALYTICAL TECHNIQUES

These have been employed for some time. Prutton, Turnbull and Dlouhy (54) performed some elementary chemical analysis on worn gears from an E.P. test and found reaction products of the E.P. additive. From this they made simple postulations as to the reaction mechanism. Godfrey (55) in an important paper describes the chemical nature of some surface films. He had stripped these from specimens, which had been subject to high speed tests where a sulphur E.P. additive was employed. Using electron and X-ray diffraction, spectrographic and chemical techniques he found the films and wear fragments to be essentially iron oxide, with some sulphide and carbide present. Furthermore he found the iron surfaces were considerably silicon enriched. His conclusion was that the E.P. additive acted by promoting oxidation of the surface, any reactions evidently being rather complicated. Fein and Randall (56) in the discussion section reported supporting evidence from their own work and once again raised the question of insoluble hydrocarbons on the surface (friction polymer.)

In a review Bisson, Johnson and Swikert (57) describe research into the effect of different iron oxides on steel. They conclude that either Fe 0 or $Fe_3 0_4$ are beneficial (in terms of wear), but that $Fe_2 0_3$ is definitely not ($Fe_2 0_3$ is "rouge" and very hard). Iron sulphide gave a high friction, as was reported by Greenhill (45) and they comment, "Effective lubrication under extreme boundary conditions is very often a function also of the nature of the oxide films present".

Allum and Forbes (58) used the Electron Probe Micro Analyser (E.P.M.A.) to give a quantitative and topographical assessment to the sulphur distribution in the wear scars from their four - ball tests. They found considerable quantities of sulphur, unevenly distributed, in the scars from tests performed in the E.P. regime. Wear scars from the A. W. regime showed little sulphur. The amount of sulphur, presumably as sulphide, increased with additives which showed better performance and increased towards the centre of the wear scars (where temperatures and pressures are greatest). They also found that the sulphur distribution extended to some depth. Similar use of the E.P.M.A. has been made for wear tracks from slow speed tests, Roberts (59) using bronzes in a low speed repeated pass machine, found tin enrichment of the surface consistent with reductions in friction, much as Godfrey (55) reported for silicon in steel. Bayles (60) also used the E.P.M.A. to study sulphur on the wear tracks of steel, made using the same apparatus as Roberts. Bayles found more sulphur inside the track than outside, but made no quantitative conclusions and unfortunately only looked at the tracks from completed tests. His work, which forms part of the basis of the experiments of this thesis, is discussed more fully in section 1.17..

Recently Baldwin (61) has described work, with an X-ray Photo-electron Spectrometer (X.P.S.), on worn surfaces from a standard wear test. His equipment revealed the sulphur present to be in the form of sulphide and produced a correlation between wear resistance of the additive used and final sulphide concentration. Both this technique and the E.P.M.A. rely heavily on complex electronic equipment to process the data, as well as operating under hard vacuum. Quantitative results must therefore be treated with caution, and it may be noted that the E.P.M.A. probes about 2 μm into the surface but the X.P.S. penetrates only about 2 nm. Therefore whilst the E.P.M.A. is affected by material down to appreciable depths within the surface, the X.P.S. only responds to the uppermost chemical layers. Both these techniques have been applied to work in this thesis - see sections 7.3. and 7.4..

A more orthodox method of obtaining quantitative data is to use radioactively tagged additives. Borsoff and Wagner (62) estimated the thickness of sulphur films on both worn gears and steel strips from static tests using this method. Their results indicated only very thin films of sulphur (assumed sulphide), but they had no way of assessing the (un)evenness of distribution of sulphur on the micro-scale. However in common with other workers they found:

i) The sulphur concentration rapidly reached a steady value, at steady running conditions. This implies an equilibrium between rate of removal and rate of formation of sulphur on the surface.

ii) The higher the degree of protection afforded by an additive, the greater the sulphur concentration on the surface.

Barcroft and Daniel (63) applied similar techniques and obtained confirmatory results. However they extended their investigations and used a variety of mechanical conditions and also they demonstrated that the sulphur penetrated to considerable depths in places. Much sulphur was found to be in the form of sulphate not sulphide and they used different additive combinations to show competition between substances on the surface. This topic has been pursued by many, for example Sakurai, Ikeda and Okabe (64) haved looked at the possible mechanism of one such interference system, using both an E.P. and an oiliness additive. Baldwin (61) considered a similar effect between an E.P. additive and an oxidation inhibitor, all of which has obvious implications to the formulation of commercial lubricants.

1.15. SURFACE REACTION KINETICS

The study of surface reaction kinetics follows directly from much of the above. For example Borsoff and Wagner (62) used steel strips immersed in a lubricant and measured the rate of reaction of sulphur on the surface. They found the reaction rate increased with both time of immersion and temperature. The latter was expected but the former result led them to suggest that the reaction was autocatalytic in nature, although the scatter in the experimental results caused them to draw only tentative conclusions.

Spikes (12) carried out some similar experiments with stainless steel and also performed slow speed friction tests, from these he deduced a relationship between reaction rate and performance for the additive. He also measured a reduction in the reaction rate when a detergent additive was present in the oil, and he was able to link this reduction with a change in performance in the friction tests. This is an important correlation between surface reaction kinetics and slow speed friction tests.

Sakurai et al (64) have followed up their earlier work and attempted to apply more rigorous kinetics to their system However the result is a complicated consideration of many factors, from which again only tentative conclusions may be drawn.

Dorinson and Broman (65) measured reaction rates in a more orthodox manner, for two different compounds, and related these satisfactorily to their relative lubricating efficientcy in high speed tests. Forbes and Reid (66) applied extensive analysis of this type to the range of compounds they had previously tested in high speed rigs. They measured heats of adsorption (and their degree of reversibility) and examined the reaction products, from which data they confirmed their hypothesis concerning the mechanism of action of an organic sulphur additive with an iron surface to form iron sulphide. They also concluded that mercaptide formation is not part of the action of these compounds in the anti-wear regime. They suggested that simple physical adsorption would appear to be the way by which protection is afforded. That is, the additive acts like an oiliness agent, as discussed in section 1.3. not by irreversible reaction with the metal as evidently takes place in the E.P. regime.

1.16. CORROSION AND PREFORMED FILMS

The study of corrosion is of interest as the reaction of E.P. additives are closely related to corrosion processes. Barcroft (67) devised an ingenious technique, which allows the rate of corrosion of a very hot iron wire (over 600C) to be determined by its change in resistance with time. The precise temperature of the wire is known from its starting resistance, and the system can be easily used with any lubricant. Sakurai, Sato and Ishida (68) used the same technique and analysed the different reaction rates they obtained at different temperatures and concentrations. They also performed X-ray analysis on the corrosion products. They conclude that diffusion is the rate determining step in the process, i.e. that the products form a barrier on the surface and reaction can only continue as iron ions diffuse through to the lubricant interface. They also derive an apparent activation energy and suggest that dibenzyl disulphide reacts unusually fast, because cracks are formed exposing fresh metal; this provides a possible explanation of the results of Borsoff and Wagner(62). Their analyses of the corrosion products show a good deal of iron oxide in all cases, whether or not a sulphur E.P. additive was present. Sulphide was detected when an additive was used, all of which adds weight to the results of Godfrey (55). Later Sakurai and Sato (69) extended the work and correlated corrosion rates with performance in high speed tests, producing some interesting results.

Grew and Cameron (70) applied the technique to a different system, the adsorption - desorption of an oiliness agent, and at much lower temperatures (less than 200C). They found a difference in the relative corrosion rates, between one lubricant with the oiliness agent and the other without, below the temperature they had previously found to be the transition temperature in their slow speed friction tests.

Unfortunately, although it is attractively simple, the corrosion studies can only be of limited value, for the corroded films produced are relatively thick (of the order of 0.1-1 µm) and uncertain in nature, apart from the fact that no mechanical stresses are applied. Nevertheless these studies have shown the complicated aspects of even these "straightforward" reaction conditions, for example the formation of oxides, cracking the surface. They have also produced, for a group of additives, the same order of reactivity as order of performance, obtained from high speed tests. All this adds weight to the "controlled corrosion" idea in E.P. additive action.

Several workers have formed appropriate films on their test specimens by suitably effected corrosion, and then assessed the films performance in a friction or wear test. Godfrey (55) found that a preformed film composed of iron sulphide and iron oxide, gave better than a film composed of either alone. Sakurai et al (64) used a preformed film, tagged with radioactive sulphur, to estimate its rate of removal in their high speed machine. Greenhill (45) as already discussed, used preformed films in his slow speed friction tests.

1.17. CORRELATION OF SLOW AND HIGH SPEED TEST RESULTS

It is a fundamental assumption of the philosophy of slow speed testing, that the mechanism of action of test additives is the same whether the sliding speed is low or high. This assumption, it is now known, is not always correct and simple deductions such as those of Bowden, Leben and Tabor (7) cannot be made so easily. Therefore the correlation of results from these two types of test must first be established or serious mistakes will follow. This has been done for some systems, but since present understanding of all the factors involved is still hazy, there is a need for further work.

Fein, Rowe and Kreuz (71) performed some simple experiments, employing an oiliness additive and measuring transition temperatures in their pin - on - disk machine. This they ran from low to high speeds and also at different loads. Their lowest speed was not as low as that commonly used on a Bowden-Leben machine, being about 1mm s^{-1}, and it appears that some of the load was carried by elastohydrodynamic effects. An increase in speed produced an increase in transition temperature, which is not expected for greater speed produces more frictional heating and thus normally lowers the transitions. Fein et al produced a relationship between the parameter $(\frac{\text{load}}{\text{speed}})$ and the transition temperature over a wide range of conditions. Fein (72) later extended this range using a four-ball machine. He obtained quantitative agreement with the earlier work, although he had to avoid the problems of frictional heating by observing the friction and wear over very short periods (10s). All of this was conducted with "unreactive oils", that is simple base stock with fatty acid additives, but no E.P.additives.

Matveevsky (73) was the first to use a four ball machine at continuous low sliding speeds (Boerlage and Blok (74) had devised a slow speed test apparatus, based on a four-ball machine, but this worked on a different principle). He applied external heating to the test specimens and produced transition temperatures much as Frewing (7) had done, and which he found were independent of load. Later he (75) correlated these slow speed transition temperatures with failure loads in some high speed tests. From the failure load he calculated a flash temperature, which he added to the ambient to give "total temperature". These "total temperatures" equalled the transition temperatures he had measured previously, and so he concluded that the factor governing the failure in both cases was essentially temperature. Again it must be pointed out that this work was on "unreactive" oils as above.

Bailey (76) extended Matreevsky's work and devised a modified four-ball machine, which he called the ball-on-triplane. In this a ball is run against the flat ends of three cylindrical pegs, which are so arranged as to give three seperate wear tracks on the ball. He ran this arrangement at low and high speeds and sought to correlate the friction - temperature relationship he obtained at low speeds with the scuffing performance of the lubricant at high speeds. He demonstrated the effect of varying the ambient temperature in the high speed tests and could often deduce a "total temperature" at which failure would occur, much as Matveesky had done. Bailey also used lubricants containing an E.P. additive and found not a constant "total temperature" but normally a constant failure load, thus demonstrating the effect of the additive.

Bailey also tried a variety of material combinations, choosing either a reactive or unreactive steel to use as the ball material. He discovered that the unreactive steel performed much worse in the scuffing tests, and concluded that important reactions took place on the wear tracks of the ball, whilst out of contact with the peg, i.e. between each succesive pass. It was because the material of the ball appeared more critical than the material of the peg, that he made this deduction and it would seem plausible that the out of contact conditions should be vital. It is whilst out of contact that the surfaces have a chance to react with the oil and sufficient time to build up a protective layer before the next pass. Bayles (60) followed up this idea together with those of Spikes (12) and employed the ball - on - triplane machine with a very pure base oil (hexadecane) and a pure E.P. additive (dibenzyl disulphide), running at low speeds. He found a drop in friction at a particular temperature (as had Spikes) which was caused by the presence of the additive. Furthermore this temperature varied with the rotational speed, although all the speeds were low enough to prevent frictional heating; the maximum sliding speed was about 10 mm s^{-1}. He linked this variation with the kinetics of the reaction, previously studied in the static situation by Spikes. By assumming all the reaction occurred out of contact and that the friction observed was dictated by the equilibrium point, when the rate of removal of the E.P. film each pass equalled its rate of formation, Bayles analysed his results and obtained an activation energy for the reaction. Bayles' assumption was that, the temperature of the drop in friction he found, was that temperature at which the reaction rate had risen sufficiently to allow enough film to be formed during the out of contact period to cause a reduction in friction. Thus as this out of contact time (O.C.T.) was reduced, the drop occurred at a higher temperature, because a greater rate was necessary to compensate for the shorter O.C.T.

One subtlety should be noted here. Previously the changes in friction described, i.e. transitions, have been rises not drops. Whereas almost all other work was concerned with the "failure" point of a lubricant during "normal" running, these tests indicated the "success" point of the lubricant during "poor" running. This was necessary to show up the action of the additive at all, but it is bound to affect the conditions within the contact, as shall be seen later. Bayles also did some work with high speed tests, and there have been very few workers who have attempted to show that the results from slow speed tests apply to high speed situations.

1.18. SUMMARY AND DISCUSSION OF THE MECHANISMS OF ACTION OF LUBRICANT ADDITIVES

A.) Oiliness additives are becoming reasonably well understood - commonly accepted points are as follows:

i) The additives themselves adsorb onto metal surfaces, sometimes as a monolayer, to form protective films of low shear

ii) Chemical reactions can occur, especially when water layers exist (with fatty acids for example), but protection to the metal is afforded in much the same way.

iii) These films will fail under extremes of pressure or temperature; temperature reducing the surface coverage by encouraging desorption.

iv) It must be remembered that even simple oils (e.g.

hydrocarbons) may exhibit properties akin to oiliness additives, because they are easily oxidised by the atmosphere to produce substances very similar to these additives.

An excellent consideration of these aspects is given by Spikes (12) and they need not be discussed further.

B.) E.P. additives are less well understood, but certain points do stand out. (It may be noted that only the action of sulphur type additives has been described. This is because they are simpler in chemical nature than phosphorus types and sulphur additives were used in the experiments described in this thesis. Generally work with phosphorus additives confirms the views being expressed, although usually the justification is more complicated, see for example Beynon (77)).

i) Chemical reaction with the metal surfaces takes place - e.g. Prutton et al (54).

ii) The extent of reaction, in running systems, increases with the severity of the mechanical conditions - e.g. Borsoff and Wagner (62).

iii) Oxides are involved in many situations (in affording protection) - e.g. Bisson et al (57), but are not essential to an explanation of additive action - e.g. Forbes and Reid (66).

iv) The rate of reaction of additives increases with temperature - e.g. Spikes (12).

v) The extent of reaction on a surface in a running machine is known to reach an equilibrium, when conditions are constant (unlike corrosion situations), and this indicates that there is a balance between rate of removal and rate of formation of the protective film - e.g. Borsoff and Wagner (62) or Bayles (60). However the chemical effect of freshly exposed metal surface upon the lubricant is not known. Complex reactions have been observed - e.g. Morecroft (78).

vi) Improved performance of E.P. additives has been obtained by the use of an oiliness additive - e.g. Sakurai et al (64). Recent work by Hironaka, Yahagi and Sakurai (79) indicates that the heat of adsorption of such an additive on FeS or Fe_3O_4 is higher than that on Fe_2O_3.

vii) The precise conditions which promote the protective effect of E.P. additives are not well defined, i.e. pressure, shear stress, shear rate and temperature.

It is necessary for all these aspects to be born in mind when considering the mechanism of any actual system, however modern thinking on the subject may be summarised so: The additive reacts with the steel, under the appropriate conditions, certainly when the temperature is raised and when other additives including oxygen do not successfully compete. The reaction product, iron sulphide or a mixture of compounds, forms a film which acts to reduce friction, prevent adhesion and thus reduce temperature rises and catastrophic failure. The best E.P. additives probably encourage the adsorption of oiliness additives present, which further reduces the coefficient of friction.

1.19. OUTLINE OF THE BASIS OF THE PRODUCT

The work in this thesis arose directly out of the work of Bayles (60), which held great possibilities for a fundamental understanding of the action of an E.P. additive - the chemical kinetics. Unfortunately the geometry of the ball - on - triplane machine is fixed, so Bayles was unable to alter the O.C.T. independently of the sliding speed. He assumed O.C.T. was the only relevant factor affected when he changed the rotational speed, which was reasonable as no evidence existed for any effect on friction of sliding speed at these low levels.

To enable the sliding speed and O.C.T. to be varied seperately, it was decided to use a reciprocating friction machine and alter the track length. Rubbing was to take place in one direction only so as to give all parts of the track the same O.C.T., and conditions so adjusted so that comparisons with the results from the ball - on - triplane could be made. A Bowden-Leben machine was available which was modified to enable these tests to be undertaken. Some investigations were also intended to assess the value of the machine in determining lubricant activity in slow speed friction tests.

CHAPTER 2.

EXPERIMENTAL APPARATUS AND TECHNIQUE.

2.1. APPARATUS, GENERAL.

The friction tests described in this thesis were carried out on a modified Bowden-Leben machine for the reasons stated in section 1;19. The extent of the modifications has resulted in a rig which bears limited resemblance to the original machine of 1939 (5). A general view of the equipment is shown in Fig. 2.1.

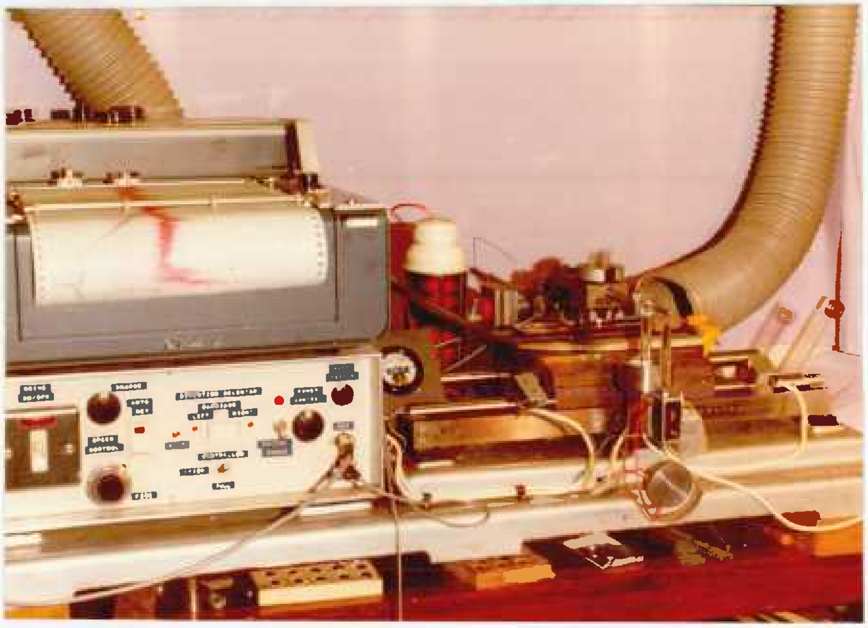


Fig. 2.1.

It consists of four basic parts;

1.) The horizontal carriage and its drive system.

2.) The control system and heater.

3.) The loading arm with its lifting mechanism.

4.) The recording apparatus.

Fig. 2.2. shows the interrelationship of the parts.

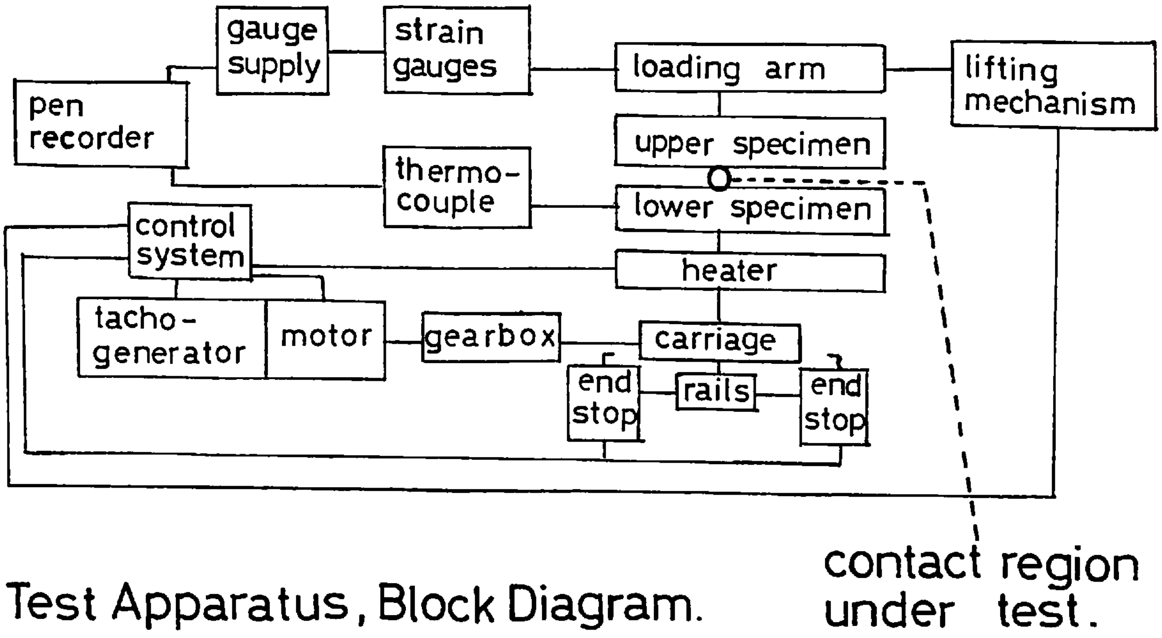


Fig. 2.2.

2.2. CARRIAGE

The carriage rested on two stainless steel rails, circular in cross-section, with one rail located in a Vee-groove on the underside of the carriage, whilst the other rested on a flat. The carriage was supported on small pads, coated with P.T.F.E., so that friction was low and sliding was free from "stick-slip". Motion was transmitted to the carriage by means of a lead screw rotated in a recirculating-ball-nut bolted to the carriage. The screw itself was supported by a bearing arrangement capable of taking thrust in either direction, and the screw was directly coupled to the output shaft of a gearbox. The input of the gearbox was connected to the armature of a special D.C. motor, a tachogenerator winding being part of the motor armature. This arrangement gave a very accurate feedback dependent on the motor speed. The tachogenerator and motor were connected to a specially constructed electronic speed controller, capable of consistent speed control over 400:1 range, with marginal loss in available torque. The motor could be driven at approx. 5000 to 120rpm, and with a gearbox ratio of 40:1 and a lead screw pitch of 5.08mm (0.200"), the traverse speed of the carriage was variable between about 10mm s^{-1} and 0.025mm s^{-1}.

2.3. CONTROL SYSTEM.

The direction of travel of the carriage was controlled by two heavy duty relays, which switched the motor and tachogenerator windings. These relays could also operate other circuits as required, such as a lifting solenoid for the loading arm and a variable resistor in the speed controller, which enabled different speeds to be used for the two directions of travel. The relays could be triggered manually, or automatically by micro-switches mounted on one of the rails which sensed the position of the carriage. The apparatus could be set to stop at the end of the traverse or to automatically reverse at each end. The position of the micro-switches was adjusted to provide the required track length over the appropriate portion of the lower test specimen.

This specimen was held in a stainless steel trough (inside dimensions 170mm long, 25mm wide and 100mm deep) which was bolted to the carriage, although thermally insulated from it by a sheet of asbestos. Location within the trough was achieved by cutting the specimen exactly to length and preventing lateral movement with a small stainless steel wedge. Around the trough a tubular electric heater was clamped, capable of dissipating 750w when connected to the mains supply. This

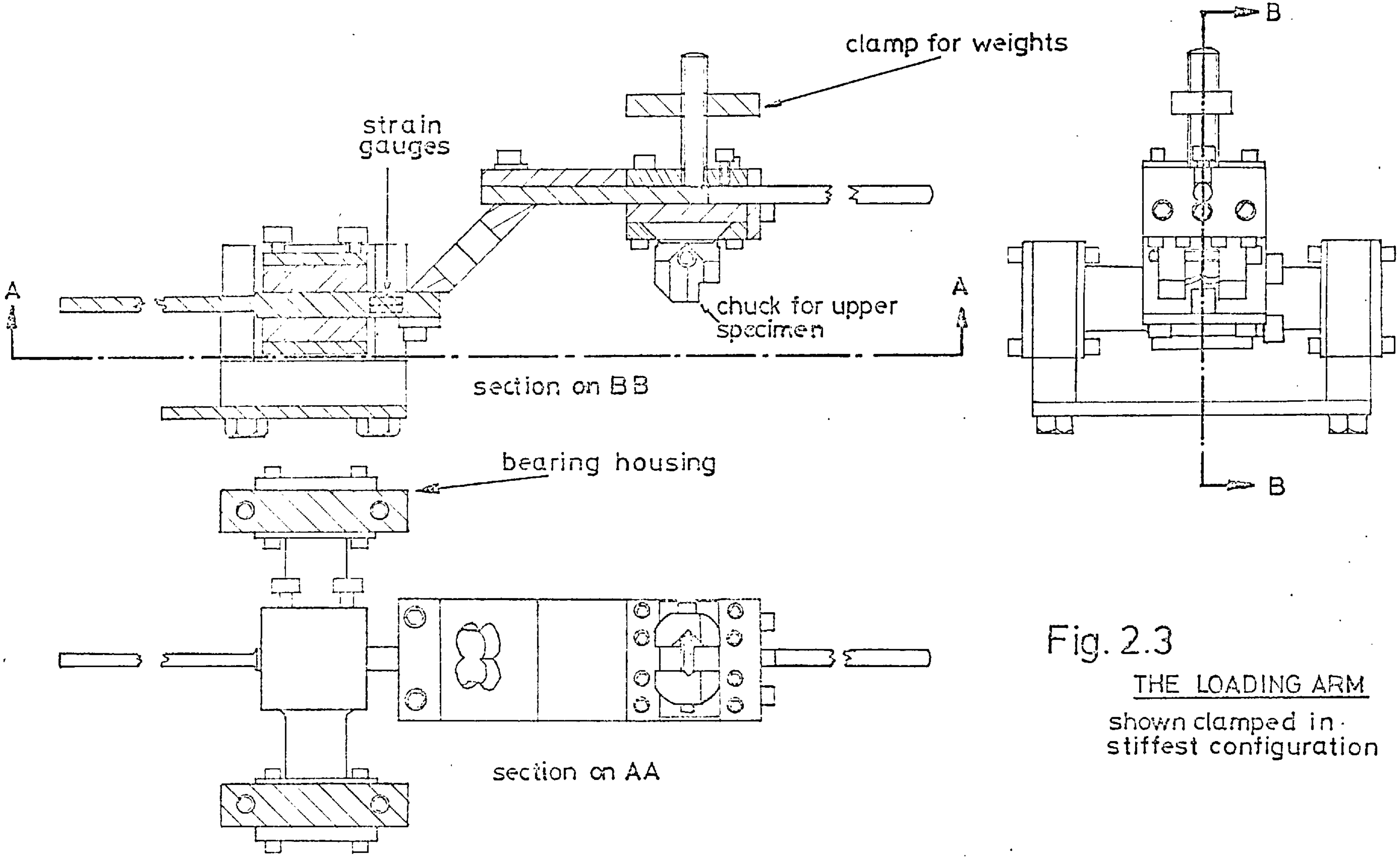


Fig. 2.3

THE LOADING ARM

shown clamped in stiffest configuration

somewhat crude arrangement had the advantage of low thermal inertia (capacity) and high heat input capability, enabling a wide range of heating rates to be obtained. Good responsive control was effected by an infinitely variable power controller. The temperature of the lower specimen was measured by a chrome/alumel thermocouple sheathed in a 1mm diameter stainless steel tube, which was clamped so as to press lightly on to the specimen close to the loading arm. A cold junction, placed in melting ice, was used as a reference.

2.4. LOADING ARM

The arm was of new design, and was designed and constructed with assistance from A. Bowyer who has been using the same equipment for his own research. Fig. 2.3. is a drawing of the arm, its main features are a pivoted assembly to ensure a constant load between the specimens and an adjustable cantilever to allow the stiffness of the arm to be varied. Friction was measured by a set of strain gauges, mounted on the cantilever, which were wired as a Wheatstone bridge and connected to a purpose-built regulated power supply of about 6.2V. Another feature of the loading arm was a chuck consisting of an adjustable "vice", which could clamp specimens of a variety of shapes via stainless steel jaws. A special arrangement was fitted which could automatically lift and gently lower the arm. Lifting was achieved by a solenoid, mounted under the arm and fitted with a pad which could be adjusted so as to fix the height to which the arm was lifted. Since the solenoid tended to drop the arm too rapidly an air damper was fitted to lower the arm slowly. The damper consisted of a perspex piston in a steel cylinder. The cylinder had a one-way valve in its base and was fixed to the body of the machine, whilst the piston was connected via an adjustable link to a large sleeve on the loading arm. The link was set so that once the arm had dropped fully on the air cushion in the cylinder, the piston continued to fall 1 or 2mm until it reached a stop. This freed the sleeve connected to the piston from the arm and thus prevented it interfering with the friction measuring capabilities of the arm.

The lateral position of the track on the lower specimen could be set by moving the whole arm and its base in a slideway, fixed on the base of the machine. Normally this slideway was clamped to prevent any free-play in the friction measuring system.

2.5. RECORDING AND CALIBRATION

A two-channel potentiometric chart recorder was used to provide a constant record of the strain gauge bridge output, representing friction, and the output of the thermocouple, representing temperature. The strain gauges were calibrated by applying a known sideways force to the loading arm, whilst held free of the carriage. A pulley and cord attached to a scale pan were used for this purpose. For larger forces, above 1 kg, the loading arm was detached and mounted on its side, so that larger vertical forces, simulating the frictional force could be applied with weights hung from a cord. The resulting calibration curve can be seen in Fig.2.4. There was no hysteresis. The thermocouple was of a standard type, its output for given temperatures can be taken from tables. With sufficient accuracy for these experiments, in the 0 - 250 C range, the sensitivity may be taken as 1mV per.

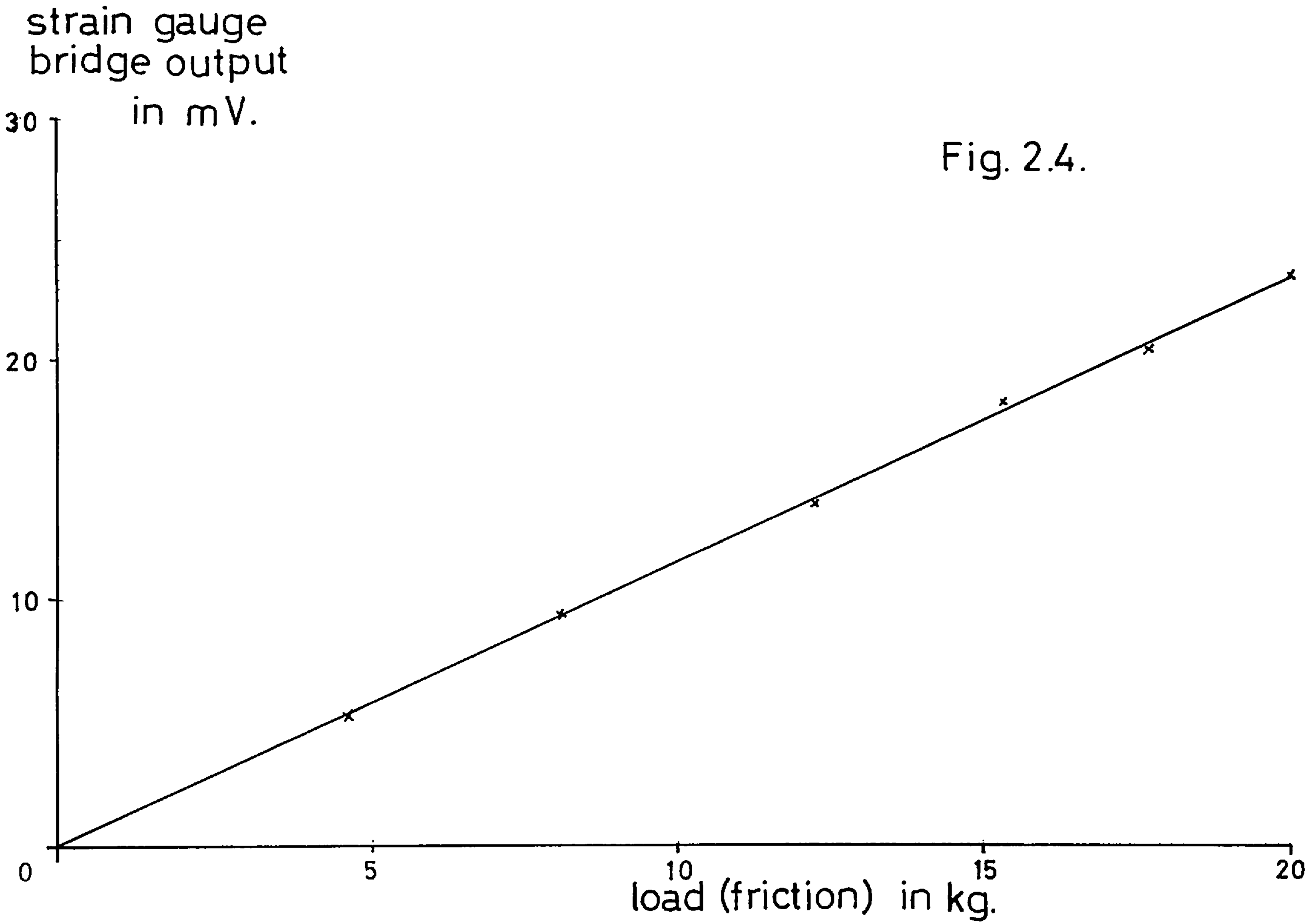

strain gauge bridge output in mV.
30
20
10
0
5
10
15
20
load (friction) in kg.

Fig. 2.4.

$25^{o}C$.

The load acting in the contact was determined with a spring balance, by "weighing" the loading arm from a point vertically above the contact. The speed of traverse was measured by timing the carriage over a set distance. For the lower speeds a dial gauge was used, which also gave an indication of the smoothness of the movement, whilst for higher speeds, a scale mounted beside the carriage indicated the distance traversed.

The accuracy to which these four variables were calibrated was a few per.cent, but the inherent repeatability in the apparatus between similar experiments was much better, less than 1%.

2.6. STANDARD EXPERIMENTAL TECHNIQUE

The majority of friction tests were carried out using the following routine, exceptions are indicated where they apply. The tests involved multiple passage of the upper specimen over the flat lower one, usually with rubbing only taking place in one direction, i.e. uni-directional sliding. In this case the loading arm was lifted at one end of the track, while the carriage returned to the other end of its travel at maximum speed. The return took a fraction of the time that the rubbing pass took. The arm was then lowered so that sliding recurred over the same track. In this way the machine simulated the sliding conditions of a pin-on-disk machine or ball-on-triplane machine like Bayles (60). The loading arm was used at its highest stiffness, that is 44kg mm^{-1}, which was quite sufficient to ensure that, even after the largest "slip", the upper specimen remained well within the original contact region.

The order of procedure was:

i) Production of specimens
ii) Production of test lubricant
iii) Washing of specimens
iv) Running of test
v) Interpretation of recorder trace

2.7. PRODUCTION OF SPECIMENS

The flat specimen was cut from bar, to the exact length required to fit the trough. The upper and lower faces were then precision ground to a very fine finish resulting in a specimen about 5mm thick; the direction of grinding was always the same as that of sliding. After grinding the surfaces were polished with dry silicon carbide paper (dry, to avoid spurious contamination of the surfaces). First 400 grit paper was used then 600 grit papers, always rubbed in the direction of sliding. By allowing the papers to clog a very smooth finish was repeatably obtained, having a C.L.A. roughness of around 0.07µm in the direction of sliding. This is an order of magnitude less than the roughness of the wear tracks produced.

At the end of an experiment the specimen would be repolished on both faces using the same technique. This did not necessarily remove the wear scar, but an unworn portion of the surface was always used in the subsequent experiment. Careful checks were made to ensure that no difference could be detected between a run employing a freshly ground and polished specimen and one employing an often polished specimen. This demonstrated the acceptability of the practice. The specimens were reground every so often, when at least 0.2mm was removed from each surface.

The upper specimens were always a new ball or roller, obtained commercially, which were already polished and required no further mechanical preparation.

2.8. PRODUCTION OF TEST LUBRICANTS

The majority of experiments employed hexadecane ($C_{16}H_{34}$) as the base oil, which has been used widely by many researchers, for example Fein (72).

It was obtained from Koch Light Ltd. as Puriss grade, in accordance with previous research work in which it has been used, it was further purified by shaking with activated silica-gel and alumina, and allowing it to remain in contact with these for at least 10 days. This process effectively removed almost all polar impurities, such as oxidation products, from the hexadecane, and after filtering it was a very pure paraffin with no detectable surface active components in it. This purification technique is based on that of Spikes (12).

The hexadecane was used as an inert carrier for the various additives that were of interest. Each batch of test lubricant was made up freshly, none being formulated more than a day before use. All the additives used were pure, usually having been recrystallised in the laboratory. All the compounds used were checked for any detectable impurities by Dr. R. Hiley using thin layer chromatography as described in his thesis (80). All compounds were found to have purity greater than 99.9%. This is in contrast to some other work, in which commercially prepared additives were used as supplied, and may have contained considerable impurities. None of the additives were used at concentrations greater than 1% by weight.

2.9. WASHING OF SPECIMENS

After polishing, the specimens were wiped and placed in a large soxhlett apparatus, filled with dry toluene (methyl benzene), and cleaned for $2\frac{1}{2}$ hours. Cleanliness is essential in boundary lubrication experiments, as demonstrated by Grew (81) and many others. The procedure used in these tests followed closely that of Spikes (12) and Bayles (60). Toluene was used as a powerful solvent, removing all greasy impurities. Acetone (propanone) was then used to remove any remaining toluene and the surfaces were allowed to evaporate dry. Only Analar grade solvents were employed.

While the specimens were soxhletting, the trough, stainless steel chuck, wedge, and thermocouple were cleaned. First any visible film was removed using silicon carbide paper, then each part was washed twice with toluene, then twice with acetone and allowed to dry. Nothing then touched these surfaces until the specimens were removed from the soxhlett. They were taken from the almost boiling toluene (B.P. = 110C) and plunged into cold acetone (B.P. = 56C) from which they were removed and placed in the trough and clamped into position. All the handling was done with clean tweezers. Once all the acetone had evaporated from the still warm surfaces, about 18ml of lubricant was added so as to cover the test surfaces.

2.10. RUNNING OF THE TEST

The apparatus was set up to give the required sliding speed and track length. Once the specimens were mounted and immersed in lubricant, the pen recorder was adjusted to place the pens on their respective zero lines. Zero friction was obtained with the loading arm lifted off the track, zero temperature when the thermocouple output was short circuited.

The carriage was then started to allow the surfaces to run-in, a procedure always carried out for at least 10 passes to ensure uniform conditions. Also any irregular running-in pattern would indicate some peculiarity, such as contaminated surfaces. Once the coefficient of friction had reached an acceptable value, usually above 0.5, the heater was switched on with sufficient power to produce the desired heating rate. When the upper temperature limit was reached, the carriage and heater controls were switched off and the arm lifted off the surface again and held free. This was done to recheck the zero friction line on the recorder because at high sensitivity thermal drift in the strain gauges resulted in a drift of the zero friction point, Fortunately this drift was repeatable and easily accounted for when interpreting the trace. It never exceeded the equivalent of 0.1 kg of friction force.

2.11. INTERPRETATION OF RECORDER TRACE

Fig.2.5. shows a section of a typical trace, and the point to note is the "roughness" of both traces, which makes precise determination of either friction or temperature difficult. The temperature is the easier to deal with, for most of the variations are due to the temperature gradients along the surface of the flat specimen caused by uneven heating. At a heating rate of $5^{o}C\ min^{-1}$ (moderate) there was a gradiant of about $10^{o}C$ along a 120mm track. With shorter tracks the variation could be less than one degree, but it must be remembered that the

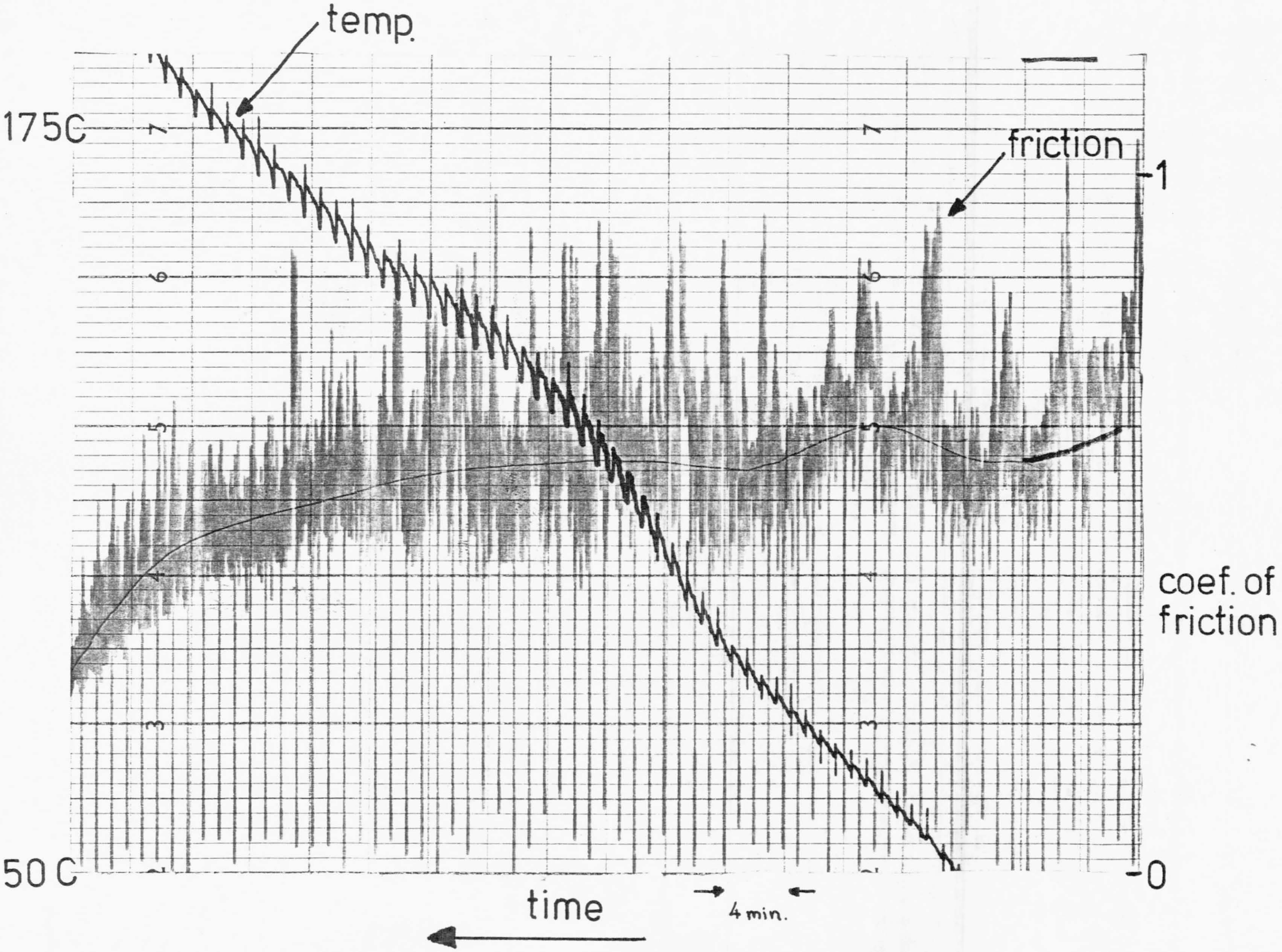


Fig. 2.5.

thermocouple could not be placed in the contact region. It was located close to the contact and touching the lower specimen, which was hotter than the upper one (by about 3 - 10°C depending on conditions). There are thus considerable errors in determining the temperature of the contact or the exposed track, but since it is the latter which is of more interest (because the critical reactions have been assumed to take place there) temperatures quoted will be from the best smooth curve drawn through the thermocouple trace. Nevertheless it must be understood that, because of the variations, no such temperature is accurate to more than ± 5°C.

The variations in the friction trace are due in part to relaxation oscillations, but more commonly, and especially at high friction, to repeated formation and shearing of metallic junctions. These cause very large, random fluctuations in the frictional force and much surface damage. In one case the coefficient of friction reached 2. This process is discussed in the next chapter, but the simplest interpretation of the trace is on the basis of mean friction. The choice of either maximum or minimum friction values would produce dubious results, and the use of mean friction does at least give a measure of the work being put into the surface. In fact, in order to reduce the size of the variations in the trace, the response of the pen recorder was deliberately slowed down so short-term fluctuations would not even appear on the trace. The friction values quoted are taken from the best mean line, drawn by eye, through the trace. Some workers, for example Frewing (8),have distinguished the changes in the "roughness" of the friction trace, this has not been done here.

Since the friction coefficients quoted have been interpreted from the results, as described above, it is not reasonable to apply an accuracy to them. The equipment used is capable of highly accurate measurements, better than 1%, but until a precise method is found by which the results may be assessed, the coefficients of friction cannot be stated to within any limits with any degree of confidence. More relevant to these studies is the repeatability of the experimental results, and this is discussed in the sections dealing with the friction tests.

CHAPTER 3

SINGLE PASS TESTS

3.1. INTRODUCTION

This chapter describes early work based on single traverse friction testing of the kind commonly employed on Bowden-Leben machines. The investigations show that this method cannot be used to study E.P. additive action, but that multiple pass tests can provide a useful tool in this field.

3.2. TESTS

The first tests were performed on a single pass system, essentially the same as that used by Frewing (10), Hirst and Stafford (37) or Grew (81). The objective of the research programme was to confirm or deny the hypothesis set out in section 1.18. This suggested that the friction drop in a system with an E.P. additive would occur at a temperature dependent solely on the "out of contact time" between successive passes, rather than the sliding speed. A simple experiment to provide suitable evidence for this could be performed on a single pass system operated at different heating rates. Assuming the hypothesis to be correct, the results of such experiments may be predicted. The friction would remain high until a sufficiently thick E.P. film had built up on the track ahead of the slider, after which the friction would fall. The temperature at which this occurred would depend, not only on the reaction of the additive, but also on the rate of heating. This is because the length of time at each temperature as well as the temperature itself governs the total amount of reaction that has taken place. Therefore if a comparative experiment were performed at a higher heating rate, the temperature of the friction drop would be higher (if the O.C.T. hypothesis were valid).

An attempt to conduct experiments of this kind revealed that they are impracticable. Although the coefficient of friction rose on appropriate "running-in" to high values (about 0.8), it did not drop at any of the temperatures reached. The load, lubricant and materials used, were those that had been successfully employed by both Spikes (12) and Bayles (60). The difference was that they conducted their tests on multiple pass machines.

3.3. DISCUSSION

The principle of a single pass test is thus: As the slider traverses the specimen, the conditions in front of it (e.g. surface roughness, work hardening state) remain constant, except for any change in the effectiveness of the lubricant (due to an increase in temperature). This is excellent for determining the "critical temperature", above which the lubricant breaks down under the particular conditions employed. On the other hand in a multiple pass friction test, any one pass will almost certainly be affected by the previous running history, since the previous traverses can alter the state of the surface. This point has been brought out by Fein (72). The effect of the previous passes is likely to be much greater when the friction is high, because surface damage is inevitably increased. However when the friction is high in a single pass test, the situation is also complicated. This high friction, which involves the creation and shearing of adhesional bonds between the surfaces, creates a wide and rough wear track and thus much tearing of the surfaces <u>within</u> the contact region. Therefore, after this kind of damage has been initiated, fresh sections of track however smooth and protected, will quickly suffer similar gross damage when they enter the contact. High friction causes gross damage and grossly damaged surfaces are more susceptible to high friction. The only possible way to stop this process is to introduce a discontinuity to the sliding. Even then, adhered particles on the slider might quickly initiate fresh damage. Therefore if a surface film is to be formed so as to prevent adhesion from occurring, its durability must be much greater if gross surface damage has already begun, compared with that needed when the friction is already low.

This point has been discussed in the past by several workers, Grew (81) and Hirst and Stafford (37) for example. They used the concept to explain why the transitions in friction they had observed with oiliness additives were not reversible, irrespective of whether the thermodynamics applicable were reversible or not.

3.4. CONCLUSIONS

It was therefore decided to employ multiple pass friction tests for the subsequent investigations, because it was known from the previous work that the system would produce useful results. However the question was raised as to the comparability of results from single and multiple pass tests. This has not often been considered. Fein (71) discusses some reasons why a multiple pass friction test should be inherently better than a single pass one, although he appreciates the complications the former system introduces.

The Bowden-Leben machine has been used occasionally to provide a measure of the durability of a preformed film, by repeatedly passing over the same track - see for example Bowden and Tabor (82). An early reciprocating friction machine was described by Cowley, Ultee and West (83), who used it in multiple pass tests to measure transition temperatures. They found that these varied with concentration in the same manner in which Frewing (10) had shown them to vary. Fein (71), as has already been described, performed similar experiments using a pin-on-disk machine in which rubbing always takes place in the same direction.

A comparison between repeated sliding in one direction and reciprocated sliding has been made by Ronay (84). He found little difference in the damage caused to the track, except for some work hardening effects. He used annealed copper specimens and so it is to be expected that work hardening would occur.

The differences between slow speed tests, performed with a single or multiple passes may be summarised as follows:

i) A single pass test may not reveal an improvement in performance of a lubricant - this has been confirmed by experiment for the system considered here.

ii) During a multiple pass test, surface conditions will change depending upon the friction developed. Thus it is theoretically possible for a dynamic equilibrium to be set up such that the rate of film formation equals its rate of removal.

CHAPTER 4

INITIAL MULTIPLE PASS TESTS

4.1. INTRODUCTION

The preliminary work described in this chapter was designed to investigate further the frictional processes in slow speed tests. This meant that metallurgical factors were investigated and a microscope was used to examine the rubbing surface during the tests. Photographs were taken to provide a record of the damage taking place. Finally some tests were conducted to assess the influence of oiliness additives on the multiple pass system. Several important conclusions were made, which are given in the summary at the end of this chapter. The information gained permitted the programme of work of the subsequent chapters to be planned.

4.2. MATERIAL COMBINATIONS

Initially conditions in the multiple pass system were selected to be close to those Bayles (60) used in his ball-on-triplane machine. However a choice of materials existed, for Bayles had used both E.N. 31 and E.N. 58 steels (although he only rubbed like on like). All four possible material combinations were employed in the tests, so that as full as possible a picture of the part played by metallurgical factors might be given. The four types of test specimen are described in Fig. 4.1. which lists their properties and composition.

Experiments were carried out using the procedure described in chapter 2. The lubricant was a 1% (wt.) solution of dibenzyl disulphide in hexadecane, the upper specimens were balls 15.88mm dia. ($\frac{5}{8}$") and loaded by 1kg against the flat. The sliding speed was

COMPOSITION & PROPERTIES OF TEST MATERIALS

	% Composition								Mechanical properties	
	C	Si	Mn	S	P	Cr	Ni	Mo	Yield point tons in^{-2}	Hardness V.p.n.
Flat specimens										
E.N. 58 B	0.15 max	0.20 min	2.00 max	0.045max	0.045max	17.0 - 20.0	7.0 - 10.0		12 - 20	180 - 200
E.N. 31	0.90 - 1.20	0.10 - 0.35	0.30 - 0.75	0.05 max	0.05 max	1.00 - 1.60			70	220
Sliders										
E.N. 58 J	0.12 max	0.20 min	2.00 max	0.045max	0.045max	17.0 - 20.0	8.0 - 12.0	1.5 - 2.5	20 - 35	200 380 *
E.N. 31 balls or pegs	0.90 - 1.20	0.10 - 0.35	0.30 - 0.75	0.05 max	0.05 max	1.00 - 1.60				870

This data taken from ref.(85)
and from hardness tests.

* certain balls had this higher
hardness - see section 5.6..

Fig. 4.1.

1mm s^{-1}, the O.C.T. was 1min, and the heating rate $5^{o}C$ min^{-1}. All the conditions are given in Fig. 4.2a. with the results in Fig. 4.2b. This has been done consistently throughout the thesis and in future, all the experimental conditions will not be listed in the text except where they differ from those of the control.

Before examining the results, shown as a friction versus temperature graph, Fig. 4.2b., several observations should be noted.

1. A suitable "running - in" period was given in all the tests before the temperature was raised, to allow the coefficient of friction to reach at least 0.5.
2. At higher temperatures (above 180C) the hexadecane was visibly evaporating and oxidation was occurring, which was indicated by a yellowing of the lubricant. The boiling point of hexadecane is about 287C and such behaviour is to be expected in the shallow open lubricant trough.
3. The heating rate chosen, approx. $5^{o}C$ $min^{-1}$was close to that employed by Bayles, and was a balance between an excessive rate which would prevent reactions from reaching eqilibrium and a low rate which would exascerbate the oxidation effects noted above.
4. The individual plots of Fig. 4.2b. are each the mean of at least three tests. Therefore they do not show the relative repeatability between tests of the same type, which is an important factor in assessing the results. The most repeatable tests were those performed with an E.N.31 ball on an E.N.58 flat. Next most repeatable were E.N.31 on E.N.31 and E.N.58 on E.N.58. Least repeatable were tests performed with an E.N.58 ball on an E.N.31 flat.
5. The control experiments, using pure hexadecane (carried out on several different material combinations with identical results) displayed a consistently high friction, which only dropped slightly

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg.	1mm s^{-1}	1 min.	$5^{\circ}C\ min^{-1}$

materials - track - slider	contact geometry
varied	$\frac{5}{8}$" dia. ball on flat

lubricant 1% DBDS wt. in hexadecane

special conditions

varied conditions

materials - track	- slider		no. of runs	repeat-ability
E.N. 58	E.N. 31	——	4	4
E.N. 58	E.N. 58	-·-·-	7	3
E.N. 31	E.N. 58	- - -	3	1
E.N. 31	E.N. 31	········	5	3

Note: The repeatability is given here as it is in all the tests, in the same manner. It is assessed on a scale from 1 to 5, in which 1 represents poor repeatability (a variation of 20°C or so in the temperature of the friction drop) and 5 represents very good repeatability (within a few °C of each other)

Figure 4.2a

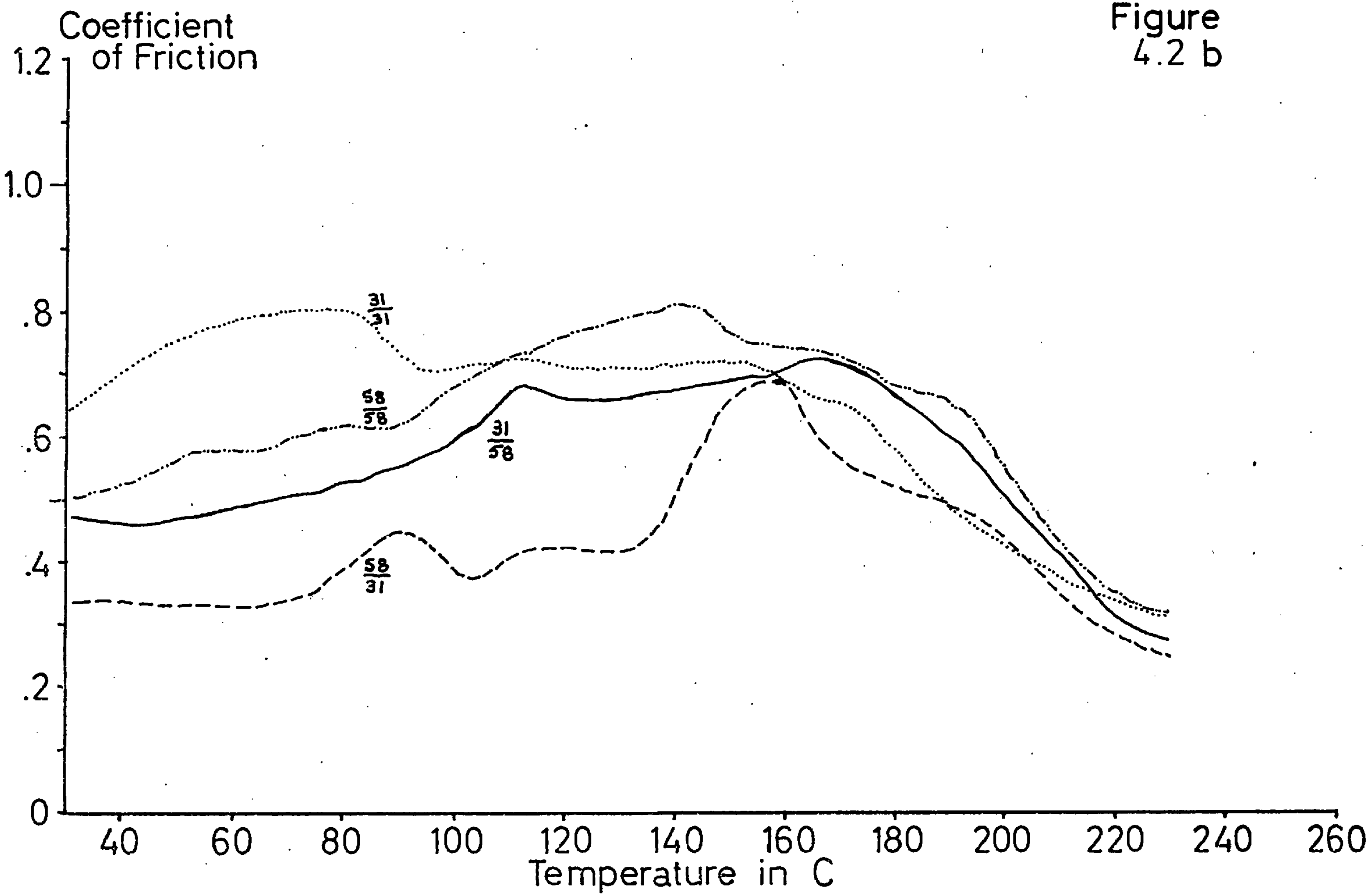

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
31/31
58/58
31/58
58/31
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

Figure 4.2 b

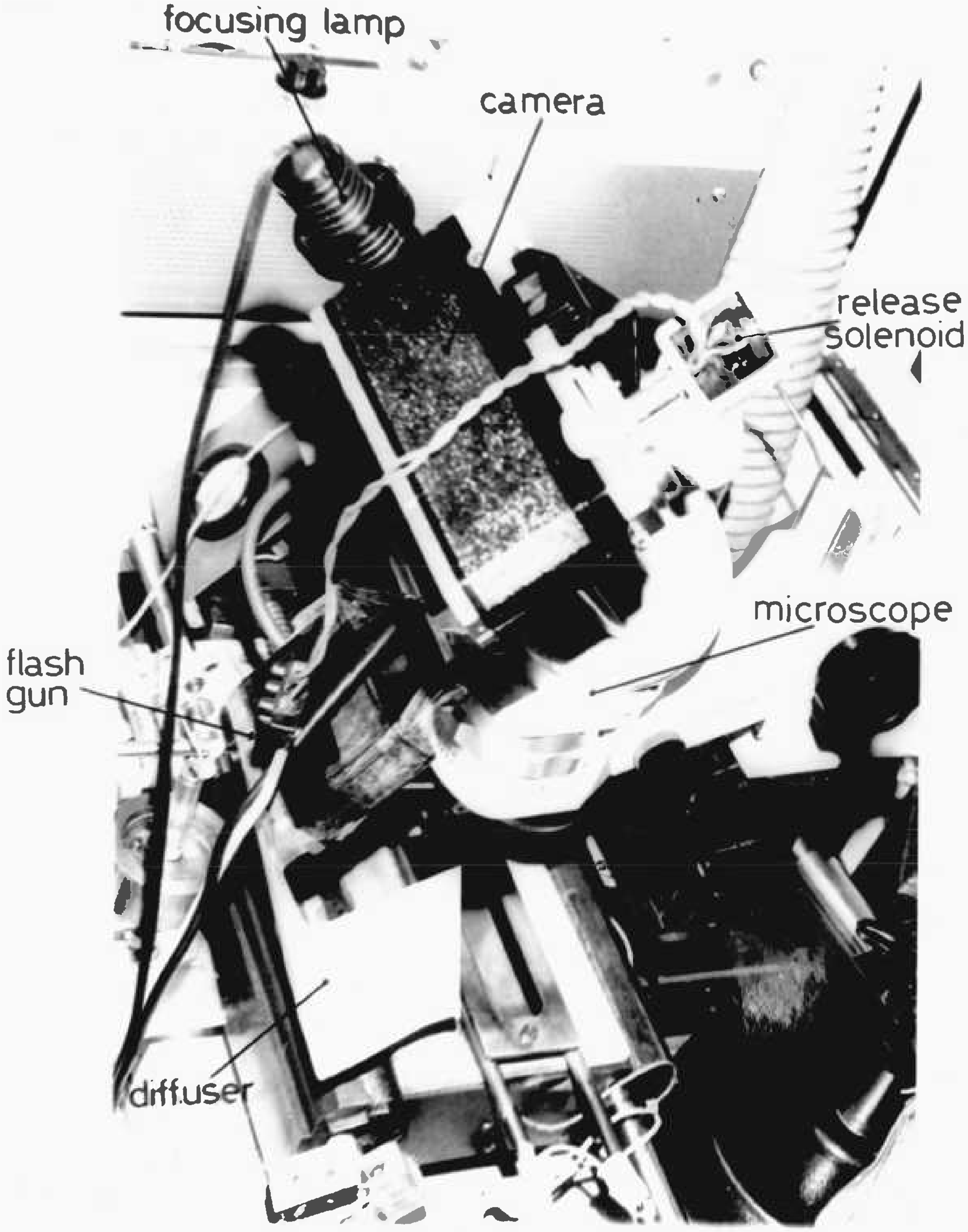
at the highest temperatures reached. These control experiments reveal the effect the E.P. additive has on the friction at elevated temperatures.

Although there are variations between the traces of the four material combinations, there is one obvious similarity between them all. They all show a change in the coefficient of friction from about 0.7 to about 0.3 when the temperature is raised from 170C to 220C.

4.3. PHOTOMICROGRAPHS OF THE FRICTION TEST SPECIMENS

To understand better the nature of the surface damage created in the above friction tests, and more importantly to see how this damage varied throughout a test, a microscope was mounted on the apparatus. The most convenient in use was a stereo microscope, which had a long working distance and three powers of magnification. Visual observations, made during a test, proved unsatisfactory, because of the fast passage of the track across the microscope's field of view. Therefore a camera was mounted in place of one of the eyepieces and arranged so as to record the state of one section of the track at the end of each pass. The final arrangement is shown in Fig.4.3.

The camera shutter was released by a solenoid, mounted on the camera case, which was operated by the reversing relays of the carriage controller. In this way each frame was exposed as the carriage reached the end of its traverse and was almost stationary. Since the loading arm was over 50mm wide, only the front portion of the track would emerge sufficiently, from under the arm, to be viewed by the microscope from above. A section of this part of the track was thus repeatedly visible on the screen of the camera, just



focusing lamp
camera
release solenoid
microscope
flash gun
diffuser

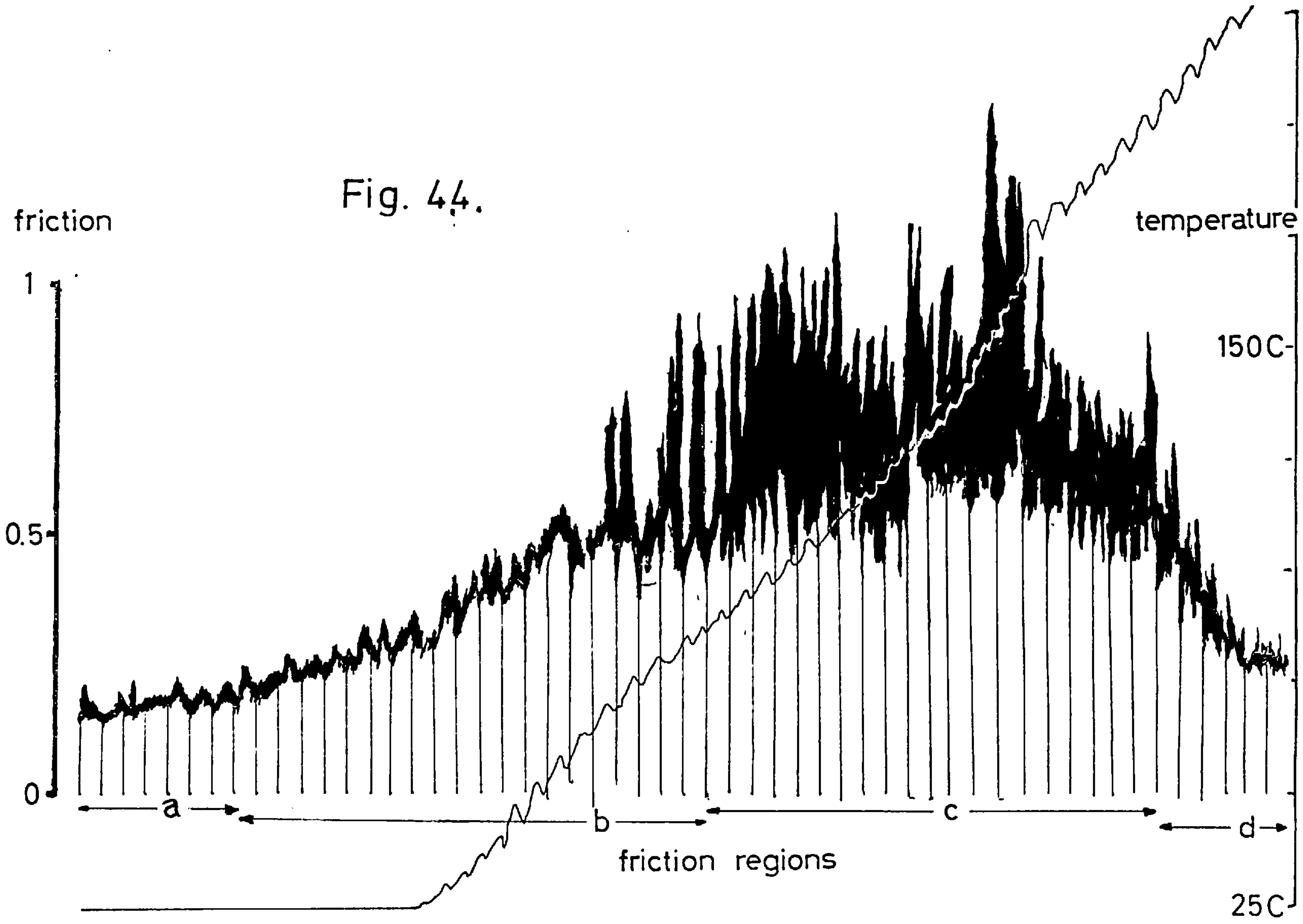
Fig. 4.3

before the carriage reversed. The microscope was focussed by eye, using the image on the camera screen. The image was made sufficiently bright for this operation by a lamp mounted over the unused eyepiece. Illumination for the exposure was provided by an electronic flash gun, synchronised to the camera shutter and mounted on the microscope body. The light from the flash gun was "bounced" off a matt white reflector across the specimen to give a diffuse and even illumination. The precise arrangement of the flash gun and reflector required experimentation to give the best results and correct exposure (no other exposure control being available). It was found that direct illumination of the specimen by the flash gun produced pictures that were too "hard", and had bright spots blurred due to dazzling. Nevertheless the flash gun was essential because the shortness of the flash (about 0.001s) "froze" any movement in the carriage or vibration in the microscope, that otherwise would have blurred the picture.

The camera had to be wound on manually after each exposure and a continual check was needed to maintain the camera in focus. This precaution was necessary because of the very small depth of field, which made precise focussing essential. Human errors inevitably meant that some frames were improperly exposed, but sufficient evidence was gathered by this technique to make several important deductions about the friction tests.

Four regions of surface damage may be identified in a typical friction trace and observed by use of photomicroscopy. Fig. 4.4. shows a friction trace, taken directly from the pen recorder and showing the friction plotted against time, including the "running - in" period. The conditions of sliding are those detailed in Fig.4.2a.

Fig. 44.



and the materials are E.N.31 on E.N.58. Photomicrographs from the same test are shown in Fig.4.5a.-d., and are presented in pairs so that the surface damage caused by the traverse may be seen by comparing the two pictures. The approximate coefficient of friction is also given. The four regions of damage are indicated on Fig.4.4. and Fig.4.5. as A – D and from the evidence of the photomicrographs are:

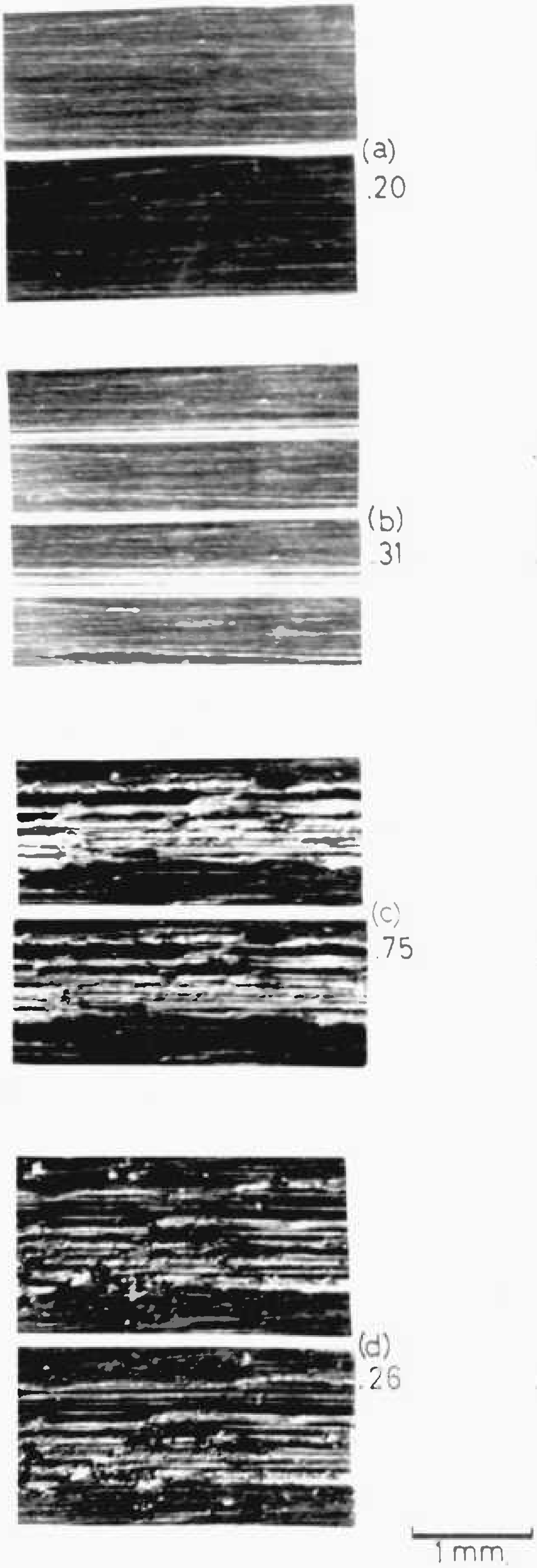
A) BEFORE RUN-IN – coefficient of friction is low (less than 0.2), the wear track is very shallow, narrow and surface scratches remain within it. No change can be observed between successive passes.

B) RUN-IN – coefficient of friction rising (upto 0.5), the wear track is widening and formed by deep, smooth sided grooves. Sometimes very little change may be detected between passes, at others new grooves can be seen to result from a single pass.

C) HIGH FRICTION – coefficient of friction is very high (above 0.5), the wear track is very rough and uneven and continuing to widen. Catastrophic damage is occurring intermittently and large fragments of the softer surface are being removed, welded and sheared. A change in the track between successive passes is always apparent.

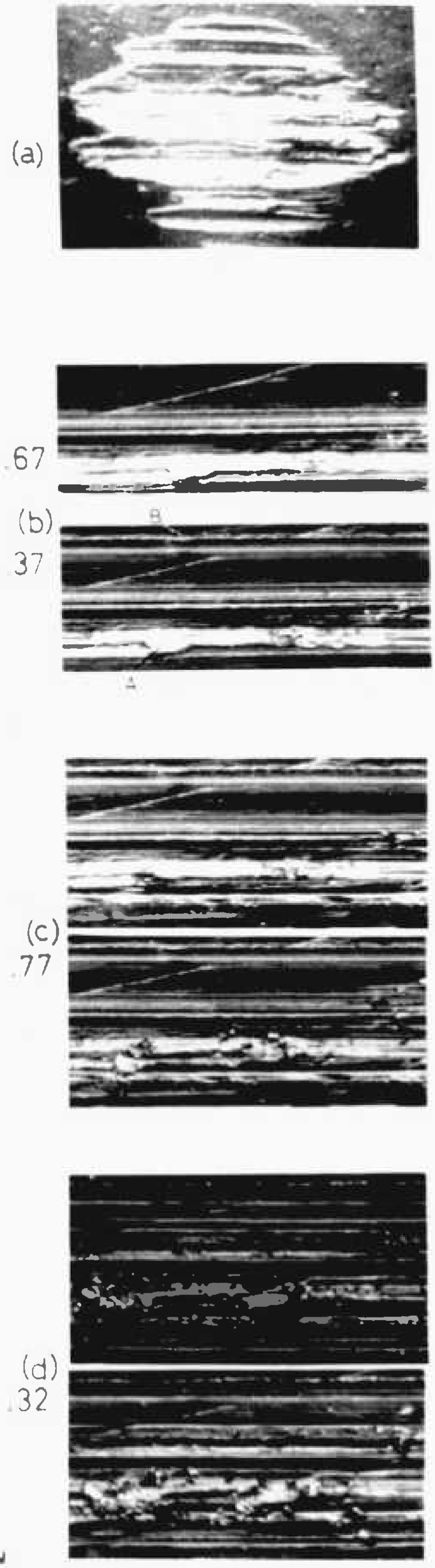
D) POST FRICTION DROP – coefficient of friction much reduced (by about half), the wear track remains wide and rough from the damage caused in region (C). There is little detectable change between passes.

Further comparisons of the same regions from tests with the other material combinations may be seen in Fig.4. 6 – 8. Part (a) of



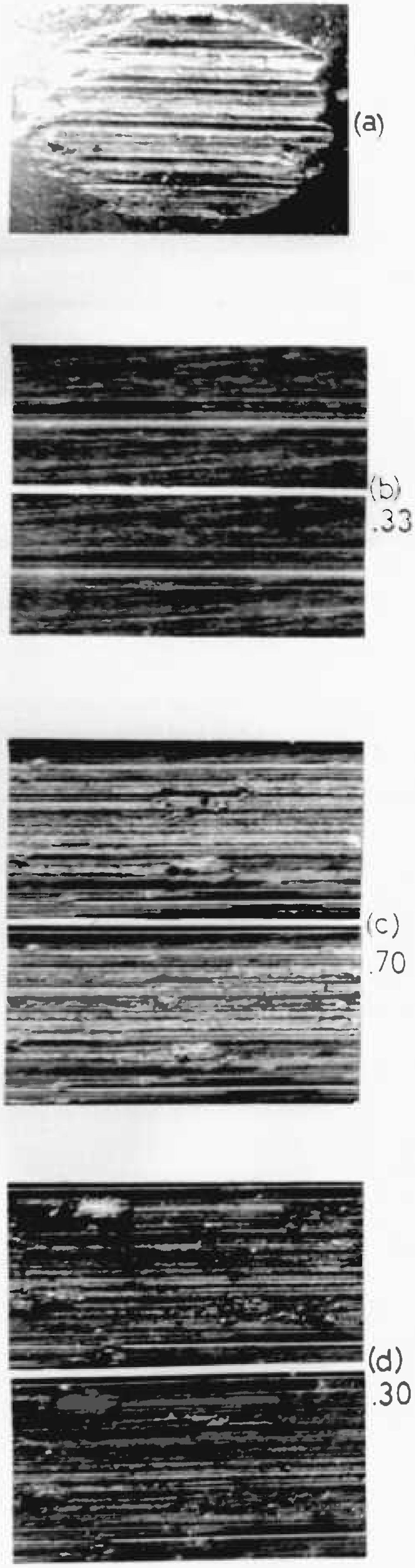
E.N. 31 on E.N.58

Fig. 4.5



E.N.58 on E.N.58

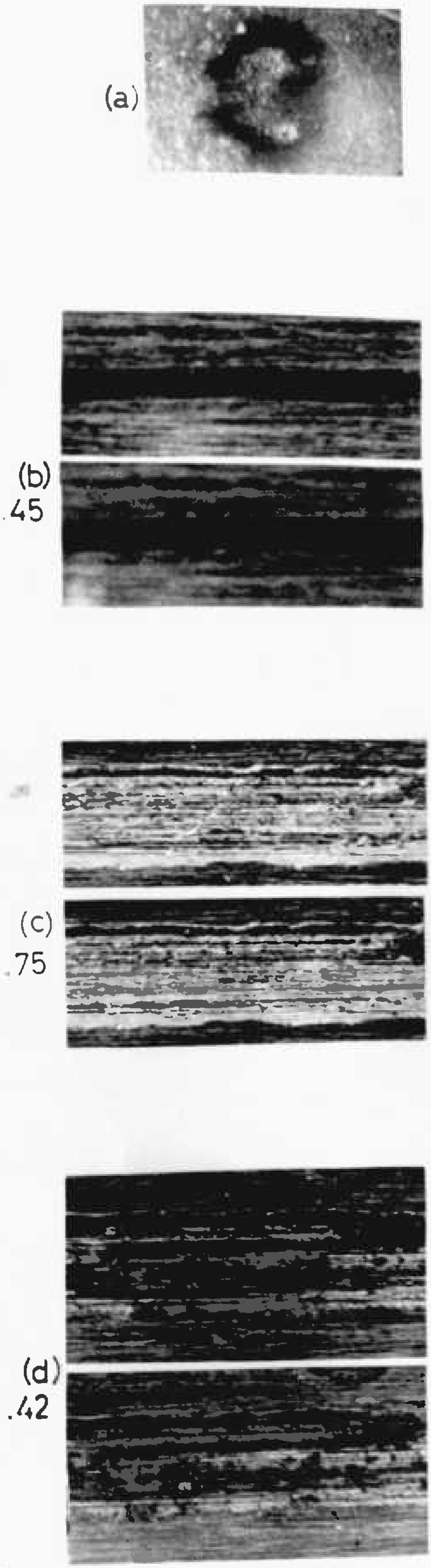
Fig 4 .6



E.N. 58 on E.N. 31

Fig 4.7

1 mm.



E.N.31 on E.N. 31

Fig 4.8

each figure shows the slider, at the end of the test, to the same magnification. Parts (b), (c), and (d) illustrate the regions of damage B, C, and D from the tests using E.N.58. on E.N.58. (Fig.4.6.), E.N.58.on E.N.31. (Fig.4.7.) and E.N.31. on E.N.31. (Fig.4.8.). To provide a vertical scale to the kind of damage in region (C), Talysurf traces were taken of the flat surface from tests that had been run into region (C). Fig.4.9a. shows the profiles of a wear track formed when E.N.58. was rubbed on E.N.58. Similarly Fig.4.9b. shows the profiles of E.N.31. on E.N.31. Both the profile across and along a part of the wear track are shown.

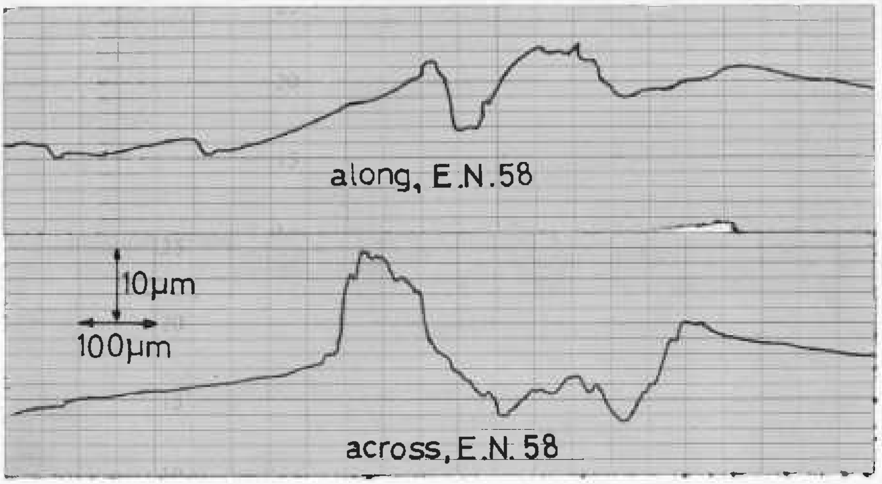


Fig. 4.9a.

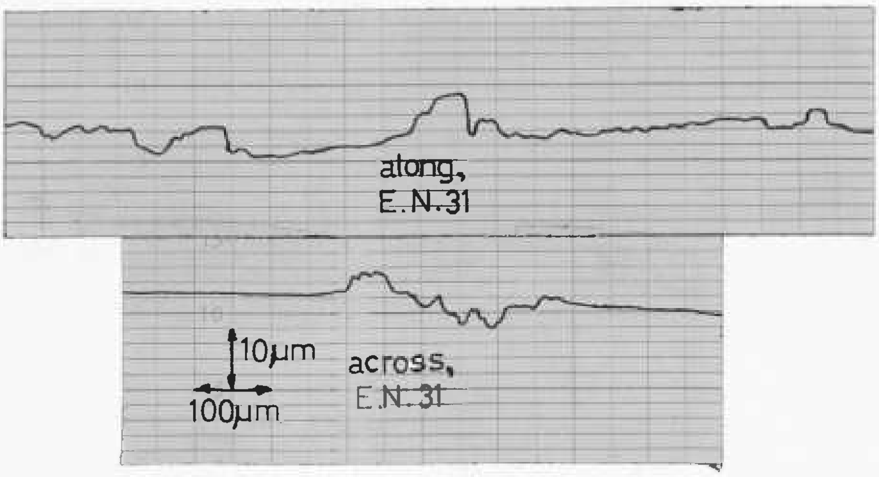


Fig. 4.9b.

Fig.4.10. shows a computer digigraphic output of a series of parallel profiles taken across a wear track of E.N.58. steel. The approximate scales are marked. The figure was produced by A. Bowyer, who employed a wear track from one of these tests.

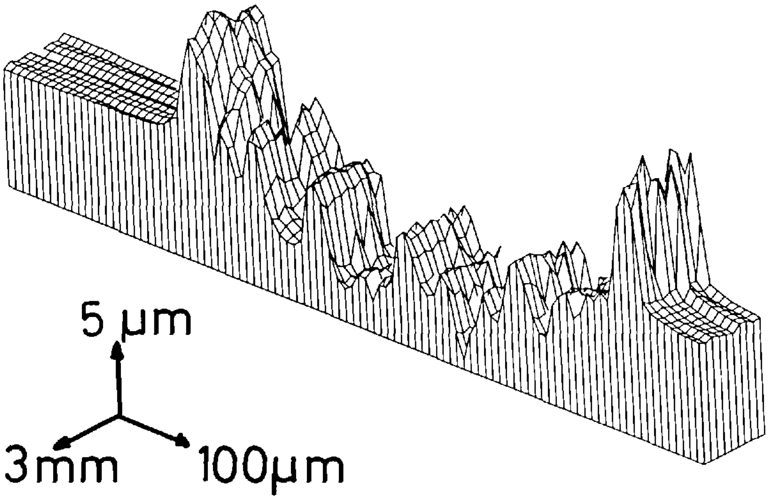


Fig. 4.10

Deductions that may be made from the photomicrographs are as follows:

1) High Friction Is Not Required For Surface Damage.

Considerable surface damage can take place without friction rising. This is revealed by the many pictures taken in region (B). Although very often no extra damage may be observed on a long section of track, when fresh ploughmarks do appear, the friction does not rise, but often falls. Thus the component of the friction involved in ploughing is relatively small, a conclusion which agrees with that of Bowden and Tabor (86).

2) The Surfaces Are Adhering.

The main characteristic of the high friction region (C) is the intermittent welding and tearing of the surfaces. This is an adhesional process as described in section 1.9.

Such adhesion implies that the rubbing surfaces are relatively free of contamination, suggesting that the cleaning techniques employed were satisfactory.

3) Friction Drop Is Caused By Prevention Of Adhesion.

The reduction in friction at high temperatures is merely a prevention of the type of damage taking place in region (C). There is no "healing" of the damaged track and it remains as rough as it was at worst. It was impracticable to observe the slider after successive passes and so it is possible that some smoothing of the slider's wear scar takes place during the friction drop.

4) Load Is Supported By High Spots.

It must be concluded that once the friction has been reduced, and the wear track remains rough, the slider will only be making contact with the track intermittently, and over a small fraction of the available area. This will also be true on occasions during regions (B) and (C). This point is illustrated by Fig.4.6b. The coefficient of friction on the first pass was 0.67, but at the second only 0.37, yet the amount of damage caused by the second pass may be seen (the extra groove at the top of the picture). Evidently a high spot formed on the slider, and during the next pass the whole load was taken on this small area. Even with the large amount of "ploughing" required to form the new groove, the coefficient of friction (a measure of the work unit) was only 0.37, (see (1) above). The size of the high spot may be judged by the previously existing protusion on the track (marked A). This caused the newly formed track to be perceptibly narrowed (at point B) by temporarily taking some of the load off the high spot.

Although a "flat" is worn onto each slider, conformal surfaces are not thereby created. Generally the load is supported on only a fraction of the apparent contact area, and therefore any particular portion of the track (or slider) will not be rubbed on every pass. This effect is accentuated by the low "stiffness" of the loading arm in the vertical plane. The two sliding surfaces may move apart without any increase in the load acting between them. This is of course not so with most practical bearing systems.

5) Hardness Of Materials Affects Scale Of Damage.

The differences between the materials allowed the following further deductions to be made.

a) The width of the wear track were dictated by the hardness of the slider. Compare for example the track widths in Fig.4.5. and 4.6. For the same track material, the width of the track is increased because of the softer E.N.58. slider.

b) The size of deformities, that is the scale of surface damage, is also affected by the hardness of the materials, both of slider and of track. Compare for example Figs.4.6. with 4.7. There were many more small scale asperities on the harder E.N.31. track as compared with the E.N.58. track. This effect correlates with the observations in (a) above.

c) Examination of Fig.4.8., in which an E.N.31. flat (V.p.n.220) has been rubbed by an E.N.58. ball (V.p.n.180) reveals part of the reason for the inconsistent frictional behaviour observed with this material combination (section 4.2.). The wear track is wide because the "soft" ball has worn considerably, yet the track shows underlying features similar to those of the E.N.31. track shown in Fig.4.7. (small scale surface deformations). Nevertheless a large scale protusion is evident, which was a portion of slider, but is now adhered to the track. It seems that appreciable amounts of the E.N.58. ball are smeared, unevenly, onto the E.N.31. track, and this effect causes the inconsistent frictional behaviour reported.

d) The converse appears to apply with the complimentary combination of an E.N.31. slider (V.p.n.870) on an E.N.58. flat (V.p.n.180). The wear track formed is narrow, Fig.4.5. since the slider is little worn, yet the scale of damage is relatively large. The greater consistency of this combination over that of E.N.58. on E.N.58. may well be due to the narrow wear track, which means that the load tends to be carried by the same points at each traverse of the slider. It would appear that transfer of the E.N.58. material from the flat to the E.N.31. slider does occur, and the frictional behaviour of this combination is indeed more like that of E.N.58. on E.N.58. rather than like E.N.31 on E.N.31.

6) Dark Areas Formed In Some Tests At High Temperatures.

The E.N.31. tracks, when rubbed with E.N.31.,displayed discoloured areas which grew and darkened during the later stages of the friction test. See Fig.4.8d. Bailey (76) reported similar black areas from his friction tests, which he considered to be formed by a sulphur compound. However the evidence produced in chapter 7 does not fully support the hypothesis.

4.4. ESTIMATION OF THE CONTACT AREA

A theoretical analysis for the deformation of a sphere, loaded against a flat plate, was given by Hertz and quoted (for steel) by Bowden and Tabor (87):

$$a = 1.1 \left[\frac{Wr}{2} \left(\frac{1}{E_1} + \frac{1}{E_2} \right) \right]^{\frac{1}{3}}$$

where a = radius of contact
W = load
r = radius of sphere
$E_{1,2}$ = Young's Modules of the two steels

For the conditions of the experiments, for example E.N.31. on E.N.58.

E_1 = 19,900 kg mm^{-2} reference (85)
E_2 = 20,900 " " "
r = 7.94 mm
W = 1 kg

a = 0.08 mm

Mean pressure in contact 50 kg mm^{-2}

The peak pressure is about 25% higher than this mean, whilst the yield point of E.N.58. steel is about 32 kg mm^{-2}. (85).

Therefore, even under static conditions, theory predicts that plastic flow will occur within the contact, at the lowest loads used. Once frictional forces are developed then plastic flow is inevitable, and the combined stresses set up large shear forces within the metal. No attempt has been made to calculate these. The model by Tabor (34) will apply. The photomicrographs provide confirmation of these preditions. All the wear tracks observed were wider than the Hertizian contact (0.16mm) (except possibly at very low frictions), indicating that plastic flow had occurred.

The actual area of contact, when governed by the flow pressure, may be found from the formula,

$$\text{contact area} = \frac{\text{load}}{3 \text{ X yield pressure}} \qquad \text{from ref. (87)}$$

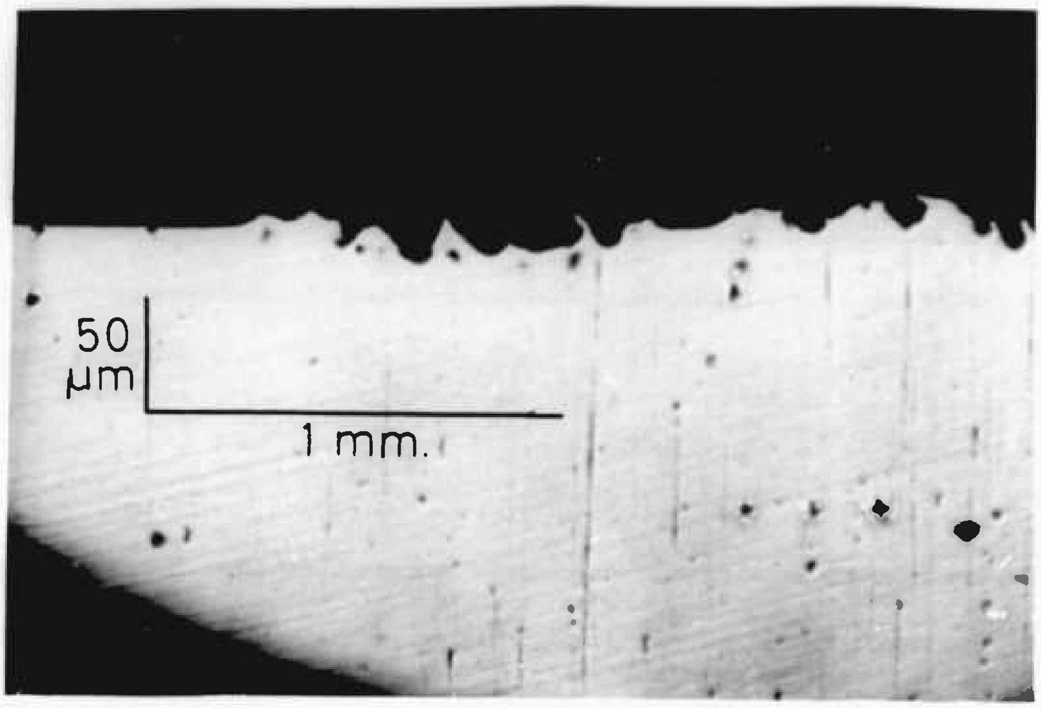
Thus with a load of 1 kg on E.N.58. steel, the contact area is approximately 0.01 mm^2.

It may be seen that theoretical estimations produce contact areas of the order of 50 times smaller than the apparent contact areas. This confirms the ideas discussed in deduction (4) of the previous section, in that during sliding the load is supported on only a few points, which may not be rubbed at every pass.

4.5. METALLURGICAL SECTION OF A TRACK

Two specimens, produced especially for friction tests described in section 7.3., were taper sectioned in the standard metallurgical manner. The sectioning was at about 10^o to the surface a taper of 5.5:1, and after polishing a number of micro-hardness tests were performed. It was not possible to etch the sections with any available etchants. The specimens were made of E.N.58. A photomicrograph of one section is shown in Fig.4.11. with the approximate scales marked.

The two specimens came from friction tests which used flat ended pegs, as the sliders, of about 4.6 mm diameter. The load was 10 kg, the other conditions were basically those as used in the tests described in section 4.2. Full details will be found in section 7.3. One specimen had been run into region (D), (section 4.3), that is the coefficient of friction had been high, and then dropped to about 0.3. The other had been run into region (C) only, because the test was terminated when the temperature reached 170C.



(a) photomicrograph of section of inset as below, ignore scratch marks.

(b) peg, inset, & recess - see sect 7.3

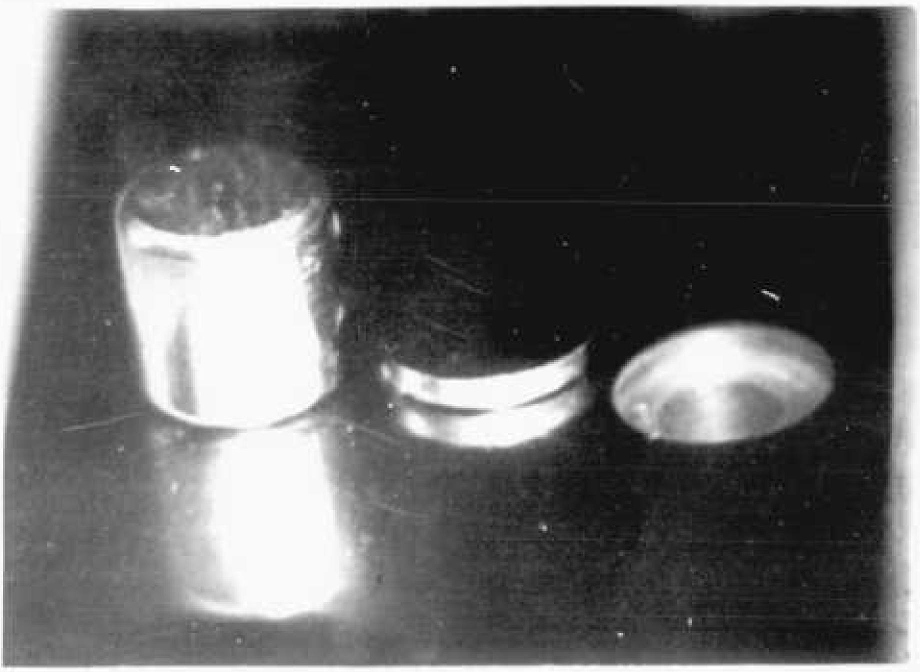


Fig 4.11

In fact there were no significant differences in the micro-hardness measurements from the two specimens, which is evidence that the drop in friction observed in these tests is not caused by a temperature effect upon any bulk metallurgical property.

The micro-hardness tests were performed on a Leitz machine at loads of 100g. The hardness at the centre of the section was 270 V.p.n. At lesser depths this rose to over 600 V.p.n. The depth to which work hardening could be detected was about 250 µm on the section or about 50 µm normal to the surface. Confirmation that the grinding and polishing of the specimens did not cause noticeable work hardening was obtained. Micro-hardness tests just below part of the unworn surface produced a hardness of 280 V.p.n. which was the same as the bulk hardness measured previously.

It is commonly known that E.N.58. steel is easily work-hardened. Ref. (85) indicates that its yield point can reach 3 or 4 times the normal value. The degree of work-hardening found is therefore not unexpected. However the way in which it may affect the frictional process is harder to determine. Certainly the real area of contact may be reduced after a number of passes, and the surface layers may have become more brittle.

Work-hardening was ignored in the major experiments of subsequent chapters. The friction tests of section 4.2 had shown the limited effect of steel type upon the friction temperature graph obtained. No further experiments on the metallurgy of the steels were performed.

4.6. OILINESS ADDITIVE ACTION

The modified Bowden-Leben machine was devised specifically for work on E.P. additives but it was decided to compare its performance with other test machines using the much more widely researched oiliness additives. Fatty acids have been used extensively as oiliness additives in slow speed friction tests, Frewing (8), Fein (72), Hirst and Stafford (37), Grew (81) for example. Therefore the use of such an acid would allow some correlation to be made between friction tests on this modified Bowden-Leben and those of other workers. A second reason for performing these tests lies in the fact that many contaminants and oxidation products of hexadecane can act as oiliness additives in the tests designed to measure E.P. additive action. It was therefore of further interest to assess the effects of oiliness additives alone on the system being studied.

Hexadecanoic acid was chosen as the additive, and 0.1% wt solutions were made up in hexadecane. This acid is an oxidation product of hexadecane, and was used in low concentrations since any impurities in the E.P. tests would only be present in relatively low concentration. The friction tests were performed with the same basic sliding conditions as those used in the tests of section 4.2. The slider consisted of E.N.31. and the flat specimen E.N.58. in all cases. The results are shown in Fig.4.12b., as two bands, with one typical trace given in each band. Quite a number of tests were conducted, but two different types of behaviour were observed. In some cases the friction rose steadily on heating, reaching high values at temperatures below 120C. In other cases the friction remained low and rose sharply at much higher temperatures (above 140C). These different transitions have been represented as two bands on Fig.4.12b.

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
varied	varied	1 min.	varied
.5 - 5 kg.	.17 - 1 mm s^{-1}		1 - 5 ^{o}C min $^{-1}$

materials - track	- slider	contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" ball on flat

lubricant 0.1% hexadecanoic acid in hexadecane

special conditions

The temperature was allowed to fall after a transition in most cases.

varied conditions	no. of runs	repeat-ability
load, sliding speed and heating rate were altered - <u>see text</u>.	14	"2"

Figure 4.12a

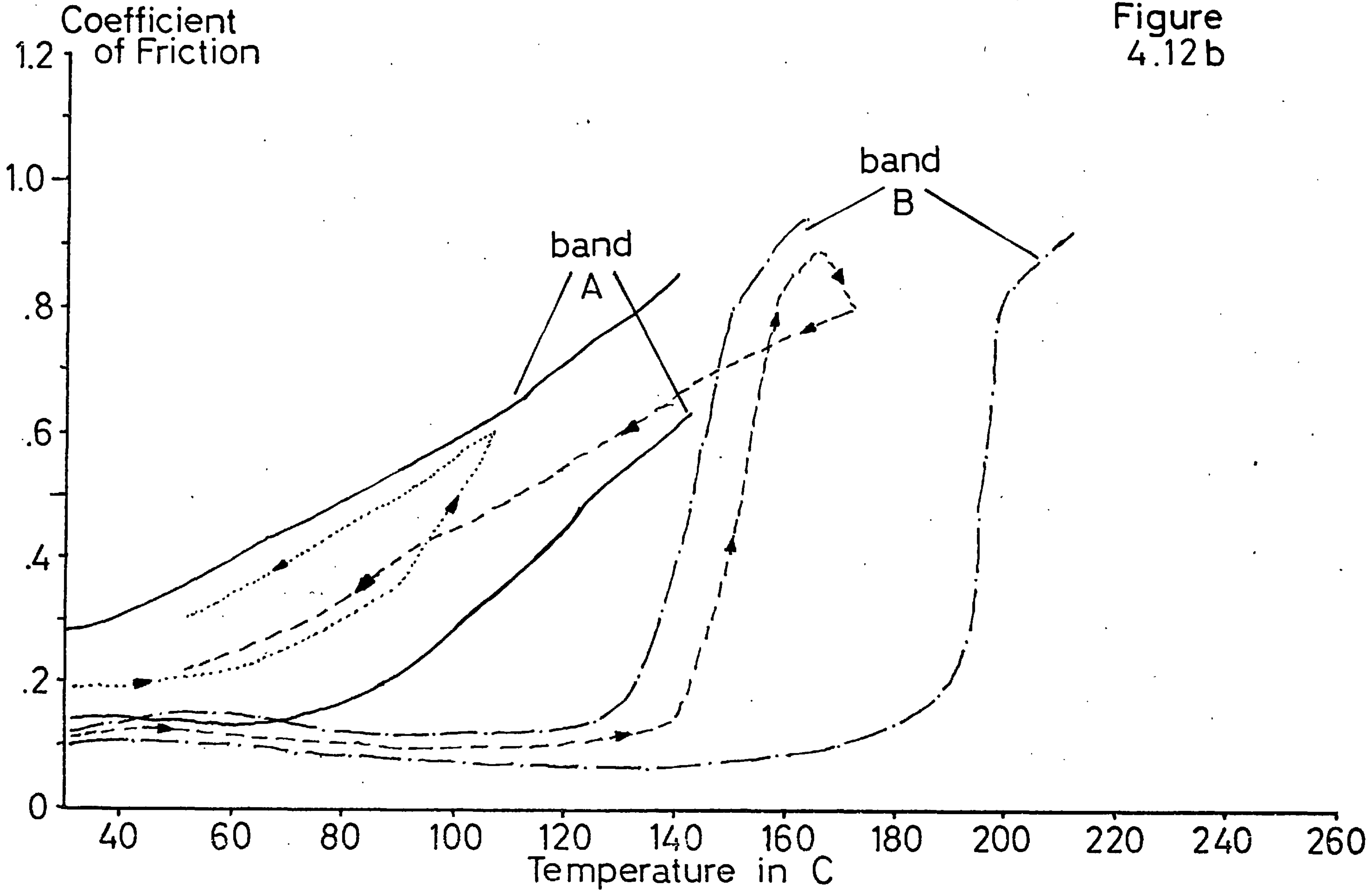

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
band A
band B
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

Figure 4.12b

At first it was thought that some particular condition such as load, was set at a critical value which meant that the transition could be either high or low because of a discontinuity in the transition temperature relationship. Such a discontinuity has been shown by Hirst and Stafford (37) for example, for one of their systems (see discussion below). On this assumption it was decided to vary the conditions, load, sliding speed, heating rate, and concentration to discover which variation would cause the results to fall consistently into one or other band. Also a check was made on the reversibility of the transition, by allowing the system to cool. No consistency was found, but several observations will help to give a comprehension of the processes involved.

1) The differences between results in the two bands may be described by the following.

   a) If the coefficient of friction at low temperatures was low (about 0.15) <u>and</u> dropped further as the temperature rose to 100C, then the transition would fall in band B.

   b) Transitions in band B were at considerably higher temperatures and the friction rose much more steeply than those in band A. Furthermore the friction often dropped after the transition in band B, but not in band A, that is there appeared to be some "over-shoot".

   c) After a transition in band B, as the system was cooled, the friction fell in such a way as to bring it into band A.

   d) Subsequent reheating and recooling of any of the specimens was tried and always produced a transition in band A, never one in band B.

2) The above observations especially (c) and (d), suggested that the critical factor was the surface roughness of the specimens.

Hirst and Stafford (37) discussed this factor in relation to the onset of plastic flow in the contact. They found a jump in the transition temperature at a particular load, which they related to the yield point of the metal in the contact. They also found the same qualitative difference between transitions at high temperatures (comparitively large and steep) and those at low ones. Sharma and Cameron (88) have shown the effect of surface roughness on transition temperature. In this situation then, if the specimens "ran-in" to a smooth track and low friction, the sliding took place with minimal plastic flow, and the transition came at a high temperature. If however the "run-in" surface was too rough, then the repeated passes would cause a continuing roughening and the transition would occur very much earlier. The observations of (c) and (d) confirm these ideas, because after a transition the track has been severely roughened and then the friction coefficients always fall in band A.

Unfortunately neither an increase nor a decrease in the load produced consistent results, which is contrary to the findings of Hirst and Stafford. This may be due to the complications which arise out of multiple pass as opposed to single pass tests, as was discussed in section 3.3.

3) An alternative explanation of the variation in the transition was investigated and dismissed. Spikes (12) indicated the importance of allowing sufficient time for the additive to adsorb in friction tests. Several experiments were conducted in which the specimens were left immersed in the lubricant for at least 15minutes before sliding was commenced. However the results did not all fall in band B. This explanation was thus rejected.

4) The broadness of band A is in some part due to the variety of experimental conditions employed. Generally the results of otherwise identical experiments could yield transitions as much as 10°C apart. Nevertheless the trends observed by Hirst and Stafford and Sharma and Cameron (88), that a reduction in concentration or increase in load would reduce the transition temperature tended to be borne out by the results obtained.

5) The majority of experimental results fell in band A and one factor, which could not be tested, might have caused the few results which fell in band B. All the specimens were cleaned using the same process, which was described in section 2.9. However it is possible that a few had traces of contaminant films, finger grease for example, when they were placed in the lubricant. Grew (81) has shown the major effect of very small amounts of such films, and in these tests the higher temperature transitions could have resulted. No way was available to check on the cleanliness and this factor cannot be ruled out as a possible explanation.

In conclusion the effect of 0.1% of a fatty acid in the lubricant may be seen from these tests. Generally it has little effect on the frictional behaviour of the system studied, if the coefficient of friction was above 0.2 and the temperature above 100C, but sometimes it could have an effect upto 180C. Secondly the lubricant performed in very much the same way in these friction tests as had been found by previous workers.

4.7. SUMMARY

Comparable conditions to those used by Bayles (60) and Spikes (12) have been employed in friction tests, performed on this modified Bowden-Leben machine. The resultant friction temperature curve is very similar. Other aspects of the tests have been investigated and the important conditions may be summarised so:

1) The precise metalurgy of the specimens (E.N.31. or E.N.58) is not critical. E.N.31. on E.N.58. produces the most repeatable results.

2) Photomicrographs of the worn surfaces indicate that the friction drop is a change from sliding when the surfaces adhere strongly to one another, to sliding which occurs without these adhesional bonds being formed. No visible healing takes place after the friction drop.

3) Work-hardening occurs on the surface of the track, but no change in this can be detected before and after the friction drop.

4) Oiliness additives can play a part in the frictional process, but only at low temperatures and low coefficients of friction. otherwise low concentrations of these additives appear to have no effect on the friction developed.

CHAPTER 5

EXPERIMENTS INVESTIGATING EFFECTS OF MECHANICAL FACTORS

5.1. INTRODUCTION

It is of interest to investigate the effect of variations in the mechanical factors on the friction trace for two reasons.

1) Since other similar friction tests have been performed on different machines, in which the mechanical conditions of sliding were inevitably different, useful comparison between the results can only be made when the effect of the variations in the factors is known.

2) The effect of varying a factor such as load, would be expected to demonstrate the characteristics of any surface film which is produced. This film will have particular mechanical properties and these may be assessed by examining the film's performance under varying conditions.

Using the frictional system described in section 4.2., there were eight factors which could be varied.

1) Out of contact time. (O.C.T.)
2) Sliding speed.
3) Track length.
4) Load.
5) Contact geometry.
6) Hardness of materials.
7) Stiffness of restraint.
8) Vertical resonance.

Each of these factors was varied, but it should be noted that it is not possible to vary the first three entirely independently. Unless the machine is stopped at each reversal, the track length is fixed by the sliding speed and the out of contact time. It was considered undesirable to alter the rubbing process in this way (by stopping the machine), although the effect of such action has become apparent through the experiments of section 6.6. Thus initially no attempt was made to separate the first three variables.

It was expected that several of these factors would affect the friction drop temperature, especially O.C.T. However apart from sliding speed, none of these mechanical factors appeared to have any real effect. This was both surprising and hard to explain. The various ideas that arose, which were usually tested and found untenable, are given and discussed in the appropriate sections. A summary is given at the end, which draws several conclusions, unfortunately mostly negative.

5.2. OUT OF CONTACT TIME

The traverse speed of the carriage was held at 1 mm s^{-1}, whilst the track length was varied to give out of contact times of 2.6, 6, 60, and 125 s. The heating rate was $5^{o}C\ min^{-1}$, except for the 2.6 s, O.C.T. experiments when the rate was $10^{o}C\ min^{-1}$. The heating rate was increased, because prolonged operation at such a high rate of repetition was likely to cause a failure in the motor or solenoids and so ruin the experiment. Experiments later showed the minimal effect of the change in heating rate (section 6.7.). Fig.5.1a. gives a table of the conditions used, and Fig.5.1b. the resulting friction values, each line being the mean from two or more tests. Two experiments were considered sufficient because the overall consistency was very good (about 5%) and as can be seen, all the results fall close together, especially within the friction drop region. E.N.31. balls on E.N.58. flats were employed because the tests of section 5.2. had shown that this combination produced the most consistent friction traces.

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	1 mm s^{-1}	varied	$5^{\circ}C$ min^{-1} (except one)

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia. ball on flat

lubricant 1% DBDS in hexadecane

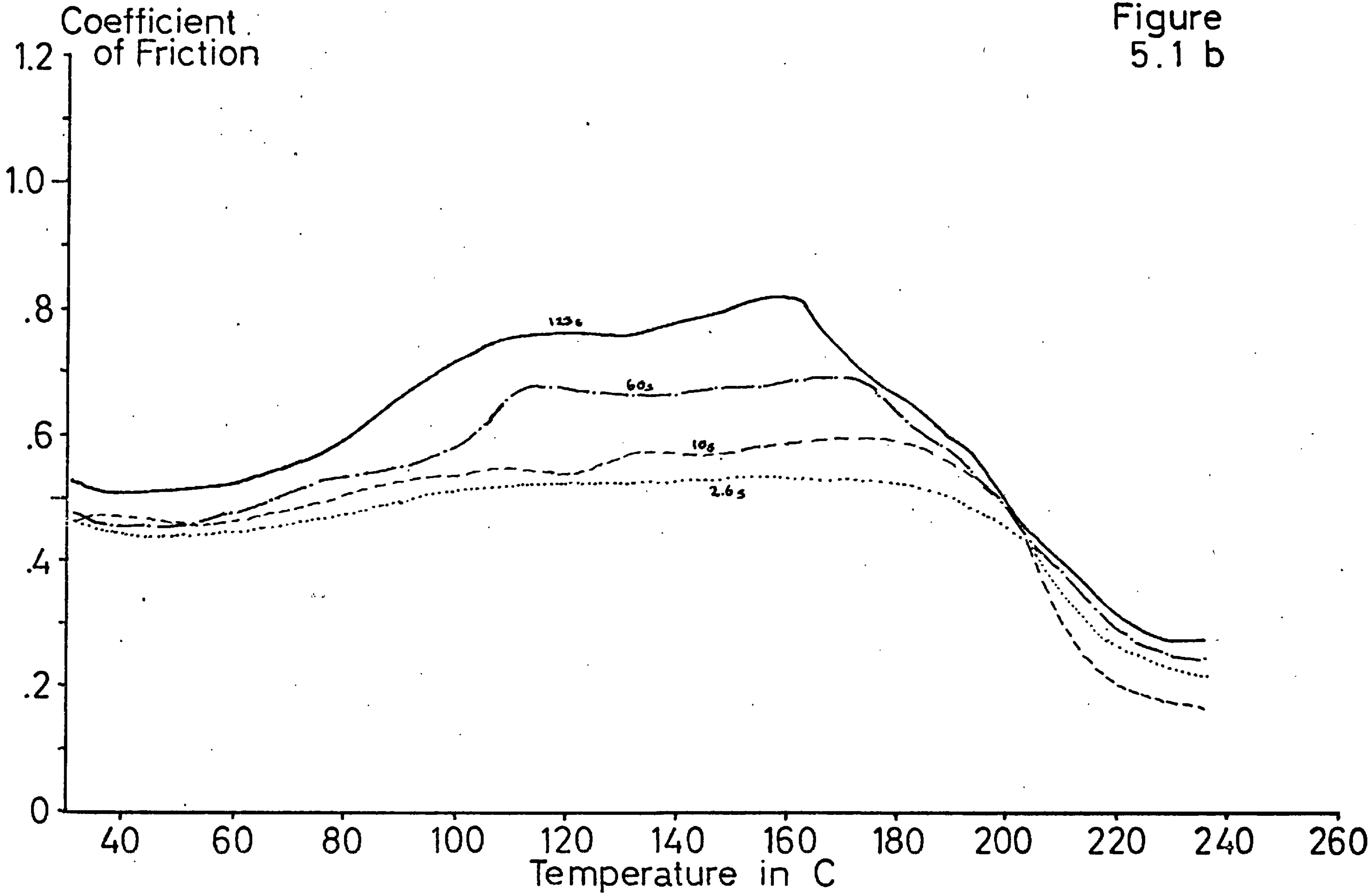
special conditions

varied conditions		no. of runs	repeatability
O.C.T.			
123 s	——	2	4
60 s	—·—·	4	4
10 s	- - -	2	5
2.6 s	········	2	5

(note: the heating rate for these tests was 10 $^{\circ}C$ min^{-1})

Figure 5.1a

Figure
5.1 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
125s
60s
10s
2.6s

A 40:1 variation in O.C.T. has shown no detectable change in the temperature at which the drop occurs. The only consistent trend was in the maximum coefficient of friction reached, before the drop. However if Fig.5.1b. is compared with Fig.5.3b., a similar variation in the maximum friction reached will be seen. The common factor between these sets of results is the variation in track length employed. Fig.5.3b. comes from experiments performed at various sliding speeds but a fixed O.C.T., and the track length varies in the same way as in the tests of this section. One reason for a change in the maximum friction observed, with track length, may be appreciated from the nature of the experiment. It has already been seen that when the friction is high, the track becomes very rough and uneven. With longer tracks the chances of the slider meeting a large protusion and requiring considerably more force to remove or overcome this, are greatly increased. Every time this happens the friction recorded shows a distinct peak. However the friction values quoted are mean values and so every peak has increased the average by a small amount. On the other hand, with short track lengths, a large proportion of the track may be relatively smooth and overall, the friction values recorded are lower.

Further demonstration of the lack of change in the friction drop temperature with O.C.T. was given by temporarily rearranging the control circuitry of the Bowden-Leben machine. The apparatus was set to reverse at the end of each pass, without lifting the loading arm off the track and traversing back over the same track at the same speed. The effect was to produce a wear scar in which O.C.T. varied with position along the scar. Experimental conditions were as tabled in Fig.5.2a. and the results are shown in Fig.5.2b. Care was taken to examine the actual pen recorder output for consistent trends

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	1 mm s^{-1}	see below	5°C min^{-1}

materials - track	- slider	contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

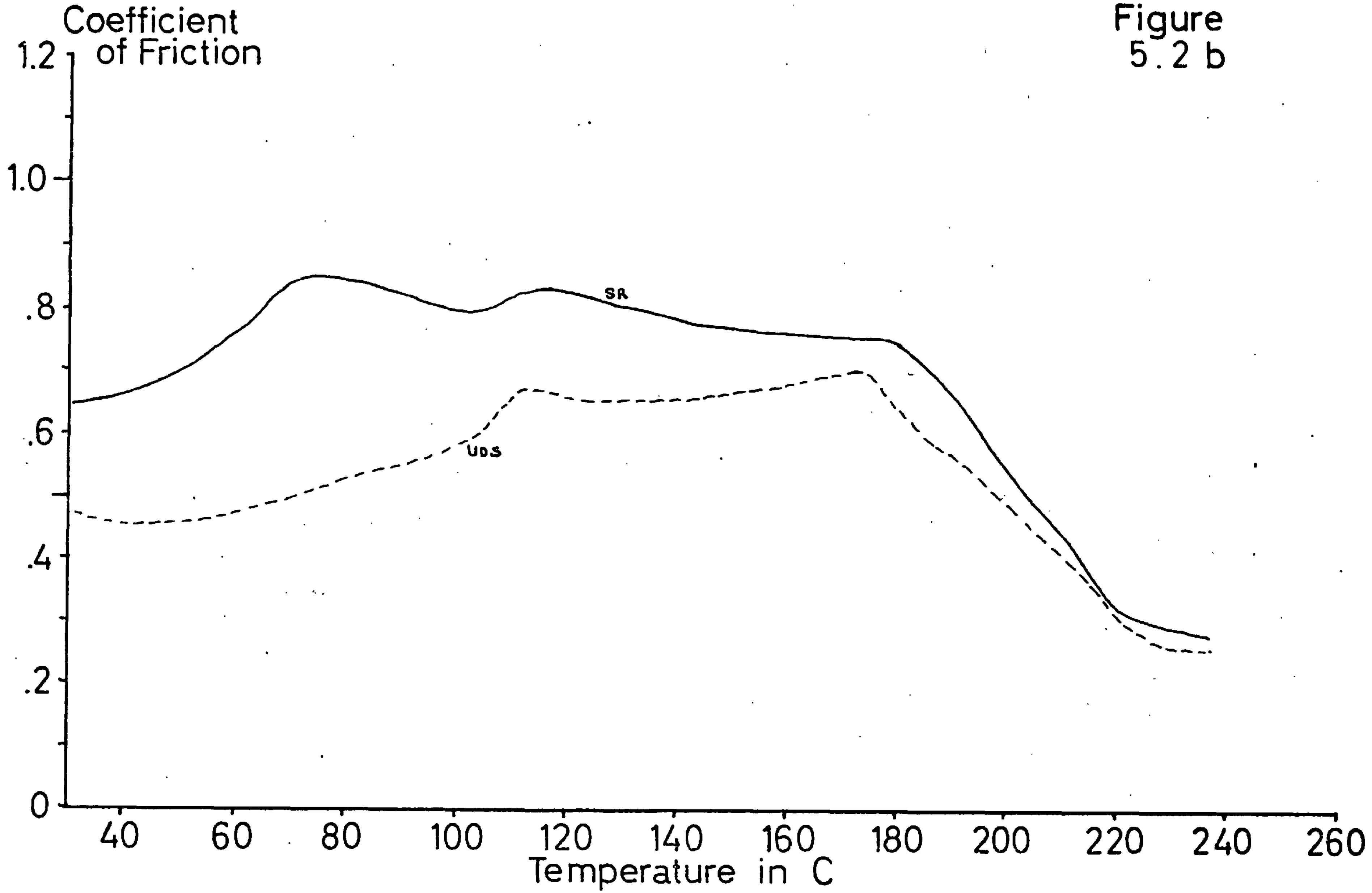
lubricant 1% DBDS in hexadecane

special conditions In one set of tests the machine was set to reverse at the end of each pass and return over the same track instead of being lifted and only rubbing in one direction.

varied conditions		no. of runs	repeat-ability
Simple reversing i.e. O.C.T. 0 - 2 mins.	〜	2	5
Uni-directional sliding O.C.T. 1 min.	- - -	4	4

Figure 5.2a

Figure 5.2 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
SR
UDS
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	varied	1 min	$2\frac{1}{2}$, 5, 10 °C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant 1% DBDS in hexadecane , Hexadecane alone

special conditions

varied conditions speed in mm s^{-1}	(heating rate in °C min^{-1})		no. of runs	repeatability
5	(10)	——	2	4
2	(10)	—··—··	3	4
1	(5)	—·—·—	4	4
.6	($2\frac{1}{2}$)	– – – –	3	4
.17	($2\frac{1}{2}$)	–·–·–·	4	4
.07	($2\frac{1}{2}$)	- - - -	3	4
.033	($2\frac{1}{2}$)	········	3	3
Hexadecane alone				
1	(5)	—·—·—	3	3
.07	($2\frac{1}{2}$)	········	2	4

Figure 5.3a

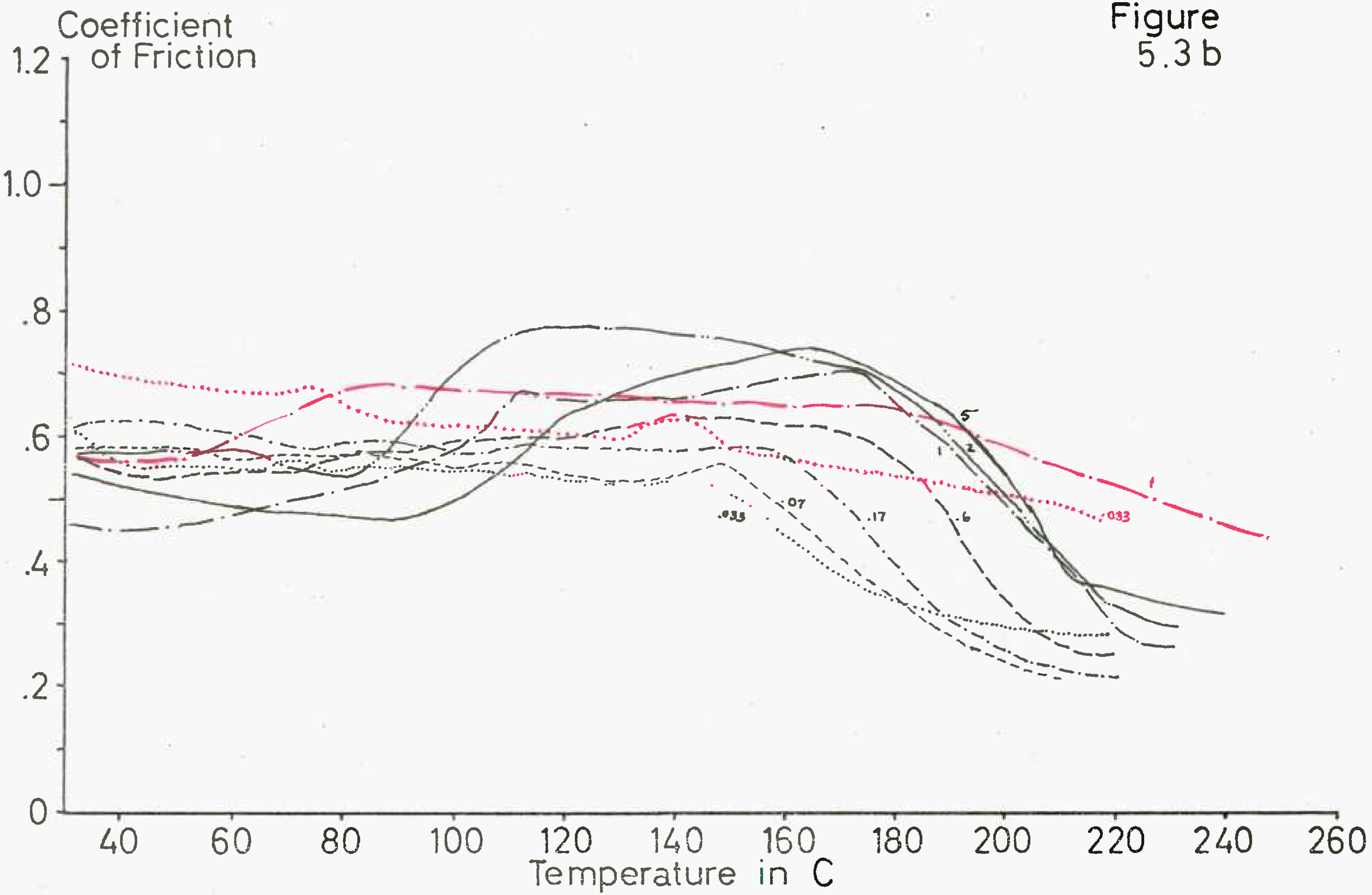

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
5
1
2
.033
.07
.17
.6
1
.033

Figure 5.3 b

in the friction trace at the ends of the track and at the centre. At the ends, each section is rubbed twice in a relatively short time but then left out of contact for a longer period (upto 2 minutes). The out of contact time hypothesis (Bayles (60)) would predict that as the slider approached an end of the track, conditions (when they favour a drop at all) will favour a low friction to be recorded, but on reversal, the recently rubbed surface would show a high friction. This was not found to be so. Friction was consistent along all parts of the track, to an equal extent at all temperatures tried. The actual coefficients of friction were very close to those found when sliding took place in only one direction.

5.3. SLIDING SPEED

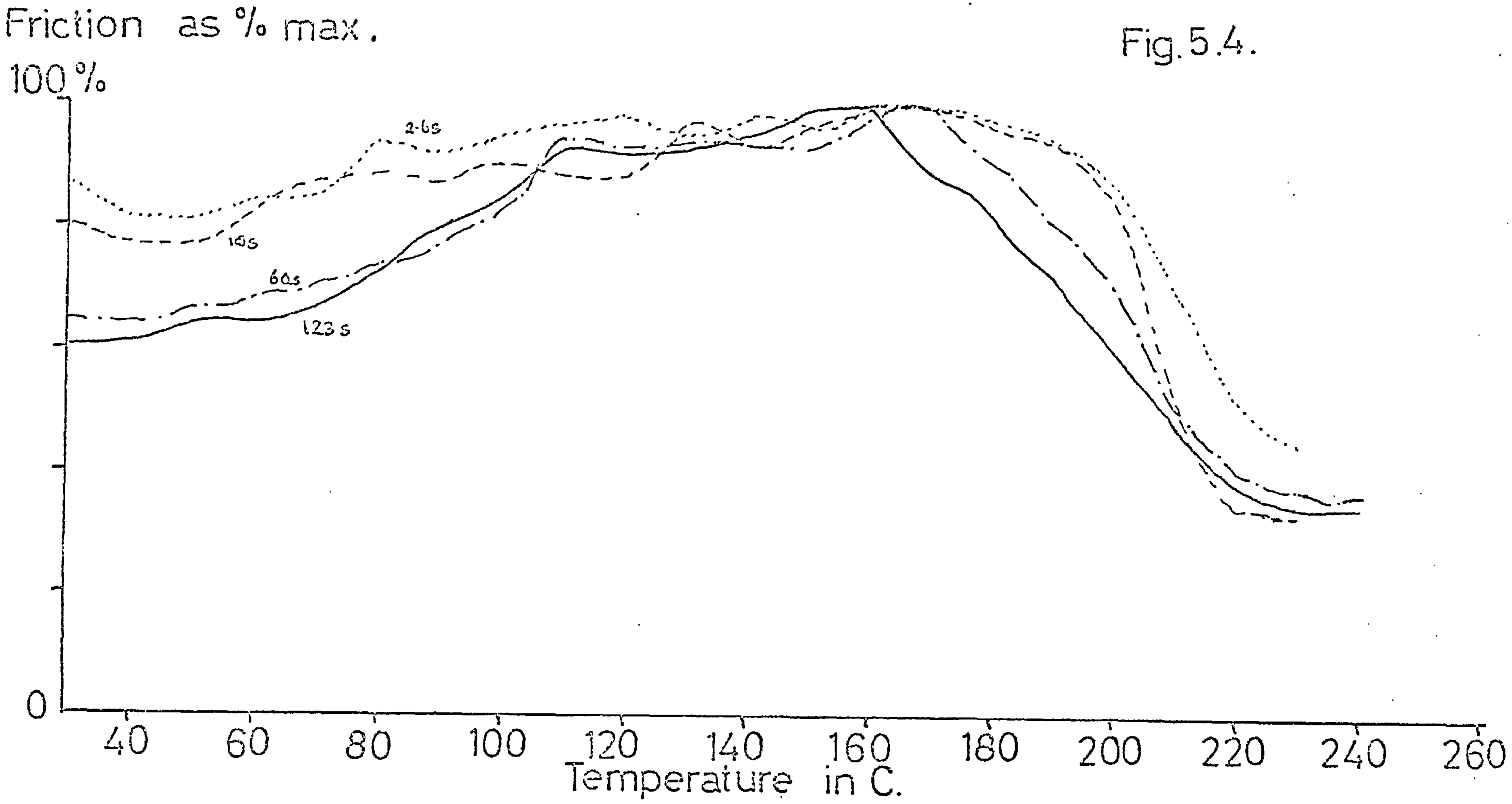
Six speeds were chosen for these experiments, 0.033, 0.07, 0.17, 0.60, 1.0, and 2 mm s^{-1}, all with an O.C.T. of 1min. Two tests were also carried out at 5.0 mm s^{-1} but with an O.C.T. of 21s (this was because the maximum track length was limited to about 100mm). Nevertheless the results of these latter tests are considered to be comparable, since the tests of the previous section have indicated the insignificance of O.C.T.

The heating rates had to be varied to prevent total evaporation of the lubricant prior to the friction drop. Reference to Chapter 6 shows that this can only introduce minimal errors. Control experiments, at each end of the range of speeds, were also performed using pure hexadecane as the lubricant. The precise conditions of the experiments are given in Fig.5.3a., the results in Fig.5.3b. A change in the friction drop temperature is evident from the graphs, it is difficult to quantify this. A means by which the temperature of the friction drop from a particular trace may be specified is required. Several possible methods were considered as follows.

It was noted, when comparing several pen recorder traces, that the starts in the drops in friction were there least consistent aspect. For example a particular trace could show high friction values until relatively late and then drop rapidly compared with the average traces. The start of a friction drop is a possible criterion for assessing the action of a lubricant, and was employed by Bayles (60) and Spikes (12). In this work it was rejected in favour of a comparison of the whole friction-temperature graph. Another possibility considered was to arbitarily choose one value of friction coefficient (for example 0.5) and use it as the "critical" value. The temperature at which the friction had fallen to this value, could then be used to characterise the result. Just such a concept was used by Hirst and Stafford (37), although they studied rises in friction with increasing temperature. This type of characterisation has the disadvantage that it ignores any variation in the maximum friction reached. Work in section 6.7 shows this maximum value to be important and the "critical friction value" concept was rejected.

One way of suppressing the variation in the highest coefficient of friction reached is to plot the friction as a percentage of its highest value. This has been done in Fig.5.4. and 5.5. for the results from Fig.5.1b. and 5.3b. respectively. Although this analysis is to some extent justified, in that it enables the friction drop temperature of the tests of Fig.5.3. to be more easily determined, it clearly complicates the issue when analysing the tests of Fig.5.1. In this case the variations may be simply explained on the basis of changes in the track length as detailed in the previous section.

Fig. 5.4.


Friction as % max.
100%
0
2·6s
10s
60s
123 s
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C.

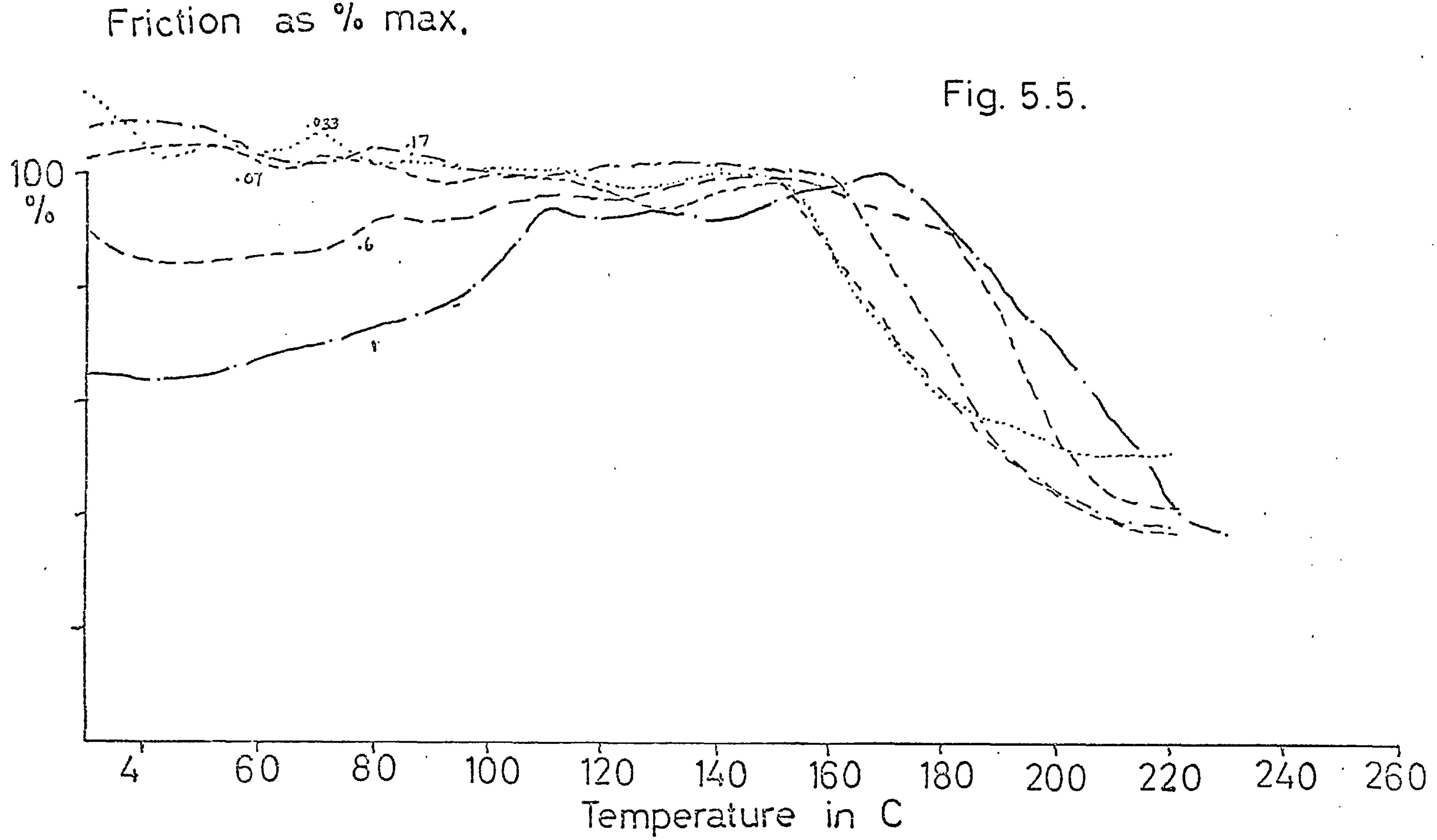

Friction as % max.
100
%
.033
.17
.07
.6
1
4
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

Fig. 5.5.

Changing the sliding speed produced an observable effect which requires explaining. Between 0.033 and 1.0 mm s^{-1} the temperature of the friction drop varied by about 25°C. At 1.0 mm s^{-1} a limiting situation was reached, with no further change as the sliding speed was increased.

Two possible explanations for this variation were propounded.

i) The real factor governing the system was the "in contact time", that is the time for which any point on the track is in contact with the slider, which is evidently dependent on sliding speed. This idea is attractive because the fixed geometry of Bayle's (60) apparatus meant that any change he made to the out of contact time resulted in a similar change to the in contact time. Thus his results would remain consistent with the theory, but merely require a substitution of "in contact" for "out of contact".

ii) The factor at work in the system is the "work rate per unit of the slider". This concept arose from the following deductions. If the friction drop is unaffected by the O.C.T. then it may be the conditions of the slider which are critical, not those of the track. As the O.C.T. is changed there is little difference to the slider, which merely meets the same section of track more often. However a change in sliding speed will alter the conditions on the slider and, especially since the coefficients of friction and wear scars remain very similar, it will cause a change in the work rate per unit area of slider by the same amount.

A possible mechanism whereby this parameter might affect the friction drop temperature can be easily suggested. If the rate of work being done is a measure of the severity of the conditions, then increasing this factor would tend to increase the degree of protection required from the additive. Since this is known to increase with temperature (from the fact that the drop occurs at all) it is not unreasonable to expect the friction drop temperature to be higher when the work rate per unit area of the slider is greater. This is in accordance with the results.

The two ideas i) and ii) above are to some extent mutually exclusive, because the first implies the beneficial effect of the contact in the process causing the drop whereas the second implies the opposite. Therefore a simple method of testing the two hypothesis is to increase or decrease the severity of conditions within the contact. This may be done by changing the load or the contact geometry. If i) above is correct then an increase in load will cause a reduction in the temperature of the friction drop. If ii) is correct then the temperature will be increased. These ideas were tested in the following experiments.

5.4. LOAD

Experiments were carried out at loads of 1,5 and 10 kg. A sliding speed of .17 mm s^{-1} was chosen, because it had previously given a friction drop near the centre of the band of results in Fig.5.3b. It was thus not close to any possible limiting case of this system, so variations in the temperature of the drop could be revealed. It did mean that the track was too short to allow the use of the microscope as discussed in section 4.3. The conditions and results of the first set of experiments are shown in Fig.5.6a. and 5.6b. respectively. E.N.31. balls were used, and a small load dependence may be seen for these. Softer E.N.58. balls were used at loads of 1 and 5 kg the results of which are shown in Fig.5.7b., and in this case no load dependence was seen. It was thus concluded that the effect of increasing load reaches a limiting

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
varied	0.17 mm s^{-1}	1 min	2½ °C min^{-1}

materials - track	- slider	contact geometry
E.N.58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant 1% DBDS in hexadecane

special conditions

varied conditions load in kg		apparent contact pressure in kg mm^{-2}.*	no. of runs	repeat-ability
1	———	3.1	4	4
5	—·—·—	9.0	3	4
10	- - - - -	15.3	2	3

* see text

Figure 5.6a

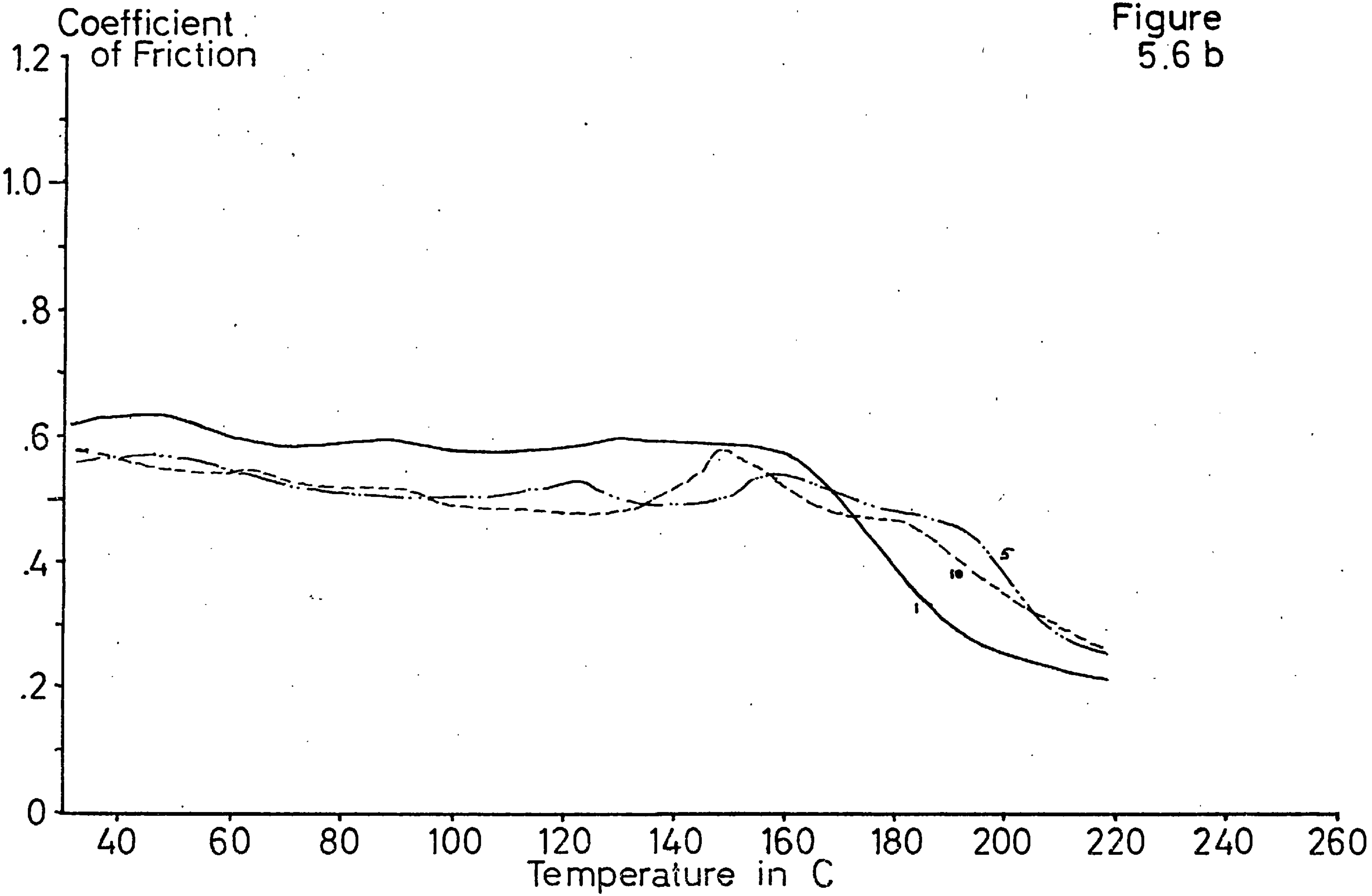

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
1
5
10

Figure 5.6 b

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
varied	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 58	$\frac{5}{8}$" dia ball on flat

lubricant 1% DBDS in hexadecane

special conditions

varied conditions load in kg		apparent contact pressure in kg mm^{-2}.	no. of runs	repeatability
1	—	1.11	2	3
5	- - -	2.75	3	3

Figure 5.7a

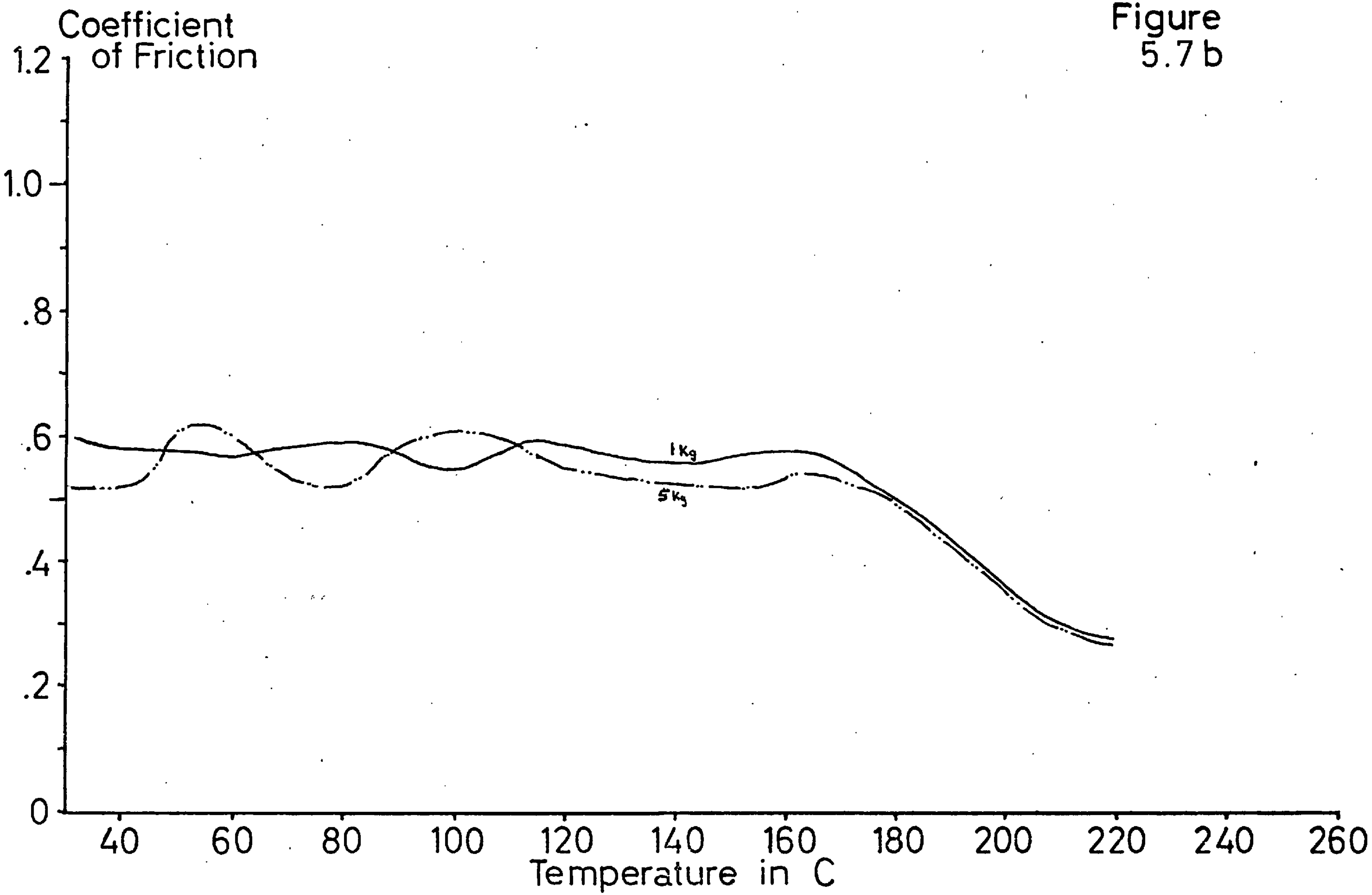

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
1 Kg
5 Kg

Figure 5.7 b

situation, quite possibly determined by the hardness of the materials. To gain a further insight into the conditions, the final wear scar on the balls were measured using a travelling microscope and the apparent contact area calculated. These were averaged for each set of experiments and the apparent contact pressures derived are shown in Fig.5.6a. and 5.7a. The apparent contact pressure increases with load, although as discussed in section 4.4. the real contact area is almost certainly proportional to load. Thus the real contact pressure is constant, as long as adhesional bonds are not affecting the contact area as discussed by Tabor (34). It should be noted how little the coefficient of friction changes with load. Indeed the effect of load on the friction trace may be summarised as minimal.

5.5. CONTACT GEOMETRY

A number of experiments were carried out with pegs manufactured from E.N.31. steel, 3/16" (4.76 mm) diameter and 3/16" (4.76 mm) long with radiused edges. They were in fact rollers for use in bearings and had the same material specifications as the E.N.31. balls. The flat end of a peg was traversed across the flat specimen by mounting it in a holder, which was clamped in the chuck in place of a ball. Considerable care was taken to ensure that the end of the roller was parallel to the surface of the flat, and this necessitated precise alignment of the loading arm and adjustment of its height (with shims). Inevitably one portion of the peg would touch the flat more heavily than the rest, but an examination of the surfaces after they had run-in showed that contact was occurring over a wide area. This was indicated not only by a wide wear track, but also by the amount of the softer E.N.58. material from the flat specimen which was transferred to the harder E.N.31. peg. As was mentioned in section 4.3., the system being studied may well be that of E.N.58. sliding on E.N.58.

Three experiments, at each of three loads, were performed and a control carried out at the highest load, using hexadecane alone. The conditions and results are given in Figs.5.8b. and 5.8a. Further experiments at 1 and 10 kg were performed at a lower speed to check of the effect of speed. These are described in Fig.5.9a. and the results shown in Fig.5.9b.

The friction traces obtained with a considerably changed contact geometry are all very similar to their counterparts. Neither the temperature of the friction drop, nor its magnitude are affected by changes in the apparent contact area or pressure. This is clear evidence against the two hypothesis of section 5.3. The first is disproved, because a large increase in the in contact time (by increasing the contact area) had no effect on the temperature of the friction drop. The second is in doubt, although it is considered that it is the real contact area which is important, and thus the rate of work being done over that area which counts.

5.6. HARDNESS

The hardness of the specimens is, of course, a metallurgical factor and may be altered by work-hardening (see section 4.5.) or by changes in the chemistry or heat treatment processes of production. It was fortuitous that two separate batches of E.N.58. balls of the same specification and from the same surplier had noticeably different hardnesses. A check could thus be carried out using two tests with each kind of ball in otherwise identical conditions. These were as in Fig.5.10a. and the resulting friction traces are shown in Fig.5.10b. There are no significant differences

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
varied	1 mm s^{-1}	1 min	5 °C min^{-1}

materials –	track –	slider	contact geometry
	E.N. 58	E.N. 31	$\frac{3}{16}$" dia flat peg on flat

lubricant 1% DBDS in hexadecane , Hexadecane alone

special conditions

varied conditions

load in kg		no. of runs	repeatability
1	———	3	4
5	—·—·—	3	2
10	—··	3	3
Hexadecane			
10	— — —	2	4
control with $\frac{5}{8}$" dia ball	- - - -		

Figure 5.8a

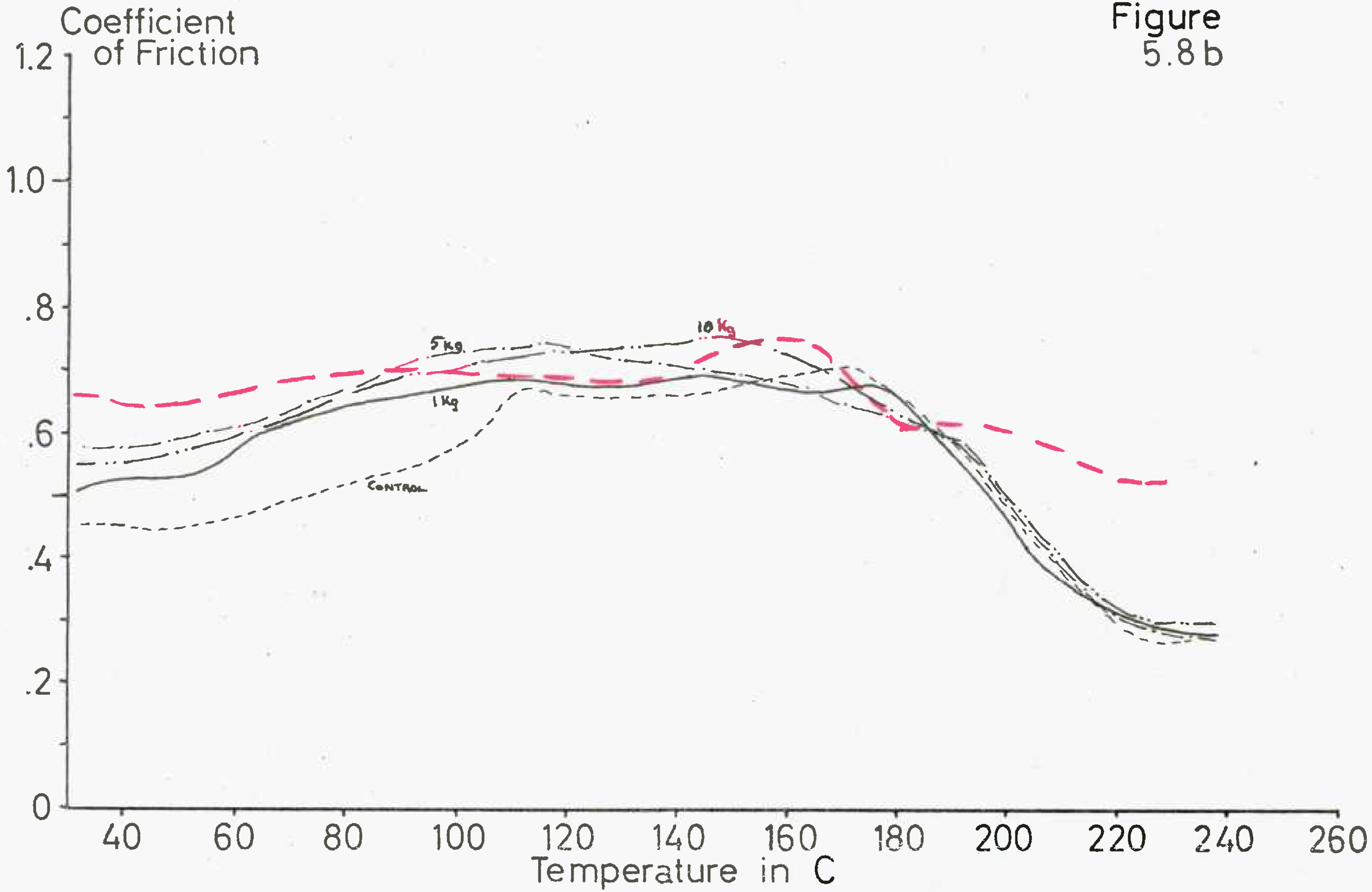

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
5 Kg
10 Kg
1 Kg
CONTROL

Figure 5.8 b

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
varied	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials	track	slider	contact geometry
	E.N. 58	E.N. 31	$\frac{3}{16}$" dia flat peg on flat

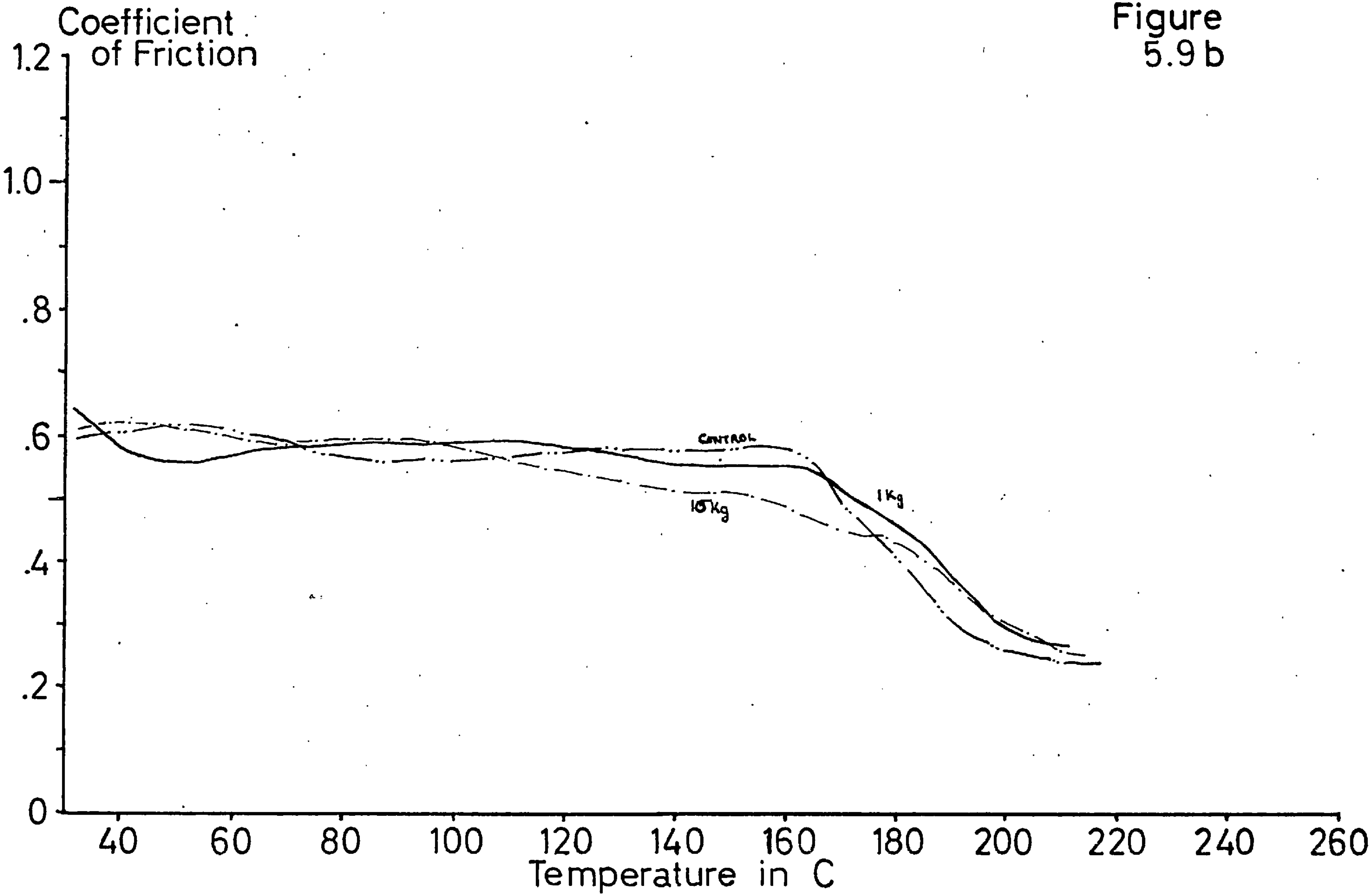
lubricant 1% DBDS in hexadecane

special conditions

varied conditions		no. of runs	repeatability
load in kg			
1	———	2	4
10	— · — · —	2	4
Control $\frac{5}{8}$" dia ball on flat 1kg load	— ·· — ·· —	4	4

Figure 5.9a

Figure
5.9 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
CONTROL
1Kg
15Kg

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track	- slider	contact geometry
E.N. 58	varied	$\frac{5}{8}$" dia ball on flat

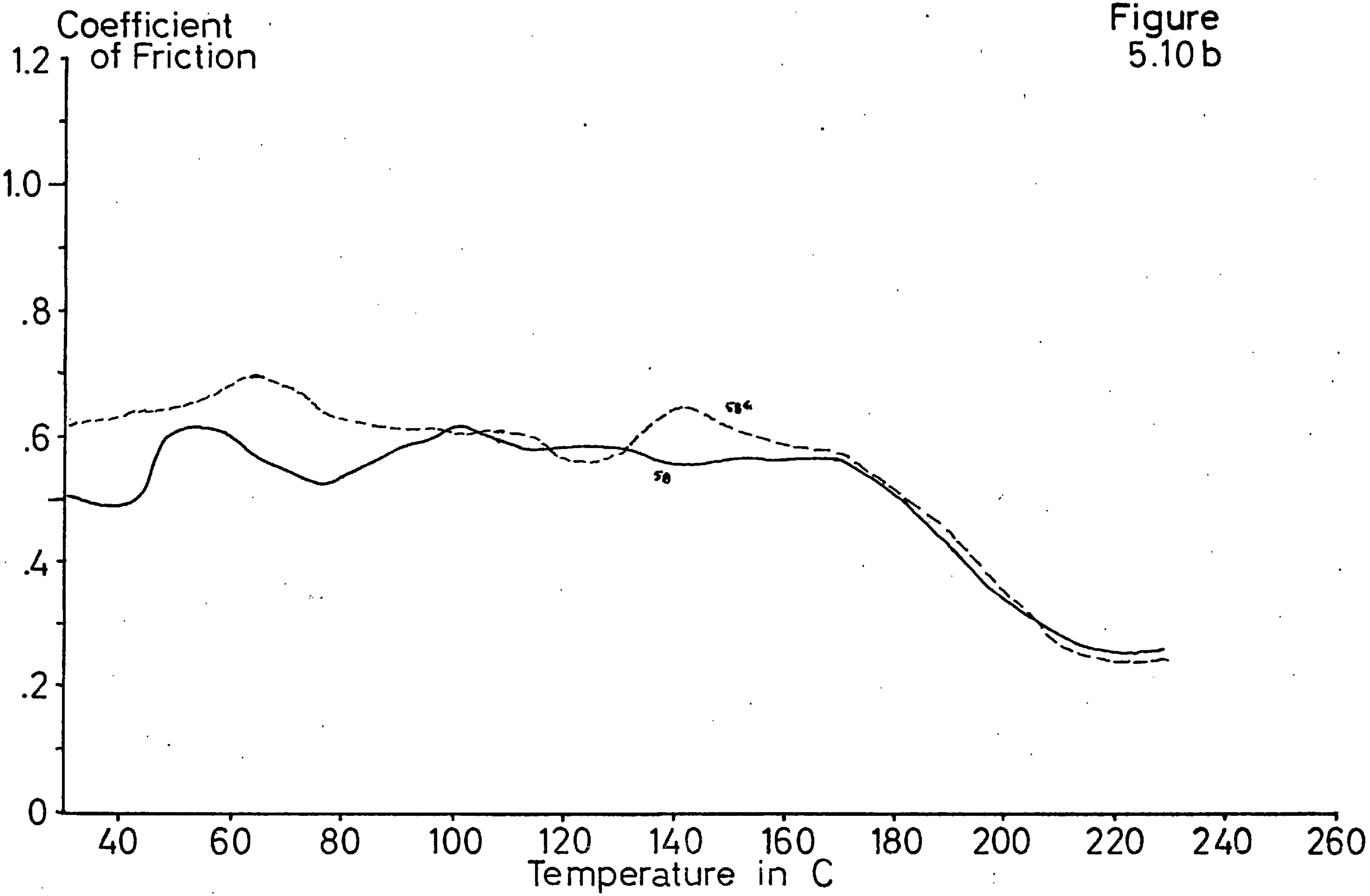
lubricant 1% DBDS in hexadecane

special conditions

varied conditions		apparent contact pressure in kg mm^{-2}	no. of runs	repeatability
Two types of E.N. 58 steel in otherwise the same specification sliders.				
E.N. 58 (normal)	——	1.11	2	5
E.N. 58* (harder)	- - - -	1.72	2	5

Figure 5.10a

Figure
5.10 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
584
58

between them. The contact areas were estimated as before and they accentuate the difference in hardness. It was therefore concluded that the hardness of the slider does not affect the friction drop, in any major way.

5.7. STIFFNESS OF RESTRAINT

The effect of varying the stiffness of the restraint used to measure friction on a Bowden-Leben machine has been reported by Hirst and Stafford (37). They found a change in transition temperature with one combination of materials and lubricants, which they could not explain. To check that the present system under investigation was not similarly affected, two experiments were carried out with the loading arm at its lowest stiffness, 0.14 kg mm^{-1} as opposed to 44 kg mm^{-1}, at which all the other tests were performed. The conditions and results of the tests are shown in Fig.5.11a and b. The reduction in stiffness by about 300 times can be seen to have produced only minor changes to the friction trace. When the stiffness was high any fluctuations in the friction did not cause the slider to move out of the contact region. At low stiffness the "stick-slip" was extreme and the slider moved in large jumps, evidently from one contact to the next. Nevertheless the overall friction trace was very similar especially at the higher temperatures. It was therefore concluded that the stiffness of the restraint played no significant part in the processes being investigated.

5.8. VERTICAL RESONANCE

An ingenious explanation of the effect of changing the sliding speed was suggested by the concept of triggering oscillations in "stick-slip" theories (see section 1.7.). Since the horizontal oscillations, that is the fluctuations in friction or "stick-slip"

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant 1% DBDS in hexadecane

special conditions stiffness of restraint varied

varied conditions stiffness in kg mm^{-1}		no. of runs	repeat-ability
0.14	———	2	3
44 (normal)	- - - - - -	4	4

Figure 5.11a

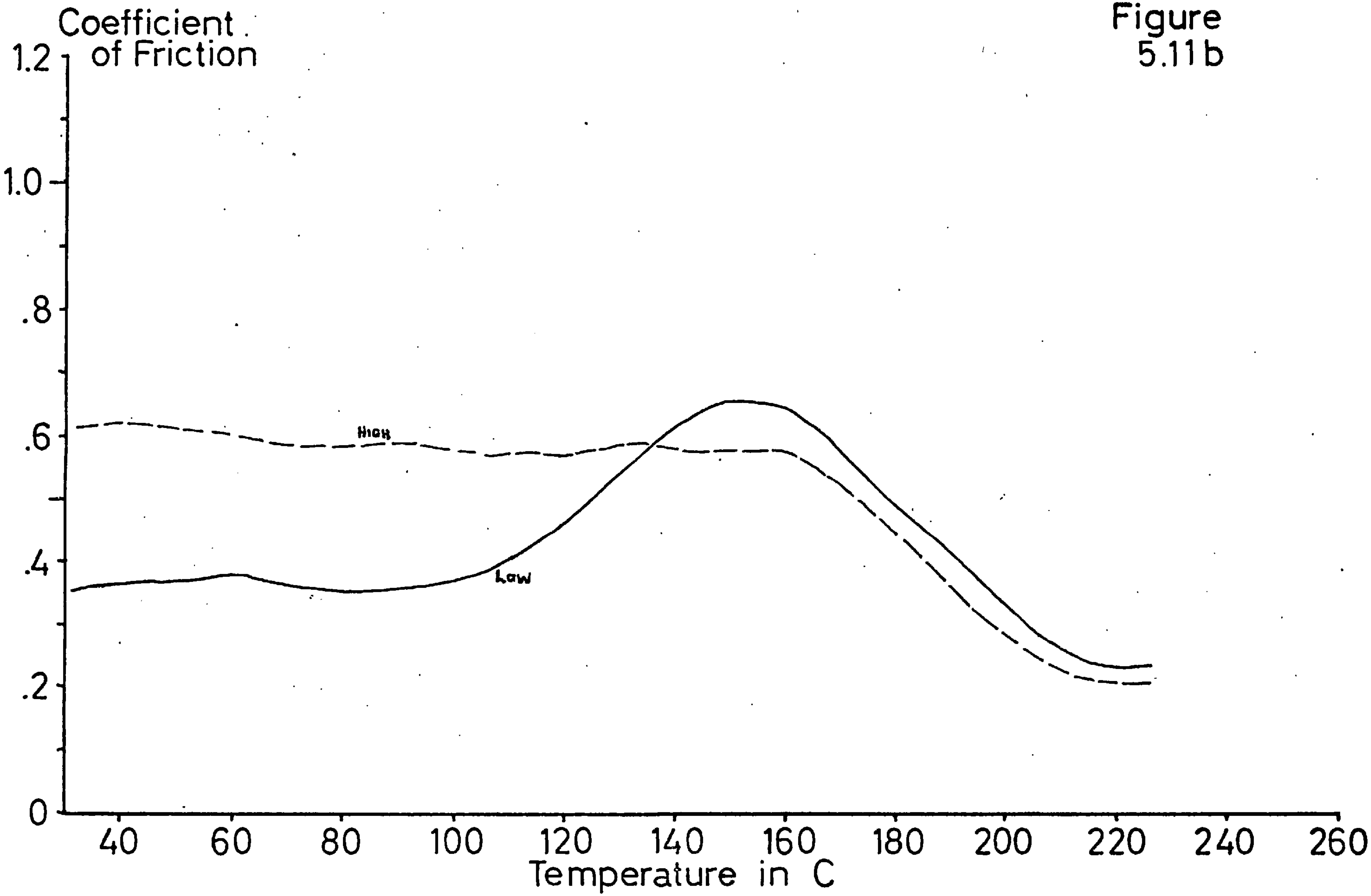

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
High
Low
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

Figure 5.11b

are interrelated to the vertical or triggering oscillations, it is possible that a change in sliding speed would affect the triggering oscillations. They in turn would affect the friction observed and could influence the temperature at which the drop occurred. The mechanism by which the sliding speed would alter the vertical oscillations would be dependent on the time taken in moving from one asperity to another. This then determines the frequency of the forcing oscillations and the resulting "stick-slip" will depend on how close this frequency is to a resonance of the system. Without analysing the system further a practical experiment was conducted by using standard transducers and a suitable signal generator.

A piezo-electric accelerometer was mounted on the loading arm, on top of the weight, and used to measure acceleration of the arm at that point. This was done by connecting it to a conventional oscilloscope. The basic resonant frequency of the arm, in that plane, was then roughly assessed. A signal generator, amplifier and transducer were then connected together and the transducer fixed to the loading arm, above the pivot line so as not to affect the load on the specimens. The transducer was then vibrated at around the basic resonant frequency of the arm, and the signal generator adjusted to set it exactly at resonance, 570Hz, (detected by the accelerometer). The amplifier was then adjusted to cause a peak acceleration of about $\frac{1}{2}$'g' on the arm at the point of contact. Two otherwise normal friction tests were then conducted and the results shown in Fig.5.12b. No significant change may be seen and this explanation of the effect of sliding speed was rejected.

5.9. SUMMARY

The experiments described above have investigated the effect

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials -	track -	slider	contact geometry
	E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant 1% DBDS in hexadecane

special conditions $\frac{1}{2}$'g' vertical vibration applied to loading arm at 570 Hz.

varied conditions		no. of runs	repeat-ability
vibrated	——	2	3
unvibrated control	- - -	4	4

Figure 5.12a

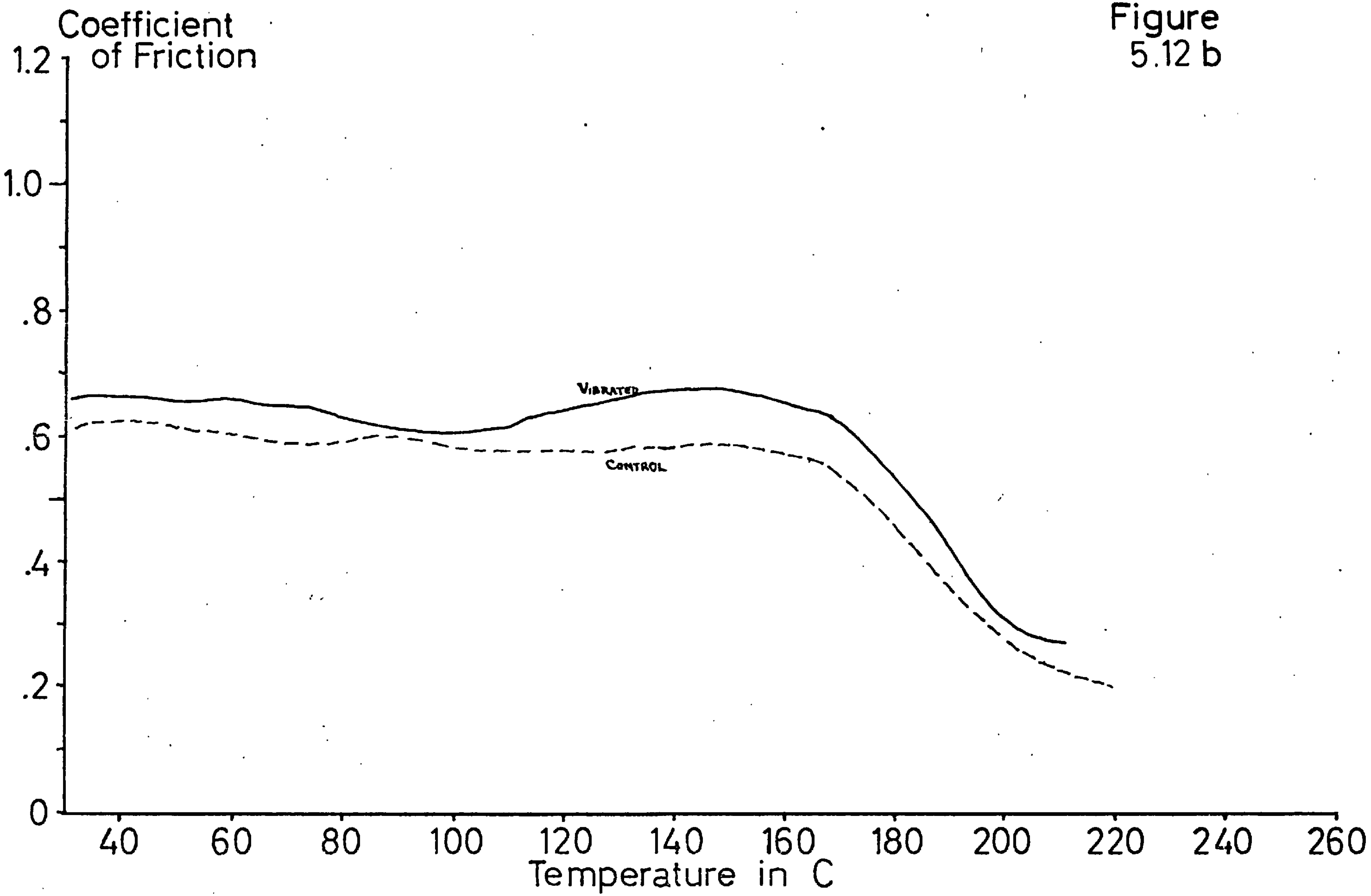

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
VIBRATED
CONTROL
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

Figure 5.12 b

of as many mechanical factors as it has been possible to vary, and although the frictional process is mechanical in nature only sliding speed has had a consistent effect on the temperature of the friction drop.

The results from the experiments of this chapter may be summarised so:

Effect on friction drop of varying:

1) Out of contact time — none
2) Sliding speed — approx. 25°C shift when changed from 0.033 to 1 mm s^{-1}
3) Track length — apparently none, however maximum friction reached is affected.
4) Load — minimal
5) Contact geometry — none
6) Hardness of materials — none
7) Stiffness of restraint — none
8) Vertical resonance — none

The following conclusions have been drawn:

The concept that the out of contact time governs the E.P. reaction, which reduces friction in slow speed tests would seem untenable. Nevertheless an explanation is required for the effect of sliding speed (which has previously been ignored in slow speed work) and also for the unexpected consistency in the friction drop temperature irrespective of mechanical conditions.

CHAPTER 6

FRICTION TESTS INVESTIGATING CHEMICAL EFFECTS

6.1. INTRODUCTION

It has generally been assumed in the interpretation of slow speed friction test results, that the mechanism of action of the additive employed is the same as that operating with the additive in a high speed test. However, whereas high speed test results are very sensitive to the mechanical conditions, the experiments of the previous chapter have shown that slow speed tests are insensitive to these factors. The important question to be answered is, what is the mechanism by which the additive creates the friction drop? First a summary of the conclusions, that can be made so far, will be of value.

1) Dibenzyl disulphide does cause the friction drop. This has been demonstrated by control experiments with pure hexadecane.

2) The drop in friction is a change from conditions of gross adhesion and tearing of the surfaces to those of smoother sliding and little surface damage.(see section 4.3.) Tabor (34) has shown how small increases in the coverage of surface films can markedly reduce the coefficient of friction from high values.

3) The only alternative to an explanation based on the formation of a surface film, is some complex metallurgical change. This has already been dismissed as most unlikely (chapter 4).

4) The temperature at which this friction drop occurs remains remarkably constant, and is high enough for oxidation processes within the hexadecane to be apparent.

5) No drop in friction has been observed to take place within one pass of the machine. (see Chapter 3) This suggests that the friction

drop is a dynamic process (that is a kind of "running-in") which is triggered by chemical factors which determine the temperature of the drop.

The experiments of this chapter were carried out to investigate the effect on the friction drop of various chemical factors such as,

1) Concentration of the additive
2) Composition of the additive
3) Reversibility
4) Thermal history of the lubricant
5) Thermal and running history of the specimens
6) Composition of the base oil
7) Oxidation inhibitor

From these it was hoped to build up a picture of the process causing the drop. However there was a limit to the range of experiments which could be performed, because the friction traces had to be sufficiently similar to enable a useful comparison to be made. Examples of the kind of problem are commented upon when they appear. Section 5.3. has already dealt with the variations in maximum friction observed and the ways in which it affected the friction drop.

Two important, and unexpected, conclusions can be drawn from the results of these experiments.

1) The thermal and running history of the specimens does not affect the friction drop temperature.

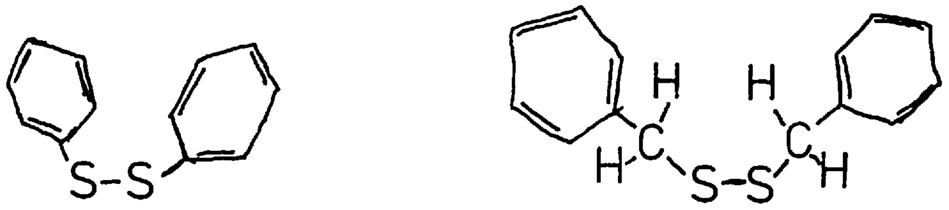
2) The extent of oxidation of the lubricant markedly affects this temperature.

6.2. CONCENTRATION OF ADDITIVE

To investigate the effect of additive concentration, a set of friction tests was carried out at low sliding speeds and reduced additive concentration (0.1%). Fig.6.1a. and b. shows the conditions and results of all three sets of experiments, 0, 0.1 and 1% concentrations. As expected the activity of the additive, at a lower concentration, was reduced. The friction traces lay between the other two. A decrease of 90% of its original value in the concentration caused only a small increase in the friction drop temperature, and reduced its extent only marginally.

6.3. DIPHENYL DISULPHIDE

Diphenyl disulphide is similar in structure to dibenzyl disulphide as shown in Fig.6.2., but the methylene group next to the benzene ring in DBDS makes the chemistry of the two quite different.



Diphenyl disulphide

Dibenzyl disulphide

Fig. 6.2.

In high speed tests in the E.P. regime, diphenyl disulphide performs significantly worse than DBDS, as reported by Allum and Forbes (50) and Sakurai et. al. (69). However in the A.W. regime, Forbes and Reid (66) have found that the two perform similarly. Diphenyl disulphide is not generally used as an oil additive whereas DBDS is found in some industrial gear oils.

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.07 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant varied concentration of DBDS in hexadecane

special conditions

varied conditions DBDS concentration in % wt.		no. of runs	repeat-ability
1	———	3	4
0.1	— — —	2	3
0	·······	2	3

Figure 6.1a

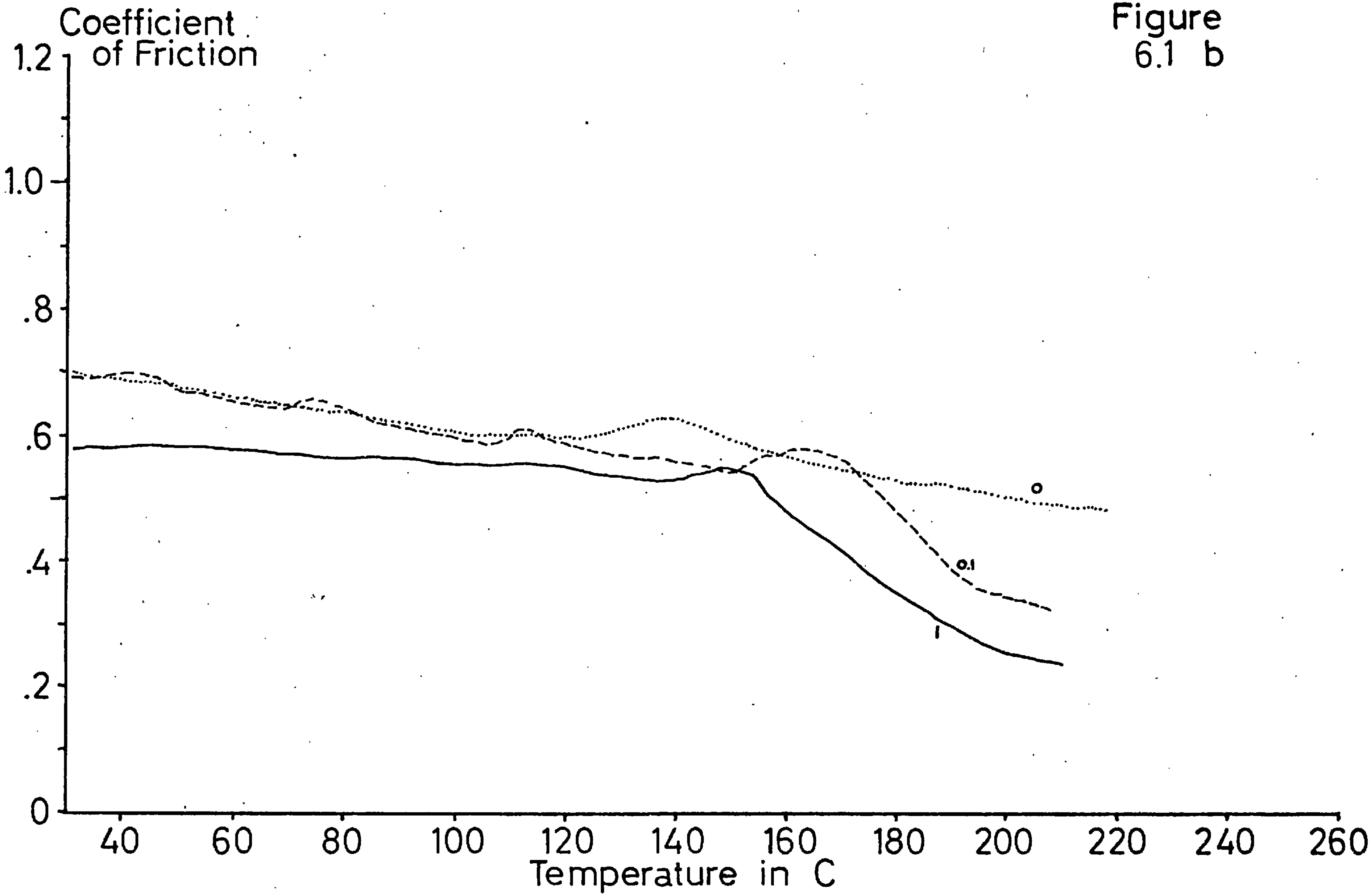


Figure 6.1 b

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
o
o.1
1

Diphenyl disulphide was obtained in a purified state from Hopkins and Williams Ltd., and thin layer chromatography revealed that it contained no detectable impurities (89). A 1% solution was made up in hexadecane and three friction tests performed. The conditions are set out in Fig.6.3a. and the friction traces obtained are reproduced in Fig.6.3b. The first experiment at a load of 1kg produced a trace in which the coefficient of friction remained low throughout (i.e. below 0.5). This was assumed to be due to some 'oiliness' action and the load was subsequently raised to 10kg to reduce this effect. The results show that the coefficient of friction initially reached as hich a value as with DBDS, but later it fell and in the region 150-210C, it displayed a trace similar in shape to that obtained with DBDS, but with friction coefficients about 40% lower. The friction drop was very similar to that obtained with DBDS, especially if considered proportionately, in the manner discussed in section 5.3. It was noted that during the later stages of the experiments, when the temperature was above 150C, the lubricant appeared more discoloured than had been the case with DBDS at the same temperature. This could well be due to some slight degradation of the diphenyl disulphide.

It must be concluded that this experimental technique does not categorise E.P. additives in terms of their practical performance. This is consistent with the results of Hiley (80), who used a slow speed ball-on-triplane machine and tested a group of polysulphides. This implies that the "rate determining step" in the chemical process involved in the friction drop is different in these slow speed tests from that governing the operation of the additive in high speed conditions.

So far only the activity of the additive has been considered. The next tests investigated the oxidation processes occurring in the hexadecane.

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
10 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track	- slider	contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" ball on flat

lubricant varied

special conditions

varied conditions		no. of runs	repeat-ability
1% wt. of each of the two additives in hexadecane			
Diphenyl disulphide	——	2	4
Dibenzyl disulphide	- - -	4	4

Figure 6.3a

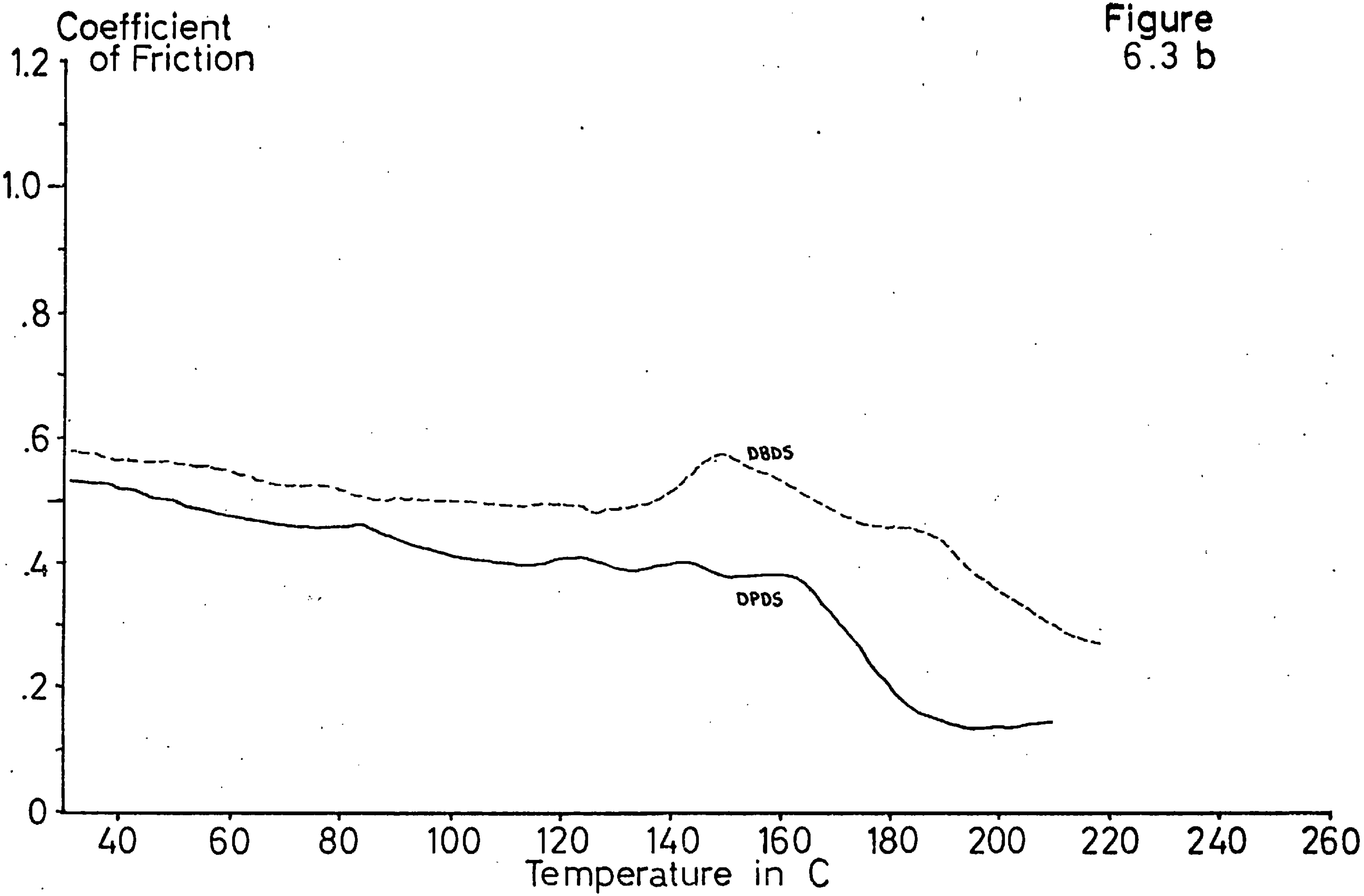

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
DBDS
DPDS

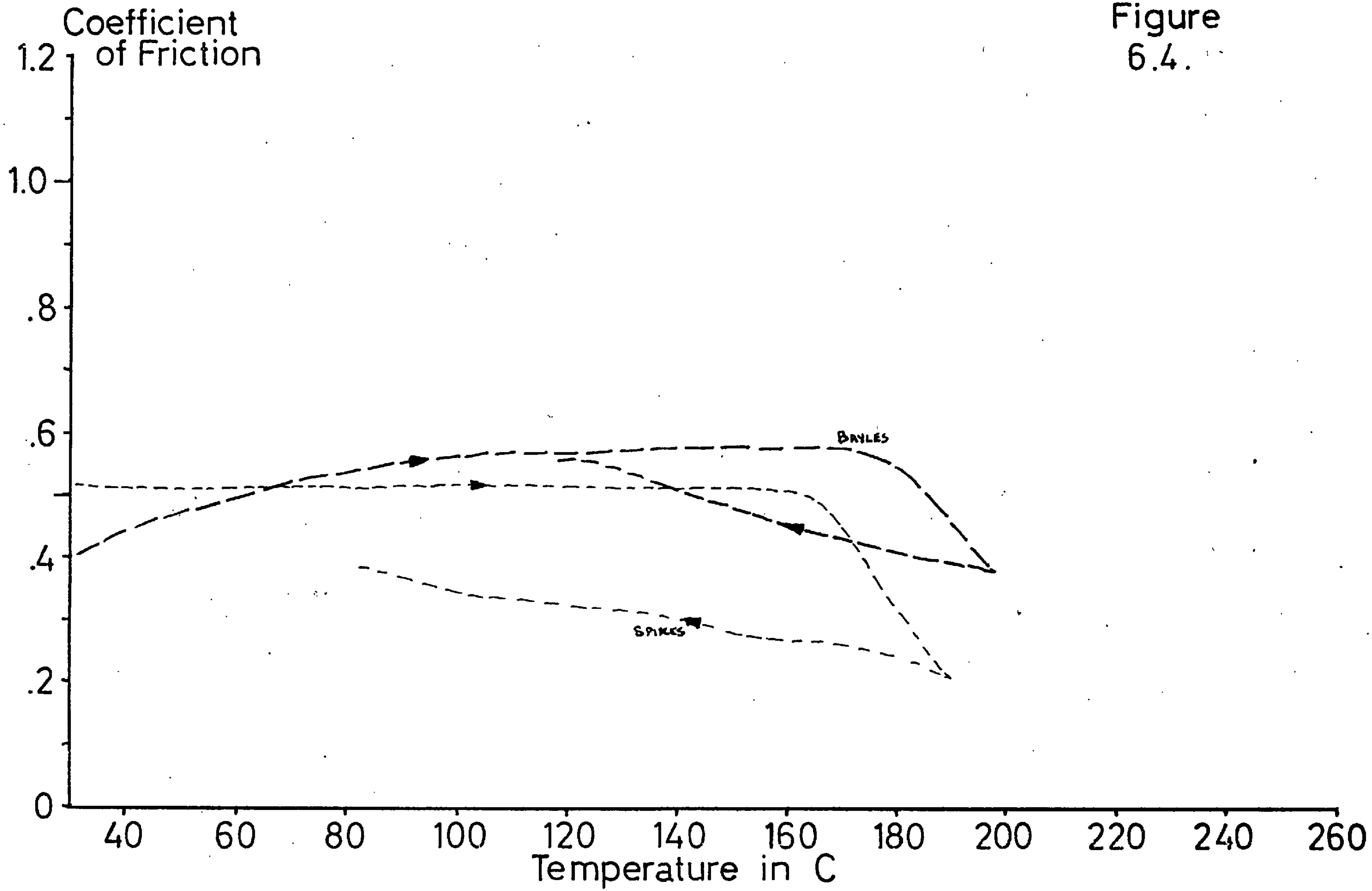
Figure 6.3 b

6.4. REVERSIBILITY

Both Bayles (60) and Spikes (12) performed experiments to demonstrate the reversibility of the friction drops they obtained. Thus when the temperature was lowered after the drop had taken place, the friction rose again, nearly reaching its original value. Fig.6.4. reproduces their results, which were for E.N.58 steel on E.N.58 and a DBDS solution in hexadecane. (It must be noted that there is some doubt about the vertical scale that should be applied to the friction trace from ref.(12)). There was some hysteresis, and the explanation they offered for the process involved was not in terms of a reversible adsorption of some species on the surfaces, but it was in terms of the dynamics of the sliding occurring. Bayles' hypothesis rested on a balance between the formation of a film by the additive and its removal by the frictional process.

Their experiments were repeated on the modified Bowden-Leben machine. Heating was stopped at 200C and the friction monitored as the system cooled. The tests were carried out at two heating rates to see if oxidation of the lubricant might be limited by this means. The conditions and results of the tests are shown in Figs.6.5a. and b. respectively. The graph indicates that very little difference resulted from the two heating rates. In both cases there was almost no "reversibility". The reason for the lack of reversibility must involve a change to either the lubricant or the metal surfaces which is not reversed by lowering of the temperature. If it is the surface that has changed, this implies the formation of a film so tough that it will resist scuffing at any temperature. This could not be easily related to the results of Bayles or Spikes. More likely is a chemical change to the lubricant at elevated temperatures, which would be

Figure 6.4.


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
BAYLES
SPIKES

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$, 5 ^{o}C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant 1% DBDS in hexadecane

special conditions when the temperature reached 200 C, the specimens were allowed to cool whilst the machine was kept on.

varied conditions Heating rate in ^{o}C min^{-1}		no. of runs	repeat-ability
2.5	—	4	2
5	- - -	2	3
Control Hexadecane 2.5	🟥	2	3

Figure 6.5a

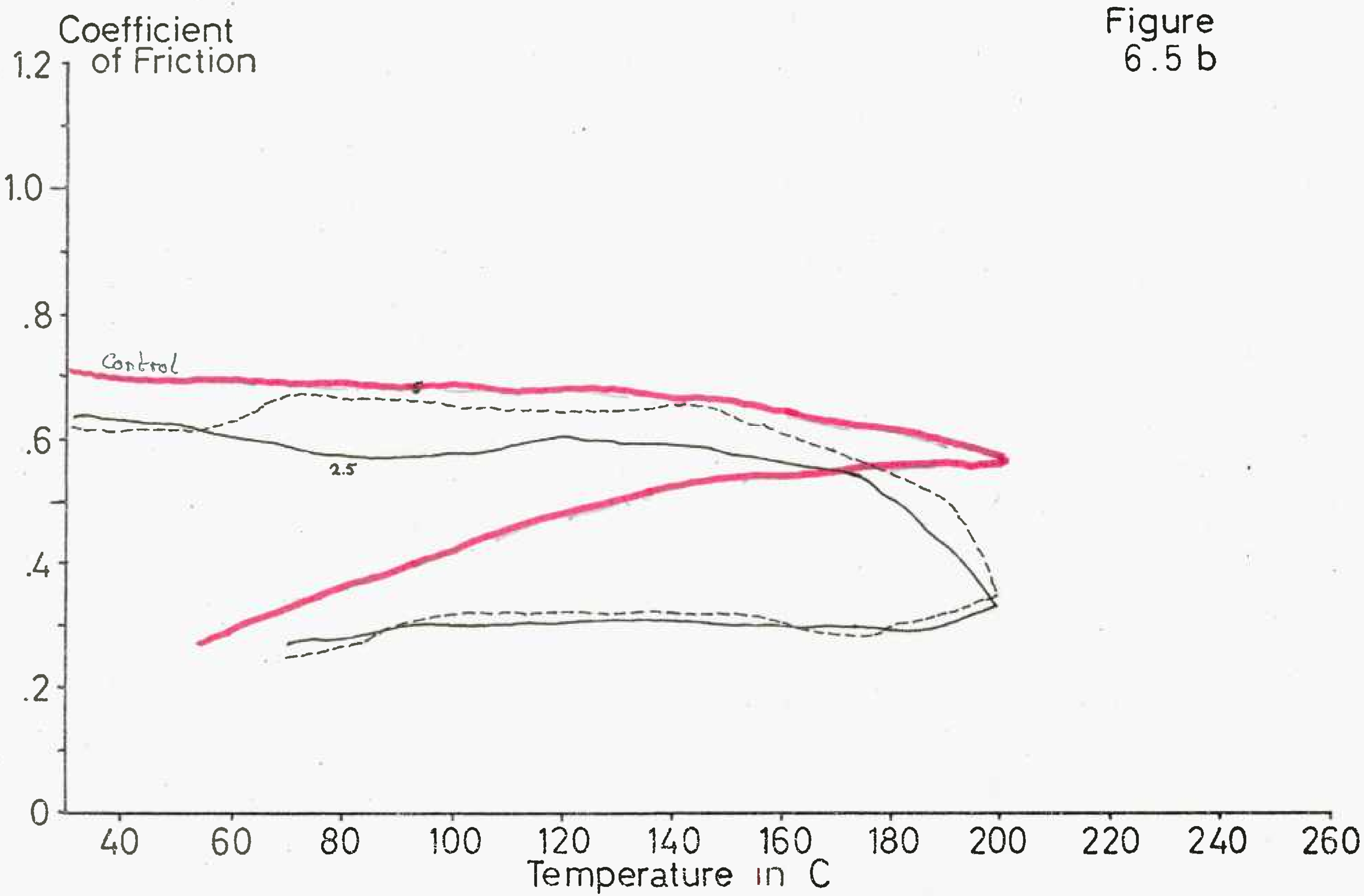

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
Control
5
2.5

Figure 6.5 b

unlikely to reverse on reduction of the temperature. Such an explanation may be reconciled to the results of Bayles and Spikes, because the geometry of their apparatus greatly decreased the amount of lubricant in contact with the air compared with the Bowden-Leben machine. Accordingly oxidation reactions would be reduced in their machines.

6.5. PREOXIDISED LUBRICANTS

Oxidation of the lubricant had been shown to affect the observed friction, and therefore samples of lubricants were deliberately oxidised to use in order to examine the effect. Pure hexadecane, and a 1% solution of dibenzyl disulphide in hexadecane were heated at about 200C. Air was continuously bubbled into the lubricant from a glass tube fed by a peristaltic pump. The temperature was monitored with a thermometer and the colour of the lubricant noted. All the lubricants were, of course, colourless at the start.

The hexadecane was exposed to an average temperature of 210C for about 20minutes. By this time it was a pale yellow colour, similar to that observed at the end of the friction tests, in which pure hexadecane had been employed. This sample was tested under conditions given in Fig.6.6a. and with the results shown in Fig.6.6b. Clearly the sample contained some oiliness agent, demonstrated by the need for elevated temperatures before the friction rose to high values. However the friction did not subsequently fall, and so these oxidation products of hexadecane alone cannot be the cause of the friction drop observed in the other friction tests.

The sample containing 1% DBDS was heated for 10 min. at an average temperature of 205C, which was sufficient to colour the oil a distinct yellow. Two samples were processed identically, but the

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	1 mm s^{-1}	1 min	5 °C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

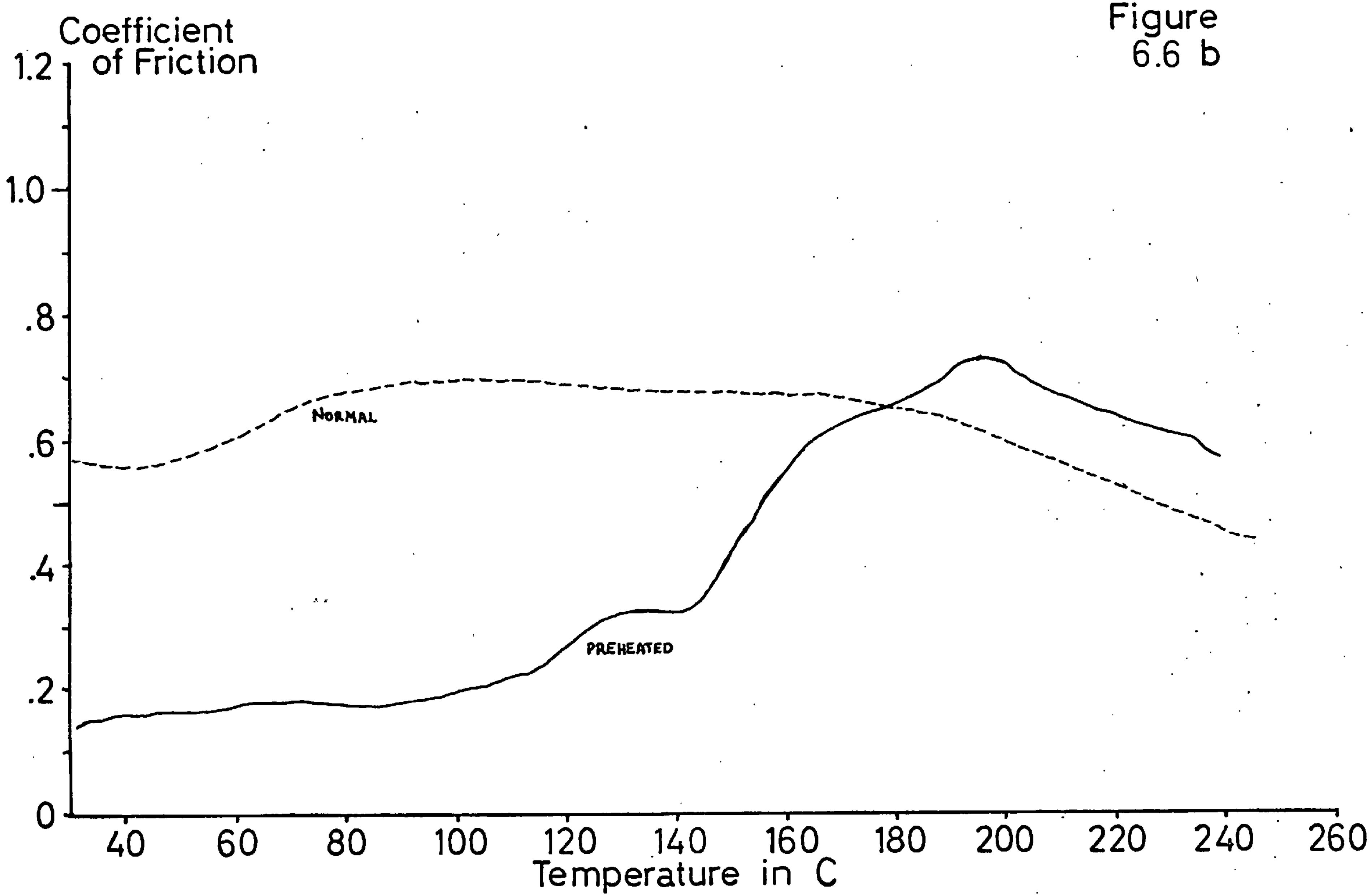
lubricant varied

special conditions one batch of hexadecane was heated in air to 200 C, and allowed to oxidise, before being tested

varied conditions		no. of runs	repeat-ability
Preheated hexadecane	——	3	2
Normal hexadecane	- - - -	3	3

Figure 6.6a

Figure
6.6 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
NORMAL
PREHEATED

second was tested in a slightly different way. Fig.6.7a. and b. show the conditions of and results from the tests conducted with the first sample. The test procedure was standard. The friction trace displayed a rise in friction only after the temperature had reached 110C, and then the friction dropped at a lower temperature than did the control using non-oxidised lubricant. A delayed rise in friction due to oiliness impurities, or oxidation products was observed as above.

However this delay in the onset of high friction had a marked effect on the running history of the track when the friction drop did occur. Very many fewer passes at high friction had taken place in these tests and this could have affected the temperature of the drop, especially if it were a kind of running-in process as suggested in section 6.1.

To take account of this possibility, the second sample was tested in a similar way, but when the coefficient friction rose above 0.5, the temperature was held below 120C for about 25 min. Thus the track was given full opportunity to"run-in"at high friction values, and only then was the heating resumed. The second sample was also tested for reversibility as in the previous section. Fig.6.8a. and b. show the conditions and results of these tests. Unfortunately one of these tests never displayed any high friction and so the graph of Fig.6.8b. is the mean of only two traces, although the consistency of these two was very good. It may be seen that there was little difference between the results of Figs.6.7b. and 6.8b. In all cases the preoxidised lubricant showed a friction drop at distinctly lower temperatures than the non-oxidised lubricant.

Analytical work to investigate the products of oxidation of

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	2½ °C min^{-1}

materials – track	– slider	contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

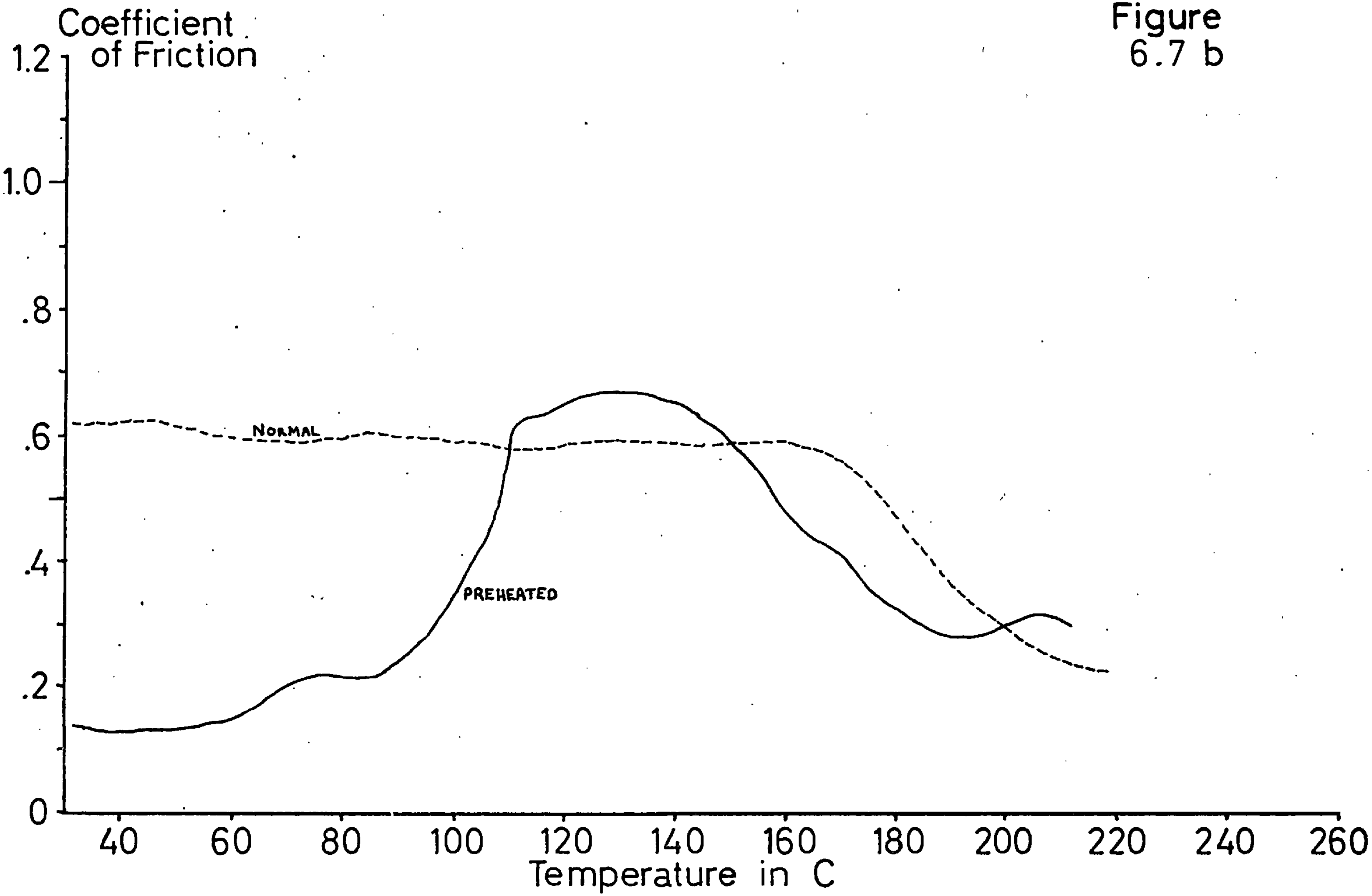
lubricant varied

special conditions one batch of a 1% solution of DBDS in hexadecane had been preheated before use to oxidise it.

varied conditions		no. of runs	repeat-ability
Preheated	——	2	4
Normal	- - - - - -	4	4

Figure 6.7a

Figure 6.7 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
NORMAL
PREHEATED

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

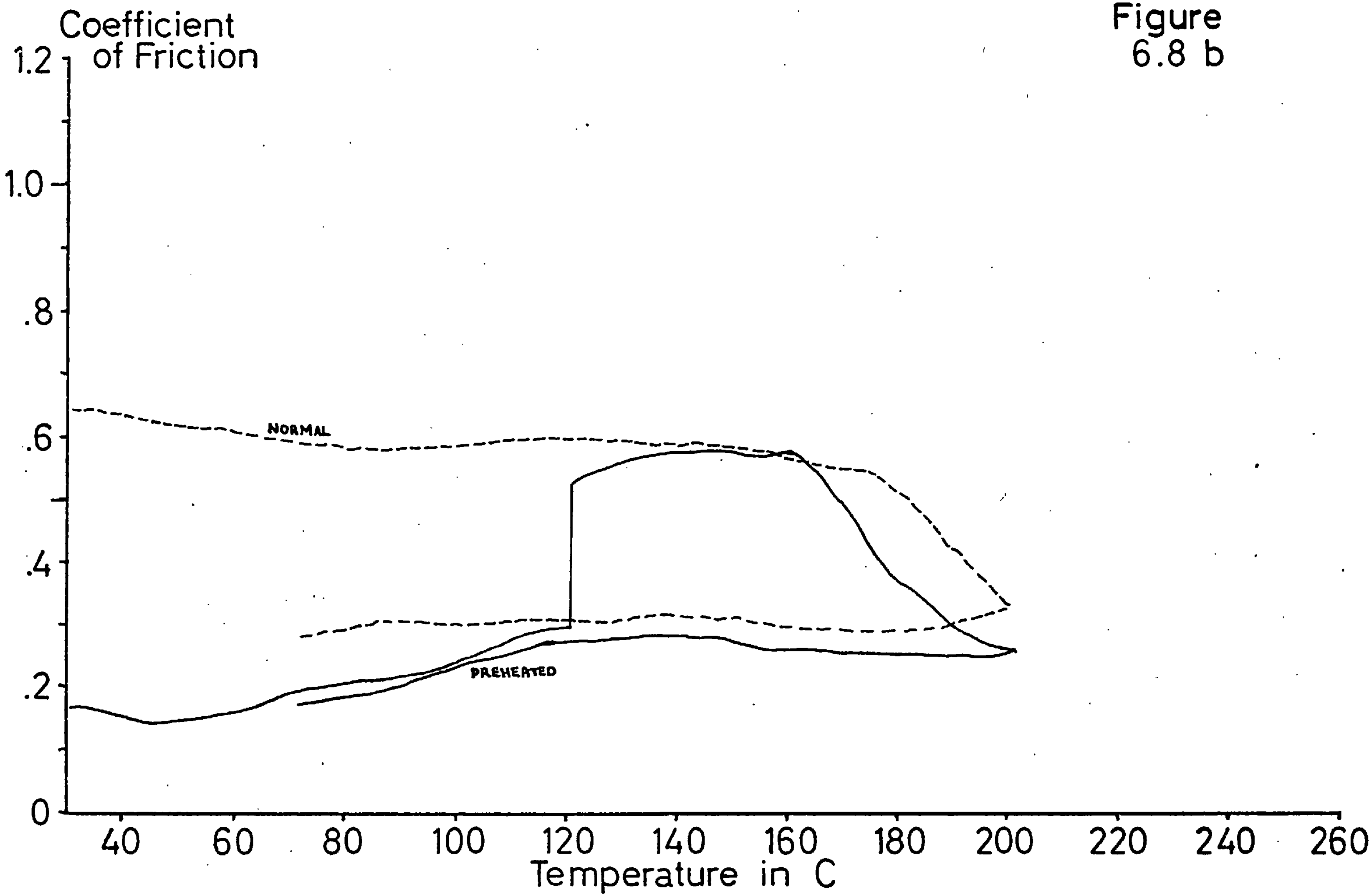
lubricant varied

special conditions one batch of a 1% solution of DBDS in hexadecane was preheated before testing in order to oxidise it. Also special procedure was applied to the test - see text

varied conditions		no. of runs	repeat-ability
Preheated	──➤	2	5
Normal	╌╌➤	4	2

Figure 6.8a

Figure 6.8 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
NORMAL
PREHEATED
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

the lubricants is presented in section 7.2.

Some later work on the oxidation of these lubricants carried out by Burch and Hiley (90) using thin layer chromatography shed further light on the above tests. The colouring of the lubricants, which had been used to indicate the degree of oxidation, was not caused by the main oxidation products. In fact the presence of 1% DBDS reduced the amount of these products found, compared with hexadecane above. It is likely that the distinct colouring of the 1% DBDS solution was due to a degredation product of the DBDS. It seems certain that the DBDS was not promoting oxidation of the hexadecane as had been previously thought.

Several conclusions may now be drawn,

1) Oxidised hexadecane contains substances which act as oiliness additives. The friction traces obtained are similar to those of a low concentration of hexadecanoic acid (section 4.6.). This is to be expected from the oxidation chemistry of paraffins.

2) These oxidation products are not solely responsible for the observed drop in friction around 180C with DBDS in hexadecane, although they may well play a part.

3) Oxidation of a 1% solution of DBDS in hexadecane causes the friction drop to take place at lower temperatures, and is likely to be an important part of the overall mechanism, which creates the drop.

6.6. EXPERIMENTS WITH VARIED RUNNING & THERMAL HISTORY

It might be expected that the exposure of clean metal surface, during the tearing and welding that occurs, will seriously affect the reactions taking place in the lubricant. This has been considered by several workers, including Morecroft (78) and has been reviewed by Eischner (91), and it appears that catalytic action can be created by this kind of frictional process. Bayles (60) suggests that "nascent" metal, created by a torn surface is involved in the reactions which form an effective surface film. The facts that firstly no friction drop had been seen to occur within a single pass and secondly that these drops often appeared to be proportional to the maximum friction value reached, indicated that the drop itself is a mechanical running-in process. This "running-in" to a low friction would be triggered by some change in the chemical conditions. If this were the case, the minor variations observed with different mechanical conditions (as in chapter 5), are easily explained. Different amounts of running-in would be required depending upon the worst state of the surface, and the running-in process would be affected by the rubbing conditions, such as speed. This concept had to be rejected after the following experiments.

The friction test was divided into two sections. Firstly the system was run until just before the friction drop. Then the sliding conditions (speed and therefore out of contact time) were altered, but the track length was kept the same. The experiment was completed and the friction trace compared with those from the two types of test done normally. The first part of the experiment was carried out with a sliding speed of 1mm s^{-1} and an OCT of 10s (see Fig.5.b.). At 155C the speed was reduced to 0.17 mm s^{-1} and the OCT became 60s (see Fig.5.b.). The heating rate was also altered. Fig.6.9a. gives the conditions.

If the concept of running-in had been correct, the friction drop would be "delayed" because of the more severe rubbing during the first part of the test. Fig.6.9b. gives the results of the tests. There was no significant delay. It may be concluded from this that

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	altered	altered	altered

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

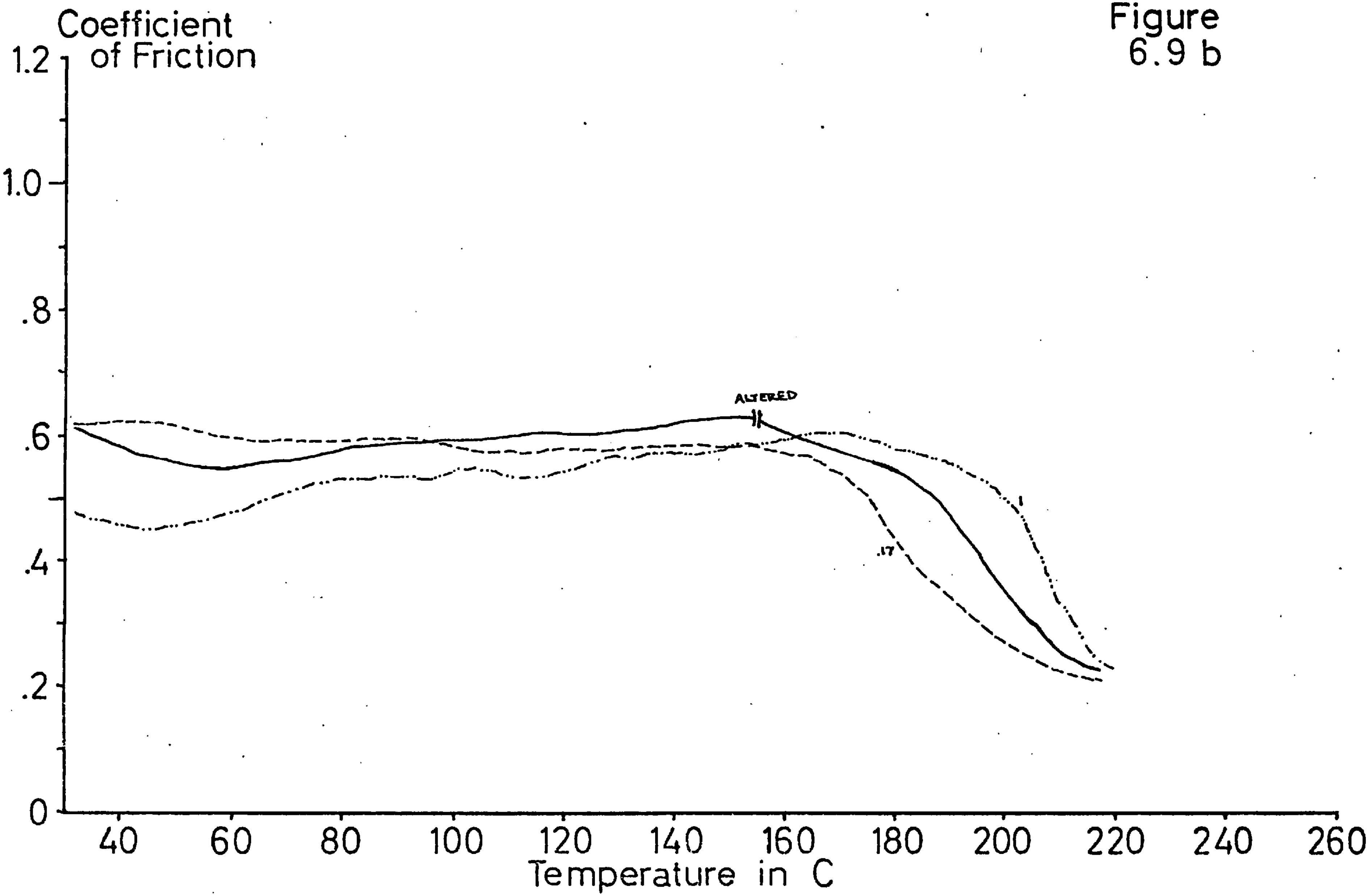
lubricant 1% DBDS in hexadecane

special conditions at 155 C the sliding conditions were altered, as is described in the text.

varied conditions		no. of runs	repeat-ability
Altered at 155 C, sliding speed 1 ÷ 0.17 mm s^{-1} O.C.T. 10 - 60 s and heating rate 5 - $2\frac{1}{2}$ °C min^{-1}	——╫——	3	4
1 mm s^{-1}, 10s, 5 °C min^{-1}	-··-··-··-	2	5
0.17 mm s^{-1}, 60s, $2\frac{1}{2}$ °C min^{-1}	- - - - - -	4	4

Figure 6.9a

Figure 6.9 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
ALTERED
.17
1

the state of the track prior to the friction drop must only play a minor part in determining the temperature of the friction drop, even though it affects its magnitude.

Further experiments were conducted to confirm this. The aim was to repeat the experiments of section 6.4., but to omit various sections of rubbing, whilst keeping the heater switched on. Thus it was hoped that those sections which had the most significant effect could be revealed. The first two experiments were conducted with normal sliding until the temperature reached 160C and then sliding recommenced when it reached 200C (and the heater was switched off). While the machine was stopped, the two specimens were held apart. The precise conditions are given in Fig.6.10a. and the resulting traces in 6.10b.

Since in these tests the actual section of the friction drop was omitted it was expected that on restarting the machine, the coefficient of friction would still be high and then fall as the surfaces quickly "ran-in". Quite contrary to expectation, the friction value recorded when the machine was restarted was only marginally higher than that recorded in the tests when rubbing was continuous. The results were repeated with sliding omitted between 125C and 200C with the same result as in Fig.6.10b.

A major conclusion could now be made, which upset many of the previous held ideas. Although the previous rubbing history of the surfaces (presumably the scale of surface damage) does affect the value of the measured friction, the rubbing process itself is <u>not</u> necessary to create a friction drop. The invariance of the temperature of the drop with O.C.T. (how often the track is rubbed) becomes inevitable since rubbing is not even necessary for the drop to occur.

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

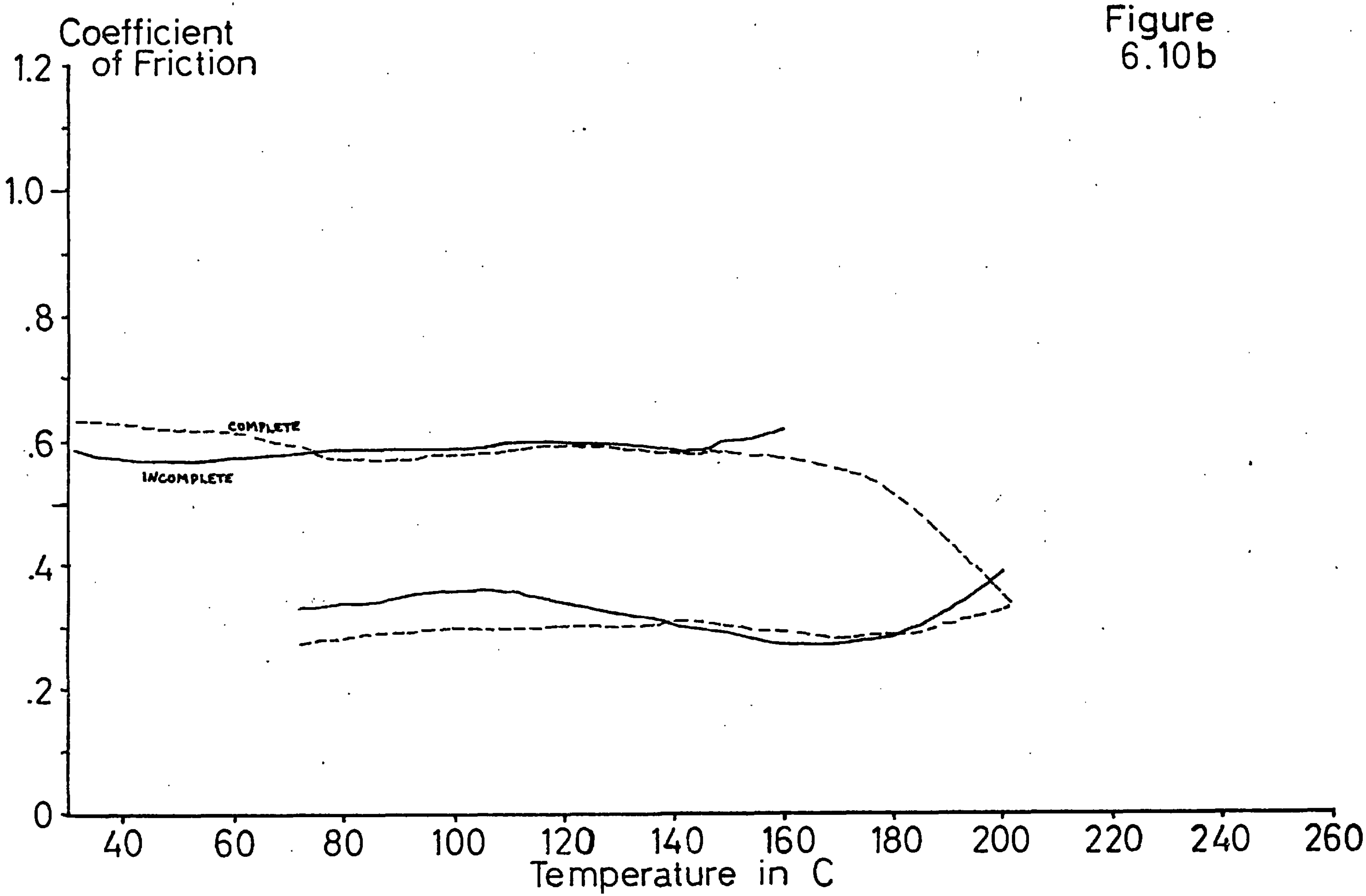
lubricant 1% DBDS in hexadecane

special conditions a section of rubbing was omitted from an otherwise normal test.

varied conditions		no. of runs	repeat-ability
Complete rubbing	———	4	2
Incomplete rubbing	- - - - - - - - - - -	3	4

Figure 6.10 a

Figure
6.10b


Coefficient
of Friction
1.2
1.0
.8
.6
.4
.2
0
COMPLETE
INCOMPLETE
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

To elucidate the importance of the thermal history of the surfaces, the following tests were conducted. The surfaces were "run-in" until a high coefficient of friction was recorded (above 0.5), using the minimum number of passes, usually 2 or 3. The surfaces were separated and the heater switched on, either to its maximum setting, which raised the temperature to 200C within 10 min., or at the lower setting, which produced a rise of $5^{\circ}C\ min^{-1}$, so that 200C was reached in 35 min. The heater was switched off before 200C, so that there was no "overshoot". Thus with the temperature at its maximum, sliding was commenced and the friction recorded as the specimens cooled.

Cooling took place as before, and the results and conditions are shown in Fig.6.11a. and b. There was considerable scatter between the results from tests with nominally the same conditions. Nevertheless a clear trend is apparent. When the lower heating rate was used a) the coefficients of friction were consistently lower and b) there were no signs of reversibility. With the higher heating rate the friction was relatively high and rose again quite often, displaying some reversibility. The higher heating rate, $18^{\circ}C\ min^{-1}$, must have been just about on the lower limit required to prevent the appropriate reactions (which cause the friction drops) from occurring. This may be deduced because some of the tests with the higher heating rate displayed friction values as low in places as sme of the friction values from tests with the lower heating rate.

It may be concluded that the friction drop is a result of certain reactions (probably involving oxidation) which take place at elevated temperatures in the lubricant. The metal surfaces may or may not be involved with the "rate determining step" which will

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	see below

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant 1% DBDS in hexadecane

special conditions Note: these friction traces were taken as the specimens <u>cooled</u> from 200 C. After running-in with a few passes, the specimens were heated without further rubbing.

varied conditions		no. of runs	repeat-ability
Specimens heated to 200 C in –			
10 min (high)	···········	4	2
35 min (low)	– – – – – –	2	3

Figure 6.11a

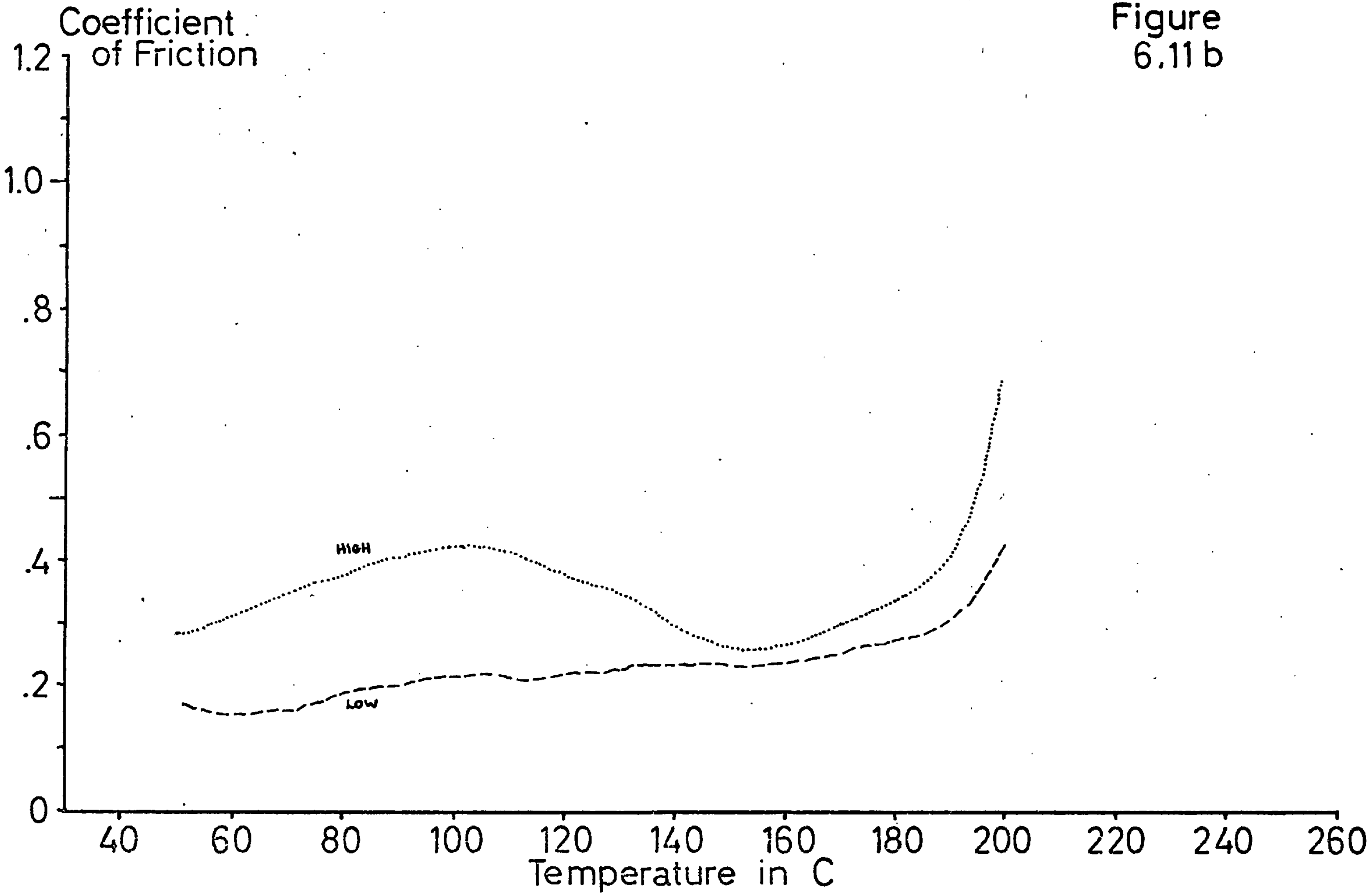


Figure 6.11 b

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
HIGH
LOW
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

govern the friction drop temperature. Mechanical factors clearly play a very small part in the processes.

6.7. HEATING RATES

Since it seemed that bulk lubricant reactions were important, it was decided to investigate the effect of a change in heating rate. As in section 3.2., it might be expected that a reduction in heating rate would reduce the friction drop temperature. This would be the case if an important reaction has to proceed to a certain point before the friction drop could begin. The temperature at which this point is reached would depend on the length of time spent at each temperature, that is the heating rate. Figs.6.12a. and b. show the conditions and results of several sets of tests.

The low heating rate tests, with a heating rate of $1.2^{\circ}C\ min^{-1}$ are presented in Fig.6.12b. The results show that the friction trace was almost indistinguishable from that obtained with a heating rate of $2.5^{\circ}C\ min^{-1}$. Thus it appears that the reactions governing the friction drop reach an equilibrium at each temperature for heating rates of both 1.2 and $2.5^{\circ}C\ min^{-1}$. A rate of $5^{\circ}C\ min^{-1}$ displays a "flattening" of the drop as shown by Fig.6.5.

When a high heating rate was used, nearly $20^{\circ}C\ min^{-1}$, the results were more complicated. Two sets of tests were performed, on different occasions, and the results differed slightly. Nevertheless in all these tests, the mean coefficient of friction rose to very high values, one or over. This is 50% higher than the maximum friction recorded in the previous tests. The only explanation for this increase that can be offered is in terms of the relative rates at which oiliness agents desorb and adsorb. Spikes (12) has described how important it is to allow full time for these processes

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17, 1 mm s^{-1}	1 min	varied

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

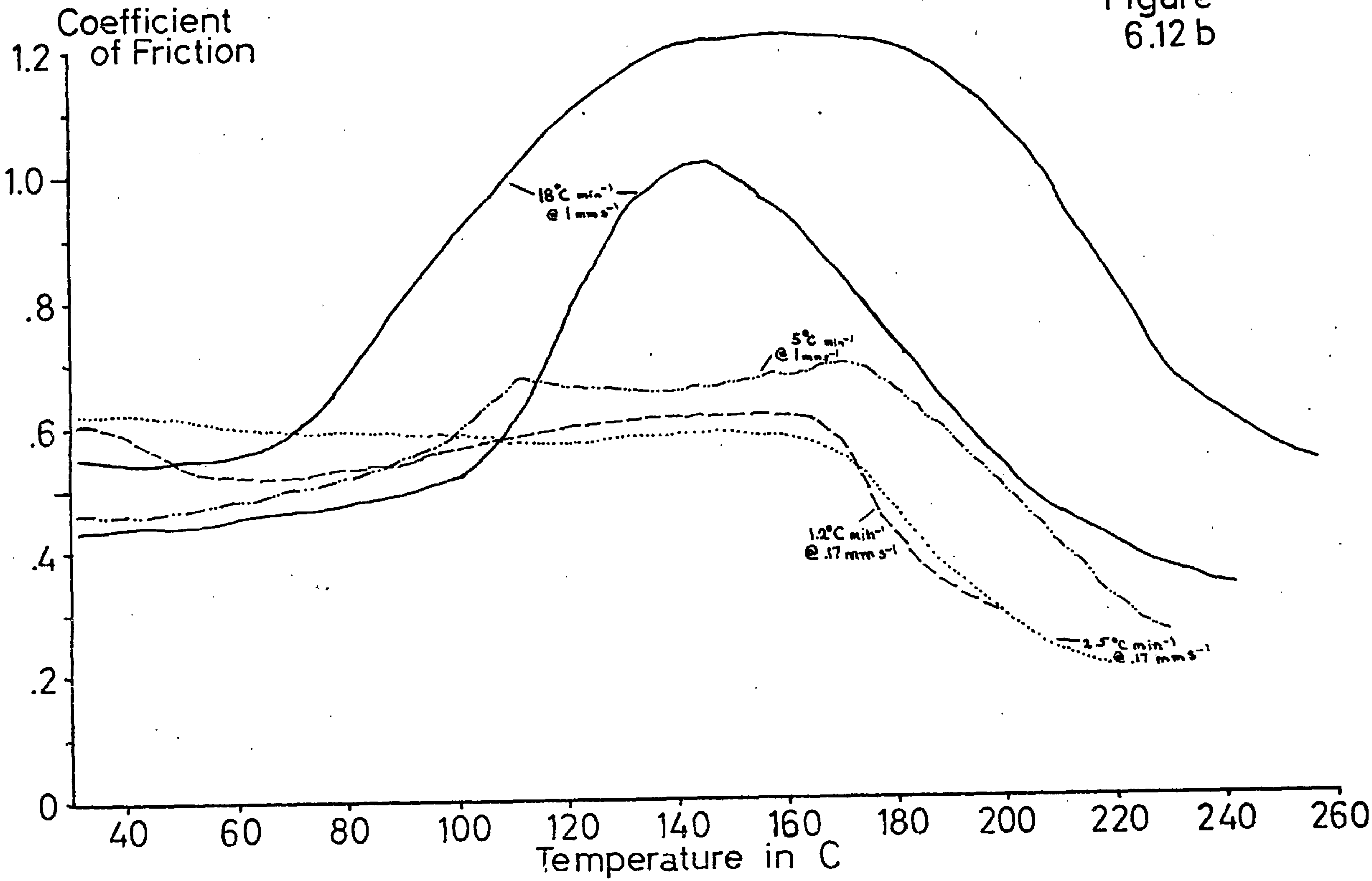
lubricant 1% DBDS in hexadecane

special conditions

varied conditions heating rate, in °C min^{-1}		no. of runs	repeatability
1 mm s^{-1}			
18	——	2,3	1,2
5	—··—··	4	4
0.17 mm s^{-1}			
2.5	········	4	4
1.2	– – – –	2	5

Figure 6.12a

Figure
6.12 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
18°C min⁻¹ @ 1 mms⁻¹
5°C min⁻¹ @ 1 mms⁻¹
1.2°C min⁻¹ @ .17 mm s⁻¹
2.5°C min⁻¹ @ .17 mms⁻¹

to reach equilibrium. If the rate of desorption were higher than the corresponding rate of adsorption, then a rapid increase in temperature would favour the desorption process further. The adsorption would not have time to catch up.

A friction drop was equally evident in these tests with a very high friction, but it is doubtful if the drops can be considered on a proportional basis, in the manner described in section 5.3. The main reason for this is to do with the adhesional bonds being formed in the frictional process. Tabor's model, discussed in section 1.9., explains how a reduction in friction is easier, the higher the friction being developed. In this situation, where very high coefficients of friction are being developed, substantially less contamination of the surfaces will be required to reduce the friction value by a half compared with that required if the coefficient of friction were around 0.7. Thus it is possible that part of the drop is due to a different cause than those observed in the control tests. Note the spontaneous drop in friction, after a very steep rise on several traces e.g. Fig.4.12.which demonstrates that very high frictions are unstable. Further complications in comparing the temperatures of these friction drops lies in the high heating rates, As mentioned in section 2.11 . the temperatures quoted are those of the surface of the flat specimen. With temperatures increasing at the rate of 20°C min, the fluctuations along the specimen and between the lubricant and the metal will add uncertainties to the measurements which cannot be ignored, nor easily accounted for.

It was thus not possible to make any firm deductions from the experiments with very high heating rates. Photomicrographs, taken in the manner described in section 4.3. indicated that the frictional process was similar to the other tests. However these tests are a good example of how difficult comparison between friction test results can be, especially when an attempt is made to compare friction drop temperatures.

In conclusion the experiments of this section have indicated that in these tests the reactions involved in the friction drop reach equilibrium at each temperature (unless the heating rates are very high- above 10°C $\min^{-1}$). This is in contrast to the findings of the reaction studies of section 1.15..

6.8. SQUALANE

Squalane (Hexamethyltetracosane $C_{30}H_{62}$) is a branched alkane, having a greater molecular weight, boiling point and viscosity than hexadecane. It was decided to use squalane, as an alternative base oil, to check that the friction drops observed are not specific to hexadecane. Unfortunately the supplies, from B.D.H. Ltd., contained 0.02% butylated hydroxytoluene, which had been added as an anti-oxidant. Careful and prolonged shaking with activated silica gel and alumina, as used for the hexadecane samples, failed to remove all the oxidation inhibitor. This was revealed by experiments, performed by Hiley (89) using thin layer chromatography.

Nevertheless a 1% solution of DBDS in squalane was used in a number of tests. The first set was a control employing just squalane. The second followed the procedure shown in Fig.6.5. as a test for reversibility, and the third followed those of Fig.6.11. in which the specimens were heated rapidly after running-in and the friction observed whilst the specimens cooled.

Figs.6.13a. and b. show the conditions and results of the first two sets of experiments. The results are very similar to the

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	2½ °C min^{-1}

materials – track – slider		contact geometry	
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball	on flat

lubricant varied

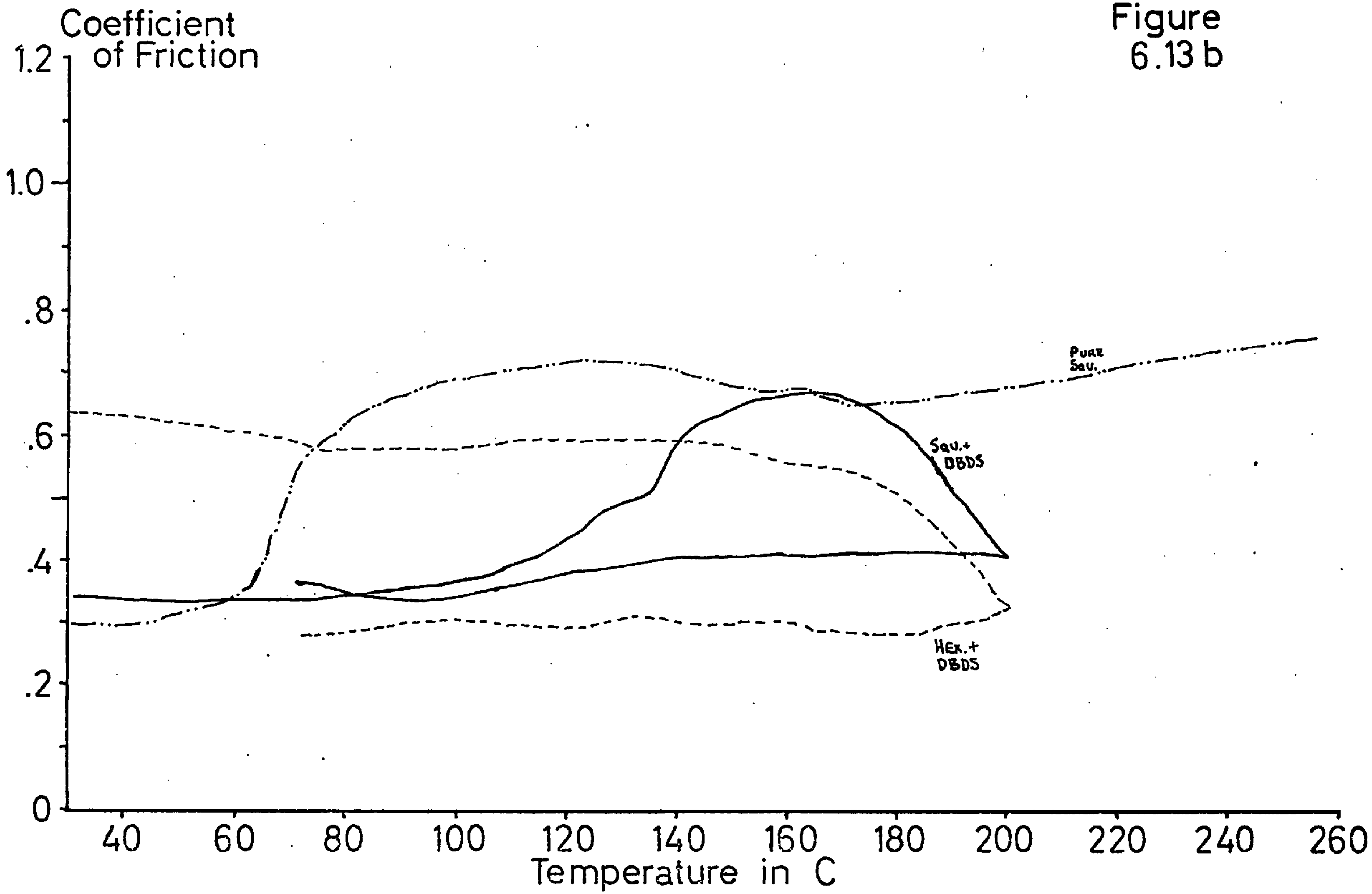
special conditions specimens allowed to cool in two of the tests.

varied conditions

lubricant		no. of runs	repeat-ability
Squalane alone	—··—··—	2	3
1% DBDS in squalane	——	2	2
1% DBDS in hexadecane	- - - -	4	2

Figure 6.13a

Figure 6.13 b



Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
Pure Squ.
Squ.+ DBDS
Hex.+ DBDS

equivalent friction tests in which hexadecane was used. The degree of reversibility is much the same and Figs.6.14a. and b., which cover the third set of tests confirm that result. In fact the course of oxidation of squalane would be expected to be very like that of hexadecane.

The above tests were of value in demonstrating that the friction traces obtained with 1% DBDS were not dependent on the use of hexadecane as the base lubricant. Another paraffin had displayed just the same results.

6.9. OXIDATION INHIBITOR

So far it had not been possible to confirm or deny whether oxidation was an essential part of the process which creates the friction drop. In an attempt to provide further evidence it was decided to use a commercial oxidation inhibitor, N Phenyl 1 naphthylamine The friction tests were carried out as normal, except that 0.1% of N phenyl 1naphthylamine was added to the 1% of DBDS in hexadecane. Figs.6.15a. and b. give the conditions and results of the first tests. The addition of the small amount of oxidation inhibitor has caused the drop to occur at a temperature 20°C higher than normal. Fig.6.16a. and b. cover the tests performed to indicate the degree of reversibility. In this case the addition of the inhibitor appears to have resulted in a reduction in the production of oiliness agents as well as in the friction drop.

Thus the use of N phenyl 1naphthylaminehas demonstrated the importance of oxidation to the process which causes the friction drop. It might be argued that the inhibitor acts by competing with the DBDS for sites on the surface. Such a mechanism was discussed by Spikes (12) for a detergent and an E.P. additive. Baldwin (61) also found

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	(18 °C min^{-1})

materials - track	- slider	contact geometry	
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball	on flat

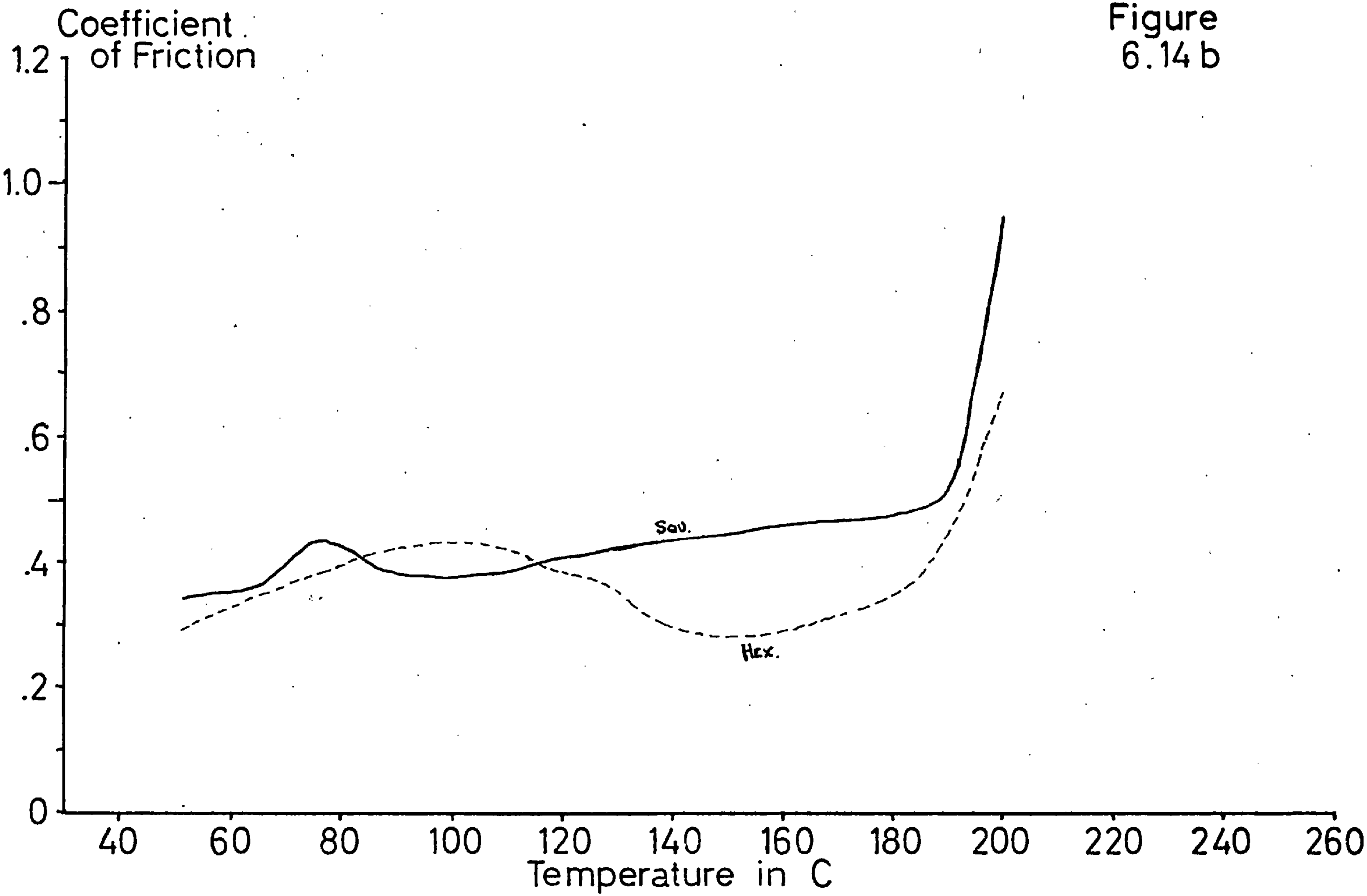
lubricant varied

special conditions Note: as in Fig. 6.11. the friction traces were taken as the specimens cooled.

varied conditions lubricant 1% DBDS in		no. of runs	repeat-ability
squalane	———	2	3
hexadecane	– – – –	4	2

Figure 6.14a

Figure 6.14 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
Sav.
Hex.

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ ^{o}C min^{-1}

materials - track - slider		contact geometry
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

lubricant varied

special conditions

varied conditions			no. of runs	repeat-ability
lubricant	hexadecane +			
	1% DBDS + 0.1% N phenyl 1 naphthylamine	———	2	3
	0.1% N phenyl 1 naphthylamine	— — —	2	4
	1% DBDS	- - - -	4	4

Figure 6.15a

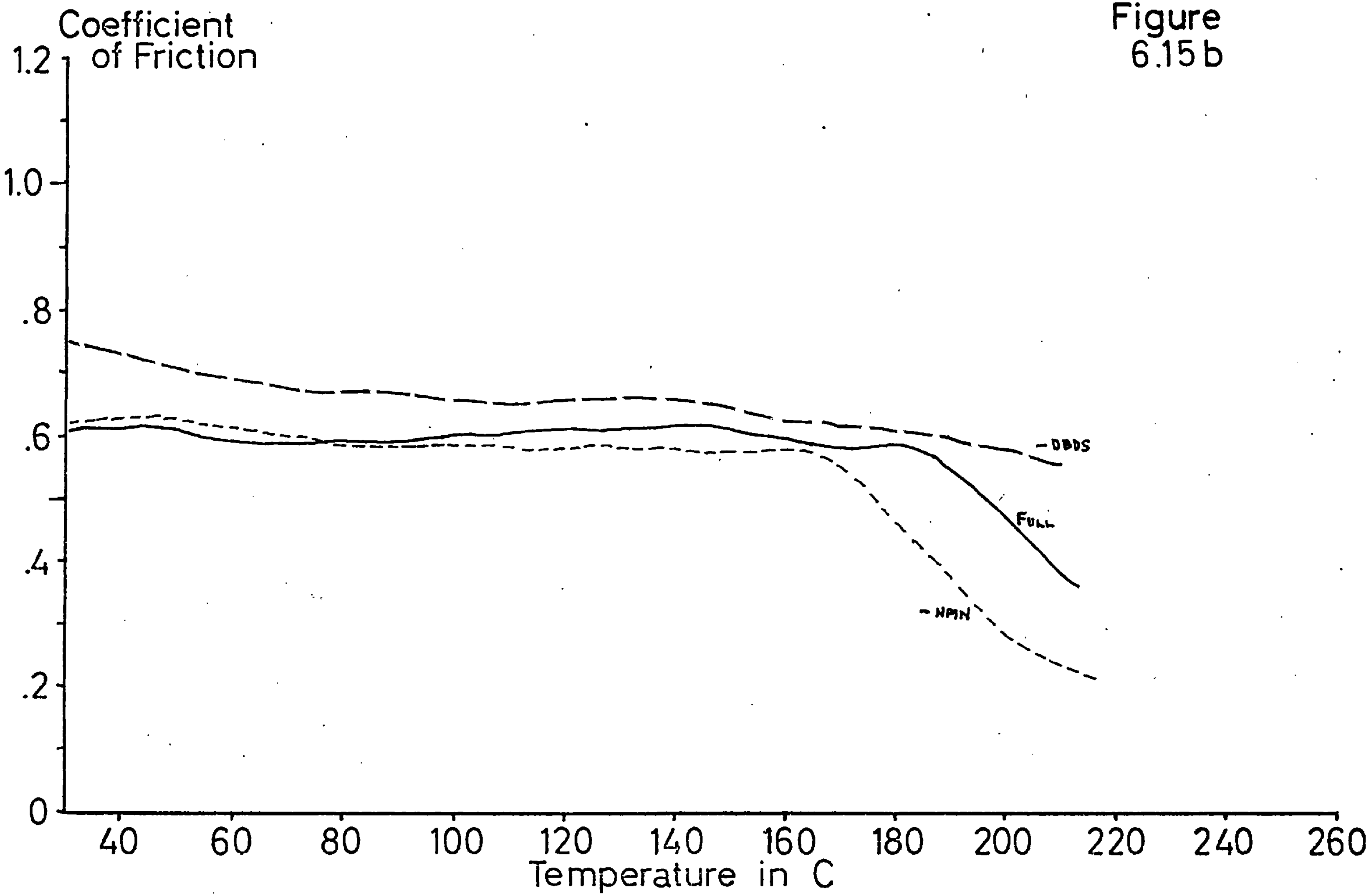

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
DBDS
FULL
NPIN

Figure 6.15 b

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials – track – slider			contact geometry
	E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

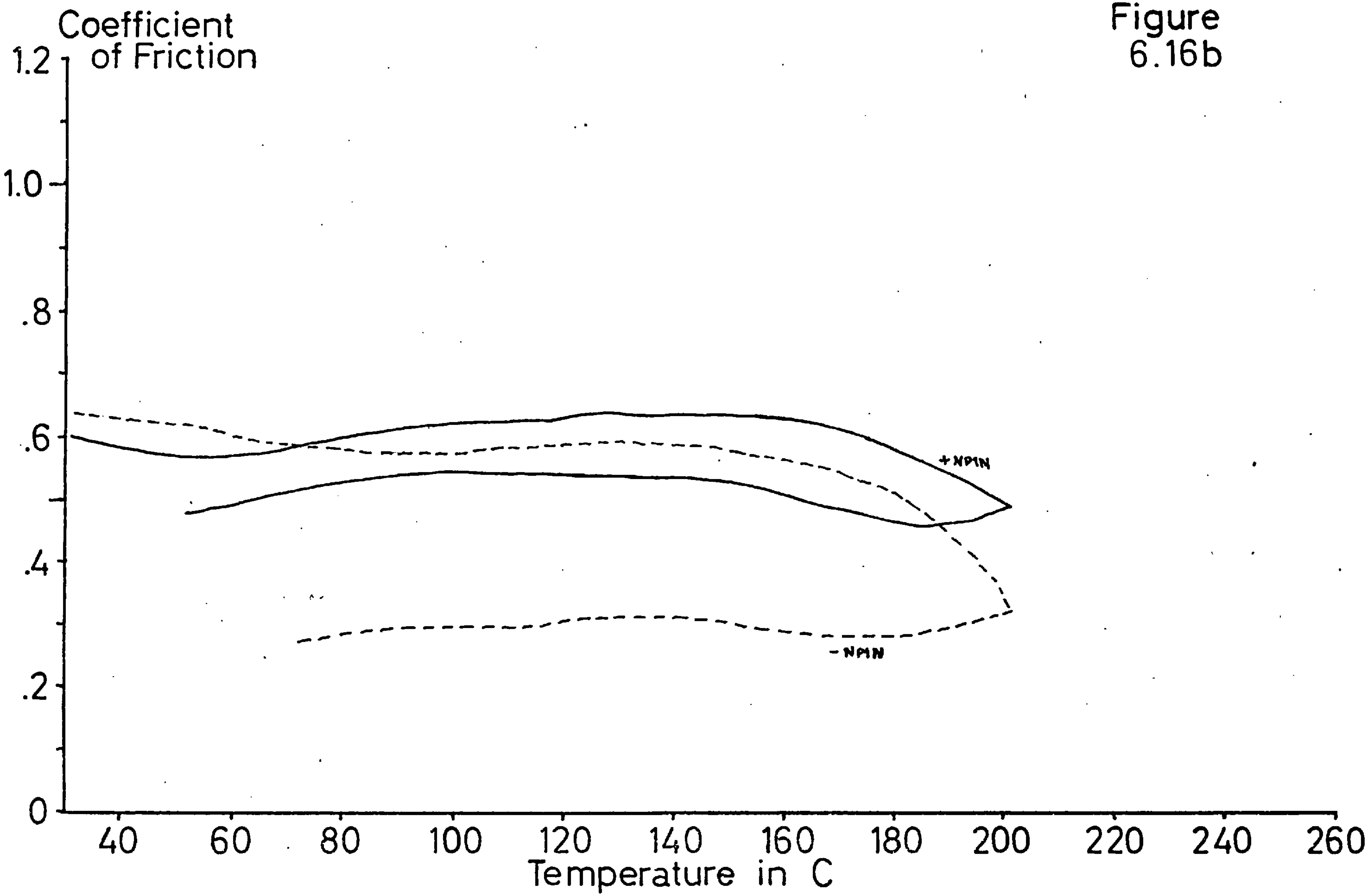
lubricant varied

special conditions specimens allowed to cool after 200 C reached.

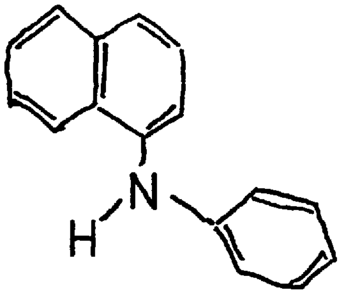
varied conditions		no. of runs	repeat-ability
lubricant 1% DBDS in hexadecane + 0.1% N phenyl 1 naphthylamine	——	2	3
nothing	- - -	4	2

Figure 6.16a

Figure
6.16b


Coefficient
of Friction
1.2
1.0
.8
.6
.4
.2
0
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C
+NPIN
-NPIN

a reduction in performance of E.P. additives, when amines were present in the base oil. However in his case the amine concentration was about 7% and in the above tests it is most unlikely that there is significant adsorption of the N phenyl 1 naphthylamine.There are three reasons for this and the first lies in the structure of the compound, which is shown in Fig.6.17..



N phenyl 1 naphthylamine

Fig. 6.17.

The structure, in which the amine group is sterically hindered, does not favour adsorption of the compound. Secondly the evidence from thin layer chromatography (89) showed that the compound adsorbs very weakly compared with a fatty acid. Thirdly, previous experiments had shown that equally small concentrations of oiliness agents, which adsorb more readily had a minimal effect on the friction trace at high temperatures.

The only alternative to the use of an oxidation inhibitor (for limiting oxidation) would be the removal of oxygen from the lubricant and the atmosphere around the apparatus. This technique has been used in the past by researchers, such as Bjerke (92) and was discussed in section 1.11. It was considered impracticable in this instance because of the design geometry of the Bowden-Leben machine. Bayles (60) had bubbled nitrogen, free of oxygen, through the lubricant in one of his tests to see if a difference in the friction traces might be detected. However he found none, and could make no firm deductions, for he did not measure the relative oxygen levels of the various tests. The problems of excluding almost all oxygen from a friction test apparatus are very great. Addition of a chemical to change the oxygen concentration is very much easier. Pyrogallol (1.2.3. Trihydroxy Benzene $C_6H_6O_3$) was considered because it is often used to remove oxygen from gasses, but it would not dissolve in hexadecane and requires an alkaline environment for its efficient functioning. It was therefore not tested. However the above ideas are reconsidered in section 6.12.

6.10. OXIDISED DIBENZYL DISULPHIDE

It became clear that not only hexadecane but also the dibenzyl disulphide was oxidising at high temperatures - see section 7.2. Some solid DBDS was deliberately oxidised by heating air to about 250C for a few seconds. The DBDS was decomposed, going progressively yellow then orange and finally red in colour and evolving hydrogen sulphide. On cooling, the "additive" was dissolved in hexadecane to make up a 1% solution, which was just noticeably pink. This lubricant was then tested in the normal way, in the hope of finding out the importance of oxidation of the DBDS in the friction drop process. A decrease in the drop temperature would indicate that oxidation was involved in the process. The conditions of the tests and the results are shown in Figs.6.18a. and b. respectively. The drop in friction certainly began at a lower temperature than was observed with ordinary

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track - slider			contact geometry
	E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball on flat

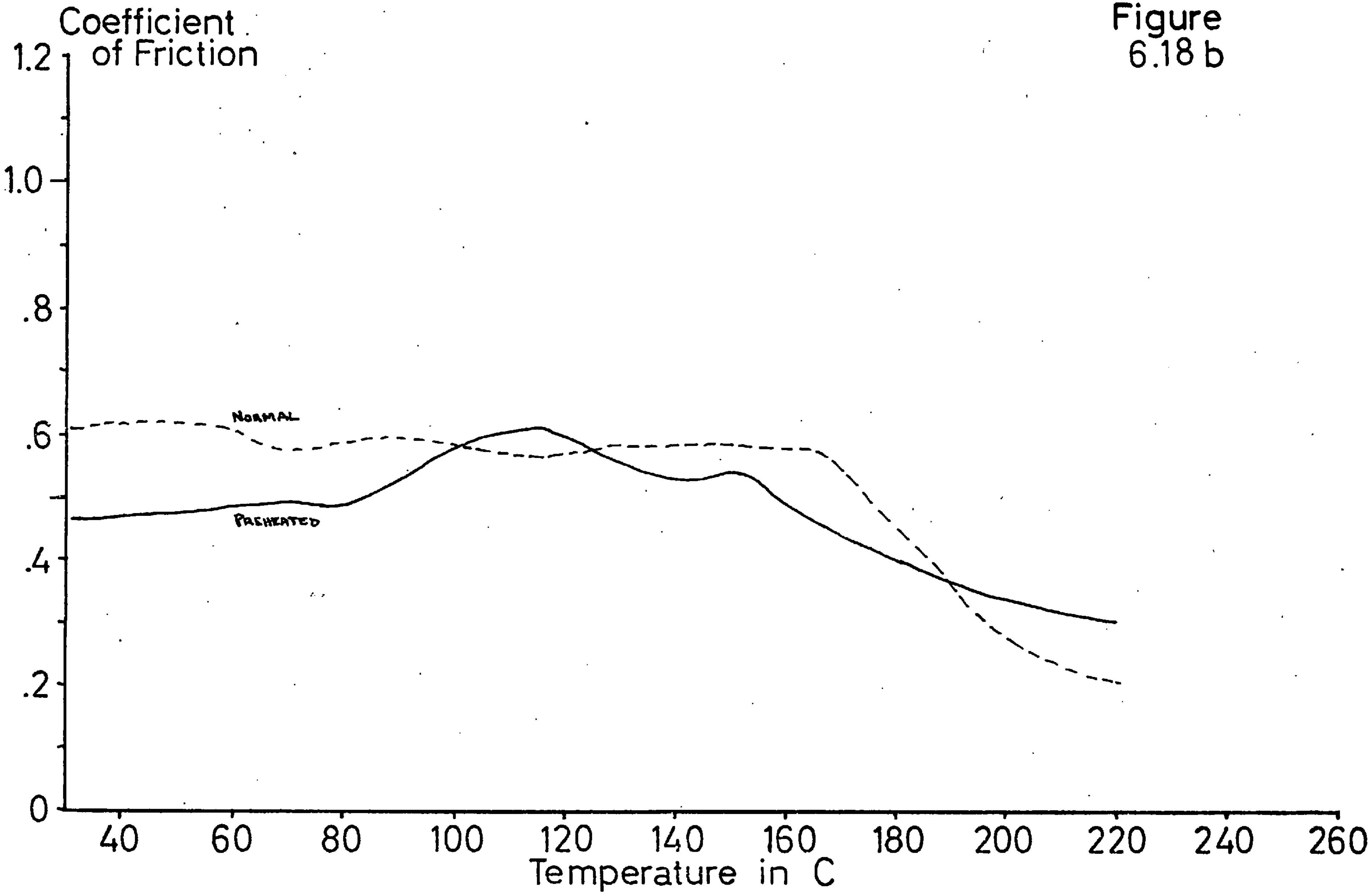
lubricant varied

special conditions the additive for one set of tests was previously heated in air to about 250 C.

varied conditions		no. of runs	repeatability
lubricant hexadecane + 1%			
preheated DBDS	——	3	3
normal DBDS	- - - -	4	4

Figure 6.18a

Figure 6.18 b


Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
NORMAL
PREHEATED
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

DBDS. However the drop was not complete until the temperature had risen much more, than in the normal case. The effective additive concentration may have been reduced by decomposition and this would account for the limited performance at the highest temperatures (see Fig.6.1.)

The evidence from these tests indicate that oxidation of the DBDS is an important part of the mechanism which causes the friction drop.

6.11. PRESENCE OF AN OILINESS ADDITIVE

As was suggested in sections 1.12. and 1.18., several researchers have proposed that if an oiliness additive is present with an E.P. additive, then the performance of either will be considerably improved. Greenhill (45) observed just such a phenomenon in his slow speed tests. Spikes (12) considered that the friction drop he observed was caused by the presence of sufficient polar molecules to adsorb onto an existing E.P. film and alter the frictional conditions. It was decided to investigate this idea and the following technique was adopted.

The production of oiliness agents by natural oxidation was curtailed by the use of 0.1% of N phenyl1naphthylamine as in section 6.9. It was known from Fig.6.16b that at 185C the friction drop would not have begun if this inhibitor was present. It was also known that without the inhibitor, and therefore with the presence of oxidation products, the friction at 185C would be under 0.5 (Fig.6.5b.). Therefore 25 g of a 1% solution of DBDS was made up and 5ml of it drawn into a clean syringe. To this smaller quantity, 25mg of hexadecanoic acid was added, and 25mg of N phenyl1 naphthylamine was added to the remaining solution. This meant that when mixed, the total solution contained 1 % DBDS and 0.1% of the other two additives.

A standard friction test was conducted beginning with the 20g or so of solution containing the inhibitor, as the lubricant, but adding the solution with the hexadecanoic acid at 185C. This caused the lubricant to cool slightly, but heating was maintained. The conditions are shown in Fig.6.19a. and the results in Fig.6.19b.

The purpose of the experiment was to demonstrate the effect discussed above by a rapid reduction in friction on addition of the hexadecanoic acid. If the friction drop occurred only when sufficient oiliness agent was present to adsorb onto an existing E.P. film, then the drop should have taken place when the acid was added. The temperature must have been sufficiently high to allow an E.P. film to build up, from the results of the normal tests. As will be seen, no rapid drop in friction was observed. It may be concluded that the production of oiliness agents is not the rate determining step in the friction drop process, that is it does not control the temperature of the drop. Whether or not oiliness agents must be present for the drop to take place cannot be firmly deduced. It would now seem less likely.

6.12. REDUCTION IN OXYGEN ACTIVITY

A most interesting hypothesis, which could explain many of the observed results, has been suggested by Spikes (93). It is based on the evidence of certain tests, already mentioned in section 1.17. B(vi), that the different oxides of iron exhibit different heats of adsorption toward an oiliness agent. Since it is to be expected that the oxygen concentration in the lubricant will decrease with increasing temperature, it is reasonable to postulate that the oxidation state of the iron oxides produced might decrease as the temperature rises. The hypothesis then states, that if the process

Conditions of Tests

load	sliding speed	o.c.t.	heating rate
1 kg	0.17 mm s^{-1}	1 min	$2\frac{1}{2}$ °C min^{-1}

materials - track - slider		contact geometry	
E.N. 58	E.N. 31	$\frac{5}{8}$" dia ball	on flat

lubricant varied

special conditions a complicated procedure was followed - see text.

varied conditions		no. of runs	repeat-ability
lubricant	1% DBDS + 0.1% N phenyl 1 naphthylamine in hexadecane		
+ 0.1% hexadecanoic acid at 185 C	———	3	1
alone	- - - -	2	3

Figure 6.19a

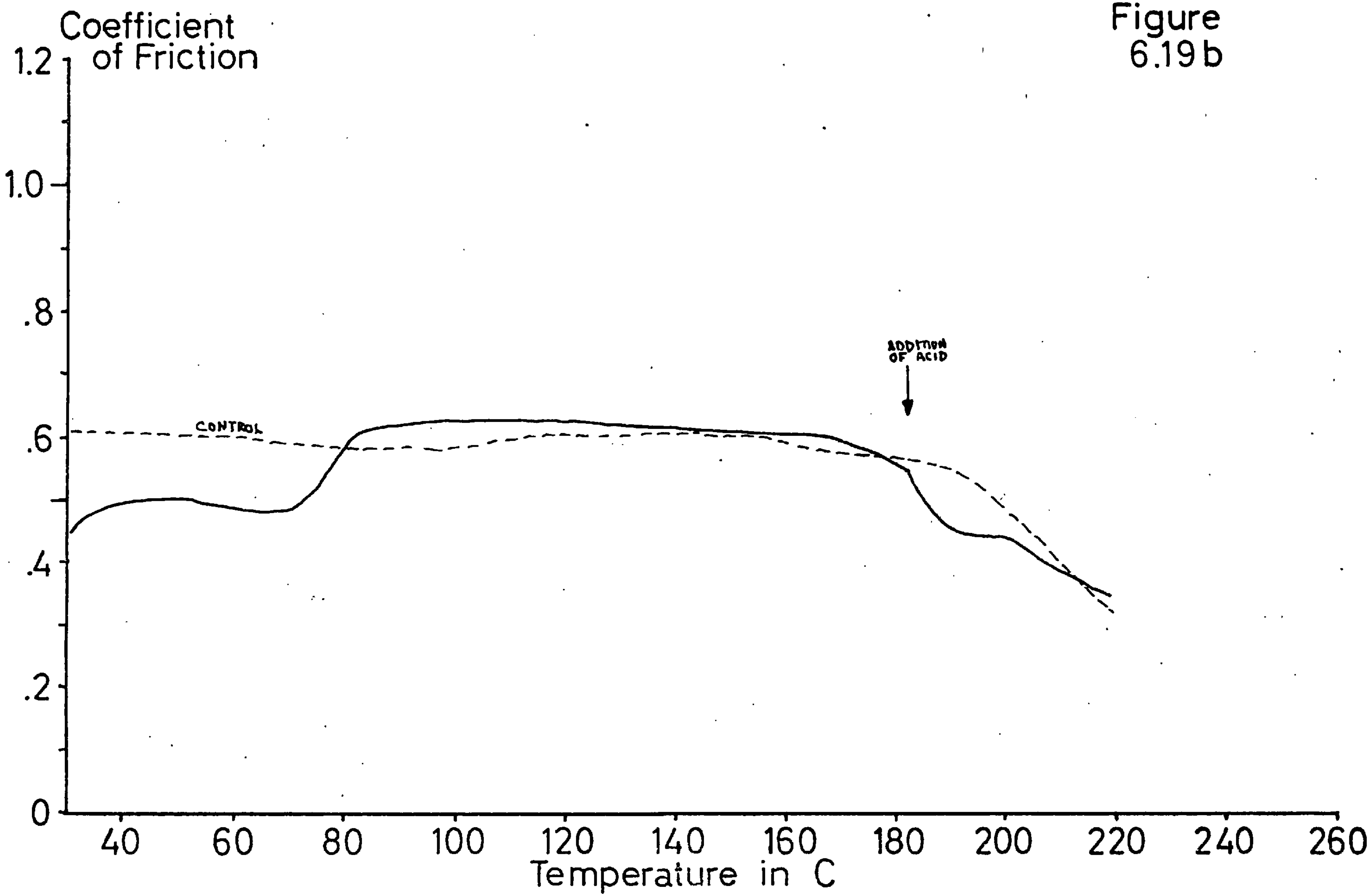

Coefficient of Friction
1.2
1.0
.8
.6
.4
.2
0
CONTROL
ADDITION OF ACID
40
60
80
100
120
140
160
180
200
220
240
260
Temperature in C

Figure 6.19b

outlined above is occurring, the observed friction drop may result from the change in oxidation state of the iron oxide on the surface at the temperature reached, so as to form an oxide on which oiliness agents readily adsorb. Once this adsorption had taken place, the degree of adhesion between the sliding surfaces would be greatly reduced, thus causing the friction to drop. The work of Hironaka, Yahagi and Sakurai (79) showed that the oxides of iron, Fe_3O_4 and FeO have surfaces on which a fatty acid will adsorb more readily than Fe_2O_3, which is in a higher oxidation state.

The only practicable way of testing this hypothesis was to alter the oxygen activity in the hexadecane. This would then shift the temperature at which the oxygen concentration fell below the level at which the significant change in oxidation state of the iron took place. It was considered undesirable to increase the oxygen activity, (and look for an increase in temperature of the friction drop) because oxidation of the lubricant was already known to be going on. The alternative of reducing the oxygen activity has already been discussed in section 6.9. It was decided, however, to attempt to reduce the oxygen concentration in the hexadecane by bubbling pure argon through the lubricant. If the hypothesis were correct, only a small decrease in oxygen concentration, and therefore activity would cause a significant reduction in the temperature of the friction drop. Unfortunately the experiments failed to produce any conclusive result.

Pure argon (from B.O.C. Ltd.) was bubbled via a glass tube through the freshly formulated lubricant (1% DBDS in hexadecane) for 20 min. After subsequent tests made with the assistance of Newley (94) it was estimated that this decreased the oxygen concentration by about 15%. This lubricant was then used in a standard test, except that argon was continuously bubbled into the lubricant close to the contact region. It was hoped that a blanket of argon would prevent oxygen from being readsorbed into the hexadecane. However as the specimens were heated, the continual flow of fresh argon across the surface evidently increased evaporation. The specimens became dry by the time they reached 170C. At this point the friction had dropped only slightly, but it was not possible to deduce any temperature for a friction drop. It may be concluded that the reduction in oxygen effected did not produce a dramatic reduction in the temperature of the drop, that is 40°C or so.

This interesting hypothesis was thus not confirmed, and with the evidence of Bayles (60), who performed a similar sort of test on his own system with negative results, it was decided to take it no further.

6.13. SUMMARY

The results of the above friction tests may be categorised by their effect on the temperature of the friction drop. The majority had no significant or consistent effect although they affected the following factors:

1) Concentration of additive
2) Chemistry of additive (diphenyl not dibenzyl disulphide)
3) Heating rate
4) Running history of the specimens
5) Base oil (squalane not hexadecane)
6) Presence of an oiliness additive (hexadecanoic acid)

The tests which produced a drop at a significantly lower temperature employed either:

1) Preoxidised lubricant

or 2) Preoxidised additive

Those which resulted in a significantly higher temperature of the drop were those in which an oxidation inhibitor was used. Thus two important conclusions may be summarised also:

1) Oxidation plays an important part in the process which causes the friction drop. Indeed it appears that oxidation of some part of lubricant, probably the additive, is a prerequisite to the drop occurring at all. The temperature at which this oxidation has proceeded sufficiently would seem critical.

2) Rubbing does not have to take place for the friction to be reduced. Therefore the formation of freshly torn metal surfaces at elevated temperatures is not necessary for the appropriate reactions to occur, as was suggested by Bayles (60). The relative insensitivity of the friction drop temperature to the mechanical conditions of sliding is therefore no longer surprising.

CHAPTER 7

CHEMICAL ANALYTICAL TECHNIQUES

7.1. INTRODUCTION

So far friction tests only have been used to determine the processes involved in the lubricant activity. This chapter seeks to confirm the deductions that have been made, by the use of chemical analysis. Two areas for analysis were available. First the lubricant itself and chemical changes taking place within it. Second the chemical species present on the metal surfaces, particularly in the wear track. The former was investigated by using Infra-Red Spectroscopy and the latter by the use of X-ray Photo Spectroscopy and Electron Probe Micro Analysis.

7.2. INFRA - RED SPECTROSCOPY

This technique has wide application in the field of organic chemistry. The adsorbtion of infra-red light of a specific frequency by a substance indicates the presence of a particular chemical group. Most I.R.Spectrometers employ two samples and produce a differential spectrum, representative of the difference between the two samples. It is possible to obtain the spectrum of a substance by using air as the other sample in the spectrometer.

I.R. spectroscopy has been used by Fein (53) to identify the oxidation products of the lubricants formed during his friction tests. It has been employed to examine the lacquers formed on cylinder walls after long running. In this case the specimens were viewed differently, by a beam of infra-red light reflected off the metal surface. The beam thus passed through the lacquer twice, but the principles used in the analysis of the spectra were identical.

It was decided to use I.R. spectroscopy when it was realised how important oxidation of the lubricant was in the friction drop process. Samples were taken from certain tests, using a clean pipette. 2ml of lubricant was sufficient, and the sample was placed in a clean stopped glass specimen tube. This was then placed in the ice compartment of a refrigerator, to freeze the lubricant. Pure hexadecane freezes at about 18C, although most samples were not pure and froze at a lower temperature. The actual depression of the freezing point could have been used to assess the molarity of the impurities present.

The samples were kept frozen until required for analysis in the spectrometer. This precaution prevented the oxidation process from continuing. All the analysis were performed by Mr. R. Chater of Analytical Services Laboratory, Imperial College. The samples were taken from experiments, as in section 6.4., in which the temperature was raised and lowered according to a set pattern. There were two reasons for doing this. Firstly in these experiments a reasonable quantity of lubricant remains at the end of the test (in most other cases the test was terminated when most of the lubricant had evaporated). Secondly this ensured that all the lubricants had the same thermal history. Fig.7.1. is a table indicating from which experiments the samples were taken.

LUBE NO.	Taken from expt. shown in Fig.	at Start or at End	Basic Composition
1	6.5. control	Start	Hexadecane
2	"	End	" + Ox.products
3	6.5. ($2\frac{1}{2}$°C min^{-1})	Start	Hex. + 1% DBDS
4	" "	End	" " + Ox. products
5	6.7.	Start	Hex. + 1% DBDS + Ox.products
6	6.16.	Start	Hex. + 1% DBDS + 0.1% Np1n.
7	6.16	End	Hex. + 1% DBDS + 0.1% Np1n + Ox. products

Hex. = hexadecane Ox. = oxidation

Np1n = N phenyl 1 naphthylamine

The analyses are listed by their spectrum no. so:

132 - Lube 1 and 2

133 - Lube 3 and 4

134 - Lube 3 and 5

136 - Lube 6 and 7

Fig. 7.1.

The four spectra of transmittance (T) plotted against frequency (f), are reproduced in Fig.7.2-5 respectively. They have been reduced (3x) and unfortunately lost some detail. In fact in performing a full analysis, Mr. Chater produced several spectra for each sample, taking particular care over certain sections of interest. His report is given in full as appendix A, and it is unnecessary to go into further detail here. His conclusions, with some comments added were thus:

1) Hexadecane, which had been used in a friction test on its own, contained considerable amounts of oxidation products. A mixture of alcohols, esters, ketones and aldehydes is the likely composition of the impurities. The acid was not detected, but any acids that were formed would be expected to react with any alcohol.

2) A 1% solution of DBDS in hexadecane oxidises when used in a friction test to form very similar products to those above, except the hydroxy (OH) group is not apparent. Therefore alcohols are unlikely to be present. Also the sulphoxide (S=O) group can be infered, which implies oxidation of the DBDS to form aromatic sulphoxides or di-sulphoxides.

3) When a 1% solution of DBDS in hexadecane is heated to 200C and exposed to the atmosphere it too is oxidised, but to form slightly different products than found in (2) above. The aromatic sulphoxides were hardly detectable and the solution appeared to contain a mixture of carboxylic acids and their ester derivatives.

4) When a 1% solution of DBDS in hexadecane is treated with 0.1% N phenyl1naphthylamine and then employed in a friction test, the effect of the I.R. spectrum is quite marked. The oxidation products mentioned in (3) had decreased by a factor of about 8. A decrease in the amount of DBDS and N phenyl1naphthylamine in sample 7 compared

Fig. 7.2

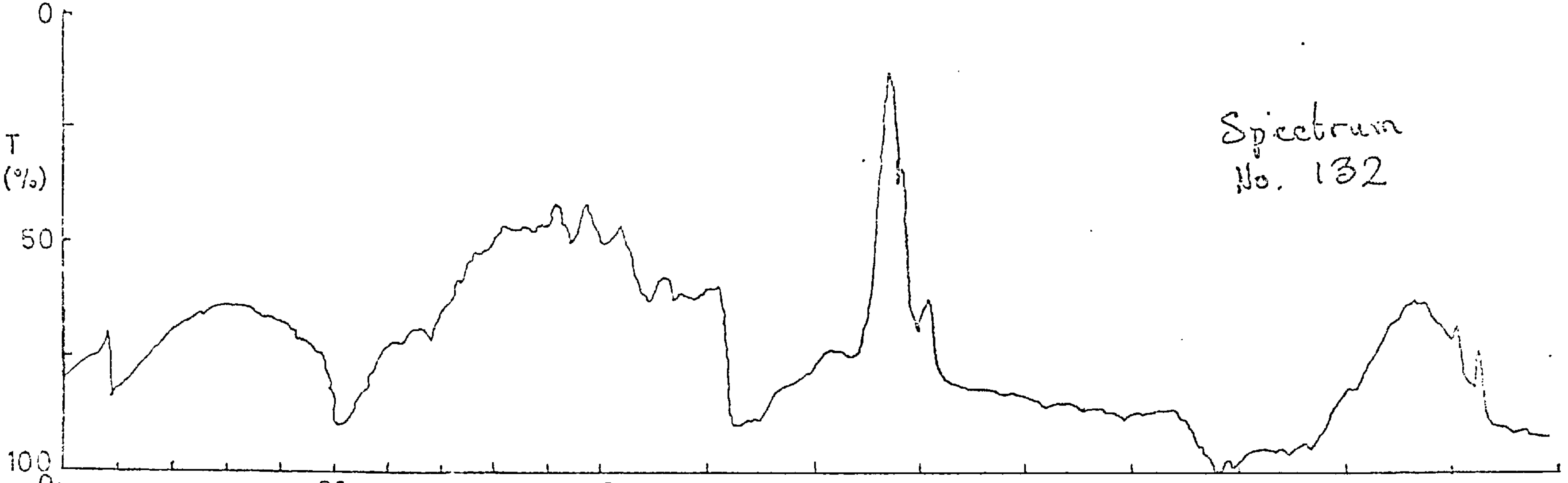
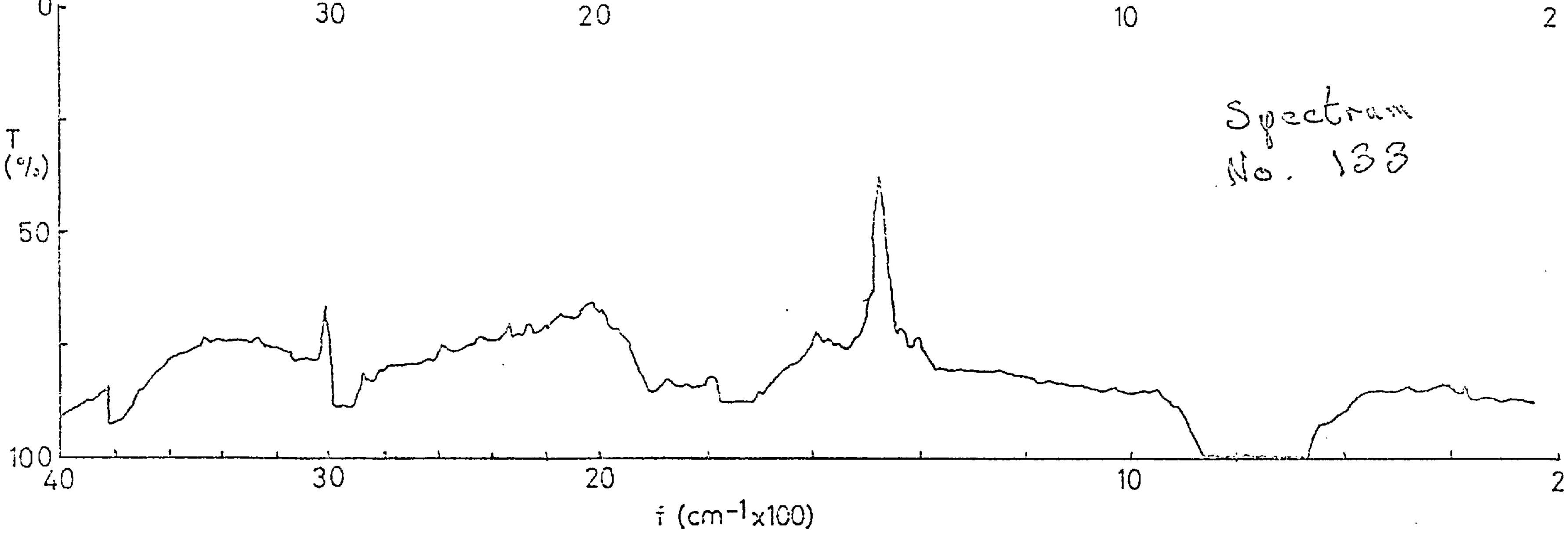

T (%)
0
50
100
30
20
10
2
Spectrum No. 132

Fig. 7.3


T (%)
0
50
100
40
30
20
10
2
f (cm-1x100)
Spectrum No. 133

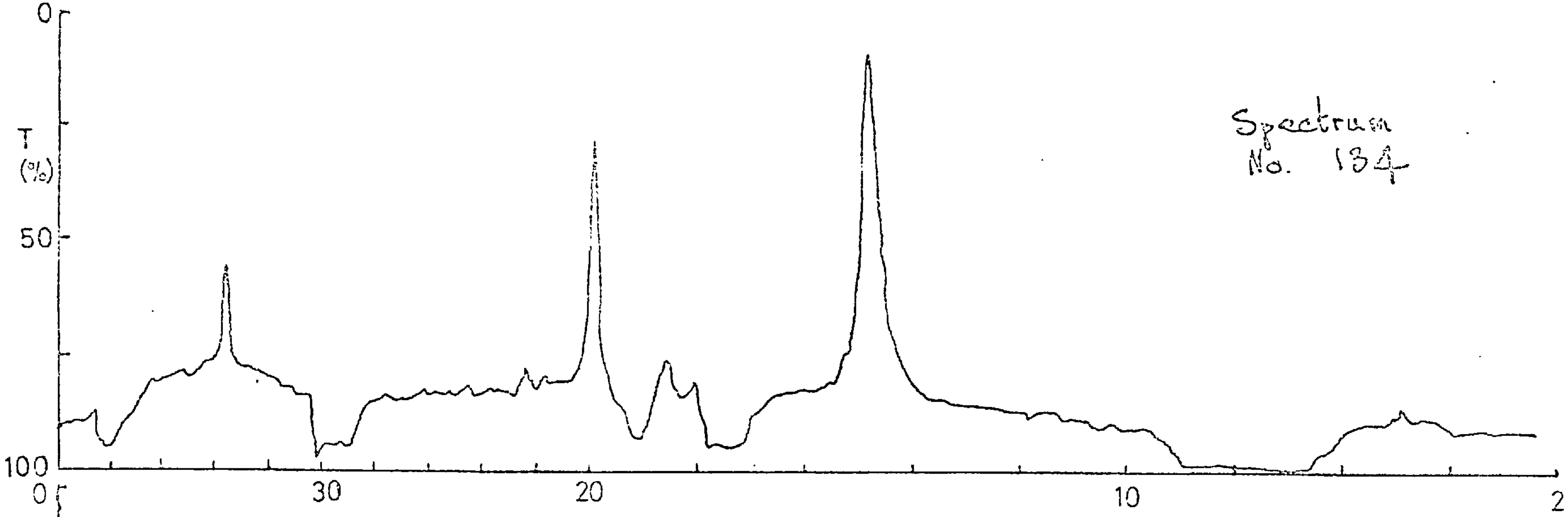

0
T
(%)
50
100
0
30
20
10
2
Spectrum
No. 134

Fig. 7.4

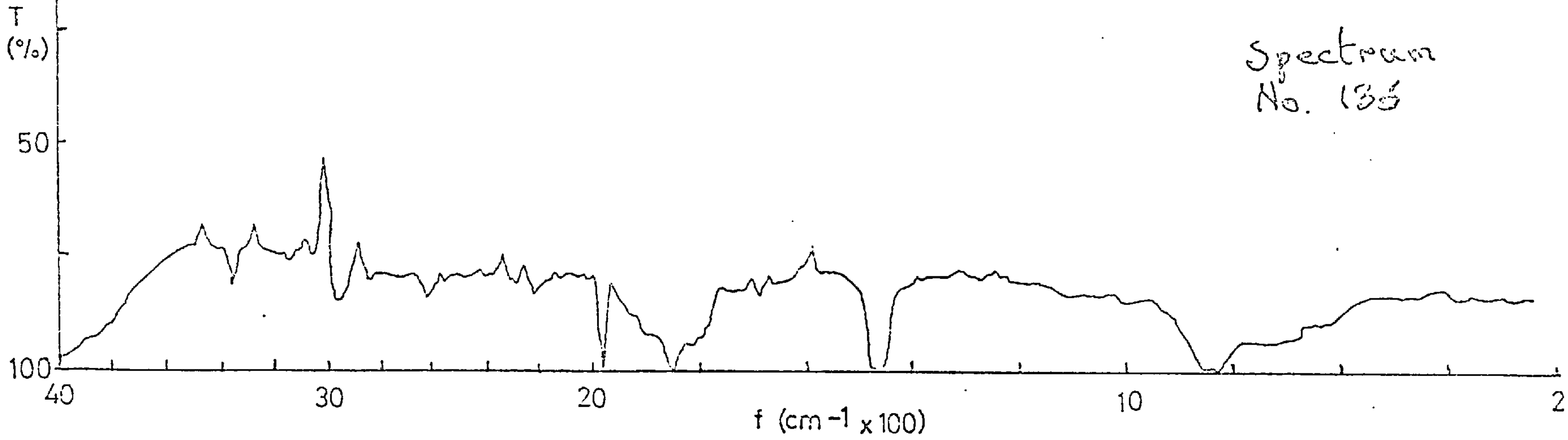

T
(%)
50
100
40
30
20
10
2
f (cm -1 x 100)
Spectrum
No. 136

Fig. 7.5

with sample 6 was also detected. Certainly the N phenyl^{1}naphthylamine appeared to reduce oxidation greatly.

All the results from the I.R. spectroscopy have confirmed the deductions made in the previous chapter regarding oxidation within the lubricant. There are some interesting aspects of the nature of the chemical group found, particularly the differences in those found in analyses (2) and (3). These may be due to the catalytic action of freshly formed metal surfaces as a result of the frictional processes, as mentioned in section 1.18. (Nevertheless no contradictory evidence to upset the conclusions of section 6.13. has been produced).

7.3. X-RAY PHOTO - ELECTRON SPECTROSCOPY

In this technique a sample surface, placed in a high vacuum chamber, is bombarded with soft x-rays of known energy. The upper atomic layers of the surface adsorb the x-rays and consequently photo-electrons are emitted. These electrons are collected and detected by an electron-multiplier, which is placed behind a set of plates charged to known voltages. These plates are arranged to filter the photo-electrons by their energy, and the voltages used are stepped over the required range so that the detector scans the emitted electrons according to their energy. The scanning is repeated until a sufficiently clear spectrum is obtained. The whole equipment is controlled by a digital computer, which processes the results, applies statistical constraints, and produces the final spectrum on a plotter.

An examination of the spectrum reveals not only which elements are present (in the top 2 nmof surface), but also the chemical bonding of each element. The technique can in theory give a quantitative indication of the atoms in the surface, because the number of electrons of that energy detected will be proportional to the concentration of those atoms with that energy. However this would require the number of scans to be precisely fixed, and also the other conditions of the analysis. Furthermore calibration, with an accurately known surface, would be needed. Comparison of the heights of different peaks cannot be used to indicate their relative proportions because the detector output is not uniform for all energies.

X-ray photo-electron spectroscopy has not been widely used in the field of lubrication research. Atkinson and Swift (95) have used the technique to assess the oxidation state of molybdenum disulphide used in their tests. More recently Baldwin (61) has examined the anti-wear properties of a group of sulphur additives. He employed a slightly different XPS machine, which analysed the whole of a cylindrical surface, that is the pins from a Falex wear test. He carefully controlled the conditions within the spectrometer, particularly the number of passes. In this way he could compare the relative heights of the sulphur peaks and so deduce the relative concentrations of sulphur on the surface in each wear test. He obtained a linear correlation between the amount of wear and the concentration of sulphide found at the end of the test. This was true for the different additives, and for a varying concentration of one additive. Fig. 7.6. shows the results with the different additives.

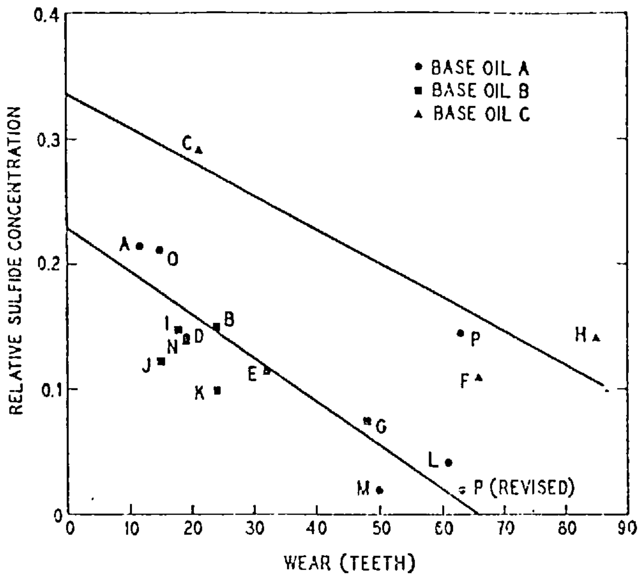


Fig. 4—Correlation between relative sulfide surface concentration and wear for compounds in Table 2.

Fig. 7.6. from ref.(61)

Unfortunately Baldwin had to assume that all the wear specimens had the same surface area, and that the different degrees of wear did not change this, by altering the surface roughness for example. Since the XPS machine gives a total count of the whole area, not a count per unit area, he had in fact compared amount of sulphide on the total surface with the degree of wear.

Baldwin's conclusions are nevertheless very important, both the correlation above, and the fact that the sulphur present was in the form of sulphide not sulphate. This indicates that oxygen may well not be necessary for the anti-wear action of the compounds.

To enable the XPS analysis to be used on the friction tests already described, some special specimens were prepared. A novel method was developed to allow sections of the track to be removed and placed in the spectrometer without touching or affecting the sensitive surface. This is essential, because the equipment only examines the top 2 nm of the surface and any contamination would radically affect the results. The previously used method of Bayles(60) of cutting a section out of the track at the end of a test, with an elastic cutting wheel was clearly impracticable. Therefore a number of 4.76 mm (3/16") diameter recesses were bored into one of the flat specimens of E.N.58 steel. These were bored to about 1mm in depth, but a pilot hole of about 3mm was drilled right through the flat specimen. This was to allow insets, fitted into the recesses, to be drifted out at the end of the experiments. These insets were parted off from 4.76mm (3/16") diameter E.N.58 bar, and pressed into the recesses as tight fits. The whole specimen was carefully reground and polished as previously. The insets were virtually indistinguishable from the rest of the surface, see Fig.4.11b.

The friction tests were conducted with the conditions as detailed in Fig.5.8a. and the results were as before, Fig.5.8b. The total load was 10 kg, the sliding speed 0.17 mm s^{-1}, the slider was an E.N.31 peg and the lubricant 1% dibenzyl disulphide in hexadecane. Two insets were analysed from different tests. The first was removed at the end of the friction test, when the temperature was about 220C and the friction had dropped. The whole flat specimen was removed from the trough and immediately plunged into acetone, in which it was cleaned and cooled. It was then taken out of the acetone, inverted over a clean specimen tube, and the inset tapped out via the pilot hole. The inset was rewashed in the tube using acetone, and the tube was then placed in a dessicator, filled with oxygen free nitrogen. This precaution was taken to prevent oxidation of the surface by the atmosphere. The second inset was prepared in exactly the same way, but that test was terminated at 170C, before the friction had dropped.

The XPS machine was operated by Dr. Chadwick of the Dept.

of Chemical Engineering, Imperial College, who kindly arranged for the analysis and supervised it. The machine, which has been specially built for the department, works exactly on the principles outlined above. A sufficient number of scans were made and averaged to produce statistically significant results. A standard spectrum from zero eV to 973.5 eV was performed and then the range from 154.5 eV to 179.1 eV was repeated and magnified. This provided a more accurate spectrum referring to the sulphur region, and on the same graph a section from 274.5 eV to 299.0 eV was also shown to provide a reference energy. In this case the 285.0 eV emission of carbon was chosen. This reference is necessary not only because a small difference in a large number is being sought, but also because the analysis is being performed to the equipment limits and the recorded energy of the emission could easily be shifted by a small charge on the specimen for example.

Interpolation of the spectra is a simple matter. Figs.7.7a. and b. show the plots for the two insets, and Figs.7.8a. and b. the two magnified sections. It must be remembered that the vertical scales are indeterminate and only the horizontal position of the peak is of interest. In both cases the sulphur present gave a peak at 168 eV ± 1 eV. Baldwin gives the energies of the various emissions of sulphur compounds,

Fig.7.9. (from ref. 61)

Ferrous Sulphide	FeS	160.8 eV
Iron Disulphide	FeS_2	161.6 "
Elemental Sulphide	S_8	162.4 "
Dibenzyl Disulphide	Bn_2S_2	162.8 "
Sodium Sulphite	Na_2SO_3	165.8 "
Ferrous Sulphate	$FeSO_4$	168.3 "

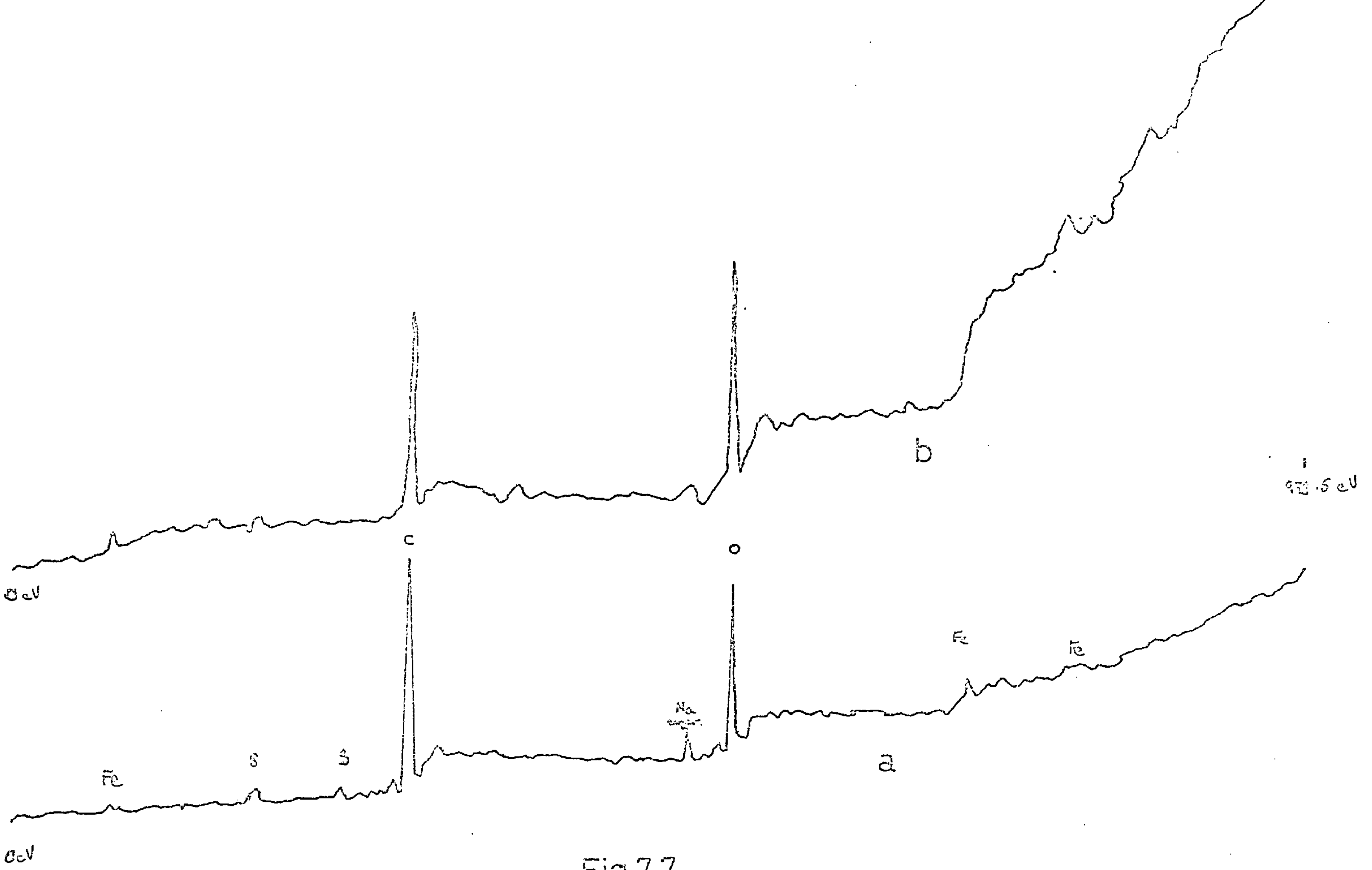


Fig.7.7.

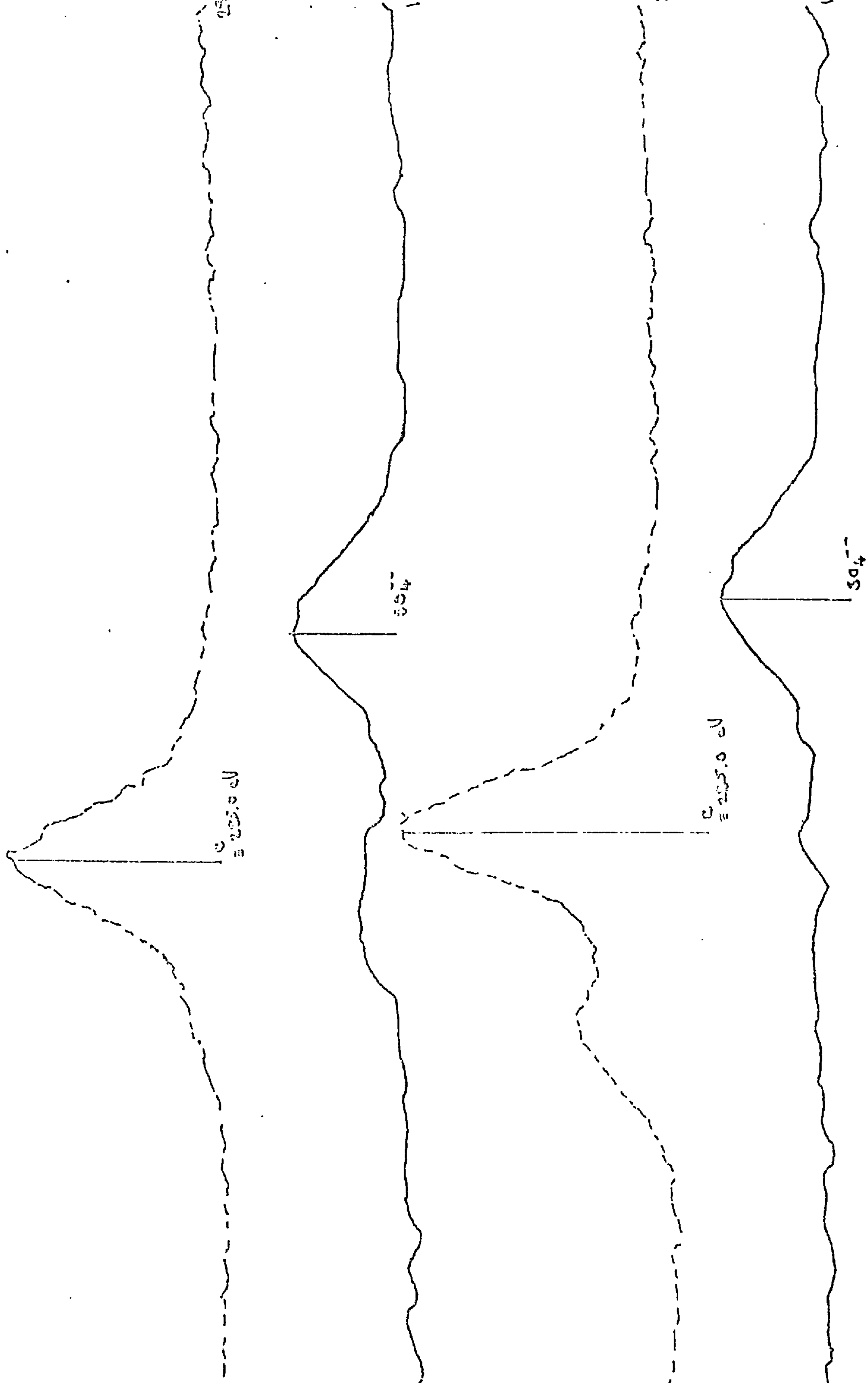

274.5 eV
299.0 eV
C
≡ 285.0 eV
154.5 eV
179.1 eV
SO_4^{--}
274.5 eV
299.0 eV
C
≡ 285.0 eV
154.5 eV
179.1 eV
SO_4^{--}
a
b

Fig. 7.8.

It may be easily seen that the sulphur on the surfaces of both insets is in a high oxidation state, probably as sulphate. It is certainly not present as either iron sulphide, free sulphur, or adsorbed dibenzyl disulphide. It may also be concluded that there was no detectable change in the oxidation state, and therefore the chemistry of the sulphur, during the friction drop.

These results confirm the general ideas produced earlier. If the sulphur had been found to be present as sulphide this would be most surprising considering the evident extent of oxidation occurring in the lubricant. Baldwin did find sulphide present, but it must be remembered that in his wear tests, the specimens are much more enclosed and there was little chance for the lubricant to be oxidised by the atmosphere. The spectra also revealed the presence of iron, carbon and oxygen as expected, the sulphur peak is quite small and it may be deduced that little sulphur was present.

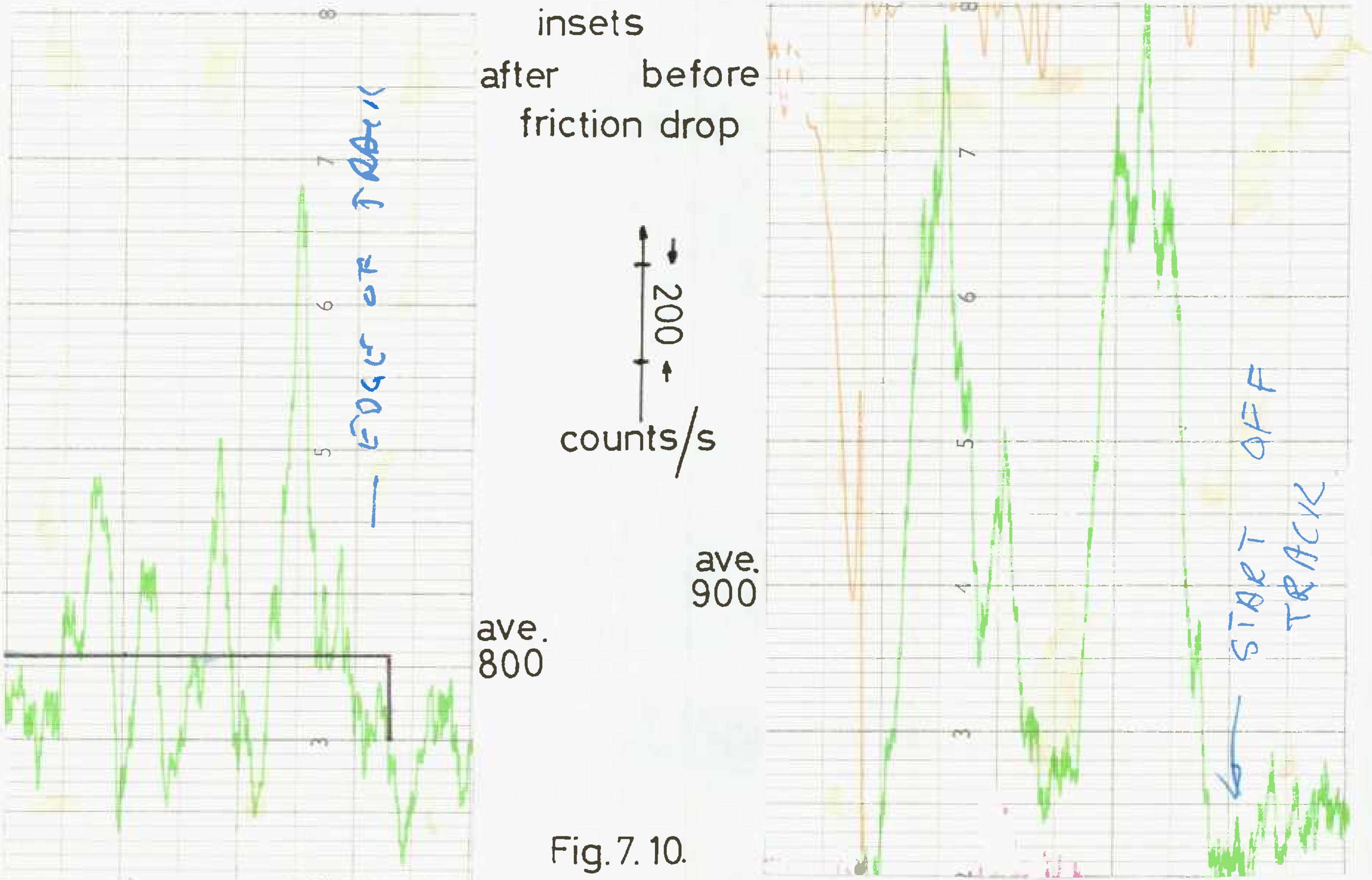
7.4. ELECTRON PROBE MICRO ANALYSIS

This technique has been more widely used than XPS, for example Allum and Forbes (58), Roberts (59) and Bayles (60). It too uses a high vacuum chamber, but in this case a beam of electrons is fired at a point on the specimen. The frequency of the resulting x-ray emission is characteristic of the particular element present. These emissions are detected by two spectrometers mounted on either side of the vacuum chamber, which are 'tuned' to a particular frequency by means of internal gratings. Thus the element of interest (or possibly two elements) only is detected. The beam of electrons is very small, less than 1 µm diameter, but may be traversed across the specimen by means of a lead screw. A larger portion of the specimen may be viewed via an optical microscope arrangement. The strength of the emission as detected is amplified and fed into a pen recorder. The analyser measures the presence of the element upto a depth of about 2 μm. However the surface layers are very much thinner than this, and although the EPMA may be calibrated with a solid block of the element, only a relative estimation of the amount of sulphur may be made in this instance.

The same insets as used in the analysis of the previous section were used, as were the two pegs from the same two tests. All the tests were carried out by Mr. Bird on the EPMA, Analytical Services Laboratory, Imperial College.

Sections of the four traces obtained are shown in Figs.7.10a.-d. In each case the trace starts a little below the edge of the wear track as viewed in the optical microscope. The average count, for a length of trace referring to within the wear track, is also shown. The apparent sulphur concentrations were all low when compared with those that had been obtained by Bayles (60) or Beynon (77). The unevenness of all the traces is due in part to the topographical variations in the surface which affect the degree of the emitted rays that are detectable.

The important conclusion from these tests is that there is no significant change in the amount of sulphur on the surface, between the start and end of the friction drop. This is in agreement with very recent work of Bayles (96) in that the sulphur levels on the metal surfaces in such tests as these, rapidly reach a limiting value as the temperature is raised.


insets
after
before
friction drop
200
counts/s
ave.
800
ave.
900
EDGE OF TRACK
START OFF TRACK
8
7
6
5
4
3

a

b

Fig. 7.10.

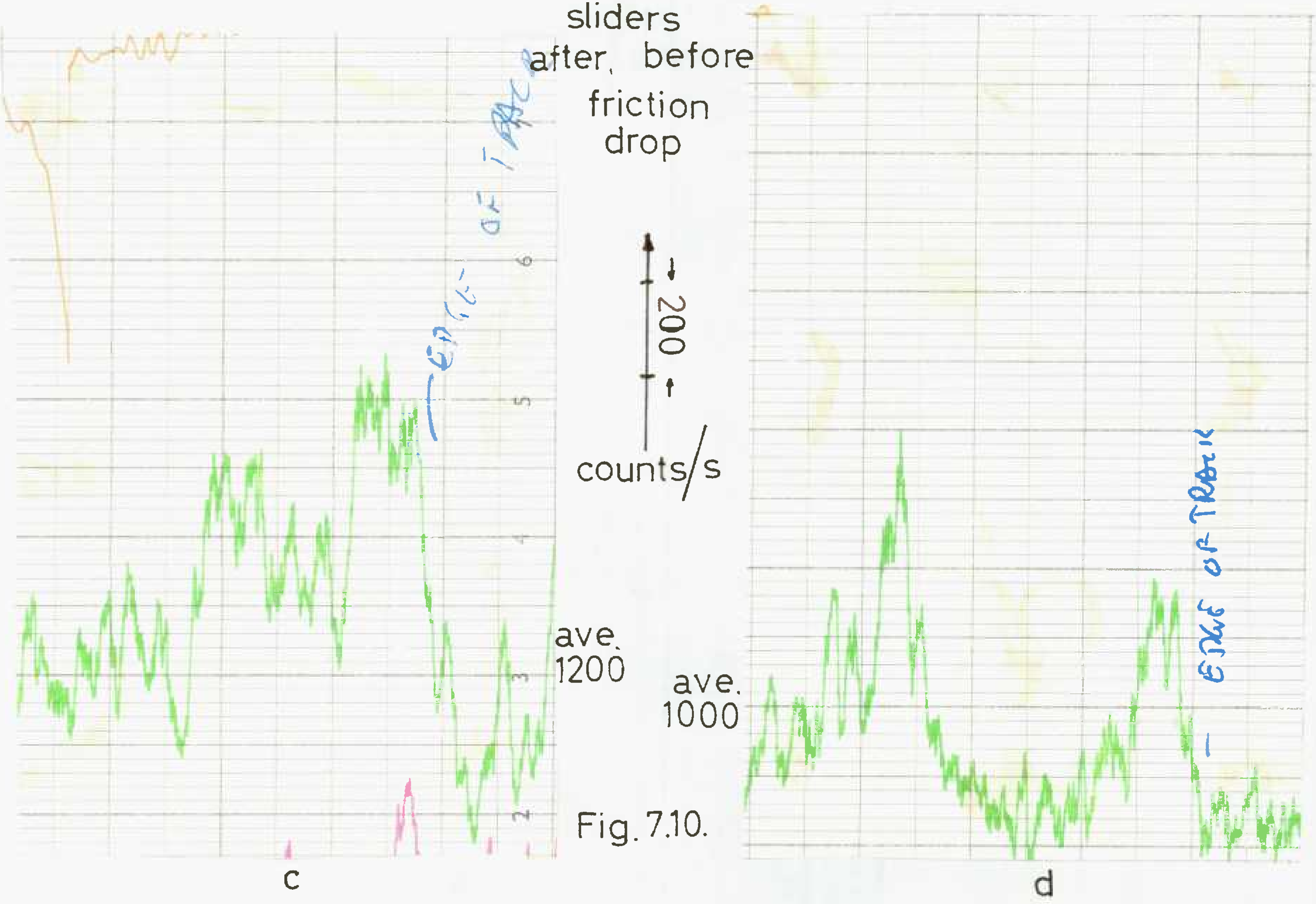

sliders
after, before
friction
drop
200
counts/s
ave.
1200
ave.
1000
6
5
4
3
2
EDGE OF TRACK
EDGE OF TRACK
c
d

Fig. 7.10.

7.5 SUMMARY

The analyses of this chapter have added considerable evidence to confirm the ideas arising out of the tests of the previous chapters.

I.R. Spectroscopy has revealed the presence of a variety of oxidation products, and provided some pointers to their likely composition. Most importantly it has indicated the effect of the oxidation inhibitor N phenyl 1 naphthylamine on these products. Its action, which previously might have been considered to have been due to preferential adsorption on the surfaces, is more clearly seen to be by reducing the oxidation reactions occurring.

X-ray photo-electron spectroscopy has shown that the sulphur on the surfaces is in the form of sulphate, both before and after the friction drop. Electron probe microanalysis has confirmed that the sulphur present is in small quantities that do not change significantly during the friction drop.

CHAPTER 8

SUMMARY OF CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

8.1. INTRODUCTION

The experiments described in this thesis have investigated as thoroughly as was possible, the action of an E.P. additive in a slow speed friction test. A wide variety of mechanical factors have been examined, and an interesting effect of sliding speed discovered. However,more interest lies in the chemical factors which play a larger part in governing the temperature at which the observed friction drop occurs.

Making definite conclusions from the results of these tests has not been easy. This has usually been because of a lack of comparability between the friction traces. Indeed one of the first conclusions to be made is that the tests were employed to determine the temperature at which the friction dropped from a 'high' to a 'low' value. However in normal terms the 'high' value would cause catastrophic failure, and the 'low' one would be considered excessive. This means that the use of this temperature to assess the lubricant's performance must be somewhat dubious. It has long been known that a change from adhesion to smoother sliding may be effected by small changes in the lubricant. Tabor (18) in 1941 described the same effect which he considered was due to oxidation of the oil. Therefore the "success" point of a lubricant cannot readily be applied to a high speed system. Neither will the rubbing conditions be comparable, nor the mechanism of action of the lubricant in the two systems.

8.2. VALUE OF SLOW SPEED TESTS

The value of slow speed tests lies in the certainty with which the load, temperature and other conditions are known. The application of analytical techniques, such as are described in Chapter 7, may allow a full understanding of the lubricant's activity in this context to be gained. This comprehension could be applied to a high speed system of similar chemistry.

If slow speed tests are to be used with E.P. additives, several conclusions from the earlier chapters will apply.

1) The precise rubbing conditions employed are not critical, except with the possibility of sliding speed, and the track length. Multiple pass tests must be used of course, and a long track will increase the liklihood of initiating surface damage which can grow and so alter the rubbing conditions.

2) The thermal history of the lubricant is of major importance. In any work at elevated temperatures the bulk reactions within the lubricant are likely to affect its performance. There is no simple way to simulate the flash temperatures generated in a high speed system, in a slow speed test. Raising the bulk temperature may create more problems than it solves.

8.3. LUBRICANT ACTIVITY IN THESE TESTS

The simplest explanation for the observed results takes into account the following findings:

1) DBDS is required to cause the friction to drop.

2) The temperature of the drop is governed by some reaction, in the lubricant, and is not much affected by the dynamics of sliding. This reaction reaches equilibrium relatively quickly at all temperatures and is most sensitive to oxidation (degradation) of the additive.

3) Oxidation of hexadecane produces substances which can maintain a low coefficient of friction in these tests.

4) Surface analysis has shown that neither the amount nor the chemistry of the sulphur on the surfaces changes during the friction drop.

The following conclusions may be drawn:

1) The O.C.T. hypothesis suggested by Bayles (60) is no longer tenable.

2) Unlike the evidence from high speed tests (58,60), the action of the DBDS is not by the formation of a low shear, sulphide film on the friction surfaces.

3) This technique cannot be used to predict the high speed test performance of an E.P. additive.

4) The reduction in friction is due to the presence in sufficient quantities of some chemical species, as yet undefined, on the friction surfaces. It is most likely some reaction product of the DBDS formed within the lubricant. An oxidation inhibitor delays its production. This product may require oiliness agents to adsorb onto it before the friction will be reduced.

It is worth considering that the action of DBDS in a high speed system could require its oxidation before it takes effect.

8.4. EFFECT OF SLIDING SPEED

So far it has not been possible to prove conclusively the cause of the effect of sliding speed. However it may be remembered that the conditions of the slider are more severe than those of the track, since it is continuously rubbed. Also that if the real area of contact is determined by the load alone, then the work done on unit area of the contact will vary very much with the sliding speed. Thus when the sliding speed is higher, a thicker surface film will be required to prevent the metal surfaces from breaking through and continuing the adhesive process. This could well account for the higher temperatures of the friction drops at the higher sliding speeds.

8.5. SUGGESTIONS FOR FURTHER WORK

Several important pointers to the chemical reactions taking place in the lubricant have already been produced. It would be worth conducting a full set of friction tests, from which samples were taken and analysed using the techniques described in Chapter 7. Additionally, thin layer chromatography could be employed to assist in identifying the various chemical species. This technique has already been tried out as previously mentioned (90).

The determination of the particular substances which cause the friction drop would then allow the action of these substances to be tested independently. In this way the activity of the lubricant in a high speed test might be better understood as, at least some, links in the causal chain of its action can be specified.

APPENDIX A

REPORT ON I.R. SPECTRAL ANALYSIS

Method:- Samples were analysed by differential I.R.Spectral Analysis. The sample was placed in the sample beam in a $\frac{1}{2}$mm nom. KBr Transmission cell. The control for that sample was placed in the reference beam of the spectrometer in a $\frac{1}{2}$mm nom. KBr Transmission cell. The cells were a matched pair. The differential spectrum was recorded initially and details of that spectrum were re-run at a slower scan speed.

For refence and interpretation purposes, absorption spectra of Lubes 2, 3 and 5 (blue traces) are recorded on the same spectra.

Precautions:- 1) Samples were removed from the fridge, warmed using hot (60^{o}C) water and used immediately. No sample remained out of the fridge for more than 3 hours.

2) Cell path lengths were measured to check their degree of match. The same cell was used for all samples and the same cell for all controls.

3) Cells were cleaned with chloroform between different samples in a process that included evacuation of the cell.

Instrument an Conditions:- P-E 621 Grating Spectrophotometer. See traces for conditions.

Results:

ASL 11947 :- Spectrum No. 132

ASL 11948 :- Spectrum No. 133

ASL 11949 :- Spectrum No. 134

ASL 12141 :- Spectrum No. 136

(1) Despite being matched cells, the imbalance is indicated by the blank (red trace)

(ii) Peaks occurring at 1209, 754 and 664 cm^{-1} in Spec. 132 are due to Chloroform ($CHCl_3$)

Interpretation:- Peaks occuring in positions where transmission is 5%T were treated with caution in the interpretation of the spectrum.

Spectrum No. 132

(i) Functional group (C=O) is infered from peaks at 1723, 1739 and 1792 cm^{-1}; C=O Str. vibration.

(a) If this peak were due to a Carboxylic Acid, a peak or two of equal intensity would be expected for the C-O group. Also, as the acid would be expected to occur as a dimer or in greater association, a broad peak in the region 2700-2500 cm^{-1} (H- bonded O-H Str.vib.) and in the region 950-890 cm^{-1} (O-H def. vibration) would be expected. Therefore Carboxylic Acids do not account for the peaks at 1723 cm^{-1}.

(b) Esters would also require a peak or two for C-O (1300-1160 cm^{-1}) as intence as that due to C=O. However the split for C=O Str. vib. peak may be a or Keto-Ester. For a long chain Aliphate Ester, the C-O Str. vib. may give the peak at 1179 cm^{-1}.

(c) The position of the C=O group peak indicates the posibility of Ketones or Aldehydes being present. The peak at 1792 cm^{-1} may be a highly strained 4 member ring Ketone or Diketone.

(ii) Long chain molecules are suggested by peaks at 1323 and 1240 cm^{-1} of C-C group Str. vibration. There is no distinct peak in the spectrum associated with skeletal vibrations again suggesting long chain molecules.

(iii) Range 3600-3200 cm^{-1} contain 3 peak tentatively associated with O-H Str. frequencies.

(a) At 3630 cm^{-1}, sharp peak suggest free O-H Str.vibrations of a Secondary Alcohol in very dilute, non-polar solution.

(b) At 3555 cm^{-1}, sharp peak is due to OH Str. vibration where the group is very regularly intramolecularly associated.

(c) Broad band at 3420 cm^{-1} is intermolecularly associated O-H Str.

vibration of the alcohol, although it may be partly due to the C=O group overtone at 3446 cm^{-1}.

Taking (a) and (b) together suggests a Diol.

(iv) The presence of unsaturated groups is inferred from the weak peak at 1620 cm^{-1}.

Spectrum No. 133

(i) Functional group C=O inferred from peaks at 1724, 1764 and 1794 cm^{-1} (C=O Str. vibration).

(a) There is no peak of similar intensity to that for C=O which may be assigned to the C–O group.

(b) In contrast to Spec. 132, free or H- bonded vibration of the O–H group are absent.

From (a) and (b) and the position of C=O Str. vib. at 1724 cm^{-1} Sat Aliphatic Aldehydes and Ketones are present. Further evidence is obtained from

(1) 1406 cm^{-1},:- CH_3 def.vib. in $-CH_3$-CO- Ketone group.

(2) Aliphatic Aldehydes may give rise to both 1325 cm^{-1} and 1406 cm^{-1} peaks (Range 1440–1325 cm^{-1}).

(3) Multiple peak of (C–C) Str.vib. of Aliphatic Ketones are found in the region 1200–1115 cm^{-1} where there are 4.

(c) Compared with Spec 132, the peak at - 1730 cm^{-1} is not similarly split but the possibility of an Ester being present should not be ruled out. The peak at 1175 cm^{-1} could be assigned to (C–O) Str. vib. of an Ester.

(ii) The spectrum indicates the presence of aromatic rings in the products.

(a) Peak at 694 and 760 cm^{-1} is (C–H) deformation O.O. plane vibration in Monosubstituted Benzene ring.

(b) (C=C) in plane deformation vibration is present at 1604, 1493 and 1440 cm^{-1}.

(iii) The possibility of the group (S=O) is suggested by the relatively sharp peak at 1030 cm^{-1}.

(iv) No single peak could be identified with the (C-S) Str. vib. suggesting that the (C-S) group does have an adjacent C=O group and that it is probably present in the group C-S=O or $C-S\overset{=O}{\underset{=O}{}}$.

Spectrum No. 134

(i) Funtional group (C=O) is inferred from peak at 1723 cm^{-1}. This peak is split with a shoulder at 1745 cm^{-1}.

(ii) Peak at 1218 cm^{-1} is single and as strong as the peak at 1723 cm^{-1}.

(a) The C-O group in Esters or Carboxylic Acids are expected to give multiple (min.2) peaks in this region (1320-1210). However, if the peak is due to (C-O) Str. vib. then the absence of intence (O-H) absorbtion peaks due to deformation or H-bonded stretch vibrations would indicate a high Aliphatic Ester. Peaks at 1348 cm^{-1} and 1408 cm^{-1} being C-H deformation vibrations of the diphatic chain.

(b) The peak could also be assigned to (C=S) Str. vibration.

(iii) The peak at 528 cm^{-1} is thought to be a deformation mode of the Carboxyl group CO.O although it may also be assigned to the deformation vibration of the C-S=O group.

(iv) Benzene Rings vibrations are not detected in the spectrum except very marginally at 680 cm^{-1}.

Conclusion:-

Spectrum 132

Oxidation products were detected in the Lube No.2 by differential I.R.Spectral Analysis. From the spectra, the functional groups (C=O) and (O-H) are identified and also possibly (C-O), (C=C) and (C-C). The products are thought to be a mixture of Alcohols,

Esters, Ketones and Aldehydes.

Spectrum No. 133

Oxidation products were detected in the Lube No.4 by differential I.R. Spectral Analysis. From the spectra, the functional groups (C=O) and monosubstituted benzene ring are identified and (C-O), (C-C), (S=O) infered. The products are thought to be a mixture of Ketones, Aldehydes, Esters and Aromatic Sulphoxides or Di-Sulphoxides.

Spectrum No. 134

Oxidation products were detected in the Lube No.5 by diffential I.R. Spectral Analysis. From the spectrum, (C=O) group is identified. Tentative assignments are made for (C-O), (S-O) and (S=O) groups. The products are thought to be a mixture of Carboxylic Acids and their Ester derivatives.

Spectrum No 136

Peaks occuring in positions where Transmittance 5% were treated with caution in interpreting the spectrum.

(i) Peaks at 1722 cm^{-1} (shoulder at 1744 cm^{-1}), 1216 cm^{-1}, 526 cm^{-1} are absent it the sample spectrum relative to the control. These peaks match closely those associated with the oxidation products of Lube No.3 seen in spc. 134 (peaks at 1723 cm^{-1} with shoulder at 1745 cm^{-1}, 1218 cm^{-1}, 528 cm^{-1}). Interpretation of these peaks as for spectrum 134. The oxidation products in spectrum 134 are approx. 8 times the concentration of these products in the sample spectrum 136.

(ii) The peak at 468 cm^{-1} is associated with (S-S) in Dibenzyl Disulphide. The concentration of this additive in the sample spectrum 136 has decreased by approx. 1/10 of its original value.

(iii) The peaks at 1602 cm^{-1} and 1580 cm^{-1} is associated with (N-H) of the additive N Phenyl-1-Naphthylamine. The concentration of this additive in the sample spectrum 136 has decreased.

(iv) The decrease in the concentrations of the two additives in the sample spectrum 136 cause the appearance of peaks at 1959, 1940, 1890, 1871, 1068, 1028, 760, 894 and 563 cm^{-1} in the difference (green) trace.

Conclusion:-

By differential I.R. Analysis, Lube 7 was found to show a decrease in the concentration of additives compared to the control, Lube 6. Also Lube 7 was found not to contain those Carboxyl Containing impurities present present in Lube 6. These impurities gave a similar I.R. spectrum as the oxidation products found in spectrum 134.

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Nov. 1975 Feb. 1976

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