KINETICS OF
EXTREME-PRESSURE LUBRICANT ADDITIVES.

by

Andrew Allan Bayles

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Lubrication Laboratory, Department of Mechanical Engineering,
Imperial College of Science and Technology,
London, SW7 2BX.

ABSTRACT

This thesis has investigated the kinetics of the reaction between steel surfaces and a simple E.P. oil, Dibenzyl Disulphide in cetane, by examining the friction-temperature characteristics of the metal-lubricant system on a variable, slow-speed, ball-on-triplane machine.

A theoretically derived relationship linking sliding speed with transition temperature has been confirmed experimentally and values for the Activation Energy of the reaction and the Heat of Adsorption of the additive to the surface have been obtained. A mechanism is proposed to explain the observed kinetic behaviour.

The function of the E.P. film in preventing scuffing failure at high speed has been examined from a kinetic stand point.

It is suggested that lubricant failure is governed by a balance between the rate of reaction of the additive with the surface and the rate of removal of the E.P. film from the surface.

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NOMENCLATURE

R	Gas Constant
T	Temperature (^{o}K)
T_R	Reaction Temperature (^{o}K)
T_S	Skin Temperature (^{o}K)
T_T	Transition Temperature (^{o}K)
$\Delta T\ max$	Maximum Flash Temperature
$[dbds]$	Surface Concentration of Additive
$[DBDS]$	Bulk Concentration of Additive
$[Fe]$	Surface Concentration of Iron
$[FeS]$	Extent of E.P. Reaction (Reaction Product assumed to be FeS for simplicity)
k	Rate constant
k_{OBS}	Observed rate constant for the reaction
k'	True rate constant for the reactions
b	Adsorption coefficient $= \frac{ka}{kd}\ e^{\frac{\Delta H}{RT}}$
ka	Rate constant; adsorption process
kd	Rate constant; desorption process.
Ea	Apparent Activation Energy
Ea_{LOW}	Energy of Activation for the reaction at low additive coverage
Ea_{HIGH}	Observed Energy of Activation for the reaction at high coverage
ΔH	Heat of Adsorption
t	Reaction time
A	Pre-exponential of Frequency Factor
V	Sliding Speed

CHAPTER ONE

LITERATURE REVIEW

1.1 INTRODUCTION

The lubrication of two surfaces which are sliding past each other may be obtained by interposing between the surfaces, a layer of some material which can be sheared without causing any damage to the surfaces. The layer firstly prevents opposing asperities coming into metallic contact; thus welding and tearing. Secondly it serves to reduce the friction between the surfaces, though this is a secondary requirement.

In a simple system consisting of two surfaces moving past each other in the presence of a lubricant, there are several lubrication regimes. When the surfaces are separated by a relatively thick film of fluid, which usually occurs under conditions of low loads and high sliding speeds, then metal-to-metal shear is replaced almost entirely by fluid shear and thus frictional behaviour is determined by the fluid properties of the lubricant. In this region the coefficient of friction is very low and surface wear is negligible. Lubrication under these conditions is termed "hydrodynamic".

When contact pressures are high, then the viscosity of the lubricating oil is affected by the pressure and elastic distortion of the surface occurs. This is the regime of "Elastohydrodynamic" lubrication.

At higher loads, or lower sliding speeds, to maintain a complete fluid film between rubbing surfaces is not always possible and the hydrodynamic film may be thinner than the surface asperities which penetrate the lubricant. This type of lubricated sliding is called "Boundary" lubrication and is effected by films formed on the contact points by physical or chemical interactions between the metal and active molecules in the lubricant fluid. Since a pure hydrocarbon cannot undergo such an interaction, agents must be added before it can function as a boundary lubricant. In normal mineral oil there is some surface-active material which is a good boundary lubricant.

Under intermediate loads, so-called "Anti-Wear" (A.W.) additives are considered to function by forming adsorbed films on the rubbing surfaces. Typical anti-wear additives are long-chain fatty acids, esters and amines, though since adsorption is the key to this regime, many long-chain polar molecules are effective to some extent.

As the pressure on the contact points increases further and contact temperatures increase, there is a lesser tendency for adsorbed films to remain on the surface and the anti-wear films break down. In order to provide boundary lubrication under these conditions, it is therefore necessary to form a more stable "Extreme-Pressure" (E.P.) film. It is with extreme-pressure lubrication that this thesis is concerned and some of the literature in this field is now briefly reviewed.

1.2 EXTREME-PRESSURE LUBRICATION

The term "Extreme-Pressure" lubrication is perhaps misleading since presumably the pressure per unit area on the actual contacting surfaces does not change with loading, rather the increased pressures result in increased contact areas. This concept was explored by Bowden and Ridler (1) who employed a dynamic thermocouple of a metal cylinder sliding over the surface of a dissimilar metal to show that even in well-lubricated systems, surface temperatures in the contact zone between sliding metals could approach the melting point of the metal. For these reasons it was suggested by Bowden and Tabor (2) that such "Extreme-

Pressure" lubricants might more accurately be termed "Extreme-Temperature" lubricants.

The property of certain elements to arrest the scuffing of metals and thereby increasing the load-carrying capacity of oils was noted in the early 1920's with the development of the hypoid gear in the automotive industry. An immediate need was created for E.P. lubricants and an empirical search for effective additives to oils was the most direct solution. Successful lubricants were found but in general, the fundamental mechanisms of their action remained obscure. Since that time, a large number of E.P. additives have been developed.

Prutton et. al. (3) and Musgrave (4) have reported that E.P. additives are principally lead or other heavy metal soaps and organic compounds of Sulphur, Chlorine and Phosphorous. Although phosphorous and chlorine additives form a very important class of compounds, they are not included in this review, which is restricted to compounds in which Sulphur is the only load-carrying atom.

Although the specific mode of action of such additives will obviously vary as to their chemical structure and composition, numerous investigators, (3 - 11) agree that an E.P. additive reacts chemically with the metal surfaces under thin film conditions to form a solid film of lower shear strength than the metal itself. It is this film which acts as the boundary lubricant.

Greenhill (5) has appropriately termed the E.P. reaction a "controlled corrosion" process, where temperature determines the extent of the reaction. It is well known in gear lubrication that an unreactive additive gives little protection - conversely, too high a reactivity is undesirable since chemical corrosion of the metals may be excessive. In order to limit corrosion, the additive must be chosen to react only when contact temperatures are dangerously high.

1.3 COMPOSITION OF THE E.P. FILM

Work by Mougey and Almen (6) in 1931 clarified the E.P. situation. They used a simulated rear-axle test rig and showed that in all cases where sulphur was the active ingredient in the extreme-pressure oil, the steel surfaces were covered with a black film which analysis indicated to be iron sulphide.

Later, several investigators adopted the approach of pretreating sliding members of test rigs with artificial chemical films and comparing the results with those obtained using untreated members.

Campbell (12) developed a very elegant method, consisting of a polished metal plate upon which was placed a slider resting against a stop on the plane which was tilted by a motor. When slip occurred between the slider and the plate, the movement of the plane was stopped: hence the coefficient of friction could be calculated from the angle of inclination of the plane when sliding was initiated. Films of iron sulphide were deposited on the plane and slider by immersion in sodium sulphide solution.

Results indicated that thin films of sulphide had little or no effect on friction force, but the coefficient of friction dropped sharply when a certain limiting film thickness was reached.

Similar results were shown by Baxter, Snow and Pierce (13) and Davey (14). These investigators used a four-ball lubricant testing apparatus (described elsewhere (15)) and found that pretreatment of the balls by various sulphide and chloride films led to marked increases in seizure load. It was concluded that the artificial sulphide films showed similar results to those obtained from oils containing active sulphur.

At the same time both Hughes and Whittingham (16) and Greenhill (5), using the apparatus described by Bowden and Leben (17) in 1939, observed that preformed films caused reductions in both friction and wear, though Greenhill pointed out that this reduction was never as great as that observed with good boundary lubricants. Davey and Campbell further noticed that the addition of paraffin oil to preformed sulphide layers resulted in a further lowering of the friction coefficient. This latter observation served to add extra weight to that of Bowden and Tabor (18), who in 1945 suggested that as the shear strength of sulphide films was not apparently low, friction at the surface would not be appreciably lowered unless fatty acids were also present. The authors put forward the theory that the sulphide film facilitated the adsorption of polar compounds on the surface. This was confirmed in a later paper by Davey (19) and more recently by Sakurai et.al. (20) who showed by autoradiography that iron sulphide films adsorb polar compounds more actively than surfaces of iron oxide.

In 1946, Prutton, Turnbull and Dhouhy (3) did some experimental work in a real lubricating situation. The hypoid gears in the rear axle of a motor car were "shock-tested" by first accelerating the car and then suddenly engaging the clutch. Chemical analysis made of the gear teeth and of the used lubricant after each test demonstrated that iron sulphide formed on the gear teeth was rubbed off into the lubricant during service.

The chemical composition of the E.P. film has been the subject of some recent controversy. Toguyachi and Takai, in a series of papers, (21 - 22) tested a variety of disulphides dissolved in paraffin oil in a four-ball machine to evaluate their E.P. properties and the influence of dissolved oxygen on their load-carrying capacities. It was found that with most of the compounds tested, the E.P. lubricating properties fell markedly when dissolved oxygen was removed from the oil. Little effect, however, was observed with dibenzyl disulphide. The authors concluded that dissolved oxygen played some part in the mechanism of boundary lubrication (21) and attributed this higher reactivity to oxidation of the metal (22).

In the following year, Godfrey (23) analysed both qualitatively and quantitatively the E.P. films formed on gear teeth by reaction with sulphurised mineral oils and showed that the major constituent was ferrosoferric oxide, whereas, iron sulphide was present in only small quantities. Godfrey suggested that sulphurised mineral oil promoted the formation of beneficial surface oxides.

Llopis and his co-workers (24) observing an increase in reactivity in the presence of oxygen, proposed that oxygen played a more complex role in the sulphuration reaction - possibly by influencing the formation of intermediate products which would then intervene in the surface reaction.

These seemingly contradictory conclusions were clarified by the work of Sakurai and his fellow researchers (25). From data obtained by X-ray analysis of surface films formed by reaction of several disulphides on a hot steel wire, they demonstrated that the chemical reactivity of the sulphur compound played a significant role in chemical reactions involved in corrosion. Oxidation reaction might predominate in the case of corrosion by disulphides less reactive towards iron, whereas with elementary sulphur, or dibenzyl disulphide, the sulphuration reaction would be predominant as these compounds have a higher chemical reactivity.

1.4 INVESTIGATIONS INTO E.P. ACTIVITY

So far it has been established that an E.P. additive functions by reacting chemically with metal surfaces at the elevated temperatures, generated in the contact. Numerous investigators (3, 24 - 31) have also shown that the performance of an E.P. additive depends to a large extent upon the reactivity of the additive towards the metal of the surface. Consequently, most researchers into E.P. lubrication have adopted the approach of measuring the extent of reaction between E.P. oils and metal surfaces.

Prutton and his co-workers (3) exposed various additive solutions to iron powder over the temperature range 150 - 250° C in an inert atmosphere. By chemical analysis of the reaction products, they were able to relate the reactivity of the additive with effectiveness in preventing seizure in "shock-tested" hypoid gears.

The problem with investigations of this nature, however,is that they are confined to relatively low temperatures compared to those already shown to exist (1) under conditions of incipient scuffing.

Levine and Peterson, (32) as reported by Barcroft, (33) achieved some success in simulating the high contact temperatures by heating steel discs to very high temperatures and dropping them into solutions of sulphur in cetane, though no reference was made in Barcoft's work, to results obtained by this method.

More recently, Barcoft himself (33) pioneered the method of electrically heating a thin metal wire immersed in an additive solution. The rate of reaction between the additive and the wire was estimated by observing changes in the electrical resistance of the wire with time. The temperature of the wire was varied by altering the driving voltage across it and was calculated from a knowledge of the resistance-temperature characteristics of the wire.

This technique effectively overcame the problem of bulk oil oxidation at the high temperatures of the experiments (up to 600° C), and was shown to be capable of measuring additive reactivities at more realistic temperatures.

Sakurai et.al. investigated the reaction mechanisms of sulphur (34), as well as chlorine, zinc dithiophosphate type (25), and binary systems of sulphur and chlorine (35), with iron and steel surfaces using the Barcroft method described above. X-ray analysis (25) of the reacted film demonstrated the dependance of effectiveness of a sulphur compound as an E.P. additive on chemical reactivity.

Investigations of this kind have only a limited usefulness. They are able to examine comparative reactivities of E.P. agents with metal surfaces under static conditions, but offer little insight into the mechanisms of formation of E.P. films on rubbing surfaces and their thickness and action in preventing scuffing.

1.5 EFFECT OF LOAD, SPEED AND TEMPERATURE ON E.P. FILM FORMATION.

Artificially produced radioactive materials have been available in quantity for only a few years but in that time they have been used as tools in many fields of research.

The radioactive isotope of an element has the same properties and hence follows the same chemical processes as the corresponding stable element..This enables the isotope to act as a radioactive label and allows the course of a reaction, or the uptake of an element to be traced. In this way, radiochemical methods have been found to be particularly useful in the field of extreme-pressure lubrication.. (20,21,24,26,28, 35 -41,45)

The first attempt to use a radioactive isotope of Sulphur (S^{35}) for this prupose was made in 1943 by Clark, Gallo and Lincoln, (36) who investigated the extent of sulphide film formation on various metal alloys using a tagged sulphurised olefinic hydrocarbon. Their work was largely exploratory but showed that sulphur-bearing films were formed even at low temperatures.

In 1957, Borsoff and Wagner (26), experimented by immersing preheated steel strips in a mineral oil solution of radiotraced debenzyl disulphide (dbds). Plots of film thickness against time demonstrated a sharply increasing reaction rate - particularly in experiments carried out at higher temperatures. The authors were unable to explain this autocatalytic behaviour but more recently, Sakurai, Sato and Ishida (34), noting a similar effect with dibenzyl disulphide, put it down to the formation of cracks or cleavage in the surface film.

Elliott, Hitchcock and Edwards (37) carried out similar tests using mild steel discs in solutions of tagged elementary sulphur and dibenzyl disulphide in mineral oil over the temperature range 100 - 200°C. Like Borsoff and Wagner, the authors showed that the reaction rate was highly temperature dependant. Unlike Borsoff and Wagner however, no anomalous behaviour was noted with dibenzyl disulphide. It was found instead that films built up steadily with time to reach an approximately constant thickness.

These "test-tube" investigations provided valuable information on the build up of E.P. films but added little to the explanation of the action of E.P. agents on actual rubbing surfaces.

Borsoff and Wagner (26) in work parallel to their static tests already described, were among the first to use a radiotracer method under dynamic sliding conditions, when they operated spur gears in a solution of radio-traced dbds in mineral oil.

Several very important observations were made. Firstly, it was found that the thickness of the film formed on the working surfaces increased with load but not with the duration of each test. Autoradiography of the gears established that film thickness was at a maximum where maximum sliding occurred. Finally, an equilibrium thickness, calculated to be of the order of 300Å was reached for each set of operating conditions, indicating that the film was continuously formed and rubbed off during service.

These observations have since been verified by the work of several investigators, though doubt still remains as to the magnitude of the thickness of the E.P. film.

Sakurai, Ikeda and Okabe (20) derived an expression to show that an equilibrium film thickness should be attained and verified this experimentally by a radio-tracer method.

In a later paper, (38) the same authors observed that this equilibrium thickness increased linearly with load over the range studied. It was also shown that a plot of film thickness against sliding speed reached a maximum and then decreased with increasing speed. The authors postulated that at the higher speeds there was insufficient time for the total readsorption of the sulphur additive swept off the surface during contact and thus the effective additive concentration was reduced.

Loeser et. al. (28) duplicated Borsoff's results using cams and tappets run in motor oils containing sulphur - 35 synthesized into zinc dialkyldithiophosphate. It was estimated that films were up to 50 layers thick. A similar value was obtained by Sakurai et.al. (20, 38) using S - 35 Sulphur compounds dissolved in cetane in a line-contact friction machine.

Hypoid gears were used in radio-tracer studies by Campbell (39), and by Barcroft and Daniel (40). Campbell used labelled dbds and found a steady thickness of 1000Å was reached on the driving faces whilst that on the coast side was about half this value.

Later, Barcroft and Daniel noted that sulphur penetrated the gear subsurface to a depth of 7000Å and suggested that a more realistic film thickness would be of the order of 3000 - 5000Å, - a value recently confirmed by Allum and Forbes (42), who used an electron probe to analyse the wear tracks formed on a four-ball machine.

1.6 THE MECHANISM OF E.P. ACTION

A mechanism for the E.P. reaction was first advanced by Prutton, Turnbull and Dlouhy (3) in 1946. These authors suggested that the reaction between sulphur-containing E.P. additives proceeded either directly or via an intermediate stage involving dissociation of the additive on the surface to give free sulphur which would then be available to react with the surface.

$$\text{(a)}\quad R-S-S-R+Fe \longrightarrow R-S-R+FeS$$

$$\text{(b)}\quad R-S-S-R \longrightarrow R-S-R+S$$

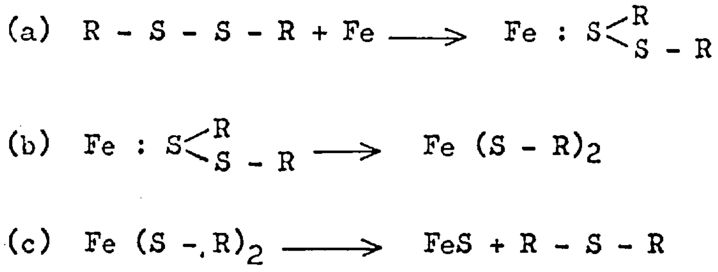
$$S+Fe \longrightarrow FeS$$

These mechanisms, represented schematically above for organic disulphides, gained some confirmation through the early work of Davey (8). However, in a later paper (43) the same author showed that the theory was an oversimplification and postulated that an iron mercaptide intermediate was first formed which then broke down to give iron sulphide. For the case of effective disulphides (eg dbds) a free radical mechanism seemed to operate as follows:-

$$R-S-S-R+Fe \longrightarrow Fe(SR)_2$$

$$Fe(SR)_2 \longrightarrow FeS+R-S-R$$

Davey suggested that this mechanism gained some support through the work of Schonberg (44), who had earlier demonstrated the ease with which the sulphur-sulphur bond was broken in disulphides. In 1957, Davey and Edwards (27), carried this theory further. From results of tests carried out on a four-ball machine with a variety of mono - and disulphides, they were able to differentiate between two lubricating properties and showed that a sulphur-containing E.P. additive could also operate in the anti-wear region under relatively mild conditions. This observation led to the following mechanism for the reaction of disulphides



(a) $\mathrm{R - S - S - R + Fe \longrightarrow Fe : S{<}^{R}_{S\,-\,R}}$

(b) $\mathrm{Fe : S{<}^{R}_{S\,-\,R} \longrightarrow Fe\ (S - R)_2}$

(c) $\mathrm{Fe\ (S - R)_2 \longrightarrow FeS + R - S - R}$

where (a) above represents the adsorption of the additive on the iron surface to form a layer capable of carrying load under mild AW conditions,

(b) shows the breakdown of the adsorbed layer to form iron mercaptide which provides lubrication under conditions approaching E.P.

and (c) the subsequent breakdown of the mercaptide layer under very severe conditions to form ferrous sulphide.

Similar mechanisms were proposed by both Llopis (24) and by Allum and co-workers (30, 31).

Llopis et.al. used Sulphur - 35 labelled compounds to establish an order of reactivity:

$\mathrm{R - S - R < R - S - S - R \ll R - S - H < R - S_3 - R < R - S_4 - R}$

and put forward a mechanism to explain this. In the case of disulphide, results indicated that the sulphur-sulphur bond split to form R - S radicals as follows:-

$\mathrm{R - S - S - R \longrightarrow 2RS \longrightarrow Fe...SR \longrightarrow FeS + R - S - R}$

Allum and Ford (30) repeated the earlier work of Davey and

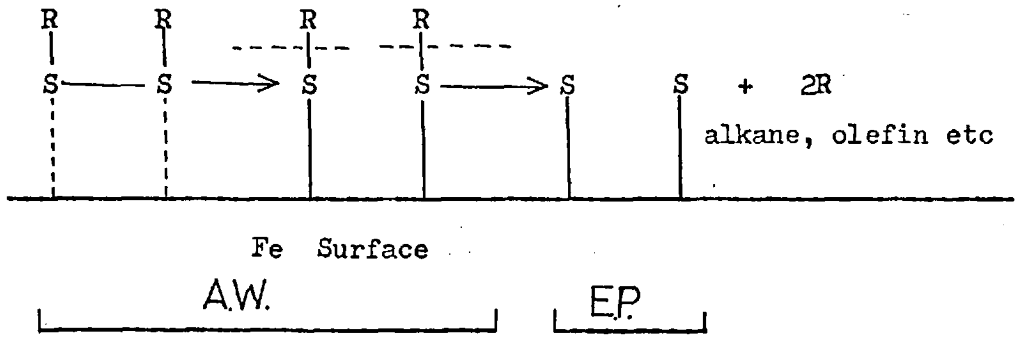
Edwards (27). A large number of sulphur compounds were analysed and it was shown that their E.P. performance was governed by chemical structure, and in particular, by the strength of the carbon-sulphur bond.

An extension of this work (31) examined the anti-wear properties of the same compounds in an attempt to clarify the early stages of the E.P. reaction.

It was established that anti-wear activity was related to the ease of formation of a mercaptide layer, governed in turn by the strength of the sulphur-sulphur bond.

On the basis of these observations, the authors suggested that disulphides, initially adsorbed on the surface, broke down by cleavage of the sulphur-sulphur bond to form an iron mercaptide. It was uncertain whether decomposition occurred on the surface or in solution prior to adsorption.

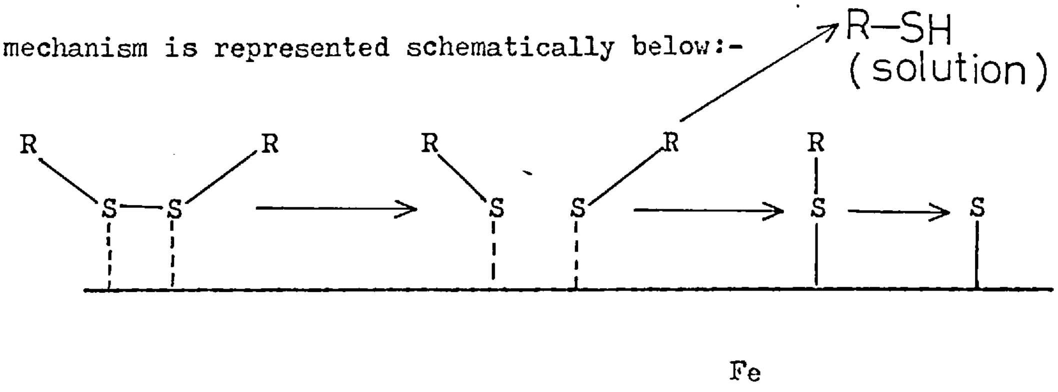
Under more severe conditions, further breakdown of the mercaptide occurred, forming a sulphur-containing E.P. film.



Spikes and Cameron (45), using a radiotracer method similar to that of Llopis et. al. (24) with dibenzyl disulphide, obtained results which correlated well with this mechanism. In order to provide supporting experimental evidence for the earlier mechanism proposed by Allum et. al. liquid phase adsorption/reaction studies have recently been carried out by Forbes and Reid (46). Results confirmed the mechanism for E.P. action but showed that differences in anti-wear behaviour between organic disulphides could not be attributed to the ease with which the sulphur-sulphur bond was broken, since, if the reaction were to proceed solely via a mercaptide intermediate, only hydrocarbon breakdown products would be expected and not the variety of sulphur-containing products observed. The authors postulated instead that anti-wear activity was governed by rates of formation of adsorbed films and by the physical properties of these films once formed.

The main product of the reaction between dbds and the iron powder was found to be dibenzyl monosulphide, which the authors initially had difficulty in explaining. However, Carruthers (47) had shown earlier that irradiation of dbds with ultra-violet light resulted in the formation of the monosulphide. Measurements of bond dissociation energies demonstrated that the carbon-sulphur bond in benzylic sulphides was weaker than that in dialkyl disulphides. It was therefore concluded (47) that with dbds, dissociation into thiyl radicals was accompanied by cleavage of the carbon-sulphur bond: dibenzylmonosulphide being formed by a combination of the benzyl and benzyl-thiyl radicals. This led Forbes and Reid (46) to suggest that the first stage in the reaction of disulphides with metal surfaces might involve homolytic fission of the sulphur-sulphur bond to form thiyl radicals, which would then be available to react either with the metal or with the bulk solution, depending on the stability of the carbon-sulphur bond in the particular radical..

This mechanism is represented schematically below:-



1.7 KINETICS OF E.P. ADDITIVES ON IRON SURFACES

The previous section dealt with the mechanism by which E.P. additives react with metal surfaces to form an inorganic anti-seizure film.

Reaction kinetics is concerned fundamentally with the rate of chemical reaction, with all factors which influence the rate of reaction and with the explanation of the rate in terms of this reaction mechanism. Greenhill(5) described the E.P. reaction as a "controlled corrosion" process and, subsequently, much of the early research into the kinetics of the reaction between sulphur compounds and metal surfaces, was carried out by researchers into the corrosion of steels by gases.

Wilson and Balke (48), in 1925, were the first to carry out investigations of this nature. Reaction rates were measured at temperatures between 300° and 400°C by measuring the volume of hydrogen evolved when hydrogen sulphide was passed through a heated steel tube. A very rapid initial rate of reaction was noted, which slowed over long periods owing to the coating of ferrous sulphide.

White and Marek (49) studied the reaction of hydrogen sulphide with mild steel over long intervals and observed that film scaling occurred leading to an acceleration of reaction rate as time increased. Prutton, Turnbull and Dlouhy (50) reacted hydrogen sulphide with steel samples in a test-tube at temperatures from 250°C - 350°C. It was found that a parabolic relationship was followed between the extent of reaction and reaction time. The authors concluded that the reaction was controlled by the rate of diffusion of iron ions outward through the sulphide film. They also reported that oxide coatings lessened the rate of reaction of steel by hydrogen sulphide and attributed this to the resistance offered by iron oxide to the outward passage of ferrous ions. More recently, Saleh et. al. (51 - 54) studied the reaction of hydrogen sulphide, carbon disulphide and sulphur dioxide with films of nickel and iron evaporated onto the walls of a glass adsorption vessel. The variation of activation energy with extent of reaction (film thickness) led the authors to suggest (52) that cation diffusion was the rate-determining step for the reaction. Results, similar to those of Prutton et. al., indicated that an oxide-coated iron surface substantially slowed the rate of corrosion.

From a lubrication standpoint, the principal interest in these investigations has been in the study of the growth characteristics of sulphide films on iron. However, other techniques have been developed in order to observe the reaction between E.P. additives and iron surfaces.

Barcroft (33) used his hot wire method with white oil solutions of dbds on stainless steel and assumed that since the surface area of the wire was very small, little additive was used up during the reaction and thus additive concentration remained nominally constant. The assumption was also made that the thickness of the formed film was such that the diffusion of iron ions outward through the film was unaffected. The data were fitted to the Arrhenius equation and linear relationships were obtained which seemed to justify the author's assumptions, though the linear dependance of extent of reaction on reaction time was not confirmed.

Very similar results were obtained by Dorinson and Broman (29) who reacted oil solutions of aliphatic disulphides with iron powder. The reacted iron was separated from the oil solution, decomposed with acid and the hydrogen sulphide evolved was measured. Reaction time between the additive and the iron was kept as short as was consistent with a measurable extent of reaction, and disulphide concentration was such that it did not change during the course of an experiment. Like Barcroft, Dorinson assumed that, under these conditions, the reaction was of pseudo-zero order and confirmed this for sulphide films of up to five monolayers depth.

A more rigorous investigation into the kinetics of E.P. additives was carried out by Sakurai, Sato and Ishida (34, 25) who used the hot-wire method developed by Barcroft with solutions of disulphides on iron wire. These authors observed that the corrosion rate of iron followed the parabolic law which indicated that diffusion of iron ions through the sulphide lattice was the slow stage of the reaction. The rate of corrosion with dbds was observed to deviate from the parabolic law with a remarkable increase in corrosion in the later stages of the reaction. This apparent autocatalytic behaviour, reported earlier by Borsoff and Wagner (26) was explained by film-cracking. With stainless steel (25) corrosion rates were very slow and the promoting action of dbds was not found at any temperature. Arrhenius plots showed the reciprocal dependence of the rate constant on the reaction temperature and value for the activation energy were found to be independant of additive concentration for all the compounds tested. Sakurai, Ikeda and Okabe (20, 38) examined kinetically both the formation and the wear of an iron sulphide film under the dynamic conditions of boundary lubrication. A radiotracer method revealed the formation of a sulphur-containing film which reached an equilibrium thickness under given operating conditions. The rate constant of the reaction and that of the wear process were estimated.

It was observed that film thickness reached a maximum, then decreased with increasing sliding speed. The authors reasoned that, at high sliding velocity, adsorbed molecules were swept off the surface during contact, so that the adsorption of the sulphur additive was disturbed. At very small contact intervals it was proposed that there was insufficient time for total readsorption. Thus the effective additive concentration, on the surface (which under these conditions was dependent upon the diffusion velocity of the compound in the solution to the surface), was reduced. This interesting result correlated well with work recently completed by Bailey and Cameron. These authors used a "ball-on-triplane" machine (55), with combinations of reactive and unreactive steels to demonstrate the importance of the "out-of-contact" period (56) in the build-up of an effective extreme-pressure film. Whereas earlier (57, 58) the E.P. reaction was considered to occur in the conjunction between sliding surfaces at the high temperatures generated, Bailey and Cameron showed that when the reactive steel was the moving member and was thus "out-of-contact" for most of the cycle, a satisfactory failure capacity was attained. With a stainless steel ball sliding against a reactive peg however, seizure was easily induced. These observations led the authors to conclude that the "in-contact" contribution to the E.P. film was small in comparison to that formed between consecutive contacts.

1.8 CONCEPT OF THE RESEARCH PROGRAMME

Though kinetic investigations have been carried out into the reaction between E.P. lubricants and metal surfaces; these have been limited in that experimental techniques have only enabled the examination of static, unloaded surfaces.

It was therefore decided to carry out the kinetic analysis of a model E.P. oil in a simulated lubricating situation, in order that the mechanism by which the E.P. reaction proceeded, might be elucidated.

CHAPTER TWO

APPARATUS AND PRELIMINARY INVESTIGATIONS

2.10 INTRODUCTION

The purpose of the experiments described in this chapter is to investigate the E.P. reaction by observing changes in the friction temperature characteristics of steels lubricated with a model E.P. oil. To avoid the complication of frictional heating, the tests were carried out on a slow speed ball-on-triplane machine.

2.20 APPARATUS

The standard four-ball machine has the inherent disadvantage that tests must be terminated and the apparatus dismantled if wear measurements are to be made. Relocation of the balls in their original positions is almost impossible after removal. Francis and Presland (59) have also shown that inconsistent behaviour can result from the upper ball rubbing in a single wear track. Profilometric examination of the wear scars showed significant differences between the tracks after one minute running under boundary conditions. After a further five minutes running, no differences were observed but surface roughness had increased four-fold. A further disadvantage is that the range of materials freely available in the form of spherical test specimens is limited. The ball-on-triplane machine (55, Figs 2.1 and 2.2) overcomes those deficiencies by replacing the bottom three balls by the flat ends of three cylindrical pegs whose axes coincide with the centre of the top ball. The geometrical arrangement of the pegs relative to the ball is shown in Fig 2.3 and was chosen so that each peg carried the same load but formed a separate

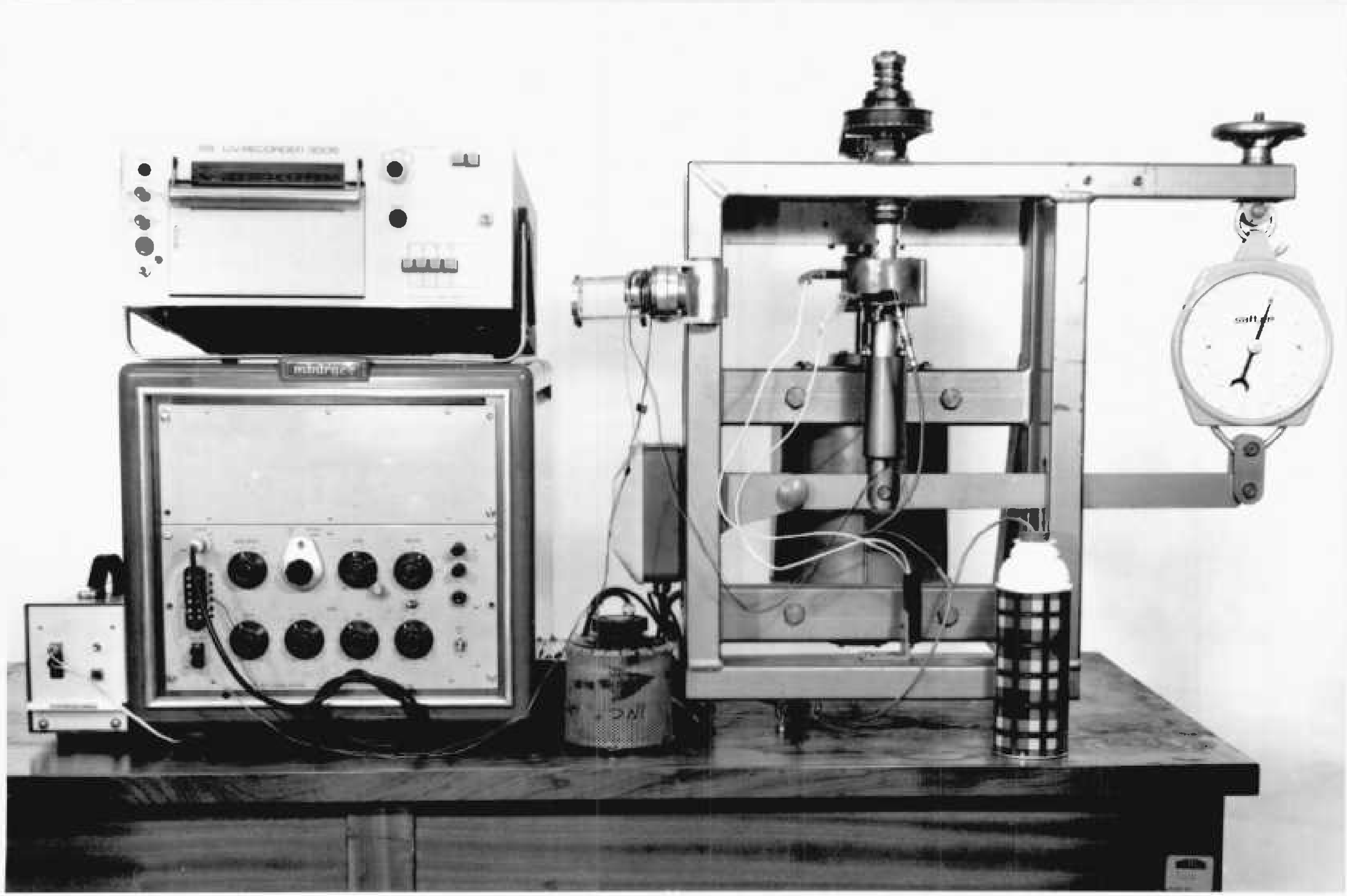


FIG 2·1 BALL-on-TRIPLANE MACHINE

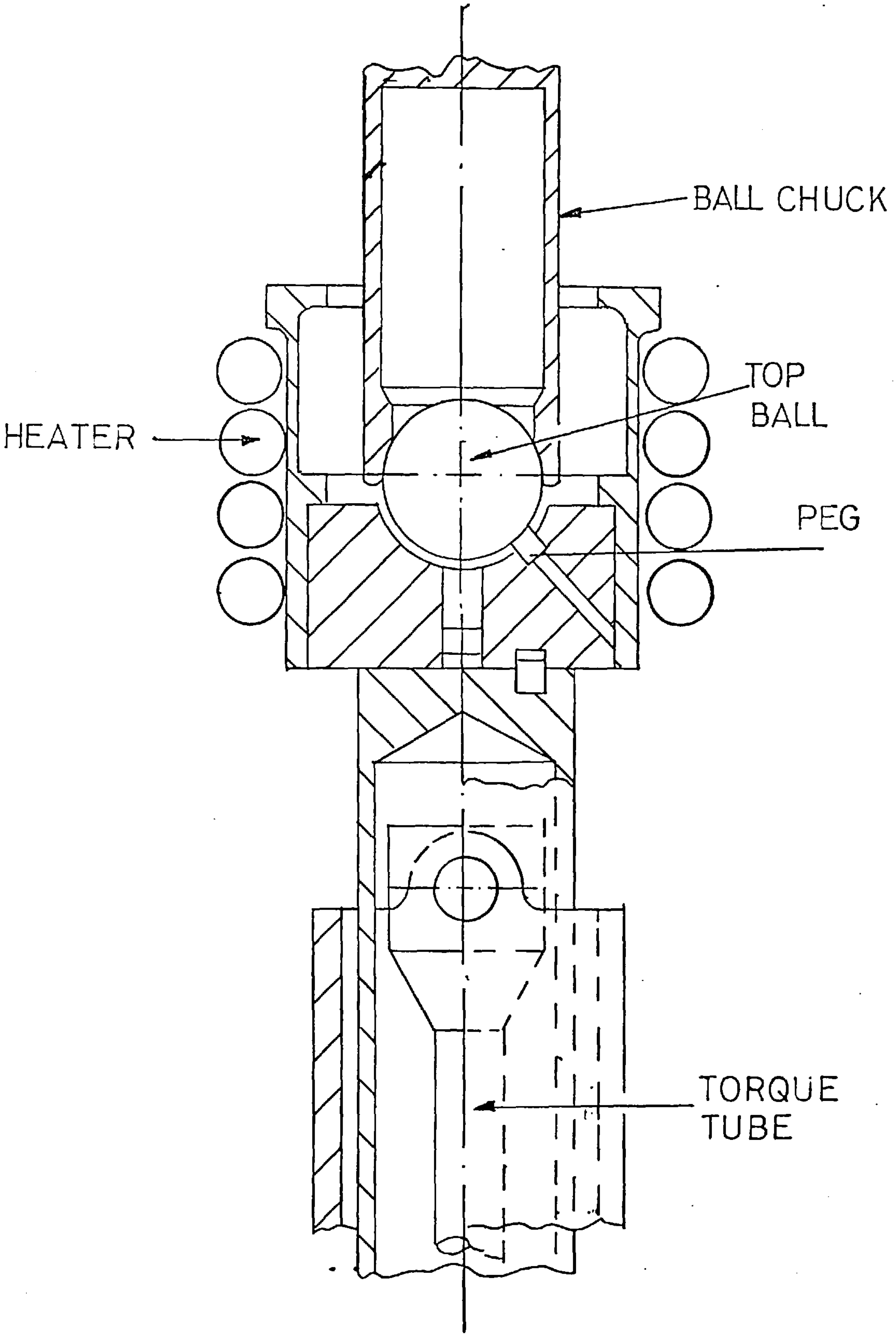


FIG 2.2 BALL-on-TRIPLANE MACHINE, SCHEMATIC DIAGRAM.

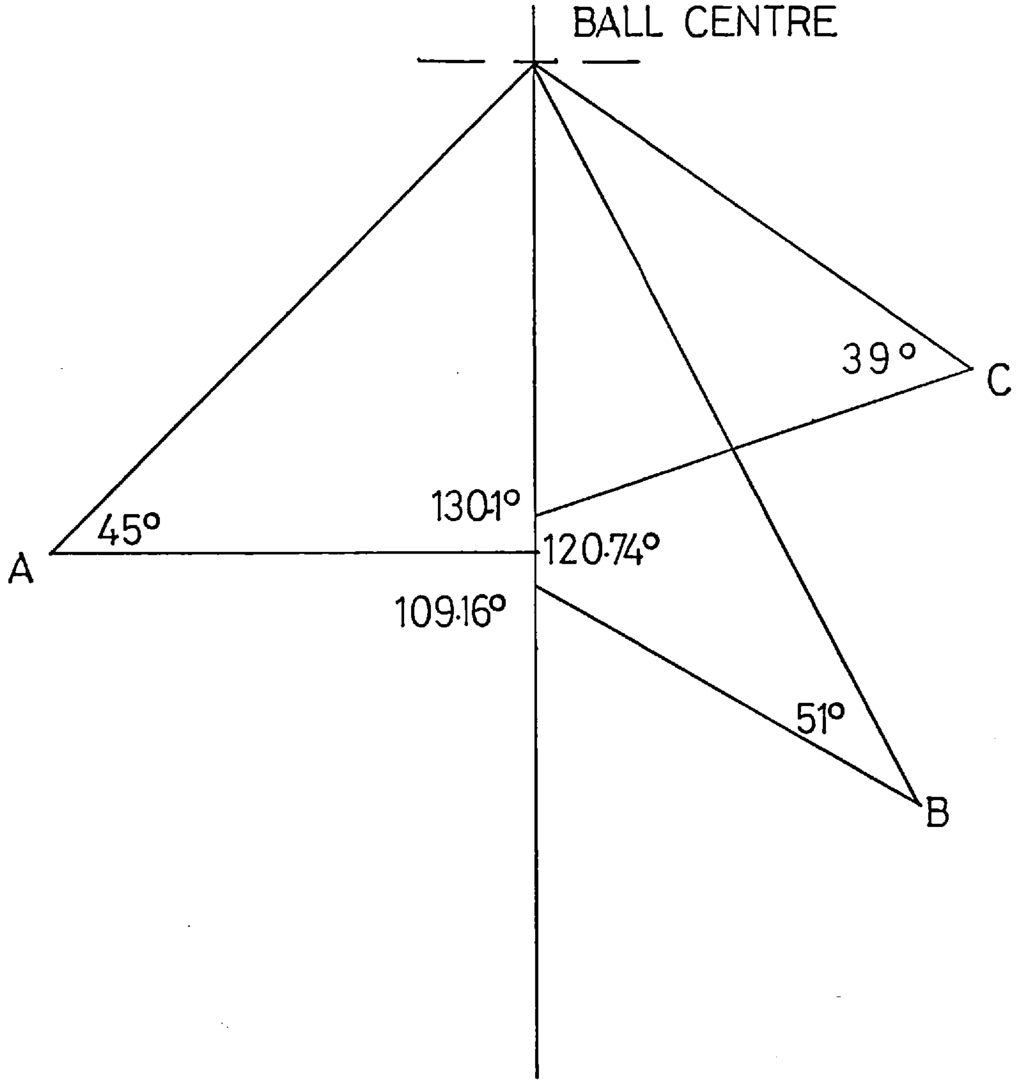


FIG 2·3 BALL-ON-TRIPLANE MACHINE PEG POSITIONS wear track on the top ball. The wear tracks can be observed through a ground glass window in the peg-cup (Fig 2.4), by means of a specially designed microscope.

The three pegs, each $^3/_{16}$ inch (4.7mms) long, $^3/_{16}$ inch diameter are held in a stainless steel cup (Fig 2.4), around which a removable stainless steel shield is screwed to retain the lubricant. The whole assembly is surrounded by the coils of a heater (Fig 2.5) controlled by a Variac transformer. Temperatures up to 300°C can be reached by this heating system and are measured by means of a stainless steel sheathed Chromel/Alumel thermocouple located near one of the pegs.

The top ball of 1 inch (25.4mm) diameter is held by an interference fit in a stainless steel chuck connected to the drive motor by means of a pulley and gear box system. (Fig 2.6). Gear boxes are available to give a range of speeds from $^1/_{1000}$ - 1000 r.p.m. (9×10^{-4} - 90mm/s).

The peg cup and heater assembly are supported on a cyndanio platform connected to a lever arm through a torque tube fitted with strain gauges. Load is applied via the lever arm by a spring balance and turnbuckle arrangement.

Signals from the thermocouple and the strain gauge bridge are fed into the two channels of a potentiometric pen recorder giving simultaneous readings of temperature and frictional torque. (Typical Trace:- Fig 2.7).

The following section contains details of preliminary tests carried out on the ball-on-triplane machine in order to establish a suitable experimental procedure. These tests took the form of some conducted earlier by Spikes (60).

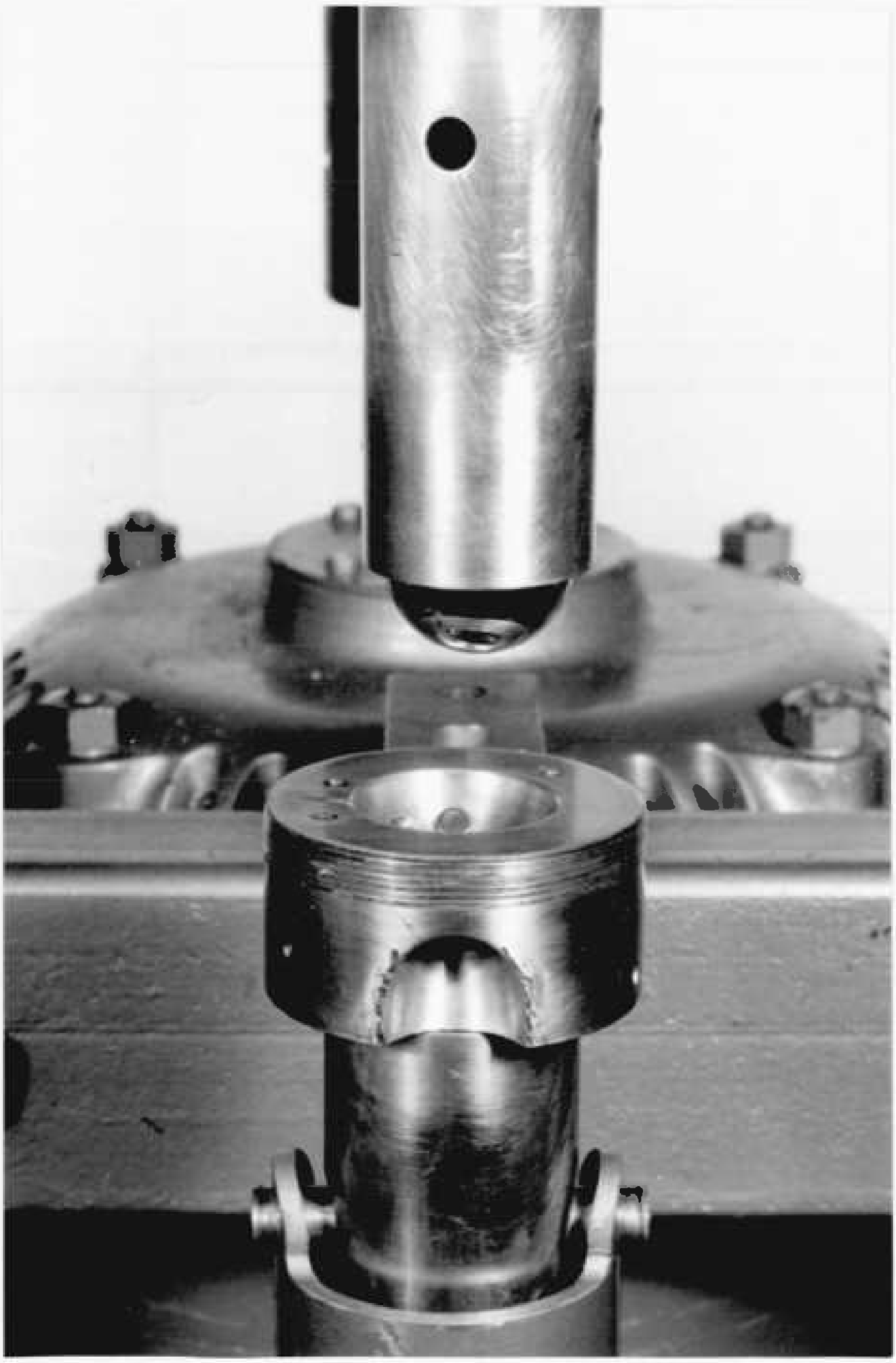


FIG 2·4 PEG-CUP.

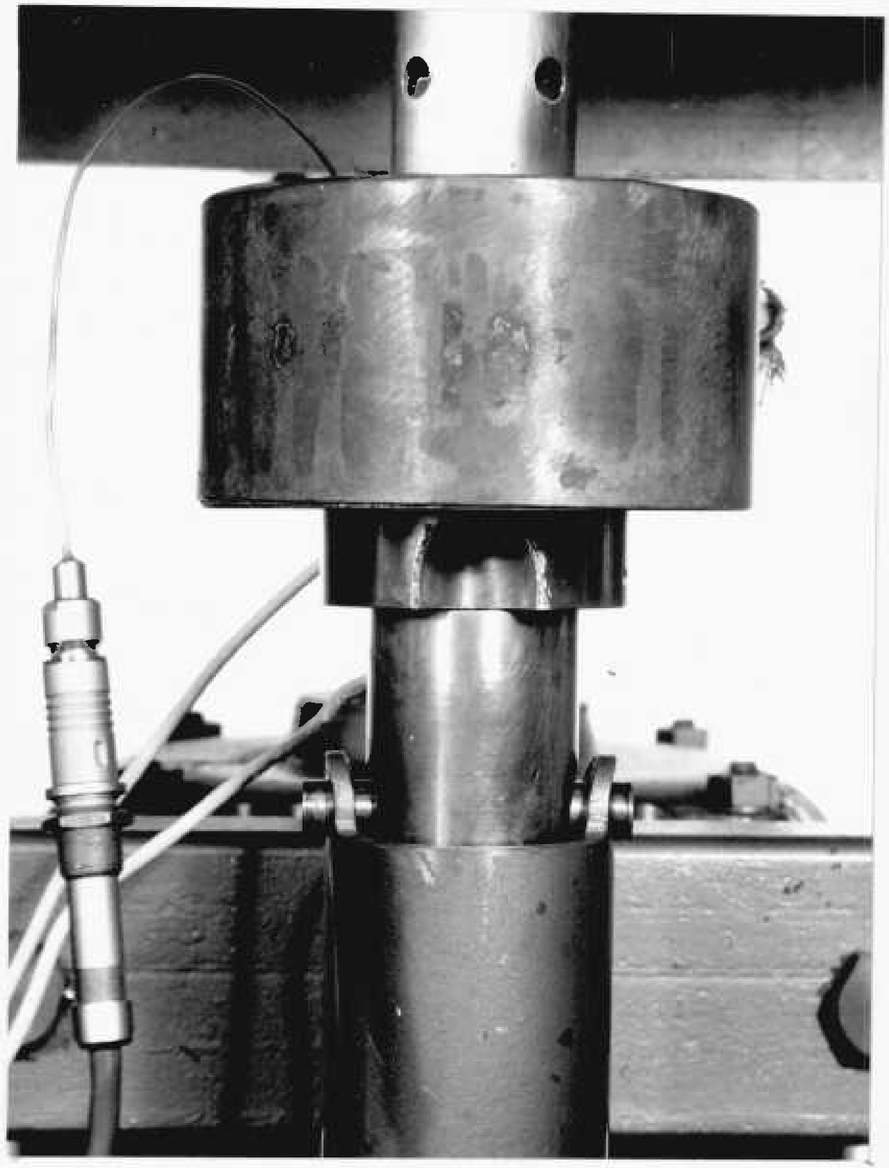


FIG 2·5 HEATER

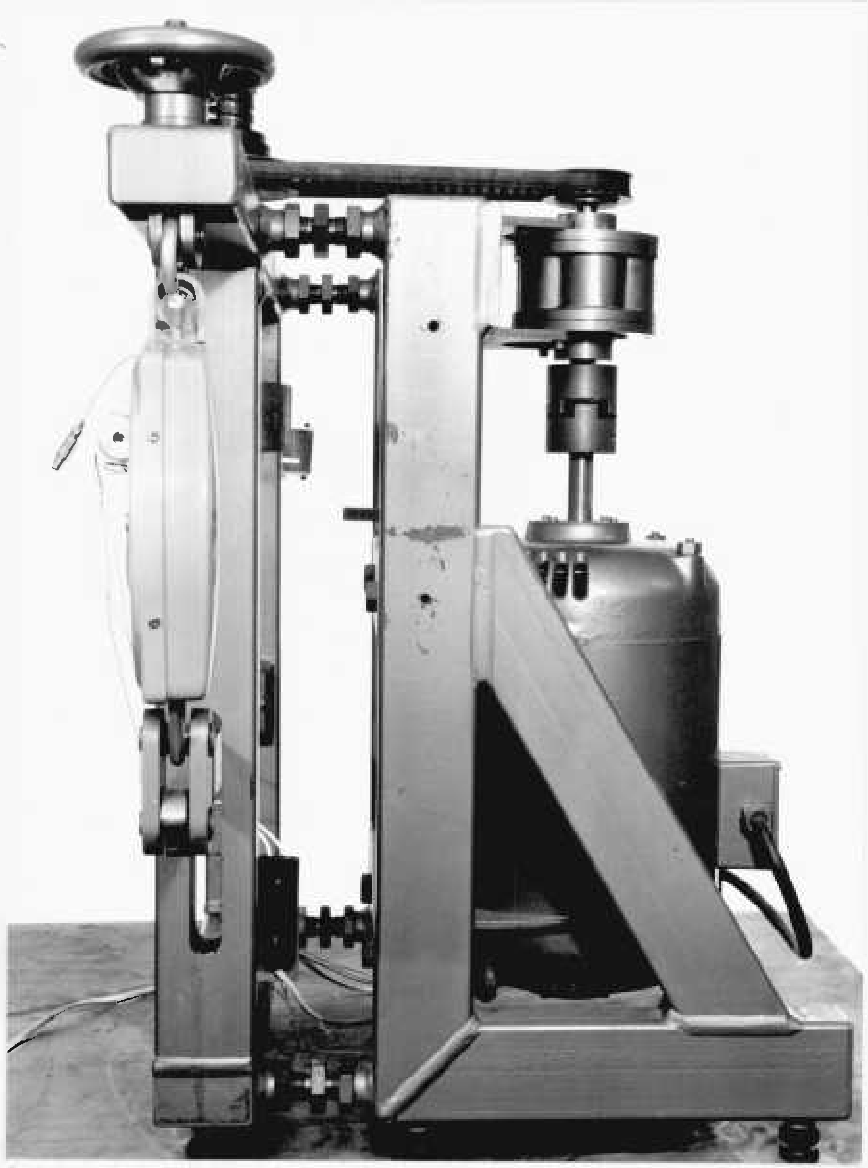


FIG 2·6 DRIVE SYSTEM

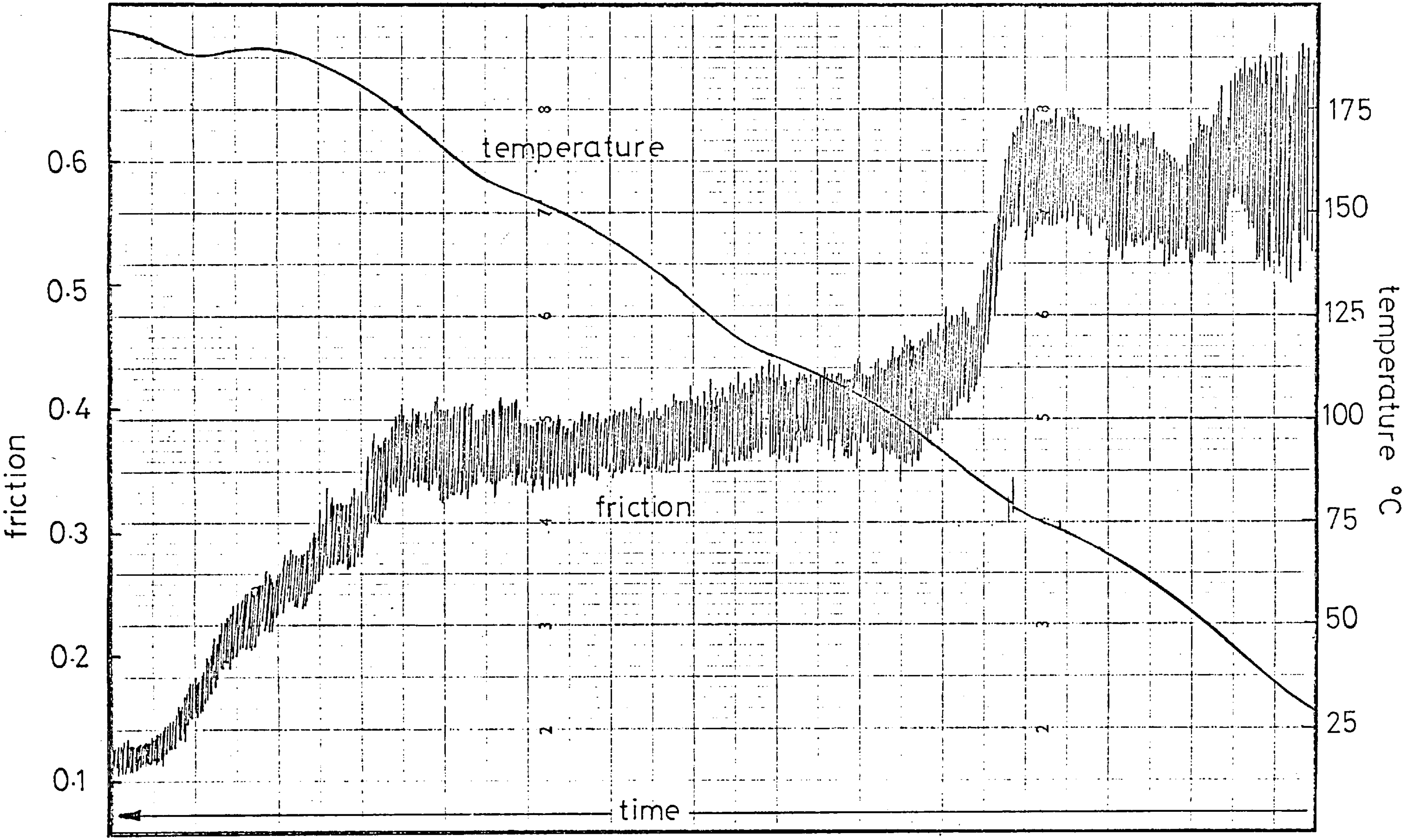


FIG 2·7 TYPICAL PEN RECORDER TRACE. DBDS on EN 31 STEEL.

2.21 MATERIALS

The test lubricant was a 1% (wt.) solution of dibenzyl disulphide dissolved in cetane (hexadecane). As the presence of any surfactant could interfere with the E.P. reaction, the cetane (of 'puriss' grade) was further purified before use by two days continual shaking with activated alumina and silica gel. Just before use, the cetane was filtered through sintered glass. The dibenzyl disulphide was of micro-analytical standard and was used without further purification. Two steel combinations, whose compositions are shown in Table 2.1 below, were used in the tests.

	C	Si	Mn	S	P	Ni	Cr	Mo
EN 31	0.90 1.20	0.10 0.35	0.30 0.75	0.050 MAX	0.050 MAX	—	1.00 1.60	—
EN 58J	0.12 MAX	0.20 MIN	2.00 MAX	0.045 MAX	0.045 MAX	8.0 12.0	17.0 20.0	1.5 2.5

Table 2.1

EN 31 steel specimens, were used as this is a standard bearing steel readily available in the form of $^3/16$ inch pegs. Some tests were also carried out on EN 58 (18/8 stainless) steel, to see the effect of steel type on the E.P. reaction.

2.22 EXPERIMENTAL PROCEDURE

The ball and pegs were cleaned thoroughly before testing by washing in a Soxhlett extraction apparatus for a minimum of three hours with analar toluene. The specimens were removed from the soxhlett and whilst still hot immersed in analar acetone. The cleaning of the chuck and cup assembly was not so critical and was carried out in an ultrasonic cleaner with analar toluene and repeated, after rinsing, with analar acetone. Just before each test, the specimens and ball-chuck and cup were removed from the acetone, allowed to dry and quickly assembled. The test lubricant was added immediately. After assembly, the strain-gauge bridge was balanced and the top ball rotated at one r.p.m. for several revolutions before load was applied. The load had to be enough to ensure full boundary conditions but not so large that the compressive yield stress of the metal was exceeded since Matveevsky (61) and Hirst and Stafford (62) have shown that loads of this magnitude can result in inconsistent behaviour. For the purpose of these tests, a load of 14lbs force (62.3N) was applied to the lever arm giving a Maximum Hertz contact pressure of 172,000 p.s.i. (1.2 GN/ m^2). After loading, the apparatus was run-in at room temperature for a minimum of ten revolutions, to allow the friction coefficient to stabilise at a high value (0.5 - 0.7). The heating unit was then switched on. In order to maintain a constant heating rate of 5°C per revolution, the assembly was heated at 80 volts (Variac) to 100°C, increased to 100 volts - to 150°C and to 120 volts above this temperature. Several runs were carried out at different heating rates to determine whether this had any effect on the friction-temperature characteristics of the ball and peg combinations.

2.30 ACCURACY

As the thermocouple recording the reaction temperature was situated in the bulk oil (though close to one of the pegs), a small systematic error in reaction temperature measurement is introduced owing to the finite heat transfer coefficient between the peg surface and the oil. In order to obtain an accurate estimation of this error, an unsheathed chromel/alumel thermocouple was soldered into the surface of a mild steel test peg, the junction being arranged to be outside the point of contact with the ball. The temperatures indicated by the two thermocouples were then compared over a number of tests. At the heat rate of 5°C per minute (at 1 r.p.m.), at which the tests described were carried out, it was observed that the thermocouple recording the true surface temperature indicated a temperature up to 2°C higher than that in the bulk oil. It is estimated therefore that surface temperatures can be recorded to within +2°C.

Figs 2.8 - 2.15 show the dependence of friction on temperature for the various ball and peg combinations. These plots are the average of three experimental runs. It was observed that the repeatability of the temperature at which friction dropped was consistent to within ± 2°C of the average value. Errors are therefore small. Friction values however, were found to fluctuate over the three runs by up to ± 10% of the mean value. This inconsistency was probably due to surface scratches and slight variations in the peg heights. For all runs with the same system, relative changes in the coefficient of friction were identical even if the absolute friction values differed slightly between runs. Since the work described in this thesis is concerned with friction change rather than with absolute friction values, accuracy is considered unimportant and error bars are omitted.

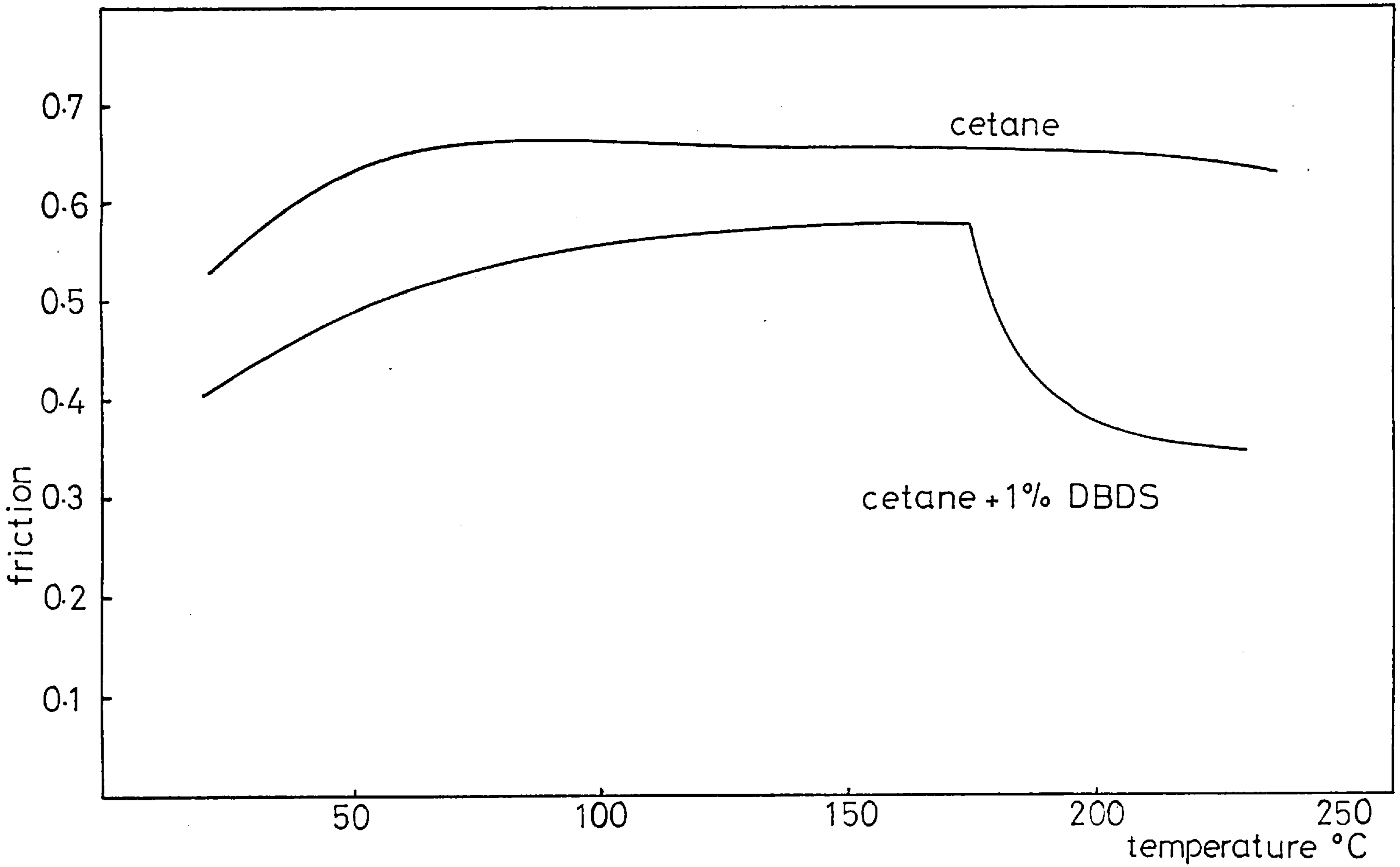


FIG. 2·8 FRICTION vs TEMPERATURE. DBDS on EN 58 STEEL, 1 rpm.

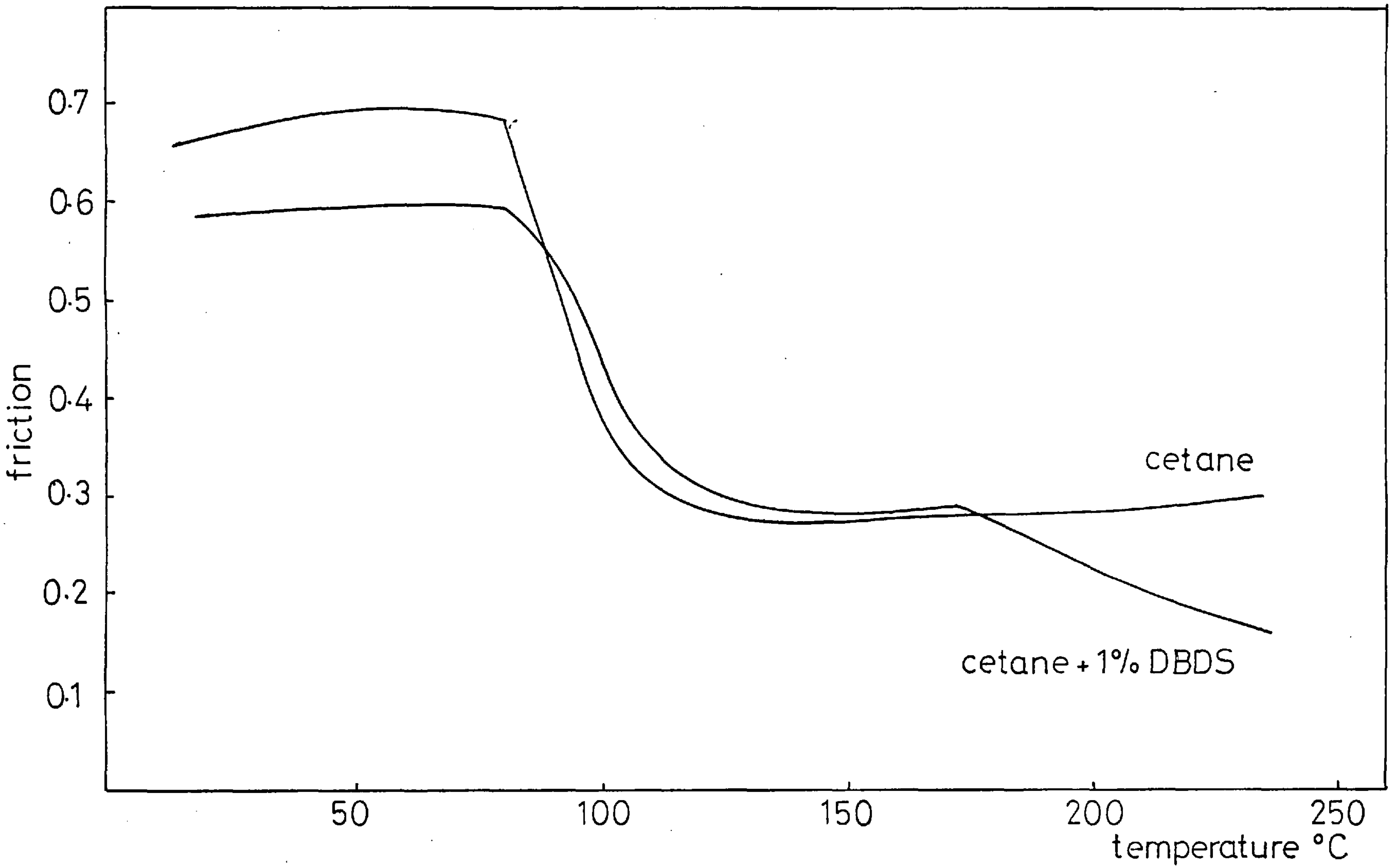


FIG 2·9 FRICTION vs TEMPERATURE. DBDS on EN 31 STEEL, 1 rpm.

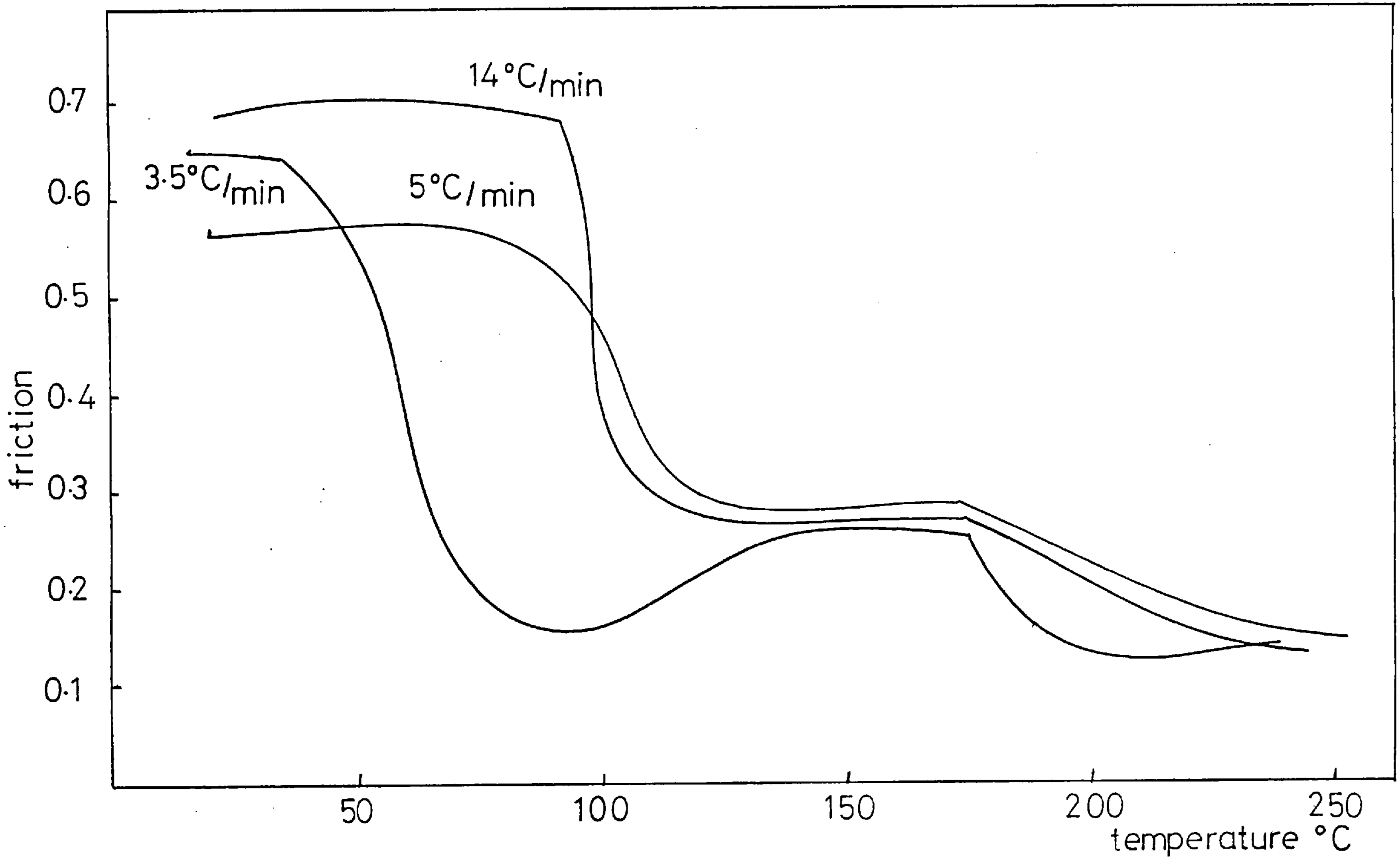


FIG 2·10 FRICTION vs TEMPERATURE. DBDS on EN 31 STEEL, 1 rpm.
HEAT RATE DEPENDENCE.

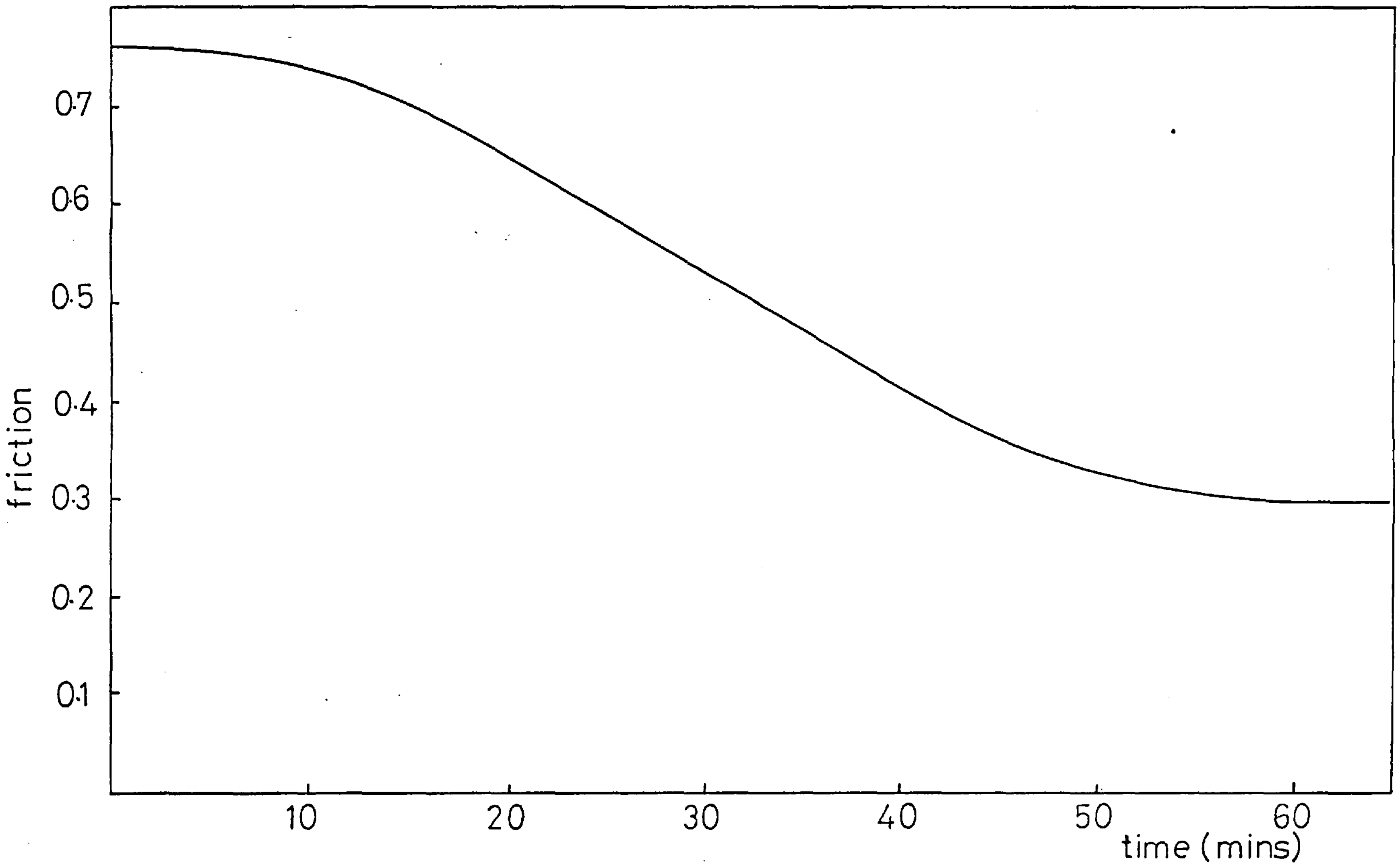


FIG 2·11   FRICTION vs TIME. CETANE on EN 31 STEEL, 1 rpm.

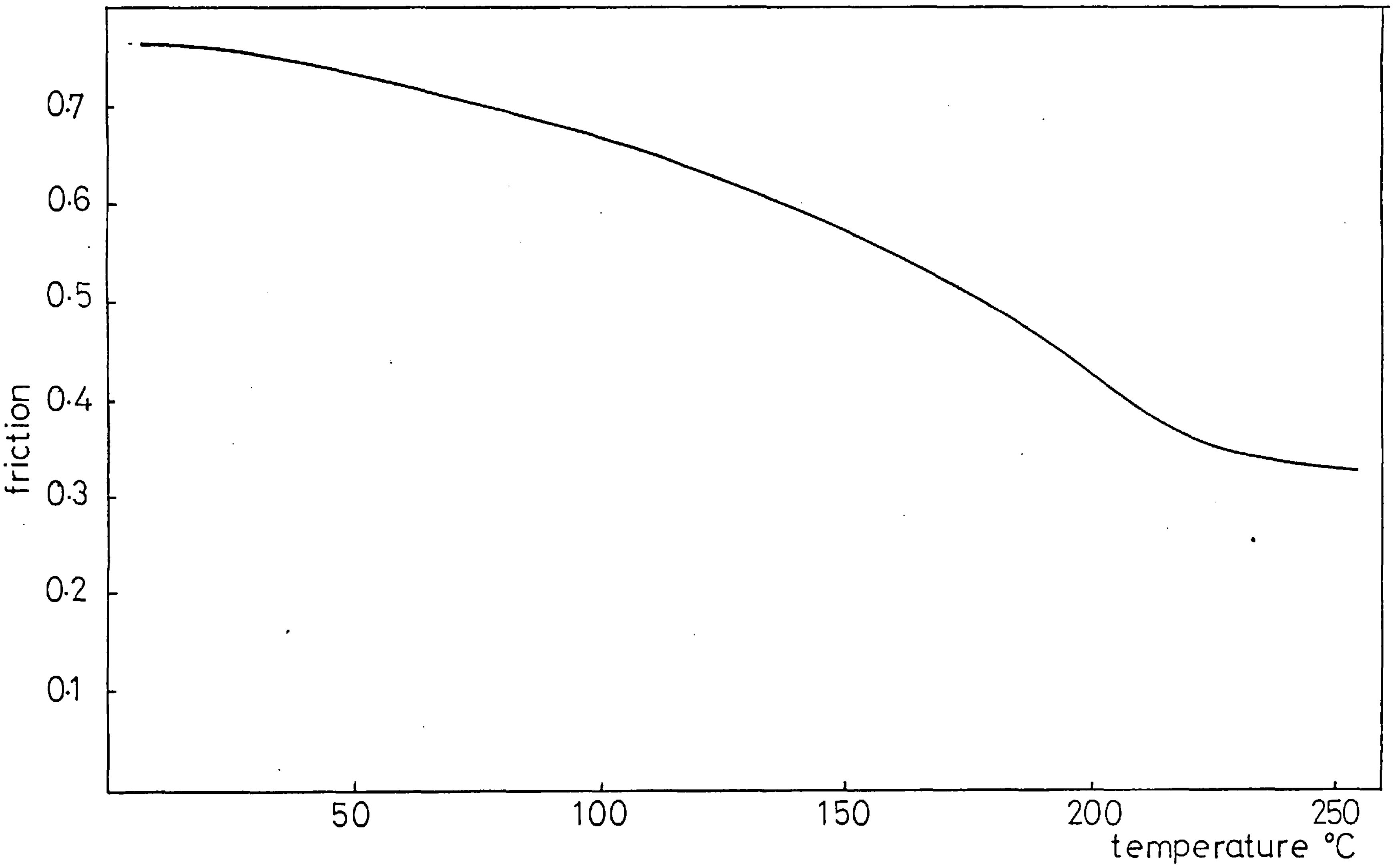


FIG 2·12 FRICTION vs TEMPERATURE . UNLUBRICATED EN 31 STEEL, 1 rpm (16·7 N load)

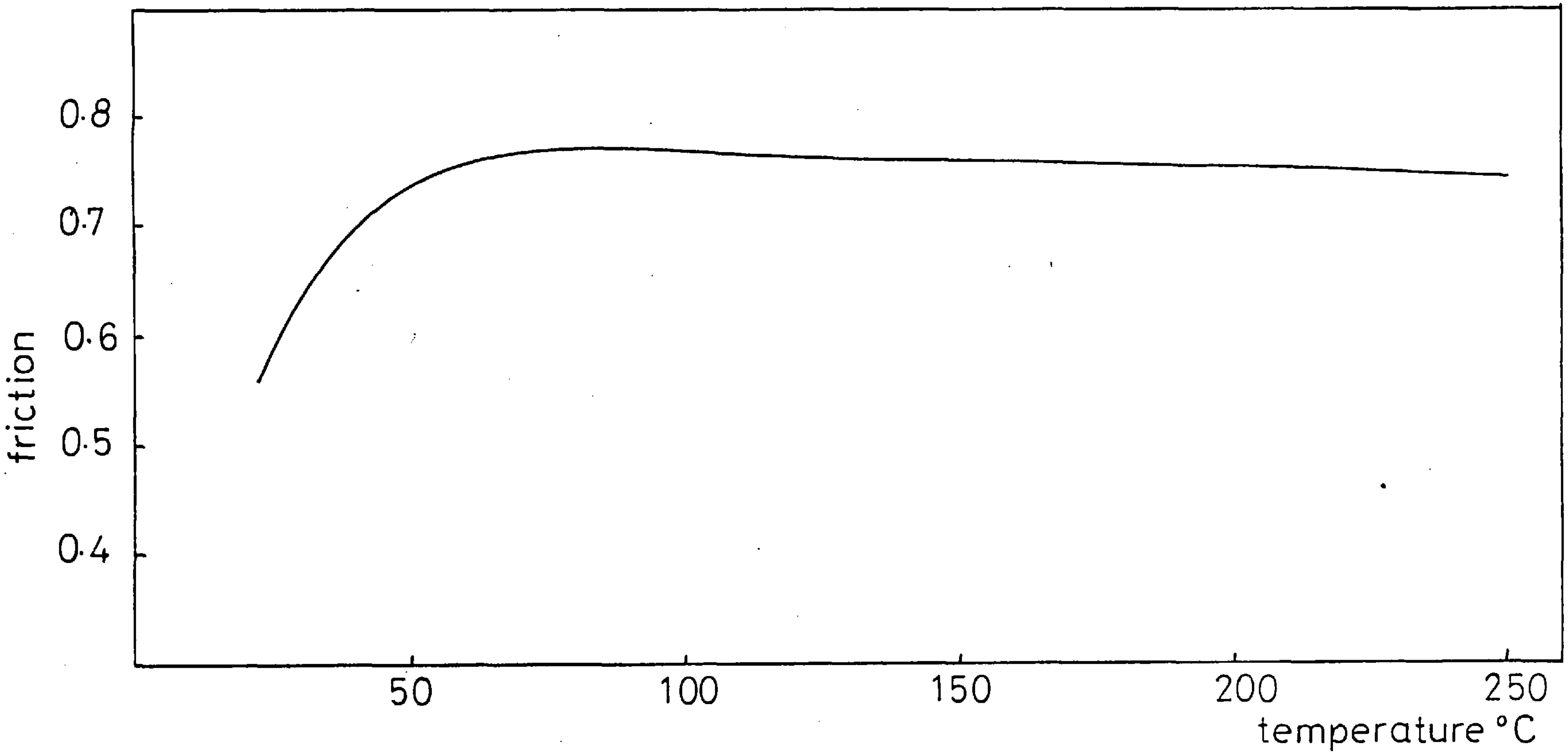


FIG 2·13 FRICTION vs TEMPERATURE. UNLUBRICATED EN 31 STEEL, 1rpm
(62·3 N load)

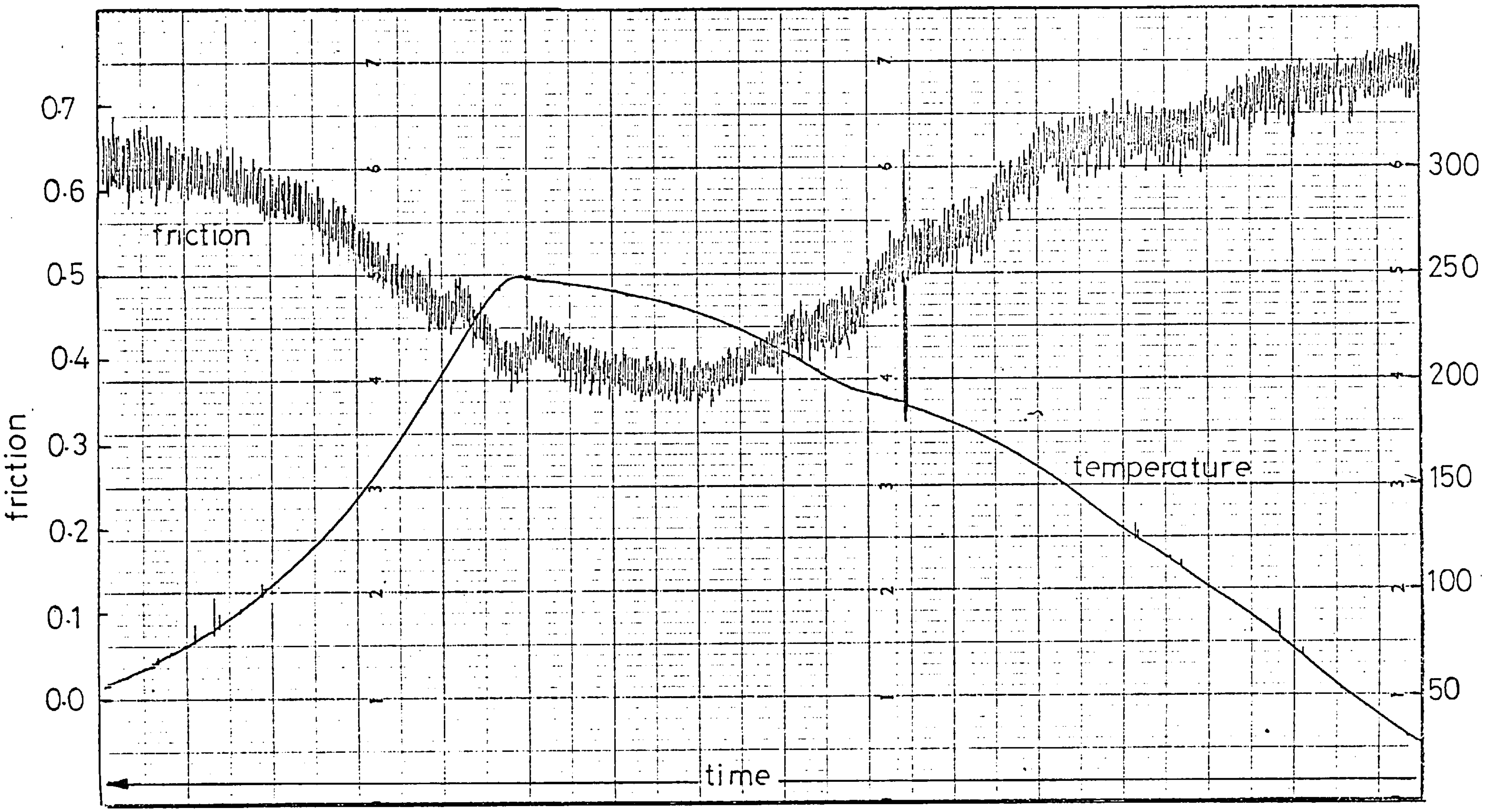


FIG 2.14 UNLUBRICATED EN 31 STEEL, 1rpm. REVERSIBILITY TRACE.

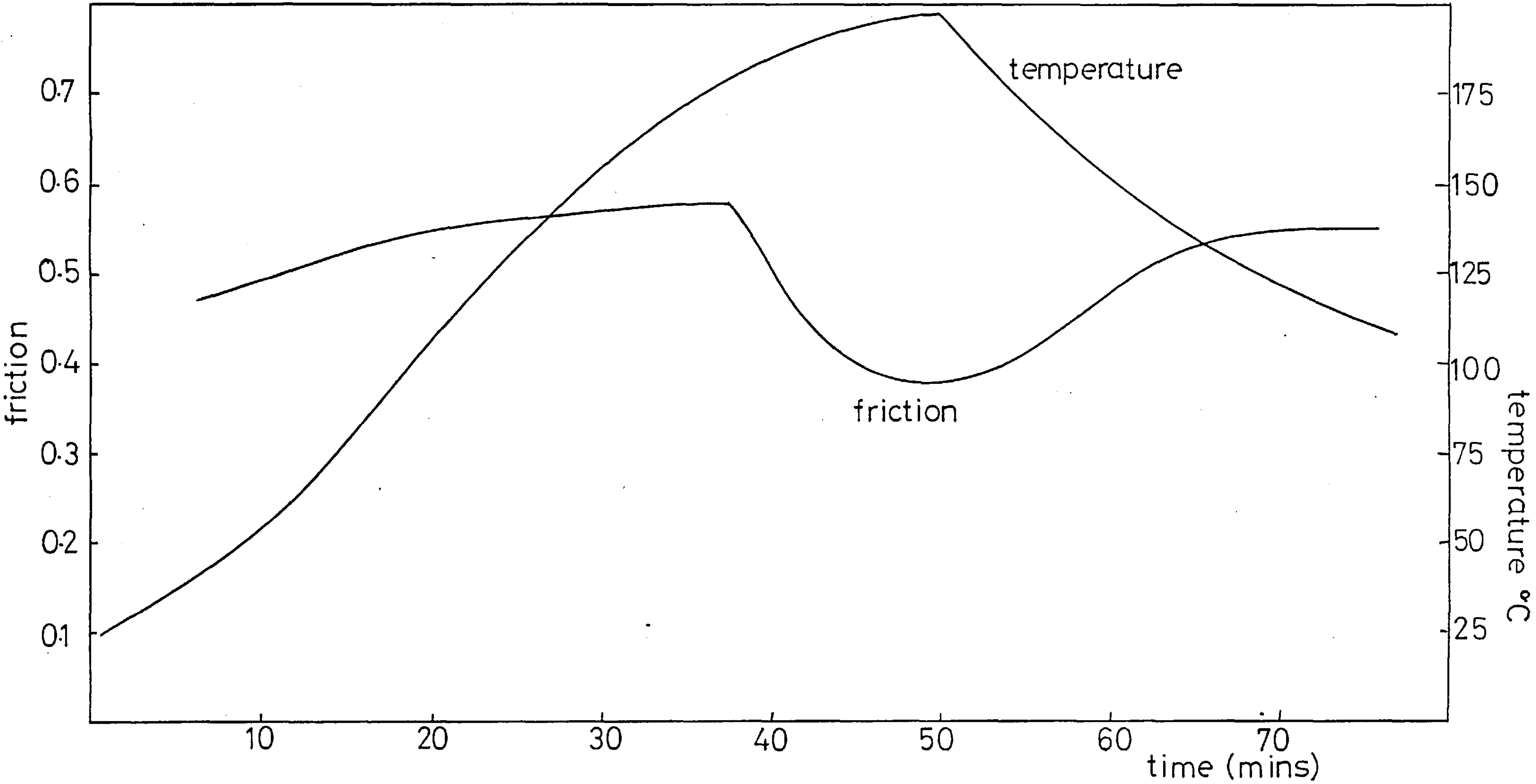


FIG 2·15 FRICTION vs TEMPERATURE. DBDS on EN 58 STEEL, 1 rpm.
REVERSIBILITY of FRICTION with TEMPERATURE.

2.40 RESULTS AND DISCUSSION - I

Steels lubricated with dbds show a drop in friction at 170° - 180°C (Figs 2.7 - 2.9) regardless of metal composition and heating rate (Fig 2.10). The appearance of the wear tracks (which showed traces of a black discolouration), and the very apparent smoothing of the friction trace (Fig 2.7) above this temperature, support the suggestion (60), that this friction drop is caused by the formation of an extreme pressure, sulphur-containing film. For verification, sample wear tracks were examined by Electron Probe Microanalysis (E.P.M.A.). The principles of E.P.M.A. and the results obtained, are outlined in the following section.

2.41 ELECTRON PROBE MICROANALYSIS

INTRODUCTION

Bombarding a surface with electrons excites electrons in surface and sub-surface atoms into higher energy levels. Excited electrons do not remain at these high energy levels but return to their normal level by emitting X-radiation of wavelength, characteristic of the elements present. These X-rays, incident on a spectrometer crystal of known lattice spacing, d, are diffracted according to the Bragg equation

$$n\lambda = 2\, d \sin\theta$$

An ionisation chamber containing a mixture of methane and argon, "counts" or measures the intensity of the diffracted X-rays. Thus, information can be obtained on the elements present on the specimen surface. The instrument used in these investigations was the Japanese Electron Optics Laboratory (J.E.O.L.), JXA - 3A electron probe microanalyser. Fig 2.16.

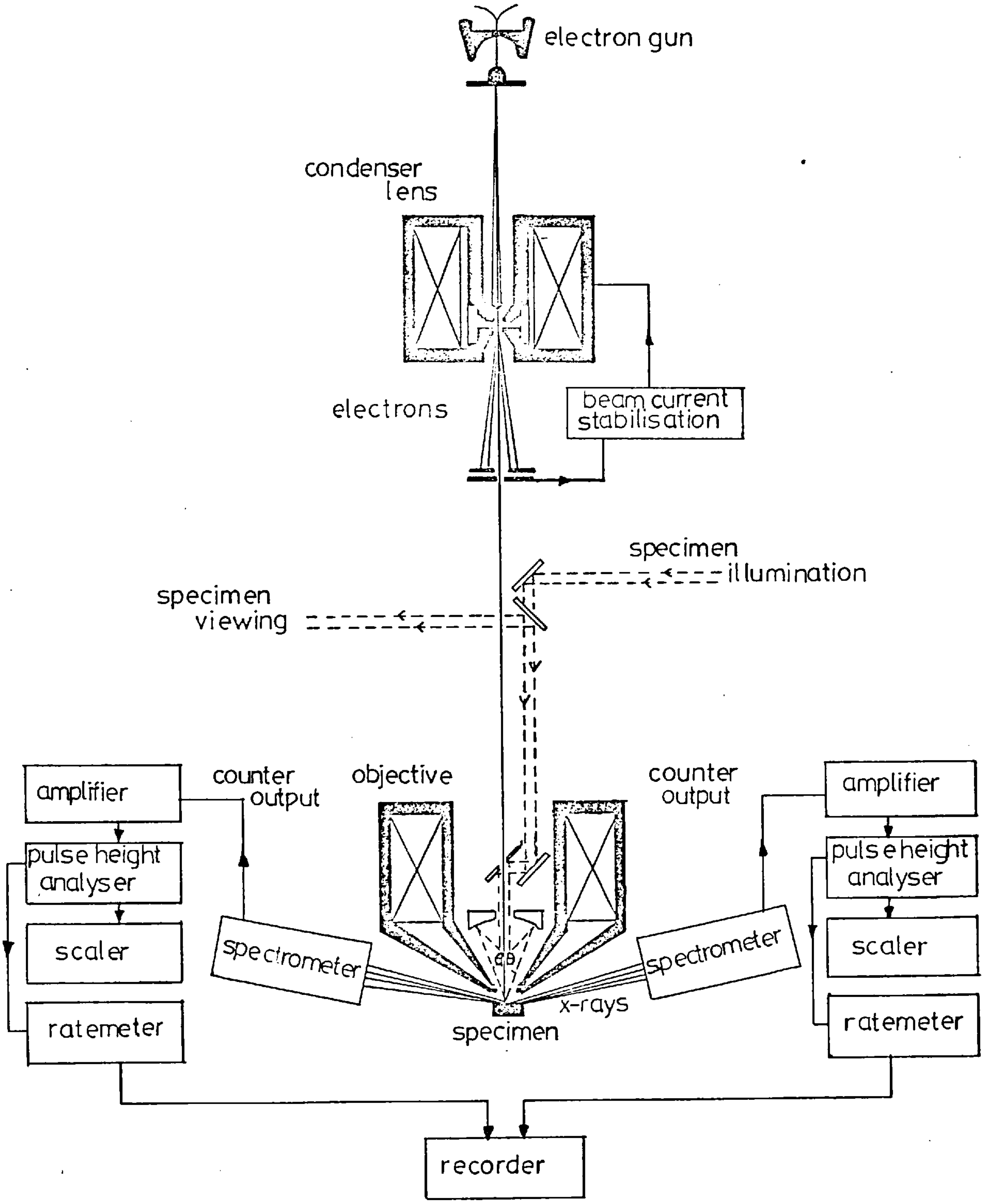


FIG 2·16 ELECTRON PROBE MICROANALYSER

The electron beam or "probe" is provided by a tungsten filament electron gun operated at 25 kV, and is focussed on the specimen surface by two magnetic lenses. Electrons strike the specimen normal to the surface and the take-off angle for resultant X-rays is 20°. Two spectrometers enable two elements to be analysed simultaneously. However, in this study both were used for sulphur. In order to determine the element distribution over a large surface area, the specimen can be driven under the electron beam at constant speed and thereby a "line-scan" of count intensity against distance is obtained. This facility was used in the investigation.

2.42 PROCEDURE

EN 31 balls were taken from tests carried out in a 1% (wt.) cetane solution of dbds and in cetane only. An unused EN 31 ball was taken as a standard to establish a datum level for sulphur in the surface of the steel. The balls were sectioned for analysis on an elastic grinding wheel and thoroughly cleaned in toluene and acetone to remove all traces of oil solution. The specimens were then mounted in plasticene in a brass holder and earthed to the holder by a painted strip of colloidal silver. Both spectrometers were tuned to the Sulphur K-α emission and calibrated to maximum count intensity against a cadmium sulphide standard. "Line-scans" were carried out across the wear tracks of each specimen.

2.43 LIMITATION OF RESULTS

Electron probe techinques are subject to certain limitations. Depending upon the density of the specimen material, the probe can penetrate the sample surface to a depth of up to 2μm, so that sulphur distributions recorded are average values of sulphur content over the depth of penetration. Also, for accurate quantitative analysis, the surface of the specimen should be flat so that no change in the X-ray take-off angle occurs. The roughness of the wear track and the slight curvature of the specimen thus made accuracy indeterminate. However, these analyses were used qualitatively only and accuracy was therefore considered unimportant.

2.44 RESULTS OF E.P.M.A. INVESTIGATIONS

(a) EN 31 BALL RUBBED IN 1% DBDS SOLUTION

Fig 2.17 shows the results of "line-scans" across the track of an EN 31 ball rubbed in a 1% (wt.) solution of dbds in cetane, large amounts of sulphur are seen to be unevenly distributed across the wear track. Photographs were taken at a single position on the edge of the area of high sulphur content. The Back-scattered Electron Image (B.E.I.) picture has a strong topographical dependence, as the amount of back-scatter depends not only upon the atomic number of the elements on the surface, but also, to some extent, upon the nature of the surface under the "probe". Sulphur, being a comparatively light element, absorbs electrons more readily than the metallic areas and thus the areas of high sulphur content are revealed in Fig 2.18 as the dark zones to the left of the photograph. Conversely, high sulphur content is represented by lighter regions on the Absorbed Electron Image (A.E.I.) photograph

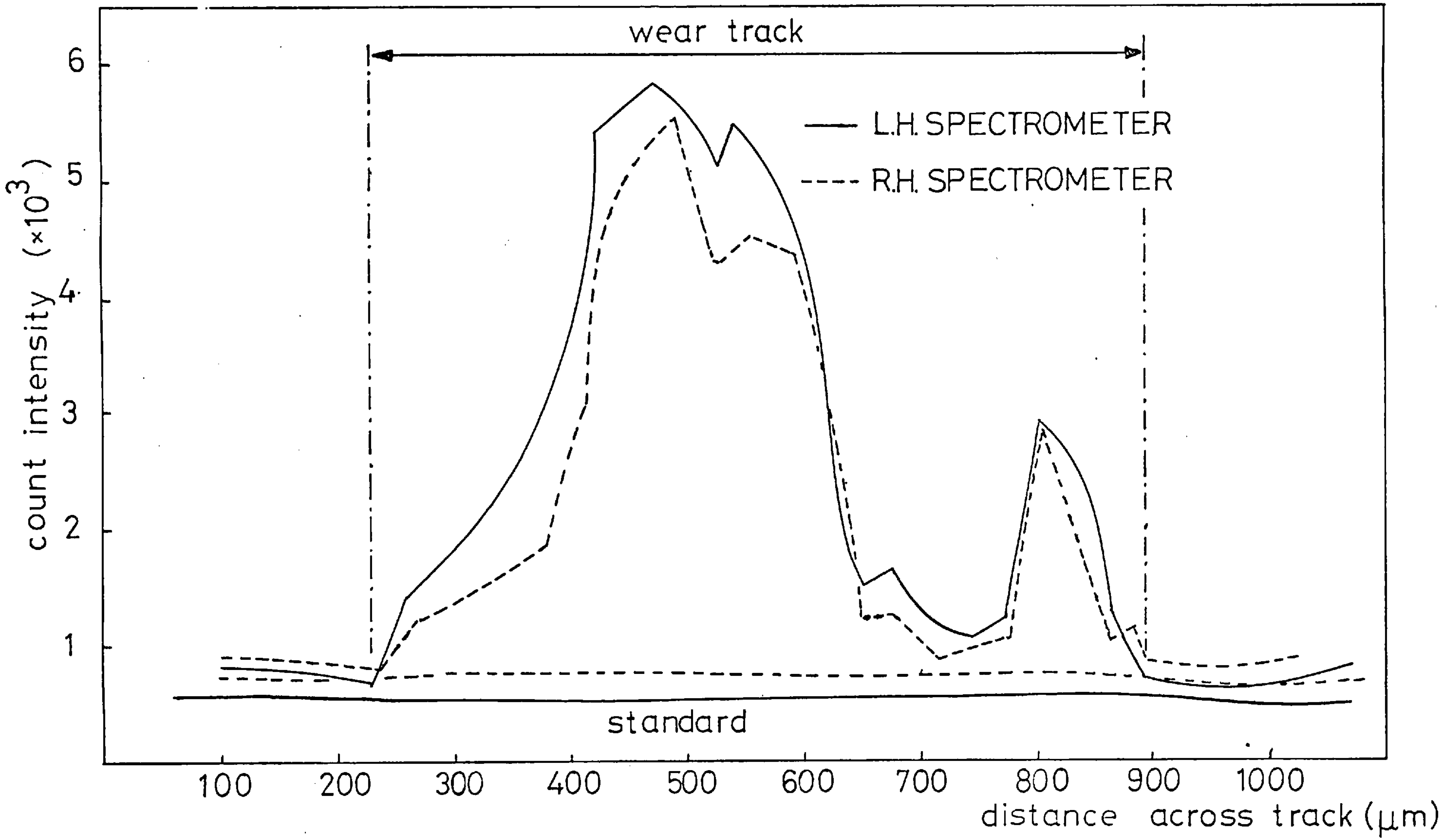


FIG 2.17 EPMA COUNT across track rubbed in DBDS solution

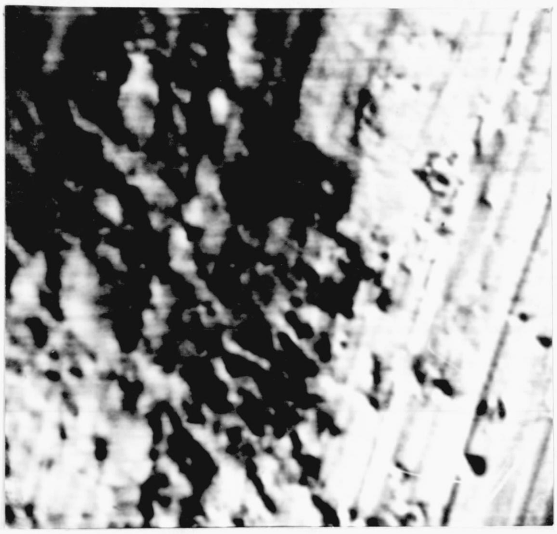


FIG 2.18 BACK-SCATTERED ELECTRON IMAGE.

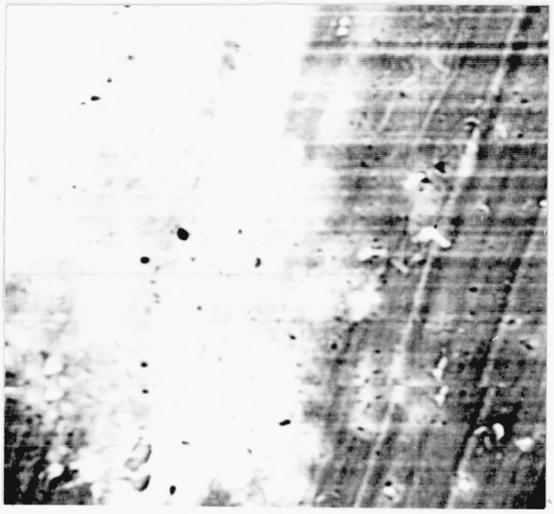


FIG 2.19 ABSORBED ELECTRON IMAGE.

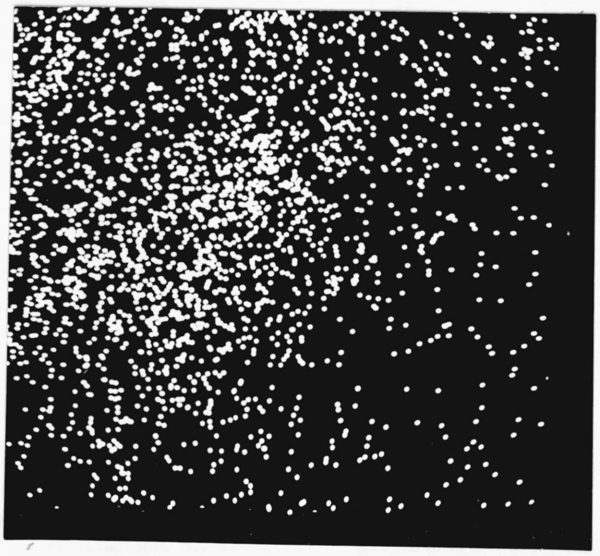


FIG 2.20 X-RAY IMAGE.

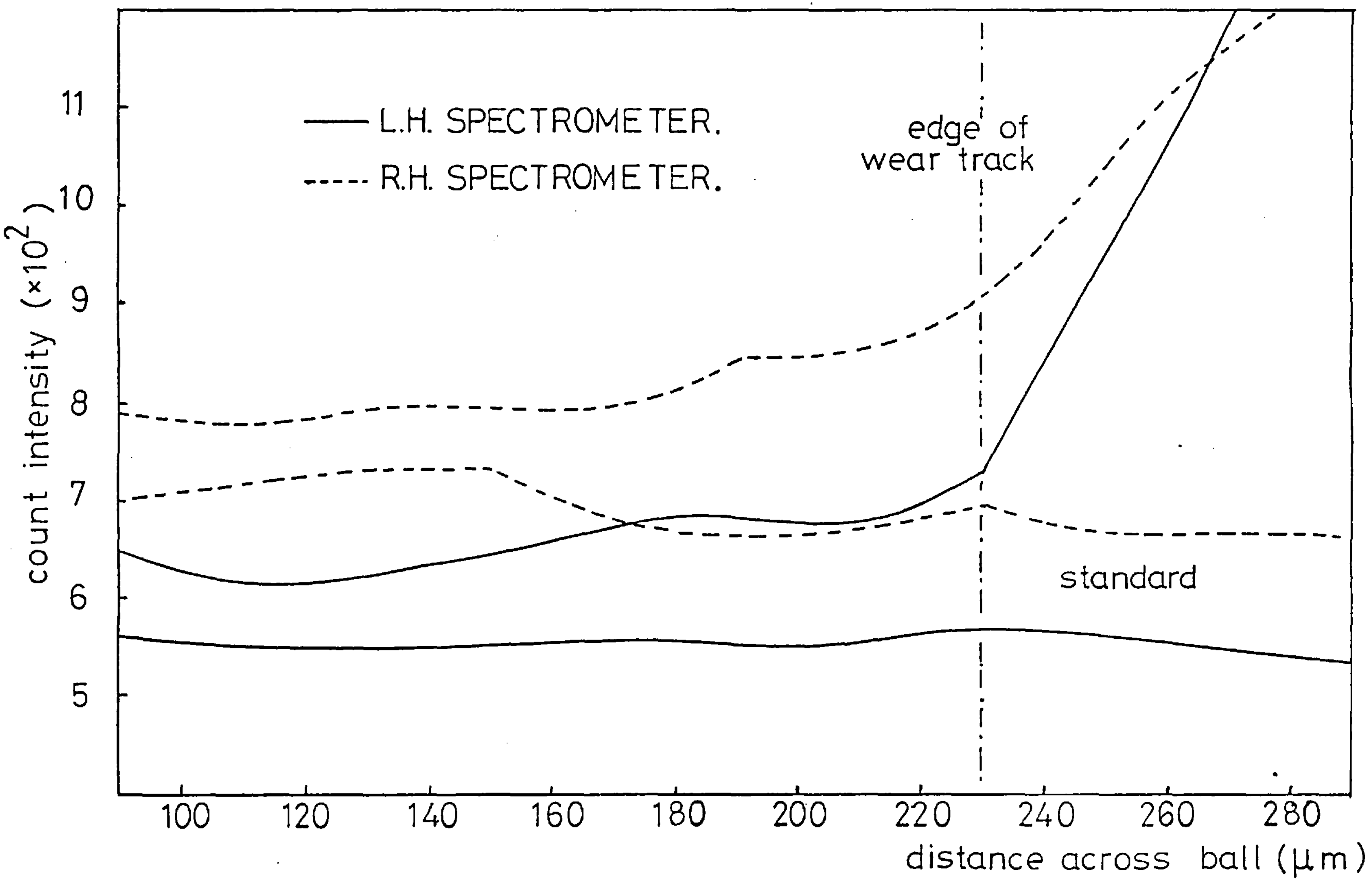


FIG 2·21 EPMA COUNT outside track rubbed in DBDS solution.

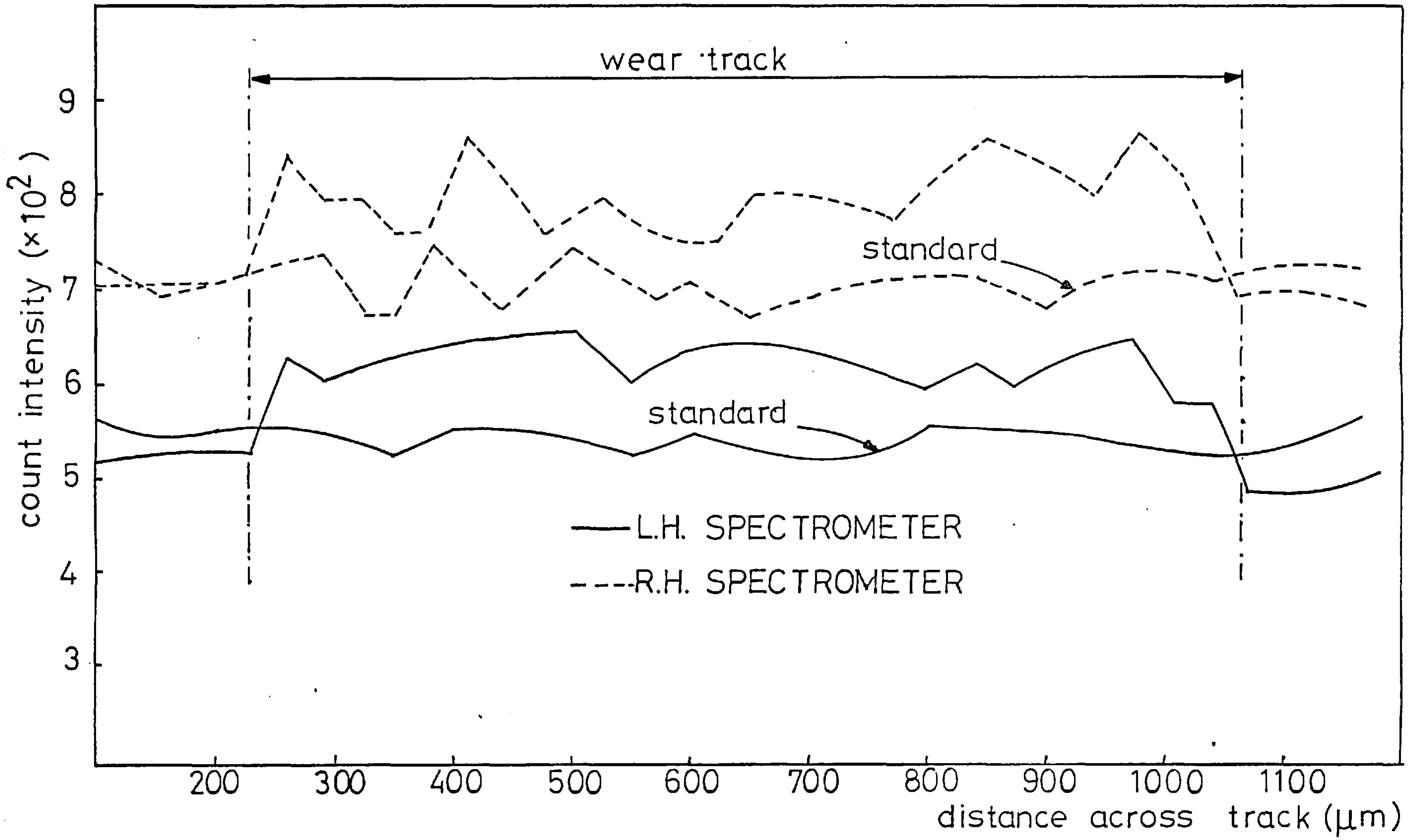


FIG 2·22 EPMA COUNT across track rubbed in pure cetane.

(Fig 2.19). The X-ray Image (X.R.I.) picture (Fig 2.20) shows the distribution of sulphur in the wear track. Each count of sulphur - Kα radiation appears as a dot on the photograph. Thus a high count rate of sulphur radiation is represented by a high density of dots.

Fig 2.21 compares the sulphur count outside the wear track of the EN 31 ball rubbed in cetane + dbds, with that of the standard. A small but definite increase in sulphur content is revealed, indicating that the extent of reaction outside the wear track is limited. This is consistent with the findings of Prutton et. al. (50) and Saleh (53), who demonstrated that oxide-coated iron surfaces substantially slowed rates of reaction and attributed this to the resistance offered by oxide films to the outward diffusion of ferrous ions (50).

(b) EN 31 BALL RUBBED IN PURE CETANE

A comparison between the standard and a ball rubbed in pure cetane is shown in Fig 2.22. The observed increase in sulphur content across the track may possibly be due to reaction of the steel with sulphur impurities remaining in low concentrations in the cetane.

It has been shown, however, that under conditions in which heavy plastic deformation exists within surface regions there is a tendency for segregation of minor alloying constituents to occur towards the surface. Plastic deformation of surfaces under load, leads to cold-working of these layers and consequently to a high density of dislocations at the surface. Sites of lower strain energy exist around lattice imperfections and solute atoms which misfit in the solvent lattice are able to diffuse readily to these sites, especially when their mobility is increased at high temperatures. In particular, surface segregation of tin in copper-tin alloys was observed by Roberts (63) and was explained on the basis of this model. Earlier, Gansheimer and Holinski (64) used E.P.M.A. techniques to show that surface segregation of silicon and chromium occured in the wear tracks of bearing steels rubbed in a four-ball tester. The concentrations of these elements in the surface layers were found to be several times that in the bulk.

The consistency of the higher sulphur count within the wear tracks above the datum level, (2.22) and the fact that the cetane base oil was carefully purified beforehand, indicate the possibility that segregation of sulphur occurs towards the steel surface under rubbing conditions.

Though these results confirm that sulphur plays a major role in protecting iron surfaces during E.P. lubrication, it is unlikely that the E.P. film is composed entirely of iron sulphide. Godfrey (23) ran gear teeth in sulphurised mineral oil and noted that the film consisted mainly of $Fe_3 O_4$, with iron sulphide present in small quantities. Sakurai et. al. (25) also found $Fe_3 O_4$ in the film formed by reacting steels with some sulphur additives. However, with more reactive dibenzyl disulphide, FeS was the major constituent of the film, which also showed traces of FeS_2. It can be seen that the composition of the film remains uncertain and probably contains a mixture of sulphides and oxides of the minor alloying constituents such as chromium and nickel (Section 3.50), in addition to those of iron. For these reasons, as well as the likely non-stoichiometric nature of the sulphide compound, it was considered impractical to quantify the sulphur levels by E.P.M.A. techniques.

It is equally unlikely that lubrication is provided solely by a chemically-reacted inorganic film. Bowden and Tabor (18) suggested that friction would not be appreciably lowered unless polar compounds were also present, owing to the relatively high shear strength of iron sulphide. Independent results obtained by Davey (14,19) and Campell (12) confirmed this. Subsequently Sakurai (20) showed that surfactants were adsorbed more actively on sulphide than on oxide surface-layers. It is thus probable that the lubricating process is aided by the adsorption of dibenzyl disulphide or of oxidation products of the cetane base oil, onto the E.P. film.

2.50 RESULTS AND DISCUSSION - II

Fig 2.9 shows a further drop in friction with EN 31 steel, seemingly dependent upon heating rate (Fig 2.10) over the temperature range 30° - 90°C. Spikes (60) demonstrated a similar effect with dibenzyl disulphide in cetane and suggested, without further study, that this drop might be due to the formation of a mercaptide layer with some E.P. properties. It is evident however, (Fig 2.9) that the friction drop is not caused by the additive, but rather is a function either of the base oil or of the steel itself.

Fig 2.11, shows the dependence of friction with time of EN 31 surfaces in pure cetane. This test was run-in to high friction, then left for one hour without rubbing. On restarting, friction remained at the high level reached on run-in, but subsequently fell with further rubbing to a value similar to that reached on heating (Fig 2.9), indicating that the rubbing process itself was responsible for the drop.

Hardy (65), similarly observed that the coefficient of friction between surfaces lubricated by surface-active molecules dropped over a period of time, from an initially high level to a lower, steady value. This "latent" period was attributed by the author to the time occupied in the orientation of lubricant molecules in the adsorbed layer. Hardy further suggested that the recorded friction value was a measure of the degree of orientation of the molecules. Supporting evidence was available in that non-polar molecules such as straight-chain, saturated hydrocarbons, did not exhibit a "latent" period.

On the basis of this hypothesis then, a possible explanation to the friction drop is the adsorption and subsequent orientation either of polar molecules present in the cetane as impurities, or, more likely, of products formed by the thermal breakdown of the cetane base oil as temperature increases. However, as the observed latent period (Fig 2.11) is considerably longer than that described by Hardy, a further explanation is necessary.

It is well known that sliding of solid surfaces under boundary conditions is accompanied by contacts between opposing asperities. It has further been shown (66), that metallic junctions formed between asperities on opposing surfaces are sheared, thus exposing areas of fresh metal. Very little appears to be known about these freshly-formed "nascent" surfaces, though it is generally accepted (67, 68) that these areas are momentarily very reactive and interact rapidly with the most reactive compounds present in the lubricating oil. It is possible that oxidation of the base oil is catalysed by the presence of "nascent" metal and that subsequent adsorption of the products of oxidation is responsible for the reduction in friction. However, the appearance of the wear track, which showed traces of a rusty-coloured deposit after testing, seems to indicate that oxidation of the steel had taken place, possibly by reacting with oxygen dissolved in the cetane base oil. The remarkable similarity between Figs 2.11 and Fig 2.12, which shows the results of tests carried out on unlubricated EN 31 steel, supports this latter possibility. Again the unlubricated wear track showed a rusty-coloured deposit.

Evidence is also found in the work of several authors. Vinogradov and his co-workers (69 - 72), established that hydrocarbons can participate actively in E.P. film formation by acting as carriers for molecular oxygen. Further work (72) compared friction tests in air with others in an argon atmosphere and demonstrated a sharp rise in the kinetic friction of steels lubricated by hydrocarbons in argon. Similar dynamic tests by Toguyachi and Takai (21,22) showed that E.P. properties fell when dissolved oxygen was removed from the oils under test. Sakurai et. al. (34), used a hot-wire apparatus (33), to show that considerable corrosion of iron wire occurred in white oil alone even at relatively low temperatures. It was concluded that the corrosion was caused by oxygen dissolved in the white oil. Fig 2.13 shows the results of unlubricated tests carried out at a higher load than those in Fig 2.12. Friction after run-in remained constant at a high value and did not fall with rising temperature. On examination, the wear tracks were badly worn and showed no signs of any deposit. However, the peg cup was found to contain small quantities of a rusty powder, samples of which were collected for analysis.

The structure of the powder was examined by X-ray diffraction and the composition of a further sample determined by electron probe microanalysis. The results of these analyses are discussed in the following section.

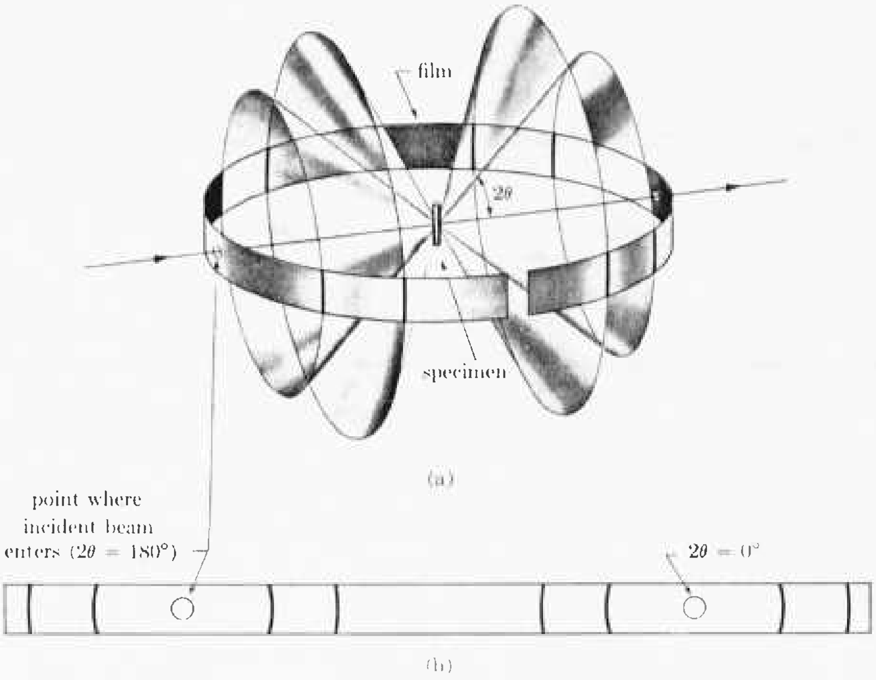


FIG 2.23

DEBYE-SCHERRER POWDER METHOD

(a) relation of form to specimen and incident beam

(b) appearance of film after exposure

2.51 POWDER ANALYSIS

In the Debye-Scherrer method of X-ray diffraction analysis, a sample of the powder is packed into a thin-walled capillary tube which is then placed on the axis of a cylindrical strip of film and rotated in a beam of monochromatic X-rays. (Fig 2.23a)

Each particle of the powder acts as a tiny crystal orientated at random with respect to the incident beam. Thus, every set of lattice planes are capable of reflection such that, effectively, the mass of powder is equivalent to a single crystal rotated about all possible axes. Cones of diffracted radiation intersect the film strip and from the resulting pattern (Fig 2.23b) the spacing of the reflecting lattice planes can be calculated. Unfortunately, however, no pattern was found, which suggested that the sample was either amorphous or of too small a crystallite size for analysis.

For examination by microprobe, a portion of the powder was mounted on adhesive tape and earthed to the holder by a carbon-coating. The spectrometers were driven to vary the angle Θ (section 2.41) - thereby effectively scanning a fixed area of the specimen over a spectrum of wavelengths. On the resulting plot of intensity against wavelength, the presence of a certain element is indicated by a "peak" at a specific wavelength. A "spectrum" scan carried out on the powder, detected only iron and traces of chromium and manganese. Results of a "spectrum" scan in the track of a ball rubbed in pure cetane, similarly revealed only the constituents of the steel and a sulphur content slightly above the datum level (discussed in 2.44b).

Owing to the low atomic number, oxygen analysis is almost impossible by E.P.M.A. techniques, as the emitted X-rays have a correspondingly high wavelength and are readily absorbed by other elements. A faint magnetic property and the appearance of the specimen, together with the fact that no other elements were detected, combine to suggest that the material consisted of "oxides" derived from the EN 31 steel.

Thus it seems that an oxidation process was continuing but at the high loading, the oxide film was scraped off immediately it was formed and so was not able to lubricate the rubbing surfaces.

This is better demonstrated in Fig 2.14, which shows the reversibility effect of temperature on the oxidation of unlubricated EN 31 steel.

At low temperatures there is no film protection and friction remains high. However, oxidation rate increases with temperature and an oxide layer is formed lowering the coefficient of friction. On further cooling, the oxidation rate decreases and friction rises as the oxide film previously built up, is scraped off the surface.

A similar reversibility effect with dibenzyl disulphide dissolved in cetane on EN 58 steel is demonstrated in Fig 2.15. Friction is observed to fall at 175°C but increases again as temperature drops below this value on cooling. Spikes (60) has shown that dibenzyl disulphide reacts with stainless steel at temperatures well below 175°C. This apparent temperature lag indicates the possibility that in order to ensure efficient E.P. lubrication, a film must be built up of sufficient thickness to withstand being totally abraded off the surface during rubbing. Work on preformed sulphide films by Campbell (12) has supported this suggestion. Fig 2.24 is reproduced from this reference and shows the friction coefficient obtained between steel surfaces treated with sodium sulphide solution as a function of the "equivalent air film thickness", which is the thickness of an air film between glass plates giving the same colour as the sulphide film observed by a spectro-photometric method. Constable (73) has shown that air-film thicknesses provide a relative measure of the thickness of a sulphide film.

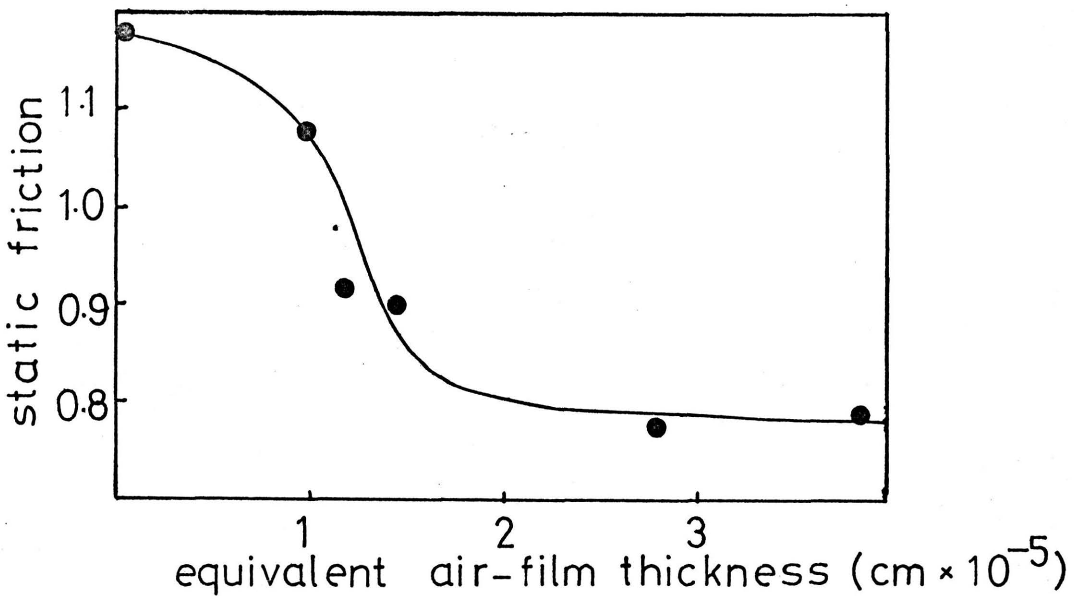


FIG 2·24

FRICTION vs FILM THICKNESS
(reproduced from (73))

Fig 2.24 clearly shows a limiting film thickness below which a high friction coefficient is obtained. Therefore, on the assumption that the E.P. reaction takes place out-of-contact (56) and that the formed film is entirely or almost entirely removed from the surface during sliding, then it seems that a critical film must be laid down during a single revolution of the top ball for effective E.P. lubrication.

2.60 CONCLUSIONS

Preliminary investigations have been carried out into the reaction of dibenzyl disulphide on steels.

The formation of a sulphur-containing E.P. layer is confirmed by electron probe microanalysis and is made apparent by a drop in the coefficient of friction between steels lubricated with a model E.P. oil.

A secondary friction drop is observed with EN 31 steel which has been attributed to oxidation of the steel by oxygen dissolved in the cetane base. Unreactive EN 58 stainless steel remains unaffected by oxidation as expected.

It is shown that the ratio between rate of film formation and rate of surface removal is of extreme importance in the build-up of an E.P. film.

On the assumption that reaction takes place outside contact and that, effectively, all chemical surface films are abraded off the surface during passage through the conjunction, then in order that the friction between the sliding members of the ball-on-triplane machine will be effectively reduced, a critical number of chemically reacted layers must be formed during a single revolution of the ball.

CHAPTER THREE

THE EFFECTS OF SLIDING SPEED ON THE LUBRICATION OF EN 31 STEEL BY DIBENZYL DISULPHIDE

3.10 INTRODUCTION

Since the extent of extreme pressure reaction depends upon the amount of time available, the results of the previous chapter indicate that extreme pressure film formation might be affected by the sliding speed.

Chapter three describes the experiments conducted to investigate this dependence.

3.20 EXPERIMENTAL

3.21 SPEED RANGE

A large range of sliding speeds was available on the ball-on-triplane machine. However, it was found necessary to limit tests to the range of speeds between $^1/50$ and 10 r.p.m. since above 10 r.p.m. frictional heating could no longer be neglected and the problem of evaporation of the base oil occurred at the higher temperatures required. Below $^1/50$ r.p.m., difficulties were encountered in controlling the rate of the rise in temperature (Section 3.22).

Speed changes were easily achieved by interchanging a series of reduction gear boxes in the drive system (Section 2.20).

The experimental techniques used in conducting these tests, have already been described (Section 2.22). However, at sliding speeds below $^1/10$ r.p.m., experiments were run-in to high friction at 1 r.p.m. before reverting to the desired speed. This was to prevent prolonged exposure of the lubricant to the atmosphere, since running-in at $^1/10$ r.p.m.

or less would have taken several hours.

3.22 HEATING RATE

Though the previous chapter demonstrated the independence of the E.P. friction drop on the heating rate, it was found necessary for practical reasons to alter the rate of temperature rise with sliding speed. Over the intermediate speed range ($^1/10$ - 3 r.p.m.), a heating rate was employed such that temperature rose by 5°C per minute. (Section 2.22). If this rate were used at very low sliding speeds ($^1/10$ r.p.m.) then a critical lubricating film might be laid down within a single revolution of the ball and results could not be compared with any degree of accuracy. Ideally, the temperature rise per revolution should be kept constant over the entire speed range, but this degree of heat control could not be achieved at very low sliding speeds. However, by a step-voltage Variac procedure, it was found possible to maintain a mean rate of temperature rise of $^1/2$°C per minute.

For tests carried out at speeds in excess of 3 r.p.m., a maximum rate of 25°C per minute was employed to minimise loss of the cetane base oil by evaporation (Section 3.21).

3.23 MATERIALS AND LUBRICANT

EN 31 steel specimens were used throughout these experiments, owing to the prohibitive cost of EN 58 stainless steel balls. The lubricant was a 1% (wt.) solution of dbds in cetane as before (Section 2.21).

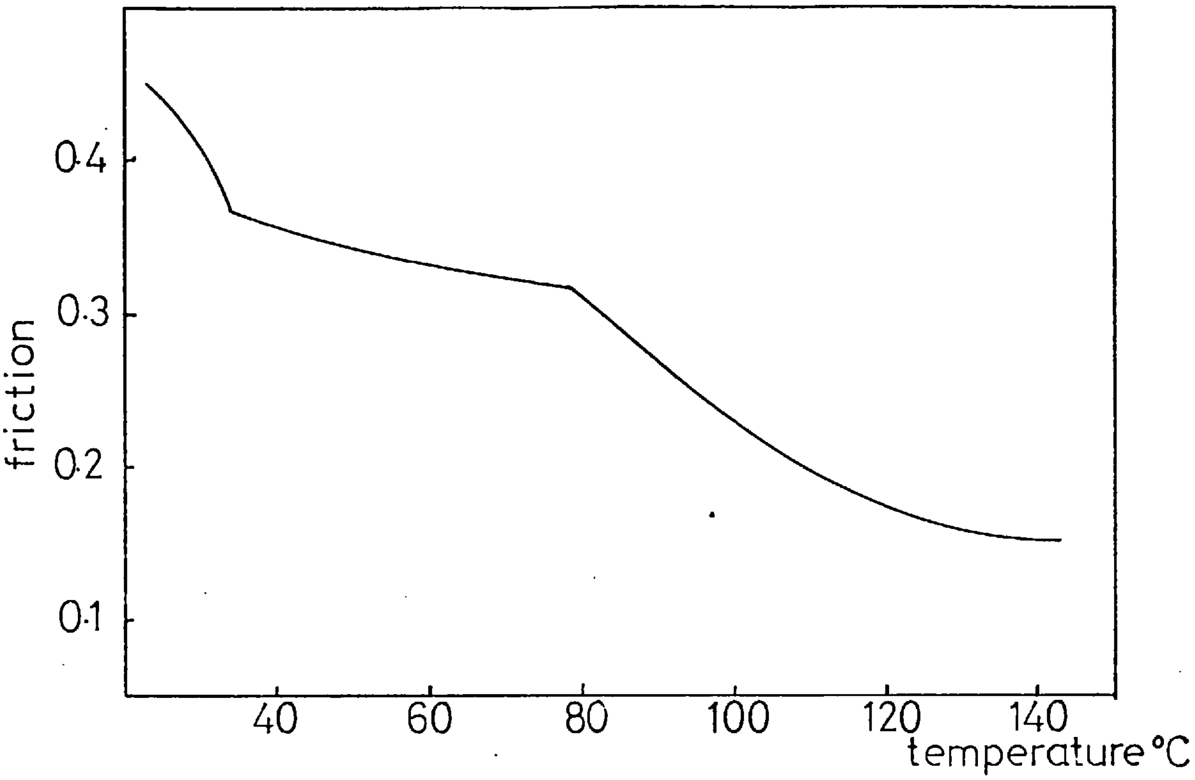


FIG 3·1 FRICTION vs TEMPERATURE. 1% DBDS on EN 31 STEEL, 1/50 rpm.

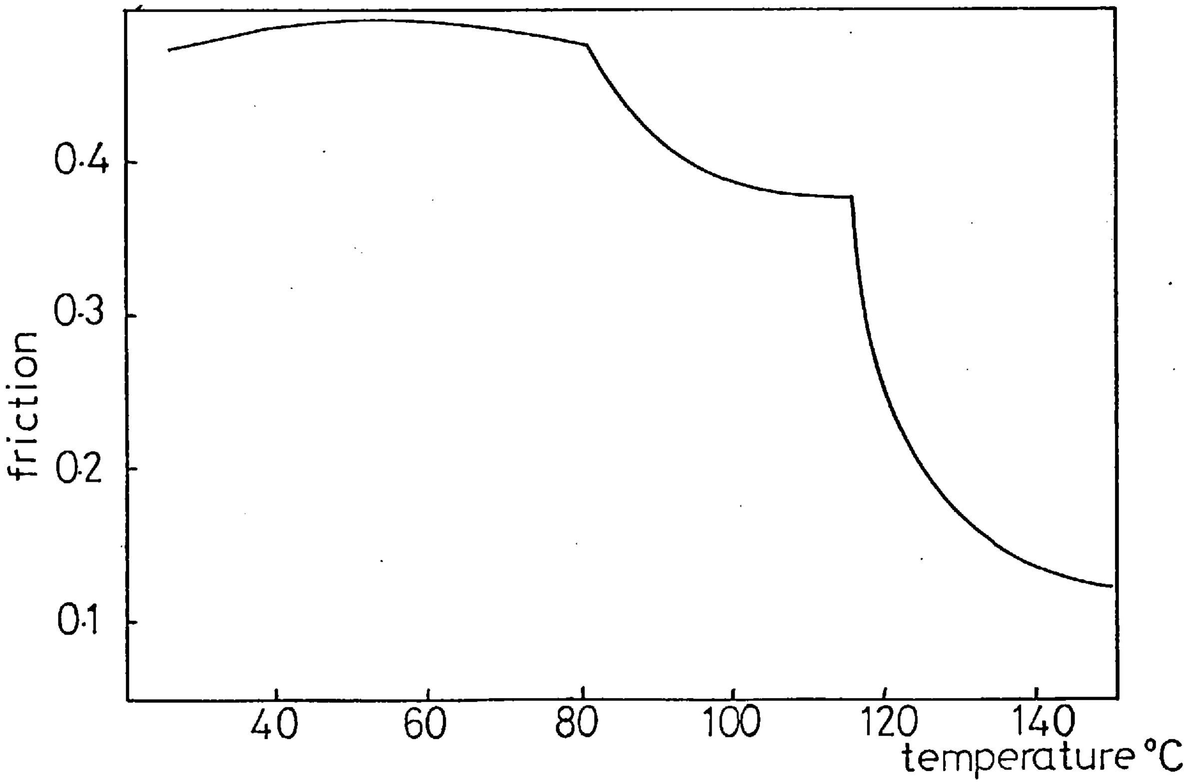


FIG 3·2 FRICTION vs TEMPERATURE. 1% DBDS on EN 31 STEEL, 1/10 rpm.

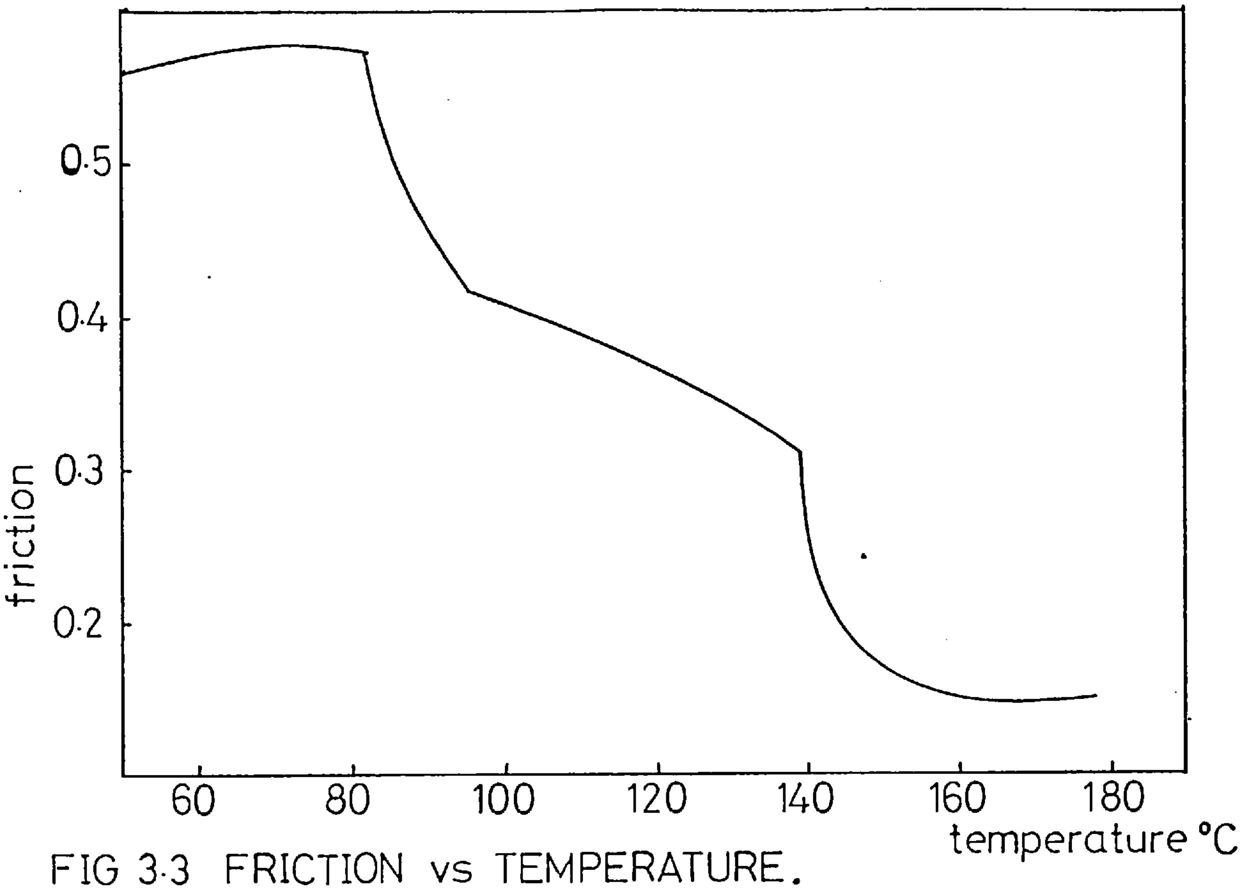


FIG 3·3 FRICTION vs TEMPERATURE.

1% DBDS on EN 31 STEEL, 1/3 rpm.

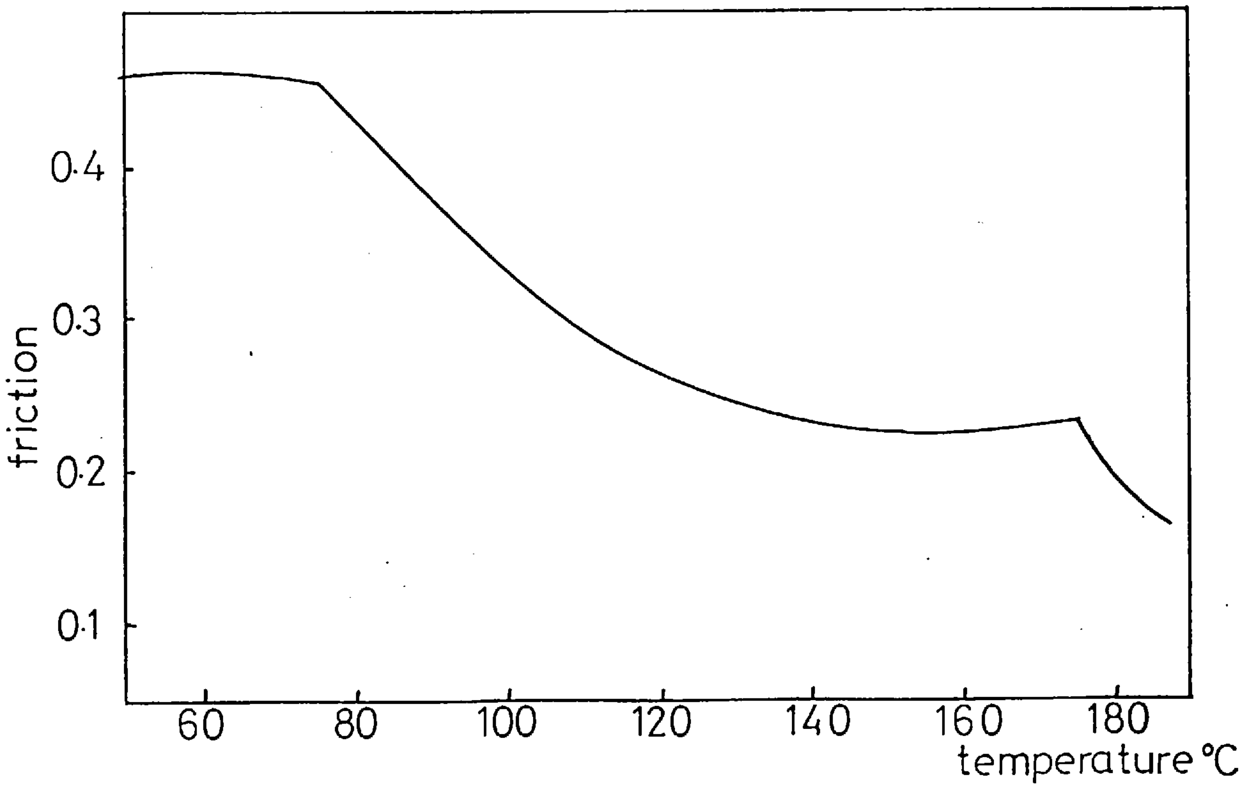


FIG 3·4 FRICTION vs TEMPERATURE.

1% DBDS on EN 31 STEEL, 1 rpm.

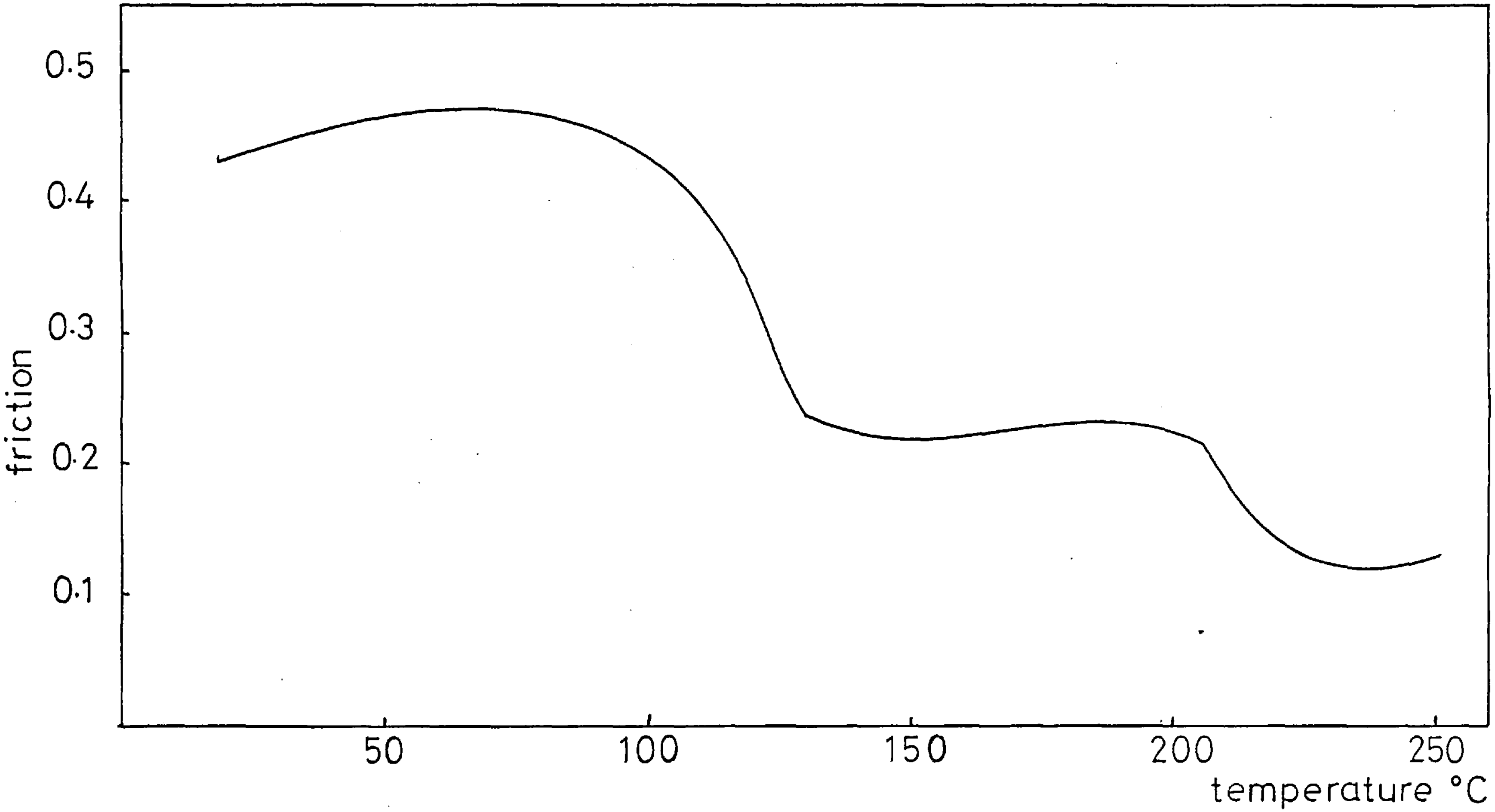


FIG 3·5 FRICTION vs TEMPERATURE. 1% DBDS on EN 31 STEEL, 3 rpm.

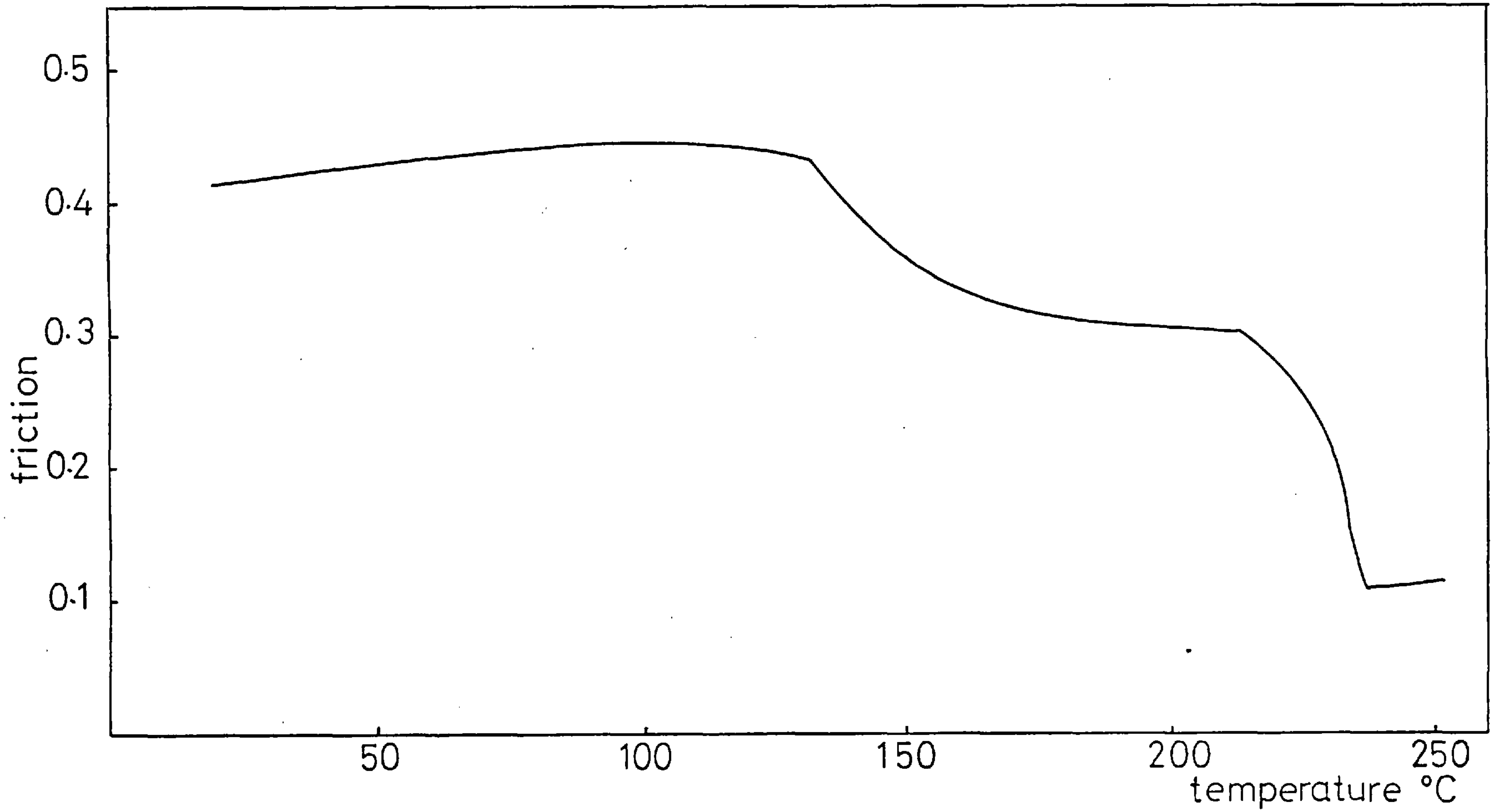


FIG 3·6 FRICTION vs TEMPERATURE. 1% DBDS on EN 31 STEEL, 3 1/3 rpm.

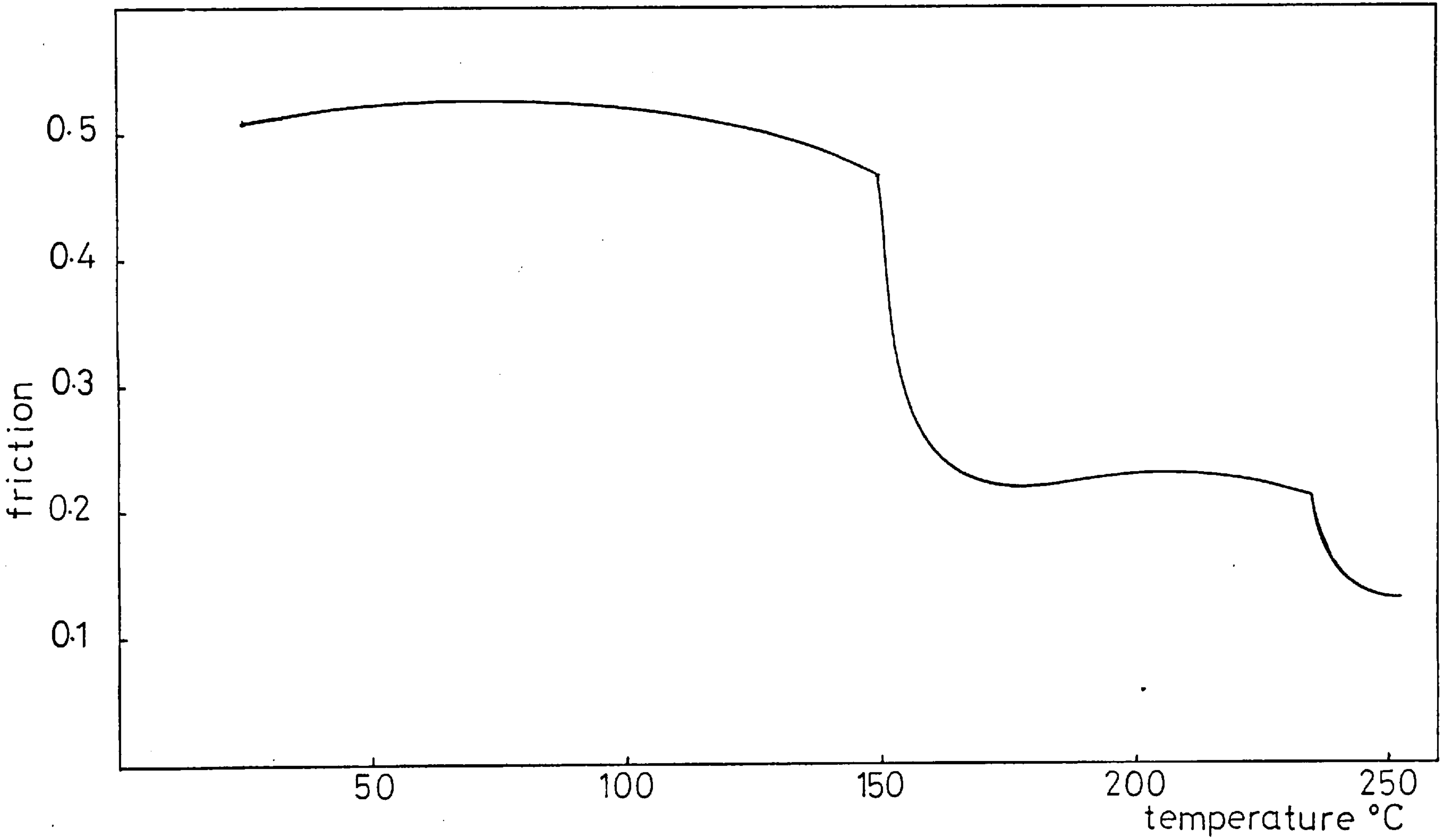


FIG 3·7 FRICTION vs TEMPERATURE. 1% DBDS on EN 31 STEEL, $6\frac{1}{2}$ rpm.

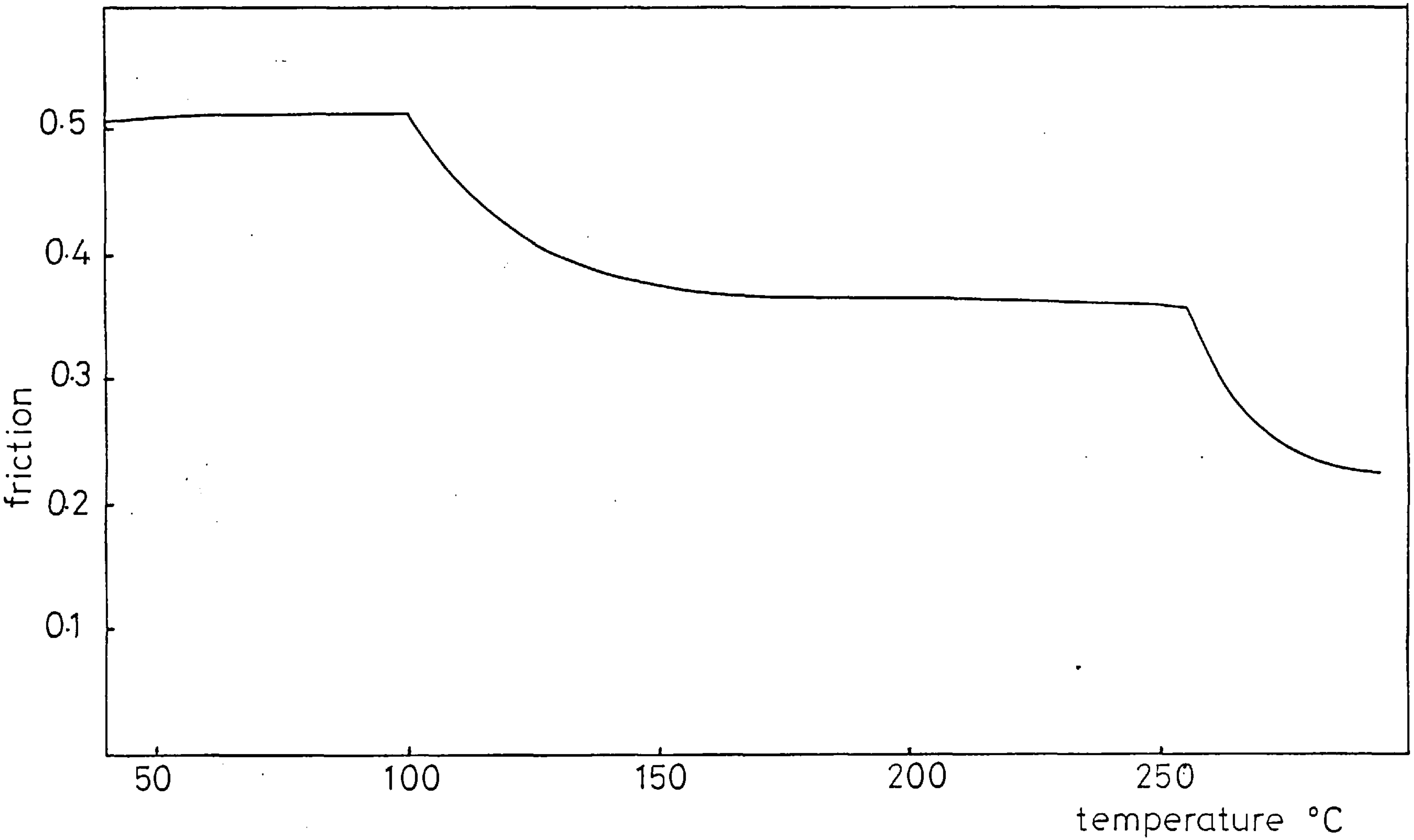


FIG 3·8 FRICTION vs TEMPERATURE. 1% DBDS on EN 31 STEEL, 10 rpm.

3.30 ACCURACY

The temperature at which the friction transition occurred was found to fluctuate within ± 2°C of the mean value of three experimental runs at each sliding speed.

At intermediate speeds ($^1/10$ - 3 r.p.m.) a systematic error in temperature measurement, due to the difference in temperature between the peg surface and the thermocouple was estimated (Section 2.30) to be +2°C at the heating rate of 5°C per minute.

Above 3 r.p.m. however, a heating rate of 25°C per minute was employed (Section 3.22) and the systematic error increased accordingly to +10°C.

At speeds of less then $^1/10$ r.p.m., the correspondingly low heating rate of $\frac{1}{2}$°C per minute (Section 3.22) reduces the measured temperature difference between the peg surface and the trailing thermocouple to negligible proportions and no correction is therefore necessary.

3.40 RESULTS

Figs. 3.1 - 3.8 show the results of friction-temperature experiments carried out on the ball-on-triplane machine at speeds between $^1/50$ and 10 r.p.m. Each plot displays characteristics similar to those demonstrated in the previous chapter in that two distinct friction drops are apparent.

The tests depicted in Figs. 3.2 - 3.5 were carried out at different speeds but at a constant rate of temperature rise of 5°C per minute. (Section 3.22). The consistency of the drop in friction in the region of 80°C in these tests confirms the earlier observation that variations in the temperature of the first friction transition are caused by differences in heating rate (Section 2.50).

This thesis however, is concerned primarily with the friction drop already attributed to extreme pressure action. The results of the previous chapter indicated that the extent of E.P. reaction (film thickness) is determined by the time between consecutive contacts, which is inversely proportional to sliding speed. The thickness of the E.P. film is also governed by the rate at which the reaction between the steel surface and the E.P. agent proceeds, which is, in turn dependent upon surface temperature. Thus, at a given sliding speed (i.e. fixed reaction time), when the increased surface temperature raises the reaction rate to the extent that a critical thickness is formed within a single revolution of the ball, the chemical film causes friction to drop as E.P. lubrication commences. It is clear that a change in sliding speed alters reaction time proportionately and so affects the temperature at which the limiting film thickness is reached.

This dependence of the E.P. friction transition on sliding speed is clearly demonstrated in Figs. 3.1 - 3.8. The resulting transition temperatures are shown corrected for systematic error (Section 3.30) in table 3.1.

V r.p.m.	$\log_{10} V$	Tm °C	Tm °K	T_T °K	$\frac{1}{T_T}$ ($°K^{-1} \times 10^{-3}$)
$^{1}/_{50}$	-1.6990	78	351	351	2.849
$^{1}/_{10}$	-1.0000	113	386	388	2.577
$^{1}/_{3}$	-0.4771	140	413	415	2.410
1	0.0000	175	448	450	2.222
3	0.4771	205	478	480	2.083
$3^{1}/_{3}$	0.5228	212	485	495	2.020
$6^{1}/_{2}$	0.8129	237	510	520	1.923
10	1.0000	255	528	538	1.859

TABLE 3.1

3.50 DISCUSSION

Assuming the most likely case of monomolecular reaction on individual metal sites, the extent of the E.P. reaction, $[FeS]$ is governed by:-

the reaction time, t,

the concentration of the additive, $[dbds]$,

the concentration of iron on the surface, $[Fe]$,

and the rate constant, k, between the additive and the steel .

Thus
$$\frac{[FeS]}{t} = k.\ [Fe]^{p}\ [dbds]^{q} \qquad \text{------ } 3.1$$

Now sliding speed, V, is inversely proportional to reaction time, t

$$V = \frac{K}{t}$$

$$V = \frac{K\cdot [Fe]^{p}\ [dbds]^{q}}{[FeS]}\cdot k \qquad \text{------ } 3.2$$

The rate constant, K, is related to the reaction temperature, T, by the Arrhenius equation,

$$k = A\,e^{-\frac{E_a}{RT}} \qquad \text{------ } 3.3$$

$$V = \frac{K\cdot [Fe]^{p}\cdot\ [dbds]^{q}\cdot\ A\ .\ e^{-\frac{E_a}{RT}}}{[FeS]} \qquad \text{------ } 3.4$$

Assuming that the reaction between dibenzyl disulphide and steel surfaces follows zero-order kinetics (Chapter Four), and also that, at the extreme-pressure friction drop, a constant critical coverage exists, (Section 4.30), then at the transition condition, the concentration factors in equation 3.4, above are effectively constant and

$$V = K_o\,e^{-\frac{E_a}{RT_T}} \qquad \text{------ } 3.5$$

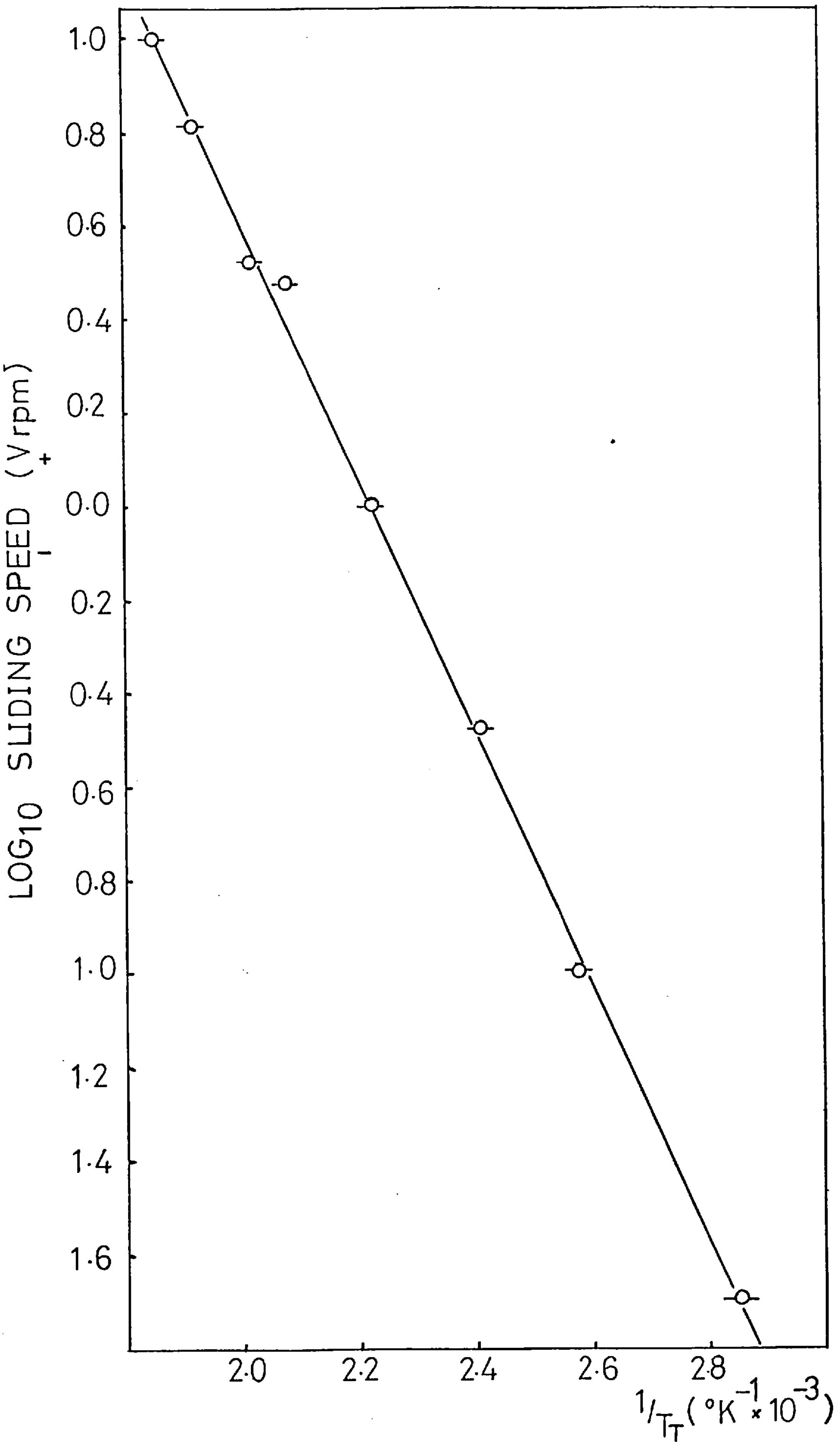


FIG 3·9 LOG$_{10}$ SLIDING SPEED vs $1/T_T$, EN 31 STEEL.
1·0 % DBDS.

or $$\log_{10} V = \log_{10} Ko - \frac{E_a}{2.3RT_T} \qquad \text{------ } 3.6$$

The linear relationship between $\log_{10}$ V and $^1/T_T$ ($^{o}k^{-1}$) predicted in equation 3.6 above, is displayed in Fig. 3.9, which was plotted from the data given in table 3.1. Error bars of $\pm$ 2°C (Section 3.30) give an indication of accuracy.

The Energy of Activation for the reaction can be determined from this plot. The Activation Energy represents the energy that must be acquired by the reactant molecules, in order to be capable of undergoing reaction and is required essentially, to stretch and ultimately break any bonds as may be necessary in the reactants.

The significance of the Energy of Activation is represented schematically in Fig. 3.10 (reproduced from ref.74), in which it is seen that the difference between the energies of activation for forward and reverse reactions is equal to the overall energy change in the reaction.

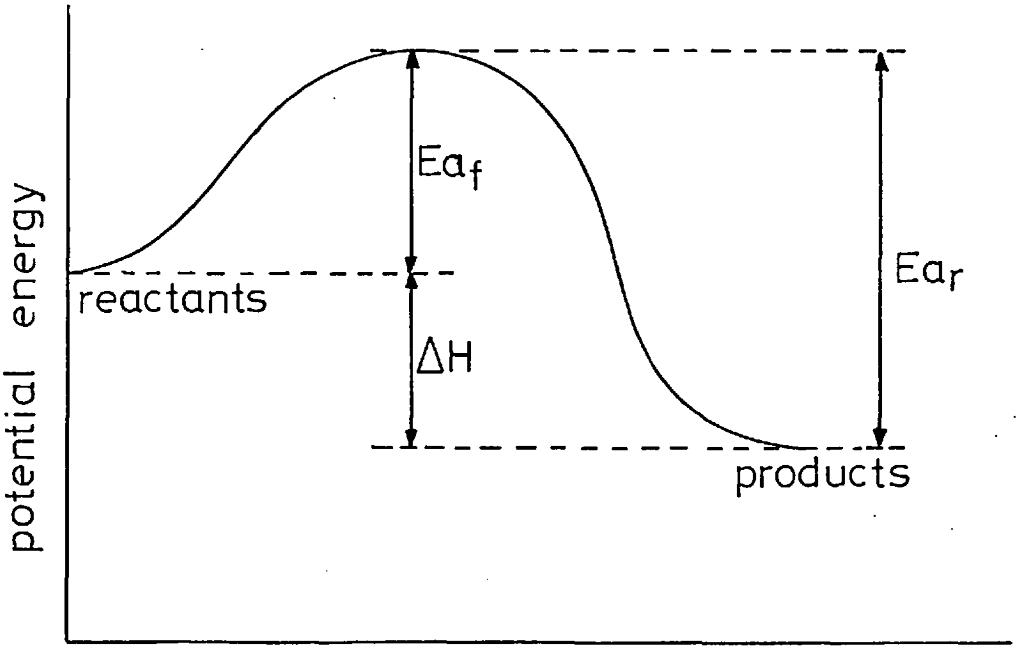


FIG 3.10

The horizontal co-ordinate in the above diagram, the reaction co-ordinate, need have no exact quantitative significance and merely represents the sequence of the reaction.

Since for a heterogeneous reaction, Activation Energy is usually a composite quantity, including not only the energy of the surface reaction, but also the heats of adsorption of the reactants and products (Section 4.30), it is referred to as the Apparent Activation Energy E_a.

On the assumption that the reciprocal of transition temperature is subject to random variation and that deviations about the regression are both independent and follow a normal distribution, a linear regression of the reciprocal of the corrected transition temperature (T_T) was carried out on the logarithm of sliding speed, by the procedure outlined in Appendix 1 at the end of this thesis.

A value of Ea for the reaction of dibenzyl disulphide on EN 31 steel of - 12.55 Kcals/mole was obtained with a standard estimate of the error of ± 0.01 Kcals/mole.

The calculated value for $E_a$above compares favourably with other values obtained for similar metal-lubricant systems.

Sakurai et.al. (34), used the Barcroft method (33), with iron wire in white oil solutions of dibenzyl disulphide at temperatures from 350° - 510°C. The Activation Energy, calculated using data given in (34), assuming a zero-order reaction, was

$$-9.80 \pm 0.5 \text{ Kcals/mole,}$$

regardless of the concentration of the additive.

A more comparable system was used by Spikes (60), who immersed discs of mild and stainless steel in a solution of radiotraced dibenzyl disulphide in cetane. The amount of reaction occurring in ten

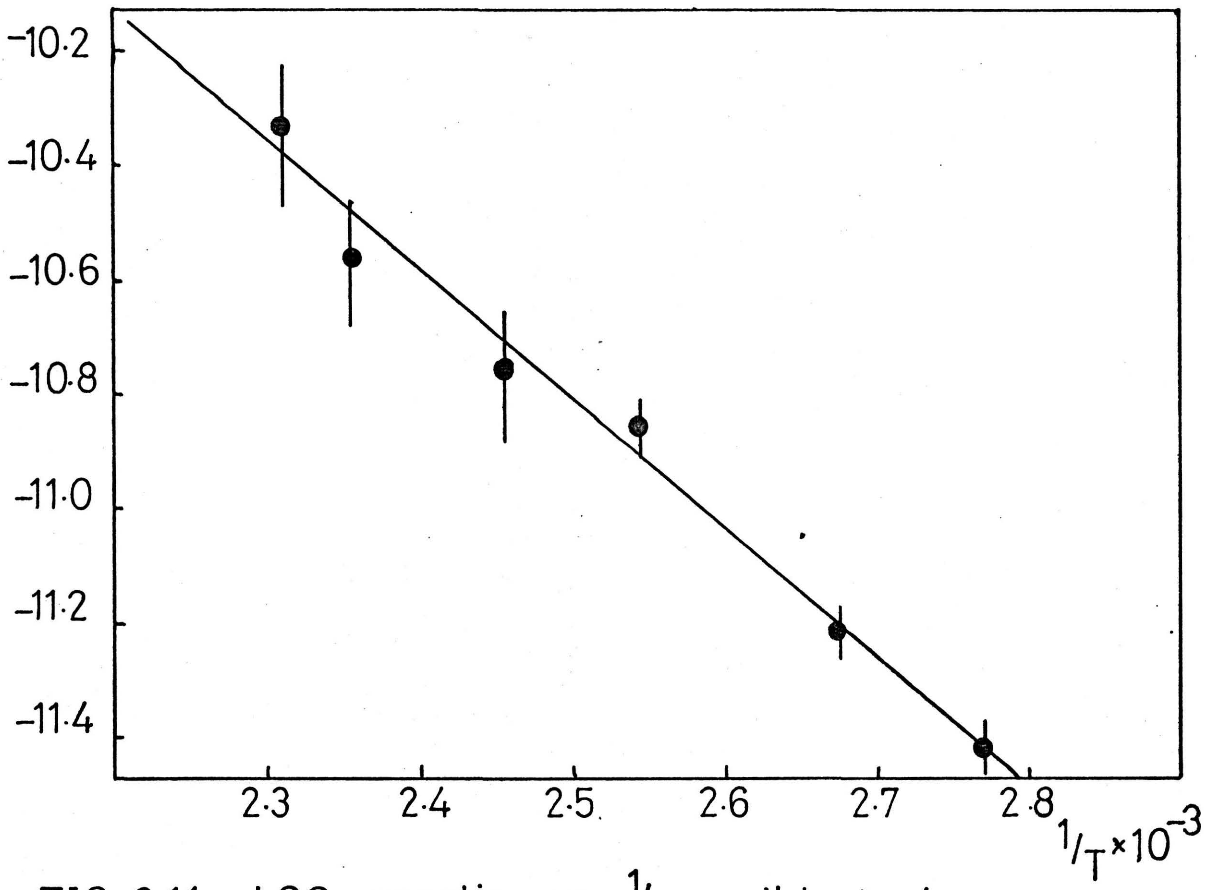


FIG 3·11a LOG_{10}reaction vs $^1/_T$, mild steel.

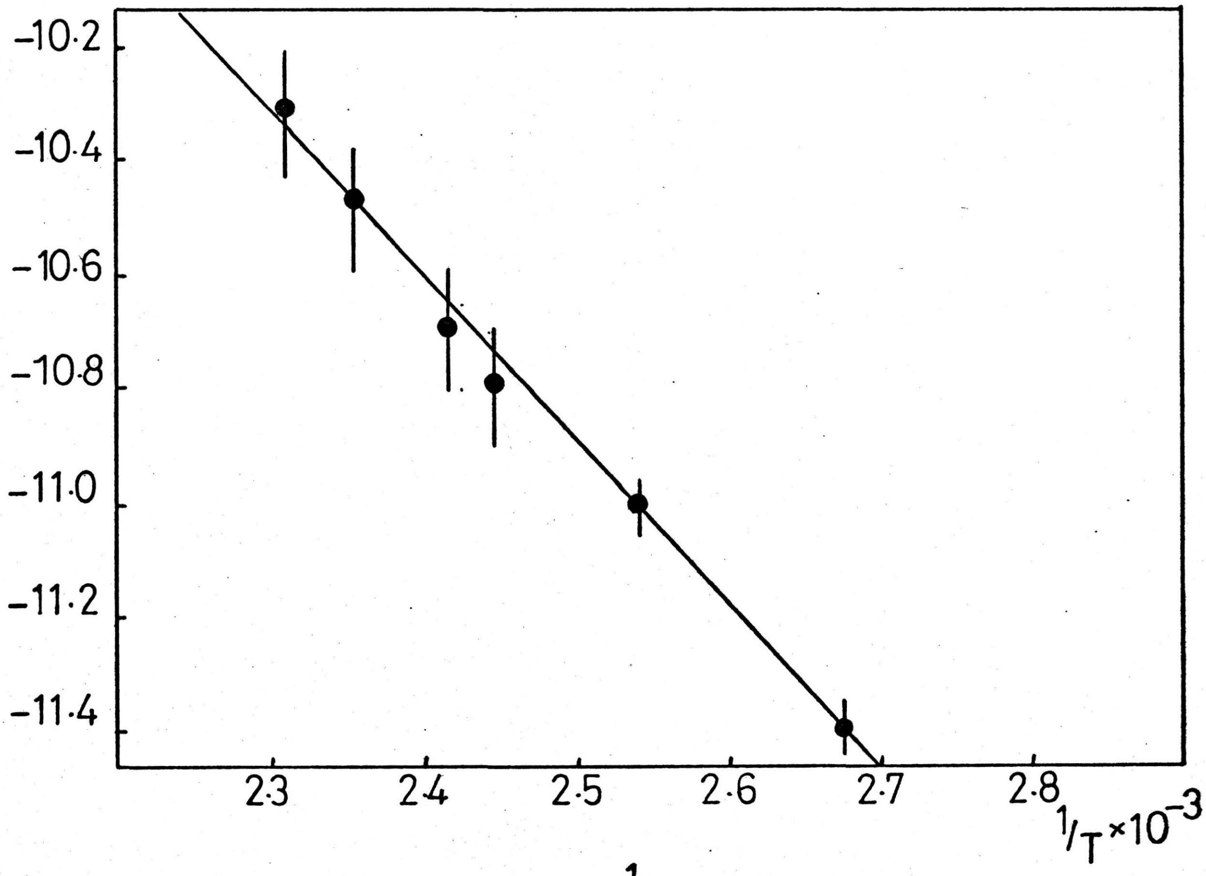


FIG 3·11b LOG_{10}reaction vs $^1/_T$, stainless steel.

minutes was measured at temperatures up to 160°C. Fig. 3.11a and 3.11b were plotted using information supplied by him, again assuming the respective reactions to be of pseudo-zero order. The resulting linear relationships support the validity of this assumption. Values for E_a of - 10.45 (standard error ± 0.12) Kcals/mole and - 13.53 (standard error ± 0.10) Kcals/mole were obtained for the reaction of dbds with mild and stainless steels respectively.

These results are summarised and compared with the results of this chapter in the table below:-

Material	E_a Kcals/mole	Error Estimate Se Kcals/mole
Iron (34)	- 9.80	± 0.50
Mild Steel (60)	- 10.45	± 0.12
EN 31 Steel	- 12.55	± 0.01
EN 58B (60) Stainless Steel	- 13.53	± 0.10

Table 3.2

It can be seen that the Activation Energy spectrum is consistent with the observed order of reactivity of these surfaces, which may indicate that the differences in E_a are due to the increasing percentages of alloying constituents in the steels.

Comparing the values for EN 31 steel with the results of Spikes' static tests for mild and stainless steels, it can be postulated that this is caused by a combination of two effects.

(a) Stainless steel has a high content of both Chromium and Nickel such that simultaneous reaction might result in the formation not only of Iron sulphide but also of Chromium and Nickel sulphides. In this case the measured Ea is a quantity combining the Activation Energies of a number of different reactions.

(b) The layer of chromic oxide on the stainless steel surface acts as a barrier to the outward diffusion of iron to the surface. (75). Thus the value of Ea for stainless steel possibly contains a contribution due to diffusional energy.

The fact that the EN 31 tests above were conducted in a rubbing situation, such that any barrier to diffusion would be removed during contact, suggests that the difference in Ea between mild and EN 31 steel is provided by the former. The magnitude of the difference in turn suggests the formation of a significant proportion of chromium sulphide on the surface of EN 31 steel, which initially appears to be inconsistent with the specified chromium content (1 - 1.6% - table 2.1). However, the surface concentration of chromium in bearing steels has been shown to be very much higher at the area of frictional contact (63), due to the segregation of chromium along dislocations to a depth of up to 8μm. (Section 2.45).

3.60 CONCLUSIONS

On the assumption that the reaction between dibenzyl disulphide and EN 31 steel is kinetically of zero order, an expression has been derived relating the logarithm of sliding speed, with the reciprocal of the absolute temperature of the friction transition.

Experimental results have confirmed this relationship.

The Apparent Activation Energy for the reaction was found to equal - 12.55 ± 0.01 k.cals per mole and was compared with values calculated for similar metal-additive systems.

CHAPTER FOUR

THE EFFECTS OF ADDITIVE CONCENTRATION ON THE LUBRICATION OF EN 31 STEEL

4.10 INTRODUCTION

The fundamental purpose of a reaction rate study is to develop a theoretical background on which interpretation of data may be based. The first stage in the development of such a model, is the determination of the reaction mechanism, which is basic to the subsequent kinetic study of any chemical process.

The term 'reaction mechanism' has two meanings. The first of these refers to the particular sequence of elementary reactions that leads to the overall chemical change whose kinetics are under study. The more recent concept of reaction mechanism includes not only a knowledge of all the individual steps in the overall reaction, but also a detailed analysis of each step as it occurs.

Whereas kinetic studies are useful in determining the individual steps of a reaction, their use in giving stereochemical details is limited. In the scope of this thesis therefore, the mechanism of the reaction will be understood to have been established when a sequence of elementary steps is shown to explain the observed kinetic behaviour.

Circumstantial evidence regarding the mechanism of a reaction is provided by the rate law which may be deduced empirically by observing changes in the concentration of one or more of the reactants as a function of time. The application of direct quantitative analysis to determine reactant concentrations during the course of an experiment is difficult. However, simplification may be achieved by studying changes

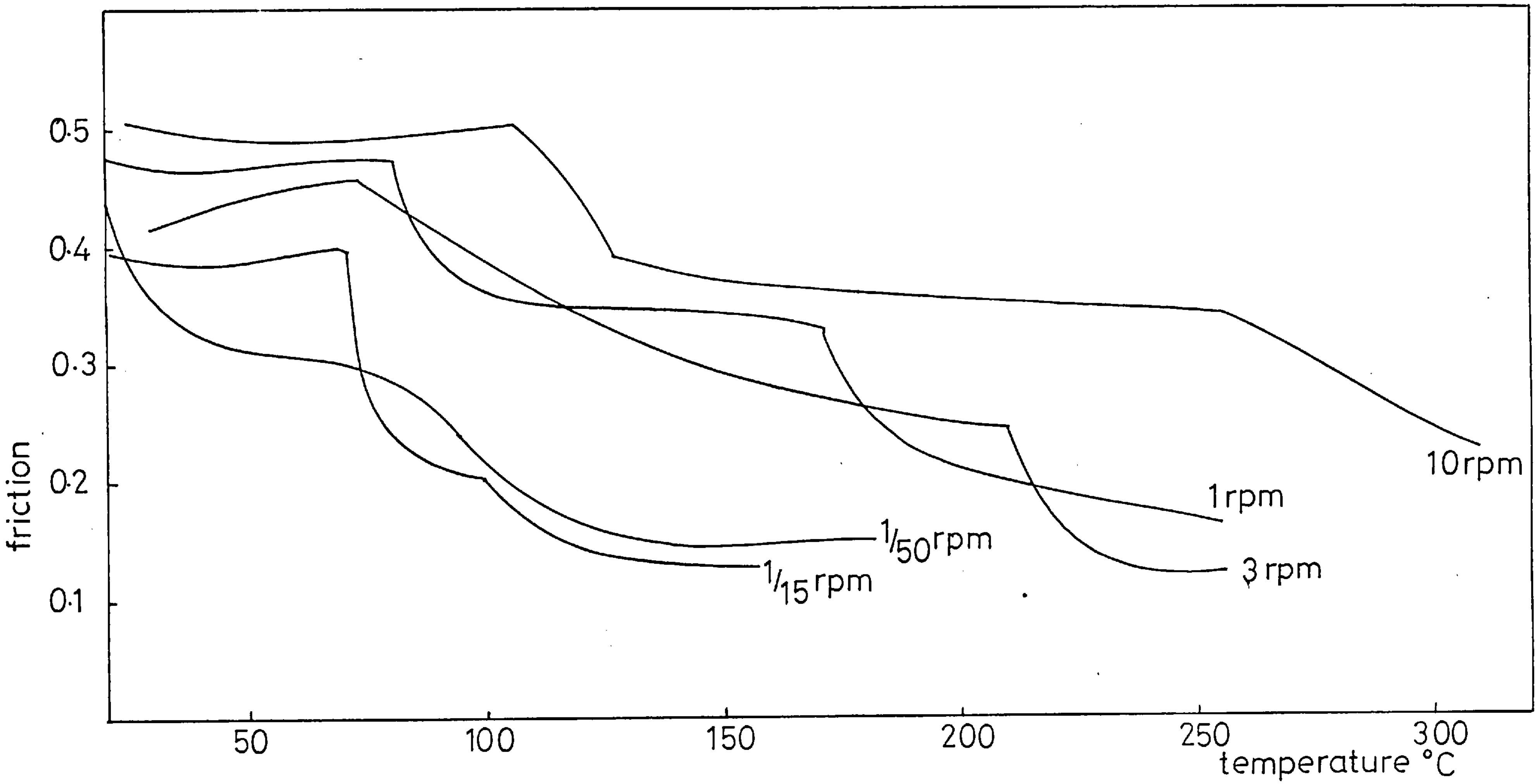


FIG 4·1 DEPENDENCE of FRICTION TRANSITION on SLIDING SPEED, 2% DBDS.

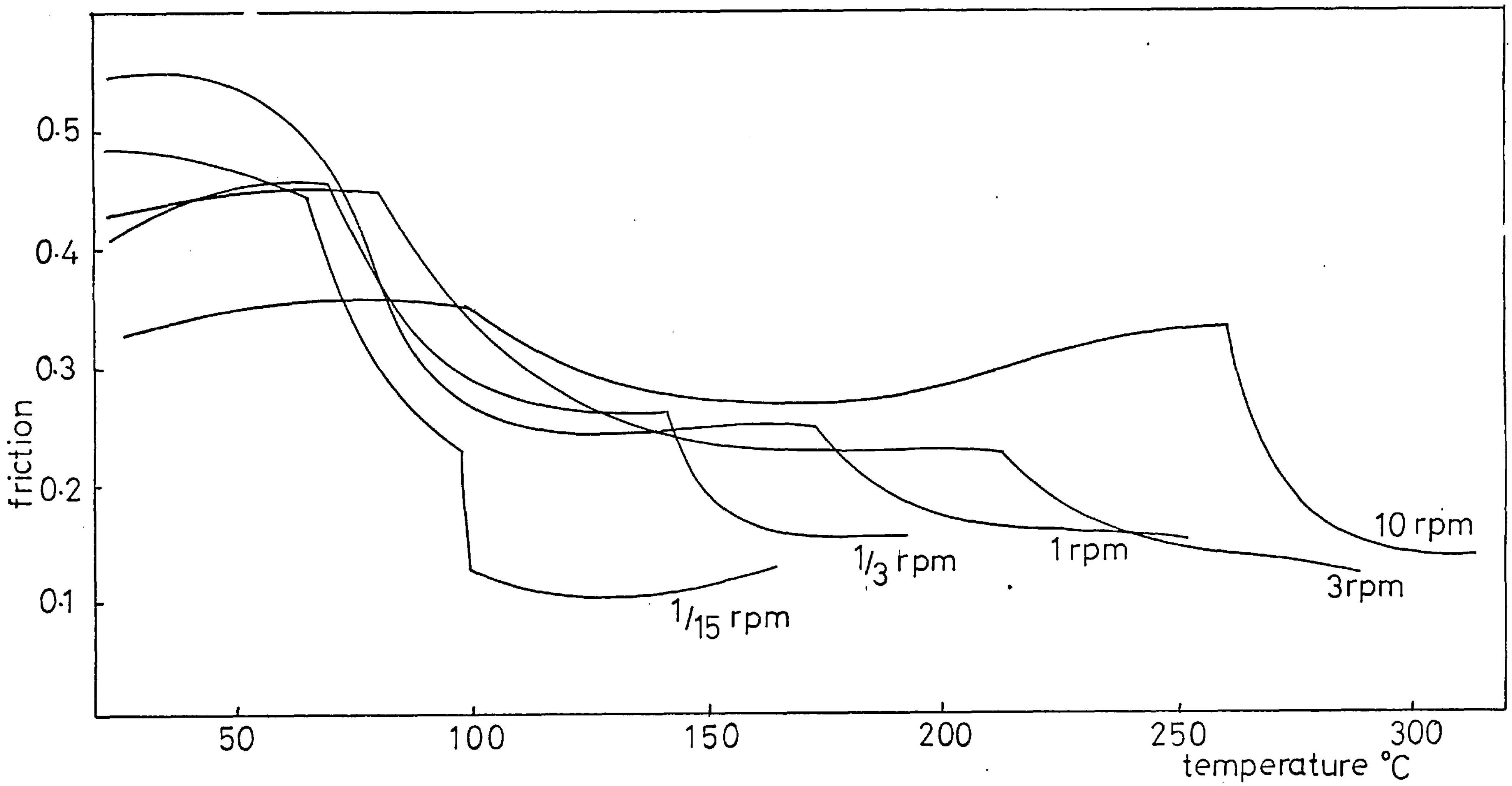


FIG 4·2 DEPENDENCE of FRICTION TRANSITION on SLIDING SPEED, 0·5%DBDS.

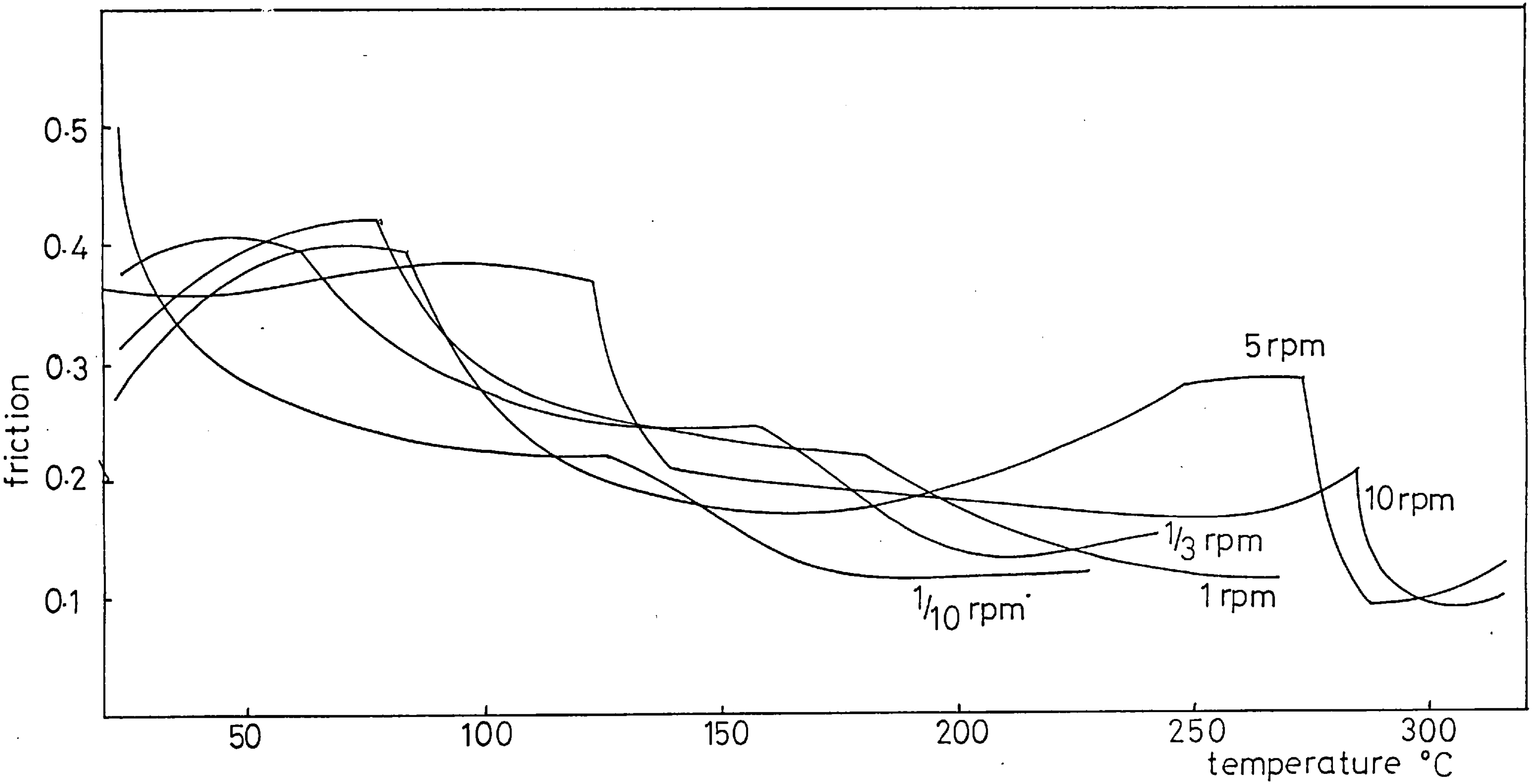


FIG 4·3 DEPENDENCE of FRICTION TRANSITION on SLIDING SPEED, 0·2% DBDS.

Conc wt% DBDS	V r.p.m.	$\log_{10}V$	Tm °C	Tm °K	T_T °K	$\frac{1}{T_T}(\times 10^{-3})$
2.0						
	1/50	-1.6990	79	352	352	2.841
	1/15	-1.1761	100	373	373	2.681
	1	0.0000	174	447	449	2.227
	3	0.4771	210	483	485	2.062
	10	1.0000	255	528	538	1.859
0.5						
	1/15	-1.1761	97	370	370	2.703
	1/3	-0.4771	139	412	414	2.415
	1	0.0000	172	445	447	2.237
	3	0.4771	213	486	488	2.049
	10	1.0000	266	539	549	1.821
0.2						
	1/10	-1.0000	127	400	402	2.488
	1/3	-0.4771	145	418	420	2.381
	1	0.0000	186	459	461	2.169
	5	0.6990	273	546	556	1.799
	10	1.0000	287	560	570	1.754

TABLE 4.1

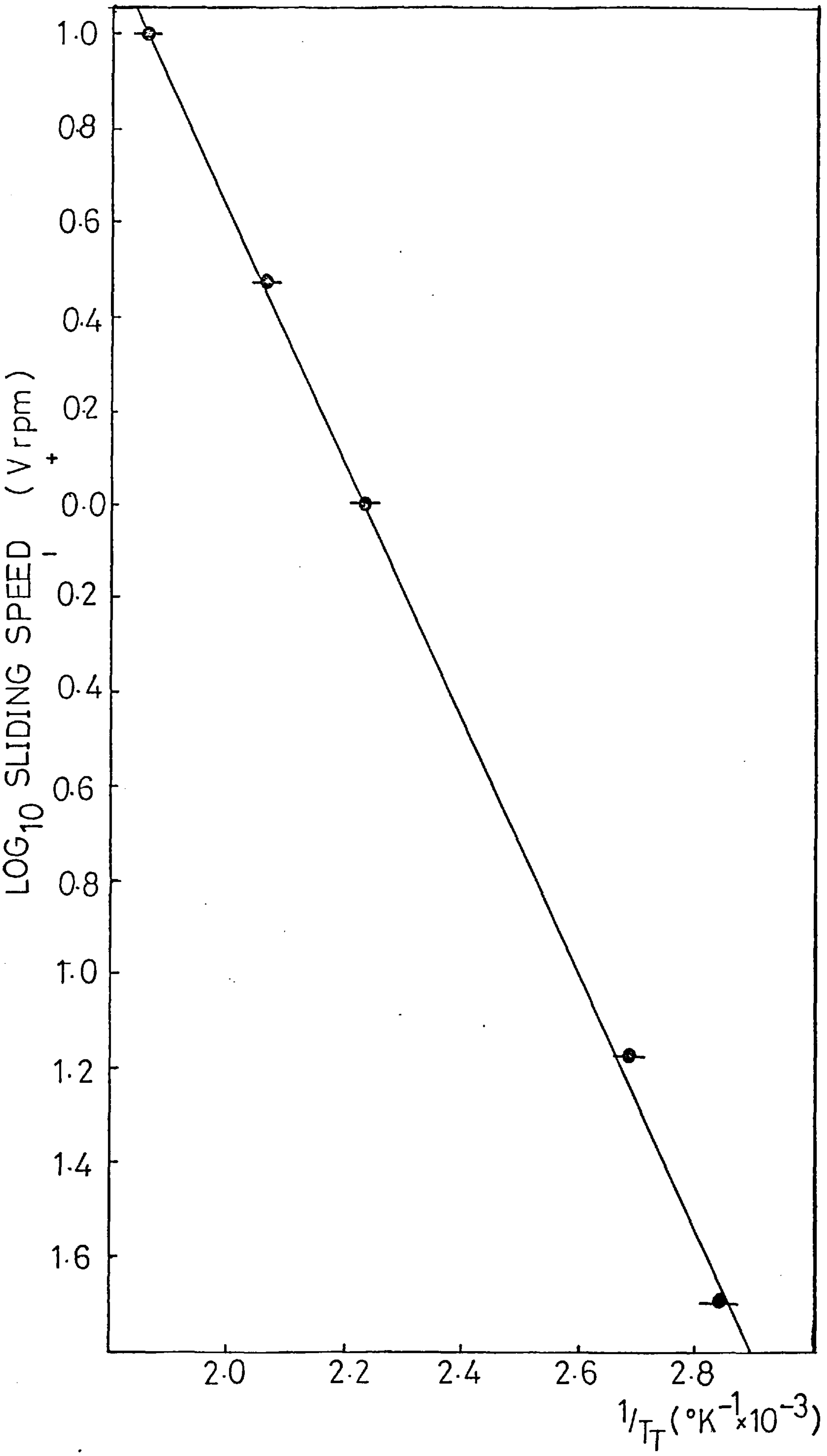


FIG 4.4 LOG$_{10}$ SLIDING SPEED vs $^1/_{T_T}$, EN 31 STEEL.
2·0% DBDS.

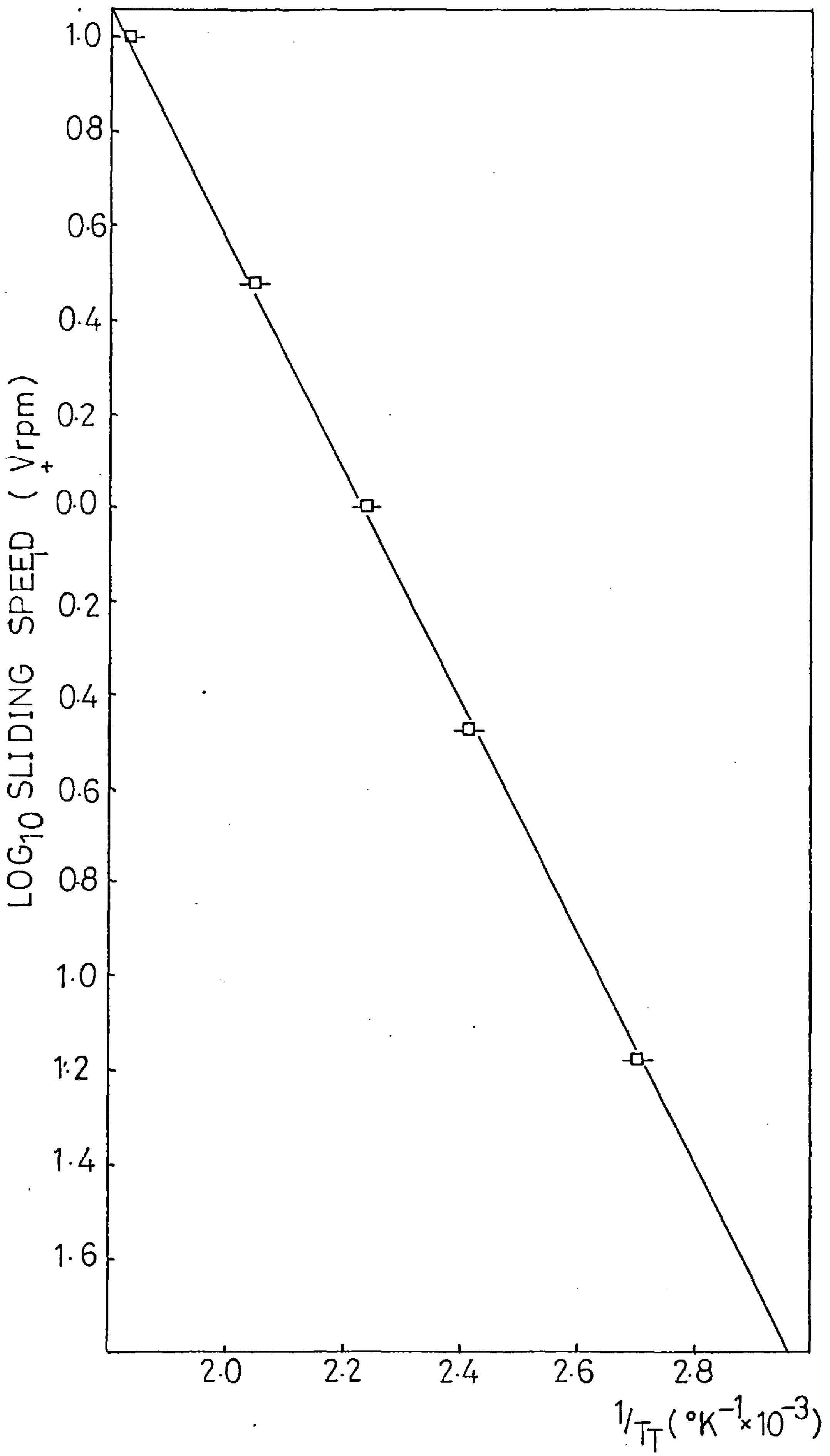


FIG 4·5 LOG$_{10}$ SLIDING SPEED vs $^1/_{T_T}$, EN 31 STEEL.
0·5% DBDS.

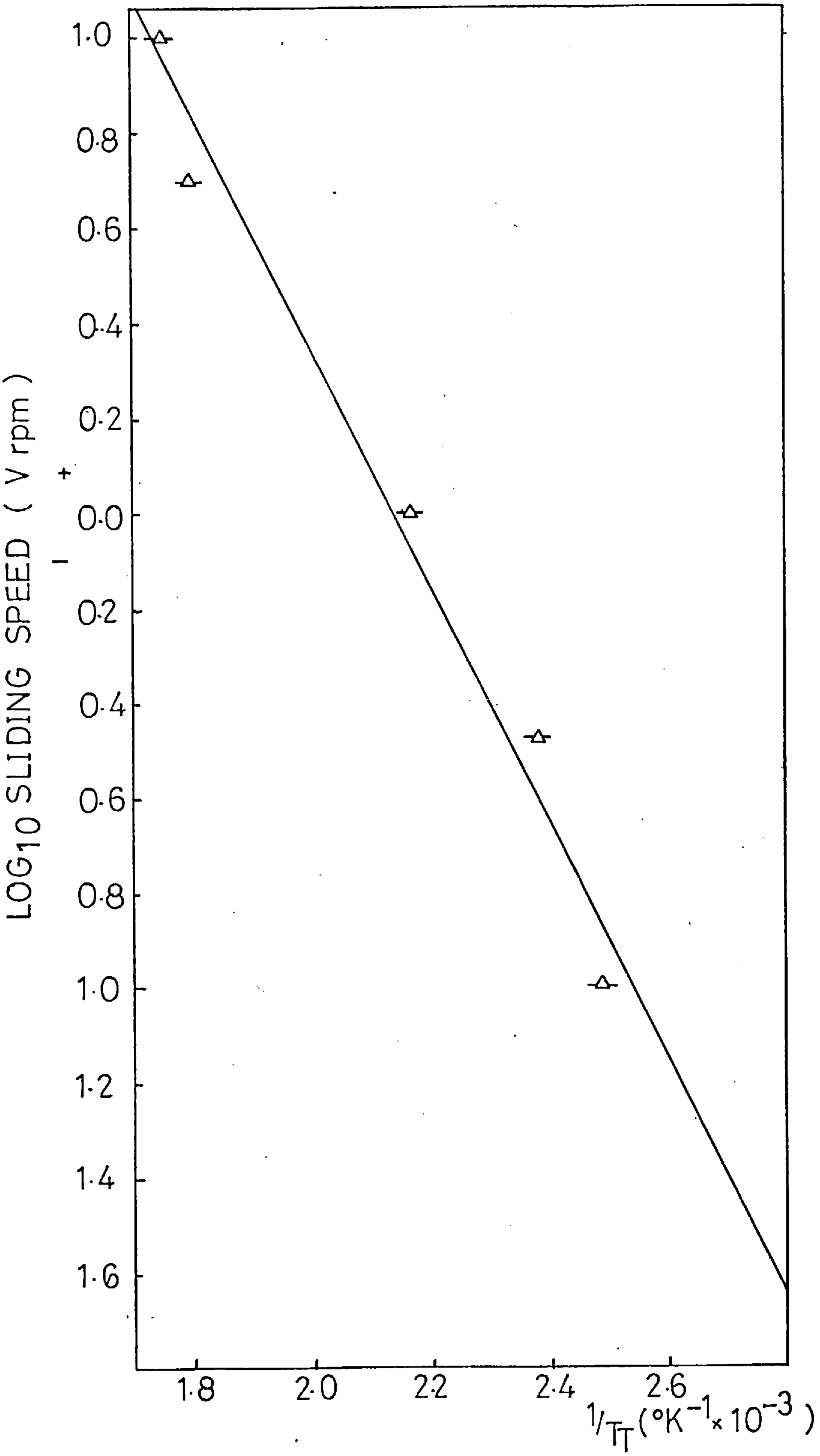


FIG 4·6 LOG$_{10}$ SLIDING SPEED vs $1/T_T$, EN 31 STEEL.
0·2 % DBDS.

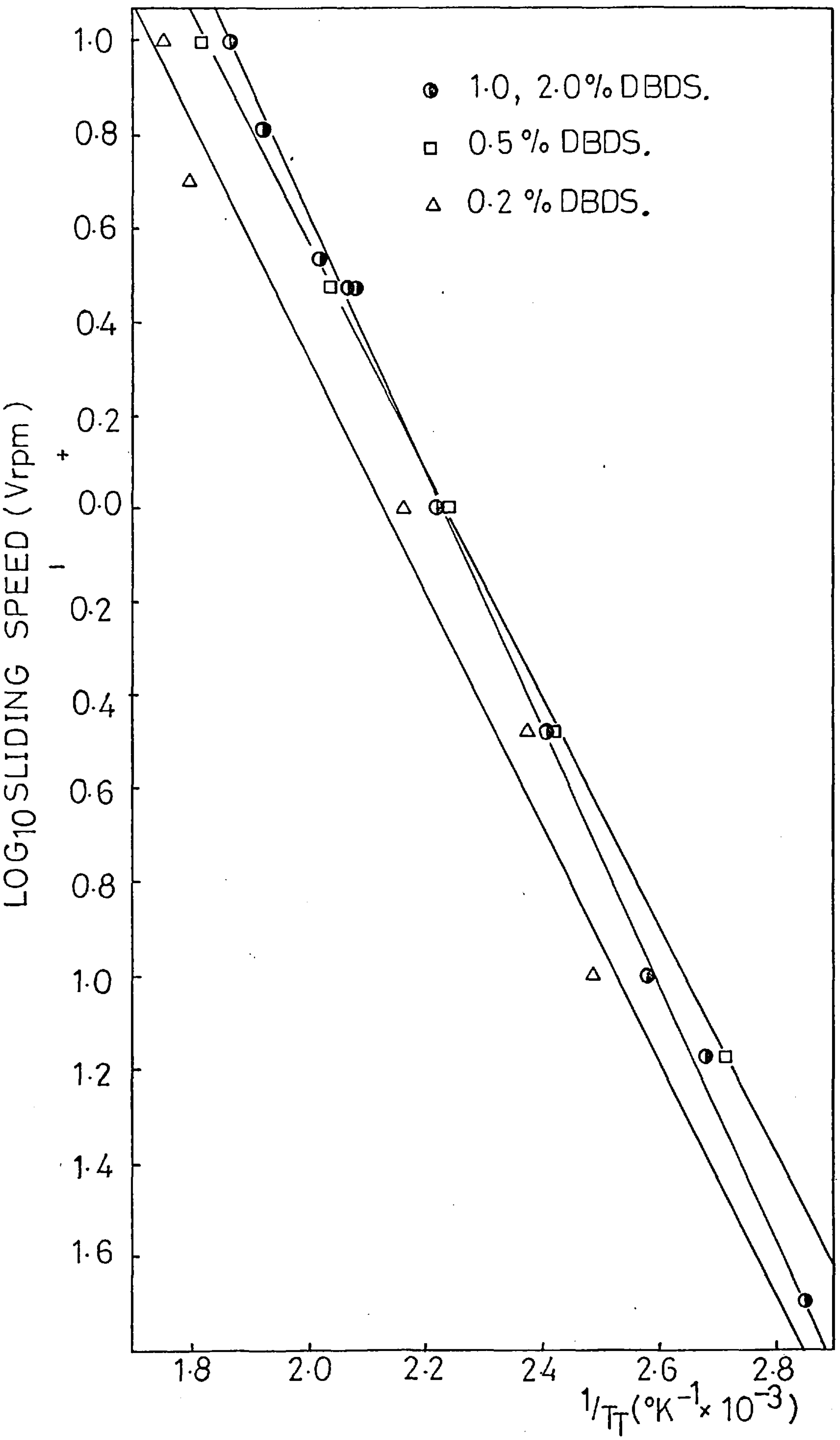


FIG 4·7 COMBINED LOG$_{10}$ SLIDING SPEED vs $^1/_{T_T}$. EFFECT of CONCENTRATION.

in reaction rate brought about by differing bulk additive concentrations.

The preceding chapters have shown that a change in the temperature at which the coefficient of friction of the system falls is indicative of a change in the reaction rate.

This chapter therefore investigates the effect of additive concentration on extreme pressure reaction rate by conducting tests similar to those described in the preceding chapter with solutions of 2.0, 0.5 and 0.2 (wt%) respectively, of dibenzyl disulphide in cetane.

4.20 RESULTS

Table 4.1 summarises the results of the friction-temperature experiments shown in Figs. 4.1 - 4.3. Linear Arrhenius-type plots of $\log_{10}$ sliding speed against the reciprocal of the absolute transition temperature are shown in Figs. 4.4 - 4.6 for each additive concentration, and compared with the results of the previous chapter in Fig. 4.7. The corresponding values for the Apparent Activation Energy Ea calculated by the regression technique previously described (Section 3.51) are tabulated below:-

Conc. dbds wt%	Ea K.cals/mole	Standard Estimate error K.cals/mole
2.0	- 12.46	± 0.02
1.0	- 12.55	± 0.01
0.5	- 11.40	± 0.01
0.2	- 11.43	± 0.10

TABLE 4.2

4.30 DISCUSSION - I

The reaction between dibenzyl disulphide and steel surfaces can be broken down into the following sequence of elementary stages..

(i) Diffusion of the reactive species to the surface

(ii) Physical adsorption of the reactive species onto the surface

(iii) Chemical reaction

(iv) Diffusion of Iron through the E.P. layer to the surface

(v) Desorption of breakdown products

(vi) Diffusion of products away from the surface.

In a complex mechanism such as this, the rate of the overall reaction is fixed by the rate of the reaction step that tends to be the slowest. Since diffusion in solution is usually a very rapid process, only with extremely active surfaces, might the overall rate be determined by stages (i) and (vi).

Similarly physical adsorption and desorption are usually faster than (iii) and (iv) since the potential energy barrier that must be surmounted before adsorption can occur is usually small.

Two steps are therefore considered by the author to be the slow step of the reaction

(a) chemical reaction at the surface

or (b) diffusion of iron through the FeS layer towards the surface.

This diffusion can proceed by either of two mechanisms. Since presumably the sulphuration reaction at the surface results in the formation of iron-deficient ferrous sulphide, which in turn leads to the presence of iron-ion vacancies in the surface layers (34), it is possible that diffusion occurs via cationic vacancies in the sulphide lattice. A similar mechanism has been demonstrated by Davies and Simnad (76) for the passage of Fe^{2+} through iron oxide. However, at the relatively low temperatures involved in these experiments, diffusion is equally possible along grain boundaries (77).

If chemical reaction at the surface (for simplicity represented as Fe+S⟶FeS) is taken as the rate-controlling step then (Section 3.50)

$$-\frac{d}{dt}\left[dbds\right] = \frac{d}{dt}\left[FeS\right] = k'\left[Fe\right]\cdot\left[dbds\right] \quad - 4.1$$

For thin layers, the diffusion of iron to the surface is unhindered (29) and thus the concentration of iron at the surface is constant.

At additive concentrations above 1 wt% dbds (Fig. 4.7), the plots are essentially independent of concentration and the reaction appears to follow zero-order kinetics with respect to the additive. This, in turn, indicates the presence of an excess of dibenzyl disulphide in the bulk solution.

Similar results were obtained by Sakurai et. al. (34) using dibenzyl disulphide on iron wire. Fig. 4.8 is reproduced from this reference.

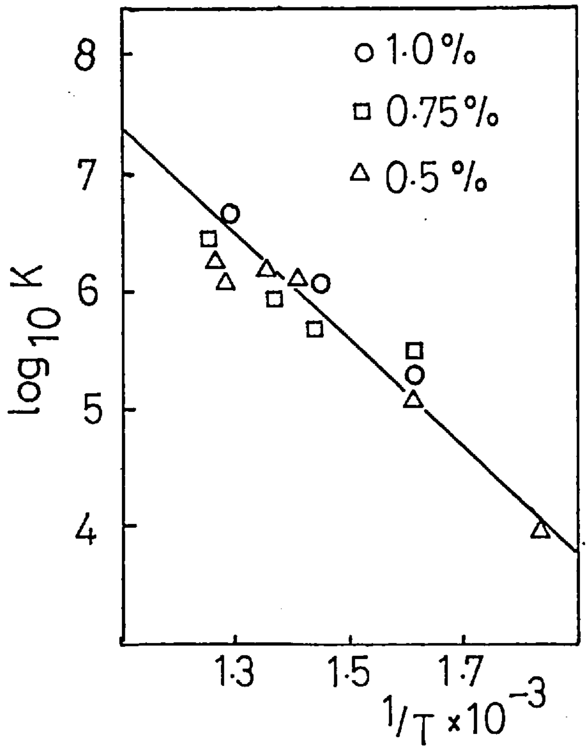


FIG 4·8

Under these conditions, the surfaces may be perpetually saturated with adsorbed molecules

thus $$[\text{dbds}] = 1$$

and $$\frac{d}{dt}[\text{FeS}] = k \qquad \text{------ 4.2}$$

which on intergration gives

$$[\text{FeS}] = kt + A \qquad \text{------ 4.3}$$

If however, diffusion of iron through the FeS film is taken as the rate step then the reaction velocity is inversely proportional to the thickness of the film (25) and directly proportional to the surface additive concentration and the number of sites available for reaction,

ie $$\frac{d}{dt}[\text{FeS}] = \frac{k' \; [\text{Fe}] \; [\text{dbds}]}{[\text{FeS}]} \qquad \text{------ 4.4}$$

As before, if the additive is assumed to be present in excess, then

$$[\text{dbds}] = 1$$

and $$\frac{d}{dt}[\text{FeS}] = \frac{k'\,[\text{Fe}]}{[\text{FeS}]}$$

The previous chapters have demonstrated that a constant critical film thickness exists at the conditions under which the coefficient of friction falls such that $[\text{FeS}]$ is constant.

It might be expected that diffusion of iron to the surface would be affected at high speeds due to the corresponding high temperature of the friction transition. However, it is generally accepted that diffusion in solids is virtually unaffected by temperatures below half the melting point of the metal (77). Therefore the surface concentration of iron, $[\text{Fe}]$ may also be considered constant and

$$\frac{d}{dt}[\text{FeS}] = k \qquad \text{as before.}$$

Thus in this specific dynamic system, where it is assumed that friction falls at a constant thickness, the observed zero-order rate behaviour at high concentrations is consistent with either mechanism. Similarly, supporting evidence for either mechanism is available in the literature.

Dorinson and Broman (29), demonstrated the linear dependence of film thickness upon reaction rate (equation 4.3) and hence confirmed the pseudo-zero order of the reaction for films of up to five monolayers thickness.

Static experiments were carried out by Sakurai et.al. (34,25) with dibenzyl disulphide on hot iron wire. The surface concentration of iron and additive were assumed constant such that

$$\frac{d}{dt}[FeS] = \frac{k'}{[FeS]} \qquad \text{(equation 4.4)}$$

which on integration gives

$$[FeS]^2 = kt + A$$

This parabolic dependence of film thickness on reaction time was demonstrated by the authors. Prutton e.t. al. (49) showed a similar relationship for the reaction of hydrogen sulphide on steel, indicating that the reaction was controlled by diffusion.

Barcroft (33) assumed thin films in his analysis but gave no indications as to the film thickness. However, a later paper by him (40) using radiotraced dibenzyl disulphide in a hypoid gear system, found that sulphur penetrated the gear surface to a depth of 7000 Å and suggested that a realistic E.P. film thickness might be of the order of 3000 - 5000 Å, a value subsequently confirmed by Allum and Forbes (42) using Electron Probe Microanalysis of a four ball wear track. E.P.M.A. studies in chapter two suggest a sulphide film of significant thickness due to the penetration of the electron beam.

Thus the balance of evidence suggests that the initial stages of the reaction are possibly controlled by the rate of the surface reaction, though as film thickness builds up, it is likely that diffusion of iron through the layer to the surface takes over as the rate-determining step.

4.40 DISCUSSION - II

The Energy of Activation can be derived from the change in rate of reaction with temperature by the formula:-

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{(equation 3.3)}$$

so that larger values of energy of activation mean a higher susceptibility of rate of reaction to temperature.

In the system described, however, at low concentrations of dibenzyl disulphide, another effect of temperature must be included. This results from the fact that the surface coverage, ie the surface concentration of reacting molecules of dbds, decreases exponentially and must be considered so that a lower apparent activation energy is obtained.

The difference between energies of activation at high and low coverages therefore provides information about the actual energy of adsorption.

Assuming that the surface concentration of iron is constant, the preceding section demonstrated that the rate of reaction between dibenzyl disulphide and the metal surface was directly proportional to the surface concentration of dbds:-

$$-\frac{d}{dt}\left[\text{dbds}\right] = \frac{d}{dt}\left[\text{FeS}\right] = k'\left[\text{dbds}\right]$$

At low coverage, the surface concentration of additive is equal to the product of the adsorption coefficient, b, and the bulk additive concentration (78),

i.e. $$\left[\text{dbds}\right] = b\left[\text{DBDS}\right]$$

thus assuming that the reaction on the surface is proportional to the number of adsorbed dbds molecules,

$$-\frac{d}{dt}\left[\text{dbds}\right] = k'\left[\text{dbds}\right] = k'b\left[\text{DBDS}\right]$$

$$= k_{OBS}\left[\text{DBDS}\right]$$

or $$k_{OBS} = k'b \qquad \text{------ } 4.5$$

where k_{OBS} is the reduced rate constant.

Under conditions where surface coverage is fractional and small, it is itself dependent upon temperature since the adsorption coefficient, b, is a quantity that decreases rapidly with increasing temperature.

i.e. $$b = \frac{ka}{kd}\, e^{\frac{\Delta H}{RT}} \quad (78)$$

or $$\frac{d \ln b}{dT} = \frac{-\Delta H}{RT}{}^{2} \qquad \text{------ } 4.6$$

where ΔH is the energy of adsorption of the additive to the surface. From equation 4.5

$$\frac{d \ln k_{OBS}}{dT} = \frac{d \ln k'}{dT} + \frac{d \ln b}{dT} \qquad \text{------ } 4.7$$

At low coverage, the true rate constant,

$$k' = e^{\frac{-Ea_{low}}{RT}}$$

or

$$\frac{d \ln k'}{dT} = \frac{Ea_{low}}{RT^2} \qquad \text{------ 4.8}$$

At full coverage, however, $\left[dbds\right] = 1$ (Section 4.30) and

$$-\frac{d}{dt}\left[dbds\right] = k'\left[dbds\right] = k' = k_{OBS}$$

and

$$\frac{d \ln k_{OBS}}{dT} = \frac{Ea_{high}}{RT^2} \qquad \text{------ 4.9}$$

On combination:-

$$\frac{Ea_{high}}{RT^2} = \frac{Ea_{low}}{RT^2} - \frac{\Delta H}{RT}{}^{2}$$

or

$$Ea_{high} = Ea_{low} - \Delta H \qquad \text{------ 4.10}$$

and the true Activation Energy of the surface reaction is lowered by an amount equal to the heat of adsorption of the additive. Comparison of the measured Activation Energies at high and low coverages in table 4.2, gives a value for the mean heat of adsorption of dibenzyl disulphide from cetane onto steel of - 1.1 K.cals/mole (standard error ± 0.1) K.cals/mole) over the temperature range 80° - 280°C.

Little information is available in the literature for comparison. However, an adsorption study on a similar system was carried out at room temperature by Forbes and Reid (46). The heat of adsorption of dibenzyl disulphide from n-tetradecane onto ground iron powder was measured by percolating the additive solution through a bed of the powder after it had first been wetted with the solvent. A value of -5.5 cals/gm

(-1.35 K.cals/mole) was obtained which compares well with that value determined above.

The heat of adsorption of surface active species onto metal surfaces, has been shown by Rowe (79) to be a measure of the strength of attachment of the lubricant molecules to the surface.

It has also been speculated (80) that the friction and wear of sliding surfaces are directly related to the heat of adsorption of the lubricant.

The Anti-Wear properties of certain organic disulphides were examined by Allum and Forbes (31). Though the authors initially put forward the theory that the anti-wear activity of disulphides was related to the ease of formation of a mercaptide layer, governed in turn by the strength of the sulphur-sulphur bond, more recent work by Forbes and Reid (46) has shown that differences in anti-wear behaviour between compounds were explained rather by differences in the rate of formation of adsorbed films and by the physical properties of these films once formed (Section 1.6).

The relatively low heat of adsorption of dibenzyl disulphide onto EN 31 steel surfaces is therefore consistent with the observed degree of anti-wear protection given by this additive (31, 81).

4.50 DISCUSSION - III

The mechanism of extreme-pressure action (reviewed in Section 1.6) is open to some controversy.

Davey and Edwards (43) postulated that the additive first reacted with the surface by a free radical process to form a mercaptide which at higher temperatures broke down to give a sulphide layer.

Allum and Forbes (31) also proposed the formation of a mercaptide intermediate though they were uncertain as to whether additive breakdown occurred on the metal surface or in solution prior to adsorption.

Forbes and Reid (46), however, speculated that if the reaction were to proceed solely via a mercaptide intermediate, then only hydrocarbon breakdown products could be expected and not the variety of sulphur-containing products which were observed. With dibenzyl disulphide the main reaction product (95% yield at 150^{o}) was dibenzyl monosulphide which was at first difficult to explain. However, irradiation of dibenzyl disulphide with ultraviolet light (82), has been shown to give dibenzyl sulphide as the main product. Carruthers (82) concluded that in dibenzyl disulphide, dissociation into thiyl radical was accompanied by cleavage of the carbon-sulphur bond; the monosulphide then being formed by combination of the benzyl and benzyl thiyl radicals.

This led Forbes and Reid to suggest that the first step in the reaction of dibenzyl disulphide with a metal surface might be the formation of thiyl radicals through homolytic fission of the sulphur-sulphur bond.

The existence of free radicals can be demonstrated by inhibitors which 'trap' the radicals as stable compounds. Toluene can act as such a radical trap since the carbon-hydrogen bond of the methyl group is weak and dissociation into hydrogen atoms and benzyl free radicals is readily achieved. The benzyl radicals formed are stabilised by resonance to a considerable degree and so are relatively inert.

Szwarc (83) has suggested that if a reaction proceeds by a radical mechanism, then the free radicals react more or less readily with toluene such that a benzyl free radical is formed.

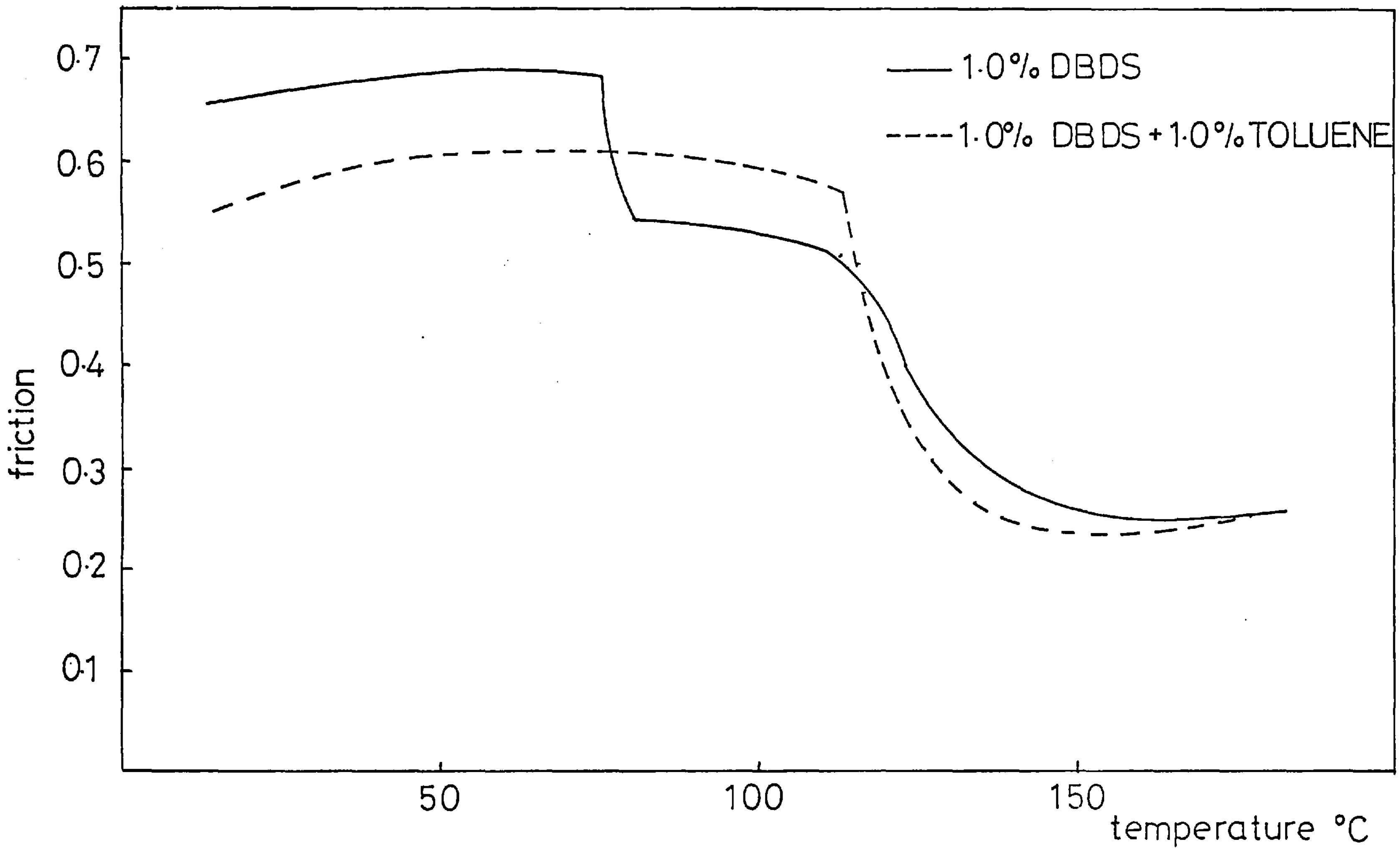


FIG 4·9 FRICTION vs TEMPERATURE. 1·0% DBDS + 1·0% TOLUENE on EN 31 STEEL, 1/10 rpm.

Tests were therefore carried out in the presence of toluene to determine whether the addition of a radical trap had any effect on reaction rate. The tests were carried out at a sliding speed of 1/10 r.p.m. to minimise loss of toluene by evaporation (Section 3.22).

The results of three tests are averaged in Fig. 4.9. The complete suppression of the first friction drop suggests the possibility that the oxidation of steel (Section 2.50) proceeds by a radical process in solution. It is equally possible however that toluene might act as an anti-oxidant by being itself oxidised to benzoic acid, thus removing oxygen from the solution. A further possibility is that toluene adsorbs onto the metal surface thereby screening the surface from corrosion though if this were the case, an effect on the value of the friction coefficient might be expected.

No significant change in the temperature of the E.P. friction drop suggests that free thiyl radicals are not present in the solution but does not exclude the possibility that additive breakdown to thiyl radicals occurs on the metal surface. This corresponds well with the reaction sequence inferred by Forbes and Reid (46), previously described.

4.60 CONCLUSIONS

Changes in concentration above 1 wt% dibenzyl disulphide in cetane have no effect on the rate of reaction which follows zero-order kinetics.

Below this concentration however, the reaction is first order and the rate constant is reduced with decreasing additive concentration.

The heat of adsorption of dibenzyl disulphide onto EN 31 steel from cetane was found to be -1.1 ± 0.1 k.cals/mole which compares well with the literature.

The reaction of dibenzyl disulphide on steel is possibly controlled in the initial stages by the rate of the surface reaction, however, as film thickness increases, diffusion of iron through the E.P. film probably takes over as the rate-determining step.

Support is offered to the mechanism of E.P. reaction proposed by Forbes and Reid (46).

CHAPTER FIVE

INVESTIGATIONS INTO HIGH-SPEED FAILURE

5.10 INTRODUCTION

This chapter reports the investigations into the breakdown of lubrication under extreme-pressure conditions, - a phenomenon of great practical importance.

The high-speed experiments were carried out before the slow-speed tests, described in the preceding chapters. It was found however to be extremely difficult to apply a true kinetic analysis to these results owing to the complication of frictional heating which could only be estimated with limited accuracy. It was therefore considered more profitable to pursue a slow-speed programme.

However, in the light of information obtained from the slow-speed tests, an attempt can now be made to explain the earlier results.

Before doing this, it will be convenient to consider, briefly, some of the literature available on 'scuffing' failure.

5.20 LUBRICANT FAILURE

Scuffing is usually considered to be due to the removal of all protective lubricant films from metal surfaces. This allows the surfaces to weld together and gives rise to the definition (84) that 'scuffing' is gross damage characterised by the formation of local welds between sliding surfaces. Though Bowden and Ridler (1) have shown that the temperature in the contact can reach the melting point of the metal, it is not necessary for asperities to reach their melting point for a weld to take place. An alternative mechanism can produce a pressure weld.

Niemann and Lechner (85) have shown that gear scuffing is the result of such a cold welding process since in their investigation, the melting points of any of the materials was not reached at any time.

In 1937, Blok (86) suggested that the failure of a lubricant was due to the local temperature in the contact rising above a certain critical value, characteristic of the particular metal-lubricant combination. This hypothesis was extended in 1939 (87) when he qualified his earlier paper by considering the critical temperature of a mineral oil to be virtually independent of load, speed and bulk temperature, provided that the latter was not so high as to cause chemical effects. Support was gained through the work of Frewing (88, 89), who investigated a wide variety of additives in white oil using a Bowden-Leben machine (17), and showed that the lubricant failed when the additive desorbed from the metal surface. This has since been confirmed by a number of authors including Askwith, Cameron and Crouch (90) who advanced the similar conclusion that surfaces will scuff as soon as the skin temperature reaches the value at which a critical fraction of the hydrocarbon layer is desorbed. Like Frewing, they also demonstrated a relationship between failure temperature and additive concentration.

The experiments carried out by Frewing were conducted under conditions where frictional heating was negligible. However, in any practical situation, the local temperature in the contact is the sum of the bulk temperature and the temperature rise generated by the friction - termed the 'flash' temperature, the translation of Blok's 'Blitz temperature'. Since in most cases, measurement of the flash temperature is not possible, a theoretical estimation of the magnitude of the temperature rise in the conjunction must be made. Such an estimation, formulated by Blok (91) has since found justification through the work of several authors.

Terauchi and Miyao (92) utilised the thermoelectric effect produced by a constantan-steel pair of gears. Unfortunately there are limitations to this technique since the temperature measured by this dynamic thermocouple is some average of the range of temperatures existing in the contact zone. Also, combinations such as constantan-steel, which produce measurable thermoelectric effects, are limited in their load-carrying ability. However, subject to these limitations, Blok's flash temperature estimations were found to agree with the temperatures measured.

Research of a similar nature was conducted by Niemann and Lechner (85), also using pairs of gears of dissimilar metals. These authors also concluded that Blok's expression was in broad agreement with the results obtained.

Much work has subsequently been conducted, investigating the constancy of the failure temperature in a number of practical and idealised cases.

Matveevsky (61) used a slow-speed four-ball machine at various ambient temperatures to find the temperature at which friction rose abruptly.

Later work, (93) using line and point contact test machines at high speed demonstrated that the total temperature calculated using Blok's expression just before failure was constant for a given material-lubricant combination, for each apparatus. The value of the total temperature calculated for the point contact machine was found to agree closely with the transition temperature measured in the slow-speed tests - indicating that failure at high speed was due to the same phenomenon to that which caused the friction transition in the slow-speed experiments.

Much research into the critical temperature hypothesis has been carried out by gear designers, in attempting to establish a failure criterion reliable enough to be practicable for engineering applications and design purposes.

Lane and Hughes (94) using a gear machine, found that within limits the scuffing of their gears could be predicted using straight mineral oils. DeGruchy and Harrison (95) also described tests on a gear rig, the results of which O'Donoghue and Cameron (96) showed to exhibit a substantially constant failure temperature.

Several papers on the topic of gear failure have been produced by Kelley and his co-workers (97 - 100). A reasonable correlation between scuffing and a constant total temperature was found using mineral oils though an attempt was made to extend the work to include reactive additive lubricants, without success (99).

The results of other work into the application of the critical temperature hypothesis to gear lubricant testing have been summarised by Kelley and Lemanski, (100) in a review paper.

Another extensive review defending the case for a constant failure temperature has recently been published by Blok (101), though the validity of Blok's criterion has been questioned on numerous occasions.

O'Donoghue et. al., (102) using a disc machine at slow speed, noted no transition phenomena unless stainless steel discs were used. It was assumed that the reason for this was that chemical attack on reactive disc surfaces, masked the transition.

Similarly, Fein (103) investigated the effects of running-in and test-procedure using a disc machine with non-reactive mineral oils and found that the failure temperature could vary by as much as 300°C.

He also concluded that chemical reaction was the cause, even though the lubricants were considered non-reactive.

Other investigations which cast doubt on the existence of a constant failure temperature have been reported (104 - 108), and Ku (108) has summed up the controversial issue - stating that 'there is strong evidence to suggest that for extreme-pressure additive oils and unconventional steels, scuffing temperature is not constant'.

Hence, it may be said from the information surveyed here, that the critical temperature criterion of failure may only be applied to non-reactive oils.

A second conclusion which can be drawn serves to confirm the views presented in Section 1.2; namely that the addition of a reactive E.P. agent can prevent this failure by forming a chemically reacted layer before temperatures are reached such that boundary or 'anti-wear' lubrication breaks down.

Rational evaluation of the failure of oils containing anti-seizure additives is much more complex than that of non-reactive lubricants.

Investigations approaching the problem from various angles have been reported in a recent review by Dyson (109), leading to a number of theories being advanced to explain the E.P. film failure phenomenon.

However, since the build-up of an E.P. film is clearly dependent to a great extent upon the kinetics of the reaction between the additive and the lubricated surface, it is by no means out of the question that the mechanism of failure might also be governed to some extent by kinetic considerations.

The work that has been carried out into this aspect of the phenomenon has been limited almost entirely to empirical tests giving

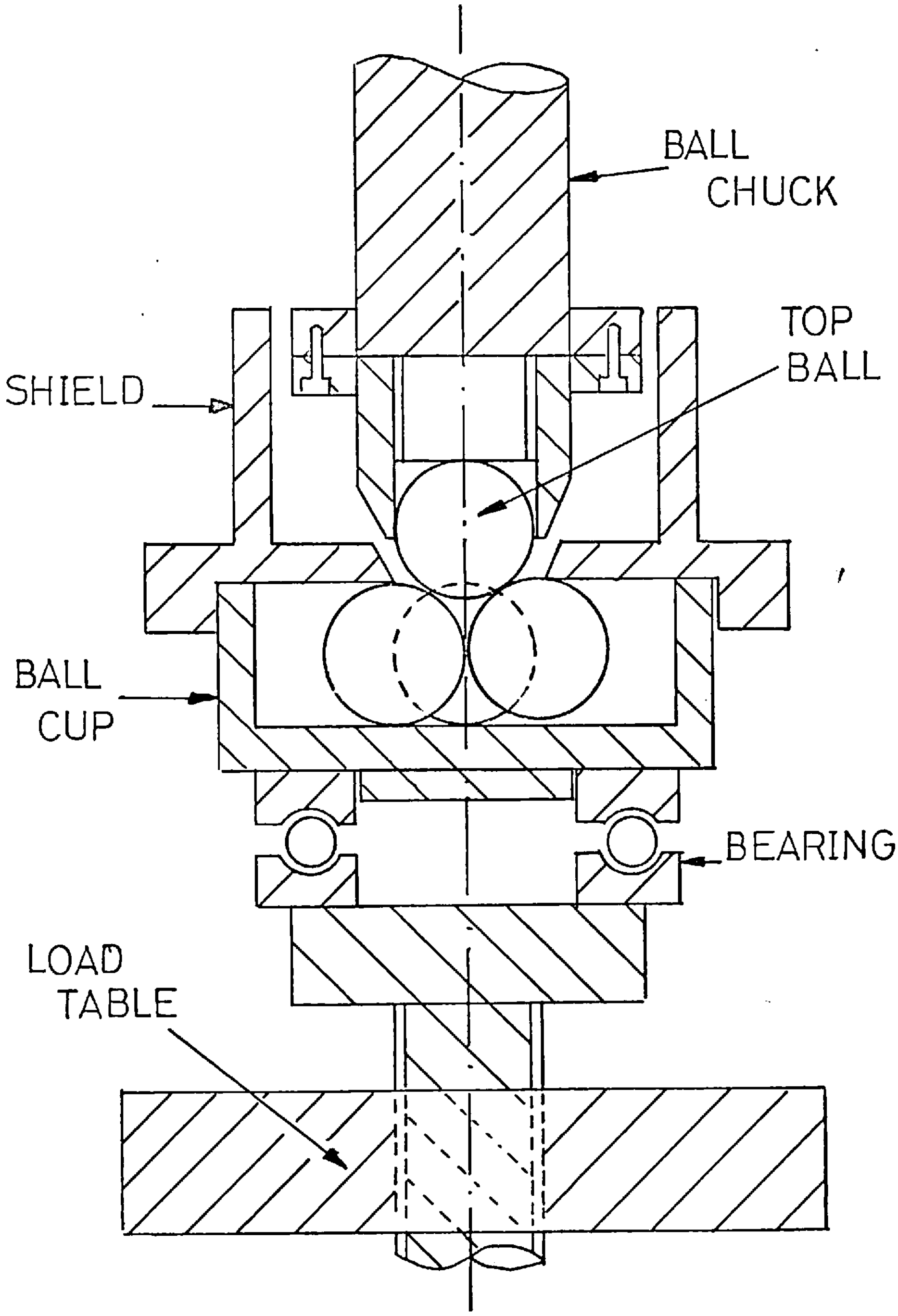


FIG 5·1 FOUR-BALL APPARATUS.

correlations between the chemical reactivities of additives and their load-carrying capacities (30, 31, 38, 41 and 42), and little research into failure has been attempted.

The work described in the following sections therefore attempts to elucidate the scuffing failure of a model E.P. oil from a kinetic viewpoint, using the foreknowledge acquired in the earlier chapters of this thesis.

5.30 APPARATUS

The high speed experiments involved in this investigation were carried out on a four-ball machine. (Fig. 5.1)

Three 1 inch (25.4 mm) balls were held clamped together in a cup containing the lubricant. A fourth ball, retained in a chuck was rotated on the bottom three balls such that the centres of the four balls formed a perfect tetrahedron. The top ball was connected to a 3 H.P. motor via a pulley and slipping clutch arrangement. A varispeed controller fitted to the motor gave a complete speed range up to 2000 r.p.m. Sliding speeds were measured by means of a tachometer attached to the drive shaft of the motor. The cup assembly was mounted via a thrust bearing on an insulating platform attached to a lever arm. Load was applied to the lever arm by a turnbuckle and spring balance system similar to that in the ball-and-triplane machine (Section 2.20).

The cup was restrained from rotation by a spring-steel leaf spring to which strain gauges were attached; enabling the frictional torque to be determined.

The slipping clutch was preset at a specific value of torque such that slip would occur before damage to the strain gauges was sustained owing to excessive deflection of the leaf spring at the high friction coefficients (0.7 to 1.0) encountered on scuffing.

The skin temperatures of the balls was measured by means of a thermocouple placed as close as possible to the trailing edge of the contact zone on one of the stationary balls.

5.31 MATERIALS

The test lubricants were 0.5, 1.0 and 2.0 weight percent solutions of dibenzyl disulphide in white oil, which was purified beforehand by the procedure outlined in Section 2.21. Tests were also carried out on the white oil alone for comparative purposes.

EN 31 steel specimens were used throughout the tests.

5.32 PROCEDURE

Before testing, the balls were cleaned in a soxhlett apparatus for several hours with analar toluene, and then immersed in anular acetone. (See Section 2.22)

As before (Section 2.22), the chuck and cup assembly were ultrasonically cleaned first in toluene, then, after rinsing, in analar acetone.

The apparatus was then assembled and the lubricant immediately introduced to reduce the risk of contamination.

Several experimental procedures were tried before satisfactory repeatability was achieved.

The procedure finally adopted was to first run the motor without load to the required speed. A preliminary test run was then carried out, applying step-load increments of 15lbs force (66.7N) to the top ball until scuffing occurred, allowing the recorded skin temperature at each load level to stabilise before a further load was added to the lever

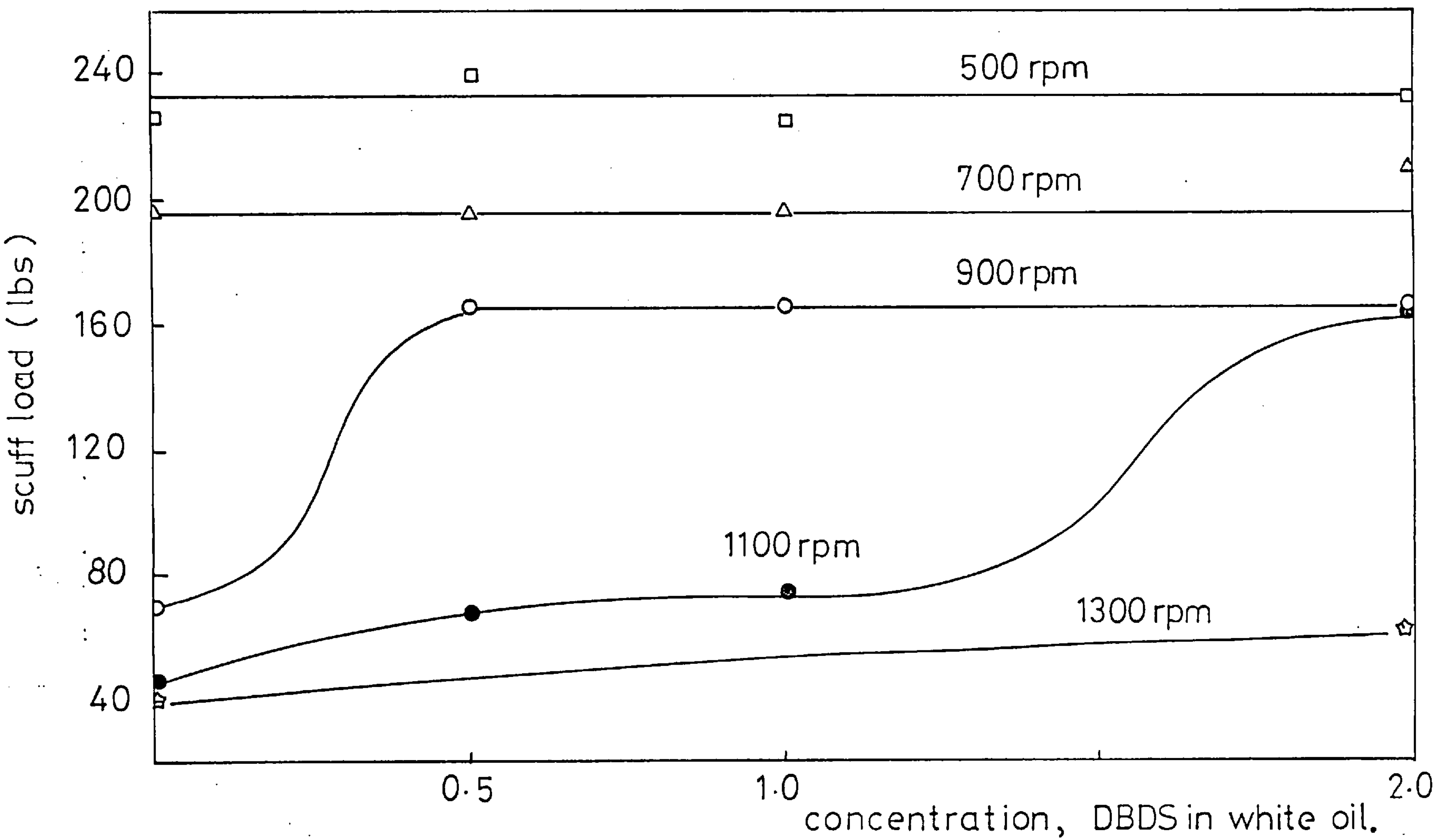


FIG 5·2 DEPENDENCE of SCUFF LOAD on ADDITIVE CONCENTRATION.

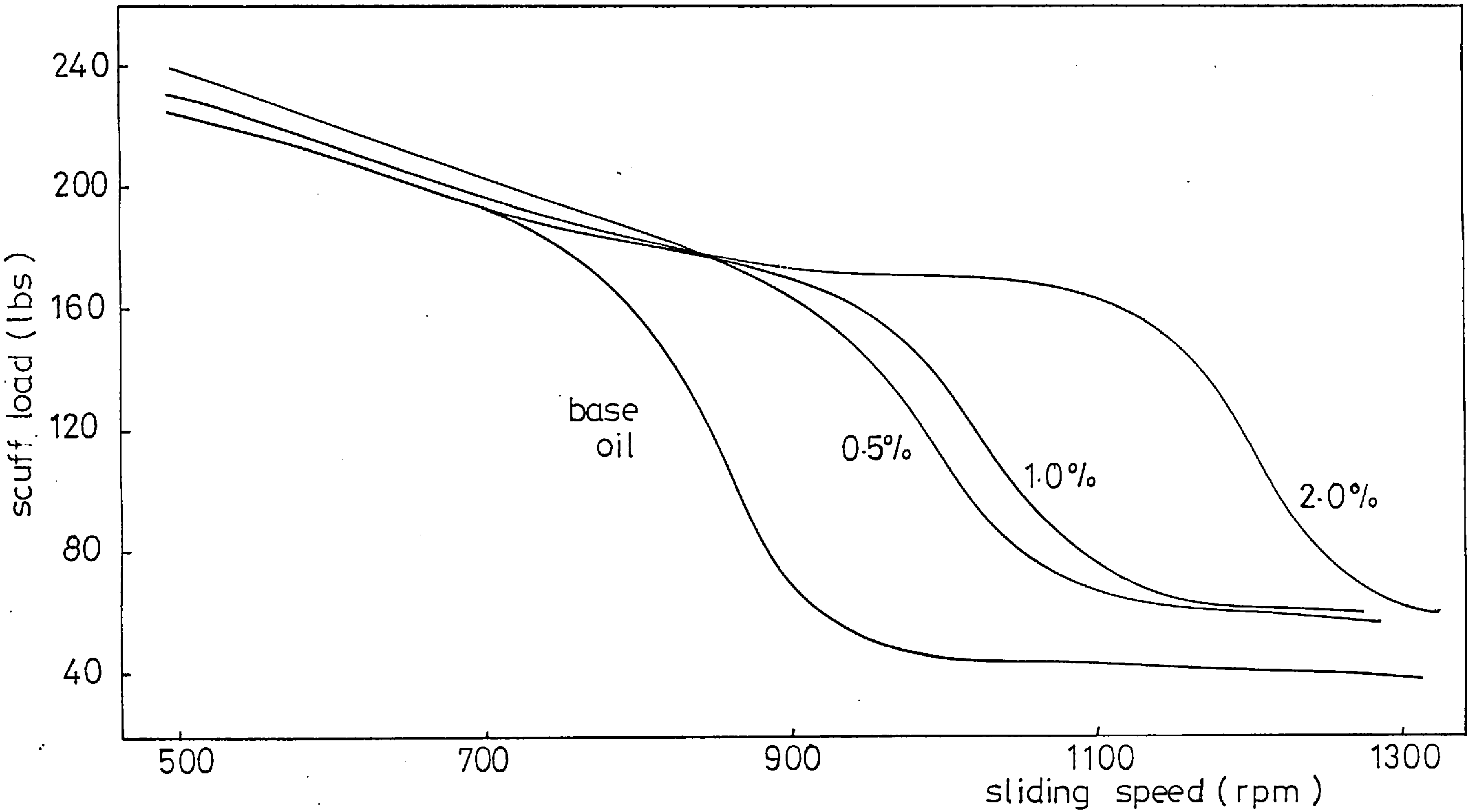


FIG 5·3 DEPENDENCE of SCUFF LOAD on SLIDING SPEED.

arm. Three further runs were then carried out following a similar procedure except that the top ball load increments were reduced to 3lbs force (13.3 N), when the scuffing load recorded in the preliminary run was approached.

Adjustment of the sliding speed was necessary after each load increment since the speed of the motor tended to fall with loading.

The onset of scuffing was recognised by sudden increases in the levels of noise and vibration, coincident with a large increase in the coefficient of friction, followed by slipping of the safety clutch.

5.33 ACCURACY

Three runs were carried out at each combination of additive concentration and sliding speed. The scuff load was taken as the average of the three tests, which were found to be very repeatable.

The recorded temperature was found to fluctuate depending on where the thermocouple was placed - a small error in location, leading to a large error in the temperature reading. This problem of thermocouple location meant that the results obtained could not be analysed quantitatively and the recorded temperature was therefore used only as a criterion for loading purposes. (Section 5.32)

5.40 RESULTS

Scuffing loads were obtained for five speeds between 500 and 1300 r.p.m. with each of the four lubricants.

The results of these tests are represented in Figs. 5.2 and 5.3 as functions of additive concentration at constant sliding speed, and of sliding speed at various constant concentrations.

Two effects can be distinguished. For tests carried out at speeds below 900 r.p.m., the failure loads are dependent on sliding speed but independent of concentration.

At 900 r.p.m. there is an initial dependence of scuff load on concentration but thereafter the same pattern was followed as in the tests conducted at lower speeds.

The tests carried out at 1100 r.p.m. are similar to those at the previous speed except that a much greater dependence of scuff load on concentration is observed.

Scuffing occurred at consistently low levels in the 1300 r.p.m. tests.

5.50 DISCUSSION

To facilitate the discussion of these results, it is convenient to consider the situation at the conjunction between the mating surfaces, as a step-load procedure is carried out at a constant sliding speed.

Under low loads, the two surfaces are probably separated by a coherent film of lubricant. The proportion of the load carried by asperities is small so that, even though the coefficient of friction for individual asperity contact might be high, there is only a small contribution to the overall friction, which is thus controlled chiefly by the fluid properties of the lubricant.

At higher loads, it is no longer possible for fluid films to be built up by the relative motion of the two surfaces and a fair proportion of the load is carried by asperities. It is at this stage that premature scuffing can occur depending on the running history of the contacts, particularly the surface temperature.

The beneficial effects of running-in are well-known. Padmore and Rushton(110) for example found that the scuffing load of gears decreased with increasing speed, passed through a minimum and then increased rapidly with further increase in speed if the load was first applied at test speed. If the load was applied from rest, not only was the scuffing load lower, but the recovery after the minimum was less pronounced. The authors concluded that when load was applied from rest, the gear teeth suffered preliminary damage during the period of running-in. The initial decrease in failure load with increasing speed can probably be related to another important effect advanced by Baber, Anderson and Ku (111) who similarly noted that the scuffing load of gears initially decreased with increasing temperature owing to the reduction in the viscosity of the lubricant, which in turn contributed to a reduction in the oil film thickness.

It is probable that the process of running-in combines several effects. Firstly, surface protection is provided by an E.P. film. Secondly, the surfaces are made to conform through a gentle wear process and finally, asperities are removed and surfaces smoothed such that less severe asperity contact occurs.

The results of the tests at 900 r.p.m. and 1100 r.p.m. show that the former plays by far the most significant role.

Since the establishment of an E.P. film is a slow process (112), it is clear that the operating history of the contacting surfaces is of extreme importance. If conditions in the early part of a test run are such that E.P. reaction occurs then asperities coming into contact at the higher loads are coated with a protective film of low shear strength and scuffing is prevented. The function of a pre-formed film in preventing seizure seems to be that the surfaces, after a step increase in loading, are thus given time to adjust to the new conditions before the film is totally removed. This is discussed more fully in the following section. If however, running-in conditions are such that little or no E.P. reaction occurs, then on a step increase in load, metal-to-metal contact occurs and scuffing ensues immediately to a degree which depends upon the prevalent severity of the conditions. It is possible, under certain circumstances, that recovery of seizure (22,113) can take place, since on scuffing, friction and hence temperature rises rapidly causing strong E.P. reaction and subsequent recovery though not before damage is sustained by the surfaces.

The effects of run-in can be seen in Fig. 5.2, since the tests carried out with the base oil at 500 and 700 r.p.m. showed no premature failure whilst at higher sliding speeds, scuffing occurred at very low loads.

The remarkable load-carrying ability of the base oil at relatively low sliding speeds is particularly worthy of comment. On examination after these scuffing tests, the balls were found to have a black substance deposited in the wear tracks. Similar black deposits, observed by Bailey (114) in the wear tracks of a ball-on-triplane machine rubbed in pure white oil were analysed by an X-ray fluorescence technique and shown to contain sulphur. Subsequent analysis of the white oil, showed that a quantity of sulphur in the region of three parts per million was present. Bailey concluded that the sulphur impurities in the white oil were in sufficient quantity to react with the wear track to form an effective E.P. layer.

The fact that a few parts per million of sulphur was seemingly sufficient to prevent seizure at 500 and 700 r.p.m., but not at higher speeds, confirms the extreme importance of the running-in conditions to the scuffing capacity of the lubricant.

These results can be explained by referring to the rate equation 4.1, given in the previous chapter.

$$\frac{d}{dt}[FeS] = k \cdot [Fe] \cdot [dbds]$$

The rate constant k, is given as before by the Arrhenius equation

$$k = A\, e^{-\frac{Ea}{RT_R}}$$

However, the reaction temperature, Tr, now contains a skin temperature term, Ts and a flash temperature contribution

thus: $$Tr = Ts + f(\Delta T\ max)$$

Assuming as in Section 4.30, that the surface concentration of iron is constant then the rate of reaction is proportional to the surface additive concentration:

$$\frac{d}{dt}[FeS] = K \cdot [dbds]$$

Slow speed work has shown that saturation concentration was reached above 1% (wt) dibenzyl disulphide in cetane. However, at 1100 r.p.m., 1% dbds was insufficient to prevent seizure, whereas a concentration of 2.0% dbds raised the reaction rate such that effective running-in was achieved. It is possible that this apparent ambiguity might be concerned in some way with the base oil. However a far more plausible possibility lies in a phenomenon noted by Sakurai and his co-workers (20,38). These authors investigated the effects of sliding speed on extreme pressure reaction rates with radiotraced dibenzyl disulphide on a line contact machine at constant load.

Since sliding speed affects frictional heating and consequently contributes to reaction temperature, then on the assumption that the surface concentration of additive was constant, the rate of reaction was expected to increase with increasing speed. It was found instead, however, that the reaction rate reached a maximum and then decreased rapidly to a low level. The authors concluded that, at high sliding velocities, the sweeping action of the repeated contacts caused adsorbed molecules to be removed mechanically from the sliding surfaces, thus reducing the surface concentration of additive and consequently, the reaction rate. The similarity between Fig. 5.3 and the plot of film thickness against sliding speed (Fig. 5.5), reproduced from this reference, (38) indicates the possibility that a similar phenomenon occurs to reduce the rate of reaction in these experiments. Obviously, at low additive concentrations more sites are available on the surfaces for readsorption and less effect would be expected. A second speed effect is that there is less time available for reaction and thus, in order to increase the reaction rate at higher speeds, to the extent where a sufficiently thick film is formed to lubricate the surfaces effectively, a higher additive concentration is necessary. This consequence can clearly be observed in the curves for the tests carried out at 900 and 1100 r.p.m. in Fig. 5.2.

Above a sliding speed of 1100 r.p.m., none of the lubricants tested were found capable of preventing premature seizure.

Fig. 5.2 also demonstrates that once scuffing due to ineffective running-in has been avoided, a constant failure level is reached for a given sliding velocity. This constancy of the seizure load is consistent with the results of the previous chapter, in which it was shown (Section 4.30) that above a certain concentration of additive, the surfaces became saturated with adsorbed molecules, such that the surface concentration was constant and equation 4.2 applied as follows

$$\frac{d}{dt}\left[\mathrm{FeS}\right] = k$$

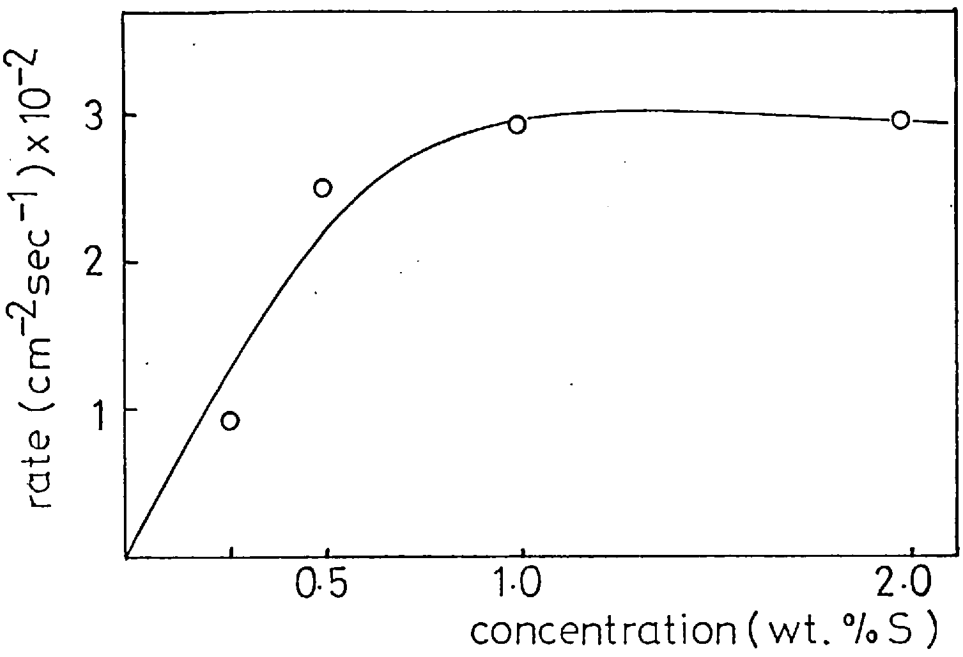


FIG 5.4 RATE vs CONCENTRATION, DIPHENYL DISULPHIDE in WHITE OIL. (38).

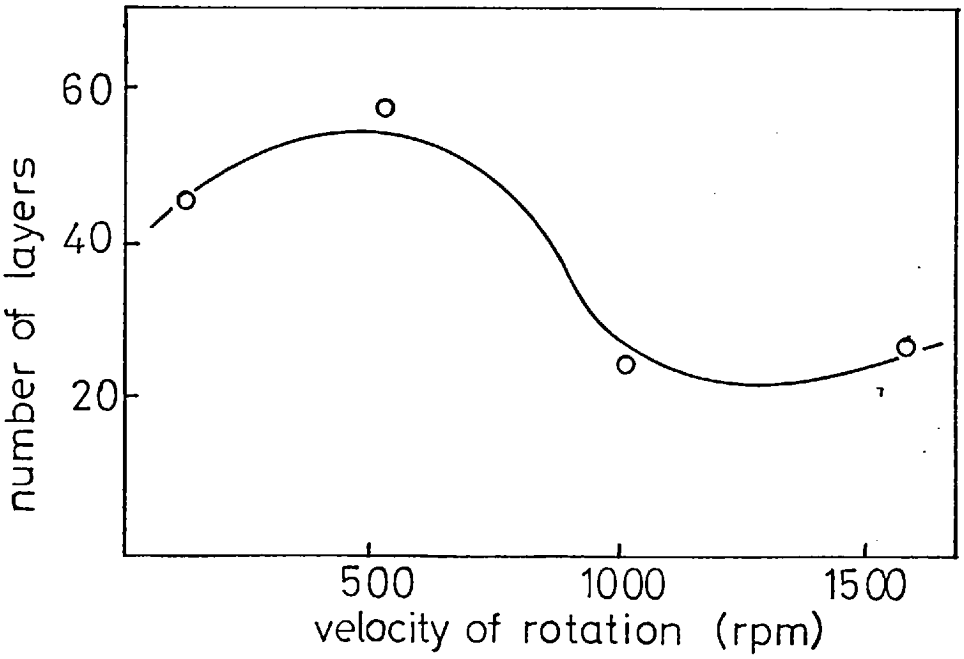


FIG 5.5 FILM THICKNESS vs SLIDING SPEED, DBDS in WHITE OIL. (38).

Thus for any given speed, the reaction rate is independent of concentration, such that a constant thickness of E.P. film would be reached. Since slow speed work has shown that a critical thickness film was necessary to reduce the friction coefficient between sliding surfaces (Chapter Two), it follows therefore that a certain thickness of E.P. film formed might lead to a specific failure load for a given speed.

This correlation of a constant failure level under conditions where surfaces are saturated with adsorbed additive molecules, is strengthened through the work of Sakurai et. al. (38) Fig. 5.4 is reproduced from this reference and shows the reaction against concentration of additive for tests carried out at 516 r.p.m. on a line-contact test machine with diphenyl disulphide (0.5 wt % Sulphur) under an applied load of 3.05 k.gms f. This curve has very similar characteristics to those of the 900 and 1100 r.p.m. tests in Fig. 5.2, in that below a certain concentration, the rate of reaction is linearly dependent upon concentration. Above this value it is constant. Sakurai similarly concluded that surface saturation with adsorbed additive was the cause of this constancy in the reaction rate.

It is shown in the following section that the formation of a sufficient extreme-pressure film under rubbing conditions depends upon the balance between the rate of reaction of the additive with the surface, and the rate of abrasion of the film. An increase in sliding speed not only affects the reaction rate by reducing the effective surface concentration of the additive (discussed above) but also increases the rate of removal of the film. The time available for reaction also decreases with increasing speed. These effects combine to reduce the thickness of the E.P. film which presumably enables failure to occur more easily. Thus the inverse dependence of scuff load on sliding speed can be adequately explained.

5.51 THE MECHANISM OF SCUFFING FAILURE

Preliminary work described in Chapter Two showed that before the friction coefficient between surfaces lubricated with a model E.P. oil could be reduced, a film of critical thickness had to be formed between consecutive contacts. (Section 2.51) It follows therefore that under a specific set of conditions at high speed, a certain film is necessary to provide adequate lubrication of the surfaces and that on removal of this film, failure would immediately occur.

Several authors have correlated extreme pressure film thickness with load. Borsoff and Wagner (26) operated spur gears in a radio-traced dibenzyl disulphide solution and showed that film thickness increased with load and that an equilibrium thickness existed for each set of operating conditions. Similarly, Sakurai, Ikeda and Okabe (20) derived theoretically an expression predicting the existence of an equilibrium film and verified this experimentally. A later paper (38) confirmed the earlier results of Borsoff and Wagner, demonstrating a linear increase in equilibrium thickness with load over the range studied. Since for tests carried out without rubbing, the thickness of the formed film might be expected to increase linearly with time (equation 4.2), the fact that an equilibrium E.P. film thickness is reached on the mating surfaces, indicates that a balance exists between the rate of reaction of the additive with the surface, and the rate of removal of the film during passage through the conjunction.

Thus:-

$$\text{Rate of formation of E.P. film} = \text{Rate of Reaction} - \text{Rate of Abrasion.}$$

An increase in load not only increases the reaction temperature and consequently the rate of reaction but also must affect the rate of abrasion. However, the fact that equilibrium thickness increases with load (26,38) suggests that the effect of load upon reaction rate is the greater. This is seemingly inconsistent with the phenomenon of scuffing failure since if load-carrying capacity were entirely dependent upon E.P. film thickness then lubricant failure by scuffing should not occur. It follows therefore that a thick E.P. film is a necessary condition but is not alone capable of preventing seizure.

If on a step increment in load there is an immediate proportionate increase in the rate of abrasion, then the film built up over the previous set of conditions must be worn away rapidly since the increase in reaction rate due to the higher frictional heating generated, which is necessary to maintain the film, is not instantaneous. During this delay, if the E.P. film is not sufficiently thick to allow the reaction rate time to be accomodated to the new conditions before metal-to-metal contact occurs, then failure follows immediately. If, on the other hand, the conditions are adjusted to before the film is completely removed then scuffing is prevented and a thicker E.P. film is formed on reaching equilibrium. That an E.P. film does allow a period for the reaction rate to become adjusted, is supported by the fact that almost invariably, scuffing was observed to occur a finite time after a load increase and not instantaneously which might have been expected.

Thus the hypothesis is advanced that the onset of scuffing is governed by a delicate balance between the thickness of the E.P. film present, the rate of removal of that film, and the time taken for the reaction rate to increase to the extent that the rate of abrasion of the film, is exceeded. It is clear that in this latter respect, the energy of activation of the additive is of great importance since the more negative this quantity, the greater the dependence of reaction rate upon temperature.

It can be concluded therefore, that the insights derived from the slow speed tests can be applied to elucidate, in quite fundamental terms, the behaviour of the lubricants tested, in relation to the prevention of scuffing failure.

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

In this concluding chapter, the main conclusions from the experimental work carried out and the possible resulting lines of research in the future are summarised.

6.10 CONCLUSIONS

6.11 SLOW SPEED WORK (CHAPTERS 2,3 and 4)

The overall conclusion that can be drawn from the slow-speed programme followed in this thesis is that a simple test apparatus can be used to examine kinetically the reaction between a model E.P. oil and steel surfaces, if the following assumptions are made:-

(i) the E.P. reaction occurs outside the conjunction of the mating surfaces.

(ii) effectively all chemical surface films entering the contact are abraded off during passage through the conjunction, and

(iii) a certain critical thickness of this chemical film must be formed within a single revolution of the ball-on-triplane machine, before effective E.P. lubrication of the surfaces is established: apparent by a large reduction in the friction coefficient.

The temperature at which the transition from high to low friction occurred was demonstrated to be dependent upon sliding speed.

On the assumption that the reaction between the additive and the steel surface followed zero-order kinetics, an expression was derived relating the logarithm of sliding speed with the reciprocal of the absolute transition temperature. Experimental results confirmed this relationship. From the resulting linear plot, a value for the Apparent Activation Energy for the reaction was deduced and compared with values found for similar metal-lubricant systems.

The rate of reaction between the additive and steel surfaces was shown to be independent of concentration above a certain value, owing to the surface being saturated with adsorbed molecules of additive. Below this value, the reaction could be fitted to a first-order rate law. From the differences between the Energies of Activation at high and low surface additive coverage, the Heat of Adsorption of Dibenzyl Disulphide from cetane onto EN 31 steel was found.

It is possible that the reaction is controlled in the initial stages by the rate of the surface reaction. However as the E.P. film thickness increases, it is equally possible that diffusion of iron ions through the formed layer, takes over as the rate-determining step.

Tests carried out in the presence of a radical 'trap' offer support to the reaction mechanism proposed by Forbes and Reid (46).

6.12 HIGH SPEED TESTS (CHAPTER 5)

Scuffing loads were obtained over a range of sliding speeds with a series of solutions of dibenzyl disulphide in white oil, and the results obtained were explained on the basis of the slow speed work already described.

The effectiveness of adequate 'run-in' was demonstrated and it was advanced that the presence of an E.P. film could delay scuffing failure by preventing immediate metal-metal contact whilst the metal-lubricant system adjusted to conditions of increased severity.

It was shown that scuffing finally occurred when the rate of abrasion of the film exceeded the rate of reaction.

6.20 FUTURE WORK

This thesis has examined the kinetics of dibenzyl disulphide using friction change to indicate film formation. Friction measurements have limitations in that film thicknesses cannot be found and must be considered constant in order that a kinetic analysis can be made.

It is considered that film thickness measurements would enable the reaction rate constant to be estimated and the Activation Energy for the reaction to be determined with increased accuracy.

Electron Probe Microanalysis has proved to be extremely useful in the qualitative examination of the sulphur-containing E.P. film. However, satisfactory quantitative information on surface films of thickness less than 5000 Å (0.5μm) cannot be obtained, since the electron beam penetrates the surface to a depth of between 0.5 and 1μm, with fluorescence effects existing over even greater depths.

These deficiencies can be overcome by the use of radiotracer techniques, which have been found to be particularly useful in the field of E.P. lubrication. These have the added advantage over techniques such as E.P.M.A. in that results are capable of distinguishing from where the E.P. film is derived. Laboratory studies of this type, using specifically β- particle emission of sulphur-35, have so far been confined to static unloaded surfaces (24,26,36,37,60) or to dynamic tests using gears (26,39, 40) and cams and tappets (28), in which results, taken at equilibrium, show the behaviour of E.P. films during running rather than the initial build-up of the E.P. film.

It is considered that an investigation into the build-up of E.P. films on 'nascent' surfaces using a tagged sulphur additive would be of extreme interest.

Conventional testing apparatus is unsuitable for radiotracer experiments. It would therefore be necessary to design a test apparatus, subject to the following major requirements:-

(i) Production of 'nascent' metal under an oil surface, and

(ii) Sufficient contact area for accurate scintillation counting.

A substantial programme based on these recommendations has in fact been agreed and is about to be commenced.

The experiments described in this thesis have investigated a simple, pure chemical system and as such have been easily controllable.

The application of similar analyses to progressively more complex additive systems would therefore provide a further direction in which this work could be extended.

APPENDIX

LEAST SQUARES REGRESSION

For an accurate determination of the value of Ea, a statistical method must be applied to the data in Table 3.1.

Consider the equation of a straight line $y = a + bx$, where a and b are parameters of intercept and slope, determining the line.

If it is possible to assume that one variable, designated x, can be recorded without error, and that the remaining variable, designated y, is subject to random variation, then the problem becomes one of linear regression which considers the frequency distribution of a single variable, whilst the other is held fixed at each of several levels.

The usual method for performing an estimation of the parameters a and b for regression problems is the method of 'Least Squares' in which the values of a and b are determined so that the sum of the squares of the deviations of y about the fitted line $\hat{y} = a + bx$ (equation A.3) is a minimum.

If $(x_1\ y_1)$, $(x_2\ y_2)$, $(x_3\ y_3)$ ---- $(x_n\ y_n)$ are n pairs of observations to be determined experimentally then the least squares estimate of b is given in reference A.1, as follows:-

$$b = \frac{\sum_{i=1}^{n} (xi - \bar{x})\ (yi - \bar{y})}{{}^{n}\ (xi - \bar{x})^2}$$

which can be simplified to

$$b = \frac{n \quad xiyi - \quad xi \quad yi}{n \quad xi^2 - (\quad xi)^2} \qquad \text{---- A.1}$$

and a is given by:-

$$a = \bar{y} - b\bar{x} \qquad \text{---- A.2}$$

where $\bar{y}$ and $\bar{x}$ are the mean values of y and x, respectively

ie $$\bar{y} = \frac{\sum_{i=1}^{n} yi}{n} \text{ and } \bar{x} = \frac{\sum_{i=1}^{n} xi}{n}$$

Knowing a and b, the regression line is given by

$$\hat{y} = a + bx \qquad \text{---- A.3}$$

After a regression line has been fitted to a set of data, it is possible to observe how accurately the y values are predicted.

The error of prediction, e is equal to $yi - \hat{yi}$ where yi is the observed value at that point and $\hat{yi}$ is the regression line value:-

$$\hat{yi} = a + bxi$$

and the estimate of the variability about the line is given by (A.1)

$$Se = \sum_{i=1}^{n} (yi - \hat{yi})^2 \qquad \text{---- A.4}$$

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ADDENDUM

Contents

The following points were considered relevant, but were not covered in the bulk of this thesis:-

A.10. Oxygen as an E.P. Additive

The running-in procedure outlined in section 2:22, was found to be necessary since two effects combine initially to cause a significant lowering of the coefficient of friction. Firstly, it is obvious that layers of chemically reacted oxide remain unaffected by solvent treatment and secondly, any contaminant present in the acetone would quickly form an adsorbed layer on the surfaces of the sliding members. It was found, however, that a few revolutions of the top ball, under load, were usually sufficient to allow the coef. of friction to stabilise at a value between 0.5 and 0.7.

It has been seen (Figs. 2.12 and 2.14) that, at low loads, a further film of oxide is formed with increasing temperature, which causes the friction to fall from this initially high level, to a value in the region of 0.35. Thus the effectiveness of oxygen as an extreme-pressure agent, under certain circumstances is demonstrated.

Several authors have similarly shown that oxygen can have a marked effect on the extreme-pressure properties of an oil.

Toguyachi and Takai (21,22) observed that the E.P. properties fell when dissolved oxygen was removed from paraffin oils containing disulphides.

Vinogradov et al (72), obtained higher coefficients of friction with steels lubricated by hydrocarbons in an argon atmosphere than similar tests carried out in air. More recently, Bjerk, (115) has found that the scuffing of steel rollers lubricated with a mineral oil was affected by the presence of oxygen.

This E.P. regime in the presence of oxygen is made more complex since the three oxides of iron; Ferric, Fe_2O_3; Ferrous, FeO; and Ferroso-Ferric Fe_3O_4, are all produced under different conditions and have different lubricating properties - particularly regarding wear. (116, 117).

Whilst Fe_2O_3 is formed on iron surfaces when an excess of oxygen is present, under conditions of limited oxygen, Fe_3O_4 is produced. Earles & Hayler, (118), have shown that at high temperatures, wear debris was predominantly ferrous oxide, which has a much lower wear resistance than Fe_3O_4, the most adherent of the oxides of iron. It was also found (118), that a transition from the production of ferric oxide debris to ferroso-ferric oxide, could be accompanied by a drop in wear rate of over two orders of magnitude.

Midgley et al (117), have similarly shown that with hardened steels, wear rate reaches a maximum with increasing temperature, then falls to a very much lower value. At temperatures below the peak, debris was ferric oxide whilst above the peak increasing amounts of ferroso-ferric oxide were found.

This irregular wear behaviour of the oxides of iron has been clarified very recently by the work of Sakurai et al (119), who measured heats of adsorption of several surface-active compounds on oxide and sulphide surfaces on iron, using a flow microcalorimeter. The heats of adsorption of stearic acid onto FeS and Fe_3O_4 were found to be very much higher than that onto Fe_2O_3. Polar compounds were therefore considered to be much more strongly adsorbed onto surfaces of iron sulphide and ferroso-ferric oxide (119). Thus the disparity between the observed wear rates of Fe_2O_3 and Fe_3O_4 is adequately explained. This conclusion, namely that surfaces formed by sulphur-type E.P. agents are more active for the adsorption of surface-active substances than those of oxidised steel surfaces (119) is consistent with the findings of chapter 2. It was observed that EN 31 steel surfaces, reacting with dibenzyl disulphide in cetane, show an initial friction transition with increasing temperature, which reduced the friction coefficient to a value between 0.25 and 0.3 (Figs. 2.9 and 2.10). This has been attributed to the formation of an oxide layer (Section 2.50). A second transition, attributed to extreme pressure action, has caused a further reduction in the friction coefficient (Section 2.40), demonstrating the superior friction properties of sulphide films over films of oxide. Thus some confirmatory evidence is available for the results of Sakurai et al. (119).

An earlier paper by the same author (25), noticed that whilst some disulphides on reaction with steel surfaces gave predominantly oxide layers, the film formed by the reaction of dibenzyl disulphide consisted of iron sulphide. Sakurai concluded that the reactivity of the sulphur compound towards iron surfaces was the reason for this apparent anomaly and that whilst the oxidation reaction might be predominant with disulphides less reactive towards iron, with dibenzyl disulphide the sulphuration reaction would predominate since this additive displays a higher chemical reactivity. Toguyachi and Takai (21,22) similarly showed that though dissolved oxygen played a part in the lubrication of steel surfaces by some disulphides, dibenzyl disulphide was affected very little by the presence of dissolved oxygen. Chemical reactivity was again put forward as the reason. However, since oxygen is particularly reactive and adsorbs very readily on iron surfaces, it seems intuitively that the reactivity theory is not the whole story. The obvious difference is that in these investigations, dibenzyl disulphide was present in concentrations of up to 3.5% by weight, whereas oxygen is present as an impurity dissolved in the base oil and is therefore available in only very small concentrations. It is possible therefore that a balance exists between reactivity and concentration, which decides whether oxide or sulphide is formed from the reaction of disulphides with steel surfaces.

In order to investigate the possible role of dissolved oxygen in the lubrication of EN 31 steel by dibenzyl disulphide several test runs were carried out in an atmosphere of Nitrogen. The Nitrogen gas, nominally oxygen free, was first passed through a bed of activated silica gel to remove any trace of water which might have been present, and then bubbled into the additive solution contained in the reaction vessel. After purging the additive solution for an hour, a test run was started following the procedure described in section 2.22. In order to prevent leakage of oxygen into the system, attempts were made to maintain a positive pressure of nitrogen above the additive solution during the test. This however proved difficult, since without adequate sealing of the apparatus, the high flow rates of gas necessary to achieve this, caused the additive solution to be disturbed. It is therefore perhaps not surprising that no visible effect was noticed on the friction temperature curves obtained by these experiments. Whereas an effect on the second friction drop perhaps might not have been expected, it is considered that some differences in the first transition due to oxidation of the steel surfaces might have been observed. That no such effect was noted can be adequately explained since it has been found that a single monolayer of oxygen can cause a significant reduction in the friction of steels (120). It has further been shown by Baker (121) that even in a high vacuum or an inert gas atmosphere, with a very low partial pressure of oxygen, a 'clean' surface will form a surface oxide layer approaching a monolayer very quickly. Baker remarks that for a working time of several hours with atomically clean metal, an oxygen partial pressure of less than 10^{-10} torr must be maintained. To maintain a minimum partial pressure of 10^{-10} torr of oxygen (or water vapour) in an atmosphere of inert gas (approximately 10^{3} torr) implies a concentration of not greater than 1 part in 10^{13}, whereas the specified minimum content of oxygen in the Nitrogen gas supplied by the British Oxygen Company was 5 parts per million by volume. It can, therefore, be seen that purities of the order necessary to achieve an oxygen free atmosphere are not feasible without high vacuum facilities. For this reason it was considered impractical to pursue this line of action further.

A.20 The Effect of load on the Lubrication of EN 31 steel by Dibenzyl Disulphide

The work of Matveevsky (61) and Hirst and Stafford (62) reported in section 2.22, has shown that the magnitude of the surface deformation under applied load, is a major factor in lubricant breakdown. When under elastic deformation, solid surface films (e.g. oxide), remain intact and can provide sufficient protection to avoid gross damage to the surfaces. However, when surface layers are stressed sufficiently to cause plastic flow, severe damage can result probably through the tearing of surface junctions. It was important therefore in the test described,to use a load such that yield point of the metal was not exceeded.

One of the two important yield criteria used in practice is that attributed to Tresca or Guest. This criterion assumes that yielding starts when the Maximum shear stress of the system equals the maximum shear stress at yield point in a simple tensile test and has been shown to give good agreement with experiment (122). The Tresca equation is outlined in Timoshenko (122) and is merely stated here in the form

$$\tfrac{1}{2}\,(\sigma_1 - \sigma_2) = \tfrac{1}{2}\,S$$

where σ_1 and σ_2 are the maximum and minimum principal stresses and S is the maximum yield shear stress. Since the quantity $\tfrac{1}{2}\,(\sigma_1 - \sigma_2)$ is equal to the maximum shear stress τ_{max}, (122), then according to the Tresca criterion, plastic flow will be initiated when the maximum shear stress exceeds half the yield shear stress of the material. For EN 31 steel, this has a minimum value of 93.2 tons/in^2 (1.46 GN/m^2) depending upon the heat treatment received by the steel, (124).

Now a load of 14 lbs.f applied to the lever arm of the ball-on-triplane apparatus, results in a maximum Hertz contact pressure P_{max}, of 172,000 psi (1.2 GN/m^2). Shigley (123) shows that for a ball-on-triplane geometry, the shear stress resulting from a given load, has a maximum value of 0.31 P_{max} at a distance of approximately half the Hertz contact radius below the surface of the contact. Thus under a load of 14 lbs force, the maximum shear stress τ_{max} is equal to 53,320 psi (0.39 GN/m^2)which is well below the shear stress limit for plastic flow (i.e. 0.73 GN/m^2). Surface deformation under this load with EN 31 steel is consequently elastic.

However, to see the effects of load on the friction temperature characteristics of EN 31 steel lubricated with dibenzyl disulphide, several experiments were conducted at two further loads. The experimental procedure has already been described (Section 2.22).

Under a load of 30 lbs force (133.5N), very inconsistent results were obtained. Whereas the first friction transition invariably occurred (though usually to a lesser extent), the friction drop due to the formation of an E.P. layer was occasionally absent. However, when this transition did occur, it did so at a similar temperature to that observed with the lighter load of 14 lbs force, though the gradient of the friction transition under these conditions was very much reduced.

It has already been noted (section 2.22) that inconsistent behaviour can result from loads of magnitude such that surfaces are plastically deformed, during rubbing (61, 62). It might be expected that initial heavy plastic deformation causes surface layers of metal to be pushed aside thus exposing fresh metal. However, presumably this deformation could lead in turn, to work-hardening of the surface layers, thus increasing the resistance to shear. Thus, in subsequent contacts, it is possible that surface films formed on the nascent metal between contacts is not totally removed and some degree of lubrication is possible. In this case, the observed behaviour would depend to some extent on the degree of plastic flow incurred. That heavy plastic deformation can occur can be illustrated through tests carried out with EN 58 J steel, which has a yield shear stress of 23.2 - 27.6 tons/in^2 (0.36-0.43 GN/m^2) at room temperature, depending again, upon the heat treatment received (124). Thus the resulting shear stresses from an applied load of 14 lbsf were well in excess of the elastic limit of the steel. The wear tracks of the EN 58 J specimens after test showed extensive damage. This is discussed further in the following section (A.30).

A further possibility to explain the irregular behaviour might be that small differences in peg heights could conceivably lead to large differences in the loading of a single peg. This in turn might result in different degrees of lubrication on each wear track and since the measured friction force is an average value taken over the three contacts, inconsistencies in the calculated friction values might be expected.

Tests carried out at loads of 3.75 lbs f (16.7 N) similarly showed anomalous behaviour. This was due primarily to the fact that the friction values prior to the friction transitions were significantly lower, leading to a less clearly-defined transition temperature. This was certainly the case with the first transition since presumably run-in at low loads did not remove all the surface films remaining on the surfaces after solvent cleaning. Similarly, the second friction drop, was to some extent screened by the first transition.

A.30. The Effect of Steel Composition on E.P. Lubrication by Dibenzyl Disulphide

The results of tests carried out with EN 58 J steel surfaces sliding together can be seen in Figs. 2.8 and 2.15. On comparison with similar tests carried out on EN 31 steel (Figs. 2.9 and 2.10), three differences can be noted.

Firstly, the unreactive steel shows no signs of a first transition which might be expected since the surface films on stainless steel consist of oxides of chromium as well as those of iron and nickel. These films can act as a barrier to the outward diffusion of iron to the surface and hence further oxidation is inhibited. (section 3.50).

A second difference is that, though a friction transition due to E.P. reaction does occur, the extent of the reduction in friction is very much less than that of the tests carried out on the more reactive EN 31 steel. On examination after these tests, the stainless surfaces were observed to be very heavily torn with a wide wear track on the ball. However, it has already been shown (section A.20), that these experiments with EN 58J steel were conducted under shear stresses exceeding the yield stress of the material, which explains the extent of surface damage. In view of this severe tearing of the surfaces, it is perhaps remarkable that the EN 58 J wear track could be lubricated to the extent observed.

The third difference is that the temperature at which the transition on EN 58 steel occurred was several degrees higher than that with EN 31 steel with an average value of $176 \pm 2^{\circ}$ C at 1 rpm. This is consistent with the decreased reactivity of stainless steels. (See section 3.50).

Tests carried out with an EN 58 ball sliding against an EN 31 peg gave similar results to those described above. The single transition again occurred at temperatures in the region of 176°. Minor differences were noted in that the coefficient of friction fell to a slightly lower value and the surfaces, consequently were not as badly torn as in the previous tests. This can be attributed possibly to differences in the hardnesses of the steels.

Tests with EN 31 sliding members have already been described. However, several experiments were run instead with EN 58 J pegs. No significant differences in the characteristics of the friction drops were noted. This adds supporting evidence to the findings of Bailey and Cameron (56) previously described (Section 1.7).

A.40. Investigation into Radical Mechanisms

A free radical mechanism for the action of disulphides with metal surfaces was first advanced by Davey (43). Later, Llopis and his co-workers (24), tested a number of polysulphides and demonstrated an order of reactivity dependent upon the number of sulphur atoms in the molecule. Recent work in our laboratory (125) has confirmed this. Llopis noted further that in the case of disulphides, results indicated that the sulphur-sulphur bond was split, forming thiyl radicals.

The effect of chemical structure upon the performance of an E.P. agent was examined by Allum and Ford (30). It was found that disulphides gave better results than the corresponding monosulphides, which tended to confirm the observations of Llopis et al. The authors reasoned that in the case of monosulphides, cleavage of two carbon-sulphur bonds was necessary to form an inorganic E.P. layer, whereas with disulphides only a single bond needed to be broken. A further suggestion was that monosulphides do not contain the relatively weak sulphur-sulphur bond, cleavage of which enabled the sulphur compound to be initially attached to the metal surface . Electron Probe Microanalysis (126) linked the E.P. performance of an additive with the sulphur content of the wear scar after test since the order of increased sulphur content followed exactly the order of increasing E.P. activity.

Further work (31) on organo-sulphur compounds as anti-Wear additives showed similarly that monosulphides were inferior to the corresponding disulphides. It was found, however, that factors governing anti-wear behaviour were not the same as those governing E.P. properties. Thus anti-wear activity could not be explained in terms of scission of the carbon-sulphur bond. It was suggested instead that anti-wear activity would be due to the ease of formation of a layer. This was governed in turn by the strength of the sulphur-sulphur bond. On the basis of these observations, a mechanism for the e.p. reaction of disulphide was advanced, in that cleavage of the S-S bond was first thought to occur forming a mercaptide. However, it was not known with certainty whether breakdown occurred on the surface or in solution. At higher loads and consequent higher temperatures, cleavage of the C-S bond was thought to occur to give an inorganic sulphur containing film.

A later study by Forbes and Reid (46) confirmed the earlier postulate that the ease of formation of an E.P. layer depended upon the strength of the C-S bond in the particular additive. However, the hypothesis that anti-wear behaviour was governed by the ease of cleavage of the S-S bond was amended. The author noted that if the reaction were to proceed via a mercaptide intermediate, then only hydrocarbon breakdown products should have been obtained, whereas the main produce for the reaction of dbds with steel was dibenzyl monosulphide. A similar result obtained by Carruthers (47) by irradiating dibenzyl disulphide with ultraviolet light led Forbes and Reid to the conclusion that the first stage in the mechanism of the E.P. reaction might involve the formation of thiyl radicals.

From this brief review, it can be seen that it is not known for certain whether the reaction of dibenzyl disulphide, with metal surfaces, proceeds by way of a radical mechanism or whether, if a radical process is indeed involved, breakdown to radicals occurs on the metal surface or in solution prior to adsorption. To investigate this possibility, several tests were carried out (Section 4.50) in the presence of toluene which can be used as an inhibitor (83) to trap any free radicals as stable compounds. The results of these tests can be seen in Fig. 4.9. Since there was no apparent change in the temperature of the E.P. friction transition (section 2.40), results indicated that free thiyl radicals were not present in the additive solution. It was noted, however, that if breakdown of the additive to thiyl radicals occurred on the surface of the steel, then no effect on reaction would be expected. This possibility was shown to agree with the reaction sequence advanced by Forbes and Reid (46).

The first friction transition already attributed to the oxidation of the steel (section 2.50) was however, completely suppressed, suggesting that this process is brought about in solution by a radical mechanism, though two further possible causes for the suppression were put forward.

To investigate further possible radical reaction mechanisms, Election Spin Resonance (C.E.S.R.), or Electron Paramagnetic Resonance (E.P.R.) techniques would be necessary. This method of detecting free radicals makes use of the fact that a radical has an unpaired electron. Since an electron is electrically charged, there is a magnetic field associated with it as a result of spin, thus effectively, each electron behaves as a tiny bar magnet. When a sample containing unpaired electrons is placed in a powerful magnetic field, the direction of the spin of the electron is reversed and in so doing, there is a net absorption of energy from the field. This forms the basis of the technique in that experimentally, the energy required to reverse the spin of an electron in an externally applied magnetic field is measured. The resulting spectrum not only detects such species as radicals, but also provides structural information and a sensitive indication of the position and environment of the unpaired electron. The disadvantage of the technique however, is that short-lived unstable radicals cannot easily be detected since they must be generated in situ in the apparatus. Without the availability of Electron spin resonance, this line of research was not pursued.

A.50. Investigations carried out into the Estimation of the thickness of the E.P. film, in preventing seizure at high speeds

Chapter Five describes experiments on the high-speed four ball machine to investigate the phenomenon of scuffing failure. At the same time, attempts were made to estimate the thickness of the E.P. film in preventing seizure, under the various conditions of sliding speed and additive concentration at which the tests described were carried out. The rationale behind the attempt, is outlined below.

At high speed, the maximum temperature in the contact is the sum of the skin temperature, Ts and the maximum flash temperature, ΔT max. However, it has already been advanced (56) that the in-contact contribution to the thickness of the E.P. film is negligible in comparison to that formed between successive contacts (Section 1.7). It is therefore envisaged that the greater part of the E.P. film is built up whilst the sliding surfaces are no longer in contact. During this period of no contact, the temperature flash decays exponentially with time (and hence distance at constant velocity) to a final value (reached just before the next contact) -which approaches that of the skin temperature. The form of this decay is set out in the diagram (Fig. A.1.) below.

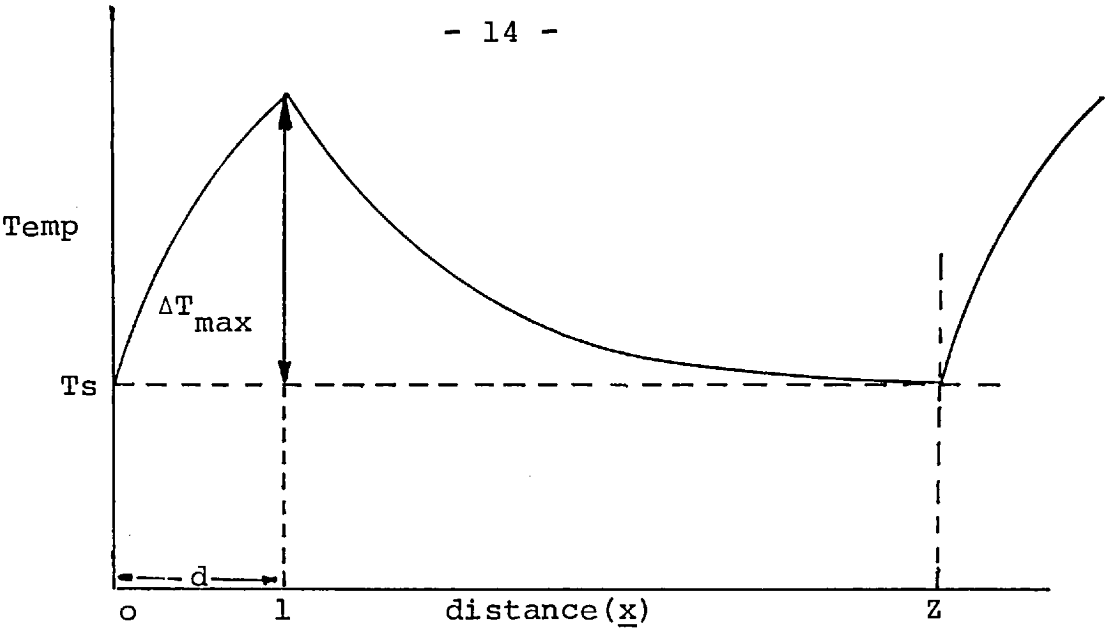

Fig. A.1. (Schematic)

Thus the temperature, T_R, at a point x past the contact is given by

$$T_R = Ts + \Delta T_{max}\left[\left(\frac{x}{d}\right)^{\frac{1}{2}} - \left(\frac{x}{d} - 1\right)^{\frac{1}{2}}\right]$$

where d is the hertz diameter of the contact. Thus $\frac{x}{d}$ is the non-dimensional distance Z; the number of Hertz diameters past the contact.

$$T_R = Ts + \Delta T_{max}\left[Z^{\frac{1}{2}} - (Z-1)^{\frac{1}{2}}\right]$$

Assuming the reaction between dibenzyl disulphide and steel surfaces to be of zero-order (section 4.30) then

$$\frac{d[FeS]}{dt} = k'e^{\frac{-Ea}{RT_R}}$$

Thus

$$\frac{d}{dt}[FeS] = k'\exp \frac{-Ea}{R[Ts + \Delta T_{max}(Z^{\frac{1}{2}} - (Z-1)^{\frac{1}{2}})]}$$

In order to integrate this expression, it is necessary to find how the change in reaction alters with distance.

Since Z = V.t, then under any given set of conditions V is constant and

$$\frac{dZ}{dt} = V$$

Now $$\frac{d[FeS]}{dt} = \frac{d[FeS]}{dZ} \cdot \frac{dZ}{dt}$$

$$= V. \frac{d[FeS]}{dt}$$

Therefore,

$$\frac{d[FeS]}{dZ} = \frac{k'}{V} \exp \frac{-Ea}{R\left[Ts + \Delta T_{max} \quad (Z^{\frac{1}{2}} - (Z-1)^{\frac{1}{2}})\right]}$$

$$= \frac{k'}{V} \exp \frac{-\frac{Ea}{RTs}}{1 + \frac{\Delta T_{max}}{Ts}\left[Z^{\frac{1}{2}} - (Z - 1)^{\frac{1}{2}}\right]}$$

Thus, assuming that reaction occurs solely out-of-contact, then the extent of reaction, [FeS] , depends upon the area under the curve (Fig. A.1.) between x = 1 and x = Z and therefore

$$\int_{[FeS]_1}^{[FeS]_Z} d[FeS] = \frac{k'}{V} \int_1^Z \exp \frac{-\frac{Ea}{RTs}}{1 + \frac{\Delta T_{max}}{Ts}(Z^{\frac{1}{2}} - (Z-1)^{\frac{1}{2}})} \, dZ$$

or $$[FeS]_Z - [FeS]_1 = \frac{k'}{V} . I$$

The expression, I, is a function of ε, β and Z where $\varepsilon = \frac{Ea}{RTs}$ and $\beta = \frac{\Delta Tmax}{Ts}$.

The integration was carried out by computer using a multiple regression technique. The regression gave:-

$$I = 0.13Z^{0.32} \exp 4.2\beta - 0.77\varepsilon$$

which in turn gives

$$\left[FeS\right]_Z - \left[FeS\right]_1 = \frac{k'}{V} \cdot 0.13Z^{0.32} \exp 4.2\beta - 0.77\varepsilon$$

Thus an estimation of the extent of reaction is given as a function of the variables, V, Z, ΔT_{max} and Ts.

Sliding speed, V, was measured by means of a tachometer attached to the drive shaft of the motor. The non-dimensional distance, Z, between consecutive contacts was calculated, knowing the value of the radius of rotation, r, by the formula,
$Z = (\frac{2\pi r}{3d} - 1)$

where d is the Hertz contact diameter given in turn (123) by $d^3 = \frac{12}{E}(1-\sigma^2).R \cdot W$ (inF.P.S units).

For steel, Poissons ratio (σ) is equal to 0.3 and Youngs Modulus (E) is equal to 30×10^6 lbsf/in^2. Similarly for the four-ball geometry, R, the reduced radius, is equal to ¼ inches. Substituting in the above expression for d gives

$d = 3.2\ W^{1/3} \times 10^{-3}$ inches where W is the normal load in lbs f.

The value of the Maximum flash temperature, ΔT max, was calculated using Blok's formula (91)

$$\Delta T\text{max} = \frac{\mu.P\left[1 + \frac{1}{\sqrt{2}}\right]V.r}{2\alpha.\rho.c\left[1 + \sqrt{\frac{\pi}{2} \cdot \frac{vr}{4\alpha}}\right]} \quad {}^{o}C$$

For the four-ball geometry using one inch balls, this expression reduces to

$$\Delta T\text{max} = \frac{0.95V\ W^{2/3}.\mu}{(1 + 0.626\ B^{\frac{1}{2}}) \cdot k} \quad {}^{o}C$$

with B, in turn equal to

$$B = \frac{3.126\ V.W^{1/3} \times 10^{-4}}{\alpha.}$$

where W,k and α are respectively

Normal load (on each ball in Kgs), thermal conductivity (Kg.sec.$^{-1}$ ^{o}K^{-1}) and thermal diffusivity (cm^{2}.sec^{-1}).

Skin temperature, Ts, was measured by means of a thermocouple placed as close as possible to the leading edge of one of the three contacts.

Values for the kinetic constants k' and Ea, were estimated from the intercept and slope of a logk versus $\frac{1}{T}$ plot given in ref (34) for the reaction between dibenzyl disulphide and iron. These values were respectively 10^{10} layers.sec^{-1} and 9.8 Kcals.mole^{-1}.

Chapter Five describes experiments carried out at various sliding speeds and additive concentrations, in which the load was increased until scuffing occurred. At the same time, the frictional torque and the skin temperature were monitored.

Thus, scuffing loads were obtained over a range of sliding speeds, together with values for friction and skin temperature recorded immediately prior to scuffing. With this information, values for the E.P. film thickness were calculated assuming that, on scuffing, the E.P. film is totally removed (i.e. $[\text{FeS}]_1 = 0$)

Thus $[\text{FeS}]_Z = \frac{k'}{V} \cdot 0.13Z^{0.32} \exp 4.2\beta - 0.77\varepsilon$

Unfortunately, these film thickness values proved to be very inconsistent. It was considered that this inconsistency was due almost entirely to inaccuracies in the estimation of the temperature parameters ΔT_{max} and Ts. Since even under conditions of constant load and constant sliding speed, the measured friction coefficient tended to vary slightly, there was a consequent variation in the calculated maximum flash temperature as this is a quantity, directly dependent upon friction. Similarly, the thermocouple indicating skin temperature could only be located with limited accuracy in each test and since the recorded temperature depended to some extent on position, there was a corresponding error in the measurement of this parameter.

In the film thickness expression above, both these temperature terms are involved in an exponential. Consequently, a relatively small error in either ΔT_{max}, or Ts, leads to a correspondingly very large error in the calculated film thickness. It was considered therefore, that without a better estimate of the two temperature parameters, the film thickness experiments described above, could not be pursued further, with any degree of accuracy.

Work since carried out in the laboratory, has shown that skin temperatures can probably now be determined by infra-red. This was not available at the time and is a somewhat complicated technique. It is the subject of a separate Ph.D,

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