TRANSITION TEMPERATURES OF LUBRICANTS

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by

Warwick John Stuart Grew

Imperial College of Science and Technology,
London, S.W.7.

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ABSTRACT

The increased failure load on four-ball machine experiments for fatty acid-alkane solutions of equal alkyl chain length was investigated.

Bowden-Leben friction temperature measurements revealed a temperature where friction rose sharply. This transition temperature increased for solutions of equal chain length.

Assuming lubricant failure at constant surface coverage, heats of adsorption were measured. Increase in lubrication ability and the greater heat of adsorption with matching chains was attributed to coadsorption of acid and alkane due to an increase in alkyl chain interactions.

Theoretical calculations of this increase agreed with experimental values.

Polynalkylmethacrylates in xylene exhibited transition temperatures which increased with a nalkyl group length.

Slow speed Bowden-Leben friction-temperature measurements with stainless steel and a mineral oil gave a sharp friction increase near 155°C.

This transition temperature with mineral oil had not be found so distinctly before this use of stainless steel. Subsequent work by other investigators who used stainless steel has shown that such tests are valuable in predicting gear and disc failure.

A theory of scuffing of engines during running in is proposed.

The mineral oil transition temperature was shown to result from desorption of friction-reducing surface active compounds present naturally. Using the hot wire method, non-additive mineral oil behaved as a corrosion inhibitor, this effect disappeared for surface temperatures exceeding 160°C, the region of the friction transition temperature. The importance of austenite in surfaces was demonstrated.

An unreactive metal-additive combination scuffed readily, whilst reactive compounds showed high corrosive wear.

The measurement of retained austenite content of carburized gears is suggested.

Whilst polar lubricants can be beneficial in reducing friction, wear and temperature; their presence caused a large reduction in scuffing load under severe high speed conditions. Even naturally occurring surface active compounds reduced the scuffing load considerably.

These effects have been explained using the proposed scuffing theory and proved experimentally.

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CONTENTS

CHAPTER I

Introduction

This introduction consists of a general introduction to the literature on friction, wear and boundary lubrication, showing some of the many important considerations. In addition each chapter contains more detailed information on each particular investigation.

Two distinct regions of lubrication are recognised, boundary lubrication and hydrodynamic; hydrodynamic lubrication is briefly explained although most of this work is concerned with boundary lubrication. It is intended just to indicate some of the parameters of boundary lubrication and other non-boundary lubrication effects, which are encountered in the formation presence and failure of boundary lubricant films, its identification and its measurement.

This work is concerned with the friction between metallic surfaces.

Consider a section through a metal surface, we may picture it as being made up of successive layers.

1. Bulk Metal

At the bottom, is the bulk metal comprising crystals, grains of crystals with grain boundaries, and possibly inclusions of foreign matter, and, if it is an alloy there may be very many structures present.

2. Bielby Layer

Above the bulk metal is deformed metal (the Bielby layer) this is the bulk metal after receiving deformation it is usually harder because of the increased density of dislocations and because of phase transformations may contain structures different to the bulk metal. This layer may not be uniform, e.g. the peak shear stress of an elastic contact is below the surface of the metal and thus transformation may be occurring below the surface too, ever making this region softer than the bulk metal.

3. Oxide Films

The deformed layer may contain oxides amongst its complicated structure, and have an oxide layer above it. The composition and thickness of the oxide layer will be determined by the temperature and pressure, the composition of the atmosphere and the ability of the oxygen to reach the oxide, and then go through to the metal surface. Embedded foreign particles will also be present in this surface.

4. Adsorbed Compounds

On the oxide layer some molecules of water vapour and other gases may be strongly adsorbed, and present too may be sulphides and chlorides of the metal, perhaps organo-metallic compounds, corrosion products, and the boundary layer.

5. The Boundary Layer

The boundary layer refers to adsorbed molecules on the surface which prevent severe metal to metal contact of sliding surfaces thus reducing friction and wear.

6. Thick Films

Because of the fields emanating from the surface and from the adsorbed molecules themselves, the boundary layer may have influence over more than one molecular layer giving rise to a thick film.

7. Bulk Fluid

Above the boundary layer and its field of influence exists the bulk liquid or gas. This is the region where hydrodynamic lubrication operates. The complete separation of the surfaces may be maintained by high pressure fluid pumped from an external source or by the pressure developed by a converging oil film in the bearing itself. Where the pressures developed are great enough to deform the solids elastically, the lubrication is called elastohydrodynamic. In hydrodynamic lubrication the tractive force is determined by the properties of the fluid, the friction is very low and the wear rate is very small. Sometimes a mixed region combining both hydrodynamic and boundary lubrication can be encountered, at lower velocities where only a partial hydrodynamic film is being generated.

Sliding Surfaces

We may now picture two surfaces sliding over each other. At the points of contact all of the components of the metal interface may singly or jointly influence the friction behaviour, indeed, the difficulty of reproducing the surface conditions can explain much irreproducability of frictional measurements.

The force required to drag one of the surfaces over the other is called the friction force and most boundary lubrication measurements are concerned with the value of this force and the associated affects of wear. Usually, the coefficient of friction is calculated, this is the ratio of the friction force to the applied load between the surfaces. For 'dry' surfaces the value is a constant over a wide range of load and temperature, i.e. Amonton's laws of friction.

(i) The frictional force is proportional to the load between the surfaces.

(ii) The frictional force is independent of the apparent area of contact.

Since the measurement of friction forces is the most frequent measurement in this work, an explanation for the constancy of the coefficient of friction and its independence of area of apparent contact is given.

The Coefficient of Friction μ

Consider a ball loaded against a flat plate, the area of contact was calculated theoretically by Hertz in 1888 for elastic deformation of smooth surfaces. Thus the radius of contact a is given by [1]

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

W = load

r = radius

E = Young's modulus of the plate or ball.

[unit csg or lb in sec]

Hence the area of contact is $\pi a^2 = A$. Thus if movement was to occur the force F required to shear the area of contact of shear stress s is given by

$$F = As.$$

i.e. $$F = CW^{2/3} \qquad C \text{ is a constant}$$

hence $$\mu = \frac{F}{W} = CSW^{-1/3}$$

Thus

For elastic behaviour the coefficient of friction decreases with increase in load. The elastic limit of the steel Y is exceeded when the mean contact pressure of the ball on the plate P_m i.e. $P_m = \frac{W}{\pi a^2}$ exceeds 1.1Y.

Thus if we consider an asperity of radius 10^{-4} cms., the load required to cause plastic behaviour for such an asperity of mild steel [2] is 4.7 x 10^{-5} grams.

Thus, when two surfaces are placed together, because of asperity contact they will touch at a relatively few isolated spots, these contacts then deform plastically until the projected area of real contact A_r is sufficient to support the load W.

Whilst the yield pressure P_m at the elastic limit is given by 1.1Y under plastic conditions $\overline{P}_m$ is approximately [2] 3Y, thus for a steel $\overline{P}_m$ is 100 Kg/mm^2, hence the real area of contact A_r where

$$A_r = \frac{W}{\overline{P}_m}$$

is now very small and thus the total load is supported by a very small area of contact. If $\overline{S}$ is the shear strength of the asperity welds, then the force required to shear them is given by

$$F = A_r\overline{S}$$

since $$W = A_r \overline{P}_m$$

therefore $$\mu = \frac{F}{W} = \frac{\overline{S}}{\overline{P}_m}$$

Hence

1. The frictional force F is proportional to the load W.
2. The frictional force F is independent of the apparent area of contact A_A.

i.e. Amonton's laws of friction.

Further information may be obtained from this relation.

Hardness

A semi-empirical relationship [3] gives the Brinell hardness as a direct function of the yield stress i.e.

$$H = 3Y \quad \text{units Kg/mm}^2$$

H = Brinell Hardness. Since $\overline{P}_m \doteqdot 3Y$ then the coefficient of friction is approximately inversely proportional to the hardness.

Temperature

The ratio $\frac{\overline{S}}{\overline{P}_m}$ is found to be virtually independent of temperature [2] over a wide range. This is because both $\overline{S}$ and $\overline{P}_m$ vary with temperature in the same manner. So far we have considered the frictional force as the force required to shear the plasticity deformed asperities, however, under relative motion a further term the ploughing force can be of significance.

Ploughing Force

Consider the sliding metal pair to comprise a hard metal and a very soft metal. The harder metal sinks into the softer metal until the area of contact is sufficient to support the applied load. Thus in addition to the force required to shear the asperity contacts, an additional force is required to displace the softer material from the front of the slider, this is called the ploughing force.

When a hemispherical slider is traversed over a flat plate a bulge appears in front of the slider, the additional frictional force to overcome this has been studied by Courtel [4] using an interferometric method.

Welding

The shear strength $\overline{S}$ of the junctions formed by asperity contact has been assumed to be of the same order as one of the metals, and the total area of real contace assumed as being the area which is just sufficient to support the load. Theories of asperity welding consider a junction growth, occuring with time with the high pressures and high temperatures developed by the sliding asperities in continual contact, this is now readily demonstrated by friction welding machines. The affect of different metal combinations is discussed later.

If we now consider the two surfaces sliding over each other, the force actually measured will be the force to overcome the least resistances to shear.

Thus, if the boundary lubrication is very good a small coefficient of friction will occur with little surface damage, but if boundary lubrication is poor and also the asperities form very strong bonds, then shearing may occur in the bulk of the metal with high surface damage.

Simple headings are now used to signify the regions of the surface and under each heading some of the factors which determine the forces required to shear this region are discussed briefly.

The Bulk Metal

Shearing in the bulk metal especially for the hard brittle metals is indicative of failure and is determined by the shape size, strength and composition of the grains. The more ductile metals give a steady friction force as they are sheared. The forces required to shear the bulk metal structure has been found to very with the crystal configuration, i.e. as expected the friction is lowest on the planes of greatest atomic density [5], thus Gwathmey [6] found the coefficient of friction between the (111) face of the face centred cubic structure of a copper crystal to be of the order of 25 whilst for the (110) face a value greater than 100 was obtained. Wilman [7] found that generally hexagonal structures require less force to be sheared than cubic structures.

Oxide Films

Clean metal surfaces have been shown to spontaneously weld when brought together in vacuum [2], for the surfaces are very reactive. The presence of an oxide film is thus very important. The shear strength of the oxide will depend upon its composition and configuration although often it is harder than the bulk metal, equally important is the strength of the bond between the metal and the oxide layer and the amount of oxide worn off by asperity contact. Hence the type of interaction may also be a function of velocity, thus if the initial interaction is between oxide films, these may be sheared exposing fresh metal, the metal may then not have time to form an oxide film before the next asperity contact. The friction will therefore depend upon the time between asperity contacts, i.e. the surface finish and the velocity, and upon the oxide growth rate, this depends upon the reaction kinetics such as temperature and the availability of oxygen. This affect has been studied by Rabinowicz [8] who considered that an oxide coating of 10^{-6} cms. is required for the oxide to act effectively.

The effect of the constituent gaseous atmosphere now becomes apparent, indeed, clean fresh metal surfaces weld spontaneously in vacuum [2]. Vinogradov et al. [9] using a four ball friction machine shows a large increase in friction and wear on changing to a Helium atmosphere, Vinogradov's laboratory [10] also considered the diffusion of oxygen through the lubricant and the effect of the solubility of oxygen in alkane lubricants. The rate of diffusion was found to be extremely important.

The Metal-Metal Interface

We may now consider the effect of the choice of metal combination upon the friction between them. This has been studied by a number of workers. Roach, Hunnicutt and Goodzeit [11] studied the performance of bearing metals against steel journals, they found that the relative positions of the metallic elements in the periodic table was of significance in establishing their resistance to scoring. One interpretation is that metal couples which tend to have complete solid solubility, without intermetallic compounds usually form friction junctions of great shear strength and are to be avoided, whilst the junctions formed between metals which exhibit a low solubility behaviour with each other, or form intermetallic compounds, are thus preferable. This applies to the B subgroup metals.

Adhesion

This effect may also be seen by considering the adhesion between the surfaces, and one of the advantages of using a lubricant is shown simultaneously. Consider a drop of liquid on a solid in the presence of a gas, then Dupre's statement for the energy W_{LS} the work of adhesion required for the surface between the liquid and the solid to be diminished by 1 sq. centimeter is given by

$$W_{LS} = \gamma_{gS} + \gamma_{gL} - \gamma_{LS}$$

where γ is the surface tension and g, L and S refer to the gas liquid and solid.

However, for equilibrium of forces for a drop resting on a surface (neglecting gravity)

$$\gamma_{gS} = \gamma_{LS} + \gamma_{gL} \cos \theta$$

where θ is the contact angle.

Hence

$$W_{LS} = \gamma_{Lg}\ (1 + \cos\theta)$$

W_{LS} the work of adhesion represents the work required for the covered surface to be diminished in area revealing fresh surface again, thus if we consider the liquid L to be a solid, a and the solid S to be solid, b, then covering of b by a will occur if the work of adhesion is high, i.e. this covering will come from mutual solubility and the formation of intermetallic compounds. Thus, for a low coefficient of friction a low value of W_{AB} is required, i.e. in agreement with Roach Goodzeit and Hunnicutts work [11, 12]. Rabinowicz [13] has given a compatibility chart for the elements based on mutual solubility and the formation of intermetallic bonds thus from the chart elements Fe vs P6, Cr vs Pb and Ni vs Pb are good for the use as sliding elements but Fe vs Ni and Cu vs Ni are bad, this agrees well with experience. Rabinowicz [13] concludes that the ratio work of adhesion to hardness of the softer metal, is a fundamental property in friction behaviour. It is now seen that one of the advantages for using a lubricant would be to lower the adhesion energy between the two surfaces, i.e. to choose a liquid which has a high energy of adhesion between both surfaces [14] much work has been done especially by Zisman [14] on contact angle and wettability and it is discussed more fully in Chapter 3 concerning oleophobic monolayers.

Reactivity of Surfaces

Conditions of high pressure and temperature exist in the friction zone and the formation of nascent metal surfaces is likely, indeed the penetration of the oxide film does not only occur under high speed shear conditions, it also depends upon the relative hardness of the bulk metal to the oxide coating, and the value of the applied load. Thus, if the oxide is hard and brittle, and the underlying metal soft and ductile, then the oxide fractures easily under light loads, thus copper oxide breaks down with increasing load [2] whilst the oxides of chromium prevent metallic contact over a wide range of load [2]. The friction zone conditions permit many reactions, thus whilst diffusion of oxygen to the friction zone to permit the formation of a lower shear strength oxide film was important in the reduction of friction of alkanes shown by Vinogradov [10], a plentiful supply of oxygen may result in corrosive wear. This was demonstrated by Fein and Kreuz [15]. Using a four ball machine, they varied the dissolved oxygen content in the lubricant, thus when availability of oxygen was low, formation of Fe_3O_4 occurred and wear was high, but with increasing availability of oxygen friction and wear decreased, until, with a copious supply, much Fe_2O_3 was formed and the wear rate increased, similar effects have been observed by Tao [16] and Bieber and Klaus [17]. Increased reactivity has been found for friction surfaces, thus Campbell [18] found increased reactivity of copper wires when they were progressively deformed by twisting, i.e. increased reactivity due to deformation, whilst Smith [19] concluded that much increased reactivity could be explained by the Kramer effect, i.e. the emmission of electrons at room temperature from nascent surfaces. Machining metal surfaces under cyclohexane, and then adding tagged nonadecanoic acid, the formation of the soap occurred, but the reactivity decreased with delay with which the acid and metal were contacted, and the decay was in a similar manner to the decay of the Kramer process indicating that the electrons were activating the chemical reaction.

St. Pierre and Owens [20] in the lubrication of aluminium, found lower coefficients of friction with cetene than with cetane (Hexadecane), this they attributed after further work to the formation of an aluminium carbon bond at the double bond position for cetene, indeed, the formation of compounds at the friction interface has been reported by Hermance and Eagon [21] and Chaikin [22] who found a dark carbonacous deposit (friction polymer) occuring on the sites of rubbing contacts in the presence of organic vapours. Rowe, Fein and Kreuz [23] conducting ten second tests at different temperatures with a high speed four ball machine with fatty acid alkane solution lubricants, examined the fluid at the end of the experiments using infra red and showed an increase in carbonyl group concentration. They then heated [24] the lubricants with powders of iron, and iron oxide to equivalent mean contact temperatures attained in the four ball machine, but found that the temperature was not of major importance in the oxidation, so concluded that the increased oxidation in the four ball machine was due to catalytic oxidation by the nascent iron surfaces. The exact effect of the addition of "extreme pressure" additives i.e. constituents added to the lubricant to form low shear strength surface films is thus difficult to interpret without experiments, although more information is obtained by studying the probably sequence of reactions [25], indeed, the addition of chloride additives to lead base alloys may result in the formation of lead chloride which has a greater shear strength than the metal itself. This has been shown by Miller and Anderson [26] by friction pendulum measurements and earlier by Merchant [27] in cutting experiments. Merchant also gives values of the shear strengths of chloride and sulphide films, thus approximately the maximum reduction in friction expected from the formation of the respective chloride and sulphide film is for iron 70% and 53% for Cu 89% and 57% but for the formation of the lead chloride an increase of 170%. Courtenay-Pratt [28] has measured the shear strength of an adsorbed layer of calcium stearate on mica. The ability to form the low shear strength film is very important and is discussed in later sections.

The Effect of Surface Active Media

The strength of a solid under cyclic stress has been found to be dependent upon surface active media. Much work has been done in Russia by Rebinder [29,30) and work in America by Westwood [31].

When the surface is subjected to deformation, ultramicrocracks appear, which on the removal of the deforming force heal, but if a surface active agent is present, the polar compound is adsorbed in the ultramicrocrack so that complete healing is no longer possible, and on reapplication of deformation i.e. asperity contact, the solid is now much weaker and rupture and fatigue failure occur more easily. Especially interesting is an experiment by Rebinders laboratory [30] in which various metals are bored with a spear-shaped drill and the amount of heat formed measured. This is done in the presence of a paraffin oil and then repeated with increasing concentrations of cetyl alcohol in the paraffin, under an applied load of .5 Kg. The addition of the alcohol acts as a lubricant and much work is expended to cause cutting, more heat being given out with increasing alcohol concentration, however, on changing to a greater applied load, the process completely reverses and now the alcohol aids the cutting via the Rebinder effect. Another possible effect of surface active compounds in rotating machinery is the peptizing action of the wear debris in the contact region so that now, the irregular abrasive particles no longer cause extra wear. This effect was noted by St. Pierre and Owens [20] who on changing from cetene to allyl stearate, found a much more polished surface although the lubrication effect was caused by cleavage of the double bond. The carbonyl group it was suggested was peptizing the wear particles.

Boundary Lubrication

So far comparatively little mention has been made to compounds which, when added to the lubricant, improve "oiliness". This property is immediately apparent when one surface is slowly pulled over the other. The coefficient of friction using a lubricant of decane or white oil is near 0.4 whilst on the addition of castor oil a fall to 0.05 may be obtained. This represents not only a large reduction in friction force but a considerable reduction in metallic transfer between between the surfaces. Thus Rabinowicz and Tabor [32], using an autoradiographic technique for cadmium surfaces showed that if the friction was reduced two fold, the metallic transfer decreased about fifty times.

It was found that oiliness could be obtained by additives of castor oil, rape seed oil, oleic acid and recently crambe seed oil.

Fogg and Hunwicks [33] published an oiliness scale in 1940 resulting from boundary lubrication tests on a Deeley machine. Minimum oiliness corresponded to dry friction $\doteqdot 0.08$. The addition of such boundary lubricants is most important and great savings may be obtained from their use.

Early work on boundary lubrication was carried out by Hardy [34]. Hardy measured the coefficient of static friction of lubricants between meticulously cleaned surfaces under controlled conditions of temperature and atmosphere. Using a glass slider he formed a table for the resistence of lubricants to seizure. This was the number of interference fringes passed through with increasing load until the application of a tangential load seizure occured. In his 1923 paper [35] he reported the existence of a latent period. Thus caprylic acid had a latent period of 45 mins. before friction reached a steady value, whilst a lubricant of 2.05 wt. % of caprylic acid in N octane had a latent period of only two minutes, both lubricants giving very similar values of coefficient of friction. An increase in temperature was found to decrease this latent period. Hardy [34] also conducted experiments using a homologous series of organic compounds, and found a linear decrease in static coefficient of friction with increase in chain length and that the viscosity of the lubricant was not a fundamental parameter in these experiments.

The Bowden-Leben Machine[36]

With the advent of the Bowden-Leben machine in 1939 many more boundary friction experiments were made. The Bowden-Leben Machine comprises a flat plate on which the lubricant is placed and a hemispherical slider which is slowly traversed across the plate. The frictional force is measured from the deflection of the rider.

In many dry and lubricated friction experiments stick slip behaviour was noticed.

Stick Slip

Stick slip is the jerky motion of one of the surfaces as it slides over the other;stick slip is considered in Chapter II.

The change of coefficient of friction with change in temperature was also determined for many lubricants including the fatty acids. In the derivation of the equation for coefficient of friction it was shown that the coefficient of friction between unlubricated surfaces was virtually independent of temperature. Experimental results have confirmed this [2] indeed Peterson [37] has determined the sliding characteristics of metals up to high temperatures and found small friction until the higher temperatures i.e. 500°C were reached when the formation of oxide films became a major factor in the friction reduction.

Fatty Acids

Many experiments were carried out on the fatty acids, since they showed good boundary lubricant behaviour. These fatty acids are the saturated monocarboxylic organic acids.

Tabor [38] conducting tests on the Bowden-Leben machine found a breakdown, or transition temperature, at which the friction increased, this transition temperature was considerably above the bulk melting point of the fatty acid and indeed, corresponded quite closely to the melting point of the respective soap i.e. chemical reaction had occured. Tabor then repeated similar tests on many different metals with a 1% lauric acid solution in parafin oil. Thus Zn, Cd, Cn and Mg all gave transition temperature in the region of the respective metal laurate, e.g. the transition temperature using Cu surfaces was found to be 97°C this compares with a softening point of 100°C of copper laurate.

Pt, Ni, Al, Cr, glass and Ag, however, all gave a high coefficient of friction and an intermittent type of sliding when lubricated with the 1% lauric acid mixture, and at 20°C a rise in coefficient of friction was noted for all of these substances.

Further tests were made on Pt using the different metallic laurate soaps, e.g. copper laurate. Using copper laurate, smooth sliding was obtained on platinum until 100°C was reached, i.e. the breakdown temperature. This temperature is identical with the transition temperature of copper surfaces lubricated with the 1% lauric acid mixture. The same procedure was then repeated for stearic acid, thus it seems clear that the lubrication of mild steel, Zn, Cd, Cn and Mg under these conditions, is effected not by the fatty acid itself, but by the metallic soap formed as a result of chemical reaction between the metal and the fatty acid, indeed this is confirmed by Bowden and Moore [39]. Using reaioactive metals they detected the metal in the ester after extracting with benzene thus Zn, Cd, and Cu experienced chemical attack whilst Pt and Au did not. Similarly Menter and Tabor [40] and Sanders and Tabor [41] made an electron diffraction study of the structure and orientation of the fatty acid films. Thus at room temperatures the film consisted of an oriented structure, with the fatty acid carbon chains normal to the surface but as the temperature was raised this orientation became less distinct and there was a temperature at which no orientation could be seen this effect was reversible, for on cooling, the orientation pattern was again observed. With fatty acids on non-reactive metals e.g. Pt, the disorientation temperature was close to the bulk melting point of the fatty acid, but on reactive metals the temperature corresponded to the bulk melting point of the appropriate metallic soap.

During this period, Frewing [42] also carried out experiments with a Bowden-Leben machine on the influence of temperature on boundary lubrication using mild steel surfaces, i.e. .13%C, .59%Mn, .05%Cr, 3.42%Ni). He considered a wide range of compounds in solution with a white oil. Compounds considered were long chain halides, acids, and substituted acids, esters, cyanides and thiocyanated nitroderivatives. He found in all cases a transition from smooth sliding to stick slip occurred, at a temperature which was a function of the concentration of the solution used, and, by plotting graphs of the logarithm of the concentrations versus the reciprocal of the transition temperature in degrees Kelvin, Frewing was able to calculate the heat of adsorption of the lubricant additive. This was found to be a constant for the homologous series of monocarboxylic fatty acids studied.

Frewing measured the heat of adsorption in this way of a large number of compounds, however, the results using carboxylic fatty acids seems to contradict Tabor's [38] work and the subsequent work [39] showing the formation of soaps with mild steel. Prutton [43] has shown that the oxide surfaces of mild steel can react with fatty acids. Tingle [44, 45] freed the metals from their associated oxide films by cutting the metal under the lubricant which was 1% lauric acid in white oil. He followed the cutting tool by a loaded hemispherical slider and thus measured the coefficient of friction. Tingle [45] found that the freshly cut metals Mg, Cd, Zn, Cu, Fe, and Al. remained virtually unlubricated, however, the same process carried out in the presence of water quickly resulted in the formation of the fatty acid soap. In Frewing's experiments, the mild steel plate was finally cleaned by boiling acetone to remove water and thus if the hemispherical slider was exposing fresh metal surface this may explain the absence of any influence of soap type lubrication in his tests.

More recent work [1967] by Timmons, Patterson and Lockhart [46] investigated the adsorption of C14 labelled stearic acid on the armco iron surfaces. Monolayers were put on the iron surfaces using retraction from mitrobenzene solution. The iron surface was carefully prepared by abrasion under flowing water, polishing with alumina and then further washing with distilled water, finally drying was carried by subjecting the surfaces to a blast of room air, after which the monolayers were prepared immediately. Desorption experiments were then carried out by heating in a vented oven, it was found that 40% of the acid seemed to be chemisorbed whilst 60% was rather weakly adsorbed indicated a process of physical adsorption. Another explanation could be that Frewing was in fact measuring the desorption of the metallic soap. Experiments by Sakurai and Baba [47] will be referred to who have found similar desorption energies and by a $\ln C$ vs $\frac{1}{T}$ relationship for a metallic soap solution in hexadecane and dekalin on platinum surfaces.

Oleophobic Monolayers

Bigelow, Glass and Zisman [48] found a similar relationship to Frewing's [42] between temperature and concentration when investigating the desorption of oleophobic monolayers. Using a platinum square surface to which a rod was attached, the platinim was immersed in the solution under investigation, the platinum square was then raised out of solution to observe whether the surface was oleophobic to the rest of the solution, the temperature was increased slowly and a temperature was found at which the dipper remained completely wetted by the solution when withdrawn, i.e. the critical temperature. Similar values of heats of adsorption to Frewing's [42] were also found.

Monolayer Measurements

It had become clear that boundary lubrication was closely connected with adsorption, and early experiments by Bowden and Leben [49] in 1940 on their 'Bowden-Leben' machine had been measurements on monolayers deposited from a Langmuir Trough. They carried out tests on the durability of the monolayer, i.e. the coefficient of friction was continuously recorded over a number of runs on the same track. It was found that for stearic acid 53 deposited films was durable for over 50 runs (the friction remaining at a constant value) whilst for surfaces on which only one film had been deposited, the friction increased rapidly after 4 runs. It was also found that the coefficient of friction for the first run was independent of the number of deposited films.

Rectification Effect

An interesting effect found in lubrication is the rectification effect, this was reported in 1929 by Viewig and Kluge [50]. It was found that on application of an alternating current between two lubricated bearing surfaces a small (microamps) D.C. current flowed. Sakurai and Baba [47] have found this effect to occur between static surfaces which were partially immersed in an organic solution containing polar molecules. They used three steel balls loaded by a weight on to a flat plate and the level of the liquid half way up the balls. As the temperature was raised a certain temperature was reached where the rectification effect ceased, and no current flowed. The concentration of the polar solute was varied and graphs log C vs $\frac{1}{T}$ were plotted so that a heat of adsorption could be calculated. Similar values were obtained to those calculated by the experiments of Frewing [42] and Bigelow, Glass and Zisman [48].

Lubricating-Oils

Boundary lubricants are often added to commercial oils, although the mineral oils often contain natural polar compounds. This was shown by Hardy [51] and by Tabor [52, 53]. Tabor tested a commercial mineral oil lubricant on the Bowden-Leben machine and good lubrication was found at room temperatures, but with increasing temperature an increase in friction occurred with a change to stick-slip behaviour, this Tabor attributed to disorientation of adsorbed products. Further increase in temperature resulted in the formation of oxidation products.

Commercial mineral oils now usually contain many additives and their effect on boundary lubrication must also be considered for adsorption is a dynamic equilibrium process. Thus oxidation inhibitors, detergents, dispersants, viscosity index improvers, pour point depressents, anti-foament additives, chlorine and sulphur and other 'e.p.' additives, corrosion inhibitors and boundary lubricants must all be considered. It will be shown that the interaction of these substances with the surface can be most important in determining failure.

Failure of moving parts is of extreme importance and much research is concerned with finding better lubricants, and materials of construction and the failure of plain bearings, rolling bearings, gears, discs, diesel and petrol engines, and gear pumps.

This work is concerned with lubricant failure.

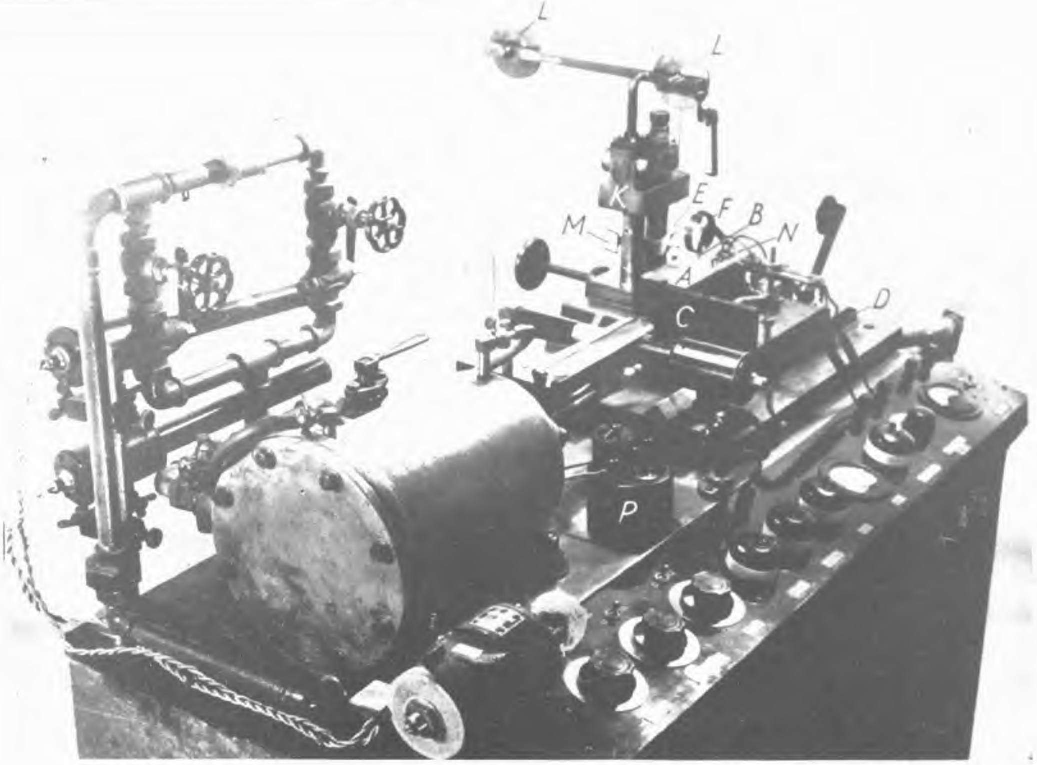
CHAPTER II

The Bowden-Leben Machine

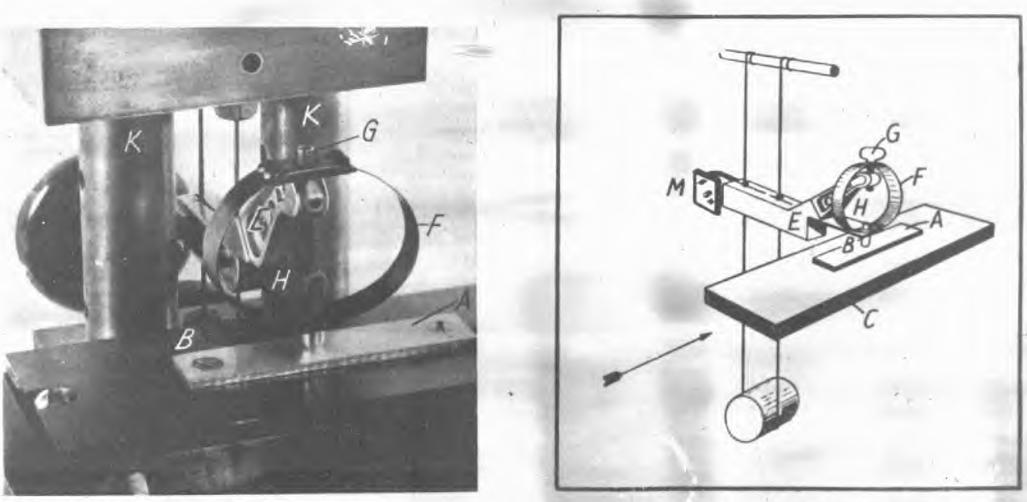
Many of the boundary lubrication tests referred to in the introduction, were carried out using the Bowden-Leben machine. A similar machine has been used in this investigation. A description of the machine and the interpretation of the results is now given.

A photograph of Bowden and Leben's original machine is shown on the following page and the description is taken from Bowden and Tabor Vol. 1 [2].

"The friction is measured between a flat lower surface (A) and a stationary upper surface which is usually in the form of a curved slider (B). The lower surface is mounted on a carrier (C) which runs on rails (D) and is driven steadily by water pressure with a force much greater than the opposing friction. This ensures steady uniform motion, free from vibration. The speed of the lower surface is adjustable and ranges from about .001 cm./sec. to a few cm./sec. The upper surface is attached to a light rigid duralumin arm (E). This is carried on a bifilar suspension of tightly stretched piano wire supported on a rigid frame (K). The load is applied between the surfaces by means of a flat spring (F) bent into a circle. The extent of the compression of this spring which is adjusted by means of the screw (G) determines the load between the surfaces. A flat piece of spring (H) prevents lateral distortion of the spring when sliding. The normal load acting between



a. General view of friction apparatus



b. Detailed view of surfaces

c. Diagram of apparatus

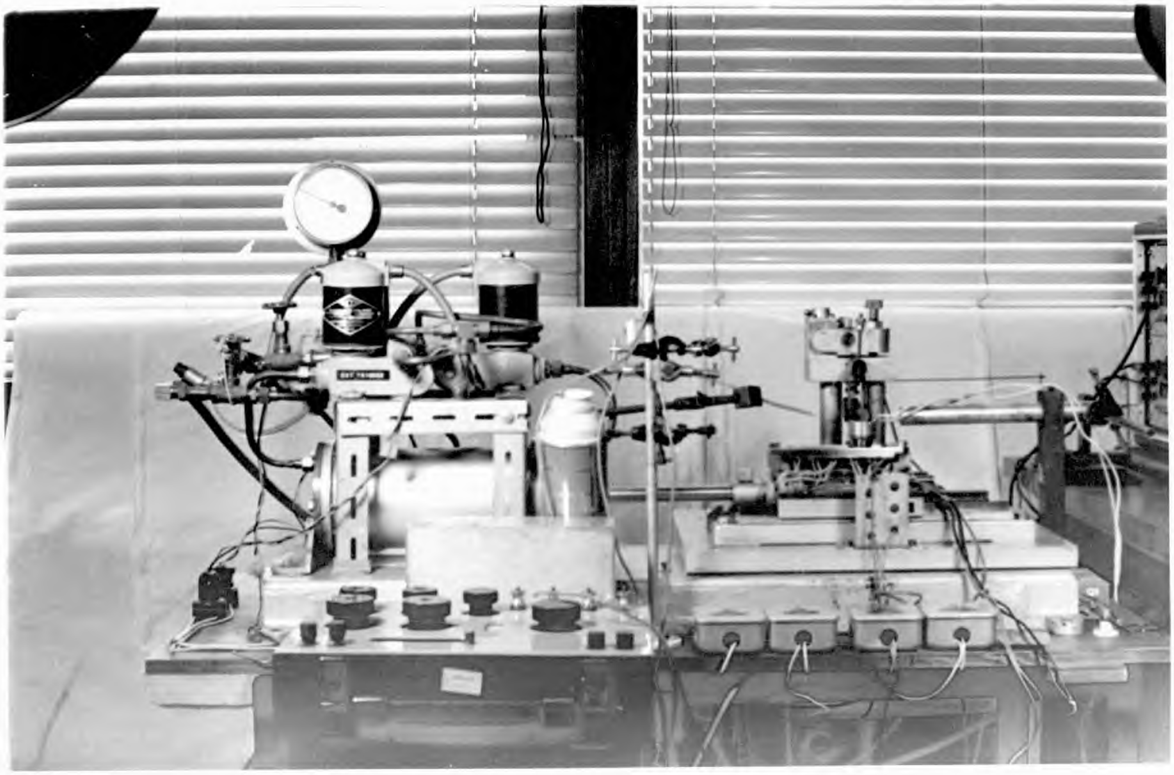
FIG. 1. Bowden-Leben apparatus for measuring friction between sliding surfaces, either dry or in the presence of boundary films.

A, lower surface; *B*, upper surface or slider; *C*, carriage holding lower surface and heating element; *D*, rails; *E*, duralumin arm holding upper surface; *F* and *G*, spring and screw for applying load; *H*, stiffening spring; *K*, massive supports for bifilar suspension; *L*, pulleys and hook for determining normal load; *M*, mirror responding to deflexion of bifilar suspension; *N*, surface thermocouple; *P*, galvanometer for determining surface temperature. Recording camera not shown.

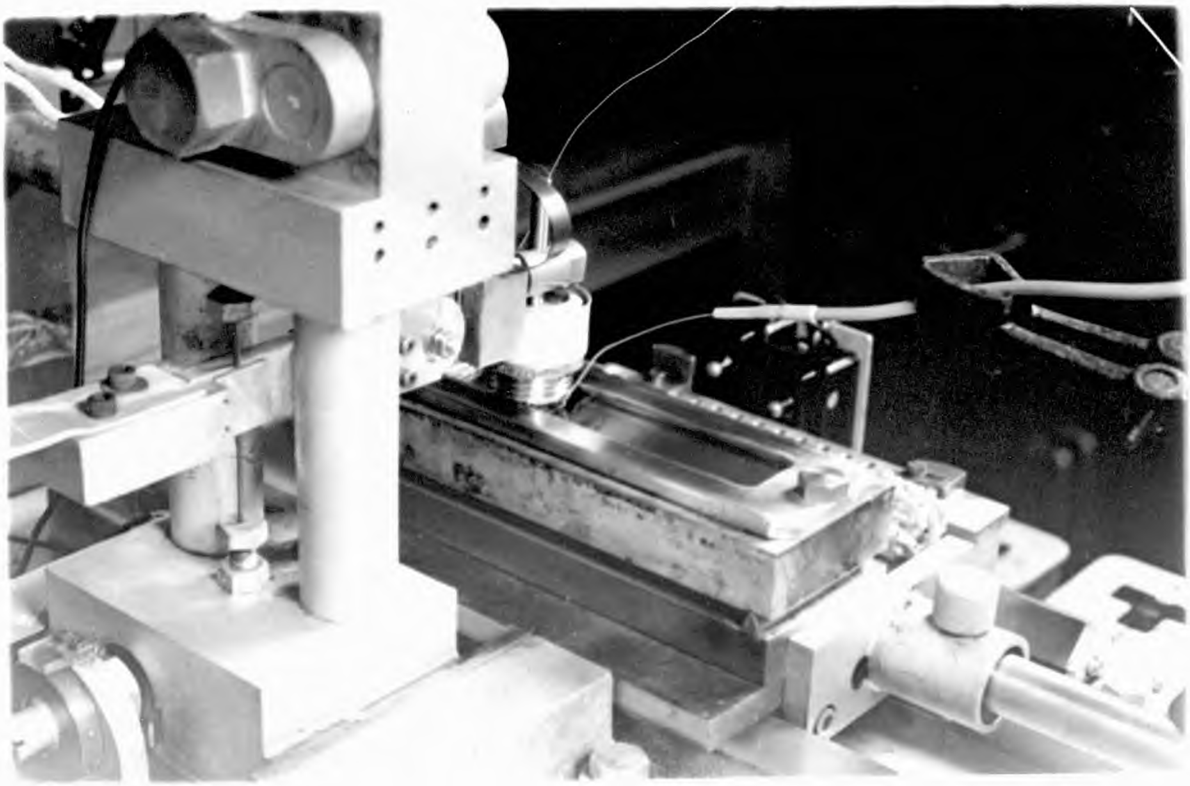
the surfaces can be measured by applying an equal and opposite load to the upper surface by means of weights and the pulleys (L). In this manner a load of up to 8 kg. can be applied by a device weighing only a few grams. Movement of the lower surface thus sets up frictional forces between the two surfaces. The torsion arm is deflected about a vertical axis and the amount of deflection is proportional to the friction force exerted between the two surfaces. The magnitude of the deflection is measured by a light beam reflected from the mirror (M) on to a horizontal slit in a moving film camera."

The apparatus used in these experiments was a copy of the original Bowden-Leben machine, however, for these experiments it was modified a little; this is seen from the photographs on the following pages. The "light beam camera" method of measuring the displacement has been replaced by a low inertia system incorporating a linear displacement transducer whose signal is fed into a fast response pen recorder. Control valves were fitted to the water system, and two micro-switches were fitted along the path of the plate holder to control automatically reversal of the piston. Most of the results were however carried out in a single pass of the plate. A new rider was fitted which could hold $\frac{1}{2}$" balls. A large stainless steel holder was made for the plate and the material under investigation clamped in this holder. The lubricant could now be applied so that at least $\frac{1}{4}$" of fluid was above the surface of the plate.

The heater under the plate was replaced by six 80 W soldering iron



The modified Bowden-Leben machine.



The modified Bowden-Leben machine.

elements encased in brass, it was found that this gave much faster heating and by using all six, a good uniform heat distribution was obtained. A heater was also fitted to the ball holder. Both heaters were independently controlled via variable voltage control units. Two thermocouples were used for temperature measurement, these were chromel-alumel encased in a sheath of stainless steel of .5 mm. external diameter. One of the thermocouples passed through a hole drilled in the ball holder and was pressed against the clamped ball rider, whilst the other thermocouple rested on the metal plate close under the ball. Further thermocouples were placed around the system but were not subsequently used since uniform and equal temperatures were obtained. Temperature measurement was made using a potentiometer reading to 1 part in 10,000 accuracy.

The velocity of the piston was set by the adjustment of fine needle valves on the water outlet side and remained constant. The water was obtained from a very large water supply tank 30 feet above the apparatus. A pressure gauge was fitted but the pressure never varied. The velocity of the piston was measured using a stop watch to measure the time a scribed mark on the piston travelled over a known distance.

Results

The first results using the Bowden-Leben machine [2] showed that the friction force between unlubricated sliding metals was not always constant, stick-slip was often obtained. An initial explanation for this behaviour may be seen on considering the sliding system as shown in Figures 1 and 2.

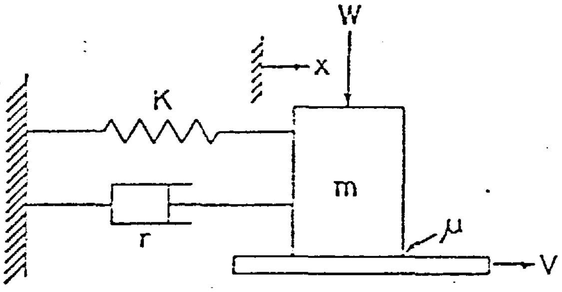


Fig. 1 Diagram of the sliding system

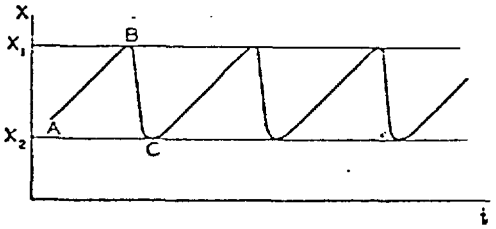
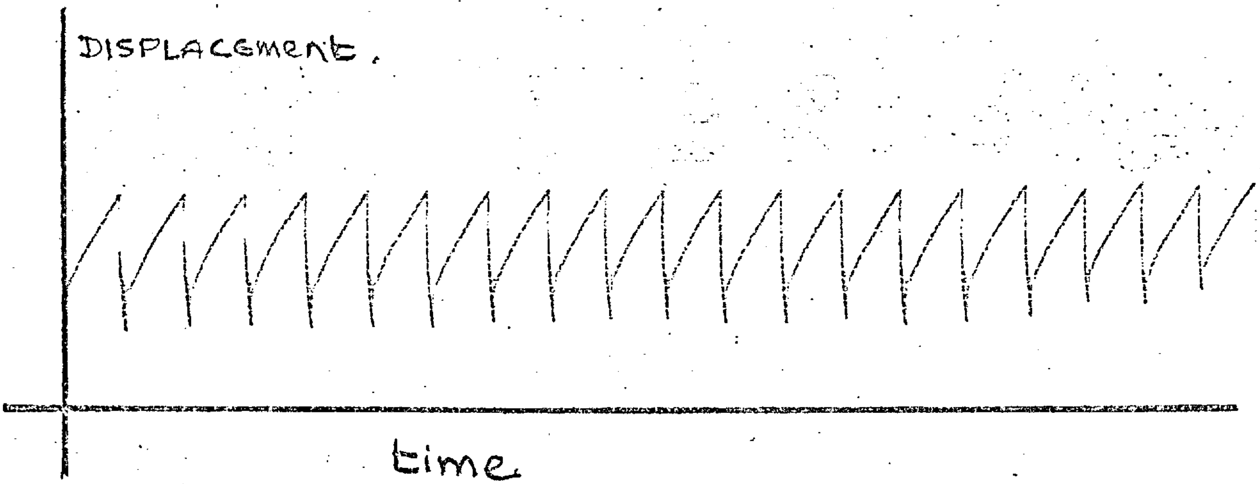


Fig. 2 Graph of displacement of slider versus time

let the coefficient of static friction U_s be greater than the coefficient of dynamic friction U_d.

The rider, therefore, moves with the flat plate at velocity V until there is sufficient spring force to overcome the static friction, the rider then moves rapidly by virtue of the lower dynamic friction force, the restoring force decreasing with decrease in extension of the spring until it comes to rest. This procedure then repeats itself.

The photograph on the following page shows a stick slip trace obtained using this modified Bowden-Leben Machine.



Stick - slip.

In the Appendix at the end of this chapter, the shape of the stick slip curve is explained in terms of the variables of the mechanical system, and hence includes characteristics of the machine.

In earlier publications using the Bowden-Leben machine, stick slip was used to identify lubricant breakdown. This clearly is not good, however, it must be admitted that usually the change to stick slip is accompanied by a rise in friction as shown in the graph given by Frewing [42].

In all cases using this modified Bowden-Leben machine the onset of stick slip whilst noted, is not used as the criterion of lubricant failure. Only changes in the coefficient of friction are used. Indeed many fluids tested on this machine were always in this regime at all temperatures. With stick slip there is a choice of where to measure the friction value, in all our tests on this machine the peak coefficient of friction has been the criterion. This peak coefficient can be identified with the static coefficient.

Bristow [54] was critical of the original use of stick slip as a criterion of lubricant breakdown. Using a modified Deeley machine, he measured the coefficient of friction of various fluids as a function of velocity and temperature. He found that after an initial fall from static to kinetic friction, the slope of the friction velocity curve could be positive or negative and varied with temperature. The change of friction with velocity is an additional damping term in the stick slip equations.

The variation of friction coefficient with velocity is most important for liquids used as transmission fluids. A clutch with high increase in friction with decrease in velocity will judder and squeal, whilst a fluid giving a rapid decrease in friction at low speeds will allow excessive plate slippage and perhaps subsequent failure.

Rounds [55] has made a comprehensive survey of the effect of additives to oils on the friction velocity curve. This is especially interesting since it demonstrates the effect of detergents, oxidation inhibitors and other additives, on boundary lubrication. Rabinowicz [56] has also studied stick slip behaviour, and applying increasing values of damping found that the slip amplitude diminished slowly at first, but, with increasing damping, suddenly dropped to zero. He then suggested that this effect occurred because the displacement between the surfaces during slip had now fallen to below 10^{-3} inches. Below this distance no metal to metal junctions were being formed. Rabinowicz [57] also suggested that the time of stick was one of junction growth. This last effect together with the variation of coefficient of friction with velocity has been incorporated into equations describing the stick slip process by Brockley, Cameron and Potter [58] and a later discussion of the process is given by Bannerjee [59].

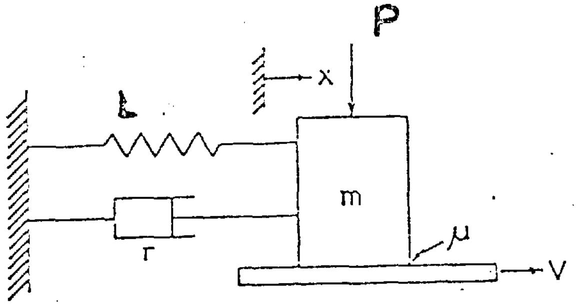
Whilst stick slip is important, for indeed its presence is most harmful in machine tool slideways nor is the squealing and jumping of brakes and clutches liked. The process has not been investigated in this work.

APPENDIX

Chapter II

The Stick Slip Process

Thus



let the mass M be loaded by the force P against a plate which is moving with velocity V

let the spring stiffness = L

let the damping coefficient = r

let the coefficient of static friction = μ_s

let the coefficient of dynamic friction = μ_D

let the displacement of the mass from the unstrained position = x

let the mass be sticking to the plate, this will continue until the force F is great enough to overcome the static friction force F_S

i.e.

$$F_s = \mu_s P$$

$$\mu_s P = Lx + rV$$

$$x = \frac{\mu_s P - rV}{L}$$

at this instant let t = 0

and slipping now begins

let the friction force be +ve

The motion will be described by

$$M\ddot{x} = -r\dot{x} - Lx + \mu_D P$$

$$M\ddot{x} + r\dot{x} + Lx = \mu_D P$$

A particular integral is $x = \dfrac{\mu_D P}{L}$

considering now the homogeneous case

$$M\ddot{x} + r\dot{x} + Lx = 0$$

i.e. $\ddot{x} + \frac{r}{M}\dot{x} + \frac{L}{M}x = 0$

let $\frac{r}{M} = 2K$ and $\frac{L}{M} = N^2$

hence

$$(D^2 + 2KD + N^2)x = 0$$

$$(\alpha^2 + 2K\alpha + N^2) = 0$$

Thus the roots of α

$$\alpha = -K \pm \left(K^2 - N^2\right)^{\frac{1}{2}}$$

α will thus have three forms.

$K < N$, $K > N$ and $K = N$; i.e. the damped, deadbeat and critically damped cases with $K = 0$ being the undamped case.

Considering the solution for

$$K < N$$

let $S = (N^2 - K^2)^{\frac{1}{2}}$

hence the roots of α are

$$\alpha = -K + is, \text{ and } -K - is,$$

Thus the general solution

$$x = Ae^{-Kt} \text{ Sin}(st + B)$$

and this particular solution

$$x = Ae^{-Kt} \text{ Sin}(st + B) + \frac{\mu_D P}{L}$$

i.e. $$x = Ae^{-Kt} \text{ Sin } st \text{ Cos } B + Ae^{-Kt} \text{ Cos } st \text{ Sin } B + \frac{\mu_D P}{L}$$

Boundary conditions

$$t = 0, \quad \dot{x} = V \text{ and } x = \frac{\mu_s P - rV}{L}$$

so $$A \text{ Sin } B = \frac{(\mu_s P - \mu_D P - rV)}{L}$$

and $$A \text{ Cos } B = \frac{V}{S} + K\left(\frac{\mu_s P - \mu_D P - rV}{L}\right)$$

this gives

$$x = \left[\frac{V}{S} + K\left(\frac{\mu_s P - \mu_D P - rV}{L}\right) e^{-Kt} \text{ Sin } st + \left(\frac{\mu_s P - \mu_D P - rV}{L}\right) \times \left(e^{-Kt} \cos st\right) + \frac{\mu_D P}{L}\right.$$

Firstly, the form of the stick slip behaviour can be most easily seen by taking the simplest case of no damping, i.e. $r = 0$ hence $K = 0$.

$$x = \frac{V}{N} \text{ Sin } Nt + (\mu_s - \mu_D)\frac{P}{L} \text{ Cos } Nt + \frac{\mu_D P}{L}$$

$$\dot{x} = V \cos Nt - N(\mu_s - \mu_D)\frac{P}{L} \text{ Sin } Nt$$

This motion will continue until the velocity of the mass relative to the plate vanishes at $\dot{x} = V$

putting $\dot{x} = V$ and solving for t

$$V = V \cos Nt - N \frac{(\mu_s - \mu_D)\ P \text{ Sin } Nt}{L}$$

i.e. $$1 = \text{Cos } Nt - \frac{NP}{VL} (\mu_s - \mu_D) \text{ Sin } Nt$$

Thus if $$Z = \frac{NP}{VL} (\mu_s - \mu_D)$$

$$1 = \text{Cos } Nt - Z \text{ Sin } Nt$$

Hence for relative values

$$t = \frac{2\pi}{N} - \frac{2}{N} \tan^{-1} (\mu_s - \mu_D) \frac{PN}{VL}$$

$$t = \frac{2\pi}{L/M} - \frac{2}{L/M} \tan^{-1} (\mu_s - \mu_D) \frac{PN}{LV}$$

$$t = \frac{2\pi}{N} - \frac{2}{N} \tan^{-1} (\mu_s - \mu_D) \frac{PN}{VL}$$

Thus the displacement of the mass from its position from the unstrained spring to the end of slip may be found by substituting this value of time in the motion equation.

$$x = \frac{V}{N} \text{ Sin } Nt + (\mu_s - \mu_D) \frac{P}{L} \text{ Cos } NT + \frac{D^P}{L}$$

Now

$$\tan Nt = -\frac{2Z}{1-Z^2}$$

where $$Z = \frac{(\mu_s - \mu_D) PN}{VL}$$

Substituting gives

$$x = (2\mu_D - \mu_s) \frac{P}{L}$$

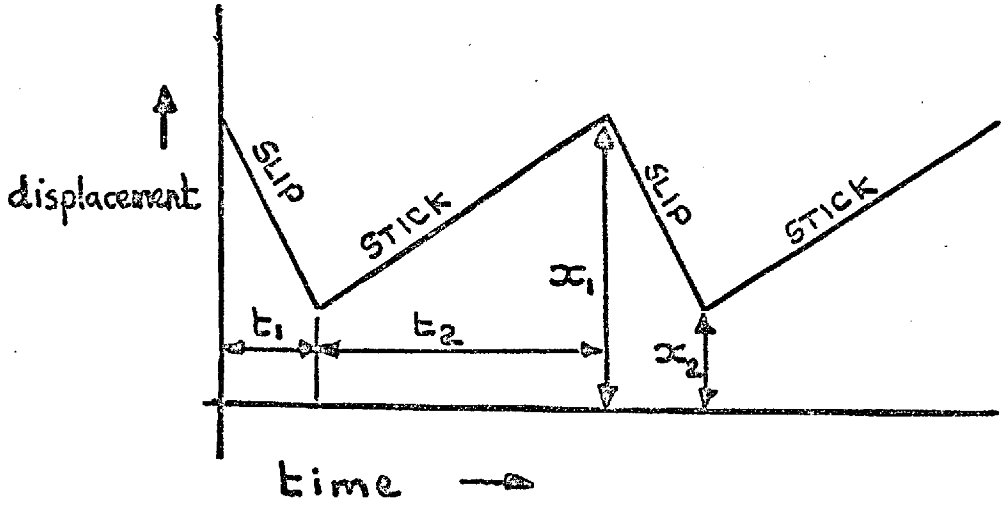
Hence the time taken by the sticking process will be given by

$$t_2 = \frac{x_1 - x_2}{V} \qquad \text{where } x_2 = (2\mu_D - \mu_S)\frac{P}{L}$$

$$\text{and where } x_1 = \frac{\mu_s P}{L}$$

$$\text{Time } t_2 = \frac{2(\mu_s - \mu_D)\,P}{LV}$$

Thus considering Fig. 3:



$$x_1 = \frac{\mu_s P}{L}, \qquad x_2 = \frac{(2\mu_D - \mu_s)}{L}$$

$$t_1 = \frac{2\pi}{\left(\frac{L}{M}\right)^{\frac{1}{2}}} - \frac{2}{\left(\frac{L}{M}\right)^{\frac{1}{2}}} \tan^{-1} \frac{(\mu_s - \mu_D)P}{VL} \left(\frac{L}{M}\right)^{\frac{1}{2}}$$

$$t_2 = 2\,\frac{(\mu_S - \mu_D)P}{VL}$$

From this we may deduce that stick slip would vanish if the static and dynamic coefficients of friction were equal, and that the time of stick decreases with the increase in velocity. Thus it would seem that to eliminate stick slip a high velocity should be chosen, but at increasing velocities the friction behaviour changes from boundary to hydrodynamic.

The amplitude of the stick slip can be reduced by increasing the spring stiffness L or by decreasing the load P.

Returning to the general equation for x. Considering the case with damping.

$$x = \frac{V}{S} + K\left(\frac{\mu_s P - \mu_D P - rV}{L}\right) e^{-Kt} \text{ Sin } Wt + \left(\frac{\mu_s P - \mu_D P - rV}{L}\right) e^{-Kt} \times \left(\cos st\right) + \frac{\mu_D P}{L}$$

$$\text{let } Q = \left(\frac{\mu_s P - \mu_D P - rV}{L}\right) \qquad \text{and} \quad d = \frac{\mu_D P}{L}$$

$$x = \frac{V}{S} + KQe^{-Kt} \text{ Sin } st + Qe^{-Kt} \text{ Cos } st + d$$

differentiating w.r.t. time

$$\dot{x} = e^{-Kt}\left[(V + sKQ - KQ) \text{ Cos } st + \left(\frac{KV}{s} + K^2Q - sQ\right) \text{ Sin } st\right] + \frac{\mu_D P}{L}$$

The effect of damping can now be seen by comparing this equation with the undamped case. The main difference is the exponential damping term appearing in the damped case. This has the effect of reducing the velocity of slip and hence reducing the time taken before $\dot{x}$ is equal to V when stick reoccurs.

This damping will reduce the amplitude of the vibrations. We are therefore interested in the maximum values of $\dot{x}$ because it is when $\dot{x}$ is larger than V that slip will occur.

Hence

let $(V + sKQ - KQ) = g$

$$\left(\frac{KV}{s} + K^2Q - SQ\right) = e$$

$$0 = g \text{ Cos } t + e \text{ Sin } st + \frac{\mu_D P}{L}$$

i.e.

$$\tan st = \frac{ge \pm [\,(ge)^2 - (e^2 - d^2)\,(g^2 - d^2)\,]^{\frac{1}{2}}}{e^2 - d^2}$$

and the correct roots evaluated.

This may be put back into the equations and the value of damping at which stick slip no longer occurs will be when

$$\frac{\dot{x} \text{ MAX } +ve}{V} < 1$$

i.e. the ratio of the maximum positive velocity of slip to the velocity of the plate, is less than unity.

CHAPTER III

Chain Matching Effects in Boundary Lubrication

In 1966 Askwith, Cameron and Crouch [60] published their paper on the chain length of additives in relation to lubricants in thin film and boundary lubrication. The forerunner to this was a letter to Nature [61] in which they reported work carried out on a four ball lubricant testing machine. This four ball machine comprised three one inch balls held tightly in a cup, whilst a fourth ball completing the pyramid was rotated at 200 r.p.m. and the load between the upper and lower balls was progressively increased until siezure occurred. It was found that using a large range of carboxylic acids dissolved in N alkanes at 0.003 molar concentration, the scuffing load reached a maximum when the number of carbon atoms in the alkane and fatty acid was equal. Askwith, Cameron and Crouch [60] showed that this matching effect occurred also for the long chain normal amines and the alcohols.

Thus Figs. 4 and 5 are taken from their paper.

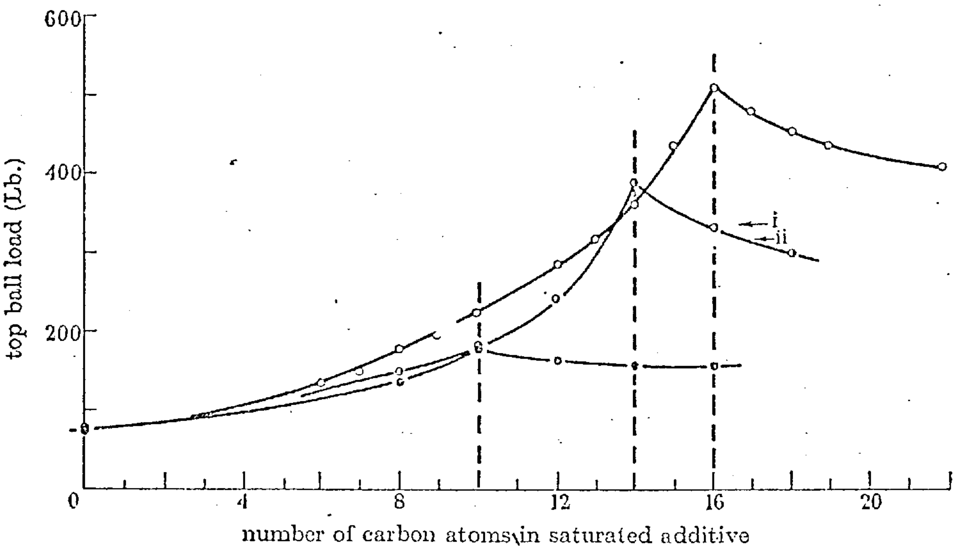


FIGURE 4. Scuffing tests with hexadecane (○), tetradecane (◑) and decane (⊖) with a range of acids. (i) oleic acid, and (ii) elaidic acid in tetradecane.

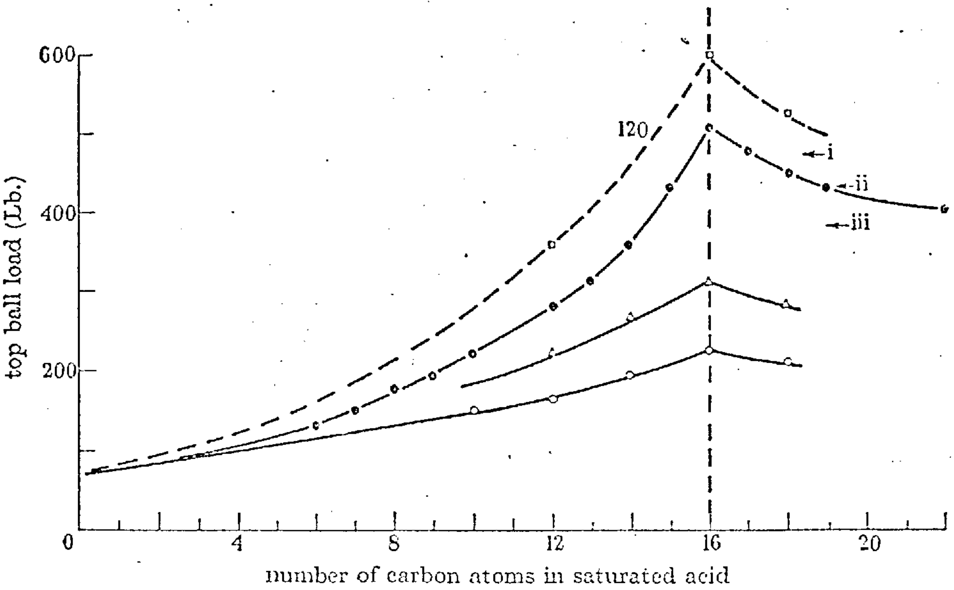


FIGURE 5. Scuffing tests with 0·03M additives in hexadecane: acids (□, 120 rev/min; ⊖, 200); amines (△) and alcohols (○). (i) Elaidic and erucic acids; (ii) brassidic acid; (iii) oleic acid.

Figures 4 and 5 taken from Ref. 60

Further confirmation of this effect was given by the voltage discharge technique and results using a pin or disc machine.

The four ball machine operating at 200 r.p.m. may be operating partly under hydrodynamic conditions, although the region prior to scuffing is necessarily boundary lubrication.

It was decided to investigate the effect of matching the alkane chain lengths of the lubricant on boundary lubrication tests using the Bowden-Leben machine and to conduct experiments measuring the coefficient of friction and its change with temperature. In this way it was hoped to study this failure in terms of desorption of the lubricant film in a similar manner to Frewing's [42] experiments of 1944.

It is clear that for a fuller understanding of the problem, a more detailed consideration must be made of the forces concerned with adsorption.

The surface of a metal, deformed metal and oxides may cause various forms of interactions to occur. These are now examined in turn.

1. The interaction between the surface of an ionic compound and an adsorbed ion.

Consider an ionic compound e.g. a crystal of NiO or NaCl and let a negative ion be adsorbed on top of one of the positive ions. The attraction of the negative adsorbed ion by surface is far weaker than if the positive ion was on its own. This is because the negative adsorbed ion will be repelled by the negative ions in the crystal, indeed the interionic distance in the crystal lattice is greater than if the ions were in the gas phase. The total electrostatic field from such a surface is quite small. Thus for a sodium chloride type crystal Huckel [62] gives the field F

$$F = \frac{8\pi\epsilon}{r_c^2} \exp\left(-\pi\sqrt{2}\,\frac{r}{r_c}\right)$$

ϵ is the charge on the electron

r_c is the shortest interionic distance

r is the distance of the adsorbed negative ion from the positive ion.

Let us consider that the adsorbed ion is of the same type as the lattice negative ion thus the equilibrium distance of the adsorbed ion from the surface will be almost r_c [62].

Hence the adsorption energy ϵ_c

$$\epsilon_c = \int_{\infty}^{r_c} \epsilon\, F\, dr$$

hence

$$\epsilon_c = -.0662\ \frac{2}{r_c}$$

We may now estimate the energy due to these forces occurring if the surface is not flat and hence the distribution is not the same, this is shown by DeBoer [62].

Thus for adsorption on an edge

$$\epsilon_{c\ \text{edge}} = -.0903\ \frac{\epsilon^2}{r_c}$$

for a corner

$$\epsilon_{c\ \text{corner}} = -.2470\ \frac{\epsilon^2}{r_c}$$

and for a position where a new row is forming of the top

$$\epsilon_{\text{end new row}} = -.8737\ \frac{\epsilon^2}{r_c}$$

hence adsorption will occur on these active sites first.

2. Interaction between an ion and a metal surface

The ion charge is said to polarize the metal in such a way that an electric charge of opposite sign is formed at a distance below the surface equal to the distance between the metal surface and the ion charge, i.e. its electric image.

Hence for an ion charge ϵ, the induced force F_i is given by

$$F_i = \frac{\epsilon^2}{(2r)^2}$$

and hence the induction adsorption energy E_i

$$E_i = \int_{\infty}^{r_o} \frac{\epsilon^2}{4r^2}\,dr = -\frac{\epsilon^2}{4r_o}$$

where r_o is the equilibrium distance between the ion and the metal surface.

3. Polarization of the surface by the adsorbed ion

If we consider the surface to be a dielectric, an ion of charge from an atom with a polarizability α induces a dipole in the atom of the dielectric such that the dipole moment μ_α is given by

$$\mu_\alpha = \frac{\alpha \epsilon}{r^2}$$

and the energy of adsorption due to this electrostatic polarization $E_{\epsilon\alpha}$ is given by

$$E_{\epsilon\alpha} = -\frac{\alpha\epsilon^2}{2r^4}$$

however, in a surface all the other atoms or groups will be polarized to some extent and in being polarized the induced dipoles are aligned in the direction of the polarizing ion and thus repel each other. Thus for a surface the adsorption energy is given by

$$E_{\epsilon\alpha} = -\frac{\epsilon^2}{4r_o}\,\frac{K - 1}{K + 2}$$

where K is the dielectric constant, and if K is a function only of electronic shifts i.e. no displacements of ions occur $K = N^2$ where N is the refractive index.

The polarization of the surface by the adsorbed ion occurs for any adsorbent, thus for an ion adsorbed on an ionic compound the induced polarization must also be taken into consideration, indeed this induced polarization effect may be of the same magnitude as the electrostatic effect considered earlier. DeBoer [62] gives examples of the magnitudes of these effects.

van der Waals Adsorption

van der Waals forces causing adsorption includes all cases in which neutral atoms or molecules either polar or non polar interact with surfaces without any sharing of the electrons taking place, i.e. the adsorbed atoms or molecules preserve their individuality.

Non polar van der Waals adsorption forces are sometimes referred to as dispersion forces and these are now considered.

4. Dispersion forces

Dispersion forces are forces of attraction and result from the polarization of each molecule due to each other molecule's continuously changing electronic cloud.

The attraction between two molecules by dispersion forces has been studied by many workers.

One equation for the mutual energy of interaction of a pair of atoms is given by London

$$E_W = -\frac{3}{2r^6} \alpha_1 \alpha_2 \frac{I_1 I_2}{I_1 + I_2}$$

where I_1 and I_2 are the Ionization energies

α_1 and α_2 are the polarizabilities

and r the distance between the two atoms 1 and 2.

It is seen that this equation is of the form

$$\epsilon_W \doteq -\frac{C}{r^6}$$

where C is a function of the properties of atoms, however, this equation is an approximation an d should really include other terms.

i.e. $$\epsilon_W = -\frac{C}{r^6} - \frac{C_2}{r^8} - \frac{C_3}{r^{10}} + \frac{C_4}{r^{12}}$$

the last term is the result of the repulsive energy developed from the interaction of the elctronic clouds at very close approach, and may sometimes be incorporated into the reduced equation by a factor f [63].

$$\epsilon_W = - f \frac{C}{r^6}$$

If we now study the adsorption of an atom at a surface the dispersion forces will be the interaction of the atom with all of the atoms of the surface.

Polanyi's equation gives from the sum of all the forces, the energy E_W as

$$E_W = - \frac{N_3 \pi C}{6 r_o^3}$$

where N_3 is the number of atoms of the adsorbent per cubic centimeter and r_o the shortest distance of the adsorbed atom to the surface.

This equation sometimes leads to erroneous results. Other treatments have been given by Forbes [63] and DeBoer [62]

The additive nature of the dispersion forces results in polyatomic molecules tending to lie flat, so that the molecules approach the surface closely. Thus molecules with double bonds show increased adsorbability due to their flatter configuration.

We may now examine the adsorption of non polar molecules by van der Waals forces on metal surfaces.

5. van der Waals forces on metal surfaces

Lennard-Jones thought that the interaction energy might be explained in terms of an image dipole picture in a similar way to the interaction between an ion and a metal surface previously discussed.

Thus he gives

$$E_W = -\frac{2\,\overline{r^2}}{12r_o^3}$$

where $\overline{r^2}$ was the mean square displacement of all the electrons in the atom, however, the values calculated by this equation are too high. Margenau and Pollard [see 62] said this was because the conduction electrons of the metal were unable to change as rapidly as the instantaneous dipoles of the non polar molecule and they have modified the equation. However experimental data on the adsorption on metal surfaces by van der Waals forces of non polar molecules indicate that the interaction energy is small [62] so that this contribution is not important compared with other interactions.

We may now consider polar van der Waals forces.

6. Polar molecules and ionic surfaces

The field associated with an ionic surface was disucssed earlier, and is small. The most important interactions of polar molecules with ionic surfaces will occur when the polar part of a molecule can approach the surface closely i.e. when the molecule has a peripheral dipole. Water thus adsorbs very strongly on most oxide films. Indeed the initial picture of a surface includes adsorbed water on the oxide.

If the electrostatic field is F and u is the dipole moment of the polar molecule, then the associated adsorption energy E_u is given by

$$E_u = -FU$$

The value of E_u for the adsorption of water on a crystal of sodium chloride is 5.25 Kcals/mole [62]. A correction may be made for small molecules by considering the charges to be at a distance l apart rather than a moment, such a calculation increases the adsorption energy of water on sodium chloride from 5.25 Kcal/mole to 5.80 Kcal/mole [62].

In a similar manner to the adsorption of an ion on an ionic crystal, the adsorption of a polar molecule on an ionic surface by polar van der Waals forces is also dependent upon the position on the crystal on which the molecule is being adsorbed, although in this case this effect is small.

7. Adsorption of a polar molecule on a metal surface

The energy of interaction between a polar molecule and a metal surface is given by

$$E_{\mu} = - \frac{\mu^2}{16\ r_o^3} (1 + \cos^2\beta)$$

where μ is the dipole moment

r_o is the distance to the metal surface

and β the angle between the direction of the dipole and the normal to the surface.

Thus this energy is a maximum when $\beta = 0$ and the dipole is oriented perpendicularly to the surface.

This energy is quite small if we consider an aliphatic ketone lying parallel to the surface

$$E_{\mu} = \frac{\mu^2}{16\ r_o^3}$$

then taking $r_o = 3.5\ A^o$ - the CO dipole as 2.7 debyes, then

E_{μ} = .15 kcals/mole.

8. Forces due to the electrostatic polarization of the adsorbed molecule

So far we have considered the polarization of the adsorbent by the adsorbed ion or polar molecule, however, a further interaction is due to the polarization of the adsorbed molecule by the electrostatic field of the surface of the adsorbent.

This energy is given by

$$E_{\alpha} = - \frac{F^2\alpha}{2}$$

F is the field at the distance of the radius r_o of the adsorbed part of the molecule, and

α is the polarizability.

Thus considering an Argon atom adsorbed on top of a potassium ion

$$\alpha = 1.68 \times 10^{-24} \text{ cm}^3$$

$$r_c = 3.14 \text{ A}^o$$

and $$F = .145 \times 10^6 \text{ esu}$$

$$E_{\alpha} = .25 \text{ Kcal/mole}$$

Whilst this effect is quite small, if we consider adsorption on one of the high energy positions of the ion such as the end position as discussed previously, the effect now depends upon the square of the field strength so that a tenfold increase in the adsorption energy due to this effect may result.

9. The electric double-layer

The surface of a metal contains at least one valency electron (conduction electron) per metal atom. Thus iron has two 4s electrons. Atomic hydrogen is adsorbed on the surfaces of metals forming a kind of surface hydride and the bond can be considered as a covalent bond the hydrogen becoming sometimes the electronegative partner, i.e. when combining with the surfaces of Zr, Ti and W and sometimes the electropositive partner as with surfaces of Pt, Ni and Fe. A double layer of charge is therefore formed at the surface which in the case of iron the positive part is pointing outwards. Thus the potential of the surface of iron is positive due to the covalent hydrogen. Clearly in the solution there must be an equal number of ions of opposite charge maintaining electroneutrality i.e. counter ions' and double layer theory deals really with the distribution of the counter ions near the charged surface.

We might expect each hydrogen atom to have a counter ion attached, but the density of the hydrogen ions may be too high for the larger cross sectional area of the counter ion to achieve this. Also thermal agitation helps to form a distribution of the counter ions over a distance from the surface. The electric potential drops rapidly at first (the Stern layer) but more slowly with increasing distance becoming zero at an infinity. More detailed treatments are given in ref. 64.

The energy effect of such a double layer has been considered by

Fowkes [63] in his paper on the attractive forces at solid liquid interfaces.

Considering the energy to be the same as for a capacitor

$$\epsilon = \frac{1}{2} QV$$

V is the potential drop across the double layer and Q the charge is given by

$$Q = qZ$$

where q is the number of counterions per unit area and Z the electronic charge per ion. The reason for the formation of the hydrogen ions in organic media for the case of fatty acids is briefly outlined below. This is because fatty acids have been used in many adsorption and lubrication studies including the experiments on chain matching.

Consider firstly formic acid, see Fig. 6. In the carbonyl group the oxygen atom is more electronegative and hence the electrons of the double bond are drawn to it, this will also affect the carbon-oxygen bond so that there is a shift of electrons, in this case, from the oxygen to the carbon atom. This shift has the effect of drawing the electrons of the hydorgen oxygen bond towards the oxygen atom of the hydroxyl group, facilitating the loss of hydrogen.

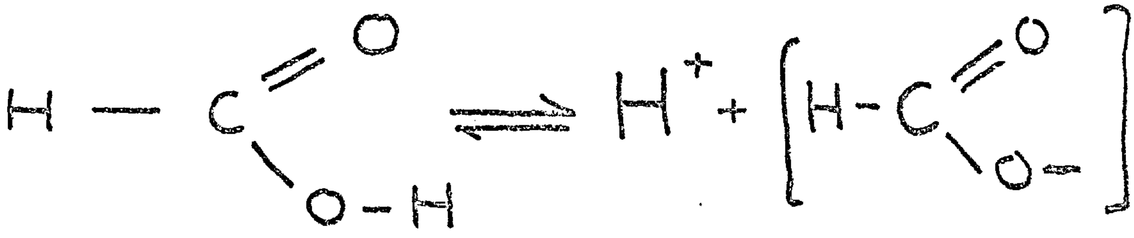


Figure 6

The replacement of the non hydroxylic hydrogen atom of the formic acid by an alkyl group, would be expected to produce a weaker acid, as the alkyl group will increase the electron availability. It is also noted that the electrostatic attraction between the partially positive hydrogen and the partially negative carbonyl group favours the cis conformation.

It is also noted that once the metal surface has adsorbed the hydrogen strongly, the double layer now has a field associated with it for attraction of molecules for adsorption.

Summary of interactions considered

Summing up then, the interactions that have been considered so far are:

1. Electrostatic (Coulomb) interaction between an ionic compound and an adsorbed ion.
2. Interaction between an ion and a metal surface.
3. Interaction due to polarization of a dielectric by an adsorbed ion.
4. Dispersion forces.
5. Van der Waals forces on metal surfaces.
6. Interactions between permanent dipoles and ionic surfaces.
7. Interaction of polar molecules and metal surfaces.
8. Electrostatic polarization by the adsorbent of the adsorbed molecule.
9. Double layer forces.

Some examples of the magnitude of these energies of adsorption are given later in the discussion section of this chapter

The examination of the literature is now continued, however, it is noted that the forces considered are not special surface forces, so that later values of van der Waals forces on surfaces will be compared to the forces of crystallisation, sublimation and hydrogen bonding.

Literature Survey

Frewing's [42] experiments, mentioned in the introduction, measured the temperature at which stick slip occurred for a series of lubricants tested on the Bowden-Leben machine using a flat plate and a hemispherical slider of a mild steel composition. He then considered the dynamic equilibrium of adsorption and desorption.

Thus

let the rate of formation of the layer of solute molecules on the surface be proportional to the concentration C of the solute in the solution.

let x be the fraction of available adsorption sites occupied.

Assuming Langmuir type adsorption and that activity may be replaced by concentration.

Rate of build up of the film is

$$CK_1(1 - x)$$

where K_1 is a constant

Rate of desorption of the film is

$$k_2x$$

where k_2 is like K_1 a rate constant.

For dynamic equilibrium these two rates are equal.

Hence

$$\frac{k_1}{K_2} = K = \frac{x}{C(1 - x)}$$

where K is the equilibrium constant.

Applying van't Hoff's equation for the temperature dependence of the equilibrium constant.

$$\frac{d \log K}{dT} = \frac{\Delta H}{RT^2}$$

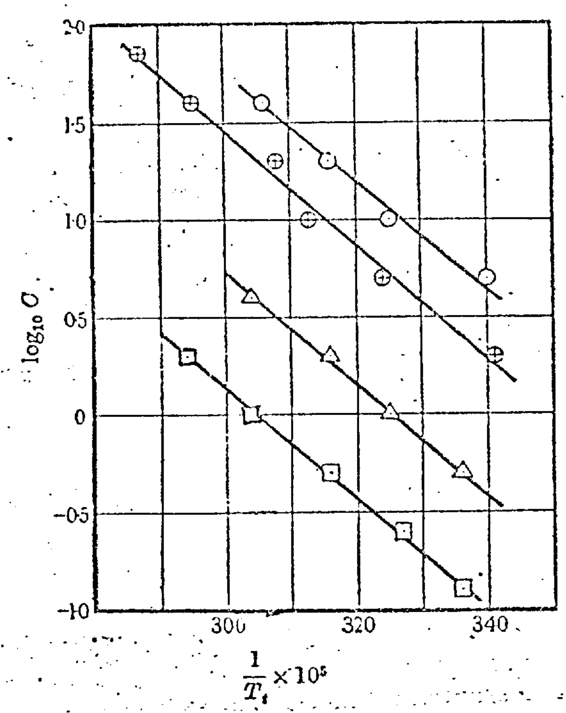
$$\log_e \frac{x}{C(1 - x)} = \frac{\Delta H}{RT} + \text{Const.}$$

and assuming the transition temperature occurs at a definite value of x, i.e. x = a,

then

$$2.3 \log_{10} C = -\frac{\Delta H}{RT_T} + \text{Const.}$$

Thus Frewing has plotted graphs log C vs $\frac{1}{T_T}$ for the lubricants as shown in Fig. 6, 7 and 8.



⊙ capric acid; △ myristic acid; ⊡ stearic acid; ⊖ oleic acid.

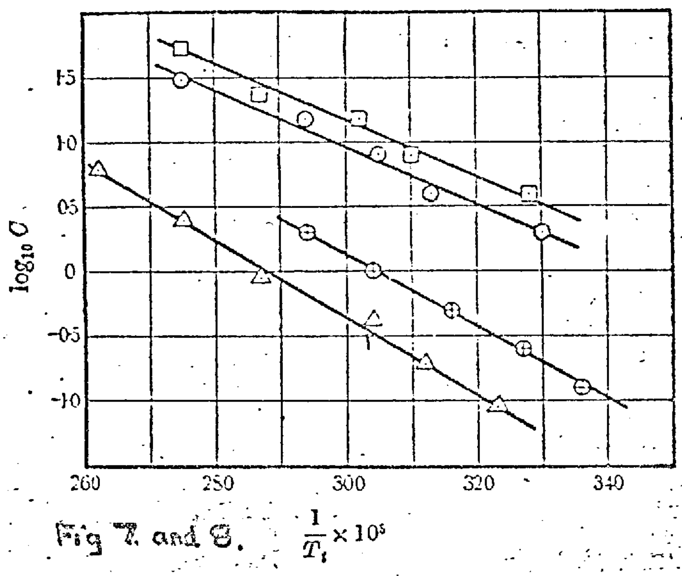


Fig 7 and 8.

⊙ α-bromo stearic acid; ⊡ α-iodo stearic acid;
△ α-hydroxy stearic acid; ⊖ stearic acid.

Figures 6, 7 and 8 from ref. 42

It is seen that from the gradient of the curve the energy of adsorption may be calculated. Frewing, however, makes an additional calculation for the fatty acids, by taking the liquid state of the acid as the associated carboxylic dimer, and the gradient as the heat of adsorption of two molecules.

The heat of adsorption of a simple molecule is then given as Q

$$Q = \frac{1}{2}(U + A)$$

where U is calculated from the gradient of the graph and is the heat of adsorption and A is the heat of association, however, the heat of association corresponds closely with the measured heat of adsorption and this calculation does not alter the value much compared to values obtained by taking the adsorption as that of a single unassociated molecule adsorbed from solution.

It is interesting to note that the heats of adsorption and association are similar. The association is due to hydrogen-bridging i.e. van der Waals forces, the same forces are acting for the adsorption of the molecule. The heat of association of formic acid is 14.125 Kcals [65] and the value will decrease with increase in chain length. The value of the heat of adsorption calculated directly from the gradient of the graph for stearic acid $C_{17}H_{35}CO\ OH$ was 13.0 Kcals/mole and the gradient of the curve for myristic acid was also 13.0 Kcals/mole. It is noted that Frewing was able to obtain a high solubility of stearic acid in white oil. Using different white oils it is reported that we have not been able to obtain the higher solubilities using Puriss grade

99.5% purity stearic acid obtained from Koch Light Laboratories Ltd. It is thought that either a similar white oil to that used by Frewing has not been obtained, or that the stearic acid used by Frewing had traces of impurities possible oleic acid which would increase its solubility in white oil.

Derivation of the equation for the calculation of the heat of adsorption of a lubricant using friction temperature measurements.

This treatment follows closely that given by Askwith, Cameron and Crouch [60].

Since physical adsorption on surfaces is usually in a state of dynamic equilibrium between adsorbed and desorbed molecules. We may consider the equilibrium to be a reaction equilibrium for the equation given below:

$$\text{unoccupied surface sites} + \text{solute in solution} \rightleftharpoons \text{occupied surface sites}$$

At equilibrium let the equilibrium constant be K,

hence

$$K = \frac{[\text{occupied surface sites}]}{\text{unoccupied surface sites} \quad \text{solute in solution}}$$

Replacing activities by concentrations, let the concentration of occupied surface sites be θ i.e. the number of occupied surface sites, and let $(1 - \theta)$ be unoccupied surface sites

and let C be the concentration of the solute in the solution.

Thus

$$K = \frac{\theta}{C(1 - \theta)}$$

which has units of $\frac{1}{[C]}$ e.g. moles/1000 gm.

Now

$$\Delta G^{o} = -RT \text{ In } K$$

then ΔG^{o} is the increase in Gibbs free energy when 1 mole of the solute goes from the solution and is completely adsorbed on the surface under the conditions considered.

Adsorption processes are usually in a state of dynamic equilibrium thus the relationship is a general one.

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

Hence

$$-\frac{\Delta H^{o}}{T} + \Delta S^{o} = R \ln \left(\frac{\theta}{C(1-\theta)}\right)$$

i.e.

$$-\frac{\Delta H^{o}}{T} + \Delta S^{o} = R[\ln\left(\frac{\theta}{1-\theta}\right) - \ln C]$$

The assumption is now made that lubricant breakdown occurs at some observable constant surface coverage. This explains why a plot of log C vs $\frac{1}{T}$ gives a straight line providing ΔH^{o} and ΔS^{o} are not temperature dependent. Also from the slope, ΔH^{o} may be calculated.

If a value is given to θ, e.g. for lubricant failure, then ΔS^{o} may also be evaluated. This has been done by Cameron [60] who took the value $\alpha = \frac{1}{2}$ and computed values of ΔS^{o} from Frewing's [42] data. He called ΔS^{o} the "entropy of scuffing".

Oleophobic Monolayers

Bigelow, Glass and Zisman [48] have found values for the heats of adsorption of the fatty acids on platinum from solutions of dicychlohexyl and cetane using an oleophobic monolayer technique.

A square of platinum carefully cleaned, was immersed in the solution and at intervals withdrawn. When the platinum dipper surface was repellant to the liquid i.e. when the liquid rolled off leaving an apparently dry surface, then the foil was covered with an adsorbed film. The dipper was then lowered back into the solution and the temperature increased until the next observation. The process was repeated until a critical temperature T_W was reached at which the dipper remained completely wetted by the solution on withdrawal from the solution. Log concentration was plotted against the reciprocal of the absolute temperature in a manner similar to Frewing's results [42].

The heat of adsorption for stearic acid adsorbed from dicyclohexyl solution was 10.0 Kcals/mole and for N octadecanol also adsorbed from dicyclohexyl was also 10.0 Kcals/mole. The relation between concentration and critical temperature was derived using statistical thermodynamics.

A method giving a conception of disorder-order theory based on a derivation by Everett is given by Denbigh [66], and derives the Langmuir Isotherm in terms of configurational entropy of the possible arrangements of adsorbed molecules on the surface sites. This derivation originally for gases may be suitably altered for the case of ideal solutions in which only one component is being adsorbed. Such a derivation is useful since it gives a picture of the molecules' being adsorbed on the surface.

It is important to note that to derive a heat off adsorption it is sufficient just to reach a constant value of $\frac{1}{1-\theta}$ for each experiment. Thus whilst equal values for ΔH^{o} were obtained both by Frewing and Bigelow, Glass and Zisman, it does not necessarily mean that lubricant breakdown occurs when the surface is no longer oleophobic. In other words the value of θ is not necessarily the same in the two cases. The formation of oleophobic monolayers has been considered in detail by Zisman et al [67] [68] who are interested in the non spreading of oils for clocks and other instruments. Systematic measurements have been made of the contact angles of a large number of pure liquids on various solid surfaces. A linear relationship has been found, for homologous series of organic liquids between the liquid/surface/contact angle and the surface tension of the liquid.

Thus extrapolating the straight lines to Cos θ = 1 see Fig. 9,

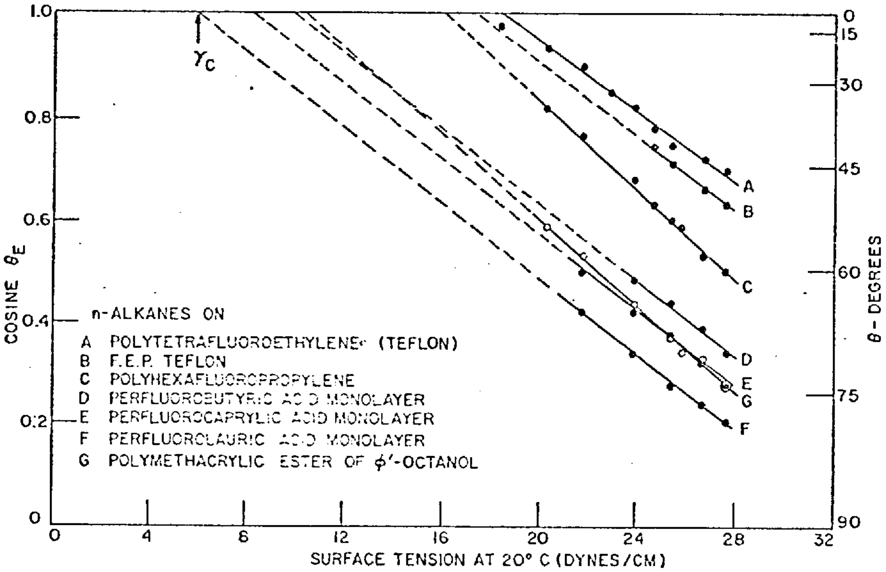


Figure 9 from Ref. 68

a critical surface tension of wetting γ_c is obtained. Therefore liquids of surface tension less than this value will spread upon the surface. The method can be extended to the spreading of oils on films, thus Shafrin and Zisman [69] give a table for the critical values of γ_c for some low energy surfaces. A close packed CF_3 surface has a surface tension of 6 dynes/cm at 20°C, a close packed CH_3 monolayer has a surface tension of 22 - 24 dynes/cm, whilst the $- CH_2 - CH_2 -$ group i.e. expected from adsorbed alkane molecules lying flat on the surface has a critical surface tension γ_c of 31 dynes/cm at 20°C.

The reason for oleophobicity of Bigelow, Glass and Zisman's experiments is now apparent. Thus the stearic acid molecule has been adsorbed, and enough of the CH_3 terminal groups of the long chain are now forming the interface so that the critical surface tension of the adsorbed monolayer is less than the surface tension of the solution.

The question of how much depletion of the monolayer occurs before the surface is no longer oleophobic has been studied by Bartell and Ruch [70,71]. Depositing close packed films of octadecylamine using the Langmuir Blodgett technique they depleted the films by dipping the slides in benzene or ether. They then measured the amount of depletion by ellipsometry. Contact angles of both advancing angles and receding angles for N hexadecane and N tetradecane were measured. It was found that the abrupt change in contact angle occurred in the region of 50% depletion. Non wetting does not require a close packed structure, only that the monolayer prevents penetration of the liquid into the monolayer. If however the solvent molecules are able to go into gaps and themselves show a terminal CH_3 group, then the film has been repaired.

Sakurai and Baba [47] previously mentioned have also found values for the heat of adsorption of fatty acids using a rectification effect. This technique has been neglected due to the papers being written in Japanese.

A small D.C. current was found to flow between a lubricant film between a flat plate and a hemispherical surface. This rectification effect vanished abruptly with increase in load or with increase in temperature. It is thought that the difference in shape of the two surfaces causes ions to form more readily in the surface having the greatest dielectric stress. The state at which the rectification effect vanishes is taken as a constant state of the adsorbed film i.e. $\frac{\theta}{1 - \theta}$ and thus plotting log concentration vs $\frac{1}{T_T}$ should enable the heat of adsorption to be calculated. Using Platinum surfaces and hexadecane as solvent Sakurai and Baba measured the heat of adsorption for a series of fatty acids, for myristic acid they found 10.4 Kcals/mole and for stearic acid 10.6 Kcals/mole. In dekalin solvent the heat of adsorption of palmitic acid was 10.6 Kcals/mole. They also carried out tests with iron palmitate and iron stearate solutions in dekaline and cetane. Heats of adsorption of 12.1; 12.7 Kcals/mole for cetane solvent were obtained respectively for Platinum surfaces. This is interesting for with steel surfaces and cetane solvent, stearic acid gave 11.4 Kcals/mole. In Frewing's experiments with mild steel surfaces there is the possibility that a fatty acid soap formed. If this soap dissolved in the solution then a process of adsorption and desorption of this soap may occur giving values of ΔH^{o} equal to 12.7 Kcals/mole.

A further method of calculating the heat of adsorption is from measurements at different temperatures of the adsorption of the liquid on to powders in which adsorption isotherms have been plotted. This follows directly from the equation we have derived,

$$-\frac{\Delta H^{o}}{T} + \Delta S^{o} = R[\text{In}\,\frac{\theta}{1-\theta} - \text{In}\,C]$$

Thus from the adsorption isotherms a constant surface coverage value is taken and the corresponding values of concentration and temperature read off.

This method is useful because it gives information additional to experiments on friction transition and oleophobicity measurements. Hence any variation of ΔH^{o} with θ surface coverage can be studied. If the surface area of the powder is known, $(\frac{\theta}{1-\theta})$ value can be determined and hence ΔS^{o} calculated. This method should yield values of $\frac{\theta}{1-\theta}$ for breakdown of boundary lubricants.

Daniel [72] measured the adsorption of stearic acid and octadecyl alcohol for a large number of powders. Measurements were achieved by sampling the solution and spreading this sample on a Longmuir trough and thus the decrease in concentration due to adsorption was calculated from the difference in film areas. Adsorbing from benzene solution it was found that for powders of silver, platinum, chromium, iron, aluminium and nickel which had been dried for a few days in a vacuum decsicator, Langmuir isotherm type curves were obtained for the adsorption of stearic acid. For powders of copper,zinc, lead and cadmium, a continuous increase in apparent adsorption occurred indicating a slow chemical reaction. The determination of the isotherms was also carried out on nickel powder for the fatty acid series lauric, palmitic and stearic acid. It was found that if the isotherm was plotted using values of relative concentration, i.e. concentration relative to the concentration of a saturated solution at that temperature, then all three acids fell closely on a single curve. Isotherms at different temperatures were measured for octadecyl alcohol and stearic acid on nickel. Values of 20 to 25 Kcals/mole for the heat of adsorption was found for adsorption of stearic acid on nickel, whilst the octadecyl alcohol gave 18 Kcals/mole. Unfortunately the surface area of the powder was not known, although Daniel [72] does say that the degree of surface coverage may cause large changes in the values of the heat of adsorption. Indeed Groszek's measurements using a calorimetric technique clearly show that this is so [73].

Another powerful technique in surface chemistry and thus boundary lubrication is contact potential measurements, this is of special interest since the formation of mixed films has been identified by its use.

In this method the surface is one of the plates of an electrical condenser the other plate, the reference plate, is a clean sample of a metal such a platinum. The platinum may be coated with polytetrafluoreothylene so that there is little tendency for vapours to adsorb on the reference electrode. On the adsorption of a surface film a difference in the capacitance occurs. This may be detected in two ways. In the one method [74] an ionizing substance such as polonium is put on the reference electrode so that the change in capacitance can be detected, or, the reference plate is vibrated [75, 76], thus in this case, the continual change in capacity causes a current to flow.

The change in capacitance caused by the presence of surface films may be determined, a brief explanation of the effect is given in the following paragraphs.

Consider concentric spheres radius r and r + d with potentials ψ_1 and ψ_2 and charges of +q and -q respectively and dielectric constant D.

Thus $\psi_1 = \frac{q}{Dr}$ $\psi_2 = \frac{q}{D(r + d)}$

hence as r becomes infinite, the potential difference

$$\psi = \frac{dq}{Dr^2}$$

let σ be the surface charge density

$$\sigma = \frac{q}{4\pi r^2}$$

$$\psi = \frac{4\pi\sigma d}{D}$$

and since it is only the surface film that has changed $\frac{\sigma d}{D}$ refers to the monolayer. Thus if we consider each molecule to be polar and the charge is at either end, and let N be the number of molecules per square centimeter of surface

$$\sigma = Ne = \frac{N\mu}{d}$$

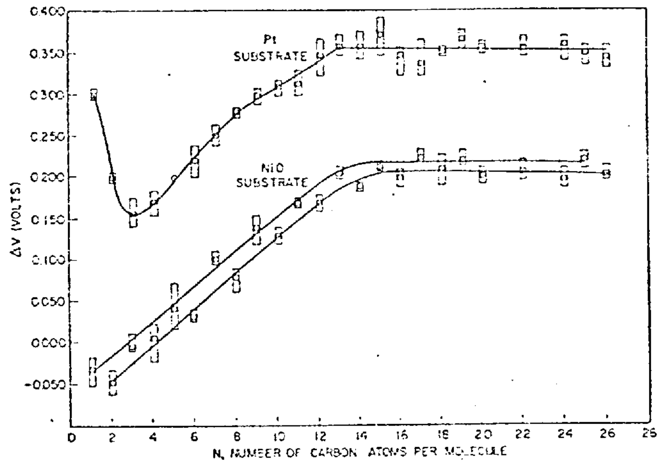
$$\psi = \frac{4\pi N\mu}{D}$$

Thus if we take D as that of the bulk solution and put all the effect into , this may then be calculated.

Bewig and Zisman [77] have measured surface potentials of N alkanes deposited by rubbing and evaporation. Clearly the N alkanes have no permanent dipole moment, values obtained, therefore are values of induced polarization from the surface fields considered earlier. Good agreement with other experiments was obtained and indicate that the alkane was lying flat. Contact angle measurements of methylene iodide drops on the film, confirmed that the surface was indicative of CH_2 groups uppermost. Bewing and Zisman [77] then made an approximate correlation between the value of the induced polarization and the structure of the metal adsorbent by consideration of the associated electrostatic fields.

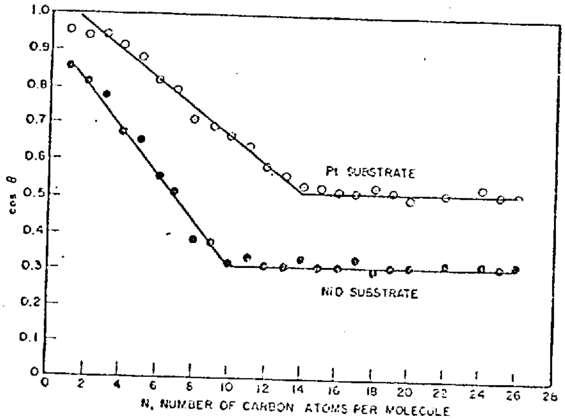
Homologous series of fatty acids have been studied using contact potentials by Timmons and Zisman [78] on various metals, but principally on platinum and nickel oxide. The monolayers were deposited by retraction from the melt or nitromethane solution and additional tests were made measuring the contact angle with methylene iodide.

Figures 10 and 11 show the principal results.



Contact potential difference data for the homologous series of fatty acids adsorbed on Pt and NiO.

Figure 10 from ref. 78



Methylene iodide contact angle data for the homologous series of fatty acids adsorbed on Pt and NiO.

Figure 11 from ref. 78

Thus, when the chain length is over 14 carbon atoms, the contact angle and the contact potential difference becomes constant. The dipole moments of the fatty acids are almost independent of the chain length.

Thus Timmons and Zisman conclude that differences in contact angle and contact potential difference, represent changes in molecular orientation and packing. Above 14 carbon atoms a constant orientation and packing arrangement has been reached. The constant value 58°- of the contact angle of methylene iodide on the monolayers on platinum is important. The greater contact angle obtained with nickel oxide was attributed to increased orientation resulting from a chemical type of adsorption between the nickel oxide and stearic acid. This conclusion was reached from temperature measurements on the nickel oxide and platinum monolayer specimens. The monolayers on platinum, after heating to 130°C and soxhlet extracting in ether for 1 hour, desorbed, whilst little change was noted in monolayer depletion on nickel oxide. This increased strength of adsorption was attributed to a chemical type of adsorption.

Zisman [79] has also correlated contact potential difference measurements with boundary friction measurements on a Bowden-Leben type machine. Figure 12 shows the effect, on increase in chain length of the fatty acid homologous series.

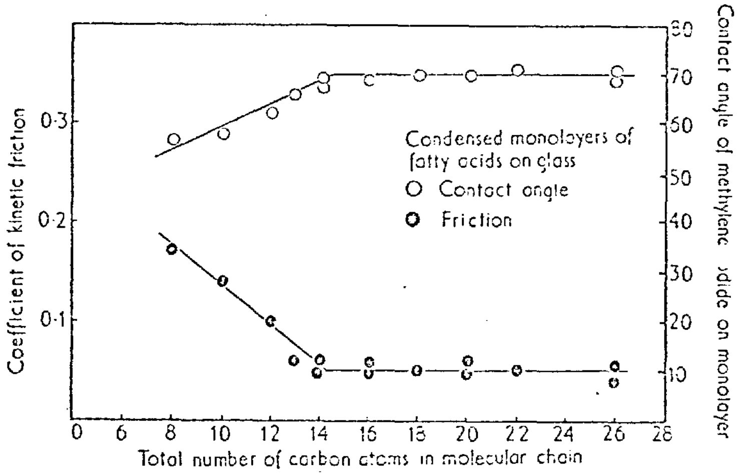
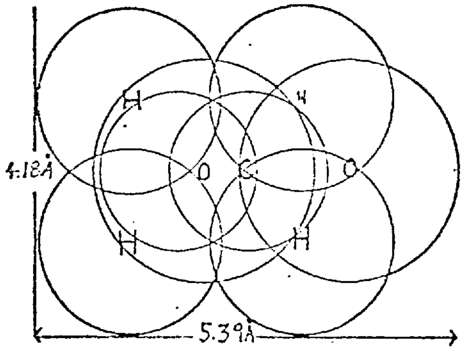


Figure 12 from ref. 79

In these tests a stainless steel hemispherical slider is sliding on the monolayer which has been deposited by retraction on glass. (Subsequent work by Timmons, Lockhart and Patterson [46] have investigated types of glass, Pyrex glass was found to be a very difficult surface to deposit a monolayer on by retraction.) The constant packing arrangement above 14 carbon atoms is again obtained and the friction measurements confirm this behaviour. Of special interest is the value of the contact angle of methylene iodide. This is 70° and corresponds to a critical surface tension of close packed CH_3 groups uppermost. This difference between contact angles of methylene iodide between the fatty acid monolayer on glass and when on platinum could be due to either orientation of the monolayer on platinum at an angle or that the packing arrangement is not so close. Electron diffraction measurements, [80] revealing that on platinum, stearic acid molecules are oriented nearly perpendicular to the surface, lead Zisman to conclude that for platinum the packing is not so close. Zisman [78] explains the alteration in contact angle and contact potential with chain length of the fatty acids to be due to methylene interactions in the chain. Thus below 14 C atoms the total interaction between chains is not sufficient to orient themselves perpendicular to the surface.

It is clear we must study the shape and packing of the fatty acids in considering adsorption and lubrication. We will take stearic acid as the example. The cross sectional area of fatty acids is conveniently measured using a Langmuir trough, determining the force area curve for the fatty acid in water. The force area curve shows two changes, the first discontinuity represents an areaper molecule of 25 sq A. but on further compression a constant area of 20.5 sq. angstoms is obtained. Vold [81] considered these results and drew the shape of the fatty acid molecule on a plane perpendicular to the chain axis as shown in Figure 13.



Projection of a *n*-fatty acid molecule on a plane perpendicular to the chain axis.

Atomic radii: C = 1.00 A. H = 1.20 A. O = 1.40 A.
Bond angles: H—C—H, C—C—C, C—C—H = 109° 30′
O—C—O = 125°; C—C—O = 117° 30′
Bond lengths: C—C = 1.54 A.; C—H = 1.09 A.; C—O = 1.28 A.

The oxygen atoms and carbon atoms are coplanar.

Figure 13 from ref. 81

She then considered packing arrangements, the most compact arrangement of vertically oriented fatty acids she showed to be 20.5 sq.Å. This is shown in Figure 14.

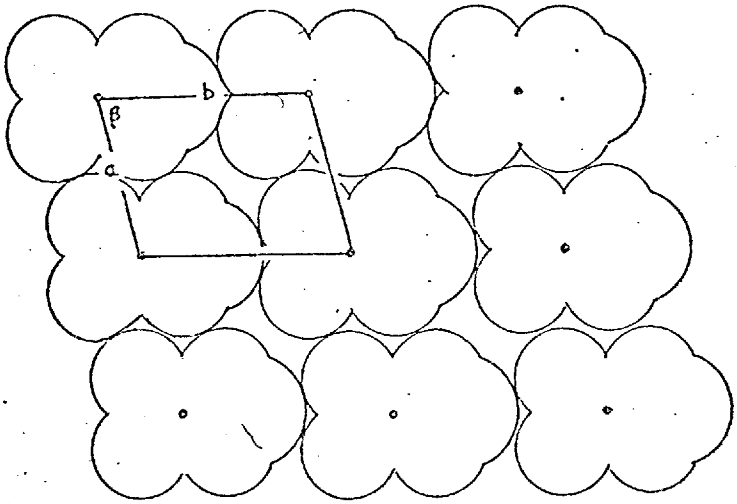
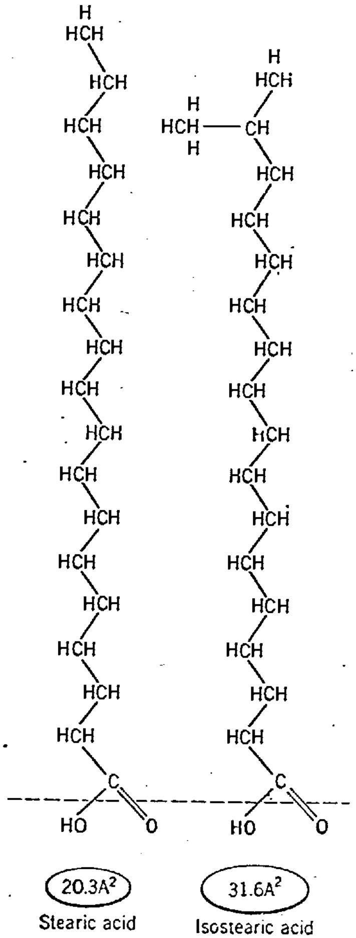


Figure 14 from ref. 81

Whilst the area which allows free rotation of the molecule is 25.2 sq. Angstroms. The length of the stearic acid chain is shown in Figure 15 and has been taken from a paper by Ries [82], also shown is isostearic acid, the length of the stearic acid chain is 24.4 Angstroms.



Stearic acid

Isostearic acid

Fig. 15

The side group on isostearic acid demonstrates the effect on change in packing area, and it will be subsequently shown that the side chain affects the alkyl chain interactions i.e. dispersion interactions by a great amount. Considering stearic acid it is seen that the cross sectional area is really determined by the acid group. Epstein [83] has suggested that with fatty acid molecules (because of the chain interactions) the tails draw together giving a sheaf of corn type structure and electron diffraction experiments seem to support this view.

The area of the sheaves in a close packed monolayer is about 1000 square Angstrons across the diameter. It is also noted that this straight spine zig-zag form is only one of a number of possible configurations. The long chain paraffins and fatty acids crystallise in a straight chain conformation. In the liquid state, because rotation is possible about the single bonds, other conformations are likely. This shows that the alkyl chain interactions are important.

We may now consider again the lubricant experiments on the four ball machine by Crouch and Cameron [61] and Askwith, Cameron and Crouch [60] in which increased failure loads were obtained when the chain length of the lubricant additive, amines, alcohols and fatty acids, matched the chain length of the carrier, alkanes. The object now is to investigate whether this effect may be explained by changes caused by the chain matching in boundary lubrication.

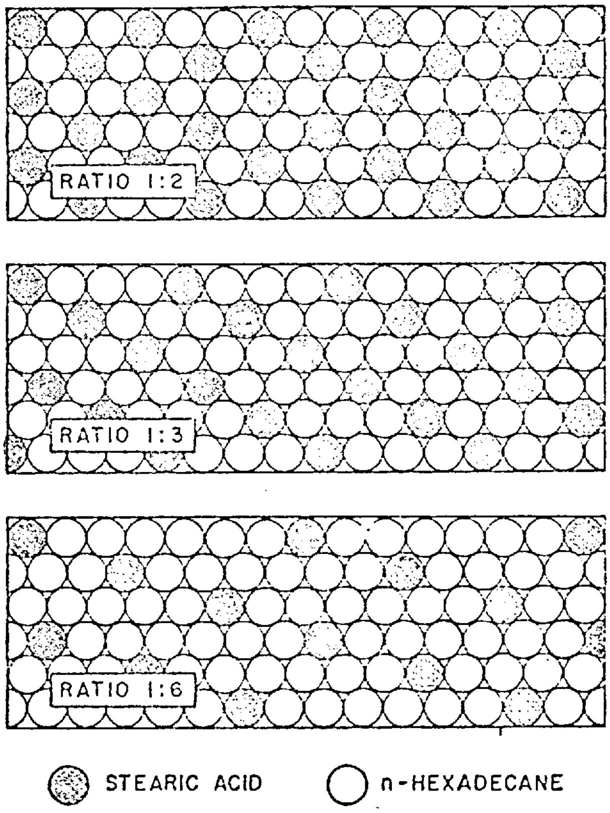
Evidence in the literature has been cited for the formation of mixed film monolayers.

In the monolayer depletion measurements of oleophobicity Bartell and Ruch [70, 71](already referred to), found that if hexadecane was spread on the surface of depleted N octadecylamine then the surface energy decreased due to more CH_3 groups in the surface. They attributed this to the hexadecane filling in the holes left by the desorbed octadecylamine. It is interesting to note the difficulty in obtaining a surface sufficiently clean for a monolayer to retract. Bartell and Ruch had much difficulty and abandoned the use of platinum and used a chromium plated steel. Their methods of cleaning given are very useful, often they used flaming of the surfaces.

Doyle and Ellison [84] investigated the coadsorption of N octadecane and stearic acid. The octadecane was labelled with tritium and the stearic acid with carbon 14. The tritium gives a less powerful beta radiation than the carbon 14. They used surfaces of Fe, Cu, Ag and Pt, but unfortunately did not obtain good retracted monolayers and so washed with cyclohexane which rinsed off some octadecane. They did, however, show that coadsorption was taking place.

Tamai [85] used a friction pendulum machine to measure the coefficient of friction of monolayers which had been retracted from solutions in which the chain length of the alkanes and fatty acids were varied. He found that there was a decrease in friction for retracted monolayers in which solvent and solute chain lengths were equal, but the work is marred for he was unable to obtain good retraction.

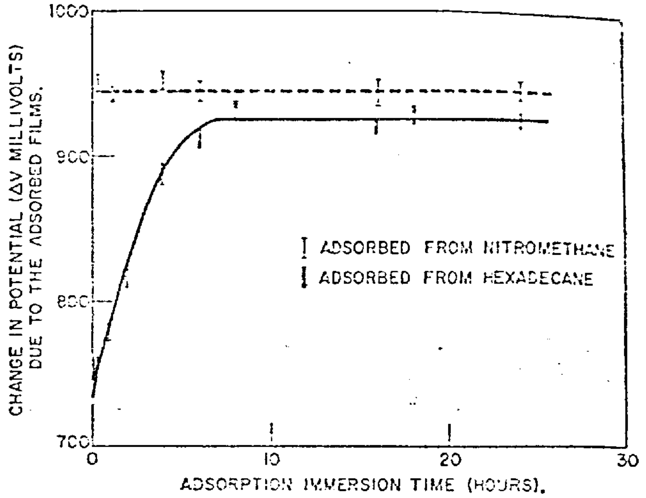
Cook and Ries [86] have studied the adosrption of mixed films using radioactive stearic acid adsorbed from hexadecane solutions. The adsorbant was the Geiger tube window itself and was mica or mica on which iron or gold had been evapourated. The tube was lowered into solution and a continuous count recorded. It was found that the iron coated surface continuously adsorbed the stearic acid, indicating chemical reaction. The mica and Au coated surface rapidly came to a constant count. The tube was calibrated by immersion in a close packed film of stearic acid on water. It was thus found that the constant count on adsorption from hexadecane solution corresponded to .15 - .33 of a monolayer. In a further experiment the mica surface was placed above a heated solution of hexadecane until the equivalent of over 9 monolayers had been condensed on the surface. This surface was then rinsed with N hexane, it was found that the surface rapidly became depleted but to a constant value of about .2 monolayers. Conducting force-area isotherms for stearic acid-hexadecane solutions over water, it was found that a high film pressure was required for a large equivalent area of stearic acid, i.e. 75 - 100 square Angstroms. They therefore concluded that these experiments show the coadsorption of stearic acid and N hexadecane.



—Schematic molecular packing of mixed monolayers of stearic acid and *n*-hexadecane.

Fig 16

Figure 16 is taken from their paper. It shows suggested packing arrangements, the ratio 1:3 in which the stearic acid molecule is surrounded by six molecules of hexadecane is most favoured. Although this diagram shows equal cross sectional areas for the hexadecane and stearic acid molecules. The chain matching of alkanes and amines has been studied by Bewig and Zisman [74] using the contact potential difference method. Firstly the long chain primary alkyl amines were adsorbed on platinum by retraction from nitromethane solution. In the same manner as the fatty acids previously discussed, with a chain length of 14 C atoms the contact potential difference and the contact angle of a drop of methylene iodide on this surface became constant. However, like the fatty acids this retracted monolayer was not close packed. The amine indicated a cross sectional area of the molecule equal to 30 square Angstroms, compared to the real area of 20.4 square Angstroms. The amines were then retracted from N hexadecane solution. It was found that the contact potential difference was much lower, yet the contact angle with methylene iodide, indicated methyl terminal groups. Further experiments measuring the contact potential difference as a function of the time of contact of the platinum with the solution, showed that, with increase in immersion time, the contact potential difference increased to the value obtained by retraction from nitormethane solution, as seen in Figure 17.



.—Contact potentials of octadecylamine adsorbed on platinum from nitromethane and hexadecane.

They then made a systematic investigation with the C_{14}, C_{16} and C_{18} amines and C_{12}, C_{14}, C_{16} and C_{18} alkanes. It was seen that as the alkane chain length became closer to the value of the amine chain length i.e. from being either longer or shorter, the contact potential difference became less time dependent, and no longer tended to approach the contact potential difference fro the film retracted from nitromethane solution. Indeed, whilst unequal chain length tests in which immersion time in the solution had been 24 hours approached the nitromethane value, the contact potential difference for chain matched experiments remained constant even after 48 hours. Bewig and Zisman [74] attributed these changes in contact potential difference to coadsorption with the amine of alkane molecules. Certainly the contact angle of a drop of methylene iodide remained constant, showing that the surface consisted of methyl groups. Assuming that the non polar alkanes did not contribute significantly to any change in contact potential difference they calculated the percentage of alkane in the film from the contact potential differences. Thus for the matched chains, the film contained between 14 and 15 percent alkane molecules. Bewig and Zisman [74] therefore suggested that a possible structure of the matched films was a regular array in which each alkane molecule was surrounded by six amine molecules.

Levine and Zisman [87] have carried out friction measurements on mixed monolayers. They used a Bowden-Leben type machine and made repeated traverses over the same track in a single direction with a uniform velocity of .01 cm/sec. After a number of traverses, the coefficient of friction was seen to increase and in this way they compared the durability of the films. The hemispherical slider was stainless steel and the films were deposited on soda glass. These monolayers, adsorbed both from the condensate and by retraction from nitromethane solution corresponded to films of maximum close packing, for the contact angle of a drop of methylene iodide for stearic acid was 71°.

They found that a monolayer retracted from hexadecane-stearic acid solution, was of inferior durability compared with monolayers retracted from stearic acid, nitromethane solution or by vapour condensation. They also found a similar relation between durability and contact potential difference for experiments in which the length of time of immersion in the solution was varied, i.e. the alkane concentration in the film decreased with increased immersion time. Similar behaviour was also obtained for a mixed film of docosylamine and hexadecane. The decreased durability was attributed to the decrease in surface density of polar molecules as a result of the incorporation of hexadecane molecules.

Therefore, there is good evidence to suggest that tests carried out in boundary lubrication may well be affected by the matching of the chain lengths of the additive and the solvent molecules.

It was decided to investigate the chain matching effect of alkanes and fatty acids using the Bowden-Leben machine and to conduct measurements of friction and the change of friction with temperature.

Experimental

The main variables to choose on operating the Bowden-Leben machine are the friction materials, their composition, hardness, shape and surface finish. The load, velocity, temperature, lubricant and the atmosphere. Since we are investigating the variation of coefficient of friction with temperature, it is good to choose values of load, velocity and surface finish and other variables which are kept constant so that any slight variation in them does not greatly affect the result. The load was 5.5 lbs (2.5 Kg) i.e. Hertzian pressure 125,000 lb/in^2 (8.080 Kg/cm^2) and the velocity as 0.02 cm/sec. Preliminary experiments showed that the results were not dependent greatly upon load and velocity. This is discussed in Chapter VI in more detail. Reference is also made to work being carried out at Imperial College, using this Bowden-Leben machine [88] on the effect surface finish, velocity and load have on transition temperatures. 18/8 stainless steel was chosen as the friction material. The chromic oxide on the steel is unreactive to fatty acids, whilst the steel is readily obtainable as balls, so that comparison tests could be carried out using the four ball machine or other friction testing machines. A flat plate and a $\frac{1}{2}$" diameter ball were the friction surface configuration, and a stainless steel plate holder and ball holder were also manufactured in stainless steel. The hardness of the plate was VDPN 230 and the ball VDPN 167. Stainless steel has a high value of dry friction so that breakdown of boundary lubrication was readily detected. The friction temperature measurements were carried out in air. The machine was modified as that nitrogen could be continuously streamed over the plate. No real difference was detected between tests carried out in nitrogen and tests carried out in air. It was found that the most important consideration was the surface cleaning. Indeed this is expected since a monolayer of surface active compounds can reduce the friction coefficient from 0.8 to 0.1. Much time was spent in search of a satisfactory method of cleaning. Many methods given by workers were investigated. It is interesting to note that the steel plate could be soxhleted for 48 hours in benzene and still remained unwetted by water. Flaming of the surfaces was also tried, this seemed initially to be successful but was not really reliable. It was found that surfaces on which retraction was obtained could be prepared by initially cleaning with acetone or other suitable solvent and then by abrasion with silicon carbide papers to grade 400. This method although time consuming was chosen for these experiments. The surfaces were checked for cleanliness before each test by measuring the static coefficient of friction of the dry surface between the slider and rider. A clean surface gave a coefficient of friction in the region of 1.0. Surfaces which gave a coefficient of dry friction of less than 0.8 were rejected and recleaned. This was done because tests showed that if the experiment was continued and the friction temperature graph for the lubricant determined that although some indication of a transition temperature was evident, sometimes it was barely visible whilst other seemingly random transitions were obtained as well.

After cleaning the plate properly, then typical examples of friction temperature curves are shown in Fig. 18. Some exhibit stick slip whilst

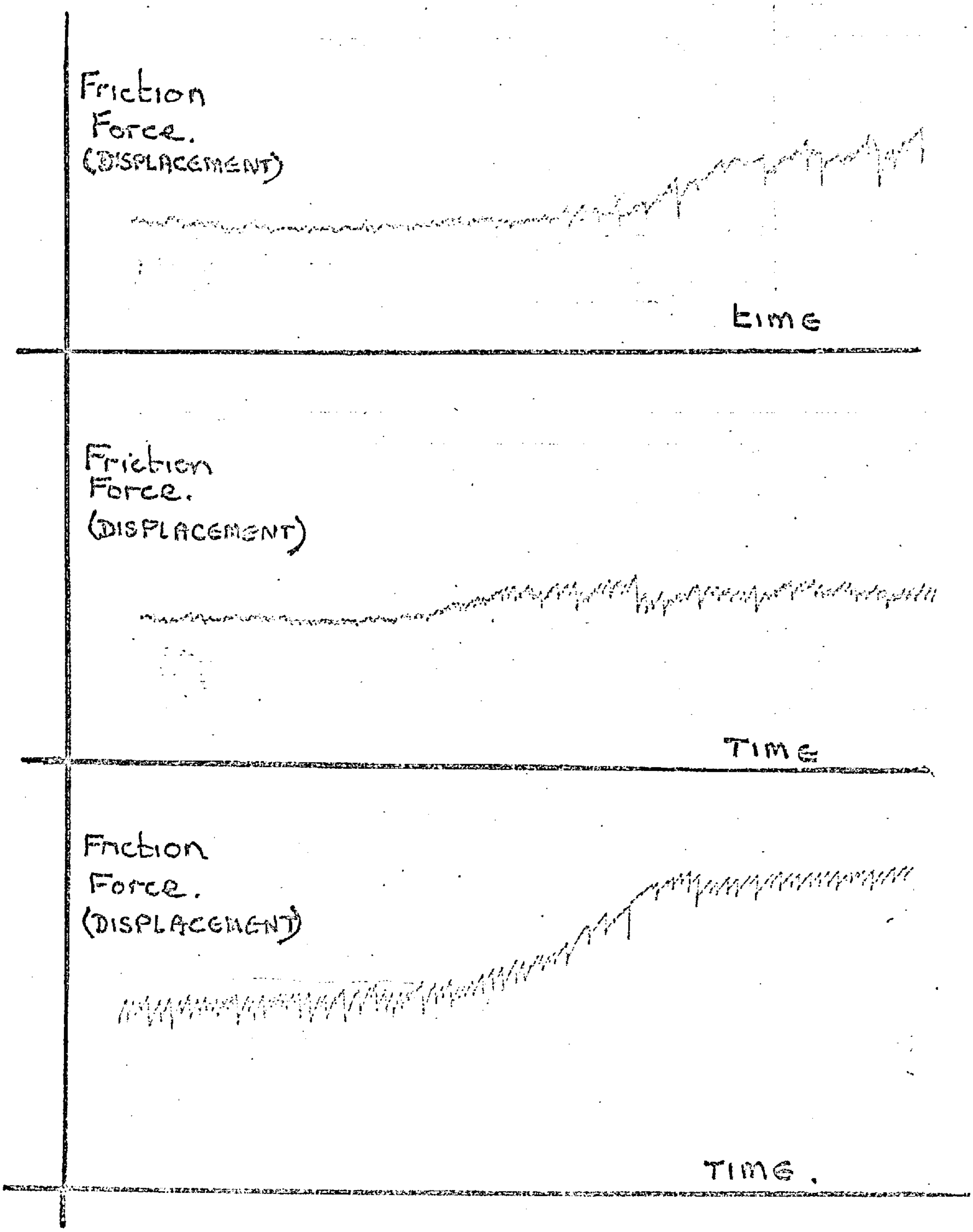

Friction Force. (DISPLACEMENT)
time
Friction Force. (DISPLACEMENT)
TIME
Friction Force. (DISPLACEMENT)
TIME.

Fig 18

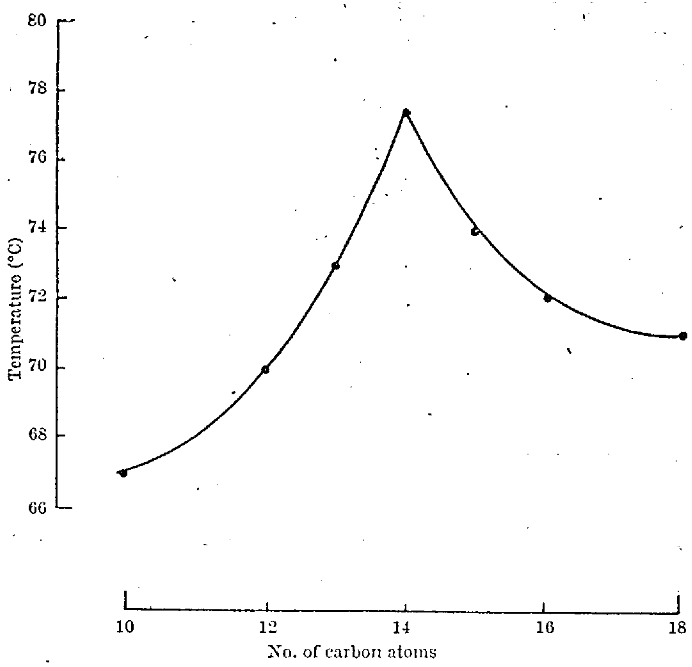
others do not. At least four runs were made for each determination of a friction temperature transition. In this way the transition temperature could be determined with an accuracy of ± 1.5°C. For the determinations in which the peak effect was determined for fatty acids in tetradecane the accuracy was ± 1.0°C. A mean friction curve was also plotted, this was the mean friction from a number of determinations of frictions vs temperature and in this way slight bumps in the curves disappeared, showing only the transition temperature.

The acids and alkanes were obtained from Koch Light Ltd. and Newton Maine Ltd. these were "Puriss" grade at least 99.5% purity. Solutions were made up in 40 ml quantities and particular attention was taken to ensure that all of the acid dissolved in the alkane. The solutions were kept in glass stoppered test tubes which had been thoroughly cleaned before use with chromic acid cleaning mixture. Indeed retraction effects could be determined with temperature on the walls of these test tubes.

Sufficient lubricant was poured onto the specimen so that the level was approximately a quarter of an inch above the plate.

The experiment was started and the heaters switched on two minutes after the lubricant had been poured in. Tests were carried out in which the time elapsed before heating was caried but no effect on the transition temperature was noticed even after a period of 24 hours. This is in agreement with Hardy's[34] findings, that the latent period was short if alkanes were present and that the latent period decreased with increase in temperature.

The plate and ball were steadily heated and whilst the plate was being traversed the friction was recorded continuously by the pen recorder. The heating rate was arranged that the whole run was completed in one traverse of the plate. Test for reversibility of the transition temperature were made, but at the transition temperature often the ball became scratched and very rough from the gross metallic contact with the plate. Thus tests for reversibility were difficult to carry out. However, it was found that if the ball had not been scratched severely or if was replaced with a smooth fresh one, that the transition temperature was again obtained with the used lubricant on a new track on the used plate. Figure 19 shows the results of transition temperatures for the fatty acids dissolved in N tetradecane (C_{14}) at 0.003 m concentration.



Transition temperature–chain length of fatty acids in tetradecane at 0·003 molar with plate and 0·5 in. ball both of 18/8 stainless steel, 2·5 kg load, velocity 0·002 cm/sec.

Fig 19.

The accuracy is at least ± 1.0°C and thus a peak effect has been obtained, for the highest transition temperature occurs for the solution of myristic acid (C_{14}) in tetradecane solution (C_{14}).

The values of temperature are also noted i.e. in the range around 73°C, this is interesting since in their paper Askwith, Cameron and Crouch [60] reported that the chain matching effect was no longer obtained in the four ball machine if the ambient lubricant tempeature eas greater than 35°C. It is suggested that a possible reason for this is that the frictional heating at the contact region could be 40°C [89, 90] and thus the total temperature in the contact area 40 + 35 = 75°C. The chain matching effect would no longer be apparent, indeed the scuffing loads would be expected to decrease.

It is concluded that the chain matching affect of solvent and solute of alkanes and fatty acids is apparent in boundary lubrication. Matching of the chain lengths of the acid and alkane causes boundary lubrication to persist to a higher temperature than solutions containing unmatched chains.

So that additional information on the chain matching effect could be obtained, it was decided to carry out tests on lauric acid (C_{12}) and to dissolve it in alkanes of different chain lengths for a wide range of concentrations, and then measure the transition temperatures. In this way the log C vs $\frac{1}{T}$ curves can be obtained and the heats of adsorption calculated from the slopes of the graphs, thus any peak effects might be seen as a change in the heat of adsorption, thus in this method lines of different gradient are compared rather than the values of single points.

Figure 20 shows a graph of the results obtained.

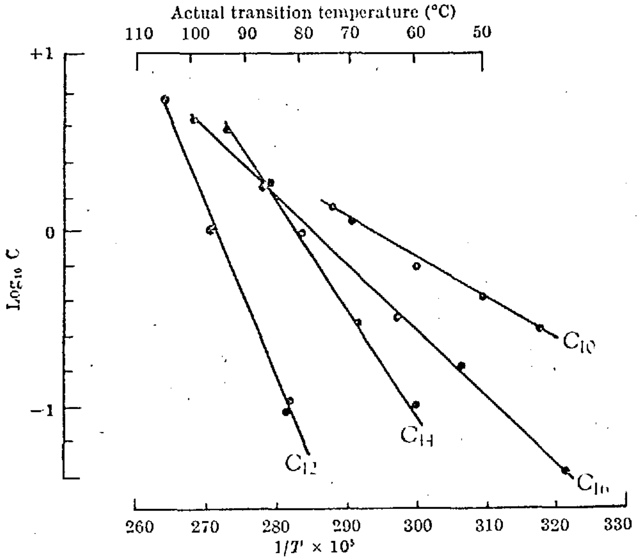


Fig. Log concentration (weight/100 g solvent)—reciprocal transition temperature °K for lauric acid in four alkanes.

<u>Figure 20</u>

Thus any horizontal line of concentration C shows the chain matching obtained for lauric acid dissolved in the given alkane solvents C_{10}, C_{12}, C_{14} and C_{16}.

Results

The following heats of adsorption were calculated.

1. Adsorption of lauric acid from decane

$$\Delta H^{o} = -11.0 \pm .67 \text{ Kcals/mole}$$

2. Adsorption of lauric acid from dodecane

$$\Delta H^{o} = -46.9 \pm 2.1 \text{ Kcals/mole.}$$

3. Adsorption of lauric acid from tetradecane

$$\Delta H^{o} = -28.3 \pm .80 \text{ Kcals/mole}$$

4. Adsorption of lauric acid from hexadecane

$$\Delta H^{o} = -17.3 \pm .46 \text{ Kcals/mole}$$

The gradients of the graphs are negative i.e. ΔH is negative. This is consistent for adsorption to take place, the free energy must be negative

$$\Delta G = \Delta H - T\Delta S$$

and the experiments show that adsorption decreases with increase in temperature, alternatively we may consider that if heat is evolved on adsorption, then ΔS is negative corresponding to a more ordered system which occurs on adsorption. A special case in which adsorption may increase with increase in temperature, is polymer solutions and these are considered later.

Beacuse it is well known that physical adsorption decreases with increase in temperature the heats of adsorption are often quoted just as numbers without particular care taken over the sign using this convention.

Accuracy of the Results

The equation connecting the transition temperature and the concentration of the solute in the solvent has been derived,

i.e. $$-\frac{\Delta H^{o}}{T} + \Delta S^{o} = R \text{ In } \left(\frac{\theta}{1 - \theta} \right) - R \text{ In } C$$

Thus there is a linear functional relationship between $\log_{10}C$ and $\frac{1}{T}$.

In the graphs concentration has been plotted as weight/100 grams. This is directly proportional to the molar concentration C for the single fatty acid.

Thus the slope of this graph multiplied by 2.303 x R, where R is the Gas Constant (R = 1.986 cals $\text{deg}^{-1}\text{mole}^{-1}$) gives the heat of adsorption in cals/gram mole. The experimental error in making up the solutions is very small compared to the error in measuring the transition temperature T. Thus a regression is taken of y on x where x is the logarithm of the concentration, and y, the reciprocal of the absolute temperature. The graphs, however, have been plotted according to the convention concerning temperature i.e. with the temperature scale as x, the absicca.

A linear regression was made for each curve and the gradient evaluated.

The variance of the regression value of the slope was also calculated [91] and hence the standard deviation of the measured values of the heat of adsorption are given. These accuracies are between 2.7% and 6.1%

Discussion of Results

The results show that chain matching of the solvent and solute has caused an increase in boundary lubrication ability over the unmatched solvent and solute solutions for conditions of increasing temperature.

It is also seen that the heats of adsorption have been calculated and an increase of the heat of adsorption has been found for the matched solute and solvent chain lengths.

In the discussion, therefore, we must consider the meaning of the values of the heats of adsorption and also resolve the apparent contradiction of these results, with those of Levine and Zisman who obtained a inferior durability of films in which chain matching occurred.

Firstly, however, the relation between the surface coverage, the heat of adosrption and temperature is again derived, but this time directly by using chemical potential, this method has not so far been published.

The relation between surface coverage, concentration and temperature

At equilibrium the chemical potential of the solute molecules in solution ℓ, equals the chemical potential of the solute molecules adsorbed on the surface S.

Therefore assuming that the adsorption is in a dynamic equilibrium

$$\mu_S = \mu_\ell$$

Hence

$$\mu_S^o + RT \ln a_S = \mu_\ell^o + RT \ln a_\ell$$

$$\mu_s^o + RT \ln a_s = \mu_\ell^o + RT \ln a_\ell$$

Considering partial molar quantities

$$h = \mu + T_s$$

$$h_\ell^o + RT \ln a_\ell - TS_\ell^o = h_s^o + RT \ln a_s - TS_s^o$$

hence

$$\frac{h_s^o - h_\ell^o}{T} = R \ln (\frac{a_\ell}{a_s}) + S_s^o - S_\ell^o$$

i.e.

$$- \frac{\Delta H^o}{T} + \Delta S^o = - R\ln (\frac{a_\ell}{a_s})$$

Assume that the activity of the liquid phase may be replaced by molar concentration C and the adsorbed molecules, let the activity be replaced by the concentration of the molecules on the surface i.e. the surface coverage. Hence if θ is the number of molecules adsorbed, surface concentration = $\frac{\theta}{1 - \theta}$

For adsorption

$$- \frac{\Delta H^o}{T} + \Delta S^o = R \ln (\frac{\theta}{1 - \theta}) R \ln C$$

Whilst we have used this equation to calculate heats of adsorption, the relation that lubricant desorption results in an increase in friction had so far just been assumed. In the introduction to this Chapter we considered the forces present which caused adsorption, similarly therefore we may consider the forces between surfaces and the effect of adsorbed molecules upon the forces of attraction between the surfaces.

Figure 21 is taken from Bowden and Tabor Vol. II [92] and shows the force-separation curve between two solid surfaces of infinite length and breadth. The energy of interaction is the area under the curve.

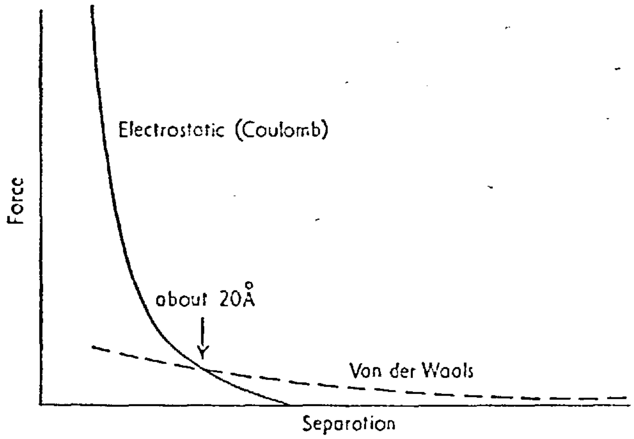


Figure 21 taken from ref. 92

It is seen that for distances greater than 20 Angstroms the electrostatic forces are very small and only van der Waals forces are significant.

Hamaker [93] calculated the dispersion energies of interaction for solid bodies of different geometrical shapes.

For parallel infinite planes [94]

$$U = -\frac{A}{12 \pi H^2} \quad \text{and}$$

$$F = \frac{A}{6 \pi H^3}$$

U is the energy attraction

F is the force of attraction

A is the Hamaker constant

H is the distance between the planes.

It has now been found, however, that with increasing distances the dispersion forces are inversely proportional to the eighth power of the distance rather than the seventh power and are called 'retarded van der Waals forces'. In the same way the forces between parallel surfaces have been found to be inversely proportional to the fourth power instead of the third, i.e. after a certain distance the forces are less. Kitchener and Prosser [95] have found experimental agreement with the predictions.

It is seen that the presence of a single perpendicular long chain molecule i.e. stearic acid 22.66 Å long [94] may prevent the surfaces coming together so that the forces between the surfaces are small. But for an alkane lying flat on the surface (perpendicular height 5.4 Å) the forces between the surfaces will be large, indeed the non polar alkanes are very poor boundary lubricants.

We will now consider the experimental values of the heats of adsorption calculated from the Bowden-Leben friction temperature measurements.

1. Lauric acid (C_{12}) in decane

The heat of adsorption of lauric acid in decane was found to be $-11.0 \pm .67$ Kcals/gram mole.

This value compares well with values obtained by Frewing for the fatty acids dissolved in a white oil. Frewing's [42] values were:

Capric acid	12.5 Kcals/mole
Stearic acid	13.0 Kcals/mole
Myristic acid	13.0 Kcals/mole

Using the oleophobic monolayer technique Bigelow, Glass and Zisman [48] obtained a value for the heat of adsorption of N ercosanoic acid i.e. (C_{20}) of 10.1 Kcals/mole, and the heats of adsorption of alkyl amides amines and other fatty acids were generally found to lie in the range 10.0 to 13.0 Kcals/mole. Although, as mentioned earlier, the heat of adsorption calculated may refer to a different surface coverage. However, the value obtained for lauric acid and decane solutions seems to be in general agreement with published results.

Another estimate of the value expected for the heat of adsorption may be indicated by other thermal properties of the system. Consider the adsorption of fatty acids on surfaces, this results in an increase in the order of the fatty acid, resulting perhaps in a close packed structure similar to the crystal structure, hence heats of crystallisation and sublimation of the fatty acids are interesting and should bear some relation to these.

Heats of Sublimation

The heats of sublimation of the fatty acids have been measured by Davies and Malpass [96] using an effusion technique. The heat of sublimation was found to be proportional to the chain length of the acid and could be expressed by the equation

$$\Delta H_{(sub.)} = 14.2 + 1.50 (N - 1)$$

ΔH is in Kcals/g.mole.

and the fatty acid is

$$C_{N-1}H_{2n-1}COOH$$

Thus there is a constant contribution of 1.50 Kcals/mole by each CH_2 group to the lattice energy, this must result from the van der Waals interactions between the CH_2 groups. The 14.2 Kcals/mole will thus mainly represent the contribution of the carboxyl group of the acid in the crystal to the total energy. Usually the acid crystallises in the associated state.

Heats of Crystallisation

Ralston [97] shows that the heats of crystallisation of the fatty acids also follow a similar equation and is given by

$$Q = -2.58 + 1.030\ (N-1)$$

where N is for even numbered carboxylic acids.

Thus methylene group interactions may well be important in the adsorption process, it is remembered that the ratio of length to diameter of stearic acid is 4.75.

The attractive forces (i.e. van der Waals dispersion forces) between long saturated chains have been examined by Salem [98] in sutdies on the stability of lipoprotein structures, for the chloroplast, can contain fatty acids such as palmitic or stearic acid combined as glycerides or phosphatides [99]. The polar regions of these lipids orient like adsorbed layers towards protein layers so the long chains orient parallel to each other and a sandwich like construction occurs [100]. Salem [98, 101] has calculated the attractive forces between the individual CH_2 group dispersion forces are locally additive. Thus the dispersion energy of attraction W_{Disp} is given by,

$$W_{Disp.} = \frac{A\ 3\pi}{8} \times \frac{N}{D^5}$$

$W_{Disp.}$	is the energy of attraction Kcals/g.mole
A	is a dimensional constant and equals 1340 Kcals per mole x Angstroms.
N	is the number of C atoms
	is the length of the CH_2 unit i.e. 1.26 Angstroms.
D	is the distance between the hydrocarbon chains in Angstroms.

Thus if the distance between the chains decreases, say, from 6.0 to 5.0 Angstroms then the energy of attraction increases by 2.4 times.

Consider stearic acid, the most close packed arrangement has an area of 20.5 A^2 the area equals $\frac{3}{2} D^2$.

i.e.

$$D = 4.8\ \text{Å}$$

$$N = 18$$

Hence the dispersion energy between two chains is -8.4 Kcals/mole.

Salem has calculated the dispersion energy for isostearic acid [98. 101] - see Fig. 15 in which there is a single CH_3 group side chain, This causes the effective diameter of the molecule to increase to 6.0 A. and hence the dispersion energy falls to -2.8 Kcals/mole.

Spink [102] has used these calculations in his experiments on the thermal desorption of stearic acid monolayers from mica and silver. Using C_{14} labelled stearic acid monolayers prepared by the Langmuir-Blodgett technique, he measured the rate of desorption for isothermal experiments carried out at different temperatures under vacuum by counting the desorbed molecules which were condensed onto a cold plate. Thus assuming the Ahrennius equation is valid the energy of adsorption is calculated.

The experimental values for the heat of adsorption on mica and silver were 43.3 ± 4.1 Kcals/mole and 10 Kcals/mole respectively. Consider the result for stearic acid desorbed from the mica surface. Electron microscope work by Ries and Kimball [64, 103] has shown that monolayers of the fatty acids e.g. stearic acid form as small circular islands and only at high surface pressures is the monolayer continuous, thus it is reasonable to assume that on desorption of a molecule of stearic acid from the monolayer, the desorbing molecule will have three nearest neighbours for hexagonal packing. Using Salem's formula Spink gives the total hydrocarbon chain interaction energy for stearic acid as 3 x -8.4 = -25.2 Kcals/mole. Spink then adds - 14.2 Kcals/mole for the carboxyl end group, so the sum is -39.4 Kcals/mole. This he compares with his experimental value of -43.3 ± 4.1 Kcals/mole.

Concerning the value of 10 Kcals/mole for stearic acid on silver Spink remarks that this is probably due to a loose packing structure.

Pimbley and MacQueen [104] have studied the desorption of stearic acid using ellipsometry, the ellipsometer continuously measured the amount of adsorbed stearic acid. Isothermal measurements were carried out at different temperatures under vacuum conditions so that an Ahrennius plot could be made. In this experiment stearic acid was condensed as multilayers onto polished metal robbons. Pimbley and MacQueen [104] found that the binding energies of the outer layers of stearic acid was 44.1 Kcals/mole for both Nickel and Platinum surfaces. The binding energy of the monolayer was found to be 36.4 Kcals/mole for Ni and 30.5 Kcals/mole for Pt. surfaces. Presumably in this case the stearic acid was more closely packed than in the Langmuir-Blodgett monolayers prepared by Spink [102]. Indeed returning to Spink's experiments, he relates the total amount of stearic acid desorbed to the fraction of a close packed monolayer desorbed from a steel surface. It is seen that whilst the % loss of close packed monolayer of stearic acid from mica thus starts at 0%, the desorption rate from silver begins at about 25%. It is clear, therefore, that the packing arrangement can be very important, and so the contact potential difference experiments by Zisman and co-workers are now re-examined.

In Timmons' and Zisman's [78] investigations of fatty acid monolayers on metals, it was found that the contact angle of methylene iodide on the monolayer was dependent upon the metal substrate e.g. 71° for Fe, 63° for Ni, 61° for Cr and 58° for Pt. Since electron diffraction experiments had shown that these monolayers were all within a few degrees of the vertical, the differences must be due to differences in packing. Bewig and Zisman [74] had already noted that the contact angle of methylene iodide on octadecylamine adsorbed on Pt was only 69° and in an earlier paper Bigelow, Pickett and Zisman [105] deduced that the apparent area of this molecule on Pt was 30 A^2 compared to 20.4 A^2 obtained on aqueous substrates. The method used, was to deplete a solution of known concentration by repeatedly taking oleophobic monolayers from the solution until it was exhausted. It was found that the contact angle remained virtually constant until the oleophobic monolayer would no longer form.

In Bigelow, Glass and Zisman's [48] oleophobic temperature measurements the heat of adsorption of N octadecanol from dicyclohexyl solution was 10.0 Kcals/mole. Bartell and Ruch [70, 71] using ellissometry show that the contact angle of trimethyl benzene on a monolayer of octadecylamine only changes to complete wetting at about 46% depletion. Their undepleted film was estimated to have an apparent area of 23 A^2. Thus at wetting the apparent area is approximately 41.7 A^2, which for a close packed hexagonal structure gives an apparent diameter of 6.9 A. Hence the van der Waals dispersion force is 1.42 Kcals/g.mole.

Thus the contribution to the heat of adsorption would be -4.3 Kcals/g.mole for an 18C atom molecule and -2.8 Kcals/mole for the 12C lauric acid molecule.

Consider now some consequences of packing arrangements possible in chain matching.

In the fatty acid molecule we have already indicated that the polar group determines the cross sectional area of the molecule and "corn sheaf" structures result. An alkane molecule, however, will be able to approach the acid chain more closely. Whilst the alkane interaction with the surface, when perpendicular to it, will be relatively weak, the increase in cohesion of the mixed film due to the alkane and acid being able to approach each other more closely may more than compensate for this loss. A more durable film is therefore produced.

Lauric acid in dodecane solution

The heat of adsorption of lauric acid (dodecane acid) in dodecane was found to be - 49.9 ± 2.1 Kcals/g.mole. Calculations are now made in an effort to explain this large heat of adsorption.

Assumptions

Let the transition temperature of lauric acid in dodecane solution be due to the desorption of a mixed surface film of alkane and acid molecules.

Let the difference in the heat of adsorption between lauric acid in dodecane solvent and lauric acid in decane solvent be due entirely to differences in the forces between the alkyl chains.

The increase in the heat of adsorption is

$$46.9 - 11.0 = 35.9 \text{ Kcals/g.mole}$$

Let us assume that the alkyl chain intereaction for the system dodecanoic acid - decane is -2.8 Kcals/mole. This value we have already caluclated from Bigelow, Glass and Zisman and Bartell and Ruch's experiments disucssed earlier. Therefore the contribution to the heat of adsorption due to $\overset{\smile}{C}H_{\bar{2}}$ dispersion forces of attraction is 38.7 Kcals/ g.mole.

Let desorption occur from a hexagonally packed mixed monolayer where there are three equidistant neighbours. Therefore, using the equation deduced by Salem [98,101] discussed earlier

$$W_{Disp} = \frac{38.7}{3} = 12.9$$

$$W_{Disp} = \frac{1250}{D^5} \times 12$$

Thus $D = 4.13$ Angstroms, i.e. this is the distance between alkane chain lengths.

It is interesting to note that the distance apart of carbon atoms of adjacent alkane chains in paraffin crystals has been shown by x-ray, an electron diffraction to be between 3.7 and 4.0 Angstroms. The distance of 4.13 Angstroms calculated above seems acceptable.

An effect which has not been considered is the repulsion of the fatty acid dipoles between each other when adsorbed on the surface possibly causing a change in orientation of the dipole resulting in a reduced strength of adsorption. It may be that the strength of surface interaction of the fatty acid therefore increases when surrounded instead by the alkane chains, so that a futher increase in the heat of adsorption would result with chain matching.

The decrease in the heat of adsorption found as the chain lengths mismatch is ascribed to the ragged effect of the surface by protruding coadsorbed alkane chains in the same described by Bartell and Ruch [70,71]

Results of Levine and Zisman [87]

We will now examine the results obtained by Levine and Zisman. They prepared, by vapour condensation and liquid retraction, condensed monolayers of fatty acids and primary amines on glass. When retraction was made from a solvent of equal chain length or near equal chain length, there was a decrease in the durability of the monolayer compared to the monolayer of the solute prepared from nitromethane or by vapour condensation. It is seen that in the unmatched case an extremely good well packed monolayer was obtained, i.e. the methylene contact angle was 71° thus there is probably a greater interaction between the surface and this monolayer, than for the case of a mixed monolayer. Whilst there is increased cohesion of the film the vertical alkanes do not have a strong surface interaction. Thus it may be expected that the pure acid monolayer gives greater durability.

Examine now the results of the chain matching experiments in solution. To compare these results with Levine and Zisman's we are comparing temperature breakdown with durability and experiments using solutions with experiments on monolayers.

It is not easy to prepare close packed oleophobic monolayers by retraction from solution. Indeed previous workers [84, 85, 70, 71] have found great difficulty, and the use of soda glass in Levine and Zisman's experiments was a great help. Thus it may be expected that the close packed monolayer prepared by Levine and Zisman would not be present under normal circumstances for friction materials. Instead a more loosely packed structure which would not be so durable would be present. Hence a mixed monolayer structure, which Bewig and Zisman found to form rapidly, may be more durable.

A further difference is that Levine and Zisman's tests are on monolayers thus there is little chance of repair and the plugging of holes. Solutions especially chain matched solutions (Bartell and Ruch [70, 71], and Bewig and Zisman [74]) can do this well. It is remembered that adsorbed molecules may be considered to be in dynamic equilibrium with the molecules in solution. Thus it is considered that Levine and Zisman's results do not contradict the conclusions of these tests nor the four ball tests of Crouch and Cameron [61].

Conclusions

It has been found that stainless steel surfaces sliding at slow speed gave a higher lubricant failure temperature for lauric acid in dodecane than for lauric acid in decane, tetradecane and hexadecane. The heats of adsorption ΔH^{o} for these solutions was calculated assuming that lubricant failure occurred at a constant surface coverage by the adsorbed molecules.

lauric acid from decane $\Delta H^{o} = -11.0 \pm 6.7$ Kcals/mole
lauric acid from dodecane $\Delta H^{o} = -46.9 \pm 2.1$ Kcals/mole
lauric acid from tetradecane $\Delta H^{o} = -28.3 \pm .80$ Kcals/mole
lauric acid from hexadecane $\Delta H^{o} = -17.3 \pm .46$ Kclas/mole

The increased lubricating ability is attributed to coadsorption of the acid and alkane producing a stronger film. This is due to the high forces of attraction occurring between the alkane and the acid which are able to approach each other closer than the adsorbed chains of the fatty acids themselves. The large heat of adsorption obtained for decoic acid in decane was found by an approximate treatment to agree with this prediction.

Subsequent Investigations

Since the time this work was completed further work has been carried out on chain matching experiments.

Harding [106] has found the peak effect for matched chains using an oleophobic temperature method similar to that used by Bigelow, Glass and Zisman [48]. He found the peak effect present for fatty acids in alkanes and N alkyl amines in alkane solutions. The monolayers were retracted on 18/8 stainless steel. No heats of adsorption were calculated.

Sharma [107] working on the same machine as the author used has demonstrated the peak effect with N alkyl amine solutions in alkanes lubricating stainless steel surfaces. He has also demonstrated the presence of the peak over a wide range in surface finish of the steel.

Gabor and Ries [108] have published a communication on chain length compatability in rust prevention. A.S.T.M. rust experiments were carried out in which steel strip carefully cleaned is immersed in the corrosive medium containing the inhibitor. In these tests the rust inhibitors were solutions of the C_{14}, C_{16} and C_{18} fatty acids in hexadecane. It was found that there was much better rust prevention for the solution of hexadecanoic acid in hexadecane i.e. no rust tetradecanoic acid in hexadecane (severe rusting) and octadecanoic acid in hexadecane (severe rusting). They attribute this effect to the formation of a mixed film of the acid and alkane when chain matching occurs.

CHAPTER 4

Polymer Solutions

Introduction

As the result of discussions with H. Gisser [109] it was decided to investigate the boundary lubricating properties of a series of poly n alkyl methacrylate polymers, and samples were sent to this laboratory. The length of the alkyl group varied from 2 to 24 CH_2 units and a table (Table I) is shown giving the molecular weight of the polymer, the alkyl chain length and the chain length of the polymer relative to the chain length of polymethylmethacrylate.

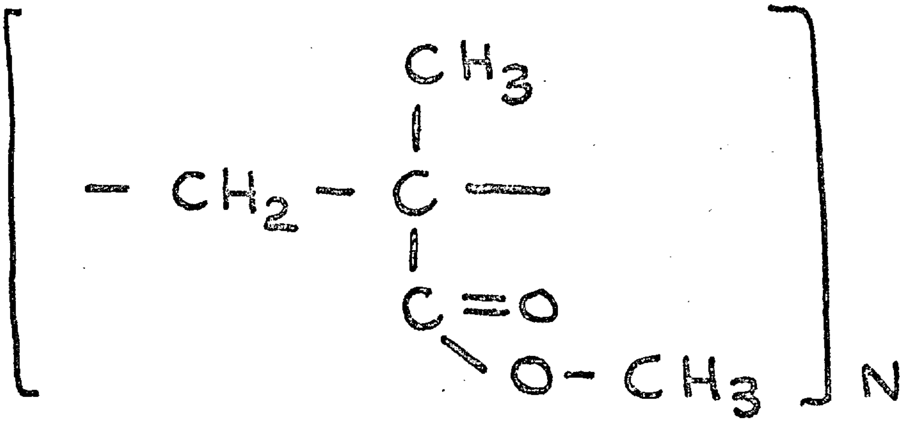
Alkyl Chain	Polymer m.wt.	Polymer chain length relative to the polymethylmethacrylate chain length
Methyl	7.6×10^5	1.0
Outyl	4.3×10^5	0.43
Octyl	2.2×10^5	0.15
Lauryl	1.4×10^5	0.072
Docosyl	15.9×10^5	0.53

TABLE I

Polymers are added to lubricating oils for use in internal combustion engines. The main results are an increase in viscosity index [110] and a decrease in viscosity with rate of shear [111].

Surface Activity

Polymethylmethacrylate whose formula is shown, and other polymers having polar groups exhibit some surface activity. Indeed some polymers have suitable polar groups added so that they behave as dispersant additives in lubricating oil [112].



Okrent [113] in his work on the affect of polymeric additives of polymethylmethacrylate and polyisobutylene on engine friction and bearing wear found some evidence that the polymers have some boundary lubricating properties. He used a V8 petrol engine, which after temperature equilibrium was reached, was motored through a dynamometer which measured friction. Simultaneously he measured the connecting rod bearing wear rates using an isotope method. He found that even when operating under conditions for which minimum friction and wear was obtained for a given oil viscosity, the addition of the polymer reduced both friction and wear. In a later paper [114] he continues this work and adds to the oil 4% by volume of surface active compounds used as detergent additives, for this addition might affect any surface active influence of the polymer additive both of which have an equal bulk viscosity at 210°F. Okrent finds that the addition of the detergent caused an increase in wear and friction for both the base oil and the oil plus polymer additive. For the polymer oil, this increase is much smaller. In the oil containing 10.8% polyisobutylene an increase in wear of .24 mgs/hr resulted whilst the base oil increase in wear was 1.39 mg/hr. Unfortunately Okrent may have used fractions of lubricating oil which contained different amounts and compounds of natural surface active comppund so that some error may be present in these results. However, it does seem that the polymer additives play some part in boundary lubrication.

Furey and Appeldoorn [115] have investigated the effect of the addition of polyisobutylene to mineral base oils on the boundary lubrication of a sliding ball on a rotating cylinder. They used their electrical resistance technique and found that the metallic contact using an additive oil was less than that of the base oil but that this difference decreased with increase in load.

Polyethylene glycols are also said to be adsorbed on surfaces. Heller and Pugh [116] found steric protection and increased stability of gold sols. They pictured adsorption of the molecules taking place at relatively few sites with long chain loops extending into the solution. Silberberg [117] predicts from a theoretical study that adsorption would be characterised by short stretches of segments attached to the surface and only short loops extending into the solution. He does say that an adsorption model like Pugh's is possible on initial adsorption but only as a non fully equilibrium adsorption.

Some adsorption isotherms of polymers on powders have been reported [118, 119] and the adsorption data is of a Langmuir type. Koral, Ullmann and Frisch [118] found that the physical adsorption of polyvinylacetate from carbon tetrachloride on to iron powder, increased with temperature.

For the adsorption to take place, the free energy change must be negative, the heat of adsorption is in this case positive and so $T\Delta S$ must be positive and greater than ΔH for

$$\Delta G = \Delta H - T\Delta S$$

This, they say, can be so for the adsorption of one polymer molecule on several adsorption sites releases several solvent molecules which were interacting with the polymer back into true solution i.e. there is a net entropy increase. The adsorption of polymethylmethacrylate from solution on to powders of iron has been investigated by Ellerstein and Ullman [119] using infra-red absorption. The polymer solution was shaken with iron powder for 14-18 hours and the supernatent liquid was studied using infra-red absorption. Thus changes in the absorbance peak height of the 5.75 carbonyl line was related to polymer concentration. After calibrating with known concentrationa the isotherm was plotted. A Langmuir type isotherm was obtained and adsorption decreased with increase in temperature using solvents of xylene, benzene, chloroform and toluene. Some difficulty was found with reversibility but apparent reversibility was obtained on going from a lower to a higher temperature.

The influence of temperature on the boundary lubrication of polyglycolethers has been studied by Cowley, Ultee and West [120]. Using a reciprocating Bowden-Leben type machine, ball bearing steels velocity 33 cm/sec. and a load 19.5 Kg. with a heating at 4 C°/min, they found a failure temperature at 146°C. They also studied the affect of molecular weight and found a linear correlation between increasing failure temperature with increase in the average molecular weight of the polyglycol fluid.

The measurement of the coefficient of friction under boundary lubrication has been studied by Gisser and Petronio [121]. A modified Bowden-Leben machine was used using a 440 C stainless steel ball (17% Cr, 1% Mn, 1%C) and S.A.E. 1020 steel (a 0.2% carbon steel) or glass as the friction plate, the tests were carried out at room temperature. The polymers used were poly (N alkyl) methacrylates (see Table I) and the effect of the length of the alkyl group of the ester side chain on the coefficient of friction was studied. Solutions were made up 1 mg/ml concentration in xylene and the graph coefficient of friction agains alkyl chain length is shown in Fig. 22.

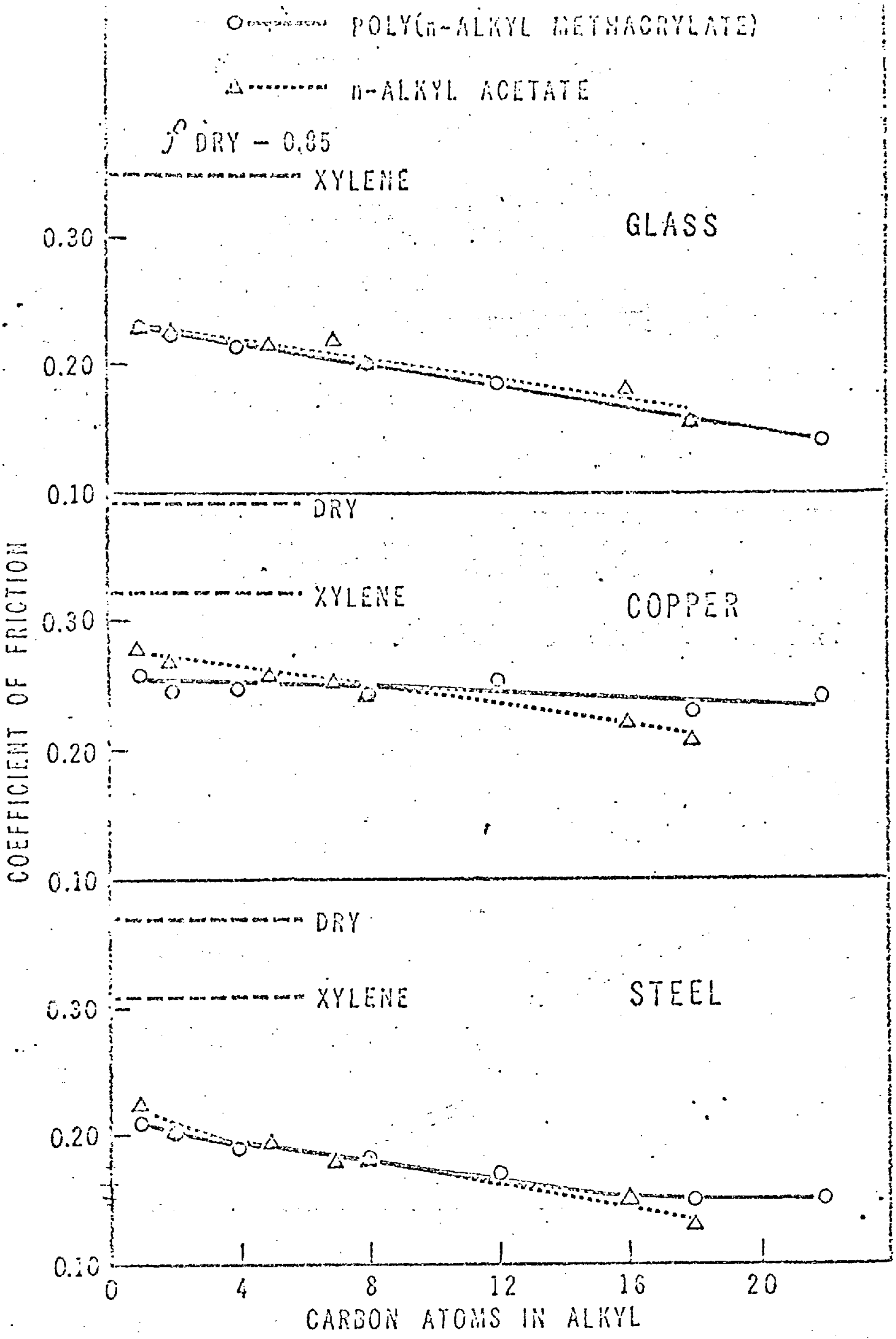


Fig. 1 Coefficient of Friction with 0.1% Poly(n-alkyl methacrylate) and n-Alkyl Acetate in Xylene with Stainless Steel Rider. Effect of Length of Alkyl Group.

Figure 22 from ref. 121

It is seen that the coefficient of friction decreases with increase in alkyl chain length. Glisser attributes this to alkyl group interactions.

It was decided that it would be interesting if these same polymers used by Gisser were subjected to a Bowden-Leben friction temperature test. Thus the temperature of failure of the lubricant film (if any) could be compared with the alkyl chain length of the poly (N alkyl) methacrylate, and the importance of such temperature friction effects discussed in the relation to the the existing use and further possible use of polymers as lubrication and wear additives, especially in respect of lubricants used in high temperature applications.

Experimental

The Bowden-Leben machine was used to measure the friction temperature characteristics of the series of poly (N alkyl) methacrylates listed in the table.

Solutions of the polymers were made in xylene at a concentration of 1.0 mg in 1 ml of xylene. The polymers dissolved readily.

The experimental conditions were as follows.

Frictional pair	18/8 stainless steel plate and ½" diameter tungsten carbide ball. Sliding friction only
Load	5½ lb vertical
Speed	.02 cm/sec
Heating	continuous increase in temperature for each run.
Method	a single pass of the plate only was taken.
Cleaning	the plate was cleaned using acetone and finally SiC papers to final paper 400 [this gives a surface

finish ≑ 10 micro inches] The ball was cleaned using acetone and paper tissues and cleanliness was checked by measuring the static coefficient of friction between slider and rider before the run was commenced.

Lubricant The properties of the polymers are given in Table I at the beginning of this chapter, and are used as 1% wt/wt solutions in xylene.

Experimental: Analar xylene was used as solvent and no transition temperature prior to complete evaporation of the xylene was found. The test procedure was the same as that used for the fatty acid alkane solutions described in Chapter 3. The friction was found to be independent of the time allowed for adsorption. Tests were begun ten minutes after the application of the solution. It is noted that Gisser allowed ten seconds before testing. A difference between these tests and those of Gisser and Petronio's [121] is the choice of the frictional pair. The polymer lubricants are poor lubricants. When a ball of stainless steel was used scratches would occasionally occur so that the rest of the pass could not be used. The ball was therefore replaced with a similar ball of tungsten carbide and in this way friction measurements along the plate were not dependent upon earlier values. The steel plate used was stainless steel 18/8 as in the fatty acid/alkane experiments.

At least three runs were taken for each experiment.

Results: It was found that the poly (N alkyl) methylacrylates in solution in xylene exhibited a friction-temperature transition. Fig. 23 shows a graph of the main results.

Friction - Temperature Curves for

Poly (n.alkyl) methacrylates in Xylene 1·0mg/ml xylene

Velocity 0·02 cms/sec, $\frac{1}{2}$" WC ball on 18/8 steel.
load 5·5 lbs normal load. Average of at least 3 runs.

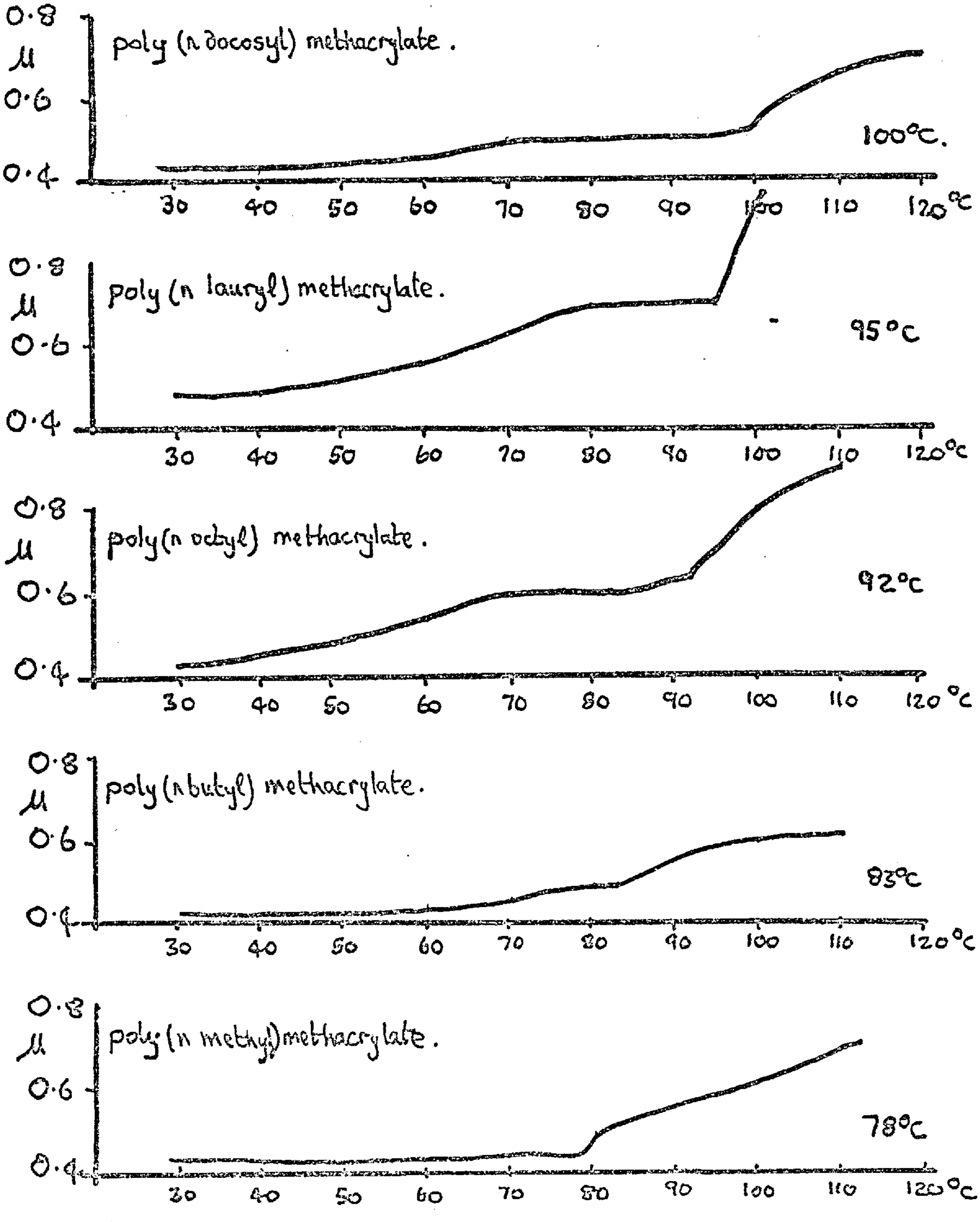


Fig 23.

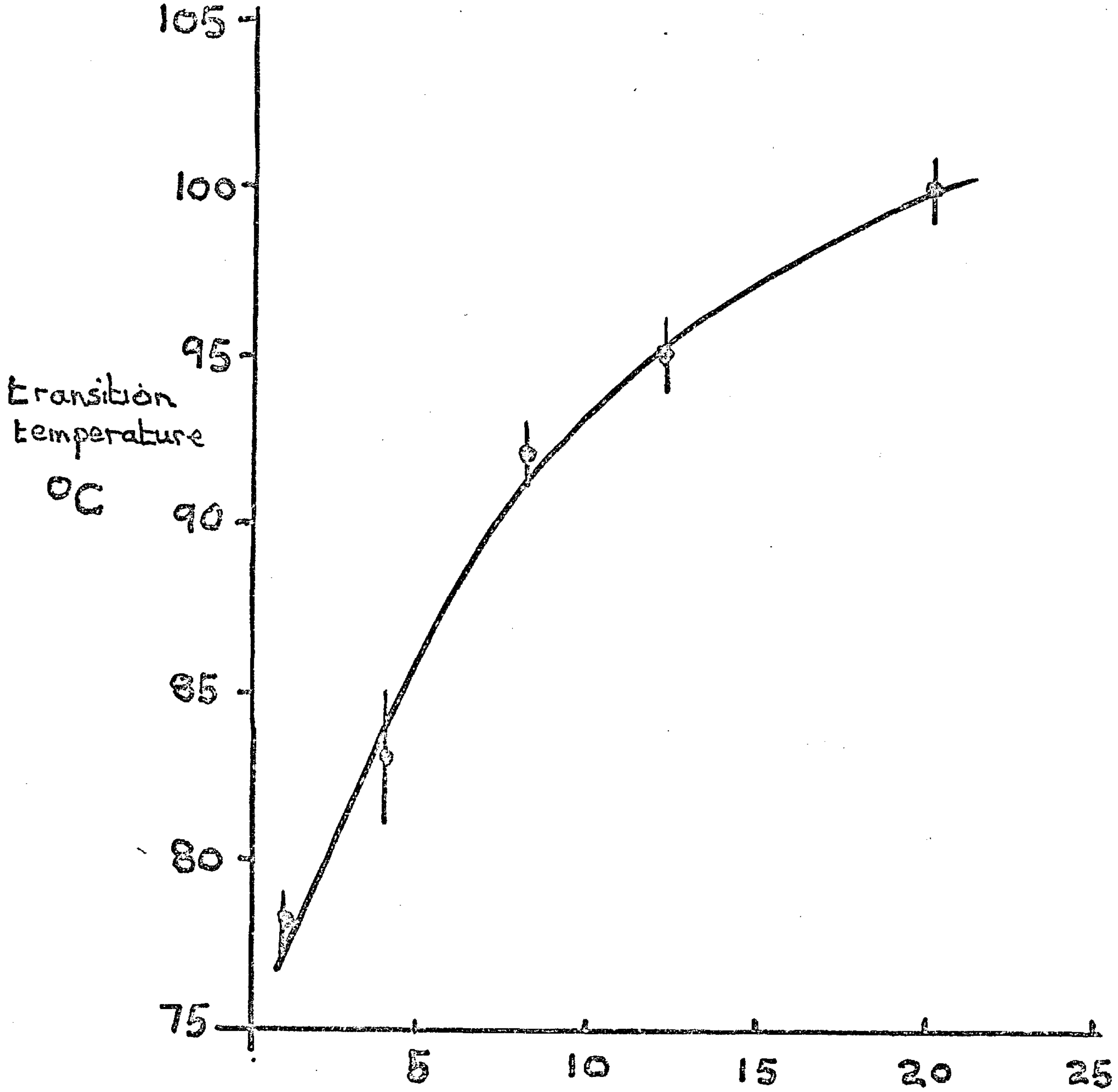

transition temperature °C
105
100
95
90
85
80
75
5
10
15
20
25
No. of carbon atoms in alkyl chain of ester group of poly(n alkyl)methacrylate.

Fig 24.

Fig. 24 shows a graph in which the critical temperature is plotted against the number of carbon atoms in alkyl group of the ester side chain.

Discussion of Results

It is seen that poly (N alkyl) methacrylates in solution in xylene exhibit transition temperatures. The longer alkyl chain length increases the resistance to lubricant breakdown. This is in agreement with the results of Gisser and Petronio [121] who found a decrease in the coefficient of friction with increase in alkyl chain length. The variation of the coefficient of friction with alkyl chain length was not investigated in detail, in the friction temperature measurement, indeed it is seen that the order changes with temperature. Gisser used much smoother surfaces and a harder substrate. It is noted that if further experiments were made, the contribution of the chain length to increased rigidity of the film could be measured as an increase in the heat of adsorption, by measuring friction temperature breakdown at different concentrations provided, that is, that the adsorption is physical.

The adsorption of the polymers may be an important factor in the lubrication of petrol and diesel engines especially in its possible interactions with other polar compounds such as boundary lubricants.

Conclusions

The coefficient of friction of a series of poly (N alkyl) methacrylates in solution in xylene was measured as a function of temperature between a tungsten carbide rider and a stainless steel plate. The transition temperature increased with the length of the ester side chain.

The adsorption of the polymers may be an important factor in lubrication especially in its possible interactions with other polar compounds such as boundary lubricants.

CHAPTER 5

Transition Temperatures of Oils

The importance of experiments determining friction temperature characteristics of lubricating oils is apparent after searching the literature on the failure of gears, discs and four ball machines by scuffing and siezure. A brief survey is, therefore given.

In 1937 Blok [122] applied equations he had derived for the temperatur developed between gear teeth to the experimental results of Almen who had used automobile spiral gears, and showed that the temperature developed at the gear teeth interface could be correlated with the scuffing load. This temperature comprises two summed parts: the bulk temperature of the gears and the flash temperature. The flash temperature is the change in temperature at the surface due to frictional heating and is dependent upon the amount of friction and the heat transfer properties in the region. It is usually positive. One form of the equation for the calculation of the flash temperature T_f of gears is given by Blok [123]:

$$T_f = 0.62 \frac{f}{b} W^{3/4} \quad (U_1)^{1/2} - (U_2)^{1/2} \left(\frac{E_R}{r}\right)^{1/4}$$

f = coefficient of tooth friction at incipient scuffing

b = thermal contact coefficient $(\lambda \rho C)^{1/2}$

λ = thermal conductivity of tooth face material

ρ = density of tooth face material

C = specific heat of tooth face material

W = actual tooth load per unit width in meshing position considered

U_1, U_2 = tangential speed of tooth faces perpendicular to the line of action

E_R = reduced Young's modulus of tooth material

r = conformity radius of contact.

This expression is given to illustrate the parameters required to make the calculation although alterations have been made to the equation to include other variables such as surface finish [124].

The surface temperature T_c is given by

$$T_c = T_b + T_f$$

T_b is the temperature of the gear wheels.

Other expressions may not specify T_B the temperature of the gear wheels but include it as a function of the oil temperature.

A number of approved standard gear and disc test machines are used to evaluate the suitability of oils. In each case the test specimens are carefully specified for shape and material.

In England the IP/IAE [125] test rig is in common use and comprises a matched pair of gears which are run to failure.

In America the Ryder [126, 127] gear test rig is in common use and in Germany the F2G [128, 129]. The following conditions are made for the I.A.E. rig:

pinion speed, initial oil test temperature, oil flow rate, initial load, load increment, running period and rest period.

> Scuffing is identified by visual examination during a rest period although onset of scuffing may be noticed during a running period.

The Ryder machine or Erdco Ryder machine specifies a similar testing procedure, the scuffing point is defined as the point at which 22.5% of the working tooth area is scuffed.

The designs of the Ryder and I.A.E. gear machines are different so that heat transfer rates would not be expected to be the same. The F.Z.G. gear tester is similar to the I.A.E. and Ryder, however, in the F.Z.G. test, the gears are flooded with oil up to their centres and the oil temperature is kept constant for the first five readings. Thus, unfortunately, the standard test rigs do not measure sufficient variables for the critical temperature theory to be applied, this is a pity especially since the evaluation of lubricants using the three test rigs does not often correlate and a new theory is required.

The Institution of Petroleum Gear Rig Test Sub-Panel correlated results from I.A.E. and Ryder gear rigs and found no statistical significant correlation between the results from the machines under some similar test conditions, Fig. 25 is a graph taken from the Sub-Panel report [130].

RESULTS FROM RYDER AT 10,000 rev/min, 74°C COMPARED WITH RESULTS FROM IAE AT 6000 rev/min, 70°C.

Reference	Oil	Ryder lb/in	IAE lb
6	M MIL-L-6082 Grade 1065 mineral	1668	26
	O MIL-L-7808	3200	68
3	MLO-57-101 (di-2-ethylhexyl sebacate)	2465	10
	MLO-57-102 (MLO-57-101 + 6 per cent dioctylphosphite)	1975	68
	Ref Oil B, MIL-O-6082 Grade 1100 mineral	2690	52
	Phenyl methyl silicone	3730	15
	PPO 500, MIL-O-6082 Grade 1065 mineral	2300	32
	GTO-133, MIL-L-7808 diester base oil	2160	32
	O-56-62, MIL-L-25336	4120	40
	MIL-O-6086 Grade M petroleum gear oil	3500	40

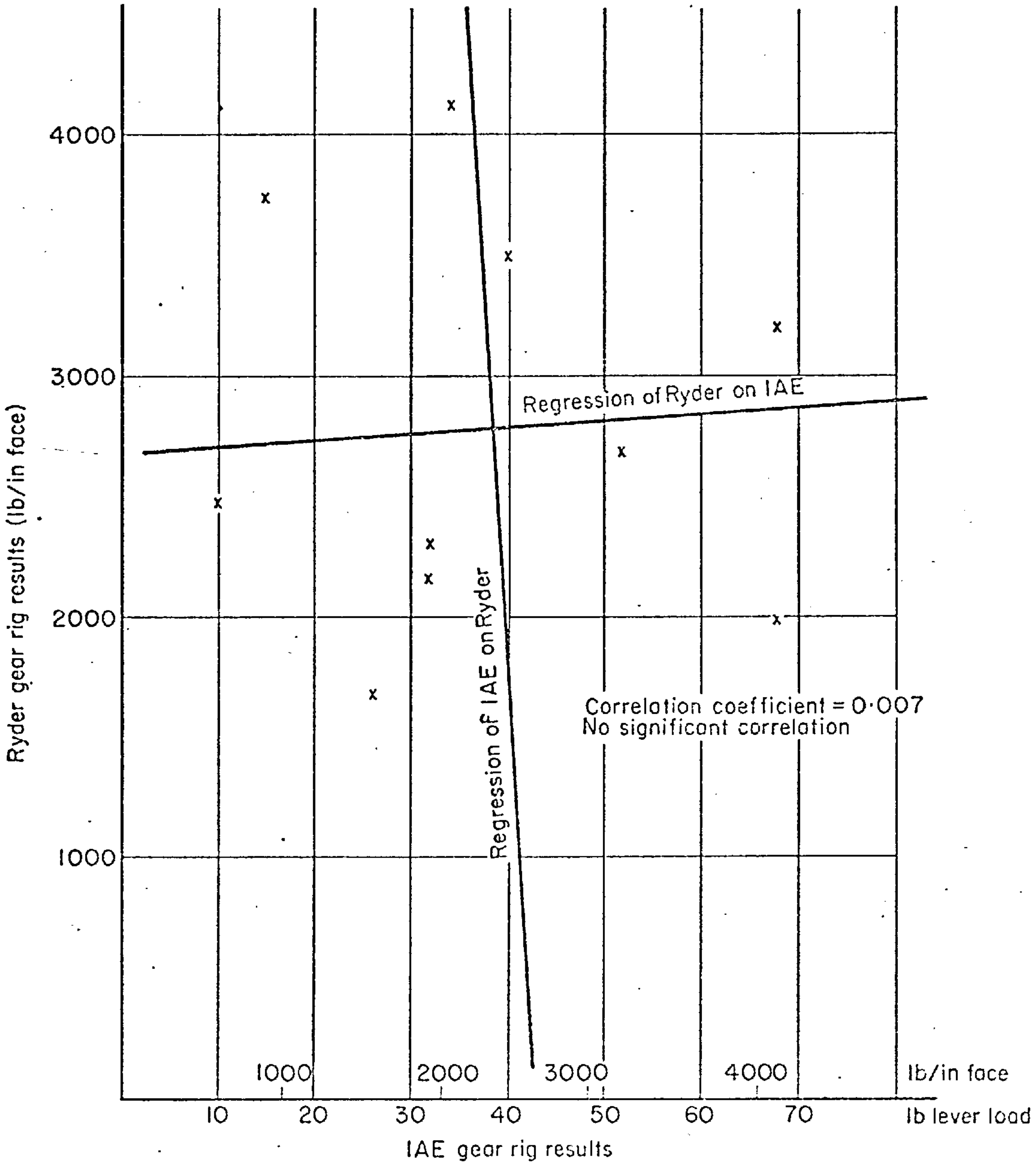
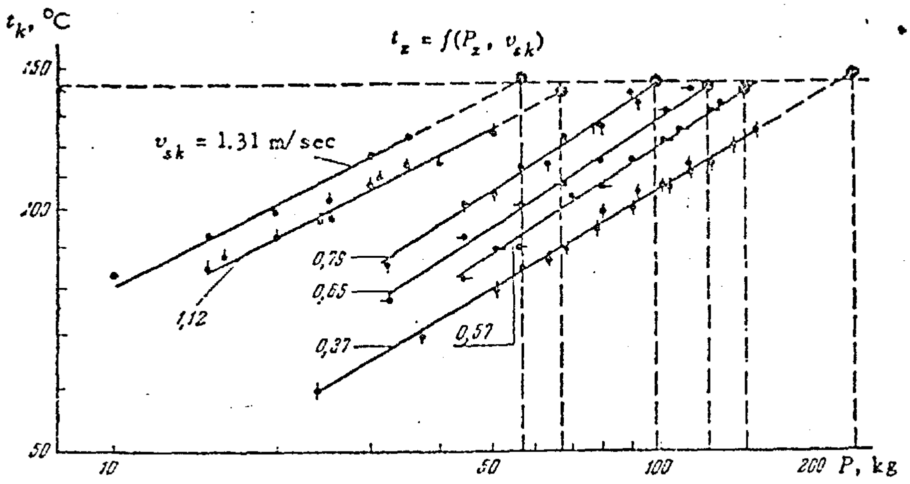


Fig 25 Correlation between Ryder Gear Rig results, and IAE Gear Rig results at 6000 rev/min, 70°C

Support for the critical temperature theory of scuffing is thus the result of investigations by workers using machines of their own design or modified machines. It must be mentioned too that it is not easy to obtain the data for a correlation with much accuracy. Kelly and Lemanski [131] observe that a 0.001 radian misalignment under 100 lb in^{-1} load causes the maximum unit load to be 25% greater than if the load was uniformly distributed.

Considerable evidence in favour of a temperature theory of scuffing exists and the critical temperature is seen to lie in the region 150 - 200°C for mineral oils.

Meng [132] has investigated Blok's theory. Meng used a roller testing machine equipped with rollers of two different steels so that a natural thermocouple was produced, mineral oils were used as the lubricant. Fig. 26 shows Meng's main results. It is seen that seizure commences at a definite temperature t_z, independent of the sliding velocity



DEPENDENCE OF CONTACT TEMPERATURE BEFORE SEIZURE, t_z, ON SEIZURE LOAD, P_z, FOR DIFFERENT SLIDING VELOCITIES

Fig. 26 taken from ref. 132

It is stressed that temperature t_z is a measurement and not calculated using a flash temperature equation.

The use of the natural thermocouple has also been extended to gears. Niemann and Lechner [133] used this method in their large test programme of gear testing. They found a good correlation between scuffing load and the temperature, but on computing the Blok equation temperatures T_oMAX, they found that whilst scuffing could be correlated well with the mean tooth temperature T_m, only poor correlation was found with the calculated Blok temperature T_oMAX. Fig. 27 is taken from one of their papers [134]

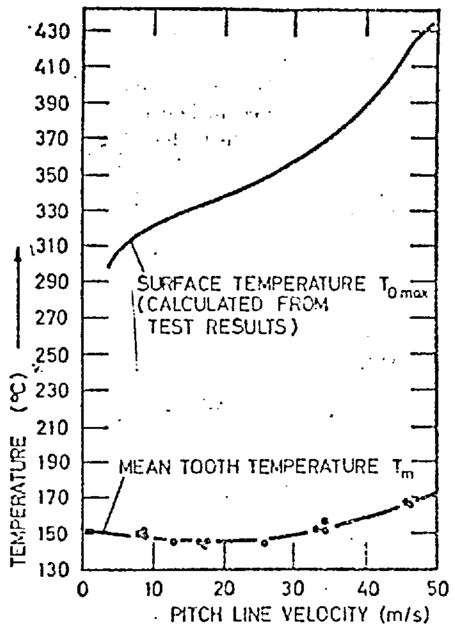
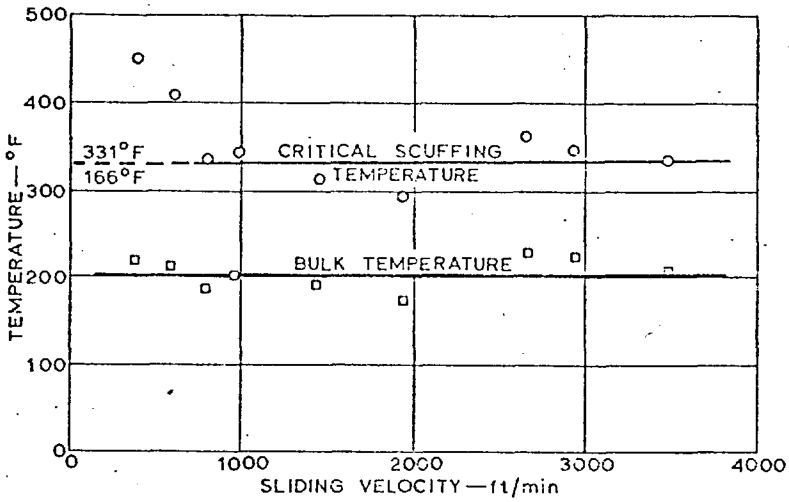


Fig. 27 taken from ref. 134

In many tests, however, the calculated flash temperature is a constant value of the bulk oil temperature, so that a graph of the calculated surface temperature plotted against speed for gear and roller tests is parallel with the bulk oil temperature. This is so in O'Donoghue and Cameron's paper [135] where a good correlation was found between critical temperature and scuffing. These results were obtained by calculation of data published by DeGruchy and Harrison of tests on an I.A.E. gear machine, Fig. 28, [136].



Temperatures at scuffing calculated from reference (3).

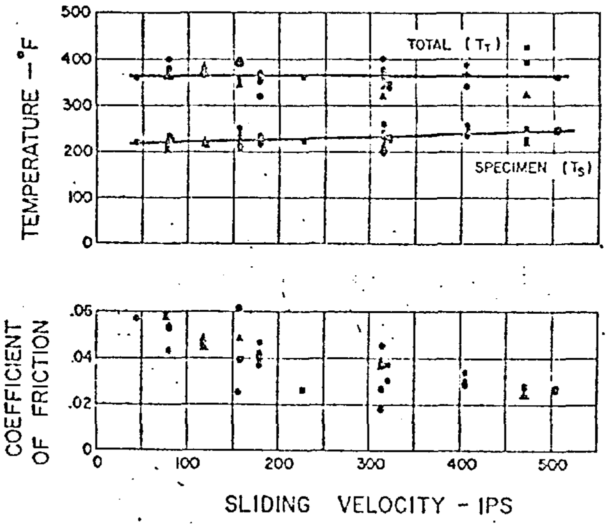
Calculated scuffing temperatures against sliding speed in discs from De Gruchy and Harrison's experiments (3)

<u>Fig. 28 taken from ref. 135</u>

DeGruchy and Harrsion measured the gear surface temperature using a trailing thermocouple, although O'Donoghue [137] has found that using trailing thermocouples a pressure too slight results in temperatures which are too low. Increasing pressure of the thermocouple against the surface causes frictional heating resulting in a temperature rise. O'Donoghue has also used thermocouples imbedded in the gear tooth.

In the tests of Leach and Kelley [138], the temperatures from a trailing thermocouple were compared with surface temperatures calculated from the knowledge of the temperature 0.25" inside the roller given by imbedded thermocouples. With the use of heat exchangers they kept the oil temperature constant and found at 160°F a non uniform error between the two surface temperature measurements of ± 50°F, however, working at 180°F the error was negligible and in this region they obtained good evidence for the critical temperature theory for rollers. Fig. 29 shows the correlation for three straight mineral oils containing no additives, their viscosities are as follows taken at 100°F and 210°F.

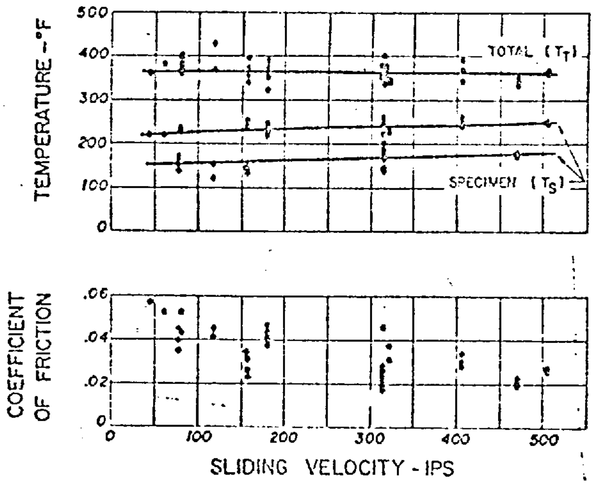
A	30.0	and	4.5
B	106.0	and	10.4
C	195.0	and	15.0



Effect of viscosity grade on the maximum mean contact temperatures at failure and coefficient of friction; Oils A (○), B (◇), and C (▣).

<u>Fig. 29 taken from ref. 138</u>

This graph has been taken from ref 138. Figure 30 also taken from ref. 138 shows the effect of roller temperature at failure obtained by keeping the bulk oil temperature at a constant value.

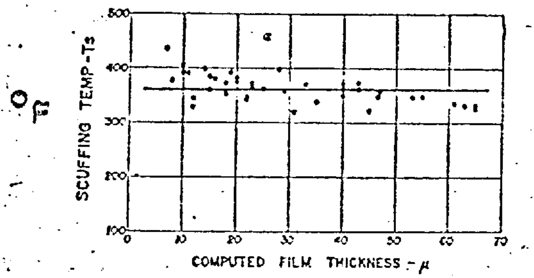


Effect of specimen temperature on the maximum contact temperatures at failure and coefficient of friction; oil A. Bulk temperature: ○ 180 F; ◇ 60 F.

<u>Fig. 30 taken from ref. 138</u>

The total temperature calculated seems to give a better correlation than the specimen temperature with scuffing, this conflicts with Niemann and Lechner's [134] tooth temperature criterion of failure, although the two curves in this graph are parallel unlike Niemann and Lechner's results. Thus whilst agreement is found for a temperature of failure criterion more work needs to be done on measurements and calculations.

Important data given by Leach and Kelley [138] is the computation of the film thickness at the point of failure using elastohydrodynamic theory, i.e. using the method given by Dawson and Whitaker [139]. The graph shows the computed elastohydrodynamic film thickness to be independent of film thickness at failure over a wide range; the graph is shown in Fig. 31.



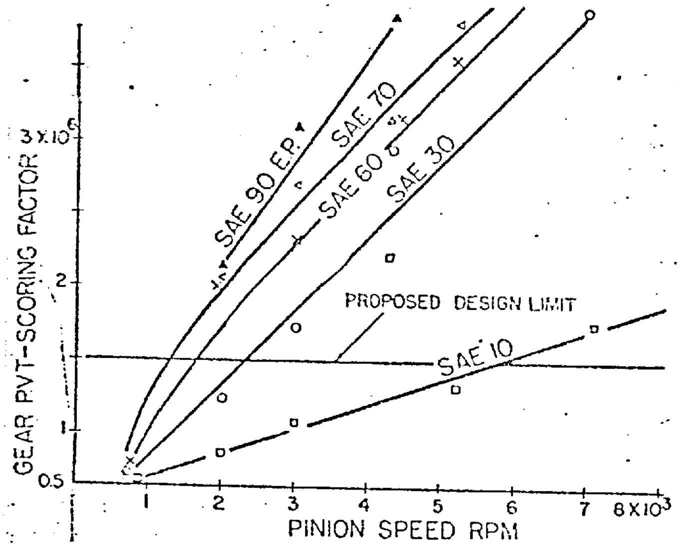
Independence of scuffing temperature to computed film thickness

Fig. 31 taken from ref. 139

Thus the hypothesis that failure occurs when the film thickness (as predicted by elastohydrodynamic theory) is no longer great enought to prevent metal to metal contact clearly does not apply in these tests. Another criterion of predicting gear failure is the P.V.T. method proposed by Almen [140] in 1948. A critical value was given for the product P.V.T. above which failure was likely to occur.

P - compressive Hertzian stress
V - tooth sliding velocity
T - the length of action measured from the pitch point to the end of contact

Shipley [141] applied the P.V.T. theory and the critical temperature theory to his experiments on scuffing using gears. Fig. 32 shows the P.V.T. criterion of failure compared with actual results, and Fig. 33 shows the results plotted this time using the temperature theory of failure using a modified Blok equation developed by Kelley [142].



Scoring test 17 to 19 ratio gears using PVT method.

<u>Fig. 32 taken from ref. 141</u>

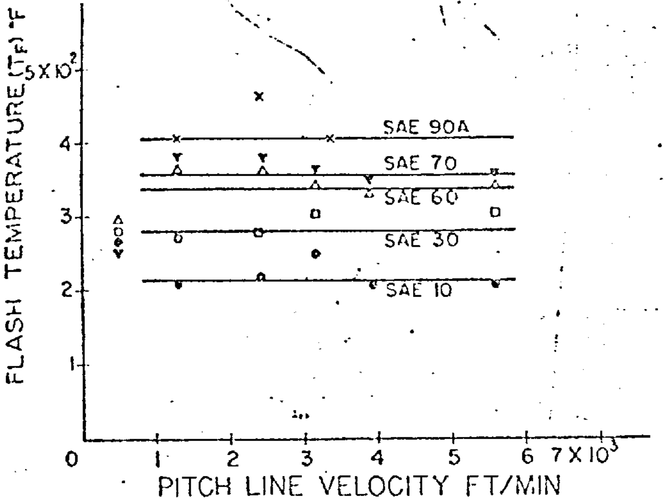
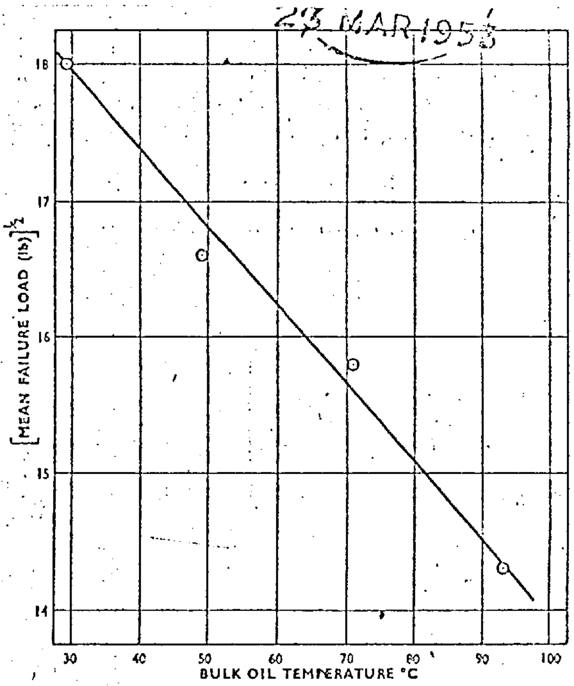


Figure 6. Scoring test results 17 to 19 ratio gears using Kelley's formula.

<u>Fig. 33 taken from ref. 141</u>

(Flash temperature in Shipley's nomenclature means the total temperature at the surface, i.e. surface temperature of the blank plus Blok's temperature rise.) It is seen that the P.V.T. correlation is very poor, whilst good correlation is found for the critical temperature hypothesis.

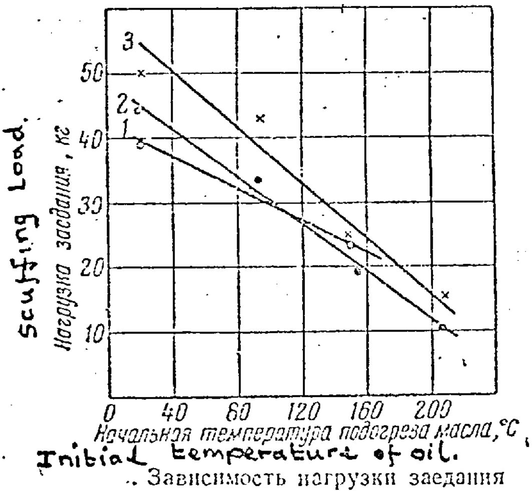
The critical temperature hypothesis may also be demonstrated by varying the bulk oil temperature and noting the change in the failure load. Thus Lane [143] has plotted the square root of scuffing load against bulk oil temperature for a two ball machine seen in Fig. 34.



Variation of failure load with bulk oil temperature. Sliding velocity 172 ft/min. Duration of run 50 sec. Oil viscosity 15 cS at 60° C.

<u>Fig. 34 from ref. 143</u>

A straight line has been obtained. Matveevsky [144] has also made similar experiments using a four ball machine. Fig. 35 shows some of his results.



.. Зависимость нагрузки заедания от начальной температуры для трех минеральных масел:

1 — трансформаторное; 2 — МСГ; 3 — МКЭ.

<u>Fig. 35 taken from ref. 144</u>

Returning to Fig. 33 from work done by Shipley [141], it is seen that the type of oil seems to affect the value of the scuffing temperature. A correlation of the oil type, specified by its viscosity as part of the critical temperature theory of scuffing has been given by Lane and Hughes [145].

Their work, using an I.A.E. gear machine is based on Blok's equation for gears which Blok [142] has modified to

$$t = C_t f \, (P^3 N^2)^{1/4} \qquad \text{.......} \ (1)$$

t is the flash temperature

C_t is a constant for the gears used

P is the total circumferential load on the gears per cm. of face width of the gears

N is pinion speed r.p.m.

f is the coefficient of friction

Thus the critical temperature t_c is given by

$$t_c = t + t_o$$

where t_o is the bulk oil temperature.

Let the scuffing load be W, the load on the lever and assume the coefficient of friction is constant under non scuffing conditions.

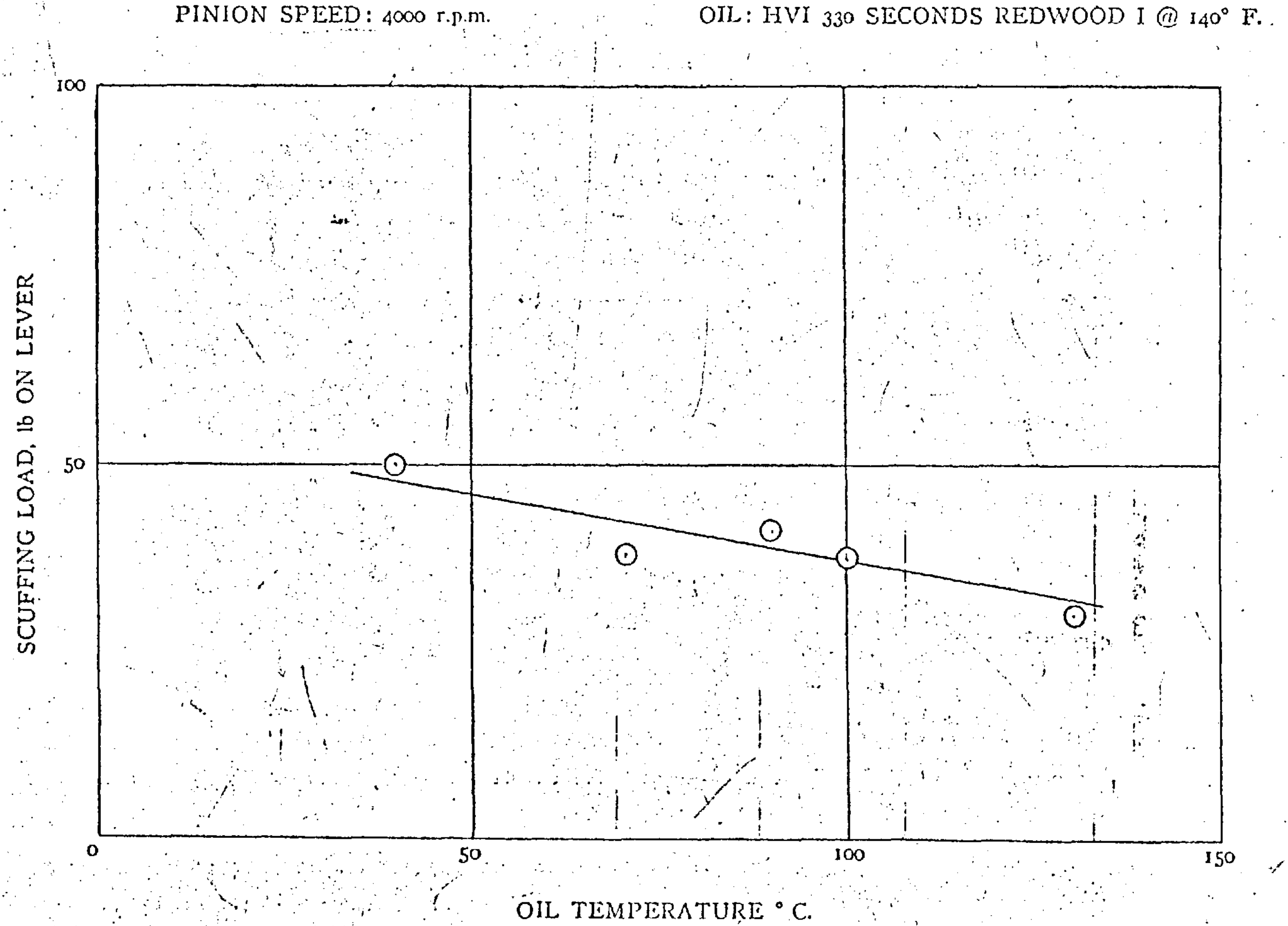
Therefore applying the critical temperature hypothesis, scuffing occurs when $t = t_c$.

Hence at scuffing

$$N^{1/2} W^{3/4} = \text{constant}$$

$$\text{i.e.} \quad N^{2/3} W = \text{constant}$$

Fig. 36 shows the log. scuffing load plotted against the logarithm of the pinion speed for two oils. The slopes of the curves are found to be approximately -2/3, confirming the theoretical value,



Effect of oil temperature on scuffing load.

<u>Fig. 36 taken from ref. 145</u>

Fig. 37 gives the variation of scuffing load with the viscosity of the oil and their method of correlating oil type with viscosity is based on this approach.

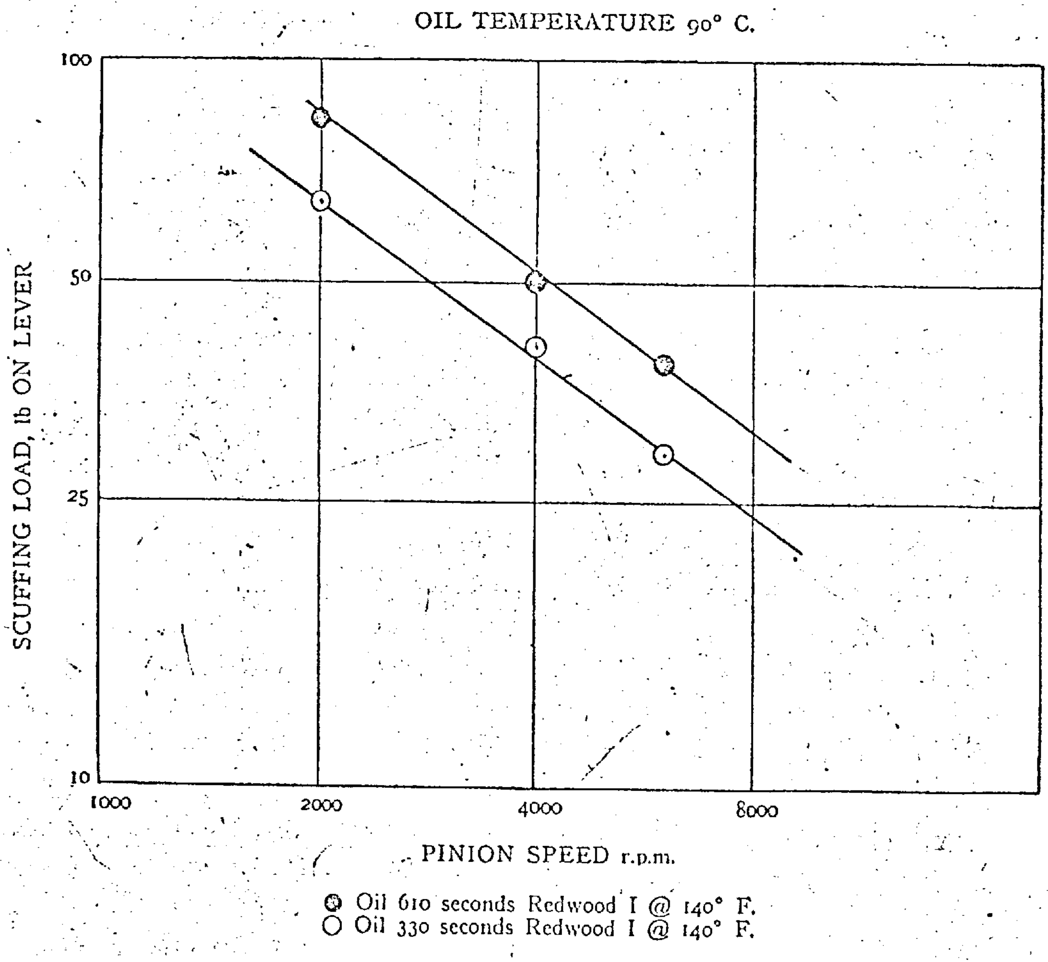


Fig. 37 taken from ref. 145

It is seen that scuffing load varies as the square root of the nominal viscosity (140°F).

Hence $W = mZ^{1/2}$

where Z = the viscosity

It is interesting to note that Fowle [146] has also obtained a similarly shaped curve.

Thus $t_c^{1/3} = bZ^{1/2}$

but

$$t = t_o + C_t f(P^3 N^2)^{1/4}$$

at scuffing $P = kW$ and $t = t_c$.

Therefore

$$W \doteqdot JN^{-2/3}(t_c^{4/3} - \frac{4}{3} t_o t_c^{1/3})$$

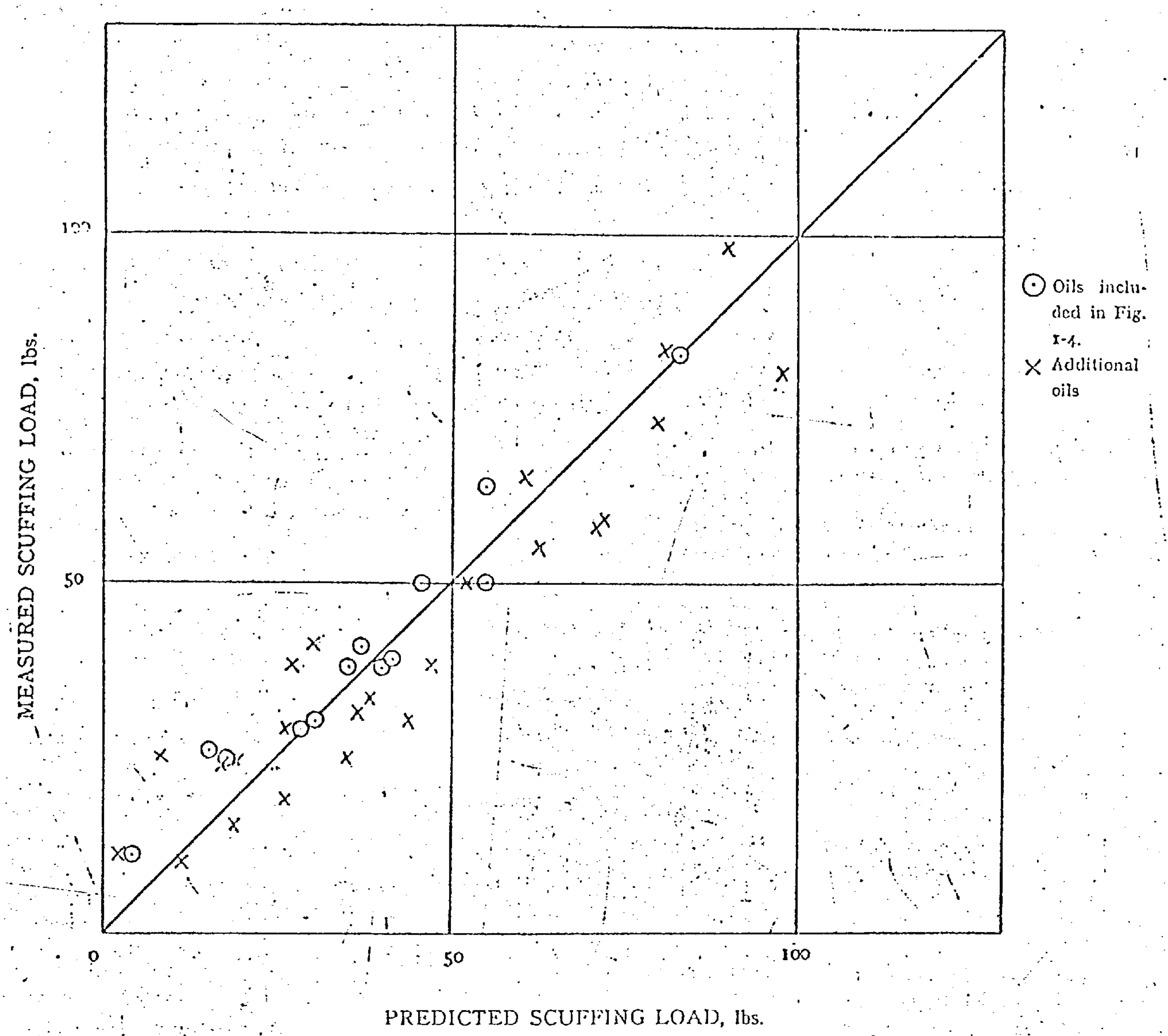
where J is a constant.

Substituting for viscosity and letting values of $Z^{1/8}$ be considered as a constant

$$W \doteqdot N^{-2/3}(AZ^{1/2} - B\theta_o)$$

The constants A and B were evaluated from the graph oil temperature against scuffing load Fig.

This equation was then used to predict the scuffing load of eight other oils and a graph, fig. 38, shows the predicted result plotted against the experimental values. A good correlation is obtained.



Comparison of predicted and measured scuffing loads.

Fig. 38 taken from ref. 145

Ali and Thomas [147] have also investigated the critical temperature hypothesis of scuffing using a disc machine. Fig. 39 shows their main results, the scuffing temperature has been calculated from the formula given by Blok. Except for low sliding velocities a critical temperature is clearly evident.

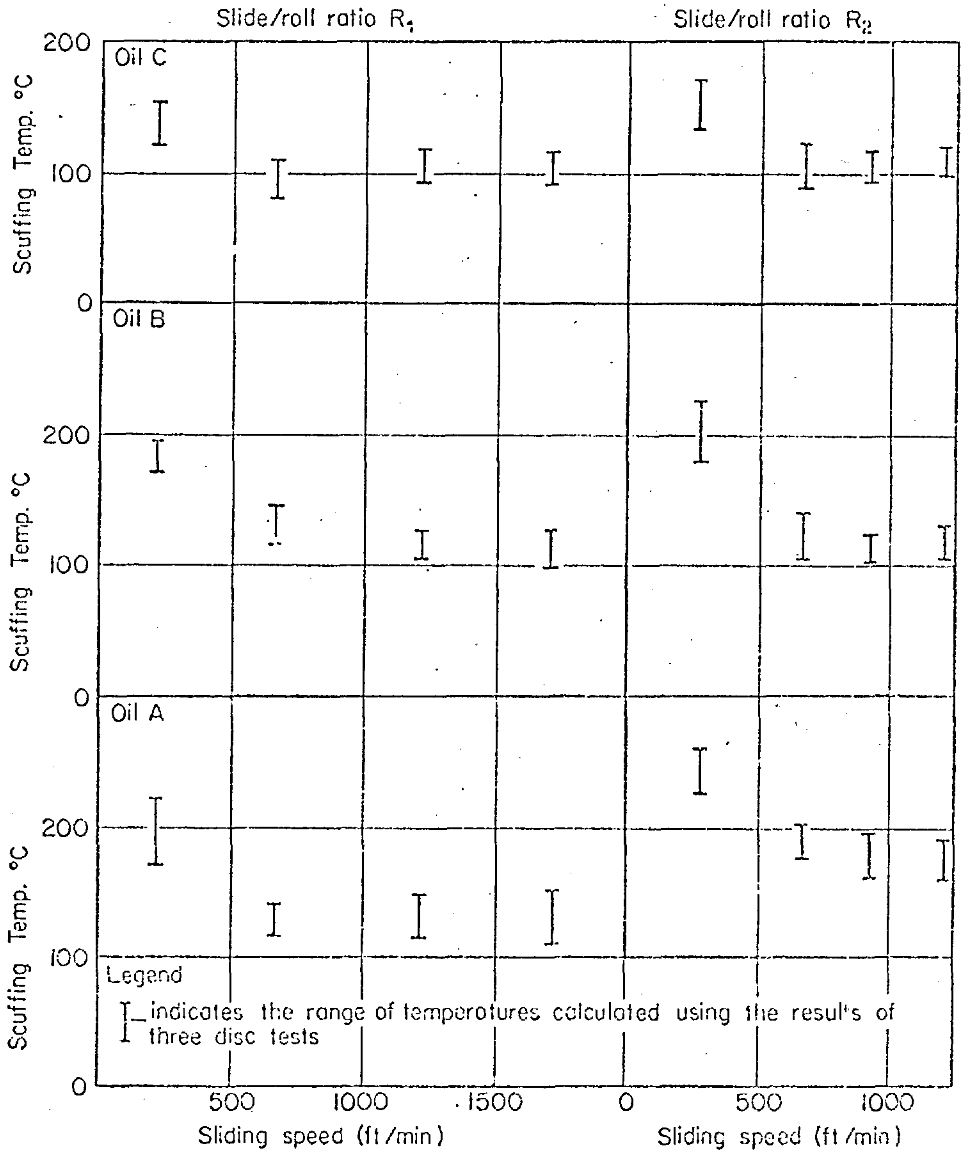
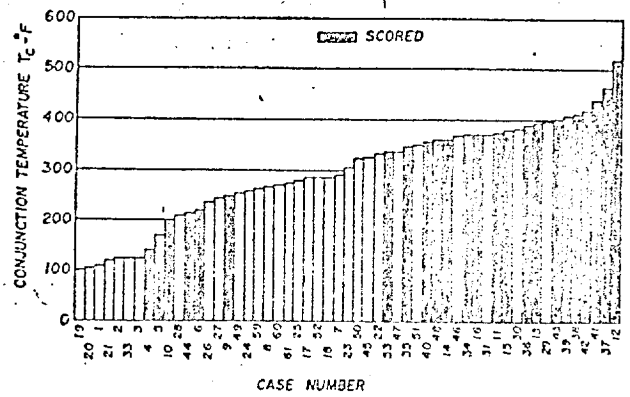


Fig. 39 taken from ref. 147

The critical temperature hypothesis of scuffing has been discussed in a review article on the lubrication of involute gearing by Kelley and Lemanski [131] and includes effects of surface finish and misalignment. Fig. 40 shows the results of 'field' tests carried out on aircraft gears. Fifty five cases were considered.



Computed temperatures with variable coefficient of friction

Fig. 40 taken from ref. 131

They found that where the aircraft gear conjunction temperature exceeded 350°F, failure was very likely. Of the values below 350°F three of the cases 4, 5 and 6 were operating under different conditions and should possibly have been excluded from the table.

Much work, therefore, has been done in support of a hypothesis for a critical temperature at which mineral oils no longer lubricate. The critical temperature at which this happens is in the range 150-200°C.

Such a finding, however, poses some questions:

Can a mineral oil ever work satisfactorily with the sump temperature above this critical value?

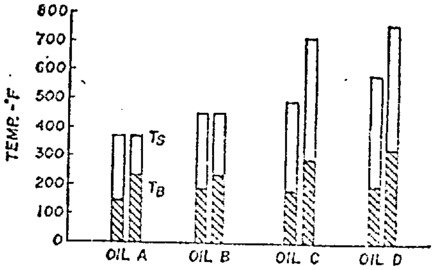
What is the action of e.p. additives?

Some results in support of the critical temperature theory were with additive oils. Thus Nemann and Lechner [133] were using a mild e.p. oil and Shipley [141] used an S.A.E. 90 e.p oil.

Certainly some engines run at oil temperatures well above 200°C without scuffing. It is clear therefore that the critical temperature theory of scuffing should include the effect of e.p. agents.

The influence of e.p. additives is seemingly rather complex, but in order to examine the mutual dependence of scuffing temperature and the action of e.p. additives some examples have been taken from the literature in the following chapters.

Fig. 41 is taken from Kelley and Lemanski's review paper [131]

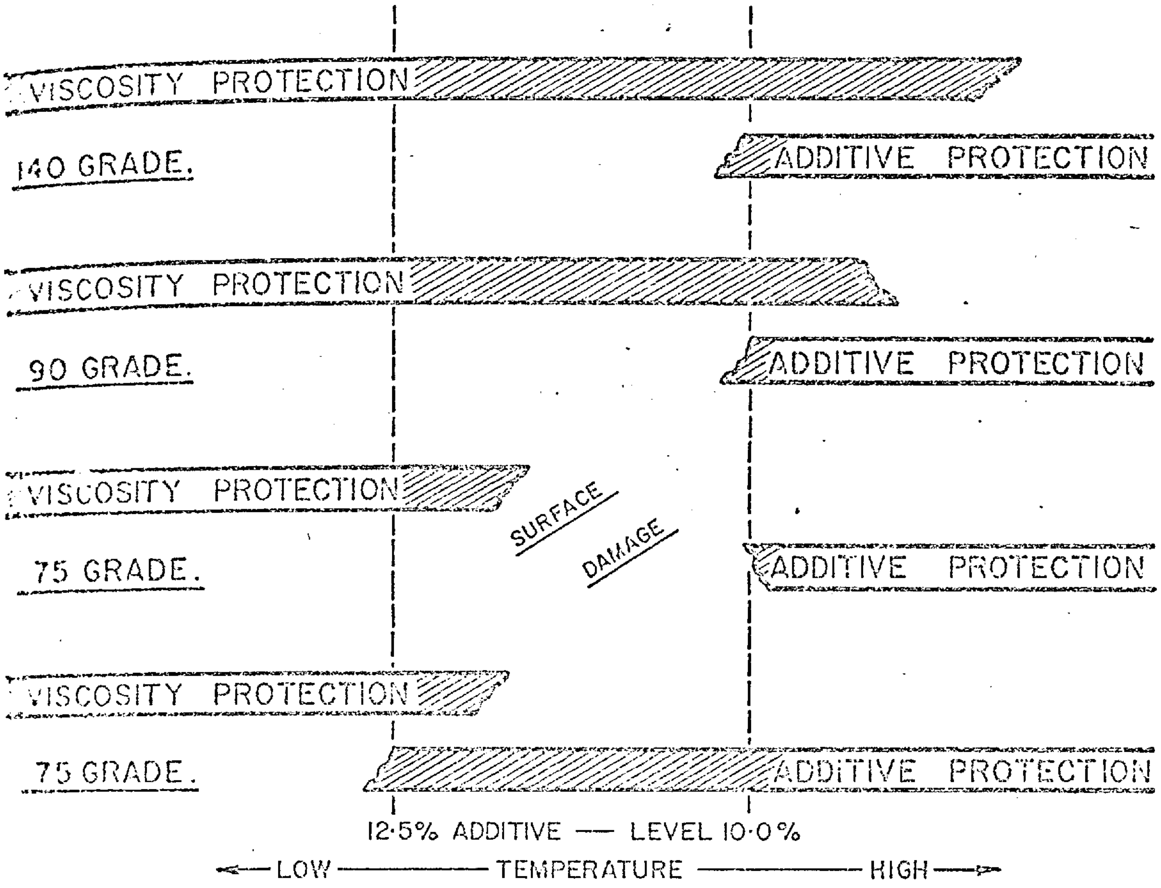


Influence of blank temperature on critical temperatures

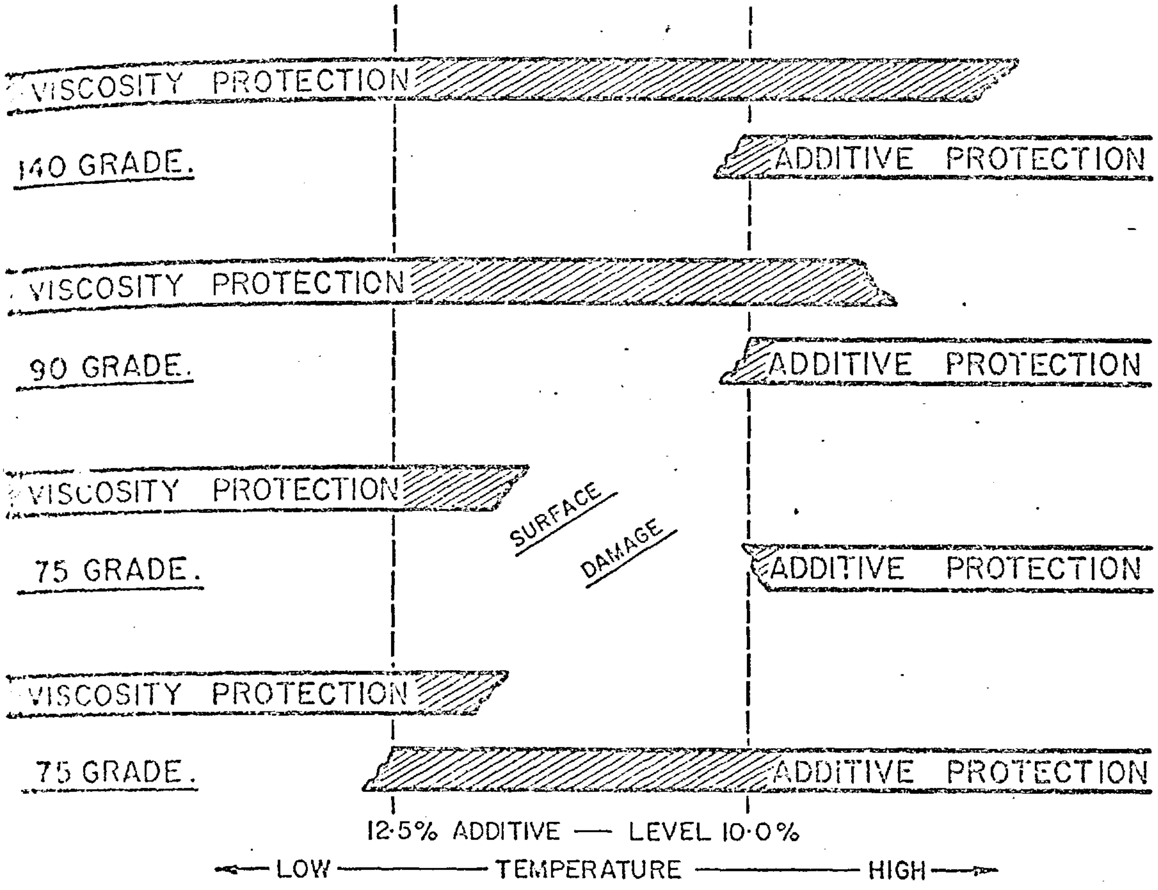
Fig. 41 taken from ref. 131

and four mineral oils A, B, C, D are considered. Oil B contains zinc dilhiophosphate and C and D sulphur phosphorus additives. The experiments demonstrate the effect of disc blank temperature on the critical temperature of failure. Oil A is a non additive oil and the total critical temperature remains unaltered by blank temperature in agreement with the work of Lane [143] and Matveevsky [144] previously discussed. Looking at the additive oils, it is seen that with a low blank temperature i.e. less than 200°F the additive does not have much effect and raises the critical temperature considerably.

This problem has been encountered in the operation of vehicles in cold climates where there is an additional restriction on using oils of sufficiently low viscosity. Whyte has called the effect a 'temperature gap' [148], Fig. 42.



Viscosity/additive gear tooth surface protection.

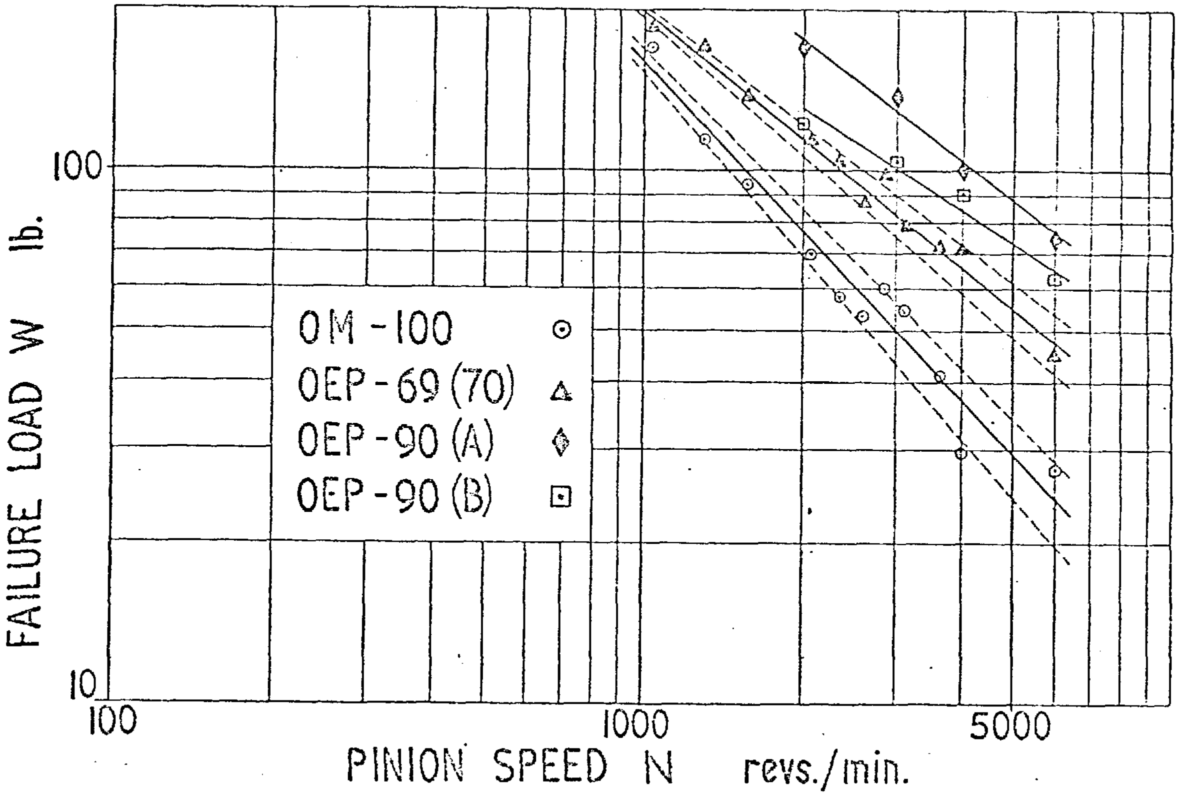


Viscosity/additive gear tooth surface protection.

Fig. 42 taken from ref. 148

There is a temperature gap because although a sufficiently high additive concentration may be added for low blank temperature operation as the axle heats up the additive becomes much more reactive and much corrosion occurs which is unacceptable.

This effect may also be seen from DeGruchy and Harrison's [136] results. Fig. 43.



Gear material EN34. Test oil flow 1 pint/min. Test oil temperature 70°C.

Fig. 43 taken from ref. 136

OM-100	is a mineral oil without e.p. additive
OEP-69(70)	is a mixed phosphorus, chlorine sulphur type additive oil
OEP-90(A)	is chlorine additive oil
OEP-90(B)	is a sulphur type additive oil.

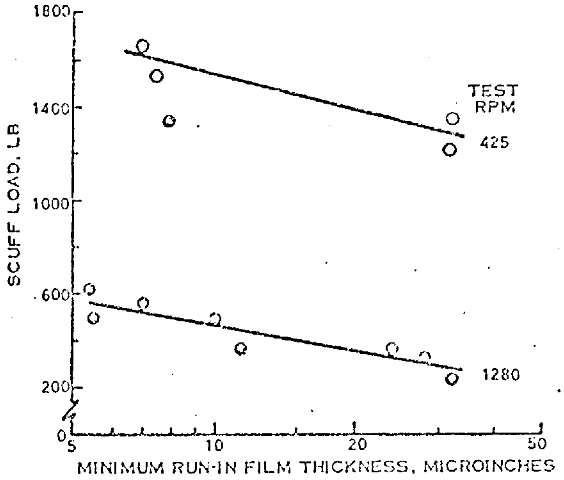
These results are taken from tests on I.A.E. gear machine and the oils are used as turbine oil lubricants. Thus increasing the pinion speed and hence the gear blank temperature, increases the effectiveness of the oil.

These important results will be considered in more detail in later chapters.

Mention must also be made of work which does not seem to support a critical temperature hypothesis.

Careful work has been carried out by Fein [149]. In his earlier experiments on four ball and disc machines he showed that the calculated critical temperature of scuffing increased with speed and viscosity and decreased with load. For any given 'non reactive' lubricant the reciprocal of the critical temperature in degrees Absolute varied linearly with the logarithm of the ratio of surface velocity to load. These results conflict with the work of Leach and Kelley in which the same lubricant was used and an almost identical machine. In his latest paper (1967) Fein discusses these conflicts and reports on many more experiments he had conducted in which the operating procedure was changed. He used ste loading, steps in speed, alternating temperatures and alternating load. A wide variation in critical temperatures were obtained. Fein, therefore, concludes that the apparent constancy of critical temperature for scuffing observed by some investigators was due to their choice of operating procedure, indeed, he accounts for his earlier correlations as being dependent on his choice of operating procedure. He concludes that the true critical temperature characteristic appears to depend upon the entire temperature, velocity, load velocity ratio, and time history of the test specimens, and that there is no simple load carrying criterion. In his investigation of the causes he found no metallurgical changes in composition of the steel to explain the behaviour and thought it was perhaps due to chemical reactions.

Attention is drawn to Fein's graph (Fig. 44) in which he calculated the minimum run in film thickness and plots this against the scuffing load which is later obtained.



Effect on load-carrying capacity of elastohydrodynamic film thickness during run-in. Solvent, neutral oil.

Fig. 44 taken from ref. 149

It is seen that a thinner film during running in is associated later with a higher scuffing load.

It will be seen later that this result as to the other effects are important in an explanation of scuffing.

This introduction is to show that experiments on determining the coefficient of friction of mineral oils and the variation of the coefficient with change in temperature might be of considerable value in the search for the mechanism of lubricant failure.

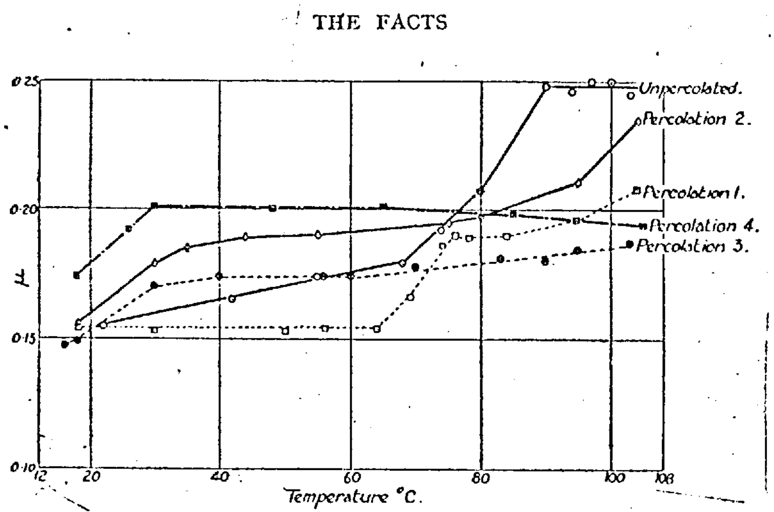
CHAPTER 6

Friction-Temperature Measurements of Mineral Oils

In the section concerned with the transition temperatures of fatty acid-alkane solutions it was seen that the presence of polar molecules on the surface could result in a low coefficient of friction under conditions of boundary lubrication.

The mineral oil fraction obtained from the crude oil normally contains polar compounds. Hardy and Nottage [150] had noticed this and carried out investigations which they published in a Technical Research Monograph in 1930. In their experiments on the analysis of commercial lubricating oils, a steel spherical slider and a flat plate were meticulously cleaned and placed at once in a chamber through which a current of clean dry air was passed. A drop of the oil was then placed on the plate and the slider was lifted by glass rods and moved so that the oil was distributed over the plate. A thread was attached to the slider and to the other end, via a light pulley, a scale pan was fixed. A fine stream of sand was then run in to the pan until the slider just moved forwards. The pan containing the sand was weighed and experiments were carried out at different temperatures. They stressed that the accuracy with which measurements could be made depended primarily on the cleanliness of the apparatus. Appendix I at the end of this chapter is taken from their paper and gives their cleaning methods. They next removed polar compounds from the oil by percolating the oil through glass beads or freshly drawn capillary tubing.

They used this oil for their friction experiments. Fig. 45 shows their results for a commercial oil B.



Percolation over Glass Beads : Oil B.
Percolated Oil. Readings in air.

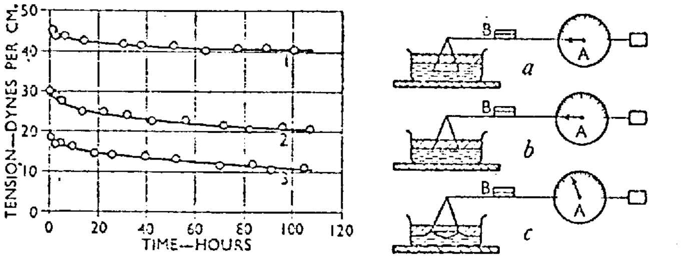
Fig. 45 taken from ref. 150

Consider the unpercolated oil first, this exhibits a friction rise from ≑ 70°C until ≑ 90°C, when the coefficient of friction becomes constant, it remains virtually constant to ≑ 108°C, the maximum temperature reached.

Percolation of the oil through glass beads raised the coefficient of friction at 30°C from 0.16 to 0.20 and further more the secondary rise in friction at 70°C - 90°C is now no longer present. The "percolation number" is the number of times the oil has been passed through a column of glass beads.

Hardy and Nottage [150] found that if the oil was left standing in a corked bottle at room temperature with air above the oil, it eventually recovered its lubricating properties.

Trillat [151] in 1937 measured the interfacial tension between oil and water using a ring tensiometer. Fig. 46 is a diagrammatic representation of the apparatus.

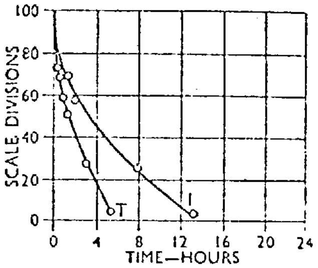


Interfacial Tension between Paraffin Oil and Water as a Function of Time

Modified Platinum Ring Method of Determining Interfacial Tension

Fig. 46 taken from ref. 151

The polar molecules present in the oil will preferentially absorb at the surface with the water, thus lowering the interfacial tension. The interfacial tensiometer measures the change of interfacial tension with time, i.e. the time required for the formation of the adsorbed layer. This is shown in Fig. 46.



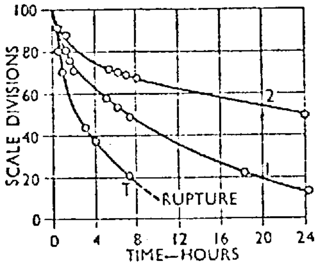
Effect of Passage over Metal Balls

T Fresh oil on water.

Fig. 47 taken from ref. 151

Trillat [151] used a commercial lubricating oil and Fig. 48 shows both the results obtained for the commercial oil and the effect of edgewise paper filtration, which decreases the polar content of the oil.

Trillat [151] then measured the interfacial tension of fresh oil which had been passed down a column of 3,281 steel balls, 3.16 mm dia. The curve is shown in Fig. 47.



[illegible] Effect of Filtration on a Commercial Oil

T Pure oil.
1 Oil filtered once.
2 Oil filtered twice.

<u>Fig. 48 taken from ref. 151</u>

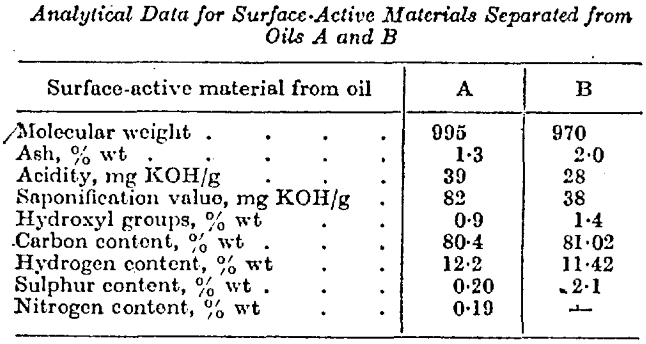
He found a similar decrease in surface activity when he passed a non polar paraffin oil to which he had added oleic acid through a long wick.

In 1940 Tabor [52] used commercial lubricating oils on the Bowden-Leben machine. He found that at temperatures in the region 40 - 80°C stick slip occurred. This effect was reversible provided there was no appreciable 'oxidation'. Subsidiary viscosity-temperature measurements were unable to explain the friction effects and Tabor attributed the rise in friction coefficient with increase in temperature to a desorption or disorientation of the lubricant film. Above 100°C Tabor found that the friction started to decrease. He said that this was due to oxidation and used this method to investigate the resistance of oils to oxidation [152].

Subsidiary viscosity-temperature measurements were unable to explain the friction effects and Tabor attributed the rise in friction coefficient with increase in temperature to a desorption or disorientation of the lubricant film. Above 100°C Tabor found that the friction started to decrease. He said that this was due to oxidation and used this method to investigate the resistance of oils to oxidation [152].

Since 1940 much work was done in testing and correlating. failure of gears and discs using mineral oils but not much work has been done on the surface properties of mineral oils. In 1961 Groszek and Palmer [153] examined the surface active compounds present in lubricating oils. They passed a quantity of oil down a chromatographic column containing magnesium oxide. After eluting the oil with much heptane they obtained the surface active material remaining on the magnesia by dissolving it in hydrochloric acid. The liberated material was extracted with 40/60 petroleum ether. They conducted various tests on these surface active compounds, obtained from two SAE 50 oils. In one test they added 2% of each respective surface active compound mixture to liquid parrafin and measured the wear scar diameter on a four ball machine. The surface active material from oil A reduced the wear scar diameter relative to that of the solvent medicinal paraffin but the other compound B increased the wear scar diameter. This latter effect was attributed (private communication) to the high acidity and corrosivity of this surface active compound at this concentration.

The surface activity of these compounds was demonstrated by carbon sedimentation tests. An infra-red absorption analysis of the compounds showed OH - C = 0 and -C - 0 peaks. Table II is taken from their paper and gives an analysis of the compounds.



Analytical Data for Surface-Active Materials Separated from Oils A and B

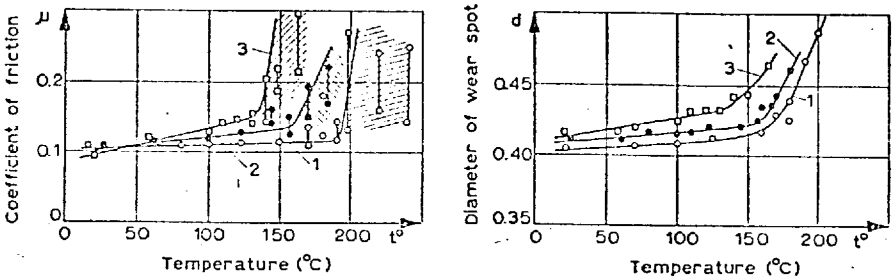
Surface-active material from oil	A	B
Molecular weight	995	970
Ash, % wt	1·3	2·0
Acidity, mg KOH/g	39	28
Saponification value, mg KOH/g	82	38
Hydroxyl groups, % wt	0·9	1·4
Carbon content, % wt	80·4	81·02
Hydrogen content, % wt	12·2	11·42
Sulphur content, % wt	0·20	2·1
Nitrogen content, % wt	0·19	—

<u>Table II taken from ref. 47</u>

Groszek and Palmer [153] also heated the oils in open beakers at 120°C and 200°C for 60 hours and noted the formation of additional surface active material. They repeated tests on these compounds.

In 1961 Matveevsky [154] published in English an account of his work carried out in Russia [155] on the properties of lubricating oils. He measured their friction in a modified 1 r.p.m. four ball machine [156]. The experiments could be carried out at different temperatures by use of heaters.

Fig. 49 shows some of his results



Friction value and wear spot diameter as function of the temperature for mineral oils whose viscosities at 100°C are: 1 = 1.15°E; 2 = 1.07°E; 3 = 2.9°E.

Fig. 49 taken from ref. 154

Matveevsky also measured the wear scar diameter after each test. Each test was made with fresh clean unscarred surfaces. It is seen from the friction temperature graphs there is no friction rise in the region of 60°C but there is a large rise in both coefficient of friction and in wear scar diameter around 150°C.

In a later paper Matveevsky [157] relates the slow speed friction temperature rise occurring at 150°C to the critical temperature theory of the failure of gears and discs which was discussed in the previous chapter.

Fein [158] in 1965 carried out low speed four ball tests similar to Matveevsky's experiments but was unable to repeat Matveevsky's results. Instead he found a wide variation in transition temperature and the transition temperature seemed to depend both upon the fraction of the oil used and also on the composition of the balls.

Experiments on the measurement of coefficient of friction and its change in value with tempeature change were then started in this laboratory using an apparatus in which a steel ball was rotated slowly against the end surfaces of three cylinders. The machine is in effect a "four ball" machine in which the three bottom balls have been replaced by flats. The apparatus has been described in detail by Lovell and Cameron [159]. The authors obtained, in some cases, a transition temperature but in other seemingly identical experiments no transition temperature was found which was most puzzling.

In a separate investigation on the transition temperatures of oils Pike [160] was unable to obtain critical temperatures with a slow speed boundary lubrication machine.

One of the major objects of this thesis has been to resolve this contradiction.

From the review of the literature, it was seen that Tabor [52] using a Bowden-Leben machine obtained a decreasing coefficient of friction with increase in temperature above 120°C and attributed this effect to oxidation, whilst Matveevsky [154] obtains a clear temperature transition at 150°C. Some variables in these experiments which might be of importance were considered and are now listed, although they are not all independent variables.

1. surface cleanliness
2. surface preparation
3. surface finish
4. oil type and composition
5. amount of oil
6. rate of heating
7. atmosphere (the gas phase)
8. sliding speed
9. load
10. steel friction combination
11. steel composition

From the previous work on the Bowden-Leben machine using alkanes and fatty acids it was found that the importance of clean surfaces could not be too strongly emphasised. To obtain clean surfaces, the method of abrasion with silicon carbide papers as used for the alkane fatty acid experiments was adopted and the dry static coefficient of friction was measured. Provided a high coefficient was obtained, the surfaces were considered clean.

The surface finish was about ten microinches. It was noted that at about 10 microinches, the friction force does not vary greatly with surface finish.

Fig. 50 is taken from work by Furey [161].

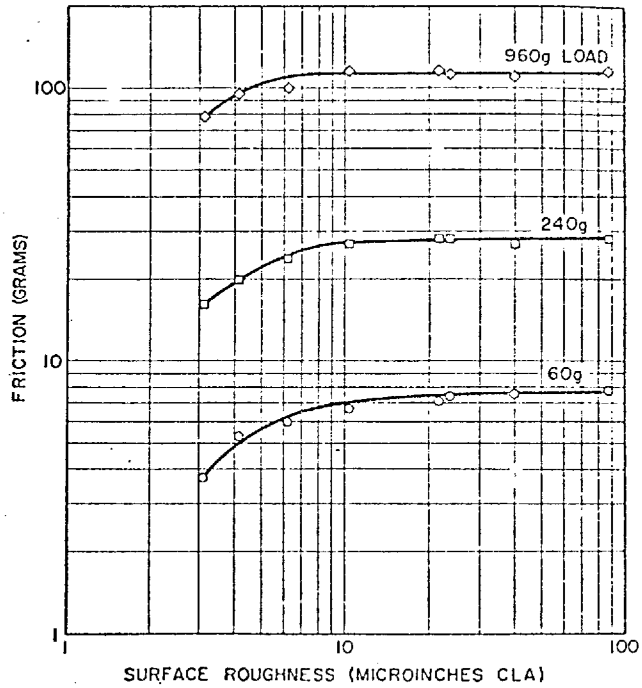


FIG. 50 Influence of surface roughness on friction

<u>Fig. 50 taken from ref. 161</u>

In the following chapter experiments were conducted on specimens of 2 microinches c.l.a. and the friction temperature is shown.

It was decided to choose initially mineral oils which contained no additives and two kinds were selected: a light stock, and a bright stock. It would be expected that the light stock might be more resistent to oxidation than the bright stock whilst the bright stock might have greater amounts of surfactants present.

The amount of oil seemed important since Tabor [52] obtained oxidation using the lubricant spread over a flat plate whilst the oil in Matveevsky's experiments was enclosed in the four ball apparatus. It was decided to have at least a $\frac{1}{4}$in. of oil above the plate. For the same reason powerful heaters were obtained so that the higher temperatures could be obtained quickly. It was decided that initially no attempt would be made to vary the composition of the gaseous atmosphere above the oil - consciously.

The sliding speed was chosen as 0.02 cm/sec. and the load was chosen as 5.5 lbs. (2.5 kg) i.e. Hertzian pressure 125,000 lb.in^{-2} (8,080 Kg.cm^{-2}) as in previous tests. Note was taken of the graph given by Matveevsky showing the results of his experiments on the variation of the critical temperature with change in Hertzian load, below 12,000 Kg/cm^{2} the critical temperature is independent of the hardness of the steel used.

The sliding pair were chosen as a steel bearing ball as the slider and a flat plate of tool steel.

Experiments were performed under these conditions. Fig. 51 shows a typical result obtained.

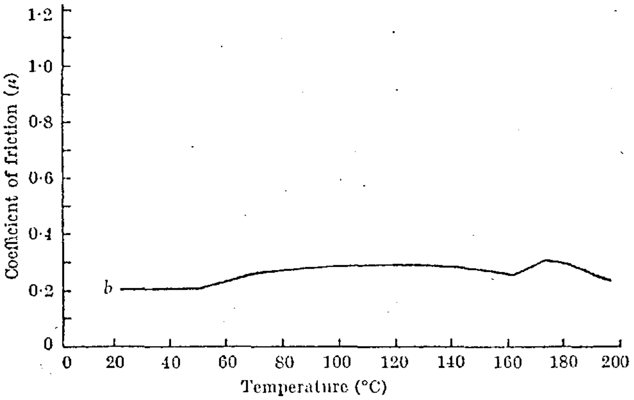


Fig. 1. Coefficient of friction against temperature for mineral oil with 0·6 carbon steel as frictional pair.

Figure 51

It is seen that there is a rise in friction at about 60°C as reported both by Hardy [150] and by Tabor [52]. At 120°C there is some slight indication of a transition temperature, but it is not of the magnitude shown by Matveevsky.

Much time and effort were then spent trying to obtain this sharp transition. The cleaning procedure, rate of healing, surface funish and velocity, load, were all varied but without success. It was then decided to change the steel composition of the sliding pair to stainless steel and to make sure that the oil came only in contact with stainless steel parts. Thus 18/8 steel balls, and plates were obtained and the ball holder and plate holder were made from stainless steel.

Immediately a clear transition temperature was obtained, this is shown in Fig. 52,

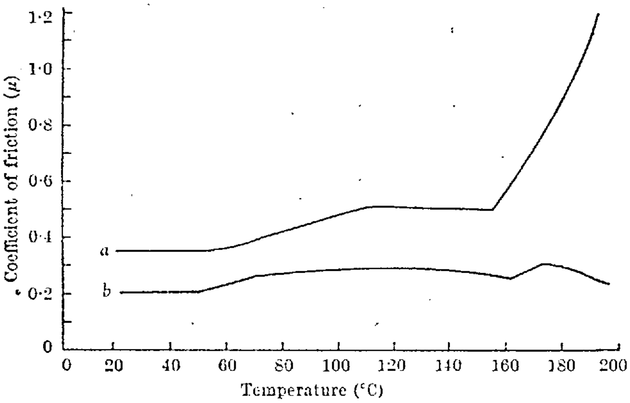


Fig. 1. Coefficient of friction against temperature for mineral oil with (*a*) 18/8 stainless steel. (*b*) 0·6 carbon steel as frictional pair.

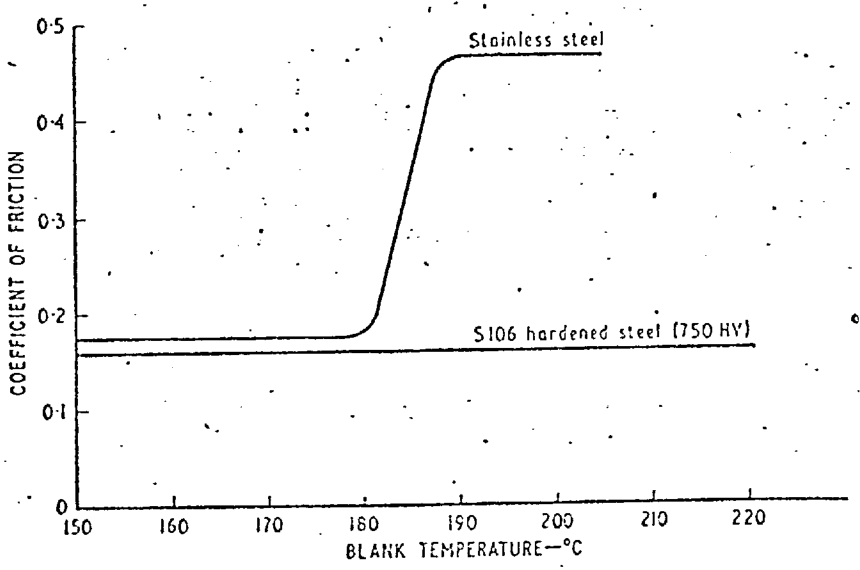
Figure 52

and further tests gave excellent reproductability. These results were reported in a letter to Nature [162].

The reasons for the transition were then considered. Tabor [52] in his experiments attributed his decrease in coefficient of friction to oxidation, indeed iron is a catalyst in promoting the oxidation of oil [163] whilst the 18/8 stainless steel surface, therefore, which containes much Cr_2O_3 [164. 165. 166] would be expected to promote less oxidation.

Groszek and Palmer [153] in their analysis of the surface active agents naturally present in mineral oils identified the presence of sulphur. The surface active compound separated from one oil was very reactive and caused an increase in wear when added to liquid paraffin in a four ball test, It was, however, added in a greater amount than that present naturally. It was thought that the surface active compounds under the conditions of the Bowden-Leben test with its high oil temperatures, might react with martensite and other reactive surfaces and so mask the transition temperature whilst with the 18/8 austenite surface, the compounds might react more slowly so that the transition temperature is obtained. 18/8 stainless steel is austenitic and austenite grains are quite resistant to etchants compared with martensite. Nital for instance hardly affects austenite but reacts vigorously with martensite.

The ability to obtain transition temperatures with mineral oils by the use of stainless steel was communicated to O'Donoghue, Manton and Asquwith [167]. They were conducting experiments to find the critical temperature of a mineral oil using a slow speed disc machine in which the discs were completely immersed in the oil. They had been quite unable to obtain a critical temperature. As soon as they changed to 18/8 stainless steel discs, clear transition temperatures were obtained. Fig. 53 shows the difference they found on changing to stainless steel.



ig *Comparison of friction–temperature traces at 26 rev/min and 17·5 lbf*

<u>Fig. 53 taken from ref. 167</u>

Fig. 54 shows critical temperature graphs for the various non-additive oils they tested.

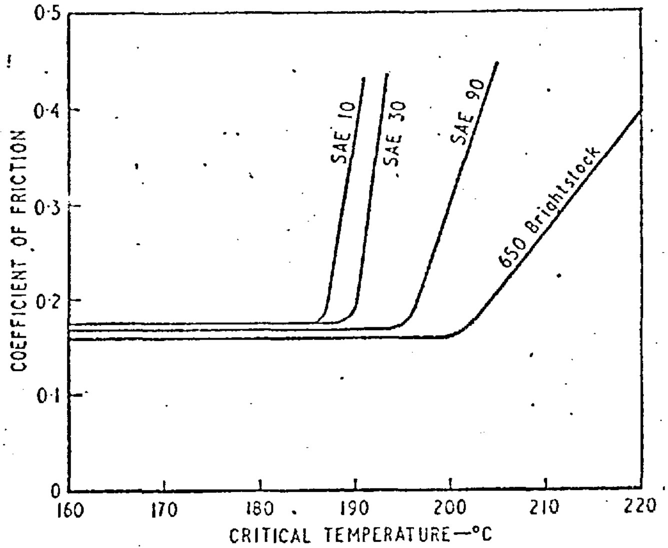


Fig. 3.1 Critical temperature traces for various Shell oils, nominally neutral mineral oils without additives

Fig. 54 taken from ref. 167

They also obtained some samples of the oil used by Ali and Thomas [147] whose disc machine results have already been considered in chapter 5 on the scuffing of gears and discs.

O'Donoghue, Manton and Askwith [167] measured the critical temperature of two of these oils on their slow speed machine, using stainless steel discs, and the value they obtained has been inserted as a dotted line on Ali and Thomas' graph, Fig. 55

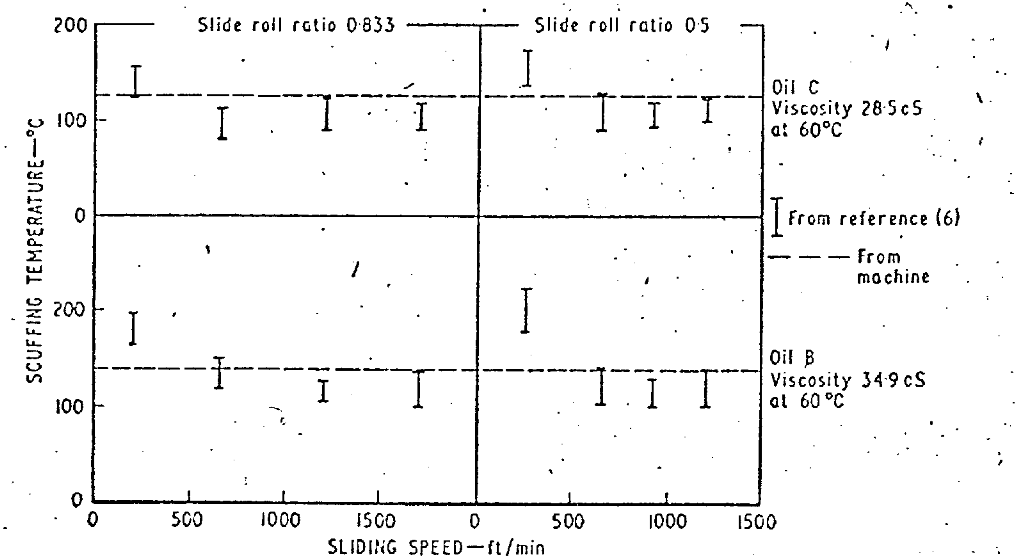


Fig 5.5. Scuffing temperature results of Ali and Thomas (6) compared with the critical temperatures determined for each oil

<u>Fig. 55 taken from ref. 167</u>

It is seen that good agreement with the calculated scuffing temperature is achieved.

Manton, O'Donoghue and Askwith propose [167] that the transition temperature of oils should be determined with a slow speed apparatus using stainless steel discs and the value should be used in the design to prevent scuffing.

Matveevsky has, however, published data [168] to show that different alloys (in his case copper) give very different transition temperatur s with stearic acid solutions in mineral oil. It is not proven that critical temperatures obtained with stainless steels are necessarily the same as those on any given hard steel. The results shown in Fig. 55 are, however, very convincing.

CHAPTER 6

Appendix 1

Details of the cleaning procedure used by Hardy and Nottage [150].

APPENDIX

TECHNICAL DETAILS

1. *Methods of Cleaning*

As the accuracy with which measurements can be made depends essentially on the cleanliness of the apparatus, details of the methods adopted to ensure such cleanliness may be of interest.

Glass.—The articles (plates, sliders, rods, etc.), are washed with soap extract and water, rinsed well with tap-water (N.B.—Distilled water should not be used as it is liable to be contaminated with a lubricating grease), and then heated to about 80° C. for 15–20 minutes in a chromic-sulphuric acid mixture. When cool the articles are removed from the solution with clean tongs (from this point onwards direct handling is to be avoided), rinsed with tap-water, and dried by draining, glass plates and sliders being supported in a vertical position with their lower edges resting on two glass rods, which have themselves been cleaned and dried in the same way. Absolute cleanliness is indicated when the water drains away from the surface as a continuous film, the upper edge of which shows a narrow band of interference colours. Adsorbed impurity on the surface of the plate or at the edges causes the film to break up into droplets or to be pushed away from the sides or lower edge. When dry, glass plates and sliders are placed at once in the chamber through which a current of clean dry air is passing.

Silica.—The tubes and chips used in the percolation experiments are cleaned in the same way as glass, but, owing to the greater porosity of the surfaces, it is necessary to dry by heating to redness.

Steel.—Gross impurities are first removed with ordinary benzene or alcohol. The surface is then rubbed vigorously on a piece of clean wet felt which has been well sprinkled with chromium sesquioxide; by this means surface scratches are removed. It is then rinsed under the tap and rubbed lightly with the clean finger to remove the finer particles of chromium sesquioxide which tend to stick to it. Polishing on felt must be continued until, when the surface is rinsed under the tap in this manner the water remains on it as a continuous film and neither breaks up into droplets nor creeps away from the edges. The surface is dried by lightly passing clean filter-paper over it, placed in a beaker, covered with freshly-distilled alcohol (absolute or 95 per cent. distilled over calcium) and the latter just heated to the boiling-point over a water-bath. Whilst still hot, the plate or slider is removed with clean tongs, rinsed twice with freshly-distilled alcohol, dried by draining, and placed at once in the chamber in a current of clean dry air.

Gas (*air or nitrogen*).—This is cleaned by passing it through a long tube packed with cotton-wool to remove dust, etc., thence through 3–5 sulphuric-acid bottles, 2 U-tubes containing soda-lime and calcium chloride respectively, 3 towers, two packed with broken potash and the third with glass wool and thence into the chamber.

CHAPTER 7

A Practical Example Demonstrating the Importance of Determining the Change of Coefficient of Friction of an Oil with Temperature

The friction temperature graphs for mineral oils obtained from experiments on the Bowden-Leben machine showed a friction rise in the region of 60°C. Hardy [150] had reported a similar behaviour for his tests in 1937 and Tabor [52] found similar rise using the Bowden-Leben machine in 1940.

The friction rise can be important and the following work in determining the friction temperature characteristics of an oil was carried out for M.I.T. Instrument Laboratories following a visit to this laboratory by them. The oil investigated is used in the bearing race of a gyroscope. Great precision is required in gyroscope manufacture for even slight errors in a gyroscope reading for vehicles travelling at very high speed may cause appreciable errors in navigation. The friction temperature characteristics of the oil was investigated since a change in temperature of the gyroscope might affect its operation.

The ball holder, balls and oil were all sent by M.I.T.

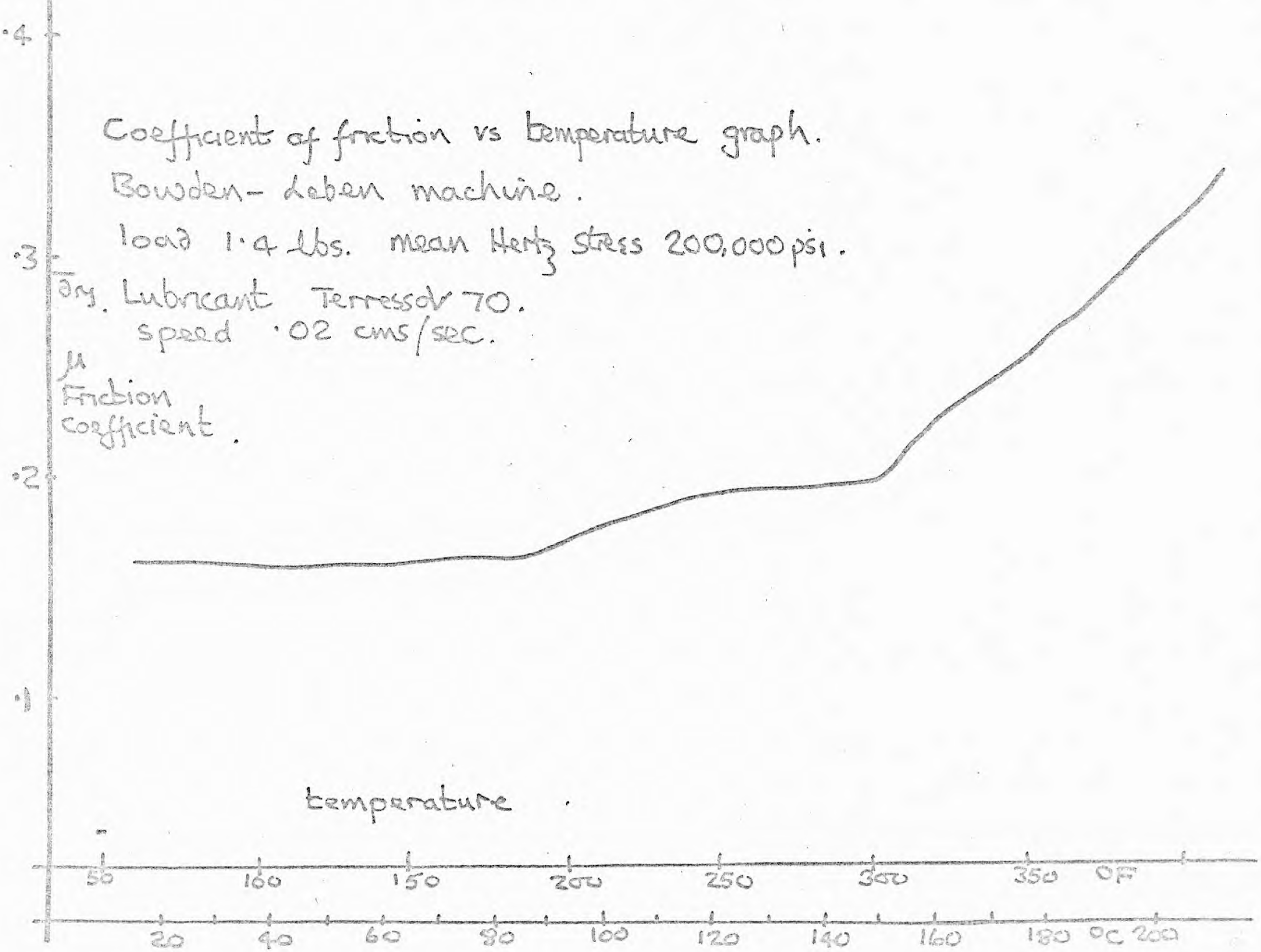
The lubricant was a mineral oil, Terresso V-78 (approximately SAE 30), and had been doubly filtered through 0.45 micron Millipore filters. The steel plate was 440 C stainless steel (17% Cr., 1% Mn., 1% C., 0.75% Mo max.) X ray diffraction showed that it probably contained 10% of retained austenite, the hardness was V.H.N. 740 and the surface finish was 2 microinches, although slight abrasion with 600 SiC papers was used to clean the surface finally.

The balls were $\frac{5}{32}$ in. diameter 440 C steel and also contained about 10% retained austenite. The Hertzian pressure at which the tests were carried out wa 200,000 psi i.e. a top ball load of 622 grams.

Results

Fig. 56 shows the friction temperature graph obtained.

Fig. 57 shows part of the friction trace obtained.



Coefficient of friction vs temperature graph.
Bowden-Leben machine.
load 1·4 lbs. mean Hertz stress 200,000 psi.
Dry Lubricant Terressol 70.
speed ·02 cms/sec.

Fig. 56

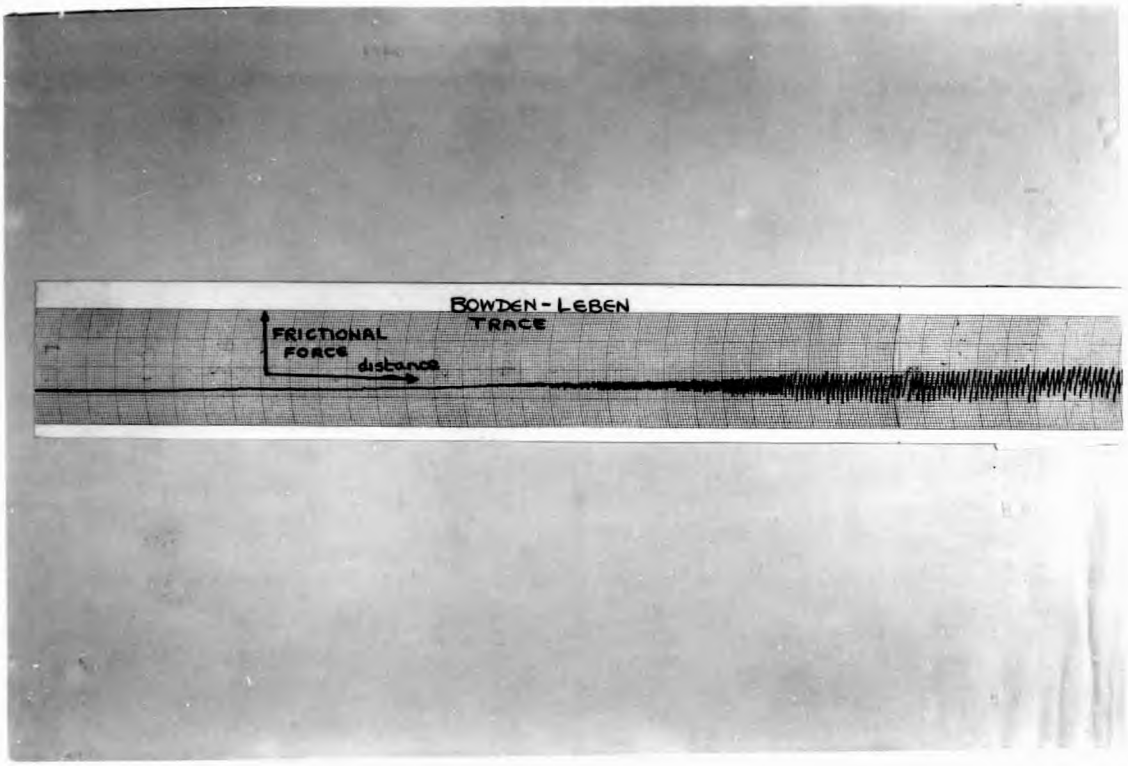


Fig. 57

Pen recorder trace from Bowden-Leben machine.

It is seen that the friction between the surfaces using this oil under these conditions increased with increase in temperature above 60°C. This was most interesting and important; further tests using other oils for gyroscopes are being done.

CHAPTER 8

The Role of Mineral Oil in Lubricant Failure

The failure of gears and discs using mineral lubricants especially non additive oils has been reviewed in Chapter 6 and it was shown that failure was dependent upon the temperature.

The failure temperature, called the critical or transition temperature has been obtained directly from friction temperature measurement by Matveevsky [154], by the author by Bowden-Leben machine tests using stainless steel specimens, and by O'Donoghue, Manton and Askwith [167] with stainless steel discs in their slow speed disc machine. O'Donoghue found that the critical temperature was reversible both by repeating the experiment with the same oil after it has cooled down, and by cooling the oil directly in the machine whilst continuing to take measurements, noting that there was a fall in friction at the transition temperature.

This does not conclusively prove that failure is a physical desorption process for there is the possibility that a chemical reaction has taken place, the products of the reaction then melting, decomposing or subliming at this temperature.

It is remembered Groszek and Palmer [153] separated surface active compounds present in oil by a physical adsorption process and the early friction experiments by Hardy [151] showed that surface activity and boundary lubrication behaviour were connected. It was therefore decided to investigate the surface active compounds present in oil more closely.

Fortunately a sample of the surface active compound A was kindly given to the laboratory by Groszek and Palmer. The properties of material A are given in Table 1 , page 175, taken from Groszek and Palmer's paper ref. 153.

Material A is a black substance similar in appearance but a little more viscous than black treacle.

Askwith, Cameron and Crouch [60] suggested that desorption of the surface agents in oils was responsible for the scuffing of gears and discs at 150°C. They quoted the work of Gorszek and Palmer [153] and the experiments of Frewing [42] and suggested that experiments similar to those carried out by Frewing on fatty acids should be carried out on the surface active agents in oils.

Frewing's work has been discussed previously in Chapter 3. He used a Bowden-Leben machine and measured transition temperature T_t for a series of fatty acids and plotted a graph log. concentration against the reciprocal of the absolute temperature. Straight parallel lines were obtained for the fatty acid homologous series, and the slope of the graphs was related to the heat of adsorption.

Therefore, similar experiments were proposed using the surface compound as the solute and a suitable solvent. A sample of the white oil left after removal of the surface active compounds was not obtained but a similar white oil was used as the solvent. Cetane and dekalin were also chosen as solvents as the representatives of straight chain and cyclic compounds.

Experimental

The friction-temperature characteristics of the surface active compound A separated from an oil by Groszek and Palmer [153] was determined for solutions of varying concentrations in white oil, dekalin (decahydronaphthalene) and cetane (hexadecane) using stainless steel surfaces on the modified Bowden-Leben machine.

The properties of the while oil are given below

kinematic viscosity	100°F	19.77 c St.
kinematic viscosity	210°F	3.98 c St.
viscosity index		110.
specific gravity		0.83

Results

All three solvents showed high coefficients of friction and did not exhibit a transition temperature when friction temperature measurements were made on the pure solvents.

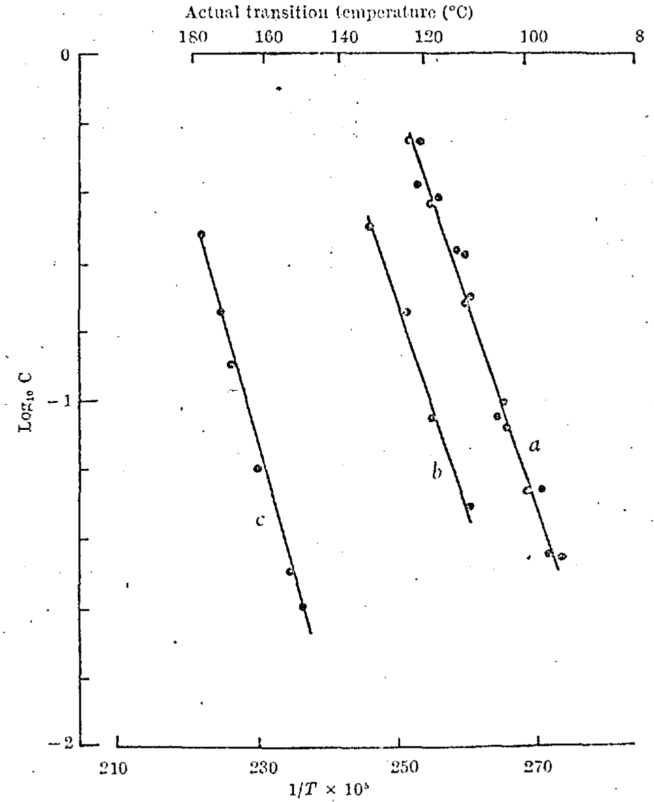
Transition temperatures were obtained for the following 3 solutions:

a) surface active compound in cetane

b) surface active compound in dekalin

and c) surface active compound in white oil

The graph log C against $\frac{1}{T}$ for these is shown in Fig. 58.



Log$_{10}$ concentration (weight/100 g solvent) reciprocal transition temperature °K. Naturally occurring surface active agent in cetane (*a*), dekalin (*b*) and white oil (*c*).

Figure 58

It is seen that three parallel straight curves are obtained for the three solvents, the heat of adsorption calculated from the gradient of the curves corresponds to -27 Kcals/gram mole. The fact that straight lines are obtained is a good indication that a physical adsorption-desorption process occurred. The surface active agent 'A' occurred in the base oil at 0.6 wt.% concentration, a similar concentration in white oil, dekalin and cetane gives a transition temperature of 190°C, 140°C and 123°C respectively, thus a critical temperature of 150°C for surface active agent in a light stock oil is reasonable.

Further tests were planned to use both the surface active compound and its original light stock oil both before and after being percolated through the activated magnisia .

It is clear, however, that a transition temperature at 150 - 200°C could be explained by the desorption of surface active compounds present in oil.

Analytical Data for Surface-Active Materials Separated from Oils A and B

Surface-active material from oil	A	B
Molecular weight	995	970
Ash, % wt	1·3	2·0
Acidity, mg KOH/g . . .	39	28
Saponification value, mg KOH/g .	82	38
Hydroxyl groups, % wt . .	0·9	1·4
Carbon content, % wt . . .	80·4	81·02
Hydrogen content, % wt . .	12·2	11·42
Sulphur content, % wt . . .	0·20	2·1
Nitrogen content, % wt . .	0·19	—

CHAPTER 9

A preliminary Study of Adsorption using Infra-Red Absorption

Introduction

So far we know that the natural surface active compounds present in oil can adsorb on steel surfaces and we know too that some of the adsorption is reversible. The surface active compounds lower the coefficient of friction indeed oxidised oils may exhibit a lower coefficient of friction than their parent non-additive mineral oils, although the associated effects such as the formation of sludge and lacquer are less desirable. Thus although it is clear that a non polar non e.p. oil such as white oil is not very effective for most lubrication requirements we must study the advantages of having surface active and e.p. additives and the influence of the type of additive and its concentration. The effects of other additives such as antioxidants, dispersants, pour point depressants polymeric additives etc. must also be considered.

The usual experiments in studying adsorption on metals is adsorption on powders which have a large surface area. In this way the adsorption isotherm may be found and thus the amount and type of adsorption evaluated. The composition of the surface active agents in oil are not accurately known nor are they readily obtained, yet a simple method of demonstrating adsorption and hence variables which influence adsorption is required.

It was decided to investigate the possibilities of infra-red absorption. Initially it was decided to look at changes in the oil. Thus if significant differences could be obtained between the oil which had not been in contact with steel powder and oil which had, then the method would be used to investigate adsorption on different metal powders, the affect of temperature and the affect of additives.

Experimental

The author is grateful to Dr. E.S. Waight of the Chemistry Department of Imperial College for advice and help and the use of the infra-red spectrophotometer, which was made by Grubb-Parsons and was similar to a type S.4. It was equipped with a Nernst filament, comb-attenuator, oscillating mirror beam chopper and sodium chloride prism. Wavelength and % absorption were recorded on a paper chart each dot on the horizontal scale representing 0.05μ i.e. 0.5μ per inch. A $\frac{1}{2}$ mm numbered cell was used for the light stock mineral oil and carbon tetrachloride put into the other cell of this matched pair. Carbon tetrachloride was chosen because it was thought that carbonyl compounds in the oil would be likely to adsorb on the powder and it was therefore intended to search in the carbonyl stretching frequency region. An absorption accuracy of ± 1% and reproductability of ± .2 was expected.

Ten grams of iron powder produced from the carbonyl 6-8 microns diameter was weighed into a 100 ml round bottom flask and 25 mls of light stock oil added. The flask and contents was then shaken vigorously for one hour after which the mixture was allowed to settle.

Fig. 59 shows a photograph of the apparatus made to shake the flask.

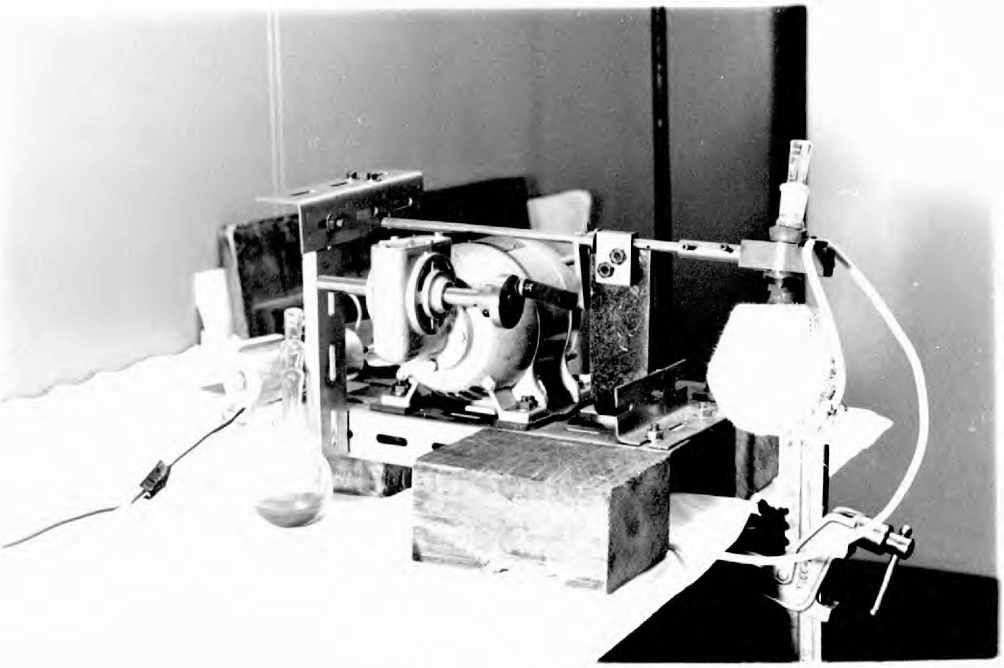


Fig. 59.

Photograph of the shaking apparatus.

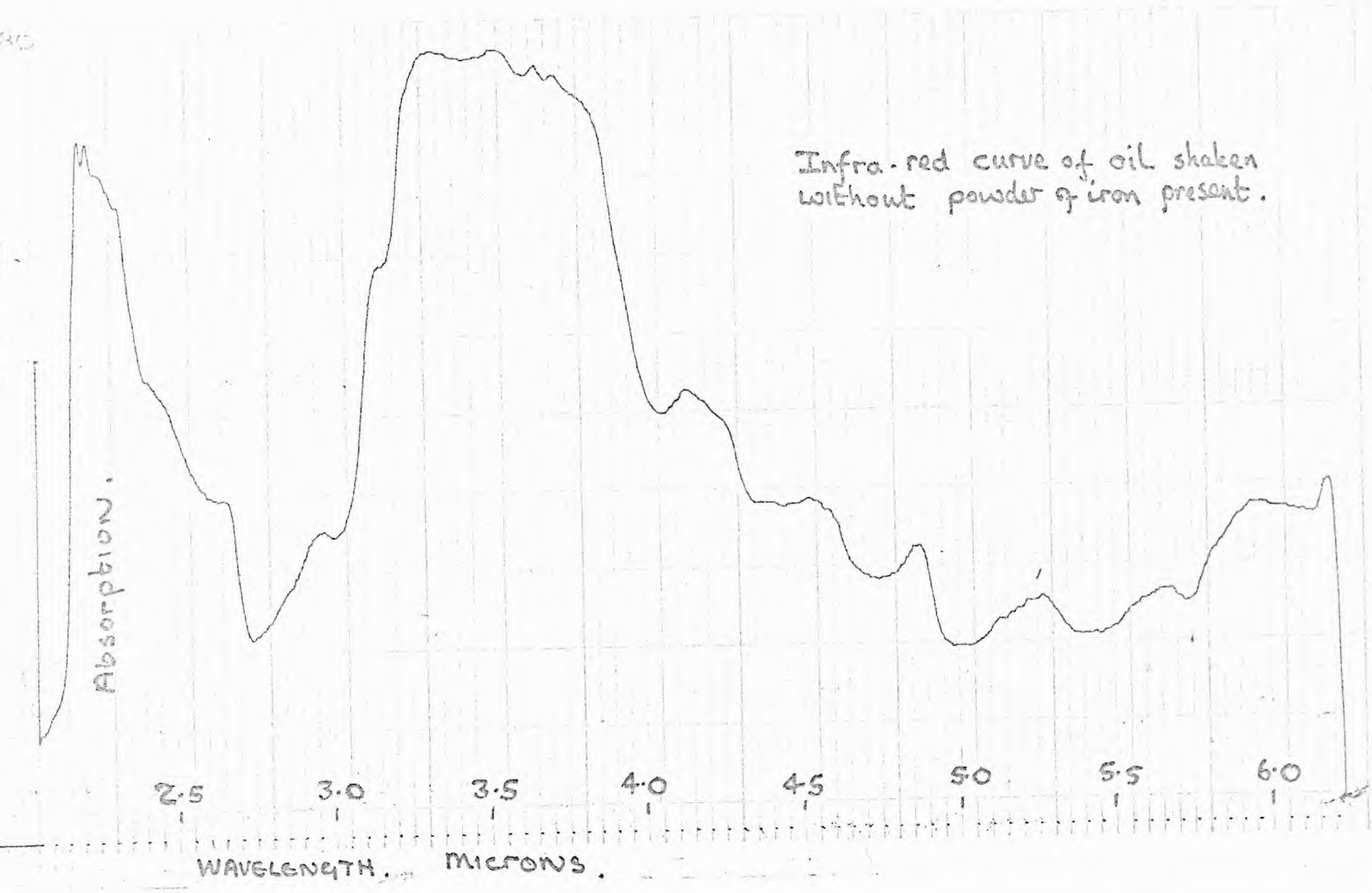
Good separation between the oil and the powder occurred. A sample of the oil was then withdrawn from the flask using a glass dropper in which one end had been drawn out to a long thin tube, so that it could enter the 100 ml. flask. The dropper was then sealed at both ends in a bunsen and subsequently taken to the infra-red machine, where this phial was again used as a dropper to fill the cell.

The experiment was then repeated but without any iron powder being present in the flask.

Fig. 60 shows the infra-red curve for the region 2 to 6 microns for the oil shaken when no iron powder was present, and Fig. 61 shows the graph obtained for the oil shaken in the flask in the presence of the iron powder.

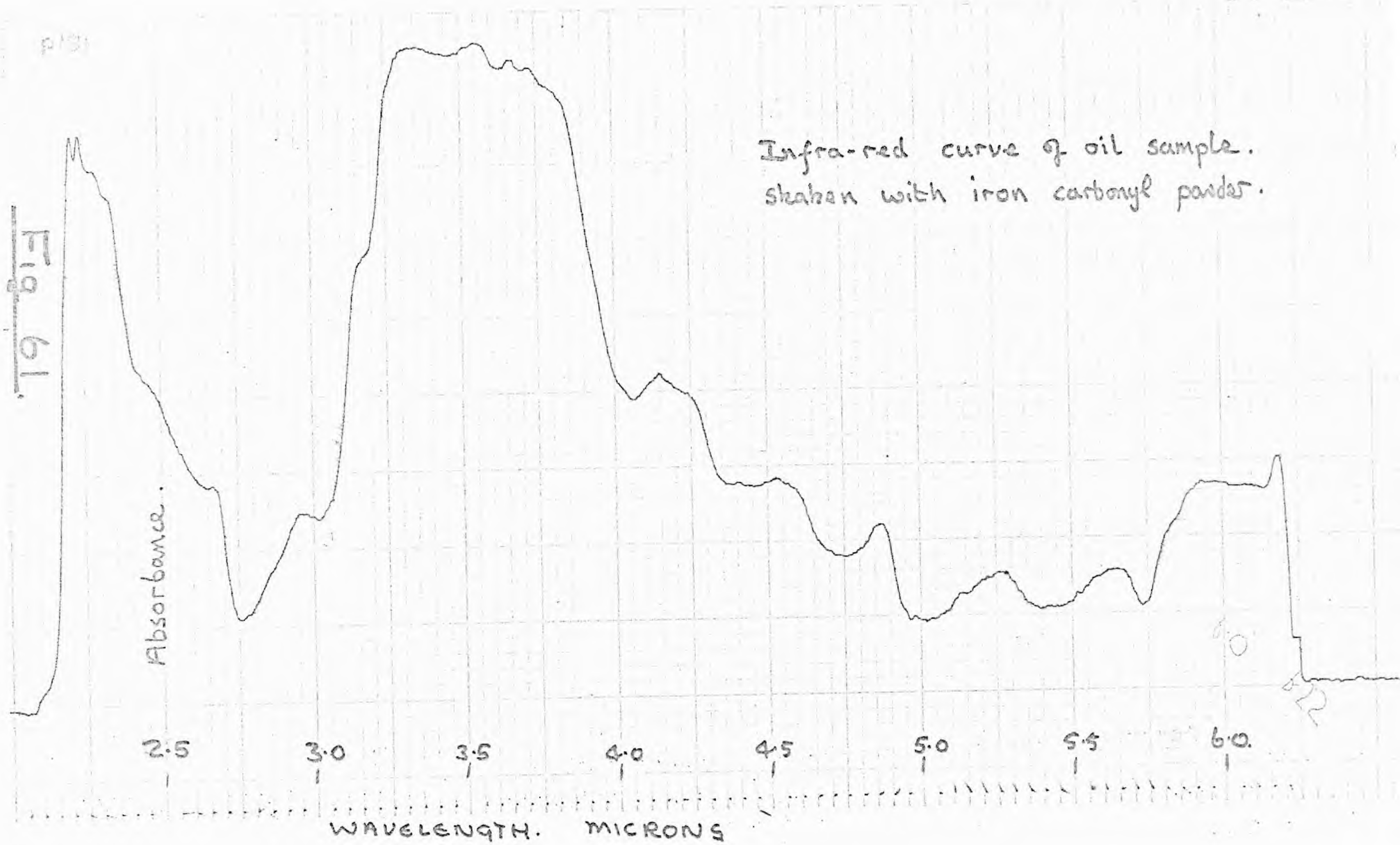
The difference between the two curves is shown in Fig. 62.

Fig 60



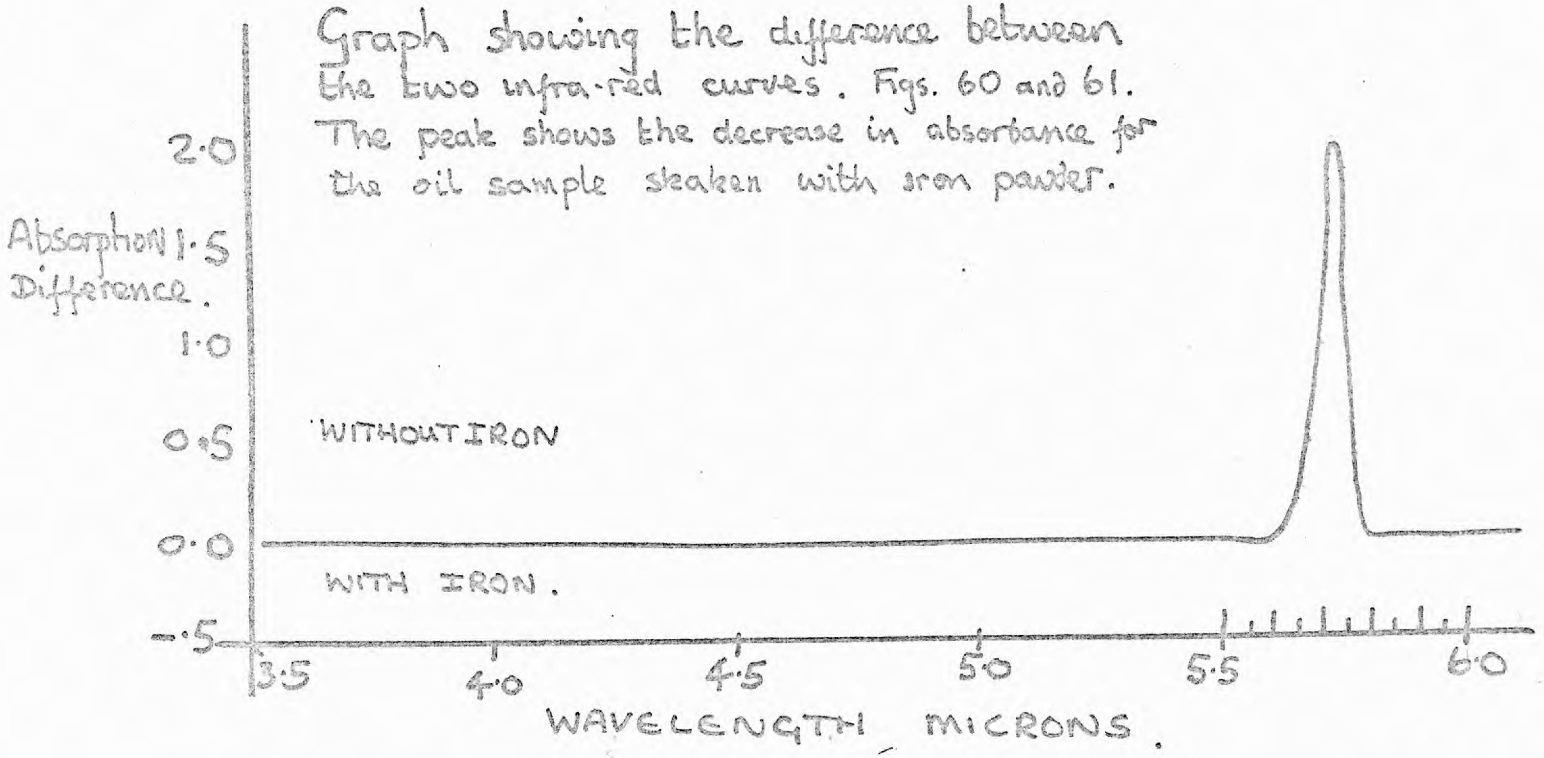
Infra-red curve of oil shaken without powder of iron present.

Fig 61



Infra-red curve of oil sample.
shaken with iron carbonyl powder.

Fig. 62



Graph showing the difference between the two infra-red curves. Figs. 60 and 61. The peak shows the decrease in absorbance for the oil sample shaken with iron powder.

It is seen that the curves are identical except in the region at 5.75 microns where the oil shaken with iron powder, gives a reduction in the absorption by the oil. This corresponds closely with carbonyl stretching vibrations of saturated aliphatic esters and aldehydes [169] and other compounds with carbonyl groups.

The decrease is attributed to adsorption of these compounds from the oil on to the iron powder.

This method of examination despite the lack of preliminary information seems promising and further experiments were planned to examine accuracy and reproducability, and then to study adsorption on to Ni.Cr. and stainless steel powders.

Some preliminary experiments were also started, showing the adsorption of cetyl amine on to iron powder so that quantitative measurements could be attempted together with experiments on competition of surface active agents for the available adsorption sites.

At this time, however, the author was given the opportunity to go to Russia as an exchange student to work in the laboratories of Dr. Matveevsky and Professor Vinogradov and this work on infra-red measurements stopped and was not pursued on return because of other interesting work, although it will be shown that a method of comparing interations of compounds with steel surfaces is of value.

CHAPTER 10

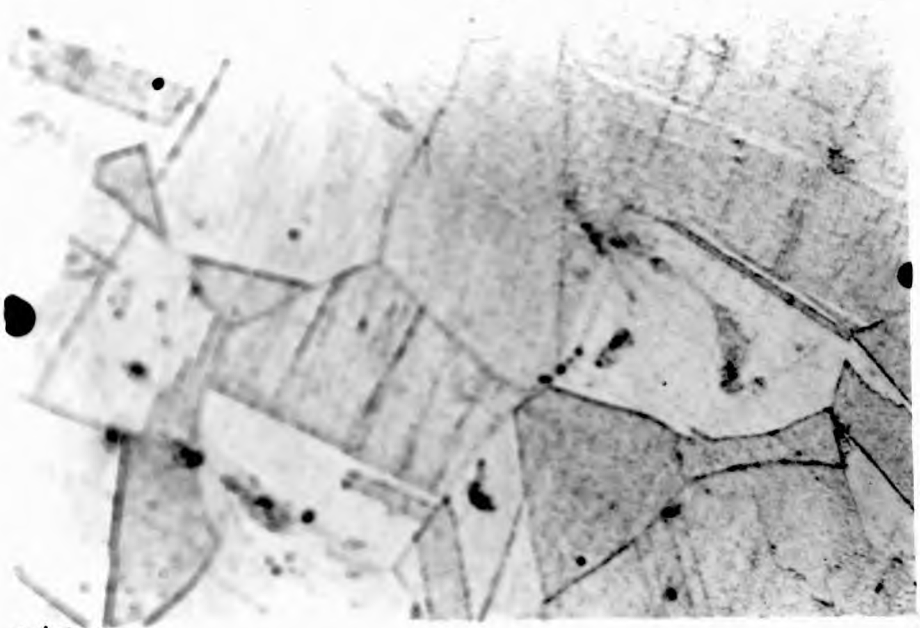
Role of Austenite in Lubricant Failure

Introduction

Chapter 6 reported that a transition temperature could be obtained on the Bowden-Leben machine using the austenitic 18/8 stainless steel surfaces, and in Chapter 8 the role of the mineral oil and its composition which causes the transition was discussed. This chapter is concerned with the part played by the steel surfaces in lubricant breakdown for it is remembered that using the Bowden-Leben machine no transition temperature was obtained using martensitic steel surfaces.

A preliminary explanation was that reactive compounds present in the oil were reacting with the martensitic steel under the conditions prevailing in the Bowden-Leben machine tests causing low friction so that desorption of surface active compounds did not cause a rise in the value of the coefficient of friction, however, in running parts such as gear teeth, the ambient temperature is much lower than the total flash temperature achieved in the contact zone and the contact time is short; thus reaction will not have occurred to the same extent and a critical temperature may still be observed for martensitic steels and plain oils especially in the running in period, where chemical reaction has occurred least.

More experiments were now planned to test and develop these theories. The 18 Cr. 8Ni stainless steel is austenitic, this can be seen from the phase diagram. A sample of the steel plate was polished and etched for 1½ minutes in a chromic hydrochloric acid mixture. The structure is shown in fig 63. and is the typical microstructure..



x650

Fig 63 Austenite microstructure.

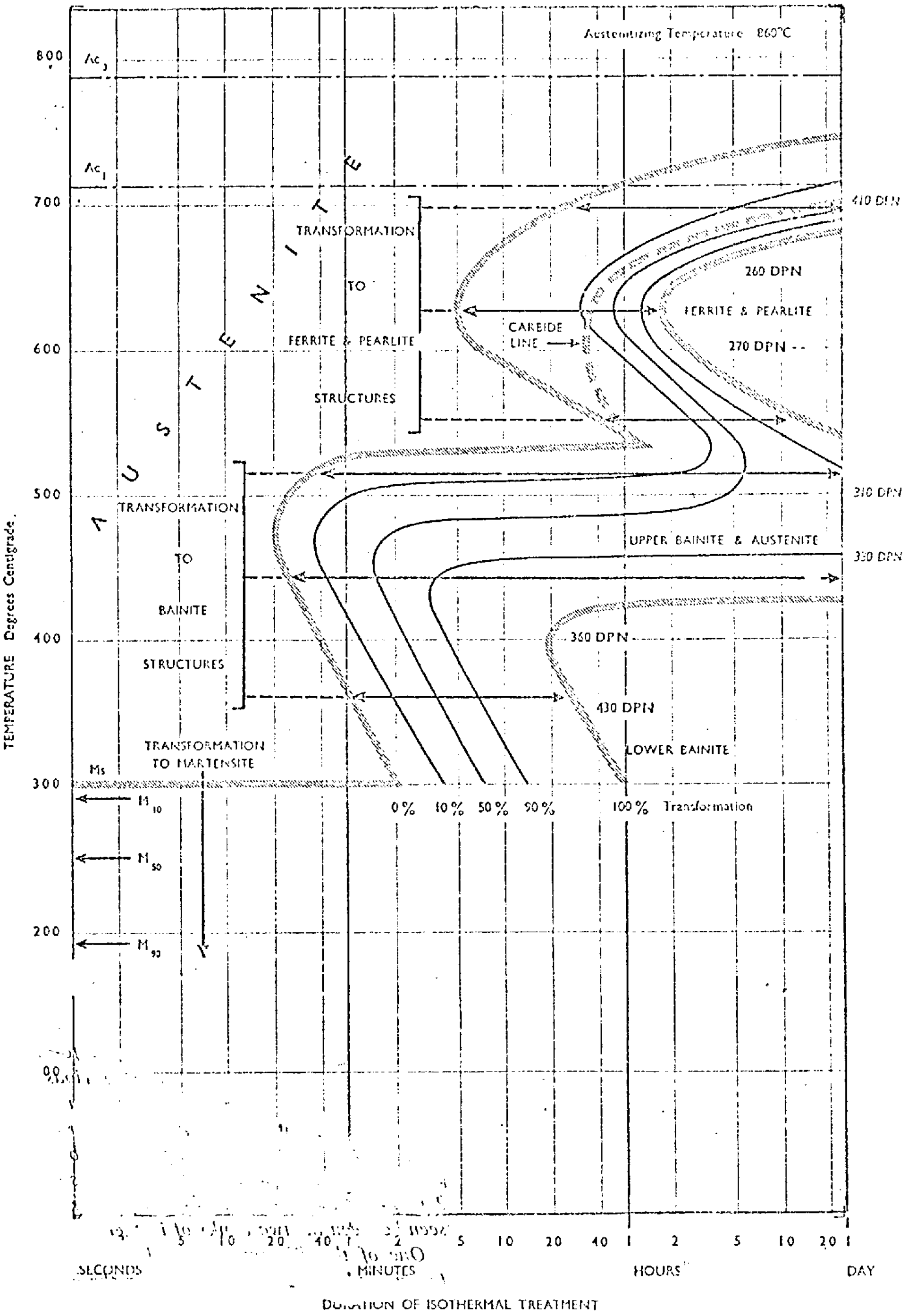
18 Cr 8 Ni stainless steel

The surface of stainless steel contains much Cr_2O_3. McCullough considers that the surface is mainly a spinel oxide $FeO.Cr_2O_3$ for the normal air oxidised surface. Yearian, Derbyshire and Radavich [165] find much Cr_2O_3 with Fe_2O_3 and Uda and Tsuji [166] suggest that there is a continuous film of Cr_2O_3 in which particles of an Fe_3O_4 type spinel are embedded. At all events it is clear that the surface of 18/8 stainless steel contains much unreactive Cr_2O_3 whilst martensitic steel does not.

The difference between the stainless steel and the martensitic steel results may be accounted for by a difference of the reactivity of the surfaces.

It is of equal interest to know if the microstructure of a steel surface contains unreactive microareas. It was thought that an austenitic structure which is unreactive compared to a martensitic structure of the same composition might affect the performance of the steel in its resistance to scuffing. Indeed the fact that austenite is relatively unreactive may be a further reason why the 18/8 stainless steel gave transition temperatures with mineral oils. The reactivity is dependent upon structure and composition.

Consider a steel which is heated to its austenizing temperature until complete transformation has occurred. On cooling transformations will proceed and are described by the phase diagram. The phase diagram gives only equilibrium states, the progress of the transformation is usually given in the T.T.T. diagram (time, temperature, transformation) Fig. 64 is a typical curve [170]. In this case EN 100 is a hypoeutechtoid steel and the broken line on the diagram refers to the start of the transformation to pearlite.



Isothermal Transformation Diagram for Low Alloy Steel (B.S. En 100) austenitized at 860° C.

Figure 64 from ref. 170

M_s is the temperature at which the formation of martensite begins and M_f the temperature at which it is completed, the formation of martensite is not time dependent and its composition is that of the austenite. On cooling a steel frequently small amounts of austenite are retained at room temperature, this is particularly so if the M_f temperature is low, indeed retained austenite is expected if M_f is below the room temperature. In general an increase in carbon content of the steel lowers the M_f temperature. The M_f temperature is depressed by a high carbon content steel although the C content might come from other structural changes in the steel, thus if a protoeutechtoid steel is being cooled, precipitation of protoeutechoid ferite causes an increase in carbon content of the untransformed steel because the maximum solubility of carbon in f.c.c. austenite is 2% whilst only 0.025% in the b.c.c. ferite thus the increased carbon content depresses the M_f temperature and hence increases the likelihood of retained austenite.

Chromium increases the stability of retained austenite [170] but Ni and Mn reduce it. Retained austenite is usually not wanted in steels for it is soft, hence sub zero heat treatment is carried out, i.e. the steel is cooled well below the M_f temperature.

It was decided to study the effect of retained austenite on lubrication failure.

Experimental

The author is grateful to P.T. Holligan and the British Iron and Steel Research Association for advice, to the British Iron and Steel Association for carburising the steel specimens and the English Steel Corporation for X-ray measurements on the amount of retained austenite.

It was decided to choose a steel in which the structure was almost wholly martensite and retained austenite and to vary the relative proportion of each. This variation can be done by carefully choosing a steel in which it is possible to operate on the left part of the T.T.T. curve. The steel chosen was heat treated to obtain maximum retained austenite content, and friction tests were carried out on the specimen. Aften completion of the measurements, the test piece was then sub zero treated to reduce the amount of retained austenite and the friction tests were then repeated. In this way the only change in the test specimen is the material transformation by liquid nitrogen immersion altering the austenite/martensite ratio.

Previous work by the British Iron and Steel Institute had showed that a suitable steel was gas carburised EN 39B. EN 39B is a case hardening steel 4¾% Ni, 1% Cr, .5% Mn and is used as a material for gears. Bars of this steel were obtained, heated to 950°C, rolled into flat strips and air cooled. This gave mainly a bainite structure. The strips were ground flat and cut into lengths suitable for the Bowden-Leben machine. The specimens were gas carburised for four hours at 925°C, cooled in the furnace to 850°C and quenched directly into oil. Gas carburising, unlike pack carburising, leaves a good surface finish and no distortion of the specimens was found. It is noted that a temperature chosen just above the austenising temperature causes only small grains of austenite to form, the small grains are less readily converted to martensite than large grains.

This heat treatment gave a retained austenite content of 24 ± 1.5%.

Fig. 65 shows a cross section of the steel flat which has been etched with nital. The steel flat was cut quickly with a thin abrasive wheel and polished. No grain change, caused by the heat during the cutting off procedure, was detected after repolishing and re-etching the specimen.

The outside edges of the specimen have not etched,this is due to the retained austenite in this region, it is noted that the corners of the specimen have a higher retained austenite component since cooling rate is more severe in these regions. Fig. 66, on the same page as Fig. 65, is a section obtained from a steel rod with hemispherical ends which had been similarly carburised and heat treated. This section has been obtained from the rod by two cuts, one along the centre line of the rod, and the other normal to it, near the end of the rod. The face shown lies along the centre line.

The extreme outside edge is dark, and is a carbon deposit on the steel, readily removed by abrasion.

The inside edge is steel containing a high carbon content, and because of the cooling procedure gives a high retained austenite content.

With increase in depth of the steel, the rate of cooling was less so that the amount of retained austenite decreases until the black region is reached. This is the region of carburised steel containing

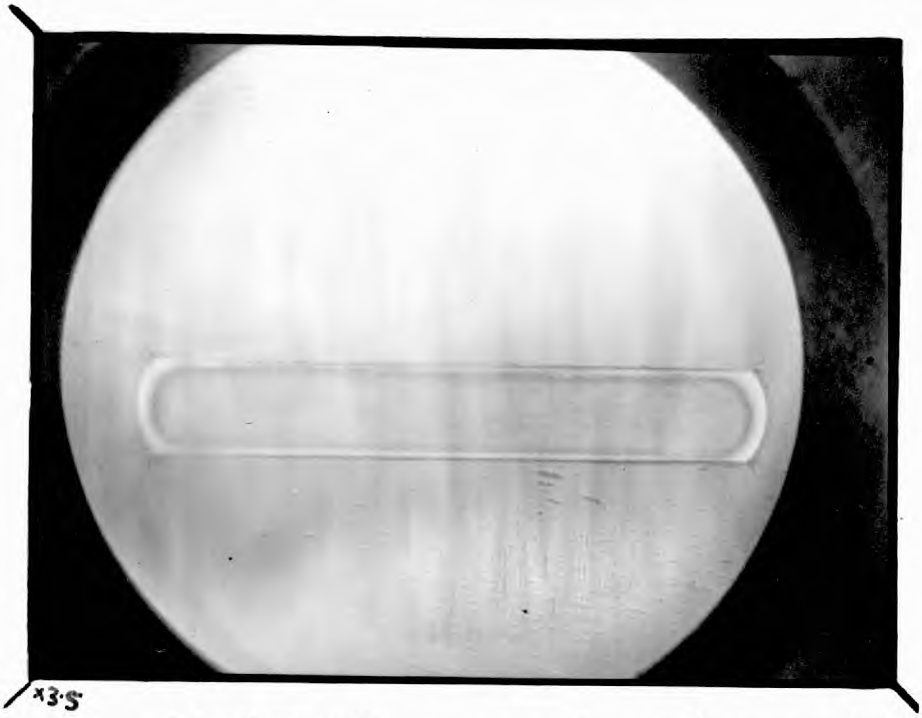


Fig 65 White area near edge contains much retained austenite

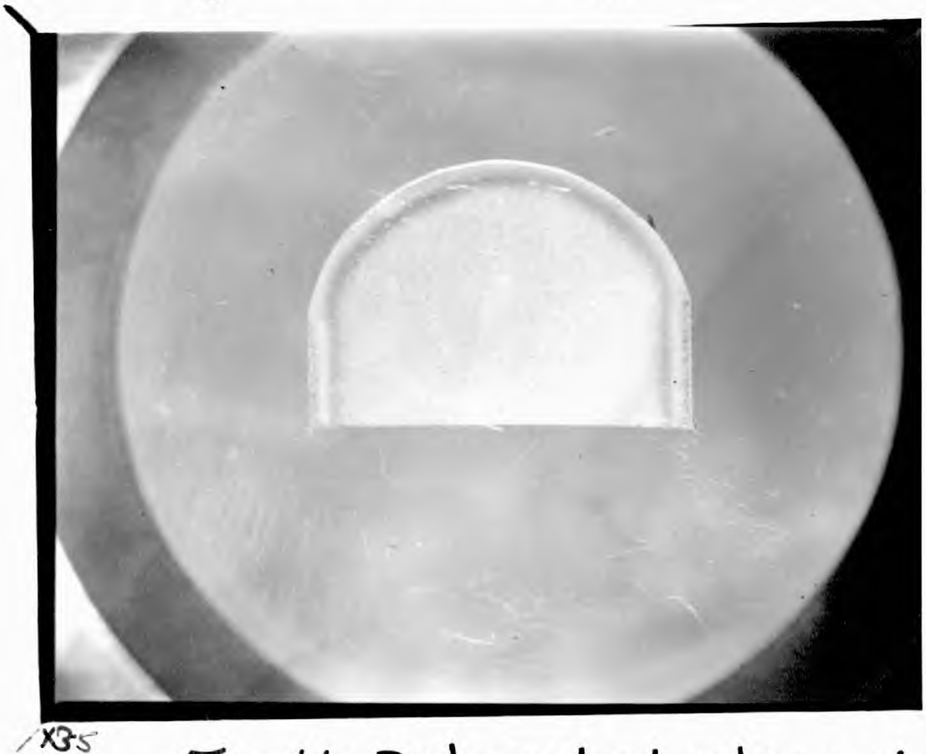


Fig 66 Dark area band contains much martensite.

only a very small amount of retained austenite its composition is almost fully martensitic.

Inside this region the original EN 39B is reached which is a bainite structure.

In Fig.67 (the black protion is the air surface of the steel). Fig. 67 shows the decrease in austenite content with increasing depth of the steel. (Magnification x 170 etched in nital 25 secs.)

Fig. 68 shows the fully martensitic structure of the carburised steel beyond which is the uncarburised EN 39B steel. (Magnification x 450 etched in nital 25 secs.)

Fig. 69 shows the edge of the surface again but at a higher magnification. (Magnification x 450 etched in nital 25 secs). The long martensitic needles are clearly visible.

Fig. 70 is the same specimen but now etched with picric acid ethenol in an endeavour to see the grain boundaries of the austenite grains. Despite this heavy etching, they are discernable.

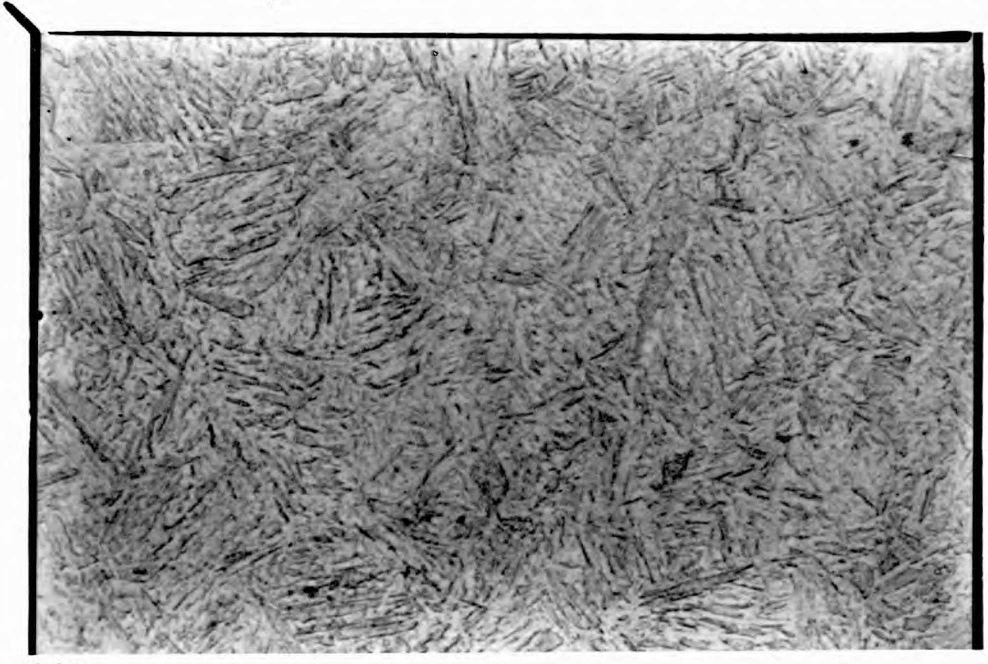
Whilst the presence of austenite and a general picture of the structure can be obtained by these micro structure photographs, an estimate of the austenite content by consideration of the etched and unetched areas may not be very accurate.

The retained austenite content of the samples was therefore determined by X-ray diffraction, using a Phillips 1310 diffractometer. The author is grateful to the English Steel Corporation for this work.

Samples of the carburised steel were then cooled at -70°C. It was found by X-ray diffraction that the amount of retained austenite

x170

Fig. 67. Decrease in austenite content with increase in depth.



x450

Fig. 68. The martensitic area.

x450.

Fig. 69. Long martensitic needles.

x600.

Fig. 70 Heavier etching revealing austenite decreased from 24% to 4.9% further cooling did not decrease the amount of retained austenite and it was decided to conduct friction measurements on these two steels.

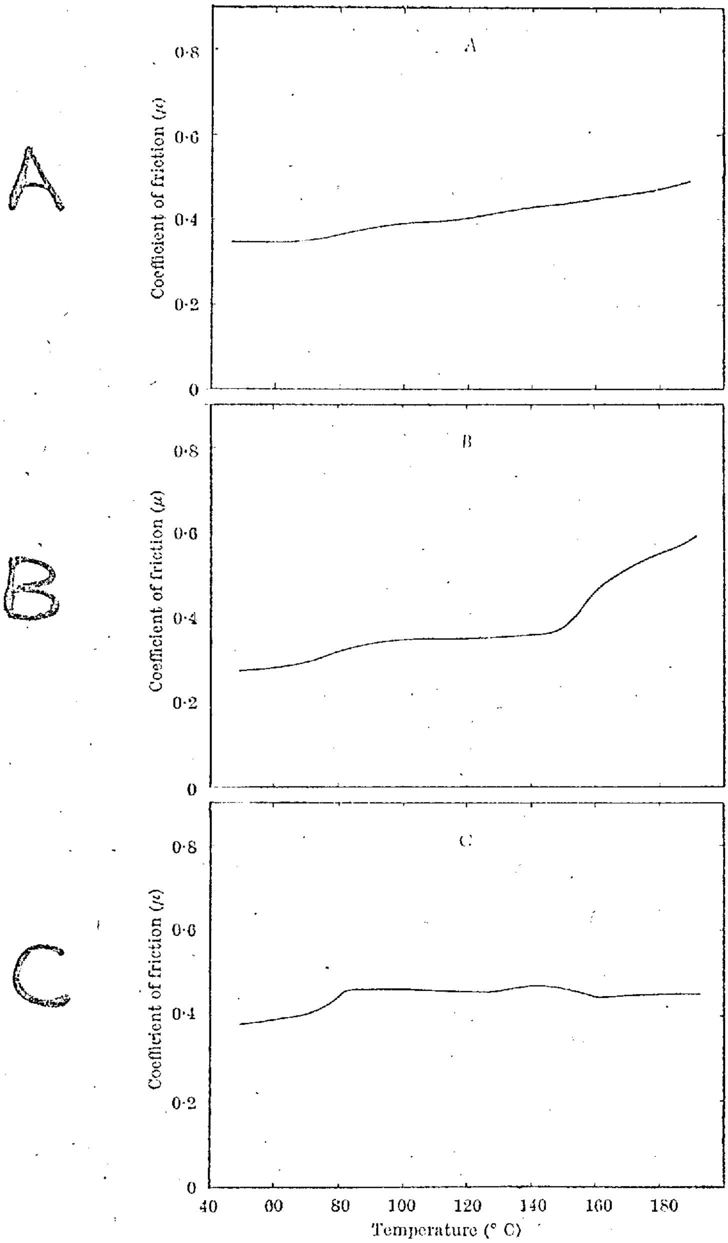
The friction temperature properties of the two steels with mineral oil lubricant were then determined on the Bowden-Leben machine.

The slider was the flat steel specimen, and it was originally intended to use the hemispherical ends of rods which had the same heat treatment as the rider. The surface finish was not sufficiently good for reproducable results so that a tungsten carbide ball was used instead.

A friction temperature determination was made for the lubricant and tungsten carbide surfaces. No transition temperature was detected.

The specimens were cleaned with acetone and silicon carbide papers and placed carefully in the Bowden-Leben machine. The oil chosen was OEP 90 turbine lubricating oil. This is a commercial lubricant and contains e.p. additives of mainly dithiophosphates. Earlier experiments with stainless steel surfaces and this lubricant, gave a clear transition temperature.

The results of the tests are shown in Fig. 71.



A, Friction temperature curve using 'Bowden-Leben' machine (average of at least four traces) using a tungsten carbide slider and an uncarburized *EN* 39 *B* rider. Velocity, 0·02 cm/sec; load, 2·5 kg; turbine oil lubricant. *B*, Friction temperature curve using carburized *EN* 39 *B* with 25 per cent retained austenite; turbine oil lubricant. *C*, Friction temperature curve using carburized *EN* 39 *B* containing 52 austenite only; turbine oil lubricant.

Fig 71

Results

In Fig. 71, Graph A shows the friction temperature curve for the uncarburised EN 39B (VHN 440) and, like the early results on the Bowden-Leben machine, it does not show a transition temperature.

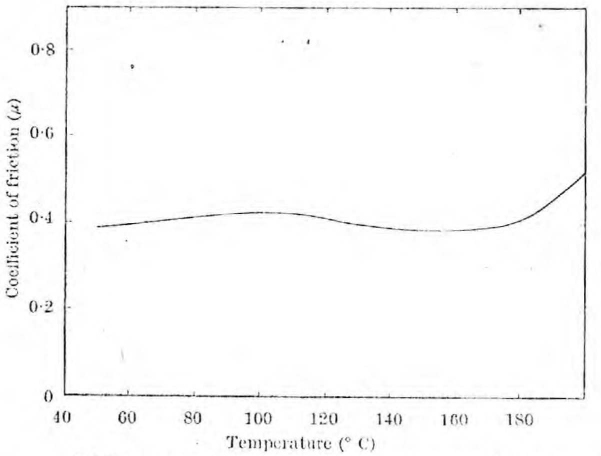
Graph B shows the friction temperature curve using the carburised steel containing 25% of retained austenite (VHN 740). It is seen that a good transition temperature is obtained.

Graph C shows the effect of changing to the 5% retained austenite sample (VHN 750). No transition temperature is obtained.

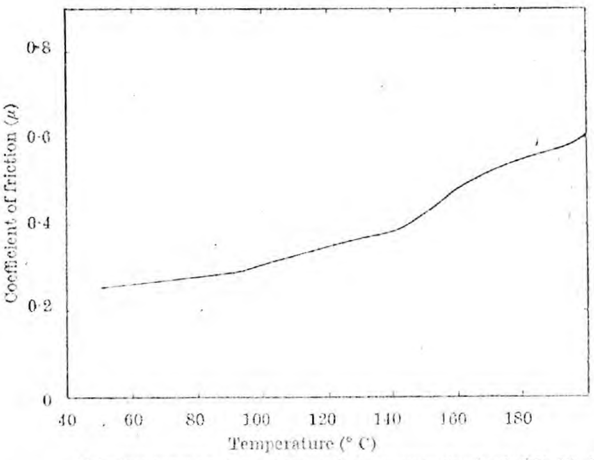
A further experiment was performed using the surface active agent 'A' separated from mineral oil by Groszek and Palmer [153]. Liquid paraffin was used as the solvent (the properties of the liquid paraffin are listed on page 175). A friction temperature test using the pure solvent and a steel specimen containing 25% retained austenite did not show a transition temperature, but instead gave a constant value of friction of 0.55.

0.59 wt % of the surface active agent was added to the liquid paraffin white oil and the friction temperature test repeated on the 25% retained austenite specimen.

Fig. 72A shows the result obtained. It is seen that the coefficient of friction has been lowered to about 0.4 but there is a transition temperature near 180°C.



. Friction temperature curve using a tungsten carbide slider and a carburized *EN* 39 *B* steel rider containing 25 per cent retained austenite; lubricant, 0·59 per cent by weight surface active compound in white oil.



Friction temperature curve using an uncarburized *EN* 39 *B* steel rider; lubricant, 0·59 per cent by weight surface active compound in white oil.

Figs. 72A and 72B

Fig. 72Bshows the effect of using the surface active compound in white oil on the uncarburised EN 39B.

It is seen that a good transition temperature is not identifiable. Thus reactive substances masking the transition temperature are contained in the surface active compound itself.

It was of paramount importance to clean the surfaces thoroughly, thus the surfaces suffered some abrasion and since the amount of retained austenite varies with the depth within the specimen it was thought that perhaps the retained austenite composition on the surface might change. Accordingly therefore, a specimen which had been much used was re-examined by X-ray diffraction for its content of retained austenite. No change was found.

Discussion

It is seen that the reason for not obtaining a transition temperature in previous experiments using martensitic steels is due to the reactivity of the lubricant with the steel under the conditions prevailing in the Bowden-Leben machine. The lubricant is heated to 200°C over a period of ten minutes. It must, however, be mentioned that some of the austenite is softer than the martensite and experiments are described later on in which martensitic balls were annealed to the same hardness as austenite balls and the affect of the difference in reactivity is demonstrated again this time using additives.

It was initially proposed that failure to obtain transition temperatures with martensitic steels on the Bowden-Leben machine did not mean that transition temperatures did not occur in real practice with gears and discs where the contact times are very short. In gears the surface tempe ature is made up of the bulk oil temperature and the momentary flash temperature. Indeed O'Donoghue, Manton and Askwith [167] have subsequently showed that the transition temperature measured using an oil and stainless steel discs gives a good correlation with the transition temperature calculated from I.A.E. gear tests with an EN 30B steel (.3C, 4.1 Ni, 1.2 Cr, .3 Mo %).

However, the correlation does not describe the events occurring in the contact zone where adsorption, desorption, chemical reaction, deformation and asperity contact may all be occurring. The result of these interactions are taken into account by the coefficient of friction. Scuffing occurs when the total contact temperature, which is a function of the instantaneous coefficient of friction reaches the critical temperature, the temperature of large scale desorption of the lubricant film, and under these conditions it is suggested, that the additives in the oil are unable to prevent failure.

The presence of surface regions on which the oil is readily adsorbed but with which e.p. additives are not very effective due to their unreactiveness with the surface, will, with chance asperity contact, cause a greater generation of heat than for a surface which is more reactive with the e.p. additive. Hence the critical temperature and thus scuffing, will, for the unreactive surface, be reached at a lower load. The Bowden-Leben results therefore predict that the presence of retained austenite at the surface of the metals will lead to a decrease in the scuffing load.

Gears and discs are manufactured using EN 39B steel since it is relatively easy to machine. It is then carburised to form the hard surface. Thus there is a likelihood of retained austenite occurring from the carburisation process and the percentage of retained austenite is also likely to vary since the hard surface of the gears is often finished by form grinding. Thus a variable retained austenite content could well explain the extremely variable scuffing loads obtained with gears and discs.

It was therefore decided to re-examine the literature to see what extent austenite or other interesting factors had been found to be important in the choice of steels used in friction and wear applications especially in relation to gears and discs, and further, to see in what way metallurgical changes, which have been reported to occur under friction conditions, might affect the scuffing performance.

Metallurgical changes have frequently been reported in the literature. However, distinction must be made between changes which have occurred <u>before</u> siezure and those <u>after</u> siezure where extremely high temperatures are developed.

The composition of the steel is also dictated by the strength required and the resistance required to failure by fatigue. Bear and Butler [171] studied the rolling contact of balls at 30,000 r.p.m. and found fatigue failure occurring due to a change in structure of the steel beneath its surface, i.e. the peak shear stress is 0.5 x Hertz radius beneath the surface). In this case the bearing steel softened and cracks slowly extended to the surface leading ultimately to failure.

Formation of retained austenite under friction conditions has been reported by Nikonov and Klebenov [172], they were interested in the spalling of rails during the braking of trains and wagons. A wheel 3 ft 4 ins dia. was rotated at a surface speed of 36 m.p.h. with a force of 2755 lb applied for 4 secs with a mineral oil lubricant against a rail. Siezure did not occur, although the heat developed raised some of the steel above its austenizing temperature and the similar high cooling rate caused retained austenite to occur. Some thermocouple measurements showed temperatures of 500°C in the first second and a cooling rate of approximately 300°C per sec.

Clayton and Jenkins [173] using a modified four ball machine found that on approaching scuffing loads when running Fe vs steel a white constituent developed, possibly austenite although they could not identify it positively.

Markovskaya and Cheryi [174] have also reported a similar effect. They found that when using pearlitic and ferritic cast irons and a diesel oil lubricant, austenite formed in the surface layers of the pearlitic steel under a sliding friction of 2.4 metres/sec and a load of 7 Kg cm^{-2}. In the ferritic iron, austenite was also detected but only when the velocity was raised to 6.4 metres per sec and the load to 20.7 Kg cm^{-2}. The austenite was detected by X ray diffraction analysis.

The effect of retained austenite on the wear of a steel (15 Cr, .5 Ni, 3.16 C) has been investigated by Popov and Brykov [175]. They found that an increase of 1% of retained austenite gives a 1.2% decrease in wear resistance.

The presence of a certain amount of retained austenite is advocated by Balter and Turovskii [176] for an increase in pitting resistance.

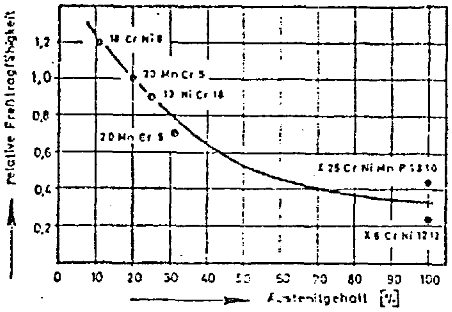
The work of Bernshtein, Kalyagina, Kapulkina and Laptev [177] is also mentioned in which they heated steel rollers to 950°C. At this temperature they rolled the steel then quenched it in water and tempered it. In this way they obtained a high percentage of retained austenite but one which was finely fragmented throughout the structure producing rollers of very high fatigue resistance.

Although the production of austenite is recorded under friction conditions the retained austenite is unstable providing the Ms temperature is above room temperature and thus deformation would be expected to reduce the amount. This has been shown by Magee [178] and Richardson [179].

Ogawa [180] has noted this effect under friction conditions where the austenite changes to the harder martensite.

The effect of gear material on scuffing failure with direct reference to austenite content has been studied by Niemann and Lechner [181]. The apparatus was a modified F.Z.G. machine which they had used for experiments on the measurement of surface temperatures in gear teeth.

Using a mild e.p. additive oil they measured the scuffing load for a number of gear steels which contained different amounts of austenite. Fig. 72c shows the results they obtained.



10. . Abnahme der Freß-Tragfähigkeit mit zunehmendem Austenitgehalt des Zahnradwerkstoffes. Verzahnung A; v = 17.2 m/s; mild legiertes Getriebeöl [illegible]; maßgebend ist der Austenitgehalt bis zu einer Tiefe von 0.3 mm unter der Flankenoberfläche

Fig. 72cfrom Ref. 181

Graph showing the affect of the austenite content on the steel on the relative scuffing load.

The austenite content was measured .3 mm under the surface of the gear and the speed was 17.2 m/sec.

The steels quoted are according to DIN 17006 specification and the alloy content in percentages is given in the Appendix at the end of this chapter.

It is seen that the scuffing load decreases with increase in austenite content. Niemann and Lechner thus advise that in carburising of the gears particular care should be taken to minimise the retained austenite.

These results agree well with the predictions made from the friction temperature measurements on the Bowden-Leben machine.

Conclusions

From the measurements on the Bowden-Leben machine, it has been shown that a transition temperature is not restricted to 18/8 stainless steel surfaces. Other surfaces on which the surface active compounds are able to adsorb and desorb may also exhibit such transition temperatures.

A transition temperature was obtained for a carburised EN 39B steel containing 25% retained austenite but not for similar specimens which contained only 5% retained austenite.

It was predicted that retained austenite in gear surfaces would cause lower failure loads, and that the wide variation in gear failure measurements might be due to this effect. This agrees with work recently published by Niemann and Lechner [181].

A literature survey showed that there is evidence that austenite can be formed under friction conditions. Some of the austenite may remain as retained austenite whilst some may be transformed to martensite.

Further measurements on the Bowden-Leben machine show that the reactive substances masking the transition temperature were contained in the surface active compounds present in the mineral oil.

Further tests on metals of equal hardness but of different reactivity towards oils and additives were now planned.

CHAPTER 10

Appendix 1

DIN 17006 steel specifications in percentages.

18 Cr 8 Ni	is	.18 C,	4.0 Cr,	20 Ni,	.5 Mn
20 Mn Cr 5	is	.2 C,	1¼ Cr,		1¼ Mn
13 Ni Cr 18	is	.13 C,	4½ Cr,	4½Ni,	
20 Mn Cr 5	is	.2 C,	1¼ Cr,		1¼ Mn
X.25 Cr Ni Mn P 18.10	is	.25 C,	18 Cr,	10 Ni,	up to 1.0 Mn and P
X 8 Cr Ni 1212	is	.08 C,	12 Cr,	12 Ni,	

CHAPTER 11

Diesel Engine Scuffing

A survey of the lubrication failure in gears, discs and engines was made earlier so that the significance of the mineral oil transition temperature obtained from the Bowden-Leben machine experiments could be considered.

One of these lubrication systems, diesel engines, is now examined again to see if the transition temperature of a mineral oil is important in the running in failure of diesel engines. The choice of the diesel engine for investigation would not seem ideal, whilst gear and disc machines are used in laboratory tests, however, at present running in failure of internal combustion engines both petrol and diesel is common and thus of great importance.

Much of the information on diesel engine scuffing was obtained from discussion or meetings in which no reports have been published, e.g. Inst. Mech. Engrs. London. Group Discussion. "Piston Rings - The Achilles Heel of the Diesel Engine". Hence little of the work is referenced.

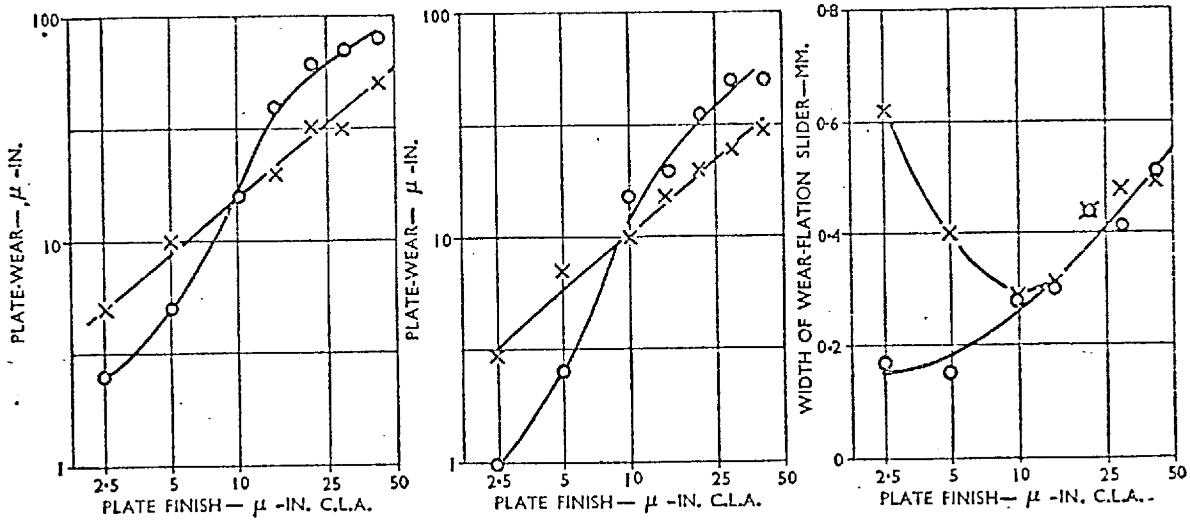
Running in failure is usually the result of scuffing between the piston rings and the cylinder or liner. Siezure does not usually occur but the scuffing is readily noticed on inspection after running in. It is remembered that methods chosen to solve the problem must be compatible with the rest of the engine i.e. such as corrosion of the plain bearings.

It seems that running in failure became prominent as the output horsepower required from the engine was increased, this consequently caused the change from cast iron, to chromium plated piston rings. Chromium plated piston rings were introduced as top compression rings and oil control rings because of their good abrasive wear resistance (hardness 850 Br. M pt 1802°C), and excellent corrosion resistance against sulphur containing diesel oils [182]. A further advantage claimed was that the crack pattern of Cr. plate causes oil retention in the pores and thus oil is taken to the cylinder wall [183].

It was found, however, that Cr. plating does not run satisfactorily against itself [184]. The failure is usually a running-in failure, and if the engine has not scuffed during the running in period, then provided actual running conditions were obtained, the chance of subsequent scuffing is much smaller.

An engine is said to be run in when it can operate at full load satisfactorily. Although the main indications of a satisfactory running in is the fall in oil consumption, fall in fuel consumption and the absence of blow by. It was found that on changing to Cr. plated rings the running in time was taking longer and that a coarser cylinder bore was required i.e. (15 - 30 C.L.A.) to prevent scuffing although much scuffing was still occurring.

Since chromium plated rings have greatly reduced wear rates compared to those of cast iron, then it is expected that the time taken for the rings and cylinder to conform takes longer hence running in takes longer. The running in time for an engine depends too upon the surface finish of the liner and upon the lubricating oil chosen. The effect of surface finish and wear between two oils, a straight mineral oil and an additive oil has been investigated using a reciprocating Bowden-Leben type apparatus by Williams and Daniel [185] and Davies [186]. They used both cast iron and chromium plated sliders on a cast iron plate to simulate the running in of an engine. The main results are shown in Fig. 73.



a Plate wear at end of stroke. *b* Plate wear at centre of stroke. *c* Slider wear.

Influence of Surface Finish on Wear: Reciprocating Wear Machine

Materials of plate and slider: 4K6 cast iron.

× Straight mineral oil. ○ Additive oil.

Fig 73.

It is seen that the wear of the plate increases with decrease in surface finish for both oils, but that using the additive oil and a smooth surface, results in a wear rate less than that obtained for the same surface finish and the non additive mineral oil, but for surface finishes greater than 10 micro inches the wear rate of the plate in the presence of the additive oil was greater than in the presence of the non additive oil.

Thus when the surface is smooth the additive oil will reduce the wear rate and hence prolong the running in time, but when the surface is rougher the additive will react with these large asperities causing a higher wear rate and hence a reduction in running in time.

The present explanation for scuffing during the running in period would be that because of non-perfect touching between piston ring and cylinder, the extra load carried by the touching parts may force the lubricant out leading to scuffing and possible siezure.

A critical temperature theory for running in failure would be as follows.

As the engine is started up, surface active compounds are adsorbed physically on the surfaces of the cylinder wall and the piston ring helping to reduce friction and wear. With increase in load the temperature of the oil and surfaces increases and at the critical temperature there is physical desorption so that the two surfaces or indeed debris going through the contact zone may scuff with the piston and liner and hence scuffing has occurred.

An important question is, however, how likely is this to occur and what is necessary to prevent or reduce the likelihood of scuffing?

We have already shown that a transition temperature may not be apparent if a sufficient amount of e.p. type reactions have occurred. It is thus proposed that a similar process occurs in diesel engines, thus if sufficient sites on the surface have low shear strength oxides, sulphides, chlorides etc. then the desorption of physical adsorbed compounds would not be over the total surface and would be, to some extent, masked. As a result, scuffing would not occur and indeed the temperature of the oil may now exceed the critical temperature with no scuffing. This theory would therefore predict:

1. That once running in has occurred the likelihood of further failure of "running in scuffing type" is rather remote.
2. A longer running in time, below the scuffing temperature would be beneficial in reducing running in scuffing, i.e. there is more time for a greater fraction of the surface sites to be covered with low shear strength films, before the critical temperature is reached.
3. Surfaces which are more reactive to the oil components under the temperatures and pressures in running, would be less likely to scuff.
4. The engine may operate satisfactorily at temperatures much in excess of the critical temperature after the running in period.

It is found in practice that these predictions are correct, however, it is equally possible to explain these effects in terms of the first scuffing theory.

There are other factors possibly in favour of the critical temperature theory. Running in tests have been carried out in which the water jacket temperature was varied, on lowering the water jacket temperature it was found that the incidence of running in scuffing was reduced, although the likelihood of scuffing in service increased.

Furuhama [187] has used a petrol engine and by using heat exchangers, was able to vary the operation temperature. Using thermocouples, he measured the piston and crank pin temperature during running in. He found a 'peak' phenomenon occurred when the crank pin temperature reached

150°C, the peak effect was a sudden rise from 150°C to 220°C and a subsequent return to the former temperature after about 30 secs. Furuhama [187] demonstrated that the peaks were a running in phenomenon only and that the peaks could lead to siezure.

Experimental

It was decided to investigate whether a 'temperature desorption' failure mechanism could account for running in failure.

Bowden-Leben friction temperature tests were carried out using a cast iron liner and a rider of sigments of piston rings as shown in photographs (Figures 74 and 75).

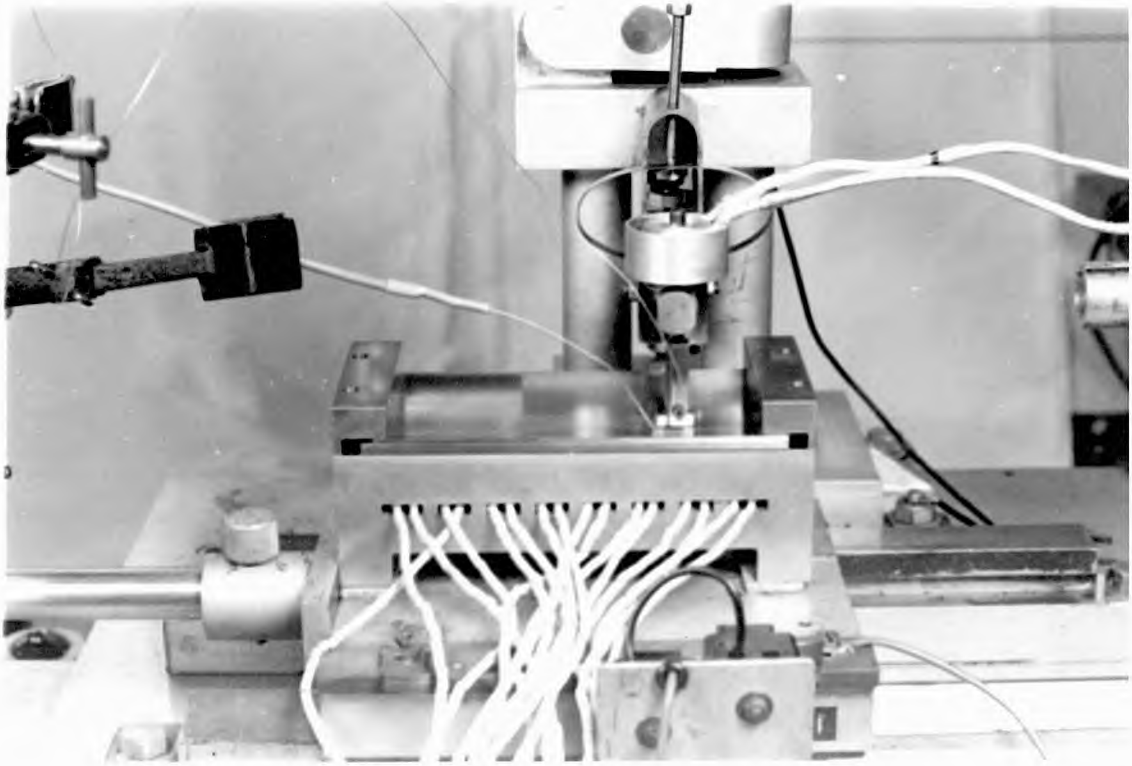


Fig. 74.

Bowden-Leben machine modified for piston ring-liner experiments.

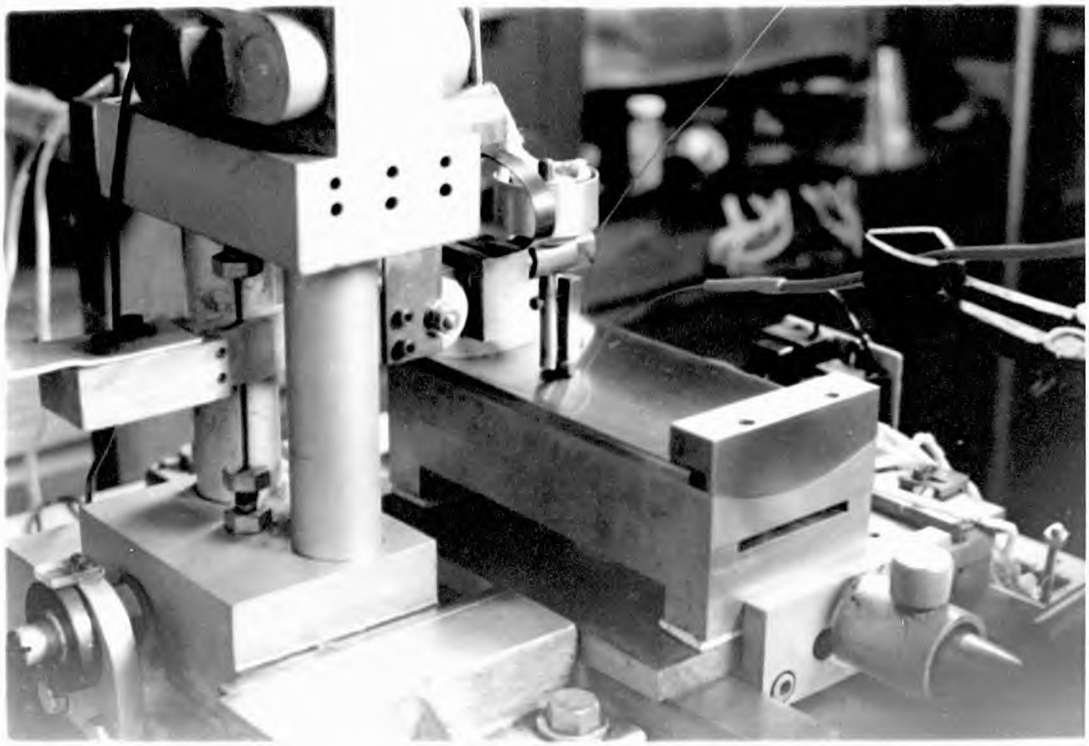


Fig 75.

Bowden-Leben machine modified for the piston ring-liner experiments

Also a test using a chromium plated slider and chromium plated piston ring was carried out. The experimental method followed closely the procedure used in previous Bowden-Leben tests. Surfaces were cleaned using abrasive SiC papers. This resulted in the surface finish of the cast iron line being approximately 5 microinches, rather than the rougher 20 microinches surface finish used when running in with chromium plated piston rings. The lubricant, light stock oil, was the same as that used in previous Bowden-Leben tests. Viscosity 5.9 cs. 210°F, 17.1 cs. 140°F, V.I. 69.

Results

Figure 76 shows that a transition temperature is detectable when running cast iron against cast iron, althouth under these conditions the rise in friction is not very large.

Figure 77 shows a much larger increase in friction at the critical temperature using a chromium plated piston ring segment.

Figure 78 shows the friction temperature curve obtained when running a chromium plated slider against the chromium plated piston ring segment. A massive and abrupt increase in coefficient of friction at the transition temperature is seen. The three graphs are now plotted together, Figure 79.

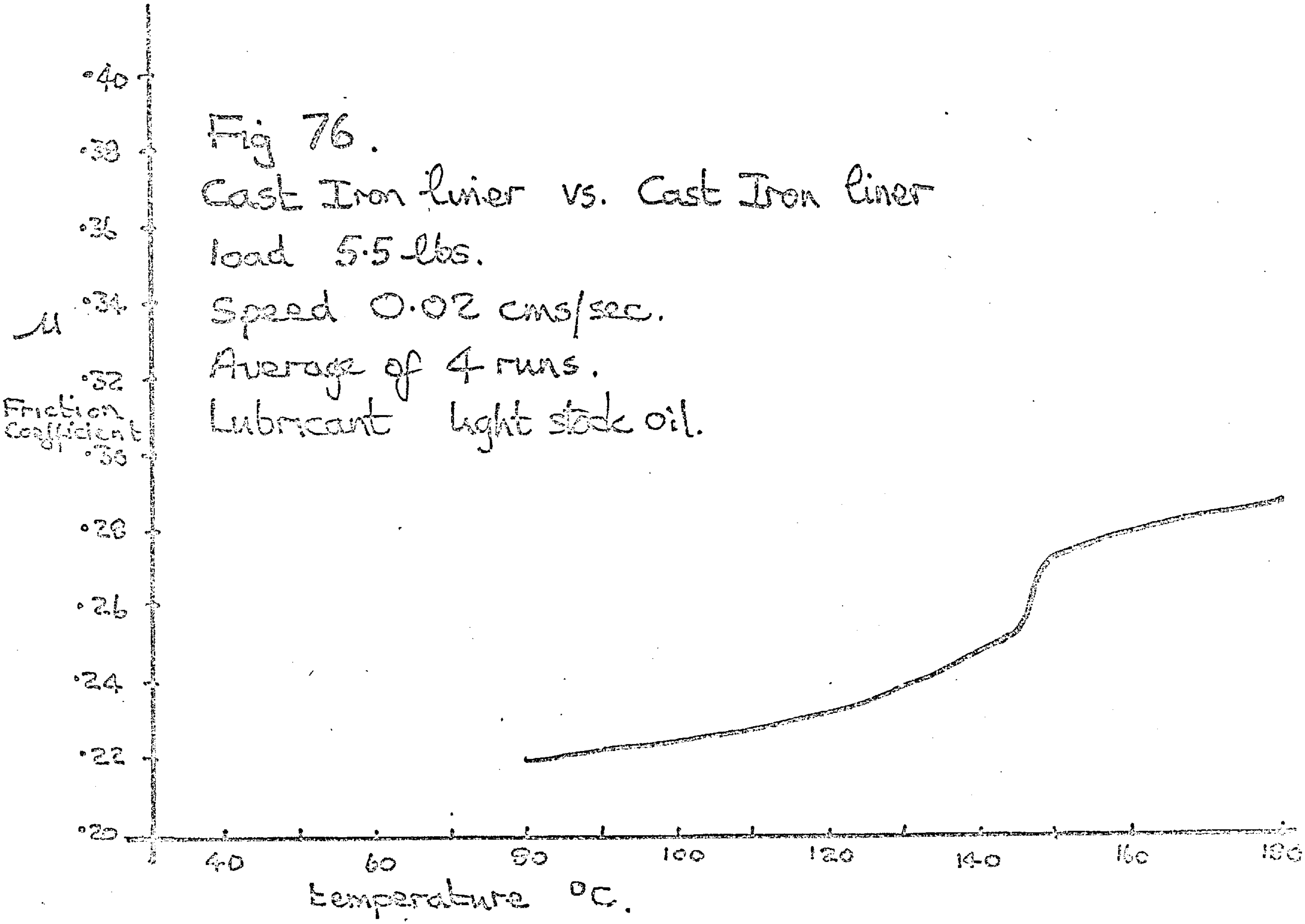


Fig 76.

Cast Iron liner vs. Cast Iron liner

load 5·5 lbs.

Speed 0·02 cms/sec.

Average of 4 runs.

Lubricant light stock oil.

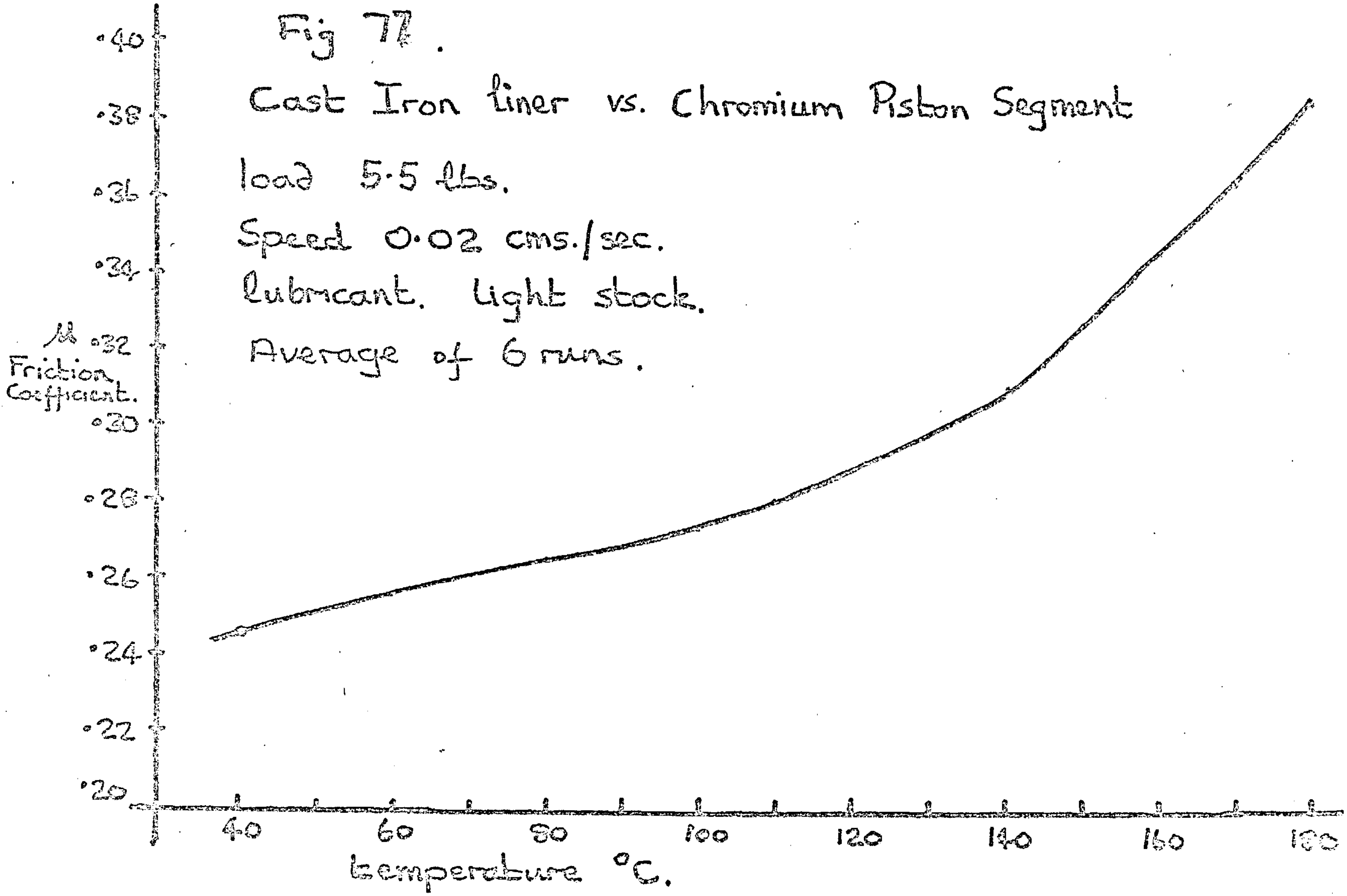


Fig 77.

Cast Iron liner vs. Chromium Piston Segment

load 5·5 lbs.

Speed 0·02 cms./sec.

lubricant. light stock.

Average of 6 runs.

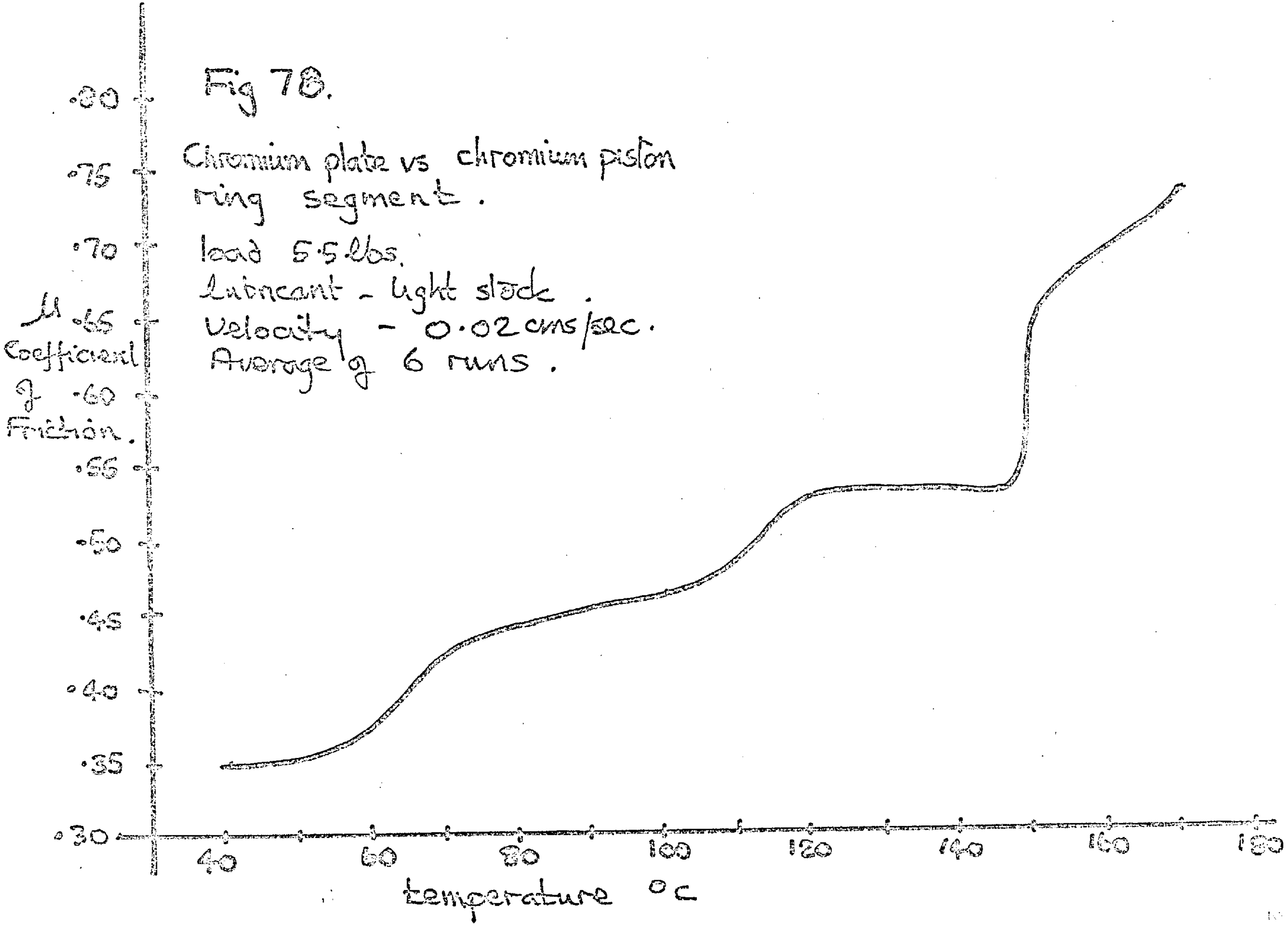


Fig 78.

Chromium plate vs chromium piston ring segment.

load 5.5 lbs.

Lubricant - light stock.

Velocity - 0.02 cms/sec.

Average of 6 runs.

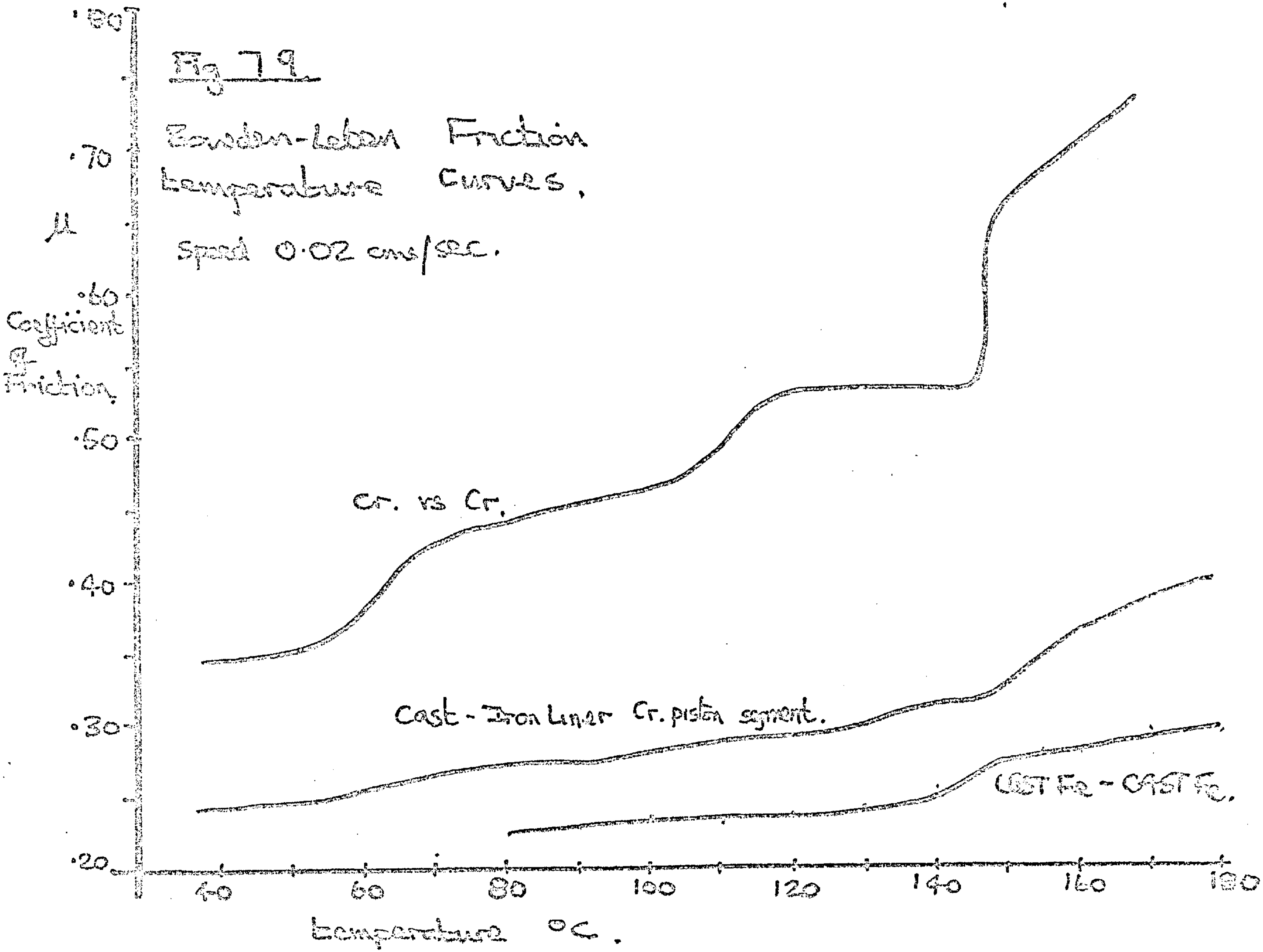


Fig 79.

Bowden-Leben Friction temperature curves,

Speed 0·02 cms/sec.

The main conclusions from these graphs are:

That a transition temperature of between 145 - 155°C is obtained using a light stock non additive oil from Bowden-Leben friction temperature measurements using metal pairs of cast iron-cast iron, cast iron-chromium plated piston ring segment, chromium plated slider-chromium plated piston ring segment. Further it is seen that using a cast iron liner segment as the slider, that on changing from a cast iron ring to a chromium plated ring, that under these same conditions the coefficient of friction of the chromium plated ring is greater, and that there is a greater increase in friction with temperature increase above the transition temperature. Indeed the tests on a chromium plated pair revealed a high coefficient of friction and a large friction increase at the transition temperature.

Thus from these experiments it would seem that the idea of a desorption type mechanism for running in failure is a possibility and the incorporation of the action of e.p. additives and the amount of physical adsorption at the scuffing temperature to the theory, would seem to strengthen the critical temperature theory of failure.

Thus the following section on four ball tests was carried out with the knowledge of these results and this theory of lubricant failure.

CHAPTER 12

Slow speed and high speed four ball tests and the affect of additives on steel

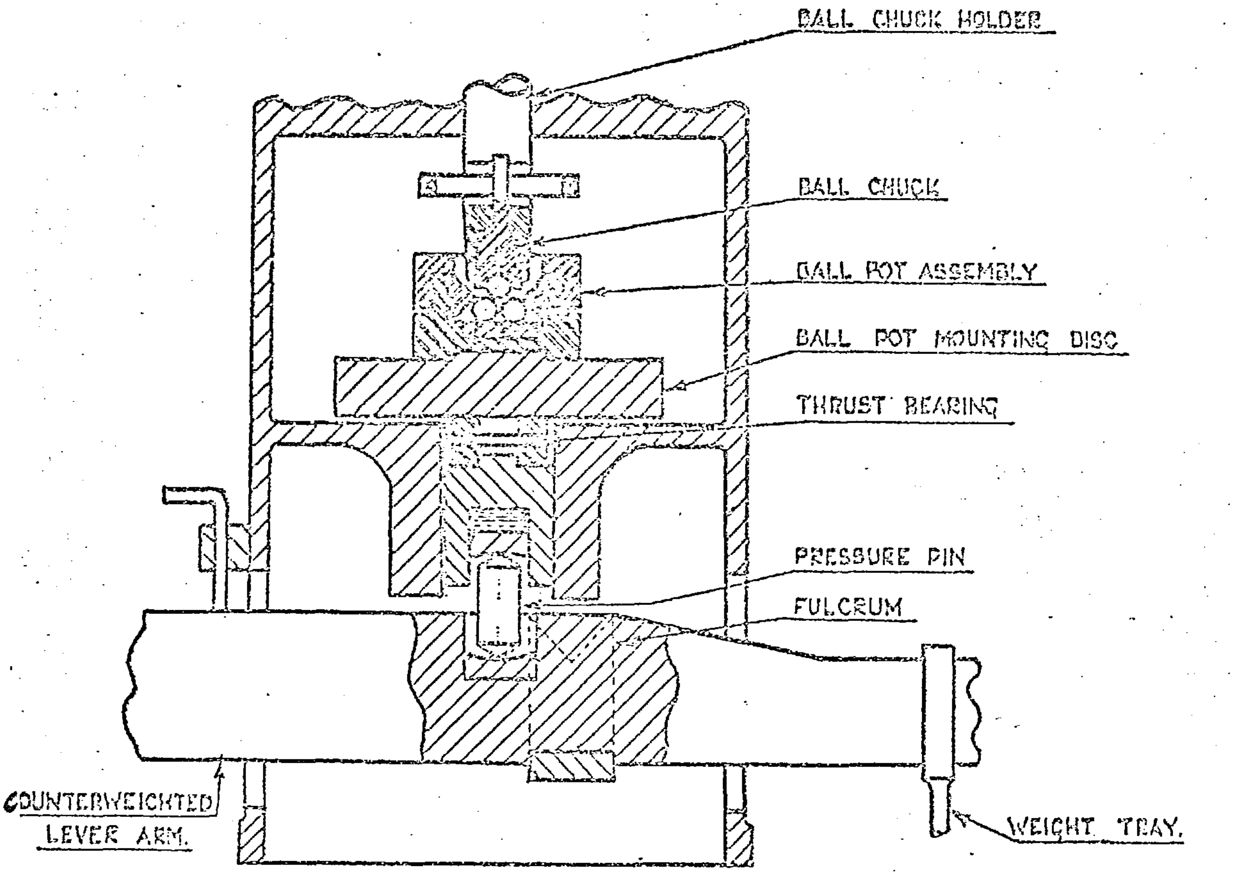
The work reported in this chapter was carried out in Moscow in the laboratories of Dr. Matveevsky and Professor Vinogradov of the Russian Academy of Sciences.

The author is grateful to Dr. Matveevsky, Professor Vinogradov, the Russian Academy of Science, the Royal Society and to Dr. Cameron for making this possible.

The four ball machine is much used in the testing of lubricants and such a test is often included in oil specifications. Figure 80 shows a Ministry of Supply D.T.D. specification four ball machine. [188]

D.T.D.581B

5



LOAD CARRYING CAPACITY TEST APPARATUS.

Figure 80

A typical test procedure is to run the machine for one minute under a given load and at contant speed, and then to measure the wear scar on the balls and the, sometimes, with new balls repeat the procedure at a higher load and to continue this process until the load is reached where the balls scuff or sieze.

So far we have demonstrated using the Bowden-Leben machine that a transition temperature can be obtained using stainless steel and an oil containing no additive and that the transition temperature may also be obtained using stainless steel and an oil containing some e.p. additive, and that this transition temperature is a possible explanation for the failure of gears and discs. Subsequent experiments showed that the cause of the increase in friction at the transition temperature was identified with the presence of natural surface active agents in the base oil, and that the cause of finding no transition temperatures using martensitic steels on the Bowden-Leben machine was due to the reactivity of the martensitic surface with the base oil, whilst an austenitic structure of the same steel composition did give a transition temperature.

The Bowden-Leben machine, however, would not seem to represent conditions of lubrication experienced by gears and discs, although the work by O'Donoghue, Manton and Askwith [167] is important in showing the relevance of Bowden-Leben type tests to actual gear machine tests. It was decided to carry out some four ball machine tests. The four ball machine, unlike the Bowden-Leben machine, comprises a rotating ball so that both the friction surfaces repeatedly come into contact. The speed of the machine may easily be varied from boundary-lubrication conditions at 1 r.p.m. to high speeds where hydrodynamic and elastohydrodynamic conditions exist, it is noted that even if the four ball test failure load is found to be directly related to boundary lubrication tests, the use of an oil which is better for hydrodynamic and elastohydrodynamic lubrication may still be of great importance, for hydrodynamic properties may determine the point at which the boundary lubrication regime is important.

The four ball machine thus, intoduces at higher speeds hydrodynamic lubrication and demonstrates the importance of boundary lubrication properties under these conditions. It is also intended to introduce e.p. additives and to note their effects under the conditions at which they are operating.

Slow speed four ball measurements

The first series of four ball tests carried out in these experiments were done using Matveevsky's KT2 machine. This is a 1 r.p.m. four ball machine and was described in Chapter 6, the chapter on transition temperatures. It is remembered that Matveevsky obtained transition temperatures with a base oil and the Russian bearing steel ШX6 whose composition is:

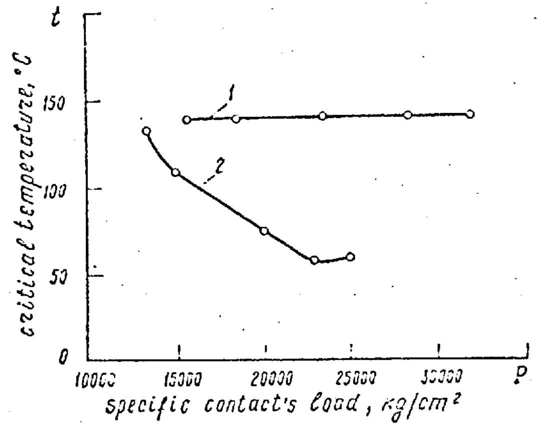
C 1.05 - 1.15%; Cr 0.4 - o.7%; Mn 0.20 - 0.40%; Si 0.17 - 0.37%

It was decided to study differences in reactivity between two steels by friction and wear measurements. It was established in the experiments using the retained austenite samples that the austenite structure was less reactive, but in these tests the steels were to be of uniform structure and of equal hardness so that a comparison of wear behaviour could also be made.

The two steels chosen were the ш X6 steel and 18/8 austenitic stainless steel.

The stainless steel austenitic balls had V.D.P. of 270 Kg/mm^2, thus the ш X6 balls were annealed in a vacuum furnace. The hardness of ш X6 was then 220 Kg/mm^2.

An operating vertical load of 11 Kg. was chosen, this gives a Hertzian pressure of 9,100 Kg/cm^2 for $\frac{1}{2}$" balls, this was chosen because earlier results by Matveevsky had shown that in this region of loading the critical temperature is not a function of the hardness of the material. Fig. 81 is taken from Matveevsky's paper [157]. Although Matveevsky's results do not include steels as soft as these being used.



Critical temperatures as a function of specific contact load:
1 Hardened steel against hardened steel (DPH 1000)
2 Mild steel against mild steel (DPH 200)

Figure 81

Experimental

The balls and ball holders were carefully washed in benzene, methylated spirit and ether and transferred using tongs to the apparatus. The thermostatically controlled heater was switched on, and when the desired temperature was reached the top ball was rotated for one minute. The friction was measured using a pen and drum chart.

After each run the wear scar diameter was measured using a microscope and all the balls were rotated to an unused area. The experiment was then repeated at a higher temperature.

The oil used was a base oil similar to a light stock oil and the additive chosen was diphenyl disulphide. Diphenyl disulphide, $C_6H_5S.S.C_6H_5$, is not considered as a very reactive e.p. additive. Sakurai and Sato [189] have examined the reaction products between diphenyl-disulphide in oil and steel using X ray analysis, much Fe_3O_4 was identified and it is thought that an oxidation reaction predominates. Sulphur and dibenzyl disulphide, however, used as e.p. additives result in the formation of sulphides.

It was decided to test over the temperature range 20 - 180°C and to initially use two concentrations of additive, 0.5% and 3.53% by weight. The tests were then carried out on the annealed WX6 balls and the 18/8 stainless steel balls.

Results

Figure 82 shows the friction-temperature and wear scar-temperature results for the stainless steel and Figure 83 shows the results obtained using the WX6 steel.

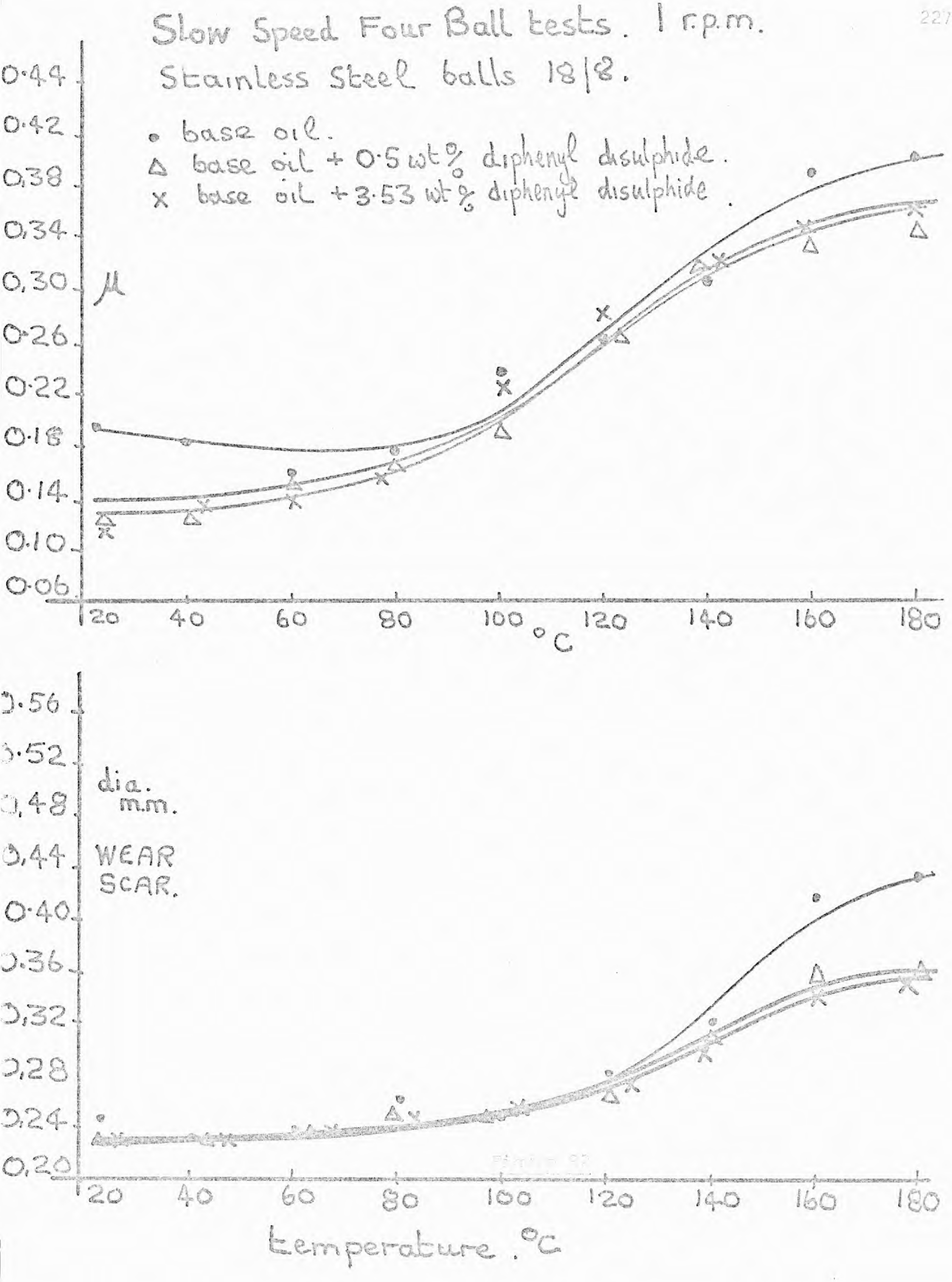

Slow Speed Four Ball tests. 1 r.p.m.
Stainless Steel balls 18/8.

Figure 92

Slow speed 4 ball tests. Sh.X6. steel.

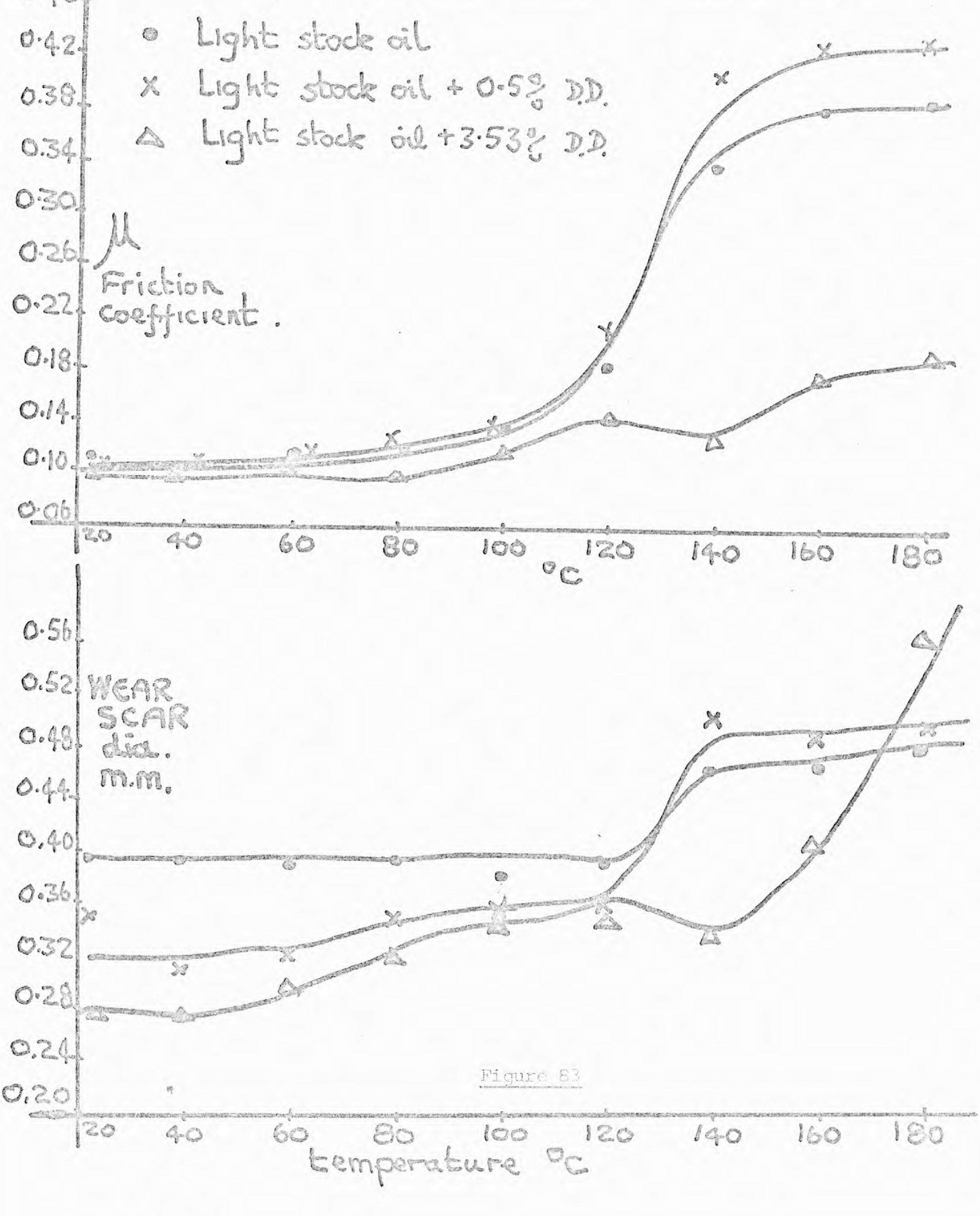


Figure 83

Tests using the stainless-steel

Figure 82 shows that friction and wear both increase greatly above a temperature region, the transition temperature. It is seen that the presence of the additive at both 0.5 wt% and at a concentration of 3.53 wt% has only a small effect on either friction or wear. There is some scatter in the results, however, the graph shows that the small effect of the additive is perhaps to decrease the friction and wear of stainless steel above the transition temperature.

Tests using the ШX6 steel

The results using the ШX6 steel are shown in Fig. 83. It is seen that the transition temperature obtained with the ШX6 steel is approximately the same as that obtained with the stainless steel.

There is some scatter of points, however, it is seen that below the transition temperature the additive seems to have little or no effect. Above the transition temperature it is seen that 0.5 wt% additive concentration has a small effect in reducing friction and wear.

The effect of 3.53 wt% addition of diphenyl disulphide additive is most interesting. It is found that below the transition temperature of the base oil, the additive oil has little or no effect on friction and wear, but when the transition temperature is reached the friction and wear do not increase but instead decrease. With further increase in temperature it is seen that friction increases a little, but that the wear increases enormously, and is greater than that of the non additive oil.

Thus at the high temperatures corrosive wear is taking place for the 3.53 wt% additive oil.

It is also noted that for the non-additive oil, the coefficient of friction with the stainless steel is greater than the coefficient of friction of the ШX6 steel and that the wear rate of the stainless steel is less than the wear rate of the ШX6 steel for conditions below the transition temperature.

Tests were then carried out using a high speed four ball testing machine.

High speed four ball tests

The apparatus used for the high speed four ball tests is the machine used by Vinogradov and Podolskii [190] a photograph is given in Fig. 84.

The proposal was to carry out similar tests as those using the slow speed four ball machine but under conditions of higher speed.

Experimental

The four balls were washed in benzene, acetone and ether and carefully transferred to the four ball machine with clean tongs. The requisite load was applied and the top ball rotated for one minute. The friction force was recorded with a pen recorder.

The wear scar diameters were measured using a microscope and the run continued with an increased load. The balls were not turned in their holder, but the run continued on the used surface. The experimental procedure is similar to the method used for high speed four ball machines found in the literature [9, 10]. The speed was chosen as 1,500 r.p.m. for the half inch balls i.e. 57.8 cms/sec. The speed enables scuffing to be readily achieved.

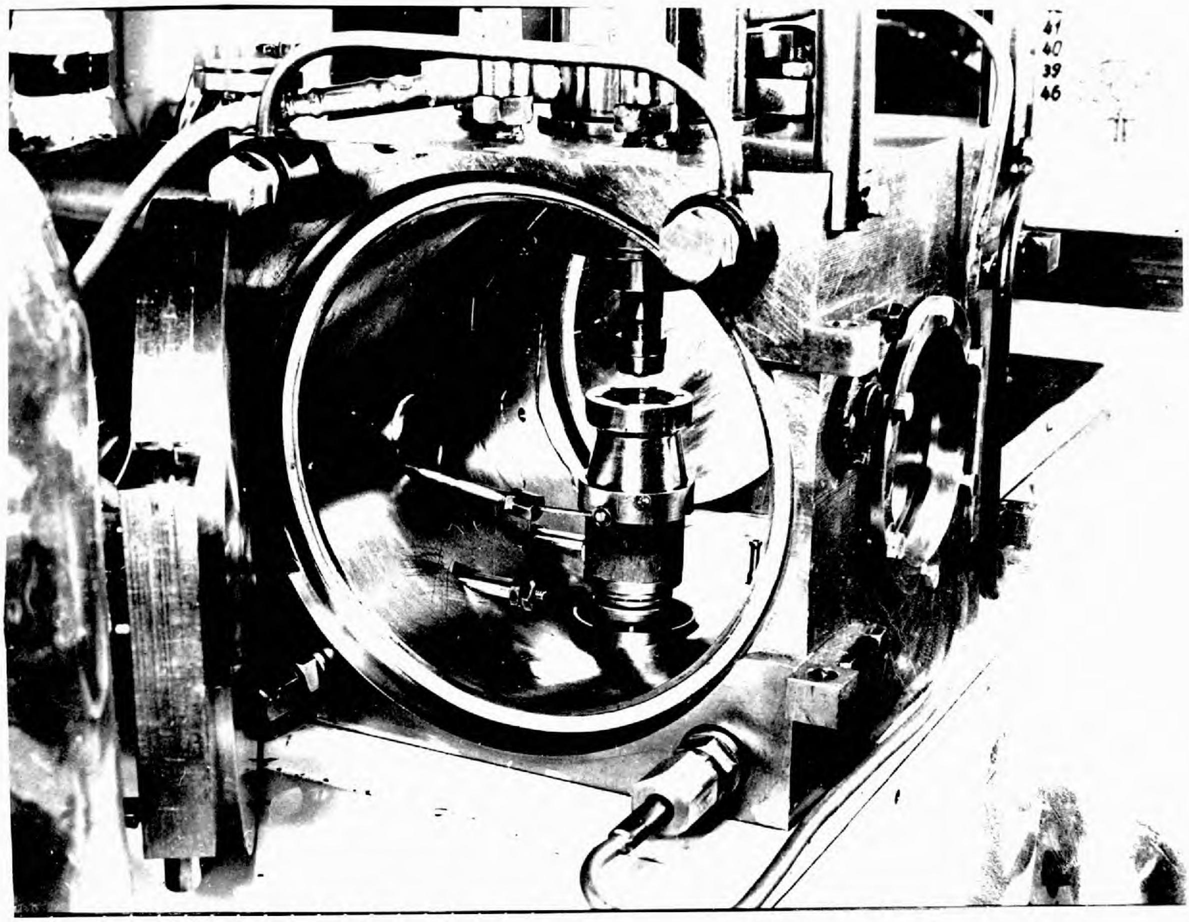


Fig. 84.

High speed four ball machine

Results

1. 18/8 Stainless steel balls

Graph 85 shows the coefficient of friction and wear scar diameter as a function of the applied load at 1500 r.p.m. The lubricants used are the light stock oil and oil with the highest concentration of additive, i.e. 3.53 wt% diphenyl disulphide. It is seen that the scuffing load is low and that there is only a slight improvement in load carrying capacity on using the oil containing the additive.

2. The Martensitic ωX6 steel

Graph 86 shows the results obtained using the ωX6 steel of hardness comparable to the stainless steel. With the light stock oil the scuffing load is much greater than using stainless steel. The effect of the additive is to increase the scuffing load by a large amount. With 0.5 wt% diphenyl disulphide additive the scuffing load increased from 60 kg to 195 kg and with 3.53 wt% diphenyl disulphide scuffing could not be obtained. It is seen that the wear curve is plotted as two lines, these are the major and minor axes of the wear scar on the ball which is an ellipse. The wear using the oil containing 3.53 wt% additive is greater than that of the 0.5 wt% additive oil for loads greater than 120 kg.

Graph 87 shows the results obtained for both steels using a log. scale.

Conclusions and Discussion

The slow speed four ball tests showed that under these conditions using the light stock, above a certain temperature, the critical temp-

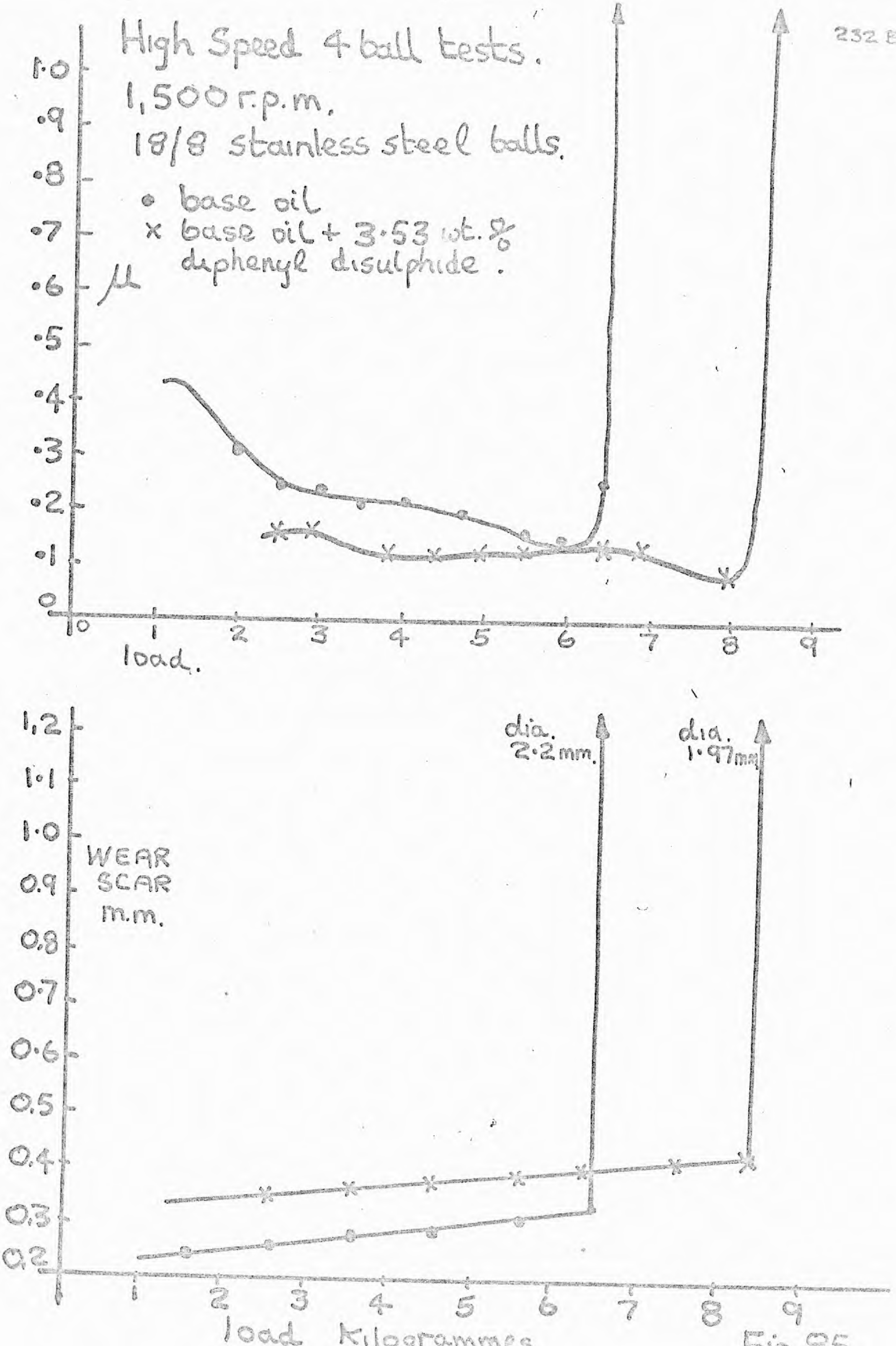

High Speed 4 ball tests.
1,500 r.p.m.
18/8 stainless steel balls.
• base oil
x base oil + 3·53 wt.% diphenyl disulphide.
μ
1·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
0
0
1
2
3
4
5
6
7
8
9
load.
1,2
1·1
1·0
0.9
0,8
0·7
0·6
0.5
0,4
0.3
0.2
WEAR SCAR m.m.
dia. 2·2 mm.
dia. 1·97 mm.
1
2
3
4
5
6
7
8
9
load Kilogrammes.

Fig 85

High speed 4 ball tests. ShX6 steel

1,500 r.p.m.

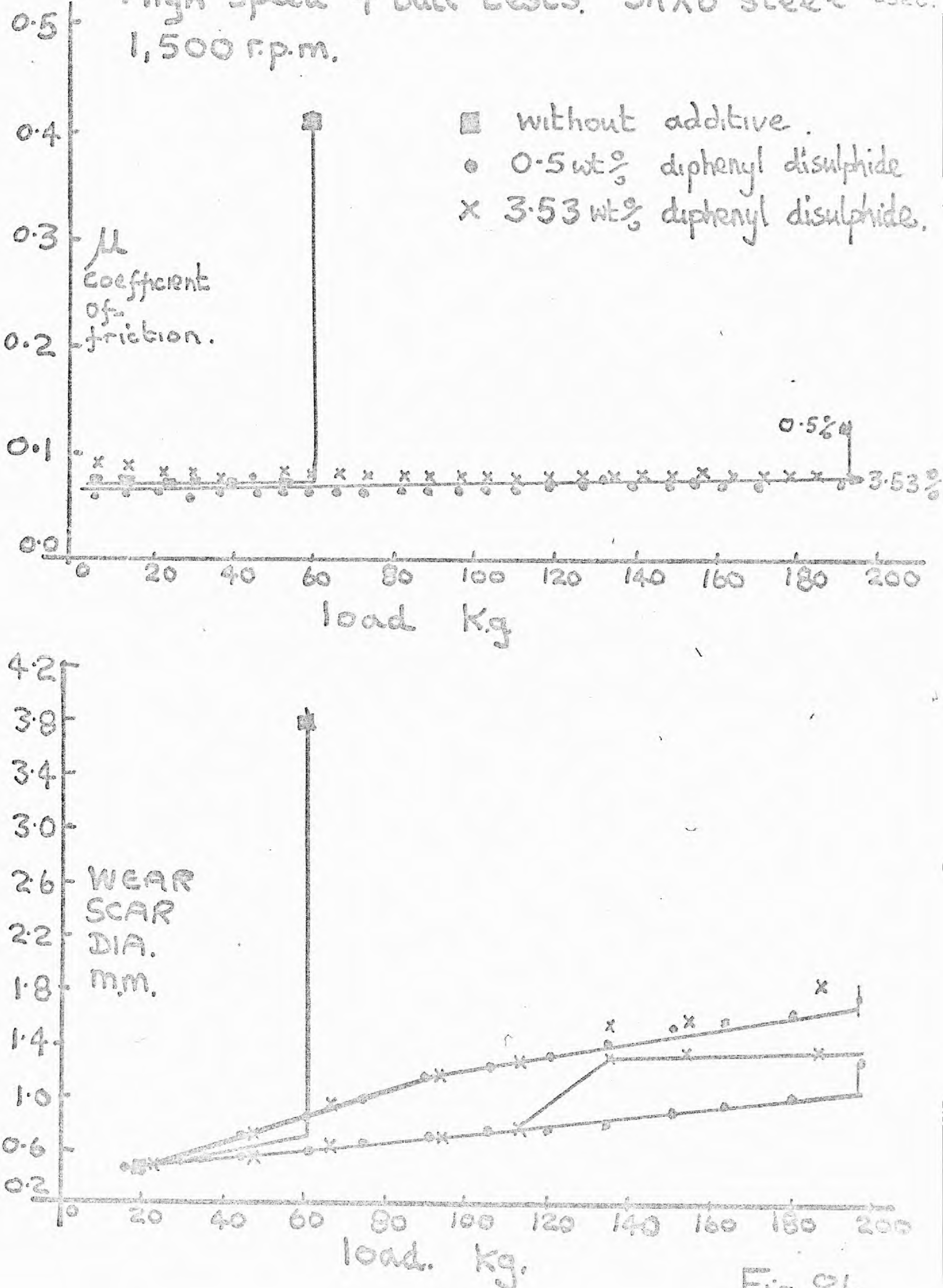
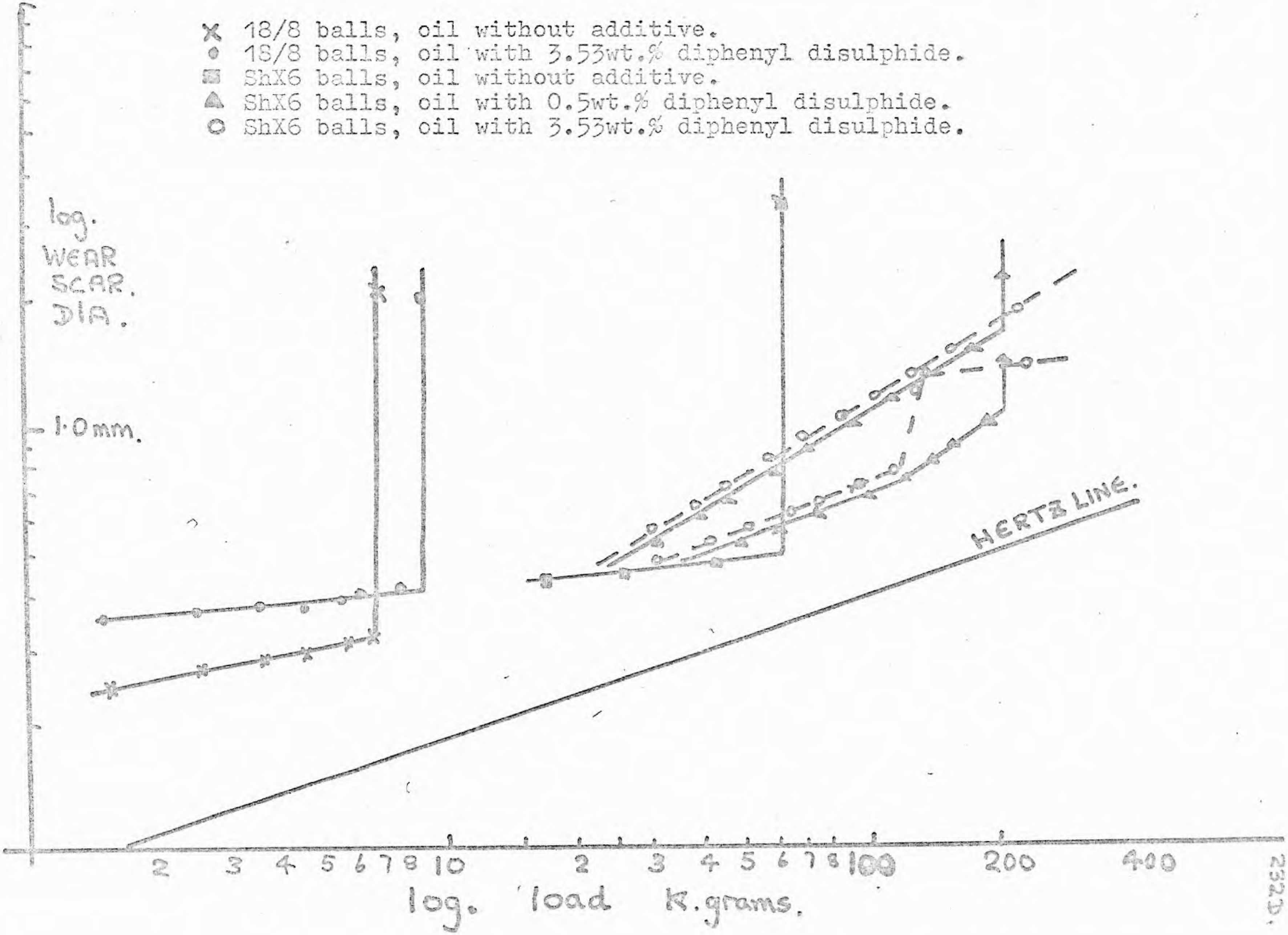


Fig 8b

Fig 97



× 18/8 balls, oil without additive.
● 18/8 balls, oil with 3.53wt.% diphenyl disulphide.
■ ShX6 balls, oil without additive.
▲ ShX6 balls, oil with 0.5wt.% diphenyl disulphide.
○ ShX6 balls, oil with 3.53wt.% diphenyl disulphide.
log. WEAR SCAR. DIA.
1·0mm.
HERTZ LINE.
2
3
4
5
6
7
8
10
2
3
4
5
6
7
8
100
200
400
log. load K.grams.

erature, the coefficient of friction increased greatly. The effect of additives demonstrated the mutual dependence of reactivity, corrosivity, wear and coefficient of friction for the two steels.

The high speed four ball tests showed that the steel structure and composition are important parameters in the failure load.

The slow speed and high speed four ball tests are in agreement with each other. The high speed four ball tests are the more usual tests, thus an important problem is to see in what way can extra information be obtained from both tests. They demonstrate the importance of metal structure and composition on failure load and consolidate the earlier work in which the deleterious effect on scuffing load of retained austenite in gears was found.

The problem now to be considered is in what way the results of these tests can improve the choice of lubricant.

In the chapter on diesel engine scuffing, a mechanism of transition temperature scuffing was proposed in which the role of the additive was most important. In this chapter the effect of additives have been considered, and perhaps an indication of further work is shown in the slow speed four ball graph, graph 83 where corrosion is seen only to appear after the transition temperature has been reached.

The following chapters are now concerned with the combined effect of polar and e.p. additives.

CHAPTER 13

Corrosion Inhibition and Desorption Effects in a Mineral Oil

Introduction

According to the transition temperature theory of scuffing we have said scuffing will occur if there is a sudden desorption under load which leaves the surface unprotected. The additive will be unable to form a coating, however, the likelihood of the additive being able to react sufficiently to prevent siezure is helped if some of the surface already has low shear strength compounds present, such as additive reaction products.

It was thought that perhaps the polar boundary lubricant was to some extent preventing the action of the additive. The process would be two methods. The first method would be by the lubricant's function i.e. to act as a boundary lubricant and reduce metallic contact, whilst the second method might be as a corrosion i.e. additive inhibitor.

This chapter investigates the effect of a polar boundary lubricant as a corrosion inhibitor.

Iron and steel surfaces even though initially covered or immersed in an oil are still likely to rust when water is present. Polar molecules are therefore added to some lubricating oils as rust inhibitors. Being slightly soluble in the oil, not only may the water not penetrate the polar film, but because of the dynamic equilibrium, the molecules may displace water. This allows repair, through adsorption of surfaces damaged by abrasion, i.e. an advantage over solid coating inhibitors depending on the main variables: the metal, the solvent, the solute, the corrosive agent, the temperature and the concentrations.

It was decided to investigate whether the desorption of polar molecules in oil to which we have attributed the sharp rise in friction found with temperature on the Bowden-Leben machine, also showed any inhibiting properties. Indeed we wish to see if such inhibiting properties disappeared with increase in temperature. Some possible experimental methods are now discussed.

It is clear that there is a close relationchip between corrosion inhibition, wear prevention and polar molecules. This was recognised by Zisman whose work on olephobic monolayers was prompted by rust inhibitor studies [191]. One of his initial experiments on corrosion was concerned with the displacement of water by a polar compound.

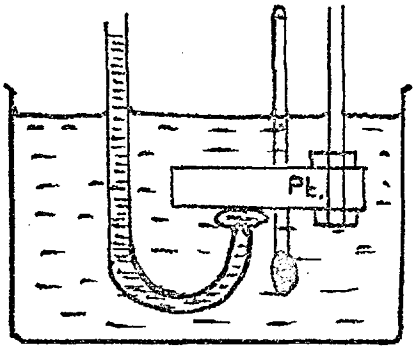


Figure 88

Thus in Fig. 88 the open end of a pipette which has been filled with the oil is inserted below the water level so that the J shaped tip is directly beneath a strip of clean platinum foil. A drop of hydrocarbon is forced out of the tip so that it just touches the foil. The drop is pressed against it for 30 minutes and then sucked back. It is found that pure hydrocarbons do not displace water from the platinum, but the addition of a polar compound such as stearic acid or octadecylamine resulted in the foil becoming both hydrophobic and oleophobic. Zisman then repeated these experiments at different temperatures. A further method he used in a later paper [192] was based on the A.S.T.M. test D665-42T. In this test the inhibitor was added to a refined oil having no rust inhibiting properties but containing 10% of distilled water. Standard steel specimens immersed in the solution were examined after 48 hours for rust. Zisman [192] carried out tests for a large number of compounds and his paper lists 76 compounds in which testing has been carried out at elevated temperatures. Thus 0.2 wt% myristic acid became a poor inhibitor above 165°F whilst 0.2% stearic acid was still satisfactory at 190°F.

Hackerman and Schmidt [193] used an electron diffraction technique to study corrosion inhibitors and found in many cases evidence of an ordered structure for compounds exhibiting good rust inhibitive properties.

In another method used by Finlay and Hackerman [194], steel powder was reduced under hydrogen at 600°C for twenty four hours and then the polar compound was passed over the steel in benzene. The powder was then treated with .1N sulphuric acid and the amount of hydrogen measured. Thus the relative inhibitor efficiency I_R was defined:

$$I_R = \frac{R_P - R_I}{R_P}$$

where R_P and R_I are the amounts of hydrogen evolved from the plain steel and inhibited steel respectively. Such a technique could be used for this investigation.

The general methods used for corrosion testing were also considered [195] i.e.

1. The change in reflectivity of a polished surface or the use of an ellipsometer to measure the increase in thickness of the corrosion product.

2. Measurements of weight changes after removing the corrosion product.

3. Potential methods such as using a Calomel cell.

4. Methods using isotope tracers such as autoradiography.

5. Isotherm measurements using powders [196].

Of these methods, radioactive tracers in e.p. additives have been much used, and some static corrosion tests have been carried out. Thus Elliot, Hitchcock and Edwards [197] used mild steel discs which they heated in test tubes containing radioactive lubricating oil. These tests were carried out at three temperatures: 100, 150 and 200°C.

Borsoff [198] immersed preheated steel strips in radioactive oil and measured the thickness of the chemical film produced. However, these results do not give sufficient readings for an assessment to be made of the critical temperature and inhibiting effect of polar oils, the object of this investigation.

It is also noted that Hackerman and Shock [199] found for oil wells, some oils gave the drilling equipment good corrosion inhibition whilst others did not.

This corrosion study has two special differences from standard corrosion studies. The polar compound in the oil may be the naturally occurring surface active compounds, thus its properties and concentration are automatically fixed for a given oil. It is expected that the corrosion tests should be carried out at temperatures up to 200°C for at these temperatures the region of transition temperature may be investigated, however, the bulk oil at this temperature is likely to oxidise. Indeed Tabor [52] using the Bowden-Leben machine found a decrease in friction above 80°C for the oil he tested. He attributed this to the formation of polar oxidation products.

The addition of an antioxidant to the oil was considered but decided only to be used as a last resort.

Two methods for the experiment were chosen to be examined in more detail (i) autoradiographic and (ii) hot wire.

Using a radioactive tracer, a flat steel specimen could be heated electrically with the oil corrosive mixture passing over it at a given flow rate. The corrosive substance could be labelled with S35 or C14 giving soft beta radiation. After a certain time, the steel plate would be washed and then counted using a scintillation counter or a photographic plate. The experiment could then be repeated using white oil rather than lubricating oil and the results compared at the different temperatures.

The hot wire method is to measure corrosion by the change in electrical resistance of the specimen, the corrosion product being non conducting. Heating is accomplished electrically by sending a current through the specimen.

The hot wire method has been used in corrosion studies [195] and more recently in studies of e.p. additive reactions with steels 200, 189, 201, 202, 203.

Temperatures in the region of 600°C may be attained using a thin steel wire, whilst the bulk oil remains at room temperature. Good correlation between chemical reactivity and the load carrying capacity of e.p. determined by the hot wire method and four ball, gear and disc tests have been reported by Barcroft [200]. Whilst the temperatures contemplated in these experiments are not likely to exceed 250°C, the hot wire method overcomes the problem of bulk oil oxidation at high temperatures, whilst retaining a quick method of corrosion measurement. It is interesting to note that Campbell and Grunberg [203] have used the hot wire method for corrosion studies at high temperatures. In order to keep the bulk oil at room temperature, they heated the wire by short pulses of current i.e. 4 milliseconds duration at 44 millisecond intervals.

The hot wire method was chosen for this investigation and other advantages and disadvantages of the method are given in the Discussion of Results section.

It was decided to compare the corrosion of piano steel wire 35 S.W.G. in two corrosive media: The one having a light stock oil base and the other a white oil base. (The white oil not having a transition temperature.)

The tests were to be carried out simultaneously in the same circuit. Thus the wires were selected to be of almost equal resistance and the two wires were connected in series. Thus any changes in current passing through the wires would result in an equal change for them both.

Experimental

A diagram, Figure 89, shows the apparatus and heating and measuring circuits used.

Switches were incorporated so that a change from measuring circuit to heating circuit was quickly accomplished. The wires chosen were eight inches long and were lightly curled and the end carefully clamped between the washers by a screw going into the end of each of the quarter inch diameter 'silver steel' rod supports.

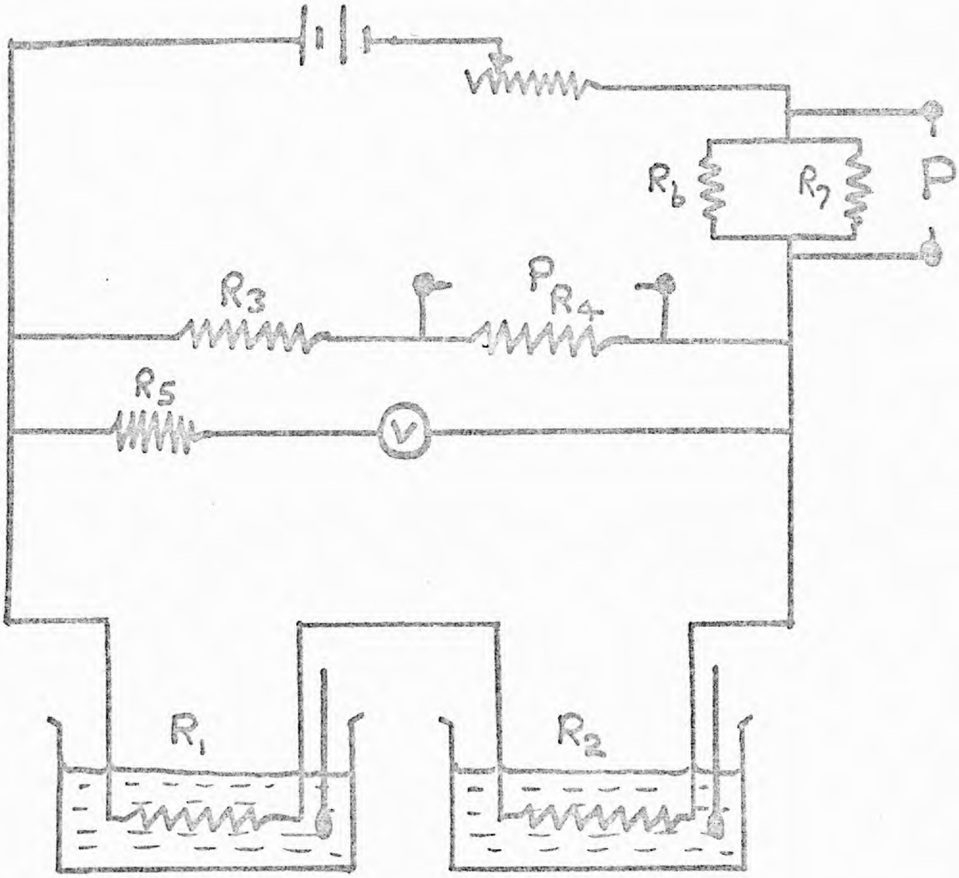
The wires and rods were cleaned firstly by rubbing with abrasive SiC paper and benzene. They were then immersed for fifteen minutes in benzene and then fifteen minutes in acetone and then quickly transferred to the corrosion mixture.

The initial resistance of each wire was measured separately in a bath of white oil which was vigorously stirred. The temperature of the white oil was measured with a calibrated 0 - 50°C thermometer.

The wires were then recleaned and put into the corrosive mixture and the required heating current sent through the wire. The time of the experiment was fifty minutes.

After this time the resistance of each wire was remeasured. The reaction decreases the diameter of the wire and thus increases the resistance. Hence the amount of corrosion of each wire for this experiment was determined. The temperature of the wires during the

Hot Wire Heating Circuit.



Hot Wire Measuring Circuit.

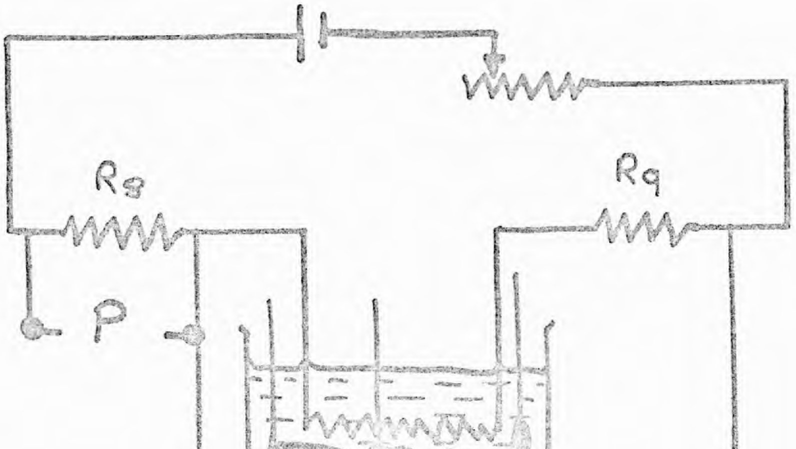


Fig 89

experiment is set by the voltage across the wires. The resistance of the wire, while current is flowing, is determined from the measurements of the potential differences across the standard resistances R_6 and R_7 and R_4 (Figure 89). The reaction temperature is obtained from a knowledge of the resistance temperature characteristics of the wire which were determined in a separate experiment.

Resistance-temperature characteristics

The resistance temperature characteristics of the wire was determined using the measuring circuit, Figure 90). For temperatures up to 170°C the wire was immersed in a temperature controlled bath containing white oil which was vigorously stirred. A mercury thermometer suspended close to the wire measured the temperature. For temperatures greater than 170°C the wire was placed in a resistance furnace, and the temperature was measured using a thermocouple. The maximum furnace temperature was 250°C. The calibration was carried out for increasing and decreasing temperatures. No permanent change in resistance of the wire was detected after calibration in the white oil and in the furnace. The absence of corrosion and of structural changes causing differences in the resistance of the wire at these temperatures was inferred from this. The resistance temperature graph was plotted and then replotted as change in resistance of the wire compared to the resistance of the wire at 30.0°C against temperature. The resistance temperature relation was also determined for a wire which had undergone corrosion and this graph was also plotted. Graph 91 shows the single linear relation obtained.

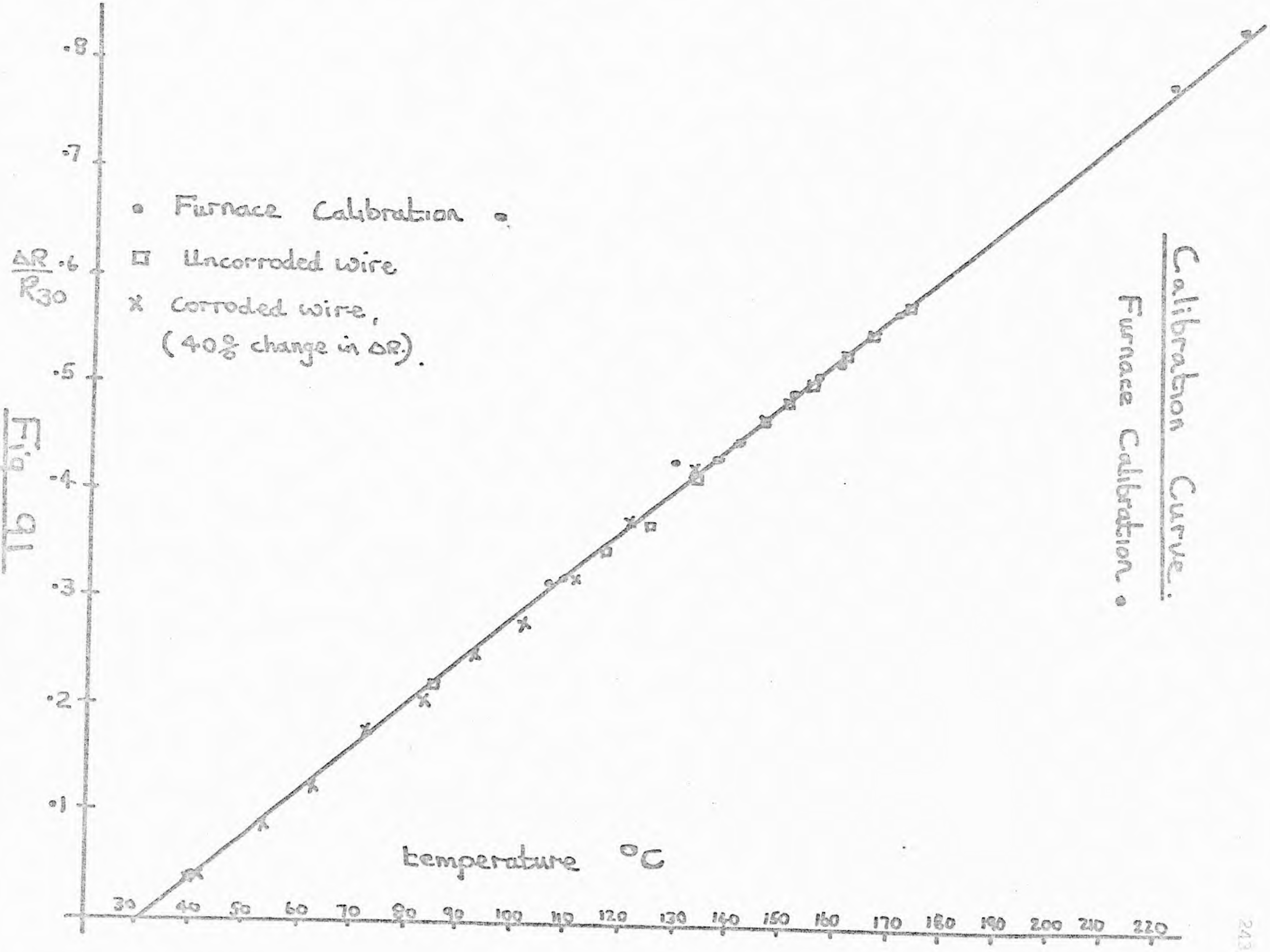
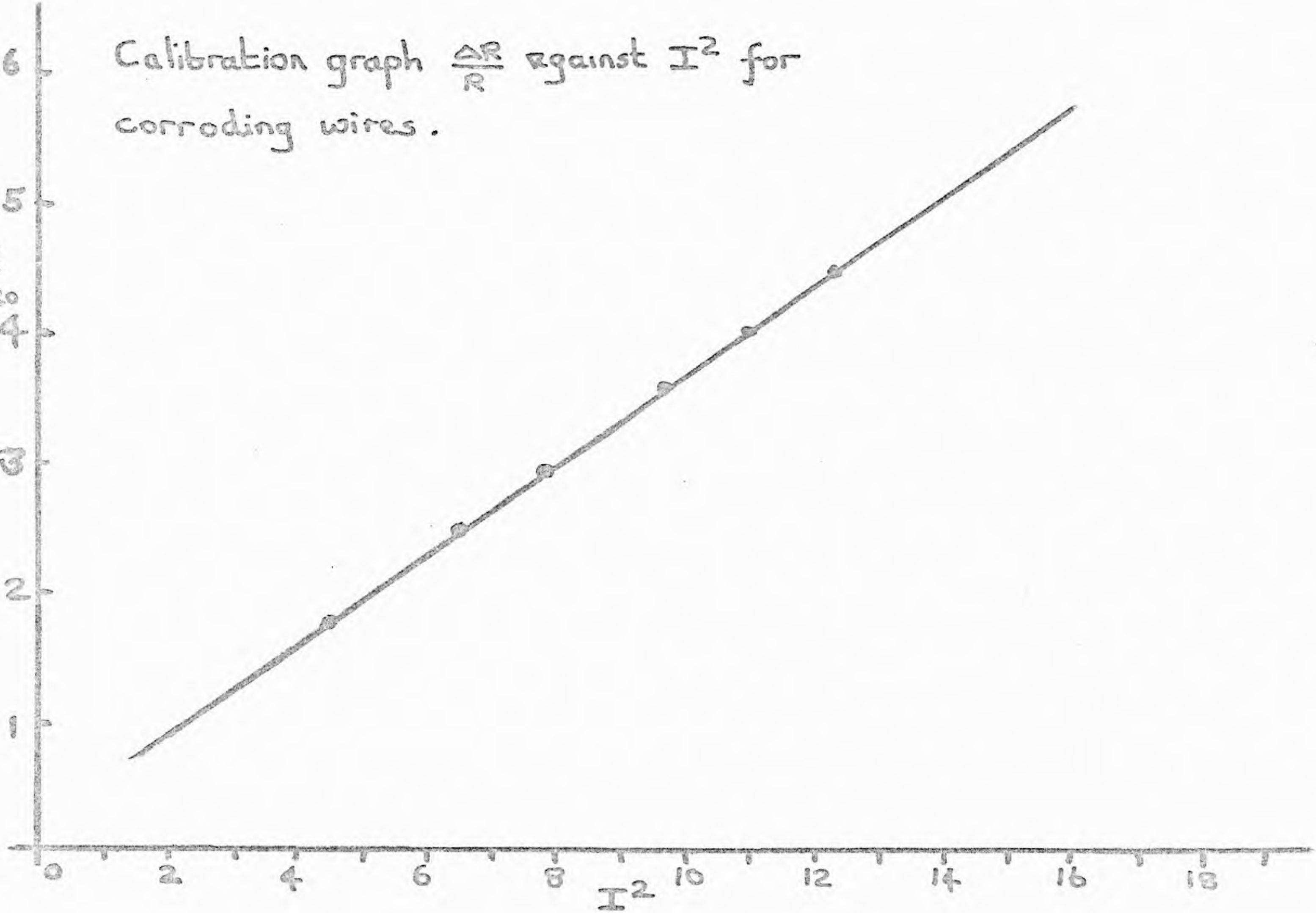


Fig. 91

Calibration Curve.

Furnace Calibration ●

Fig 92



Calibration graph $\frac{\Delta R}{R}$ against I^2 for corroding wires.

The corrosion mixture

The two oils to be compared were: (i) the light stock oil containing no additives used on the Bowden-Leben machine experiments which gave a transition temperature of 155°C and (ii) a liquid paraffin B.P. Tests on the Bowden-Leben machine using stainless steel with the paraffin did not detect a transition temperature. The paraffin had very poor boundary lubricating properties, i.e. its coefficient of friction was very high. The viscosity of the white oil is as follows:

59°F	36.38 c.p.	sg .85
210°F	2.7 c.p.	sg .80

After preliminary trials the corrosive substance was chosen as glacial acetic acid. Some toluene was also added so that a single phase mixture was obtained.

The solutions made up were:

120 mls	white oil or light stock oil
120 mls	glacial acetic acid
200 mls	toluene.

The mixture was made directly into the glass dishes in which the wire corrosion tests were conducted. All glassware was cleaned with chromic sulphuric acid cleaning mixture.

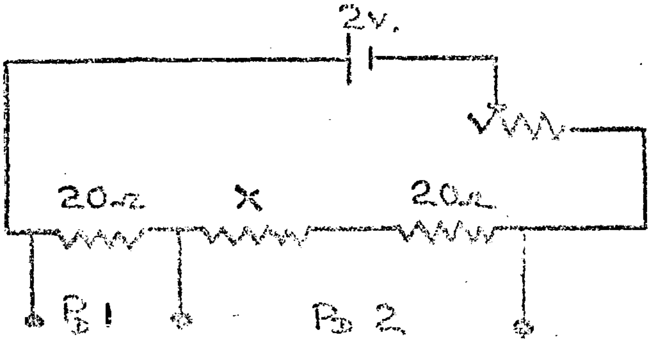
Electrical Circuit

The values of the resistors in the circuit, Figure 90, were varied according to the value of the current flowing through so that the potentiometer was able to operate at maximum accuracy.

As a typical example, a corrosion experiment is now considered and the result calculated illustrating the way in which the results were obtained.

Typical Calculation

(a) Measuring Circuit



P is the potentiometer

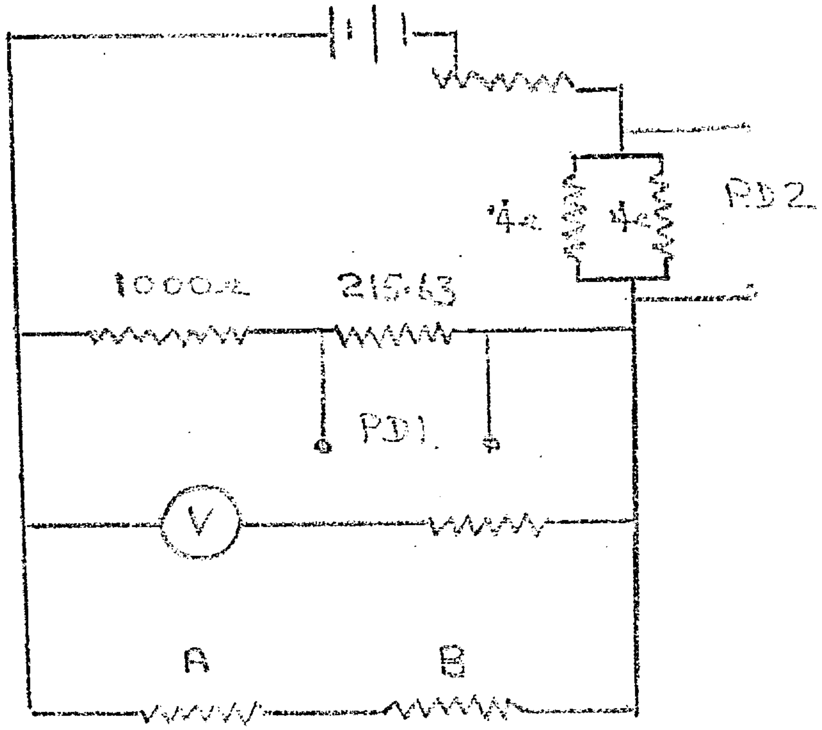
X is the resistance of the wire to be corroded

A refers to the light oil stock corrosion test

B refers to the white oil corrosion test.

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	R_{30}	Temp.	% change at 50 mins
A_{cs}	0	2795	2919	.88730	.86148	38.4	25.0
B	0	2795	2925	.93023	.90316	38.4	28.5
A_{cs}	50	2795	2950	1.10912	1.07684	38.7	
B	50	2794	2961	1.195418	1.16063	38.7	

Heating Circuit



$$A + B = R$$

$$R = \frac{12.75146}{\frac{(2)}{(1)} - .0009275}$$

Time mins	P.D.(1)	P.D.(2)	R	% increase in resistance	Temp.
0	1.2430	.6480	2.45036	138.9	125°C
47	1.4784	.6380	2.9612	140.7	130°C

The increase in resistance at 47 minutes is compared to an unheated resistance of 94% of the final corroded resistance for the calculation of $\frac{\Delta R}{R}$ for temperature measurement.

Since the heating effect is dependent upon the square of the value of the current flowing through the wire graph $\Delta R/R_{30}$ vs I^2 was plotted for the results obtained using the corrosion experiments, Graph 92. A good linear relationship is obtained. For temperatures higher than this it was decided, therefore, to set the temperature by fixing the current obtained from extrapolation of the $\frac{\Delta R}{R_{30}}$ against I^2 graph, graph 92, and to keep this current at a constant value. It is reported in the discussion section that accurate potential measurements were required the potentiometer was manually operated and thus over the time of operation a constant current is required to pass through the resistances.

The corrosion tests were carried out from 70°C to 190°C.

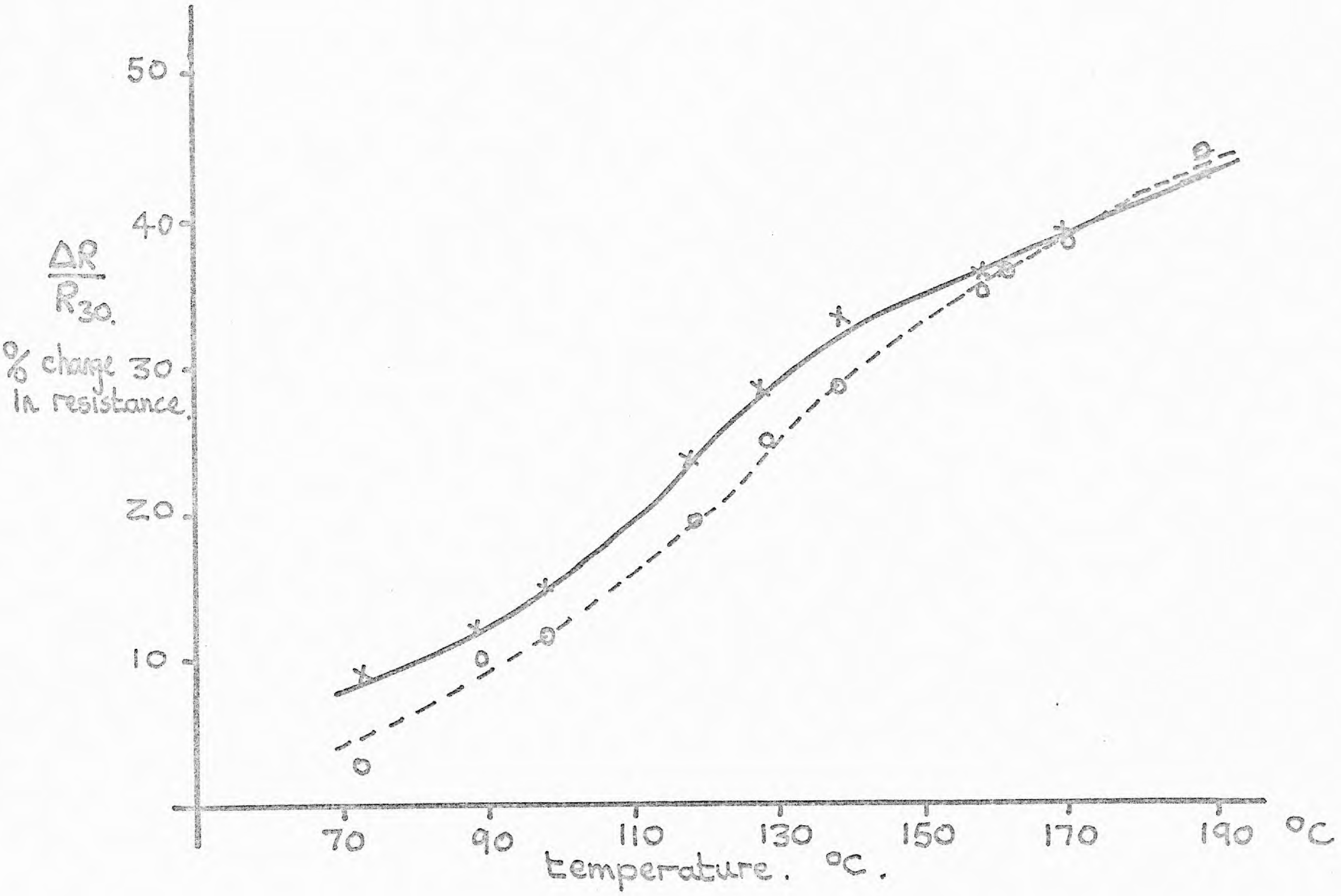
Results

The results are shown as a graph, graph 93,. The change in resistance of the wire due to corrosion is plotted against temperature of the wire for the two corrosion mixtures. It is seen that in all cases up to 160°C there is less corrosion of the wire with the light stock oil mixture. Above 160°C there is little difference in the corrosion of the wire for the two corrosive mixtures indeed at 190°C the corrosion of the wire in the light stock oil is greater than that obtained using the white oil.

Thus the natural polar groups in this light stock oil have a cossosion inhibiting effect on the attack of the steel up to the temperature region of 160°C.

This result will be compared to the friction temperature measurements using stainless steel surfaces and this light stock oil, reported earlier where a transition from low friction to high friction was obtained at 155°C.

Fig 93


$\frac{\Delta R}{R_{30}}$
% change in resistance
50
40
30
20
10
70
90
110
130
150
170
190
°C
temperature. °C.

Discussion of Results

The results are plotted as a percentage change in resistance against temperature, it is noted that the graph may also be plotted in terms of change in thickness of the wire. Thus,

Let R = resistance of the wire

r = radius of the wire

subscript 1 = initial state

subscript 2 = final state

K = constant

$$R_1 = \frac{K}{r_1^2} \; ; \qquad R_2 = \frac{K}{r_2^2}$$

Thus

$$2r_1\Delta r = \frac{K\Delta R}{(R_1 + \Delta R)R_1}$$

i.e.

$$\Delta r = \left(\frac{\Delta R}{R_1 + \Delta R}\right)\left(\frac{\pi}{2}\right)$$

Thus for a 12% change in the resistance of this wire 35 s.w.g. (thickness 0.0084 ins) the consequent change in radius is 0.00045 ins.

Accuracy of Experiment

Wire surface temperature

The difference in temperature between the centreline temperature and surface temperature of the wire has been calculated and is given in Appendix 2. It is seen that at a surface temperature of 110°C the centreline tempeature exceeds this value by only 0.074°C. Thus the temperature of the wire is assumed to be uniform.

Some advantages and disadvantages of using electrical resistance methods in corrosion studies have been discussed by Champion [195]. It is important that the wire is uniform and without notches or other defects. Pitting is said sometimes to be a problem especially with small diameter wires, and it is essential that a good contact is made between the wire and the holders.

In these experiments fresh wire without visible defects was always taken for each run and particular care was taken in making a good contact between the wire and holder.

Choice of wire

The wire chosen was a piano steel. Barcroft [200] in his experiments used stainless steel, Sakurai et al [189, 201, 202] used piano wire whilst Campbell and Grunberg [203] used iron wire. However, the tests of all these workers were carried out at temperatures in the region of 600°C. Thus a more reactive wire and corrosive medium is required for sufficient corrosion to occur at 200°C.

Choice of corrosive medium

Preliminary experiments showed that sufficient reaction was not occurring at these low temperatures on using the e.p. additives used by Barcroft, Sakurai et al and Campbell and Grunberg. Glacial acetic acid was chosen for, although being a weak acid it gives a sufficient hydrogen ion concentration to produce a rapid attack on iron. Acetic acid is used as a 1% addition in water for a standard corrosive spray test of steels [195, 204]. It was found, however, that the addition of toluene to the acetic acid oil mixtures was required for the solution to remain a single phase for the experiment. Because of depolarisation of hydrogen in the corrosion process by oxygen or air [205] the corrosion rate is dependent upon stirring efficiency. It was decided, therefore, to have no stirring and to have for each experiment, identical volumes of solution, lengths of wire and container vessels. Carrying out the experiments without stirring has an additional benefit in limiting the temperature rise of the corrosion mixture.

The potentiometer used was nominally capable of measuring voltages to an accuracy of 1 in 10,000. The standard resistances were specified as being accurate to 0.1% although their constancy is probably better than this. It is noted that such an accurate potentiometer is required since an error of 3.3 in 10,000 in potentiometer reading causes an overall corrosion value error of 5%.

Temperature measurement

In the section on experimental procedure, it was stated that the temperature for the corrosion tests was selected from the curve $\Delta R/R_{30}$ vs I^2, graph 92, which had been constructed from actual corrosion tests. This was chosen because by monitoring the current a more accurate control could be kept on the temperature. It does, however, mean that the curve has been extrapolated. It is remembered that even if there is some error in actual temperature, since the two wires are in series, the accuracy of the difference between the test using the light oil and the test using white oil is unaltered.

Campbell and Grunberg calibrated their wire by putting Sn and Pb flashes on the wire and noting the current at which the Sn and Pb melted.

It is expected that the temperature accuracy of these results may be no better than ± 3°C. The accuracy could be improved by using a constant current supply and a potentiometric pen recorder indicating the resistance of the wire. A method was devised to vary the current after measuring the new radius of the wire after corrosion by potentiometric measurements so that the temperature of the wire could be kept constant. However, it was found that the balancing time and supplementary calculations were too time consuming especially when a constant watch had to be maintained on the condition of the batteries. The results do show, however, that the mineral oil has corrosion inhibitive properties and that this effect vanishes in the region of 160°C. This is compared to the friction temperature measurements on the Bowden-Leben machine where a transition temperature was obtained for this oil at 155°C.

Conclusions

It was found that using a light stock mineral oil in a corrosive mixture the corrosion of a piano steel wire was less than the corrosion obtained when using a purified white oil. Thus the light stock oil containes natural corrosion inhibitors.

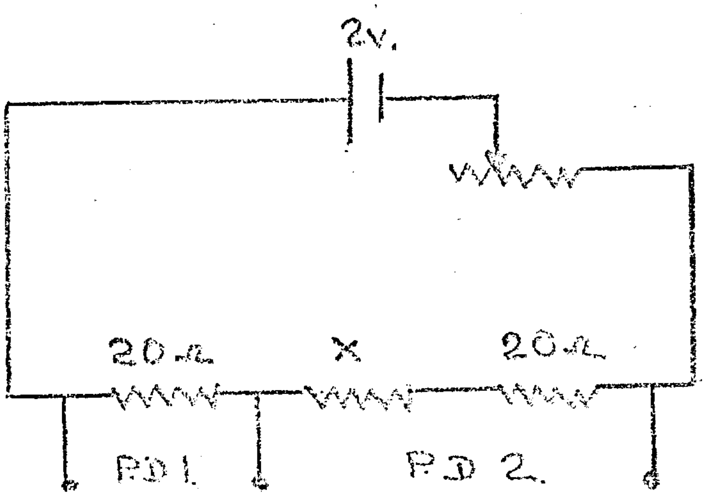
Using the hot wire method the corrosion tests were conducted over a temperature range from 70°C to 190°C. It was found that in the region of 160°C the corrosion inhibitive effect of the mineral oil over the white oil disappeared. This effect is compared to friction temperature measurements made on the Bowden-Leben machine using this oil and stainless steel surfaces. The friction temperature measurements revealed a sudden increase in friction at the transition temperature 155°C.

CHAPTER 13

APPENDIX I

Corrosion Test Results

Measuring Circuit



Test No. 1 Temperature 73°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	.28060	.2991	1.318603	1.30563	33.8	4.86
$B_{W.O.}$	0	2810	.2970	1.13188	1.04654	33.8	18.64
$A_{L.S.}$	110 mins	2835	.3031	1.382716	1.36903	33.0	
$B_{W.O.}$	110 mins	2823	.3000	1.25398	1.24156	32.8	

Test No. 2 Temperature 89°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	2786	2914	.91888	.914286	31.7	10.9
$B_{W.O.}$	0	2789	2910	.867694	.863770	31.7	11.4
$A_{L.S.}$	50	2795	2935	1.00179	.995779	31.0	
$B_{W.O.}$	50	2795	2933	.987476	.981551	31.0	

Test No. 3 Temperature 98°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	.27905	.2920	.928149	.923508	32.1	12.0
$B_{W.O.}$	0	.27940	.2924	.930565	.925912	32.1	14.8
$A_{L.S.}$	50	.2781	.2927	1.0398	1.03460	32.0	
$B_{W.O.}$	50	.2790	.2939	1.06810	1.06276	32.0	

Test No. 4 Temperature 118°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	2790	29345	1.0358423	1.010568	36.4	17.7
B	0	2789	29445	1.11501	1.08780	36.4	21.6
$A_{L.S.}$	50	2789	2959	1.219075	1.189329	36.2	
B	50	2786	2975	1.35678	1.323675	36.2	

Test No. 5 Temperature 127°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	.2795	.2919	.88730	.86148	38.4	25.0
$B_{W.O.}$	0	.2795	.2925	.93023	.90316	38.4	28.5
$A_{L.S.}$	50	.2795	.2950	1.10912	1.07684	38.7	
$B_{W.O.}$	50	.2794	.2961	1.195418	1.16063	38.7	

Test No. 6 Temperature 138°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$C_{L.S.}$	0	2799	.2947	1.057521	1.031717	36.5	28.5
$D_{W.O.}$	0	2800	.2941	1.007143	.982569	36.5	33.1
$C_{L.S.}$	50	2796	2986	1.35908	1.32592	36.8	
$D_{W.O.}$	50	2797	29845	1.34072	1.3080	36.8	

Test No. 7 Temperature 158°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	27913	29155	.889908	.876737	34.1	34.97
$B_{W.O.}$	0	27905	29245	.960401	.946187	34.1	35.7
$A_{L.S.}$	45	2790	2956	1.18996	1.15545	37.6	
$B_{W.O.}$	45	2789	2969	1.290785	1.25335	37.6	

Test No. 8 Temperature 160°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	2794	2935	1.009305	.979934	38.0	35.9
B	0	27955	2920	.9019327	.875686	38.0	35.8
$A_{L.S.}$	50	2781	2970	1.359223	1.33258	35.1	
B	50	2786	2955	1.213209	1.189430	35.2	

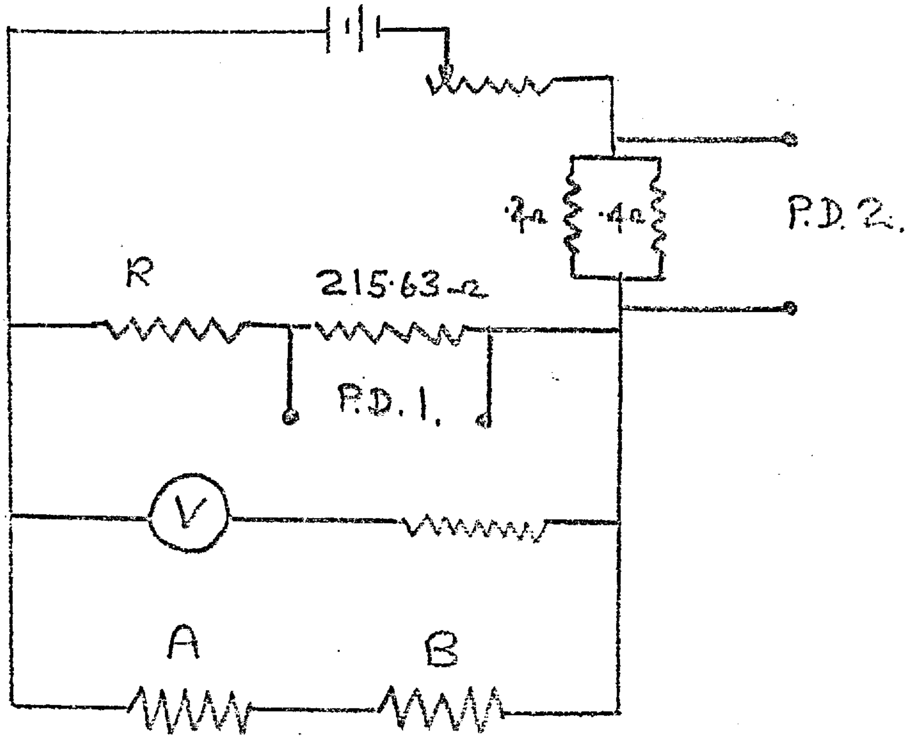
Test No. 9 Temperature 170°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	2781	2909	.920532	.90691	34.3	37.8
$B_{W.O.}$	0	2786	2879	.66762	.657739	34.3	38.4
$A_{L.S.}$	50	27745	29505	1.26870	1.24992	35.0	
$B_{W.O.}$	50	27805	2909	.92429	.9106105	35.0	

Test No. 10 Temperature 190°C

Mixture	Time	P.D.(1)	P.D.(2)	Resistance	Resistance 30°C	Temp.	% change
$A_{L.S.}$	0	.2861	2991	.908773	.904252	31.4	44.5
$B_{W.O.}$	0	.2856	3016	1.1205	1.11493	31.5	43.5
$A_{L.S.}$	50	2816	.3000	1.20682	1.30682	30.6	
$B_{W.O.}$	50	2811	.3036	1.60085	1.60085	30.6	

Heating Circuit



R unless stated differently is 1000·0Ω.

Heating Results

Experiment No.	Time mins	P.D. (1)	P.D. (2)	Resistance	Current	$\frac{\Delta R}{R}$	Temperature °C
1	0 110	.7920 1.0053	.4105 .4206	2.46461 3.05455	2.1	.1784 .1701	74 72
2	0 45	.9011 .9642	.5135 .5045	2.2413 2.44139	2.55	.24 .23	90 87
3	0 50	1.0276 1.1834	.5633 .5580	2.33013 2.70665	2.8	.26 .29	95 102
4	0 45	1.13440 1.5785	.6195 .5900	2.7720 3.76013	3.1	.358	117 120
5	0 47	1.2430 1.4784	.6480 .6380	2.45036 2.9612	3.3	.389 .407	125 130
6	0	1.6295 1.7880	.7155 .7030	2.91020 3.25086	3.5	.445 .424	140 136

Experiment No.	Current	I^2	$\frac{\Delta R}{R_{30}}$	Temperature
7	.380	14.4	.53	158
8	.381	14.5	57	160
9	.395	15.6	.675	170
10	4.25	18.06	.66	190

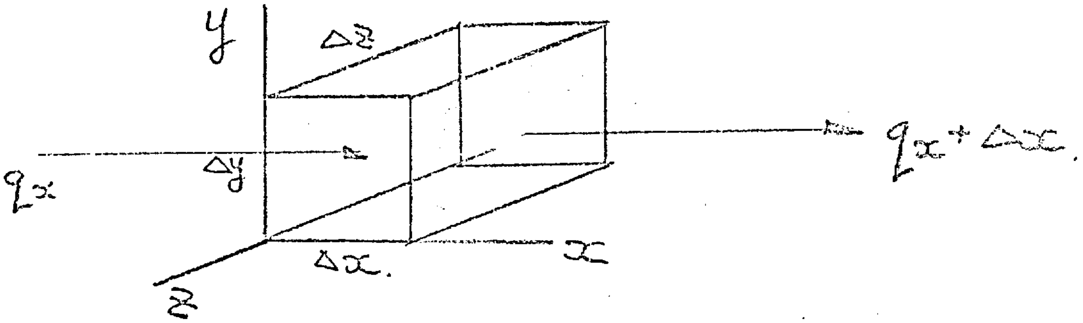
CHAPTER 13

APPENDIX II

The surface temperature of the wire

The temperature distribution across the wire is now calculated so that if it is found that the resistance of the wire and thus, temperature, varies over the cross sectional area then the surface temperature may be corrected.

Consider an element of the wire



the net rate of heat conduction into the element is of temperature T in the x direction

$$q_x - q_{x+\Delta x} = \frac{\partial q_x}{\partial x} \Delta x$$

Hence

$$\frac{\partial q_x}{\partial x} \Delta x = - \frac{\partial}{\partial x} (- K \frac{\partial T}{\partial x} \Delta y \; \Delta z) \; \Delta x$$

Similarly in the y and z directions

$$- \frac{\partial}{\partial y} (K \frac{\partial T}{\partial y} \Delta z \; \Delta z) \; \Delta y$$

and

$$- \frac{\partial}{\partial z} (K \frac{\partial T}{\partial z} \Delta x \; \Delta y) \; \Delta z$$

Let a current flow through the wire and let the energy be transferred away as heat. Let W_i be the heat generation per unit volume and time, i.e. Btu/ft^{3}hr.

Hence

the rate of heat generation within the element is

$$W_i \, \Delta x \, \Delta y \, \Delta z$$

Let C be the specific heat of the wire

Let f be the density of the wire

and t the time.

Thus by conservation of energy, the increase in internal energy will be given by

$$c \frac{\partial T}{\partial t} \Delta x \, \Delta y \, \Delta z \, f$$

Thus equating the sum of all energy particles

$$\frac{\partial}{\partial x} (K \frac{\partial T}{\partial x}) + \frac{\partial}{\partial y} (K \frac{\partial T}{\partial y}) + \frac{\partial}{\partial z} (K \frac{\partial T}{\partial z}) + W_i = fc \frac{\partial T}{\partial t}$$

Thus if K is constant

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} + \frac{W_i}{K} = fc \frac{\partial T}{\partial t}$$

changing now to cylindrical coordinates

$$[\frac{1}{r} \frac{\partial}{\partial r} (r \frac{\partial T}{\partial r}) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2}] + \frac{W_i}{K} = fc \frac{\partial T}{\partial t}$$

Consider the hot wire. Assuming a steady state $\frac{\partial T}{\partial t} = 0$; $\frac{\partial T}{\partial z} = 0$ and for circular symmetry $\frac{\partial T}{\partial \theta} = 0$

Hence

$$\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{W_i r}{K} = 0$$

i.e.

$$\frac{dT}{dr} = \frac{W_i r}{2K} + \frac{c_i}{r}$$

$$T = \frac{W_i r^2}{4K} + c_1 \ln r + c_2$$

for the solid wire T is not ∞ at $r = 0$. $c_1 = 0$, let $T = T_o$ at $r = r_o$

Hence

$$T - T_o = \frac{W_i}{4K}(r_o^2 - r^2)$$

at $r = 0$ the centreline let $T = T_c$

$$T_c - T_o = \frac{W_i r_o^2}{4K}$$

W_i is the heat generation per unit volume and time. The resistivity of the 35 s.w.g. wire is 1.35 Ω per foot.

$$\text{Heat generation} = I^2R \ \text{Btu/ hr ft}$$

$$W_i = \frac{I^2R}{\pi r_o^2}$$

$$T_c - T_o = \frac{I^2R}{4K\pi}$$

Let K the thermal conductivity be 13 Btu/hr ft F°, and let the current be 3 amps.

$$T_c - T_o = 0.074^{\circ}C$$

whilst the temperature obtained from the $\frac{\Delta R}{R_{30}}$ curve is 110°C.

Hence the temperature distribution across the wire is for these calculations may be neglected.

CHAPTER 14

The Deleterious Effect of a Boundary Lubricant

In the four ball tests using the 1 r.p.m. machine for the 3.53% additive, Figure 83, it was noted that the diphenyl disulphide additive seemed only to be acting after the transition temperature had been reached.

In the hot wire experiments it was shown that corrosion of the steel wire by acetic acid was less when in a solution with light stock oil solvent, than in solution with a liquid paraffin solvent and that the inhibiting effect remained only whilst the temperature was below 160°C, the region of transition temperature of the light stock oil obtained from friction measurements on the Bowden-Leben machine.

It is now suggested that the addition or presence of a polar boundary lubricant is of value, because when added wear and friction decrease but this deneficial effect does not always apply. It applies only when the boundary lubricant is below its transition or desorption temperature, and further, the presence of boundary lubricants may cause the scuffing of gears, discs and engines.

Thus it is suggested that for conditions of lubrication where a high siezure load is required the initial beneficial effect of the boundary lubricant decreases wear and limits the amount of asperity interaction so that when the more severe conditions are reached in which the boundary lubricant desorbs the surfaces are left unprotected. Scuffing may therefore occur according to the theory discussed in the chapter on diesel engines.

This theory of lubricant failure is now examined in this chapter in the next series of tests. Firstly, however, a literature search was conducted to find whether published results agreed or disagreed with this theory.

In Chapter 5, a review of the literature on scuffing of gears, discs and engines was given, and some experiments on which the oil contained e.p. agents were discussed, these are now recalled. Kelley and Lemanski [131] conducting disc experiments found that the failure temperature and scuffing load was dependent upon the disc blank temperature, Figure 41) for it is seen that e.g. below 140°F the e.p. oil is little better than the straight mineral oil and it is only after a disc temperature of 300°F (150°C) has been reached that the scuffing load using the additive oil increases considerably.

Whyte [148] has noticed a similar effect in the lubrication of the axles of army vehicles in Northern Canada, which he called the 'temperature gap', Fig. 42. The gap is the temperature range over which no satisfactory lubricant was obtained. Below this temperature a viscous oil was precluded because of the cold climate but operature was possible with a less viscous oil which contained a high additive concentration, however, this same oil when operating above the temperature gap $\doteq$ 290°F (143°C) caused too much corrosion and at the higher temperature an oil containing much less additive would be satisfactory. The results of DeGruchy and Harrison [136], Fig. 43, were also discussed. They found that the effectiveness of the additive increased with gear pinion speed and thus gear temperature and Fein [149], Fig. 44, found that a higher scuffing load was associated with a thinner running in film i.e. in agreement with the theory of failure given in the chapter on diesel engine failure, Chapter 11.

The literature did not yield much information on the definite deleterious action of a boundary lubricant.

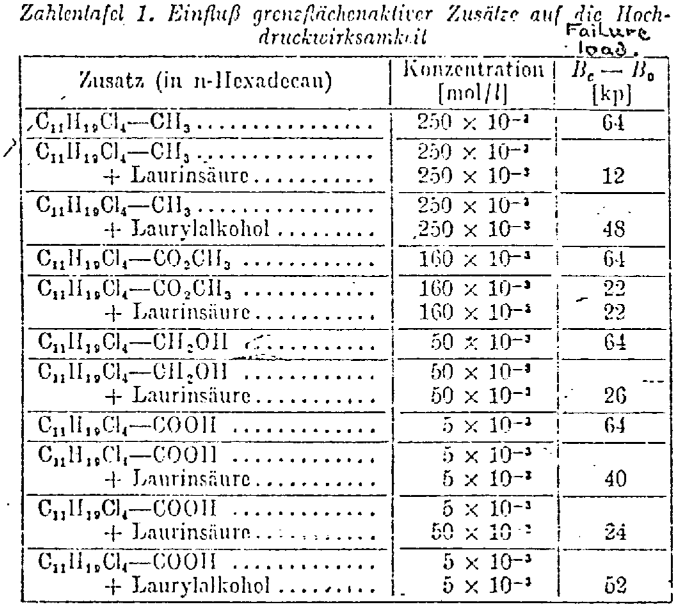
In a paper by Gänsheimer [206] in 1960 he reports that the siezure load using an Almen-Wieland machine is less with a lubricant micture of paraffin oil molybdemum disulphide and nonoic acid than for the lubricant of molybdemum disulphide and paraffin oil alone, for concentrations below 10% MoS_z. This he attributes to the low load carrying polar nonoic acid being adsorbed on the surface to the exclusion of the molybdemum disulphide.

Okrent [114] (1961) noted that oil soluble soaps and surfactants having detergent properties reduce the effectiveness of antiwear additives and thus are not used much in gear oils.

More recently, December 1968, (indeed after these tests had been carried out) Studt [207] investigated the effect of polar groups on the scuffing load, thus Fig. 94 is from Studt's paper. It is seen that the addition of lauric acid or lauryl alcohol in all cases reduces the failure load.

Rounds [208] in a large series of tests in which he measured the coefficient of friction of thrust ball bearings over a speed range of 0 - 1000 ft/min found that the effectiveness of an additive often depended upon the base oil used, and that in some instances a greater additive action could be obtained by using a more refined oil base.

In a review paper in 1956 on lubricant additives, Smalheer and Mastin [209] stressed the importance of the United States Army axle tests as a



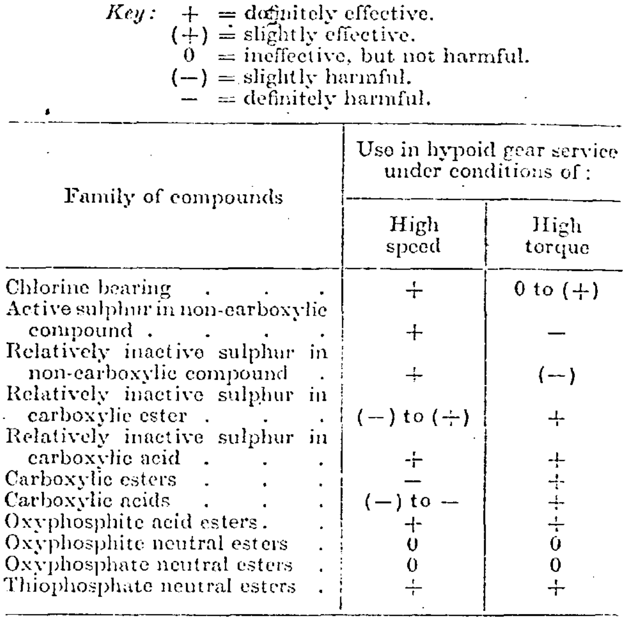
Zahlentafel 1. Einfluß grenzflächenaktiver Zusätze auf die Hochdruckwirksamkeit

Failure load.

Zusatz (in n-Hexadecan)	Konzentration [mol/l]	$B_c - B_0$ [kp]
$C_{11}H_{19}Cl_4-CH_3$	250×10^{-3}	64
$C_{11}H_{19}Cl_4-CH_3$	250×10^{-3}	
+ Laurinsäure	250×10^{-3}	12
$C_{11}H_{19}Cl_4-CH_3$	250×10^{-3}	
+ Laurylalkohol	250×10^{-3}	48
$C_{11}H_{19}Cl_4-CO_2CH_3$	160×10^{-3}	64
$C_{11}H_{19}Cl_4-CO_2CH_3$	160×10^{-3}	22
+ Laurinsäure	160×10^{-3}	22
$C_{11}H_{19}Cl_4-CH_2OH$	50×10^{-3}	64
$C_{11}H_{19}Cl_4-CH_2OH$	50×10^{-3}	
+ Laurinsäure	50×10^{-3}	26
$C_{11}H_{19}Cl_4-COOH$	5×10^{-3}	64
$C_{11}H_{19}Cl_4-COOH$	5×10^{-3}	
+ Laurinsäure	5×10^{-3}	40
$C_{11}H_{19}Cl_4-COOH$	5×10^{-3}	
+ Laurinsäure	50×10^{-3}	24
$C_{11}H_{19}Cl_4-COOH$	5×10^{-3}	
+ Laurylalkohol	5×10^{-3}	52

Figure 94 from ref. 207

good method of evaluating lubricants. The specification requires two tests, one a high speed test and the other a low spped-high torque test. Over many years of testing they found that some lubricant additives were helpful for passing one test, but definitely harmful for passing the other test. These conclusions were quite reliable. They give a table, Figure 95, giving the performance characteristics of a number of families of organic compounds to both tests.



Key:
+ = definitely effective.
(+) = slightly effective.
0 = ineffective, but not harmful.
(−) = slightly harmful.
− = definitely harmful.

Family of compounds	Use in hypoid gear service under conditions of:	
	High speed	High torque
Chlorine bearing	+	0 to (+)
Active sulphur in non-carboxylic compound	+	−
Relatively inactive sulphur in non-carboxylic compound .	+	(−)
Relatively inactive sulphur in carboxylic ester . . .	(−) to (+)	+
Relatively inactive sulphur in carboxylic acid . . .	+	+
Carboxylic esters . . .	−	+
Carboxylic acids . . .	(−) to −	+
Oxyphosphite acid esters .	+	+
Oxyphosphite neutral esters .	0	0
Oxyphosphate neutral esters .	0	0
Thiophosphate neutral esters .	+	+

Fig. 95 from ref. 209

It is seen that the compounds unfavourable to the high speed axle tests are carboxylic acids and esters, i.e. the polar compounds, whilst the polar compounds are effective for high torque-low speed applications. Thus we now examine the results expected from these tests from our scuffing theory.

High torque slow speed test

In this test, heat generation is slow, the boundary lubricant will act in reducing wear and friction and thus temperature. However, with high torque and slow speed, some surface sites will form low shear strength additive compounds so that when the temperature of desorption is reached the running in type scuffing will not occur.

High speed test

Here the heat generation is much higher and since the load is not high initially the boundary lubricants will act effectively so that very few low shear strength additive surface compounds are formed. When the scuffing temperature is reached there is massive desorption and scuffing. Whilst without the polar compounds there would have been no massive desorption but continuous additive action.

Thus the scuffing theory agrees with the experimental results of Smalheer and Mastin [209].

It was therefore decided to conduct further tests to investigate this hypothesis.

Apparatus

The apparatus used was a high speed four ball machine shown in Figure 96. A schematic diagram is given in Figure 97. It is seen that there is provision for heating both the cup assembly and the rotating shaft.

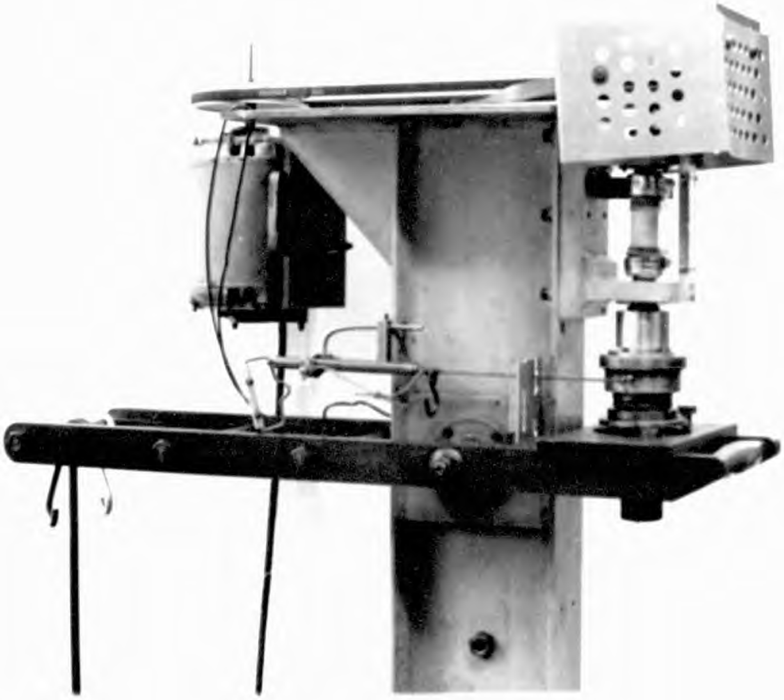


Fig. 96

High speed four ball machine.

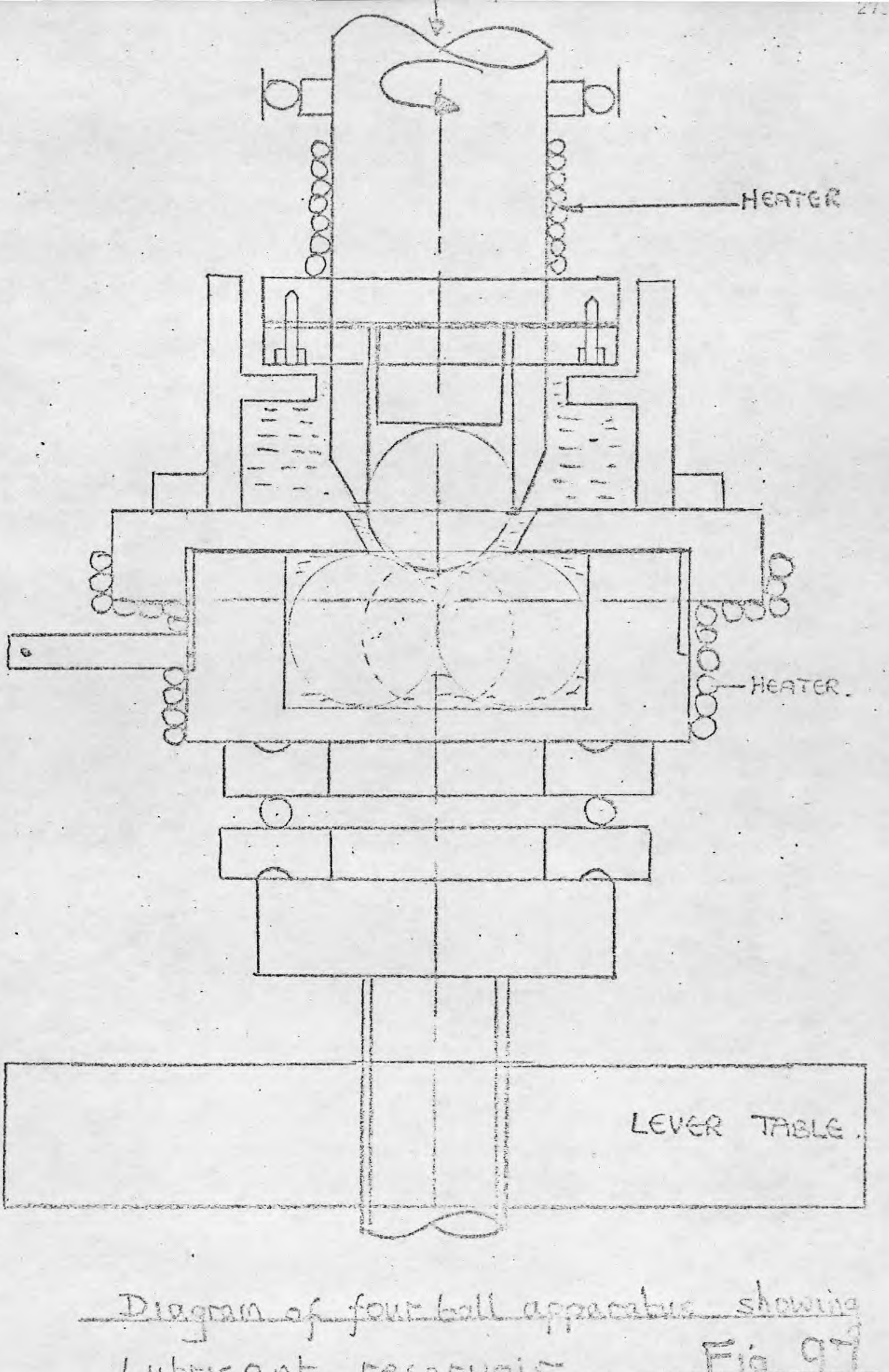


Diagram of four ball apparatus showing Lubricant reservoir Fig 97

The heating wires were connected to variable voltage supplies and a good temperature distribution could be obtained. The temperature was measured using thermocouples.

The speed of rotation of the top ball of one inch diameter was 1000 r.p. (30.25 ins/sec) (77 cms/sec) the balls were ball bearing steel E.N.31 and thus the test operates at a higher speed than the standard four ball test specification of 1500 r.p.m. with half inch balls i.e. 22.6 ins/sec. Friction was measured using a spring balance, and the load was applied with weights.

Experimental

Great care was taken to ensure that the balls were clean. They were soxhleted in benzene for at least six hours and then washed in acetone. On transferring the balls from the acetone to the cup or holder assemblies, which had also been washed thoroughly in benzene and acetone, clear continuous interference fringes could be seen as the acetone evapourated. If this effect was not seen but instead patches occurred or there was slight discolouration then the ball was rejected. New balls were used for each test. The test procedure was as follows:

The clean balls were carefully transferred with tongs to the ball holders and the lubricant was added. The top ball was loaded with 30 lb increments whilst in the rest period, the balls running and then resting for 30 second intervals successively.

From initial tests for repeatability it was found that the lubricant wa not covering the friction zone completely at the high speed so that premature failure was occurring. The lubricant reservoir was therefore raised about three inches above the balls using the additional oil holder as seen in the diagram. Results then became repeatable as will be shown in the result section.

The Experiments

The experiments were divided into two parts.

The first set of experiments were to show that indeed the effect of a boundary lubricant surfactant can be deleterious.

The second set of experiments were to demonstrate that the transition temperature desorption theory of scuffing was a satisfactory explanation for this effect.

The base oil was liquid paraffin and contains no boundary lubricant, a Bowden-Leben friction temperature test confirmed that there was very poor lubricating ability and no friction transition temperature. The liquid paraffin is from the same source as used in previous tests. The additive was diphenyl disulphide as in previous tests.

As an example of a lubricant having a surface active compound the light stock oil was chosen. This is a lubricant having the surface active compound in it naturally.

The initial temperature of the lubricant and apparatus was room temperature 22°C; no temperature control was made during these tests.

The tests were carried out according to the procedure given earlier and the results are shown in Table 96 .

Results

LUBRICANT	LIGHT STOCK OIL	LIGHT STOCK +1.1% DIPHENYL DISULPHIDE	LIQUID PARAFFIN	LIQUID PARAFFIN + 1.1% DIPHENYL DISULPHIDE
SCUFFING	200	350	170	650* 650*
LOAD LBS.	170	290	170	710*
	200	320	170	880*
AVERAGE.	190	320	170	
INITIAL TEST TEMPERATURE	22°C	22°C	22°C	22°C
BOWDEN LEBEN TRANSITION TEMPERATURE	150°C		NONE	
WEAR SCAR DIAMETER	$>\frac{1}{8}''$	$>\frac{1}{8}''$	$>\frac{1}{8}''$	FOR 710 LBS 0.058"

* WOULD NOT SCUFF

* In earlier tests the maximum loading was 650 lbs. which was increased up to 880 lbs. for subsequent tests.

Figure 96

Thus it is seen that under these conditions the liquid paraffin with diphenyl disulphide additive exhibited a much higher load carrying capacity than the light stock oil containing the diphenyl disulphide additive. Indeed scuffing was unobtainable on this machine for the white oil additive tests.

The second series of tests were to show that the transition temperature desorption theory of scuffing is a satisfactory explanation for this effect.

It was decided to choose the white oil as the non polar lubricant and choose the white oil with cetyl (C_{16}) amine additive as the polar lubricant. Diphenyl disulphide again was the extreme pressure additive.

Firstly it was shown that the polar lubricant with cetyl amine and with the e.p. additive gave a lower scuffing load than the white oil with only diphenyl disulphide additive, Table 97. The transition temperature was measured for the white oil, amine diphenyl disulphide solution on the Bowden-Leben machine using stainless steel surfaces, a transition temperature of 100°C was found.

Thus the four ball test for the white oil cetyl amine diphenyl disulphide lubricant was now repeated but at a temperature of 100°C. For these tests both the cup assembly and the top ball holder shaft were heated, and thermocouples were positioned in the lubricant mixture, touching one of the bottom balls, and also the top ball shaft.

It is seen that at this temperature, i.e. operating above the transition temperature, the scuffing load has increased. The lubricant then behaves like the white oil with diphenyl disulphide, Table 97.

However, it may be said as an alternative explanation that the increase in scuffing load obtained for this high temperature test is due to the increase in reactivity of the diphenyl disulphide additive.

Therefore, a further test was performed. A lubricant solution was made up containing the same amount of diphenyl disulphide and white oil but with a greater concentration of cetyl amine, so the transition temperature is raised. Using Blok's flash temperature equation [122, 123, 124] falsh temperature of about 55°C is expected, although because of vibration the instantaneous load and hence temperature might be higher resulting in a lower scuffing load than expected. Thus the cetyl amine concentration was increased from 0.3 wt% to 1.0 wt% this increased the transition temperature from 100°C to 175°C.

The experiment was now repeated with this lubricant at 100°C, it is seen that the scuffing load decreased. The system is therefore operating again in the region in which the transition temperature has been reached and has led to failure.

The results of these tests together with the earlier tests are now shown in Figure 96 and Figure 97.

LUBRICANT	LIGHT STOCK OIL	LIGHT STOCK +1.1% DIPHENYL DISULPHIDE	LIQUID PARAFFIN	LIQUID PARAFFIN + 1.1% DIPHENYL DISULPHIDE
SCUFFING	200	350	170	650* 650*
LOAD LBS.	170	290	170	710*
	200	320	170	880*
AVERAGE.	190	320	170	
INITIAL TEST TEMPERATURE	22°C	22°C	22°C	22°C
BOWDEN LEBEN TRANSITION TEMPERATURE	150°C		NONE	
WEAR SCAR DIAMETER	$>\frac{1}{8}''$	$>\frac{1}{8}''$	$>\frac{1}{8}''$	FOR 710 LBS 0.058"

* WOULD NOT SCUFF

* In earlier tests the maximum loading was 650 lbs. which was increased up to 880 lbs. for subsequent tests.

Figure 96

LUBRICANT	LIQUID PARAFFIN +0.3% WT. CETYL AMINE	LIQUID PARAFFIN +0.3% WT. CETYL AMINE +1.1% DIPHENYL DISULPHIDE	LIQUID PARAFFIN +0.3% WT. CETYL AMINE +1.1% DIPHENYL DISULPHIDE	LIQUID PARAFFIN +1.0% WT. CETYL AMINE +1.1% DIPHENYL DISULPHIDE
SCUFFING LOAD LBS.	320 260 260	350 320 320	710* 710* 710*	260 300 260
INITIAL TEST TEMPERATURE	22°C	22°C	100°C	100°C
BOWDEN LEBEN TRANSITION TEMPERATURE	86°C	100°C	100°C	175°C
WEAR SCAR DIAMETER	$> \frac{1}{8}''$	$> \frac{1}{8}''$	0.058"	$> \frac{1}{8}''$

*DID NOT SCUFF.

Figure 97

Results

These results demonstrate clearly that under these conditions, the addition or presence of a polar boundary lubricant can have a large and deleterious effect on the scuffing load.

The results obtained from these tests agree and support the transition temperature theory of failure considered in this and previous chapters.

DISCUSSION

Accuracy

The load increments were of 30 lbs thus it is seen that in nearly all of the tests the failure load accuracy was ± 30 lbs; it can also be seen that the differences in scuffing load between tests in which comparisons have been made are very large indeed, i.e. a difference in failure load of 400 lbs. The maximum loading in earlier tests was 660 lbs. This was increased up to 880 lbs for subsequent tests after obtaining more weights.

General Discussion

The object of the last two chapters were to see in what way lubricants could be improved. It has now been demonstrated that the presence of polar material in the oil is not always an advantage and can cause a decrease in the failure load. Indeed these results show that even the natural surface active compounds present in a mineral oil can lead to a lower scuffing load.

Thus two regions in which boundary lubricants may function are described. In the first region the contact temperature is always below the transition temperature. In this region the addition of boundary lubricants reduce wear and friction and are advantageous. The second region is where the temperature of the contact is likely to reach the transition temperature of the boundary lubricant. Initially the first region operates, but as the load increases the transition temperature is reached and scuffing is likely, depending upon the history as discussed in the chapter on diesel engine scuffing. In these tests which were severe, scuffing always occurred in agreement with the theory. Thus when operating in this severe region it is better not to have a polar boundary lubricant present which may desorb. Indeed these results show that even the surface active compounds present in lubricanting oil can lead to a lower scuffing load and that for such severe conditions it is better to use an e.p. additive in a non polar lubricant like liquid paraffin (white oil).

The Hertzian diameter for the liquid paraffin diphenyl disulphide lubricant at the top ball load of 710 lb is 0.031 ins whilst the measured wear scar diameter was 0.058 ins thus there is not severe chemical corrosion, it is remembered that the light stock oil test with the same amount of e.p. additive failed at a top ball load of 200 lbs, whilst scuffing could not be obtained with the white oil diphenyl disulphide mixture even at 880 lbs top ball load.

The maximum top ball load of 880 lbs was not exceeded for it was seen that the driving motor was having difficulty in starting.

Onset of scuffing was easily recognised. A sudden large amount of squealing occurred with a huge increase in friction. Continued running under these conditions only caused greater noise and friction force with massive wear.

It is noted that these results have been obtained using four ball conditions which are more stringent than the standard four ball test specification. The high speed shock axle tests referred to by Smalheer and Mastin [209] are also severe tests. It is, therefore, suggested that perhaps the standard four ball test should include tests at a higher speed as well.

Conclusions

Under severe friction conditions the presence of a polar boundary lubricant can have a deleterious effect on the scuffing load.

This effect was also noticed for the surface active compounds present naturally in commercial mineral oils. A more highly refined oil containing no surface active agents and the same quantity of diphenyl disulphide additive as the commercial oil gave a much higher scuffing load. The presence of polar compounds in oils can be beneficial in reducing friction, wear and temperature, providing the temperature is below the transition temperature.

If the polar compounds exhibit a transition temperature and if this is quickly attained due to severe high speed conditions, then there is a likelihood of scuffing at the transition temperature. Whilst a non polar additive oil may not scuff at these conditions.

ABSTRACT

The increased failure load on four-ball machine experiments for fatty acid-alkane solutions of equal alkyl chain length was investigated.

Bowden-Leben friction temperature measurements revealed a temperature where friction rose sharply. This transition temperature increased for solutions of equal chain length.

Assuming lubricant failure at constant surface coverage, heats of adsorption were measured. Increase in lubrication ability and the greater heat of adsorption with matching chains was attributed to coadsorption of acid and alkane due to an increase in alkyl chain interactions.

Theoretical calculations of this increase agreed with experimental values.

Polynalkylmethacrylates in xylene exhibited transition temperatures which increased with a nalkyl group length.

Slow speed Bowden-Leben friction-temperature measurements with stainless steel and a mineral oil gave a sharp friction increase near 155°C.

This transition temperature with mineral oil had not be found so distinctly before this use of stainless steel. Subsequent work by other investigators who used stainless steel has shown that such tests are valuable in predicting gear and disc failure.

A theory of scuffing of engines during running in is proposed.

The mineral oil transition temperature was shown to result from

desorption of friction-reducing surface active compounds present naturally. Using the hot wire method, non-additive mineral oil behaved as a corrosion inhibitor, this effect disappeared for surface temperatures exceeding 160°C, the region of the friction transition temperature. The importance of austenite in surfaces was demonstrated.

An unreactive metal-additive combination scuffed readily, whilst reactive compounds showed high corrosive wear.

The measurement of retained austenite content of carburized gears is suggested. Whilst polar lubricants can be beneficial in reducing friction, wear and temperature. Their presence caused a large reduction in scuffing load under severe high speed conditions. Even naturally occurring surface active compounds reduced the scuffing load considerably.

These effects have been explained using the proposed scuffing theory and proved experimentally.

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Friction Transition Temperature Effect of Matching Surfactant and Carrier

WE have reported[1,2] how straight chain hydrocarbon solvents have a specific effect on lubrication with surface active agents. Using a slow running 4-ball machine we showed that lubrication was best when the chain length and shape of the surfactant accurately matched the solvent. We have now confirmed these results using the temperature at which the friction increased sharply in a standard 'Bowden–Leben'[3] machine, kindly lent us by Tube Investments, Hinxton Hall. While this change can be determined with mild steel and fatty acids[4], it is very hard to detect with mineral oils. The best way we have found to observe it is to use stainless steel (18 per cent chromium, 8 per cent nickel) for the frictional pair. Friction-temperature curves for a mineral oil with 18/8 stainless steel and with 0·6 per cent carbon steel are shown in Fig. 1. The rise at 60° C for mineral oil has also been reported by Tabor[5].

If it is assumed[2] that the system obeys the Langmuir adsorption iosthorm and that the critical transition temperature from low to high friction occurred when half the adsorption sites were covered, it is possible to connect the concentration C of surfactant in moles/1,000 g solvent and the absolute transition temperature T_c by the relation

$$\Delta H^0/T_c = R \ln C + \Delta S^0$$

ΔH^0 = standard heat of adsorption change

ΔS^0 = standard entropy change.

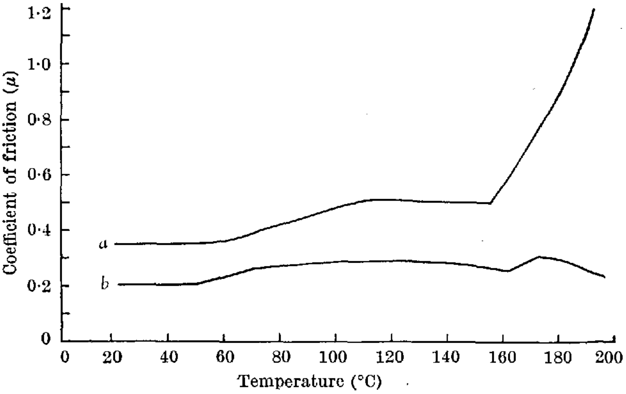

Fig. 1. Coefficient of friction against temperature for mineral oil with (*a*) 18/8 stainless steel. (*b*) 0·6 carbon steel as frictional pair.

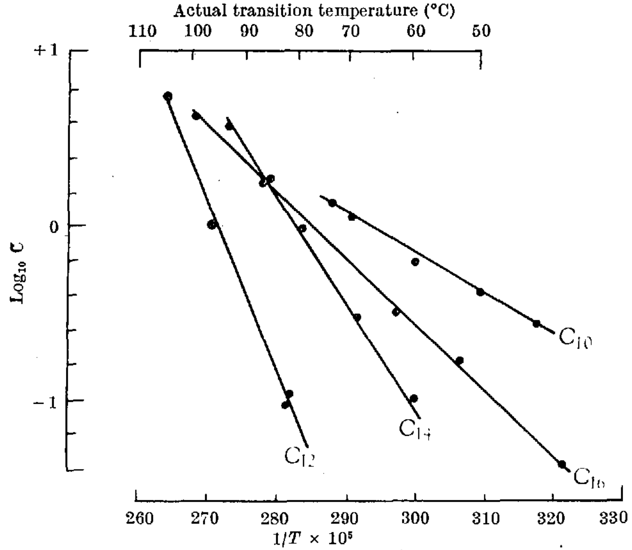

Fig. 2. Log concentration (weight/100 g solvent)—reciprocal transition temperature °K for lauric acid in four alkanes.

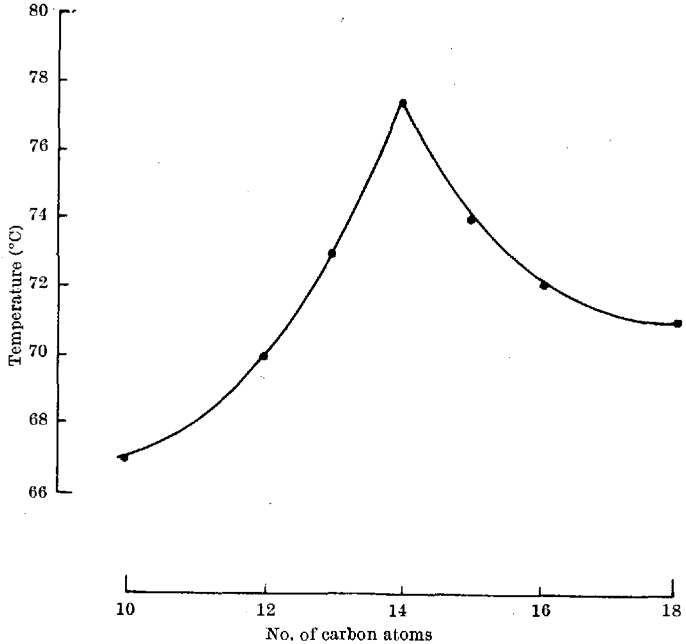

Fig. 3. Transition temperature–chain length of fatty acids in tetradecane at 0·003 molar with plate and 0·5 in. ball both of 18/8 stainless steel, 2·5 kg load, velocity 0·002 cm/sec.

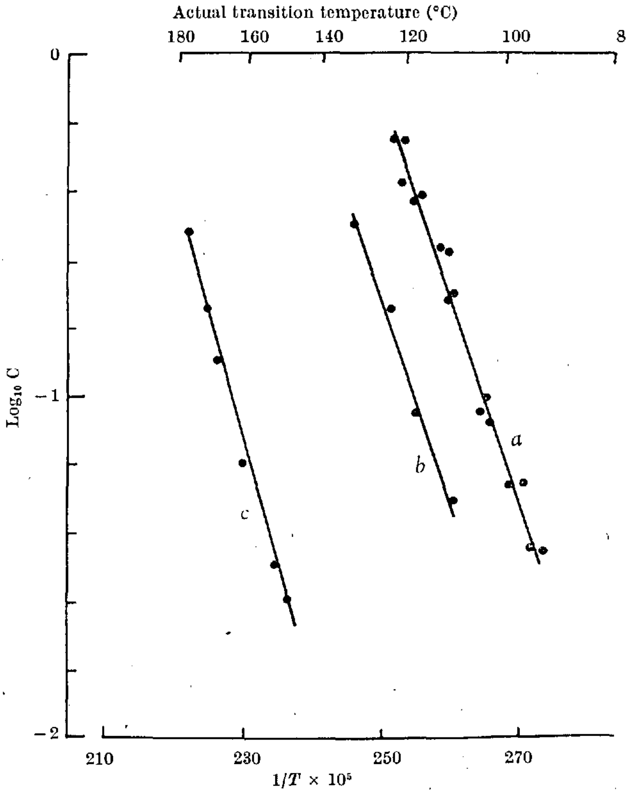

Fig. 4. Log_{10} concentration (weight/100 g solvent) reciprocal transition temperature °K. Naturally occurring surface active agent in cetane (*a*), dekalin (*b*) and white oil (*c*).

The effect of matching chains was shown by dissolving lauric (dodecyl) acid in various alkanes (C_{10}, C_{12}, C_{14} and C_{16}) and plotting log concentration against $1/T_c$.

The same effect was also demonstrated by dissolving various acids in tetradecane at 1/300 molar concentration and measuring the transition temperature. The temperature was measured by a fine chromel alumel thermocouple positioned close under the ball. By averaging the friction traces of at least four runs, clear transitions were observed. The friction rose very markedly at the transition and the surfaces scored, so rendering observations on the reversibility of the process difficult. When the entire test was completed rapidly the effect seemed reversible for fatty acids. A plot of temperature against chain length shows a peak (Fig. 3).

Also it was suggested[2] that the critical temperature of 150°–200° C observed in many experiments on lubricated systems such as gears[6,7] was caused by a desorption of the surface active material isolated by Groszek and Palmer[8] which is normally present in oils. We dissolved the same material as that used in ref. 2 in hexadecane, dekalin and white oil, three solvents which matched the material progressively closer. The log concentration $1/T_c$ curves are shown in Fig. 4. This lends support to the supposition put forward in ref. 2 identifying this critical temperature with desorption and gives a rational basis for the critical temperature scuffing mechanism for gears and disks.

W. Grew
A. Cameron

Imperial College of Science and Technology,
Department of Mechanical Engineering,
Exhibition Road, London.

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Role of Austenite and Mineral Oil in Lubricant Failure

THE suggestion[1] that the failure of lubrication in gears is caused by the actual contact temperature reaching a critical value (150° to 200° C) at which the desorption of surface active compounds present in oils occurs has been supported[2] by evidence obtained from modified 'Bowden–Leben' friction apparatus. With mineral oils, the friction change could not be observed in this apparatus with a tool-steel friction pair, but it showed up sharply with stainless steel (18 per cent chromium, 8 per cent nickel). The mechanism of the difference between the two is the subject of this communication.

With a similar apparatus we used a steel (*EN* 39 *B*) which was chiefly bainite (hardness, Vickers pyramid number 440) but no austenite. In Fig. 1*A* the friction temperature curve, using an Admiralty turbine oil, *OEP*-90, and a tungsten carbide hemispherical slider, is shown. By gas carburizing and suitable quenching of the *EN* 39 *B* steel, the surface contained martensite and retained austenite. The friction temperature trace is shown in Fig. 1*B* for a 25 per cent retained austenite sample (Vickers pyramid number 740). A transition temperature shows up clearly, and Fig. 1*C* shows the friction temperature trace for a 5 per cent retained austenite sample (Vickers pyramid number 750). No sharp increase is found.

In carburized steel, the retained austenite content is highest just below the surface; the finish grinding of gears must often result in changes in austenite content, and the importance of this large change in the friction temperature characteristic, consequent on the presence of austenite, must be recognized in gear testing. The scuffing loads are extremely variable and such a scatter could well come from the change in austenite content. Niemann and Lechner[3] have demonstrated that alloys containing austenite reduce the load carrying capacity of gears.

The previous communication[2] did not give any reason for the transition temperature being absent in tool steel when using plain mineral oil (light stock). Mr A. Eyres suggested that the reactivity of the sulphur compounds usually present in plain oils should be studied.

We considered that sulphur compounds, for example, might react slowly with austenite but sufficiently rapidly with martensite so that, when the critical temperature was reached in the slow speed friction machine, physical desorption would be masked and a transition would not be seen. A similar mechanism would also occur for oils

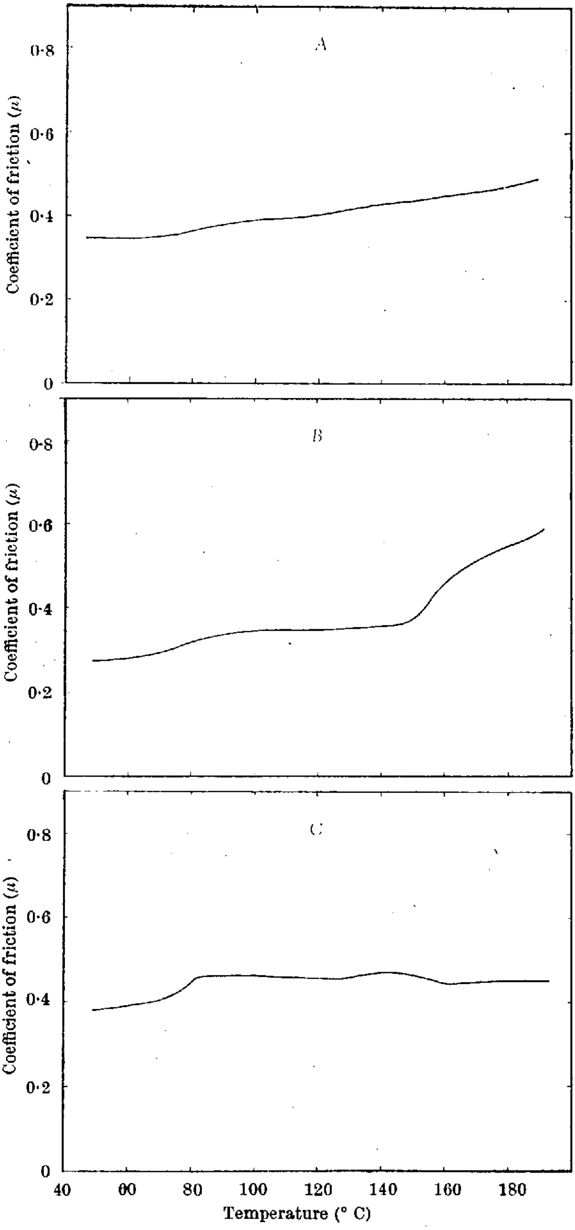

Fig. 1. *A*, Friction temperature curve using 'Bowden-Leben' machine (average of at least four traces) using a tungsten carbide slider and an uncarburized *EN* 39 *B* rider. Velocity, 0·02 cm/sec; load, 2·5 kg; turbine oil lubricant. *B*, Friction temperature curve using carburized *EN* 39 *B* with 25 per cent retained austenite; turbine oil lubricant. *C*, Friction temperature curve using carburized *EN* 39 *B* containing austenite only; turbine oil lubricant.

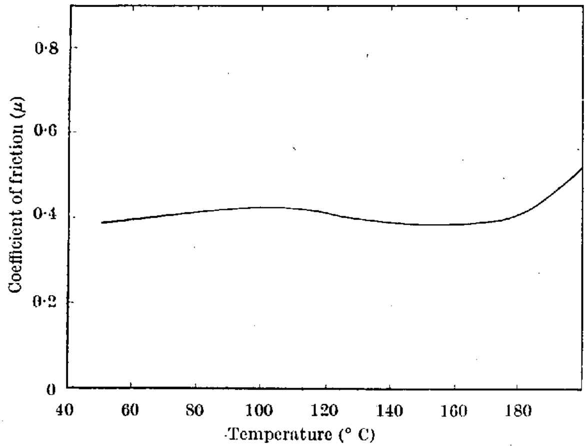

Fig. 2. Friction temperature curve using a tungsten carbide slider and a carburized *EN* 39 *B* steel rider containing 25 per cent retained austenite; lubricant, 0·59 per cent by weight surface active compound in white oil.

containing extreme pressure additives. In running machine parts, such as gear teeth, the ambient temperature is much lower than the total flash temperature achieved in the contact zone and the contact time is short; thus the reaction will not have occurred to the same extent, and a critical temperature will still be observed for martensitic steels and plain oils and, especially in the running-in period, where chemical reaction has occurred least, for oils containing extreme pressure additives.

Groszek and Palmer[4] isolated surface active compounds present in oils by percolation through columns of activated magnesium oxide and reported that the compounds exist at a concentration of about 0·4 per cent and contain sulphur. No transition temperatures were obtained from the friction temperature curves for the 25 per cent retained austenite sample or uncarburized *EN* 39 *B* when using white oil (oil from which surface active compounds have been removed) lubricant, but when 0·59 per cent of the surface active compound was added to the white oil a quite different result was obtained for the two surfaces. The carburized steel containing retained austenite showed a critical temperature (Fig. 2), but the uncarburized steel gave no sharp critical temperature (Fig. 3). It is suggested that this effect is caused by some reactive compounds in the surfactant reacting faster with martensite than with austenite and thus excludes the possibility that the absence of a critical temperature was a result of oxidation products formed in the 'Bowden-Leben' system but not necessarily in gear and disk systems.

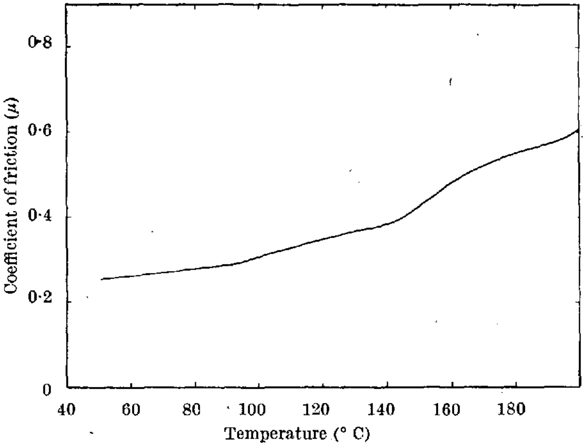

Fig. 3. Friction temperature curve using an uncarburized *EN* 39 *B* steel rider; lubricant, 0·59 per cent by weight surface active compound in white oil.

These findings are clearly very important for the choice of gear steels.

We thank A. Groszek for the surfactant, and the British Iron and Steel Research Association for carrying out the heat treatment and the X-ray determination of the austenite content. We also thank P. T. Holligan and Dr Bruce Kelley for many useful discussions. One of us (W. G.) thanks the Mobil Oil Co., Ltd., for the award of a bursary.

W. Grew
A. Cameron

Department of Mechanical Engineering,
Imperial College of Science and Technology,
London.

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