CHEMICAL REACTIONS IN LUBRICATED SLIDING CONTACTS

by

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ABSTRACT

The literature concerning the phenomenon of friction polymer is reviewed and analytical methods suitable for its examination are discussed in detail.

A series of sliding experiments have been carried out in an attempt to generate a friction polymer. Surface deposits have been extracted using dichloromethane and studied by various methods, in particular mass spectroscopy.

The lubricants and additives employed have been a series of C_{16} aliphatic compounds with different functional groups, ranging from hexadecane to hexadecanedioic acid.

A number of chemical changes have been observed to occur at the point of sliding, especially using the alcohols hexadecan-1-ol and 1,16-hexadecanediol. With no compounds, however, was polymerisation observed to produce more than a doubling of molecular weight.

The 'friction polymer' often refered to in the literature is thus concluded to consist of a mixture of degradation products rather than a true polymeric material.

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LIST OF SYMBOLS

The symbols used in the text have the following meanings unless otherwise specified.

a	Hertz radius, (m)
α	Thermal diffusivity, (W m^{-1} $^oC^{-1}$)
α^o	Angular measure, (^{o})
BP	Boiling point, (^{o}C)
C	Specific heat, (kg m^2 s^{-2} $^oC^{-1}$)
c	Velocity of light, (m s^{-1})
d	Lattice spacing, (μm)
E	Energy, (J)
E	Young's modulus, (kg m^{-2}) (in Appendix II)
e	Charge on an electron, (C)
E_b	Binding energy of an electron, (J)
E_{ke}	Kinetic energy, (J)
g	Acceleration due to gravity, (9.806 ms^{-2})
H	Magnetic field strength, (A m^{-1})
h	Plank's constant, (6.6256 J s)
I	Intensity
L	Top ball load, (kg)
λ	Wavelength, (m)
μ	Coefficient of friction
m	Mass, (kg)
m/e	Mass to charge ratio of an ion
MP	Melting point, (^{o}C)
MW	Molecular weight
ν	Frequency, (Hz)

n	An integer
P	Mean Hertz pressure, (kg m^{-2})
p	m/e ratio of a parent ion
R	Reduced radius, (m)
r	Radius, (m)
ρ	Density, (kg m^{-3})
T	Temperature, (^{o}C)
T_b	Bulk temperature, (^{o}C)
ΔT_{fm}	Maximum flash temperature rise at a contact, (^{o}C)
T_t	Total temperature, i.e. bulk temperature plus flash temperature, (^{o}C)
θ	Angular measure, (^{o})
V	Volts
v	Velocity, (m s^{-1})

INTRODUCTION

Boundary lubrication involves the formation of a film on a metal surface to alter its nature and so protect it during sliding. Additives used to specifically achieve this are called boundary, or friction modifying additives. They are typically sulphur or phosphorous containing compounds or long chain surfactants such as oleic acid. Often encountered is a film which appears to arise not specifically from the boundary additives, but from the hydrocarbon base stock. This usually appears as a brown resinous deposit around the contact region. A similar substance is frequently found in unlubricated systems such as on the contacts of electrical switchgear and gyroscope slip rings. This material has become known as 'friction polymer'.

The presence of friction polymer in a lubricated system is associated with a decrease in friction and wear - particularly in the mixed boundary/elastohydrodynamic lubrication régime. In electrical contacts its formation is undesirable since it is electrically insulating.

Friction polymer appears to be produced by a wide range of lubricants and metal-metal sliding pairs. It is generally accepted that it is a mixture of compounds, but there is some controversy concerning carbon chain length and molecular weight. Some believe the mixture to consist of short chain molecules, whereas others maintain that high molecular weight products are formed. The effects of temperature and particularly pressure in a sliding contact would tend to give a longer chain product, but the trend caused by catalytic

effects of possibly nascent metal surfaces cannot be so easily predicted. The exact nature of a friction polymer probably depends on the lubricant, the sliding surfaces and the conditions of sliding. However none of the reports describing friction polymer has offered proof of its being a true polymer - neither have the species necessary for its generation been ascertained.

It is the aim of this thesis to discover what chemical species are necessary to produce a friction polymer, and to determine its molecular weight and chemical nature.

CHAPTER 1

LITERATURE SURVEY AND SCOPE OF WORK

1.1 LITERATURE SURVEY

Shaw first reported in 1948 that freshly formed metal surfaces initiated chemical reactions[1]. It has since become generally accepted that such surfaces, often called nascent metal surfaces, exhibit catalytic behaviour not shown by surfaces which have been formed for some time. Heterogeneous catalytic behaviour depends on the presence of active sites on the surface. There are often high energy flaws such as vacant lattice sites, electron traps, crystalline edges or steps in crystal surfaces. Reaction with these sites occurs very quickly to reduce the overall energy of the system, so after a relatively short time the surface is no longer active in the same way. Nascent surfaces have been used to specifically initiate polymerisation[2].

The first reference to an insulating 'polymeric' film formed on a metal surface was by Hermance and Egan[3] in 1958. They found that electrical contacts made of precious metals showed intermittent open circuit. Associated with this was the presence of a brown powdery substance just outside the contact area and a translucent film at the contact point itself. The latter was formed by impaction of the powdery material. Hermance and Egan called this deposit 'friction polymer'. Further investigation showed that its occurence was independent of whether or not the contact was passing a current. Using

a pin on disc machine with a palladium pin and disc and benzene vapour as the lubricant, friction polymer was shown to decrease friction and wear. Examination of several metal-metal pairs and a number of organic vapours as the lubricant revealed that although platinum and particularly palladium gave considerable quantities of material, nickel gave none. The organic compounds were listed according to the amount of friction polymer formed. Generally C_1 - C_4 alkanes, C_1 and C_2 amines and alcohols produced little or none, whereas compounds such as styrene and acrylonitrile gave relatively large amounts. Between these extremes lay the higher alkanes, alkenes, amines and alcohols together with benzene, toluene and limonene. No acids appear to have been tested. Analysis showed the deposits to be a mixture of compounds containing carbonyl and carboxyl groups even when they were apparently not present initially. The explanation offered for the formation of friction polymers involved the mechanical shearing of adsorbed molecules followed by recombination of the fragments to form long chain molecules. The mechanism of incorporation of oxygen into the products was not clearly explained. Rubbing was found to be necessary, but elevated temperatures were not. The catalytic effects of the metal surface were somewhat complex since there were no poisoning effects such as are found in normal catalysis using the platinum group metals (platinum, palladium, rhodium, indium, osmium and ruthenium).

The occurence of a brown deposit on and around the contact area of sliding pairs has since been reported by a number of researchers[4 - 30]. Its presence has been used to explain often otherwise inexplicable results. Hermance and Egan found that the friction polymer which they produced was a relatively delicate material, and certainly not able to give the performance that some others have attributed to it. However, it must be borne in mind that Hermance and

Egan did not characterise their material; they only found it to be a mixture. Neither did they, it appears, pay much heed to the nature and quantities of any impurities in the chemicals they used. It is therefore quite possible that other workers found different products, their composition and properties depending on the metals, lubricant and sliding conditions. In only one instance has a friction polymer been thought to be prowear[5]. It has generally been shown to have antiwear and antifriction properties[3,4,7,8,15,18,22].

Silicones and siloxanes are readily polymerised by the effects of heat[32-35]. The products are typically cross-linked polysiloxanes[36-38] which often appear as yellow solids. Since a number of those who have reported 'friction polymer' were using partially or fully formulated oils, it might be that the deposits they observed may have been caused by silicones added as antifoaming agents.

Some studies have been carried out on chemically pure surfaces. One such piece of work was by Buckley[31] who operated a pin on disc machine inside the vacuum chamber of an Auger spectrometer. This enabled him to follow the reactions occuring when an aluminium oxide rider was rubbed against an iron disc. The lubricants used were readily polymerisable monomers such as vinyl chloride. Their sorption was sometimes found to be dependent on the sliding conditions. Polymerisation reactions were shown to be dependent not only on the simple ability of a molecule to polymerise but also on its structure.

Research into the formation of friction polymers can be divided into three distinct parts.

(1) The formation of insulating films on precious metal electrical contacts resulting in failure of the contact.

(2) The nature of friction polymer formed when steel slides on steel with organic vapours or liquids as the lubricant.

(3) The deliberate formation of polymeric films in situ on metal surfaces to reduce friction and wear.

Polymer formation on precious metal contacts has been investigated by Hermance and Egan[3], Campbell and Lee[39] and Chaikin[40,41]. Campbell and Lee used an enclosed test apparatus and vapour lubrication. The sliding members were a cylindrical roller loaded against a rotating shaft. Most of the work was concerned with palladium sliding on palladium with limonene as the lubricant. This system did produce friction polymer, but when benzene was substituted for limonene a red oxide film was formed rather than an organic material. This is in contrast to Hermance and Egan who found that benzene on palladium gave copious amounts of polymer[3]. If however the palladium was first dipped in a stearic acid solution, benzene vapour produced considerable quantities of friction polymer. It was suggested that polymerisation depended on the shearing of the acid molecules to give free radicals which subsequently react together. The presence of radical traps should therefore prevent the formation of friction polymer, but this was not examined experimentally. Campbell and Lee concluded that the factors affecting polymerisation were (1) catalytic activity during sliding, (2) the effects of high pressure at asperity contacts and (3) the formation of hydrogen peroxide and other peroxides as a result of electron emission from nascent metal surfaces[42]. Interestingly the platinum group metals proved to be quite active but chromium and iron, important constituents of bearing steels, gave no deposits whatsoever. The deposit produced by Hermance and Egan was insoluble in aqua-regia but evolved carbon dioxide with chromic acid[3]. To determine whether or not friction polymer had been formed, Campbell and Lee applied the same criteria to a vinylite resin replica of the wear scars. This method allows a test to be carried out without interference from the

base metal.

Chaikin[40] on the other hand used a fine wire probe to measure the electrical resistance of the surface. A high resistance was taken as indicative of the presence of friction polymer. The contact resistance method was supplemented by the use of an electron microscope. Once again palladium was found to be particularly active.

In a subsequent paper[41] Chaikin reported that when a metal surface with an organic material on it, was rubbed, it was not electrons which emerged from the organic layer, but positively charged ions. These were generated by the interaction, with the organic film, of electrons released from the metal surface. The electrons had a very low energy, about 2 - 3 eV, but because the organic layer was electrically insulating, the field across it was probably of the order of 10^9 Vm^{-1}. This is in the range of dielectric breakdown for even a good insulator. The electrons would thus be accelerated through the layer and cause extensive alteration to the structure of even relatively stable molecules. This mechanism indicates that the reactions occuring are radical reactions. Chaikin did in fact observe a reduction in the amount of friction polymer when radical traps such as tetraethyl lead were present. Hermance and Egan did not observe this, but their method for determining the presence of free radicals required the radicals to be relatively long-lived and freely available. Chaikin explained the difference by postulating that the radicals were at no time 'free', but were formed and reacted within the organic film.

The formation of friction polymer on sliding steel surfaces has been studied by Fein and Kreuz et al.[43 - 46]. Fein et al. first noted a polymeric product when using hexadecane solutions of carboxylic acids in the four-ball machine. The study, initially aimed at determining the effects of lubricant oxidation, found that 'friction polymer' was formed whether or not the acid solutions had undergone

oxidation. Hexadecane did not produce any polymeric material itself, the presence of an acid was necessary. In 1965 Fein and Kreuz[44] reported the results of their research into the effects of different chemical structures on friction and wear. The test apparatus was a four-ball machine operated at high loads and low speeds. Unsaturated molecules gave friction polymer whereas saturated molecules yielded an iron oxide wear debris. Cyclohexane and benzene were taken as model lubricants both for vapour and liquid lubrication studies. The concentration of oxygen (as O_2) was found to be important. With vapour lubrication a decrease in the oxygen concentration led to an increase in the amount of friction polymer produced. This also applied to liquid cyclohexane, but the converse was true for liquid benzene. In all cases the presence of an organic product was associated with low wear rates.

In a later work Fein and Kreuz[45] looked specifically at the material produced by cyclohexane vapour. This gave a friction polymer which was soluble in both chloroform and cyclohexane. An analysis of the material accumulated from several tests showed that it contained 8% iron - mostly as iron (II). This figure was proportional to run duration and the oxygen concentration. The organic part contained carbonyl and carboxyl groups. The hydrocarbon chains were mostly branched chain aliphatic. Hydrolysis by hydrochloric acid yielded a product containing 29% acid and 63% neutral material. The polymer itself became less soluble, or dispersible, in cyclohexane with increasing test duration. Its molecular weight showed a similar trend. Polymer from a two hour run showed about a third to be in each of the ranges 300 - 400, 400 - 850 and over 800, whereas after sixteen hours only one half of the sample had a molecular weight of less than 850.

It was postulated that this organometallic reaction product formed

a viscous layer at the load bearing conjunction - provided that only a little unreacted hydrocarbon was present. The viscous film promotes an elastohydrodynamic lubrication régime. Under flooded conditions the volume of parent hydrocarbon would be too large to develop the necessary viscous film. This contradicts the idea that flooded lubrication is ineffective because of the restricted availability of oxygen at the load bearing conjunction[47]. Confirmation of this came in a later paper[46]. The addition of liquid lubricant caused the solution of the protective polymer layer resulting in failure.

Others who have found friction polymer but who have not studied it in any detail include Scot et al.[48] and Reda[49] who used a new analytical device called the 'Ferrograph'. This piece of equipment detects magnetic particles and has so far only been used to study wear processes. Both Scot and Reda found 'metallic' wear debris held together by a sticky polymeric material, but neither attempted to analyse it. Salomon[50] produced a friction polymer in which he detected the groupings CO_2^-, C=O, CH_2 and CH_3. Probably the first person to report that friction polymer was not necessarily a polymer, but could be a mixture of small reaction products, was Klaus[51]. This represented a significant step forward, since up until then, friction polymer was accepted as being a true polymer. The only proof of molecular size had come from Fein[45] who obtained a product at least four times as heavy as his starting material, cyclohexane. Considering the mechanisms of formation of friction polymer so far advanced, it is just as reasonable to expect the presence of a mixture of smaller molecules as a product consisting solely of very large molecules.

Zaslavsky et al.[52,53] and Furey[54-61] have done a considerable amount of research into the specific generation of friction polymer on

steel surfaces to give antiwear, antifriction and extreme pressure action. Zaslavsky et al., in an excellent work, tested a number of additives and additive mixtures, but unfortunately none were named so the published papers actually give very little information. It is clear however that hydrocarbon base stocks did not produce any friction polymer.

Furey, who accepts that friction polymer is not a true polymer[62], has concentrated his efforts on the production of polyesters from a mixture of diacids and diols in a hydrocarbon carrier. During sliding the acid and alcohol groups react together to form a polyester. This reaction is facilitated by the effects of temperature and the metal in the contact region acting as a catalyst. This system can be used to produce a tailor-made protective film exactly where it is needed - where metal-metal contact occurs - which is a good reason why the method might well find commercial use.

A model for boundary lubrication which does involve the formation of friction polymer type materials has been proposed by Beerbower[63,64]. Unfortunately such behaviour has not yet been suitably quantified for incorporation into a mathematical model.

1.2 SCOPE OF THIS THESIS

Research into the phenomenon of friction polymer has, so far, been unsystematic. Little heed appears to have been taken concerning the nature and quantity of any impurities in either the base stocks or additives. This means that the lubricants were essentially unknown. Although base stocks have often been single hydrocarbons, there have been instances of the use of rather complex mixtures such as white oil. Additive selection has not been such that the effects of functional groups could be ascertained. It was therefore decided to adopt the following method to try to obtain a greater understanding of the

formation of friction polymers.

(1) Discover whether or not a pure alkane, in this case hexadecane, produced friction polymer, and,

(2) Determine the effect of various functional groups in the terminal position. The groups chosen were $C{=}CH_2$, $-NH_2$, -OH and -COOH. The ester hexadecyl hexadecanoate was also studied and compared to a mixture of the alcohol and acid. The diol and diacid were examined both individually and as an equimolar mixture. All the additives were used as up to 2% solutions in hexadecane.

Purity is clearly very important, so considerable care was taken in the purification and analysis of the compounds used. Since friction polymer is formed on metal surfaces, all the methods currently available of analysing surfaces were investigated with regard to their suitability for this study. Mass spectroscopy was used extensively since this is one method which would give positive proof of whether or not friction polymer is a true polymer.

The organic compounds used were ultra-pure, but to maintain some semblance to real life commercially available EN31 steel was used for the rubbing members. These were in the form of a ball and rollers suitable for use in the laboratory's ball on triplane apparatus. The cleanliness of these and any part of the triplane apparatus in contact with the lubricant solutions was of course of the utmost importance.

The overall plan then was to begin with a pure alkane which would not, on past experience, be expected to yield any friction polymer, and work systematically to the mixed diol-diacid system which is known to generate polymeric films in situ on sliding steel surfaces.

CHAPTER 2

ANALYTICAL TECHNIQUES

2.1 INTRODUCTION

The work in this thesis is dependent upon the successful analysis of surface films. Many different analytical methods are currently available, including a number of quite sophisticated machine techniques. Very few of the latter have, however, been adapted to surface analysis.

This chapter describes preliminary experiments to assess the suitability of each analytical technique for investigating polymeric films. Each method is briefly outlined and its advantages and limitations reviewed.

2.2 INFRA RED SPECTROSCOPY

Infra red spectroscopy is a common method of structural analysis used extensively in chemistry.

2.2.1 Theory

In a molecule the atoms are continually in a state of vibration, moving closer to, then further from, each other. This motion has a certain energy associated with it. Similarly molecules are bending from side to side (fig. 2.1). This motion also has energy associated with it.

If energy is supplied to the molecule, it will bend and the atoms will vibrate with greater amplitude, the frequency remaining unchanged. In infra red spectroscopy energy in the form of infra red radiation is

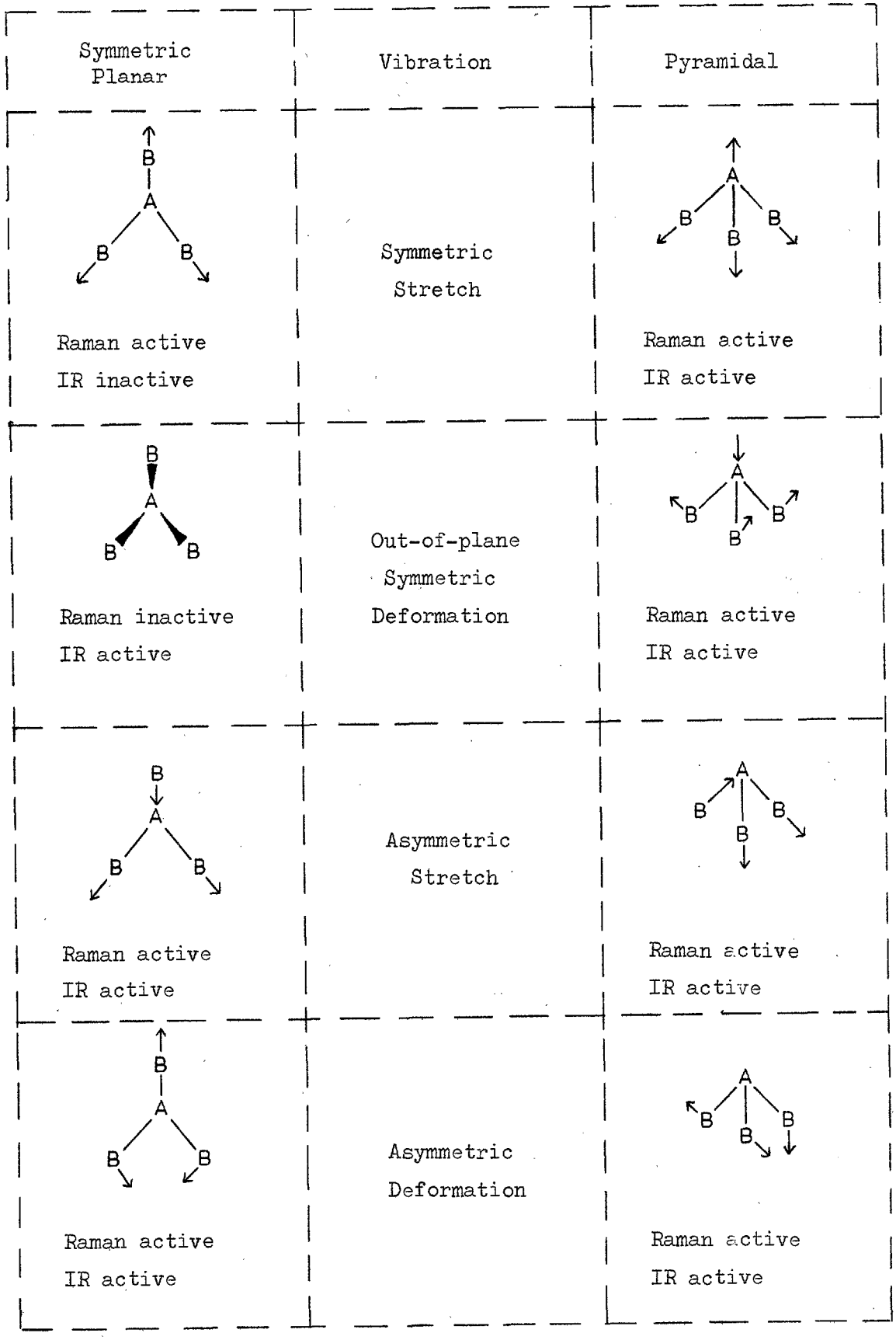


Fig. 2.1 Activities of vibrations of planar and pyramidal AB_3 molecules.

put into the molecules and the frequency and amount of energy absorbed is measured as a spectrum. The excited molecules lose their energy by intermolecular collisions and transfer of energy from one mode to another.

2.2.2 Practical Techniques

Clearly if the radiation is only passing through a few molecules very little energy will be absorbed since only about one molecule in a thousand will be raised to an excited state. This very small absorbance will be difficult to detect. Similarly, too great a number of sorbent molecules do not produce a good spectrum due to too great an absorbance of energy.

The normal practice is to use transmission spectroscopy with pure liquid samples held between transparent windows by capillary action or with solutions in fixed pathlength cells (pathlength ~0.1 mm for a 5% solution). Solids are ground up with a paraffin mixture, nujol, which has a refractive index close to that of the solid. (A solid on its own would scatter too much radiation.)

To look at a surface using infra red spectroscopy is more difficult. There is a method commercially available called Attenuated Total Reflectance Spectroscopy (a.t.r.). The sample is pressed firmly against the back face of a small prism of higher refractive index than the sample. It is mounted so that the radiation suffers total internal reflection at all non-vibrational frequencies. At vibrational frequencies the refractive index of the compound changes and the reflected beam is attenuated. The geometrical arrangement is shown in fig. 2.2 overleaf.

This can be used to look at a film on a flat surface, providing the film is thick enough to absorb sufficient radiation. A thinner film can be observed by causing the infra red beam to pass through the

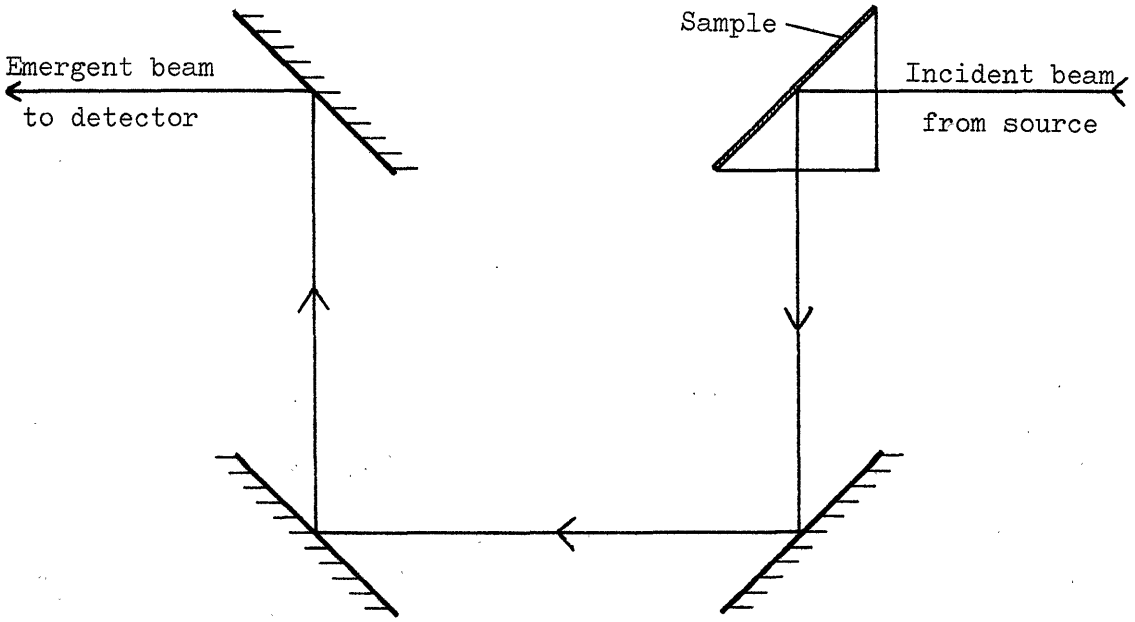


Fig. 2.2 Principle of the Attenuated Total Reflectance unit.

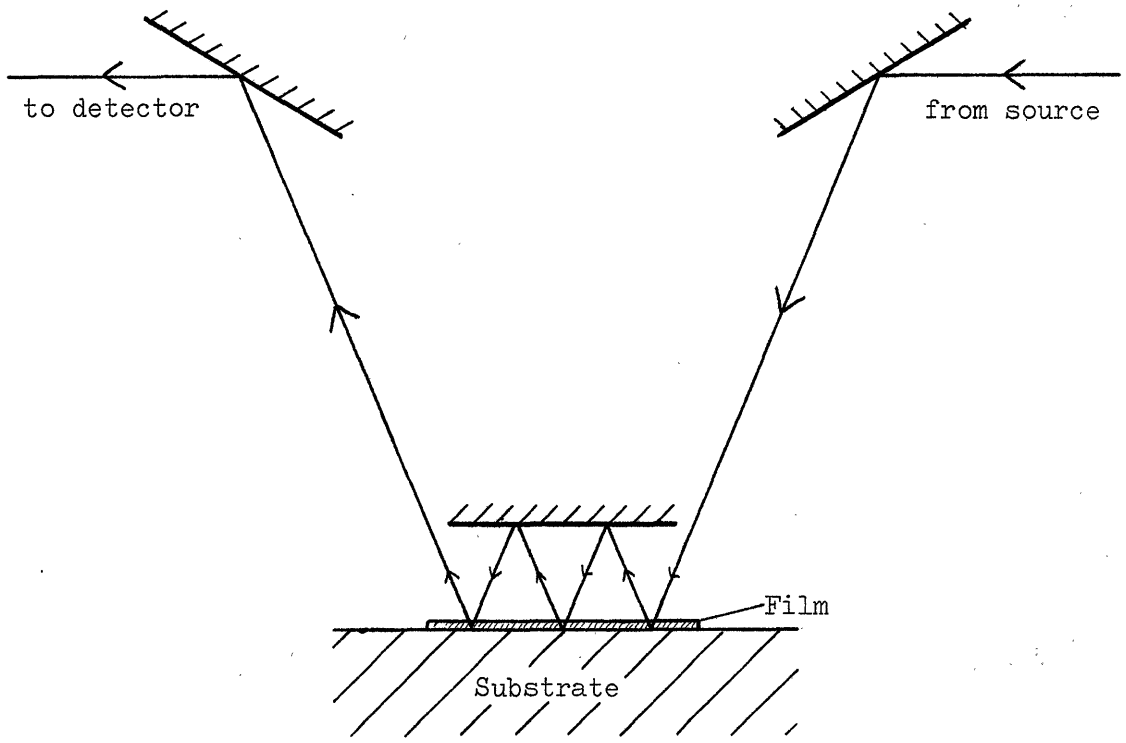


Fig. 2.3 The optics for multiple reflection infra red spectroscopy shown schematically.

sample several times as shown in fig. 2.3. This is known as Multiple Reflection Infra Red Spectroscopy. This depends on the substrate being a good reflector. If it is not, then the infra red beam will be almost totally attenuated. Pritchard,[65] however, found that optimum results are obtained not by multiple reflection, but by using a single reflection at a glancing angle of about 5° thereby increasing the path length. This removes the problem of loss of intensity caused by a poorly reflecting substrate.

2.2.3 Limitations

In practice it was found that the films formed on the wear tracks of 19.06 mm (3/4") balls were very thin indeed, and a single reflection as obtained with normal attenuated total reflectance did not give adequate absorption. Multiple reflection did not work for two reasons.

(a) The surface of the ball was curved so using a flat mirror, the only one available, the emergent beam did not line up correctly with the subsequent optics.

(b) The ball had been run in a test rig with the result that the surface of the ball was far from smooth. This roughness caused scattering of the infra red beam and hence too great an attenuation. (A comb can be driven into the reference beam in a multiple beam spectrometer so that reference and sample beams are of comparable intensity. However when both beams become very weak, stray background radiation and electrical noise from the instrument renders it impossible to obtain anything resembling a spectrum.)

Glancing angle reflectance suffered the same problem of scattering by the rough substrate surface.

Had infra red spectroscopy worked, it would have given information concerning the types of bonds present, and thus would have indicated which atoms were bonded to each other. It would not have positively

identified the presence of a polymer, since for example a C-C bond in a linear chain is the same in C_6H_{14} as in $C_{200}H_{202}$ and infra red spectroscopy only detects bond types and their local environment. Another limitation of infra red spectroscopy is that transmission infra red data is readily and plenteously available viz. the America Institute of Petroleum infra red spectroscopy data tables, but there is not much reflectance data. There is, for a given bond, a change in the frequency of absorption using reflectance spectroscopy compared with transmission work. Thus to verify a spectrum, a pure sample of the suspected material ought to be prepared and directly compared with the 'unknown'.

2.3 RAMAN SPECTROSCOPY

2.3.1 Theory

If photons undergo collisions with molecules, assuming the collisions to be perfectly elastic, the photons will be deflected unchanged. If a detector is placed at right angles to the incident beam, photons of the same energy as those of the incident beam will be detected. If however the collisions are inelastic, that is energy is exchanged between a photon and a molecule, the detected photons will have an energy greater than the incident photons if they gained energy, and an energy less than the incident photons if they lost energy to the molecules. The latter is favoured. This scattering with a change in energy is called Raman Scattering. As with infra red spectroscopy only certain energy changes are allowed because of certain selection rules which apply[66]. Infra red activity depends on a change in a dipole in the molecule whereas Raman activity depends on a change in polarizability, thus infra red and Raman spectroscopy complement each other.

2.3.2 Experimental Techniques and Limitations

It is theoretically a simple matter to shine a laser beam at a glancing angle at the worn track on a ball and observe the scattered radiation. However in practice the same problems as those found in infra red spectroscopy of obtaining a great enough path length, so that there is sufficient material present to absorb energy, apply. This technique was therefore considered to be unsuitable for further investigation.

2.4 X-RAY ANALYSIS

2.4.1 Introduction

Normally X-ray analysis depends on the sample being either a solid with a crystalline structure or an ordered liquid. The crystals themselves must be greater than a certain size, otherwise there are too few diffracting atoms. The elucidation of the structure of an unknown material using only X-ray analysis is very complex. A structure has to be guessed, its diffraction patterns calculated and compared to those of the unknown. Only when a good correlation has been obtained can the experimental results be used to work back to the actual structure. In this work X-ray analysis was considered for the analysis of the iron oxides for which data is already available on the J.C.P.D.S. Powder Data File[67]. Three different types of diffraction were attempted. They were a back reflection powder method, and the diffractometer method for examining a surface, and a transmission powder technique for looking at a loose powder.

2.4.2 Back Reflection Powder Method

The geometric arrangement is shown in fig. 2.4 overleaf. Monochromatic X-rays strike the surface to be examined. X-rays are

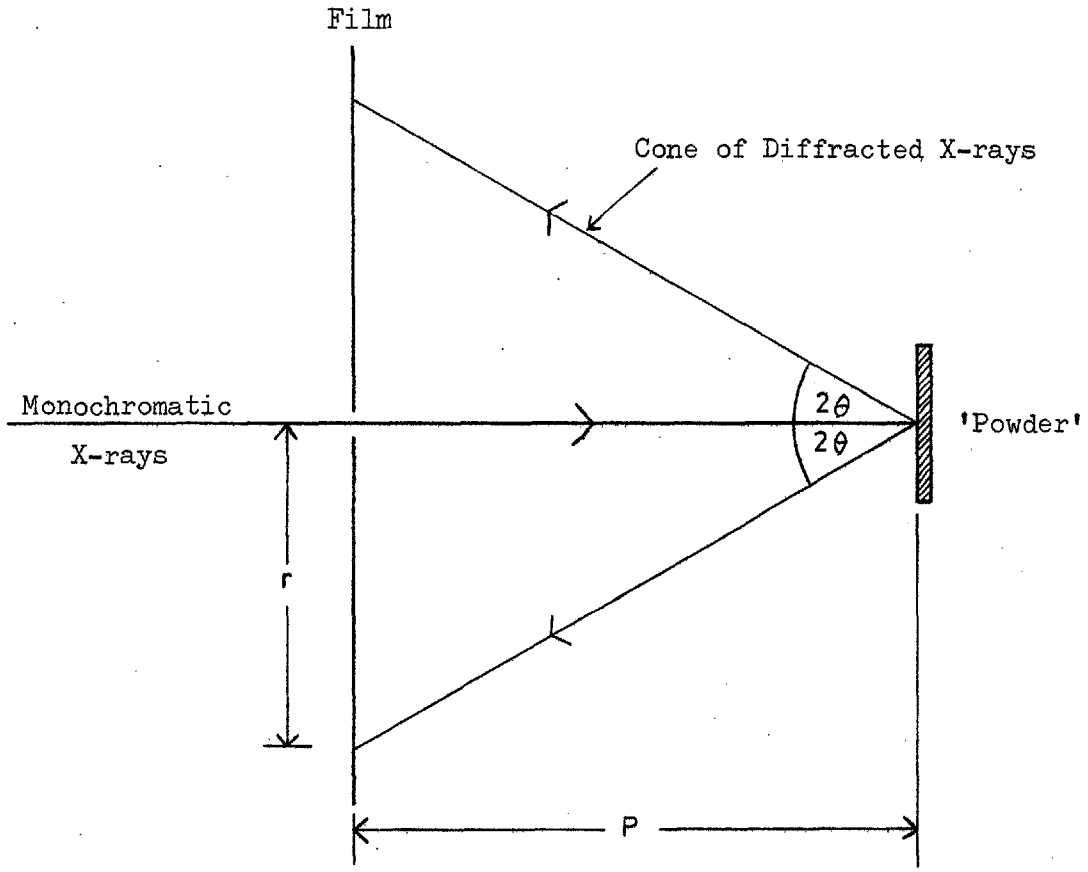


Fig. 2.4 The geometric arrangement for the back reflection powder method of X-ray analysis.

diffracted at angles which satisfy the Bragg equation

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

where n is an integer, λ the wavelength of the X-rays and d is the interatomic spacing in the crystal. The cones of diffracted X-rays describe concentric circles on the film. Knowing the distance of the sample from the film, P, by measuring the radius of the circle, r, the angle 2θ in fig. 2.4 can be calculated. If this is substituted in the Bragg equation, d, the interatomic spacing can be found. The values of

d so obtained are compared with standards on the powder data file.

Limitations. In this work the 'powder' was on a curved surface. This means there is some uncertainty as to the distance between the film and the sample. However the use of a thin beam of X-rays overcomes this so that sufficiently accurate values of d can be obtained. A rather more serious problem was fluorescence, which caused the film to be badly fogged. This was attributed to nickel in the ball. The specification for EN31 steel does not mention nickel, so it was assumed to be absent, however due to scrap recycling it is quite possible to have traces of nickel present; it would only be a trace which would be required. Nickel was later confirmed by E.P.M.A. studies. There is a technique for overcoming the fluorescence problem. The film is reversed so that the emulsion is on the back rather than the front as is normal. The diffracted X-rays now have to pass through the film to reach the emulsion. By choosing a suitable film thickness it is often possible to stop the fluorescence so that only the diffracted X-rays reach the emulsion. This was tried, but to no avail, since the intensity of the fluorescent radiation was comparable to that of the diffracted radiation. A single faint halo was observed during development of the film, but it was too faint and too broad to yield any sensible information. This suggested that the sample might be amorphous, or have crystal units too small to diffract a sufficient number of photons. There may also have been too small a quantity of material present. The amount of material present could not be altered significantly, so the following technique was applied.

2.4.3 The X-Ray Diffractometer

The X-ray diffractometer often overcomes the problem of too thin a specimen experienced with the back reflection method. With back reflection the X-ray beam strikes the sample normally. The

diffractometer uses an oblique angle of incidence so that a greater path length is traversed. The apparatus is shown diagrammatically in fig. 2.5.

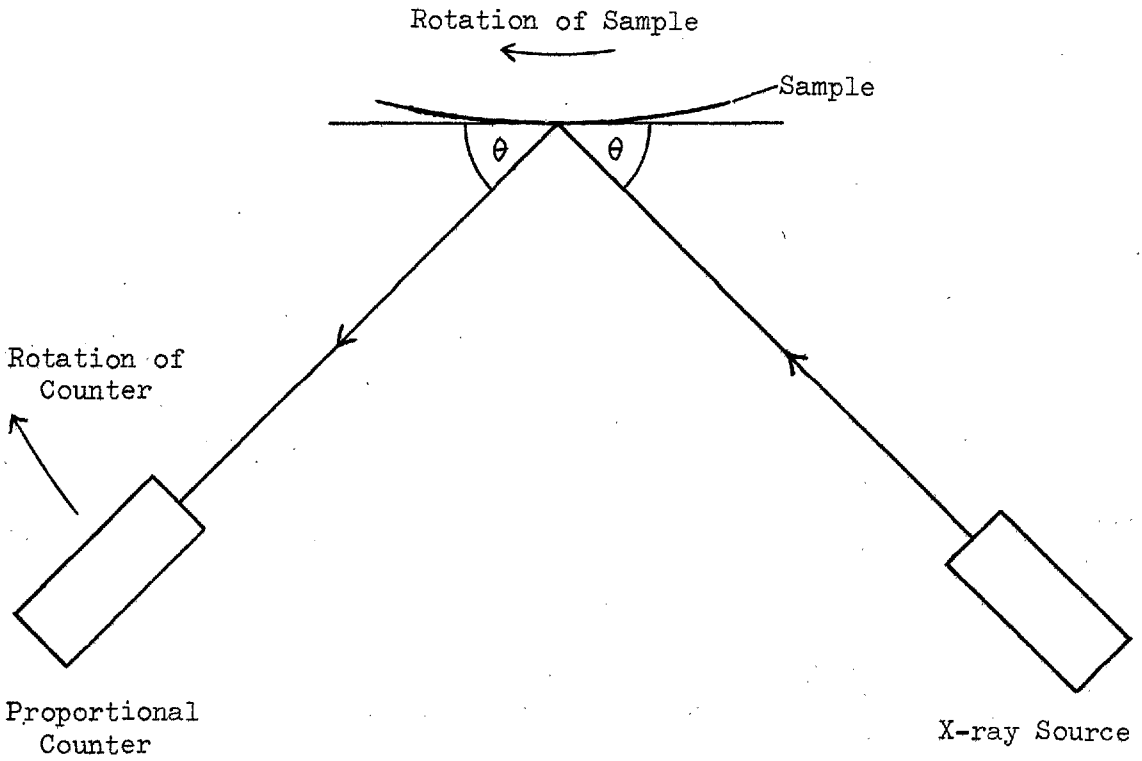


Fig. 2.5 Diagrammatic layout of the X-ray diffractometer.

The sample is rotated at α^{o} min^{-1} whilst the detector is rotated at $2\alpha^{o}$ min^{-1}. The detector, in this case a proportional counter, only receives diffracted X-rays when the angle θ satifies the Bragg equation

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

The result of rotating the sample is a plot of the change of intensity of the diffracted X-rays with changing angle θ; fig. 2.6 overleaf. From the trace the angle θ can be determined at which a peak in the intensity curve occurs. These values of θ are then substituted in the

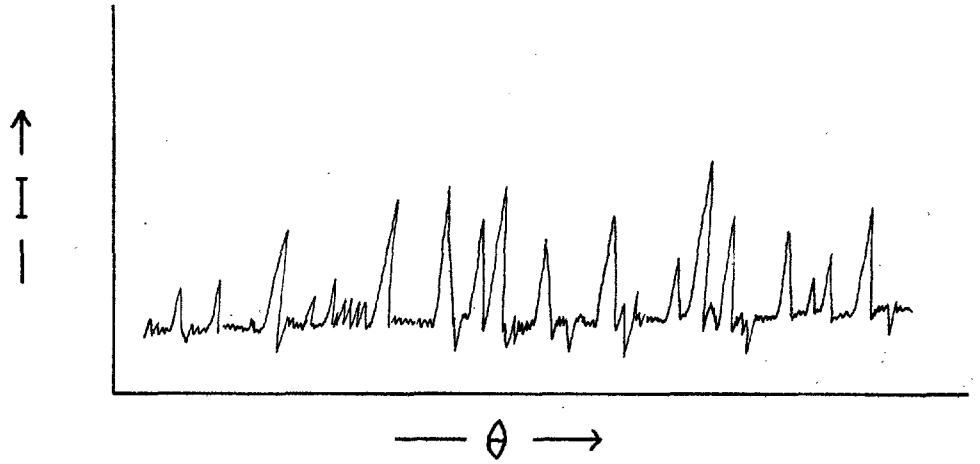


Fig. 2.6 Typical trace of intensity of diffracted X-rays, I, versus angle of incidence of X-ray beam θ^{o}.

Bragg equation to obtain the interatomic distances d, which are then compared with data from the powder data file.

Limitations. Using this method two peaks were obtained, but they were both very broad. No meaningful value of θ could be obtained. This loss of resolution was considered to be due to the curved surface of the sample. In any case however, two peaks are not sufficient to fingerprint a compound from the data file.

Considering the problems of both the back reflection powder method and the use of the diffractometer, further work using X-ray techniques to examine the surface was abandoned. However transmission powder analysis was used for examining wear debris.

2.4.4 Transmission Powder Analysis

This method is for use when a finely divided loose powder is available. It cannot be used for examining surfaces or large particles; the former because they would essentially be opaque, and the latter because they would cause diffraction. The principle of the method is shown in fig. 2.7 overleaf.

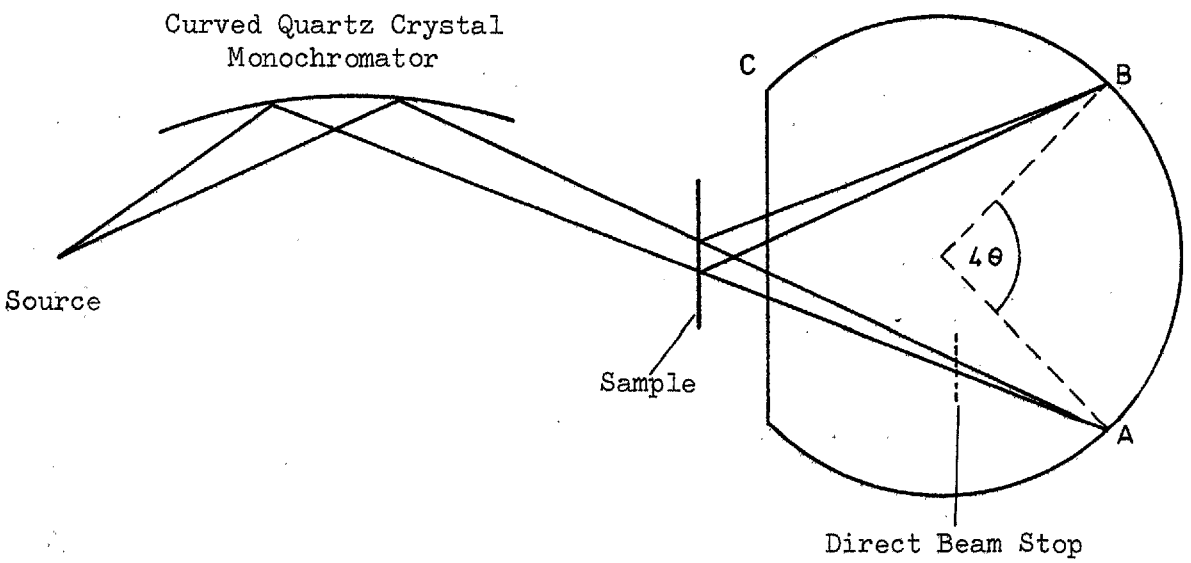


Fig. 2.7 Schematic diagram of transmission powder X-ray analysis.

A beam of X-rays is focussed using a curved quartz crystal. The focussing is achieved by diffraction, not by reflection. Because the X-rays are diffracted from the first layer of atoms only, the emergent X-ray beam is monochromatic. ($\lambda = 2d \sin\theta$, d is fixed, so for a given θ the wavelength of the X-rays, λ, only has one value. Varying the angle of incidence, θ, will vary λ.) The incident beam passes through the sample and impinges on a film in the camera AC at A (fig. 2.7). This corresponds to a d spacing of infinity. Some of the X-rays are diffracted by the sample at discrete angles. This produces a series of lines on the photographic film. The arc on the film AB in fig. 2.7 corresponds to 4θ, where θ is the diffraction angle. Knowing the dimensions of the camera, the angle θ can be read off directly from the developed film. To prevent fogging of the film the direct beam is

'stopped' by a metal plate, which is only removed momentarily to give the d = ∞ line.

Limitations. This method of analysis is used for crystalline powders. If the particle size of the powder is too great the X-ray beam is diffracted by the particles themselves. Such a powder can be ground to obtain a smaller particle size. However if the powder is amorphous there are too few diffracting atoms per particle, so no diffraction is observable.

The total analysis of an unknown is very involved. The technique is best used for the verification of a suspected structure by comparison with standards.

2.5 ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (E.S.C.A.)

2.5.1 Introduction

Electron Spectroscopy for Chemical Analysis, or E.S.C.A., is a relatively new technique of chemical analysis which can be used to examine liquids, gases and solids[68]. It is also particularly useful for examining surfaces and surface films[68].

2.5.2 Theory

In principle an electron beam impinges on the sample to be analysed. This causes an electron to be ejected from its normal shell. The electron leaves the atom with kinetic energy E_{ke} given by

$$E_{ke} = h\nu - E_b$$

where h is Planck's constant, ν is the frequency of the monoenergetic electron beam and E_b is the binding energy of the displaced electron. For a given electron beam the kinetic energy of the ejected electron depends only on the binding energy which varies from element to element for a given shell. When two atoms combine with each other the binding

energies of the electrons change. The kinetic energy of an ejected bonding electron will therefore be different from an electron in the same shell of the same element which is not involved in bonding. This change in kinetic energy is called a chemical shift, and is characteristic for different bonds. For example, if the L shell electrons in carbon are examined, their kinetic energy, assuming the same energy electron beam displacing them, will be different for a C-H bond, a C-O bond or a C-C bond. The electrons in inner shells are also affected by bonding, but to a lesser extent than those in the outer shell. Both 'bonding' electrons and non bonding electrons are ejected. Thus a spectrum of energies is produced. It shows both which elements are present, and also to which elements they are bonded.

With modern detectors the counting of only a few electrons is not too difficult. Unlike X-ray techniques, which depend on electrons being in excited states, E.S.C.A. makes use of electrons in their ground state. There are more electrons in their ground state than in excited states. The combination of these two facts, the large number of suitable electrons available, and the ability to detect small numbers of electrons, means that only very small quantities of material are required to obtain a useful spectrum. For example, a gas sorbed on a surface provides a good spectrum. There is also no problem with low atomic number elements (viz. X-ray fluorescence where low atomic number elements have a very low fluorescent yield so cannot be detected.).

2.5.3 Limitations

Considering the capabilities of this analytical technique, its ability to detect and identify very small quantities of low atomic number elements, and indicate their chemical environment would seem to make it ideal for examining the formation of surface films. The chief drawbacks of E.S.C.A. are its great sensitivity and the need for a

vacuum. If a ball were taken from a test rig after running in an oil it may have a surface film on it, but it will also have a film of the supernatant lubricant on top of that. If the sample were then introduced into the E.S.C.A. machine the film of lubricant would interfere with the detection of the surface film. Similarly any materials absorbed from the atmosphere during transfer from the test rig to the vacuum chamber may also interfere. The vacuum may remove the adherent lubricant film, but if some remained, bombardment by electrons may cause chemical reaction. This may produce new products, or modify products from the running in the test rig. There can be problems arising from the presence of high vacuum oil from the pumping system[68].

These drawbacks together with the lack of free access to E.S.C.A. equipement rendered developement along these lines impossible. Buckley[69] appears to have had some success using the Auger facility of an E.S.C.A. machine, but the samples were produced in a vacuum chamber attached directly to the analysis chamber.

2.6 ELECTRON PROBE MICROANALYSIS (E.P.M.A.)

2.6.1 Theory

Bombarding a substance with electrons causes electrons in inner electronic shells to jump into outer shells with the absorption of energy. These excited electrons however do not stay in the higher energy state but drop back into a lower energy inner shell. As an electron drops from the higher energy level E_2 to the lower energy level E_1 energy is given out in the form of X radiation. The wavelength of the radiation is given by:

$$E_2 - E_1 = h\nu = hc/\lambda$$

where h is Planck's constant, ν is the frequency of the X radiation,

c is the velocity of light and λ is the wavelength of the radiation. Since the energy levels are characteristic for each element, for a given element, the difference $E_2 - E_1$ will be unique. The X-ray photon will therefore have a characteristic wavelength. If these X-rays are incident on a crystal of known lattice spacing, d, they will be diffracted at angles given by the Bragg equation:

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

where θ is the angle through which the photons are diffracted. These photons can then be detected and counted using a suitable detector. This is the principle on which the electron probe microanalyser works.

The particular instrument used in these investigations was the Japanese Electron Optics Laboratory (J.E.O.L.) JXA-3A electron probe microanalyser. It is shown diagrammatically in fig. 2.8.

The electron beam or probe is provided by a tungsten filament electron gun operated at 25 KV. It is focussed on the specimen surface by two magnetic lenses. The 1 μ diameter beam of electrons ideally strikes the surface under investigation normally. This activates a pear shaped volume up to 2 μm below the surface and about 2 - 5 μm in diameter. From this small volume X-rays are emitted over a solid angle of 4π. Only a small proportion of the resultant X-rays can be collected. This is achieved using two spectrometers, one on each side of the specimen. They can be arranged to either analyse for two different elements simultaneously or to both analyse for a single element.

In order to examine a larger area of the surface, the sample can be driven under the probe. This is an important feature, since the probe looks at such a small area, that any inhomogeneity will be quite pronounced. Scanning the surface either plots inhomogeneity or averages it out. This scanning facility was used extensively in this

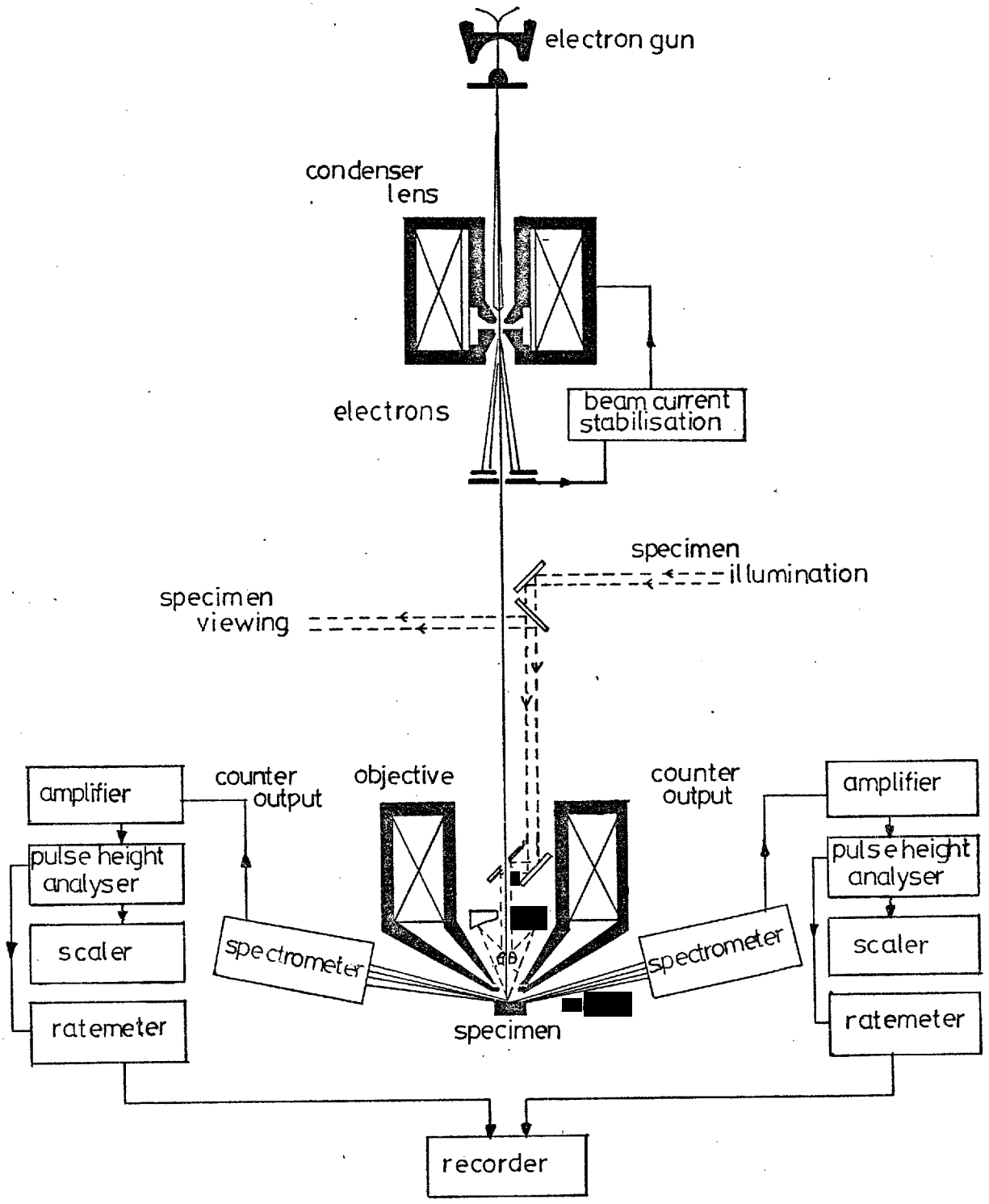


Figure 2.8 ELECTRON PROBE MICROANALYSER

work.

For the detection of carbon, a crystal with a large d spacing is required because of the long wavelength X radiation emitted. True crystals are not available, so pseudo-crystals of the lead stearate family are used. A flow counter with a very thin window is used to detect the X-rays. A problem with carbon analysis is that the X-rays have such a long wavelength that they are readily absorbed by the matrix of the sample being examined. Therefore the degree of precision for the analysis of this element is less than for heavier elements.

2.6.2 Experimental Procedure

A ball was taken from the test rig immediately after a run was terminated. It was washed in toluene and then with acetone to remove lubricant. It was sectioned using an elastic wheel. Such a section is shown in fig. 2.9. The sample was held by plasticine in a brass sample holder. It is necessary for the sample to be electrically earthed, otherwise it becomes electrostatically charged during electron bombardment and the subsequent discharge might damage the sample surface. Earthing was achieved by painting a strip of colloidal silver between sample and sample holder. Since the wear tracks were the interesting part, the section was arranged so that the wear track appeared on the geometric top.

The spectrometers were 'tuned' using a suitable standard. This is usually the element, but for sulphur cadmium sulphide has to be used since sulphur would be burned up by the heat produced by the electron beam. The sample was traversed under the probe and a 'line scan' of count rate versus position produced. The worn area was compared to the non worn area. Both were compared to a section from a cleaned unrun ball.



Figure 2.9 A section of a ball prepared for electron probe micro-analysis. The dark lines are the wear scars.

2.6.3 Limitations

The electron probe microanalysis technique is subject to certain limitations. The probe will penetrate to a depth of 2 μm, depending on the density of the sample. The total count for a given element could therefore be due to either

(i) a very thin film on the surface of the section or

(ii) an average over the depth of penetration of the probe or

(iii) a combination of both.

With low atomic number elements a considerable amount of the Kα X radiation produced would be absorbed in the substrate matrix. It is thus reasonable to assume that for carbon the X radiation dominantly originates from surface films. For accurate quantitative analysis the sample should ideally have a surface ground flat and polished with 0.25 - 1μ diamond paste. In this work the sample was a ball, so the surface was curved. It had also been rubbed against another piece of steel, so the surface was rough (fig. 2.10). The latter caused the X-rays to leave the surface at a range of angles rather than a single angle. This makes accurate counting of the photons impossible, resulting in the accuracy being indeterminate. For this reason the results were regarded only as qualitative. This technique nevertheless gave much useful information, which is discussed in the relevant sections.

2.7 MASS SPECTROSCOPY

2.7.1 Introduction

Mass spectroscopy is a very useful method for helping to determine the structure of a molecule. In some cases it is possible to use solely mass spectroscopy to ascertain a molecular structure. Although the technique can be used to examine a surface film, its main use is for conventional analysis. One of its important advantages is that

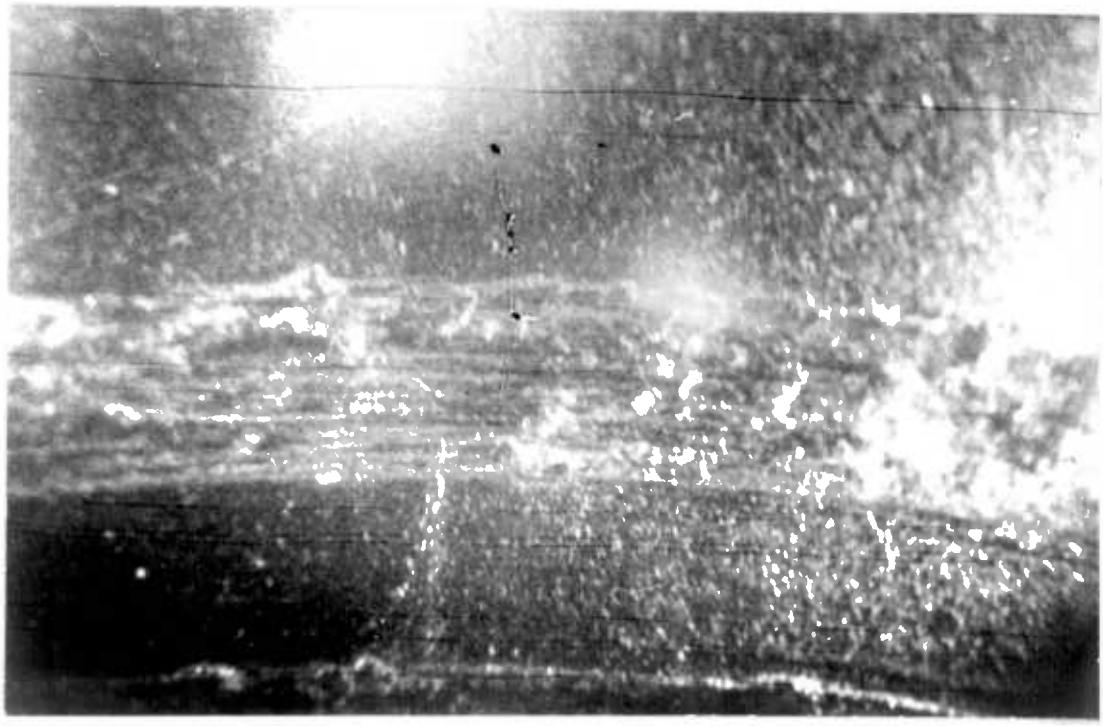


Figure 2.10 A close up view of the wear scar on a ball showing the roughness of the surface.

only a small sample is required.

The instrument used in this study was an AEI MS9 machine which is of the double focussing type. The principle of mass spectrsocopy is described in the next section.

2.7.2 Principles of Operation

The sample under investigation is bombarded in a vacuum of 10^{-5} - 10^{-7} Torr by a beam of electrons. If the energy of the electron beam is about 10 - 15 eV then a positive ion will be formed from a molecule by the removal of one electron (10 - 15 eV is the ionisation potential for most organic molecules.). The positive ion is called the molecular ion. If the energy of the electron beam is increased still further then the molecular ion will undergo decomposition to form fragment ions. These are characteristic of the original molecular structure. If the electron beam energy is increased above 70 eV doubly charged species tend to be formed by the removal of two electrons from the molecule. This tends to complicate analysis of the results, so, if possible, this condition is avoided.

The positive ions produced by bombardment are accelerated by a small electrostatic field maintained between the repeller plate X and the first accelerator plate Y (fig. 2.11). After passing through a slit in Y, the ions are further accelerated by a higher field between Y and Z and enter the analyser through a slit in Z.

The analyser in a single focussing machine is a uniform magnetic field. The ion beam which has been accelerated through the voltage V enters the magnetic field at right angles to its direction of motion. Ions of mass m and charge e enter the field with velocity v given by

$$eV = \tfrac{1}{2}mv^2 \qquad (1)$$

and traverse the magnetic field H in a circular orbit of radius r according to the equation:

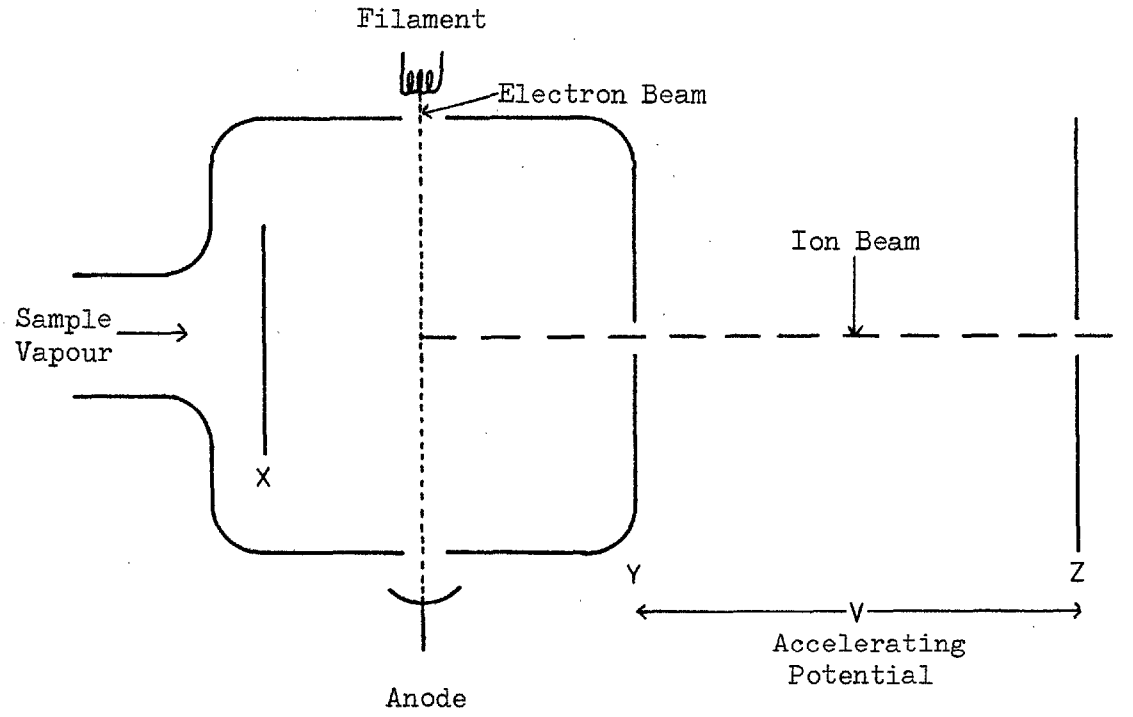


Fig. 2.11 The ion source of a mass spectrometer.

$$Hev = \frac{mv^2}{r} \qquad (2)$$

Eliminating v from these two equations gives:

$$\frac{m}{e} = \frac{H^2 r^2}{2V} \qquad (3)$$

The magnetic field separates ions of the same m/e ratio. In practice ions of a given mass do not all have the same kinetic energy, so describe circles with a range of radii, the beam is therefore not focussed. To overcome this a radial electrostatic field is applied. This gives focussing of ions of the same kinetic energy at a slit immediately before the magnetic field is applied (fig. 2.12) and results in better resolution. An instrument using both electrostatic and magnetic fields is called a double focussing mass spectrometer.

It is a feature of the geometry of the machine that the radius of the path described by all the ions must be the same. To achieve this,

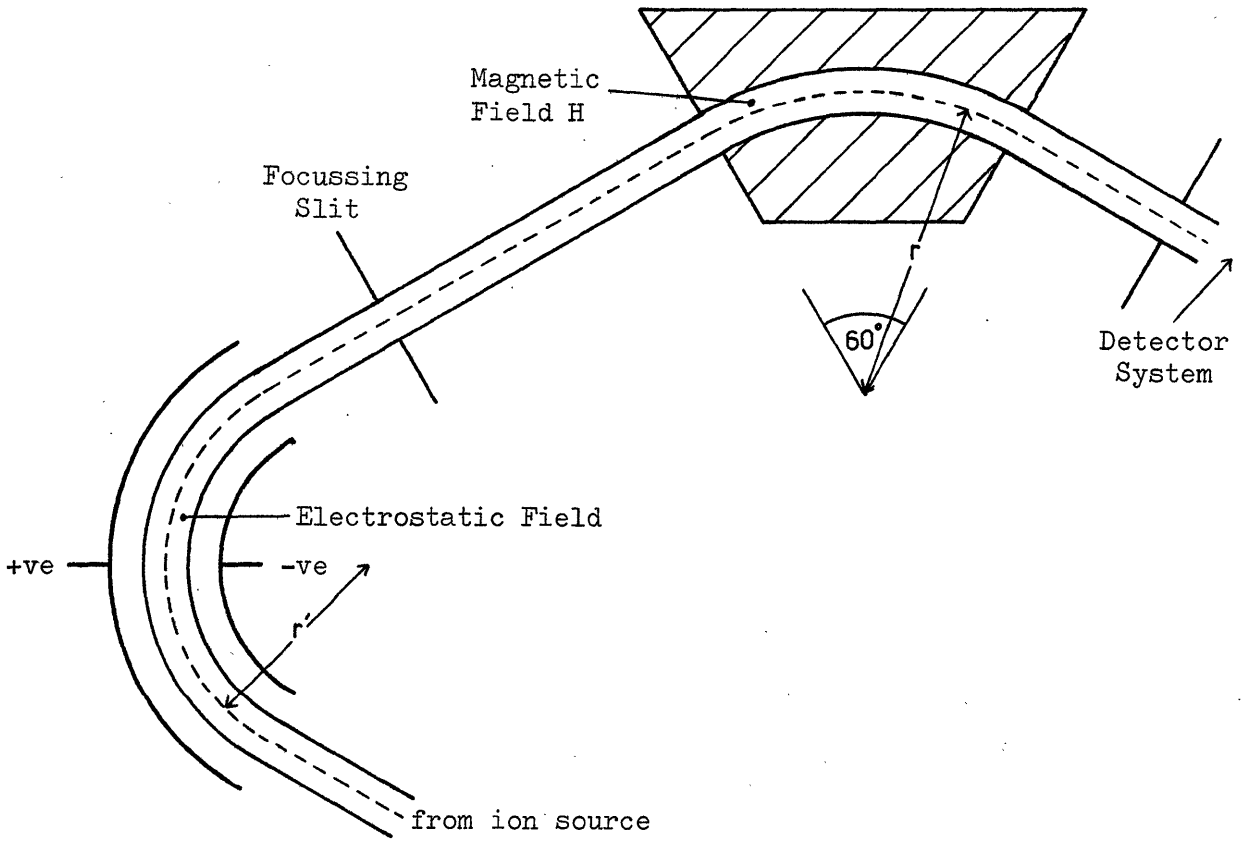


Fig. 2.12 The focussing of the ion beam by both an electrostatic and a magnetic field as in a double focussing mass spectrometer.

either the magnetic field can be varied, a constant accelerating potential being maintained, or the accelerating potential V can be altered whilst keeping H constant. The former technique is unsuitable for fast scans because of the inductance of the magnet. Also $m/e \propto H^2$ (equ^n. 3) so m/e is very sensitive to small changes of H. A variable accelerating potential is employed. A scan can be obtained in about two seconds with the particular instrument used in this study. Its resolving power ($m/\delta m$) is about 10 000, which is not good by the latest machines ($\sim$60 000) but is quite adequate for this study.

The output from the spectrometer was displayed using a uv recorder. The bar-graphs in this thesis were derived from the recorder output.

2.7.3 Interpretation

The spectrometer will detect changes of one mass unit, and can therefore be used to detect the presence of isotopes. It will, for example, show the presence of ^{13}C in an organic compound. This being so, a molecular ion M^+ derived from an organic molecule will have associated with it a peak at mass M + 1. The intensity of this peak is proportional to the amount of ^{13}C present. Therefore an alkane of high molecular weight will produce a peak at mass M + 1 of greater intensity than a low molecular weight alkane, since the possibility of a ^{13}C atom being present in the molecule will be greater for the larger molecule. Similarly, in a larger molecule, there is a greater possibility of the presence of two ^{13}C atoms. This gives rise to a peak at mass M + 2. Knowing the natural isotopic abundance it is possible to calculate the expected intensities of the peaks. Conversely, by measuring the isotopic peak heights, and knowing the natural abundance of the isotopes, it is possible to determine how many atoms of an element are present in a particular fragment. Similarly, isotopic abundance can be used for identification. This is particularly clear for bromine which has isotopes, ^{79}Br, natural abundance 50.52%, and ^{81}Br of natural abundance 49.48%. Two peaks are observed at masses M and M + 2 of almost identical heights. There is no peak at M + 1.

As was mentioned at the beginning of the previous section, a molecule will fragment in a manner which is characteristic of the groups it contains. It is possible, however, for a fragment ion, once produced, to further fragment whilst it is being accelerated, possibly undergoing elimination or a molecular rearrangement. There is also the possibility that an ion may collide with another ion or molecule, and react with it. Since a high vacuum is used, only a few ions are present in any given volume, so the probability of this is quite small. However

it may still occur and must be considered when interpreting spectra.

The fragmentation processes will be described in more detail when specific compounds are examined using mass spectroscopy.

2.7.4 Limitations

Reference to fig. 2.11 shows that the sample is introduced as a vapour. Clearly, therefore, the sample must be vapourisable. There is little difficulty with a liquid or a fairly low melting solid. However a high melting solid may undergo thermal decomposition. For this reason the minimum temperature possible is always used to obtain a spectrum.

Although mass spectroscopy is a tool for use with liquids and solids, it is possible to examine a surface film. This is done by introducing the substrate, with the film sorbed on it, into the heated sample vapourisation chamber. Some of the film may vapourise and pass into the ion source. This is particularly so with physisorbed films where increasing the temperature decreases the amount adsorbed. Chemisorbed films are more difficult to remove since they are more strongly bound to the substrate. Increasing the temperature in order to remove some sample often destroys the film. This was found to be the case when sections of balls were introduced into the sample chamber. No spectra were obtainable.

Mass spectroscopy was successfully used for the examination of:

(i) 'pure' lubricants to ascertain purity,

(ii) used lubricants to detect chemical changes and

(iii) films stripped from ball surfaces.

The information obtained for each substance examined is presented and discussed in the relevant chapter.

2.8 CHROMATOGRAPHY

2.8.1 Introduction

It is well known that some materials are adsorbed by other materials. This property is utilised in all forms of chromatography. If an adsorbate is flowing through a tube containing an adsorbent, adsorbate molecules will be adsorbed onto the adsorbent. They do not remain adsorbed indefinitely, but desorb. Since there is a flow, the desorbed molecules will move along the tube a little way to be readsorbed. The flow of adsorbate through the adsorbent can thus be regarded as being a series of steps. The molecules are adsorbed, desorbed and moving, and readsorbed.

For a given adsorbent the tenacity with which an adsorbate will be held depends on the nature of the adsorbate. Clearly, if a molecule is strongly sorbed, it will spend most of its time stationary and very little time moving. Similarly, if a molecule is only weakly adsorbed, it will spend most of its time moving, and very little time stationary adsorbed on the adsorbent. If, therefore, a mixture of strongly sorbing molecules and weakly sorbing molecules is passed through the tube of adsorbent, during a given time interval, the weakly sorbing molecules will have travelled a greater distance along the tube than the strongly adsorbed molecules. This process then has separated the two types of molecules.

The two types of chromatography used in this study were thin layer chromatography (TLC) and gas liquid chromatography (GLC).

2.8.2 Thin Layer Chromatography

In TLC the adsorbent is a uniformly thin (0.25 - 0.75 mm) layer of activated silica gel supported on a glass plate. A drop of a solution of the mixture to be separated is spotted about 10 mm from an

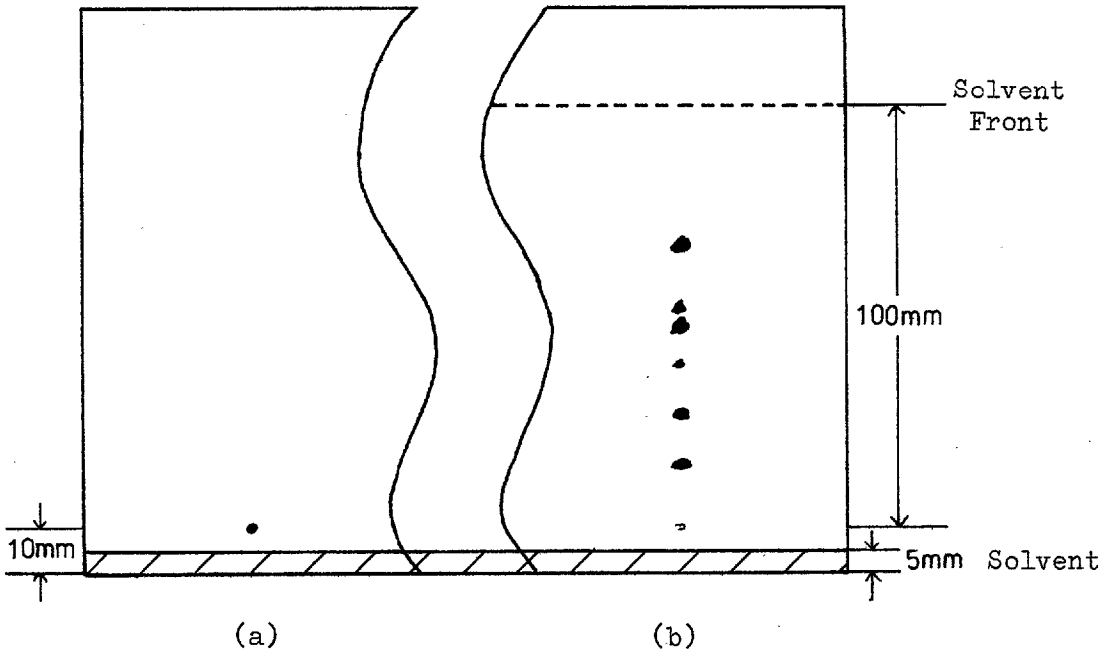


Fig. 2.13 A thin layer chromatography plate (a) before the separation process and (b) after separation. The spots may only be visible after development and not during the actual separation.

edge of the plate. The plate is placed vertically in a tank containing about 5 mm depth of a solvent (fig. 2.13). It is important that the solvent level is below the spot, and that the atmosphere in the tank is saturated with solvent vapour. The solvent rises up the silica gel by capillarity. When the solvent has risen a certain distance, the plate is removed from the tank and the solvent dried off. If a colourless mixture is to be separated, the spots will be invisible. For any measurements to be made they must be rendered visible. This is done by spraying the plate with a suitable developing agent. The choice of agent depends on the products, since some visuallising agents are quite selective for a particular functional group. They act by forming a

coloured compound with the material of the spot. There are also general developers, such as a methanol/concentrated sulphuric acid mixture. On heating, this mixture chars organic compounds indicating the presence of any material as a dark brown or black spot. This destroys the compound and gives no information concerning its structure. It is however useful in determining whether a compound is pure or not. The particular silica gel used contains an inorganic luminophore which fluoresces strongly under short wave ultra-violet light. If a material is present on the plate which absorbs in the ultra-violet range, it will appear as a black spot when the plate is examined under ultra-violet light.

Limitations. Although samples of the order of micrograms can be separated, the technique is not very successful when a very small amount of one material is present in another. For this reason, and the fact that identification poses problems, since, like X-ray powder techniques reference to standards is necessary, this analytical procedure could not be used for the determination of polymerised material in hexadecane. It can obviously not be used to examine a solid directly. Its main use was restricted to the determination of the purity of starting materials. The solvent used for elution, and the method of visualisation are mentioned where TLC has been used.

2.8.3 Gas Liquid Chromatography

The other form of chromatography employed was gas liquid chromatography (GLC). The adsorbent is a liquid supported on a solid held in a long (~2 m) thin (~3 mm) tube. This unit is called the column. An inert gas, usually nitrogen, is passed through the column in order to carry the sample along it. The sample, which must be a liquid or a gas, is injected into one end of the column. It is vapourised immediately in the hot injection port. The sample vapour passes through the column, being sorbed and desorbed by the liquid as

previously described. Adsorbtion decreases with increasing temperature therefore, if the column is cold, some materials may be so strongly adsorbed that they make little or no progress through the column. If the column is heated, however, these compounds will become less strongly adsorbed and will move through the column. For this reason a temperature programme is normally applied. This may consist, for example, of (i) holding the column at a fixed temperature for some time, (ii) increasing the temperature at a uniform rate and (iii) holding the column at this second temperature. This procedure may be repeated several times with the same or different heating rates to achieve a good complete separation. The complexity of temperature programming depends on the particular instrument.

Having separated a mixture into its component parts, it is necessary to detect these parts. There are two types of detector in everyday use, one is the flame ionisation detector (FID), the other is the hot wire detector (HWD).

In the FID hydrogen is burned at a flame. A potential difference is maintained across the flame between two electrodes. A flame produces ions, so there will be a certain current flowing across the flame. If a material is introduced into the flame which burns, more ions will be produced. The current across the flame will increase. This change in the current is amplified and displayed, usually using a pen recorder.

For a given set of separation conditions, the time taken for a compound to pass from the injection port to the detector is characteristic of that material and is known as the residence time. Note that with TLC the time was fixed and the distance varied, whereas with GLC the distance is fixed, time being variable. By introducing samples of known pure compounds, residence times can be compared with that of an

unknown and the sample may be identified. There are available fairly extensive tables of residence times. However, since there has been little in the way of rationalisation of column materials, they are not always useful. A good example of the use of GLC is demonstrated in the determination of the impurities in hexadecane (Chapter 4).

A GLC machine may be interfaced with a mass spectrometer, the mass spectrometer being used as the detector. GLC separates a mixture; the mass spectrometer determines the molecular weight and functional groups present. This is a powerful analytical tool, particularly when linked directly to a computer which can identify each component and quantify the amount present. Unfortunately this set-up was not available at Imperial College. Use of a GLC/mass spectrometer combination nevertheless was obtained. However poor spectra were produced which did not give any significant information. The interfacing of GLC and a mass spectrometer is not easy since the chromatography unit has a working pressure of typically about 80 psi, whilst the mass spectrometer operates at 10^{-5} - 10^{-6} torr.

Limitations. Chromatography cannot be used for the direct examination of a surface. It can be utilised to look at materials stripped from surfaces. Of itself chromatography gives little or no information concerning molecular structure. Its primary use is in the separation of mixtures. The components of a mixture can only be identified by comparison with standards.

In attempting to identify an unknown polymeric material this technique was considered to have little use. It was found to be valuable in ascertaining whether or not a compound, usually a starting material, was pure. In the case of hexadecane the impurities were also identified by comparison with standards.

2.9 WET CHEMICAL ANALYSIS

2.9.1 Limitations

Wet chemical analysis was by and large precluded from this investigation on two grounds.

(i) The quantities of material involved were very small. Ideally they should be studied on the surface where they were found. This not being possible, they were produced as dilute solutions in a hydrocarbon solvent. Conventional organic analysis requires the separation of a mixture into its component parts. This would present great difficulties considering the quantities involved.

(ii) The analysis would only indicate the functional groups present. It would not show the presence or absence of a polymer.

It is clear therefore that for a successful analysis one must use machine techniques rather than classical wet chemistry.

CHAPTER 3

APPARATUS AND PRELIMINARY INVESTIGATIONS

3.1 INTRODUCTION

The formation of friction polymer has been reported to have occurred under a wide range of conditions of load, sliding speed and temperature. To be able to evaluate the usefulness of any analytical technique, it must be employed under conditions where there is material present to analyse. For this reason early investigations were designed effectively to duplicate a typical set of conditions of load, sliding speed and temperature. As can be seen from table 3.1 the number of possible combinations was quite large.

Many experiments had been done using the Four Ball rig. It was therefore decided to use the Lubrication Laboratory modification of this - the ball on triplane apparatus[70].

3.2 BALL ON TRIPLANE APPARATUS

This apparatus, shown in fig. 3.1 was a development of the standard four ball test rig. It consists of an upper ball which is rotated against the flat ends of three 3/16" rollers whose axes coincide at the centre of the ball. The geometrical arrangement of the rollers is shown in table 3.2. Each roller carries the same load but produces a separate wear track on the ball. This overcomes the problem with the four ball rig where inconsistent results have been shown to be due to the lower balls rubbing in the same wear track[71].

Lubricant	Load	Speed	Temperature	Test apparatus	Reference
Benzene	20 g	120 Hz	Room	Stylus on plate	41
"	50 kg	$3.5\ 10^{-3}$ ms^{-1}	Room	4 ball machine	44
Mineral oil + iodine	5 kg	$3.5\ 10^{-3}$ ms^{-1}	Room	4 ball machine	10, 11
White oil	15 kg	0.5 ms^{-1}	21°C	4 ball machine	29
"	15 kg	$3.3\ 10^{-3}$ ms^{-1}	25°C	4 ball machine	91
"	15 kg	0.4 ms^{-1}	25°C	4 ball machine	91
"	0 - 148 Pa	2.29 ms^{-1}	121°C	Friction drive	9
"	118.4 Pa	0 - 5.08 ms^{-1}	121°C	Friction drive	9
"	1 kg	0.56 ms^{-1}	25°C	Ball on cylinder	91
"	3 kg	0.4 ms^{-1}	25°C	4 ball machine	91
Cyclohexane (vapour)	50 kg	$3.5\ 10^{-3}$ ms^{-1}	25°C	4 ball machine	44, 45
" "	14 kg	0.23 ms^{-1}	20°C	4 ball machine	52
" "	23 g	0.13 ms^{-1}	Room	Pin on shaft ($\frac{1}{2}$" shaft, 3/8" rider)	39
" "	---	0.56 ms^{-1}	Room	Ball on cylinder	10

Table 3.1 Synopsis of lubricants and conditions for which friction polymer has been reported.

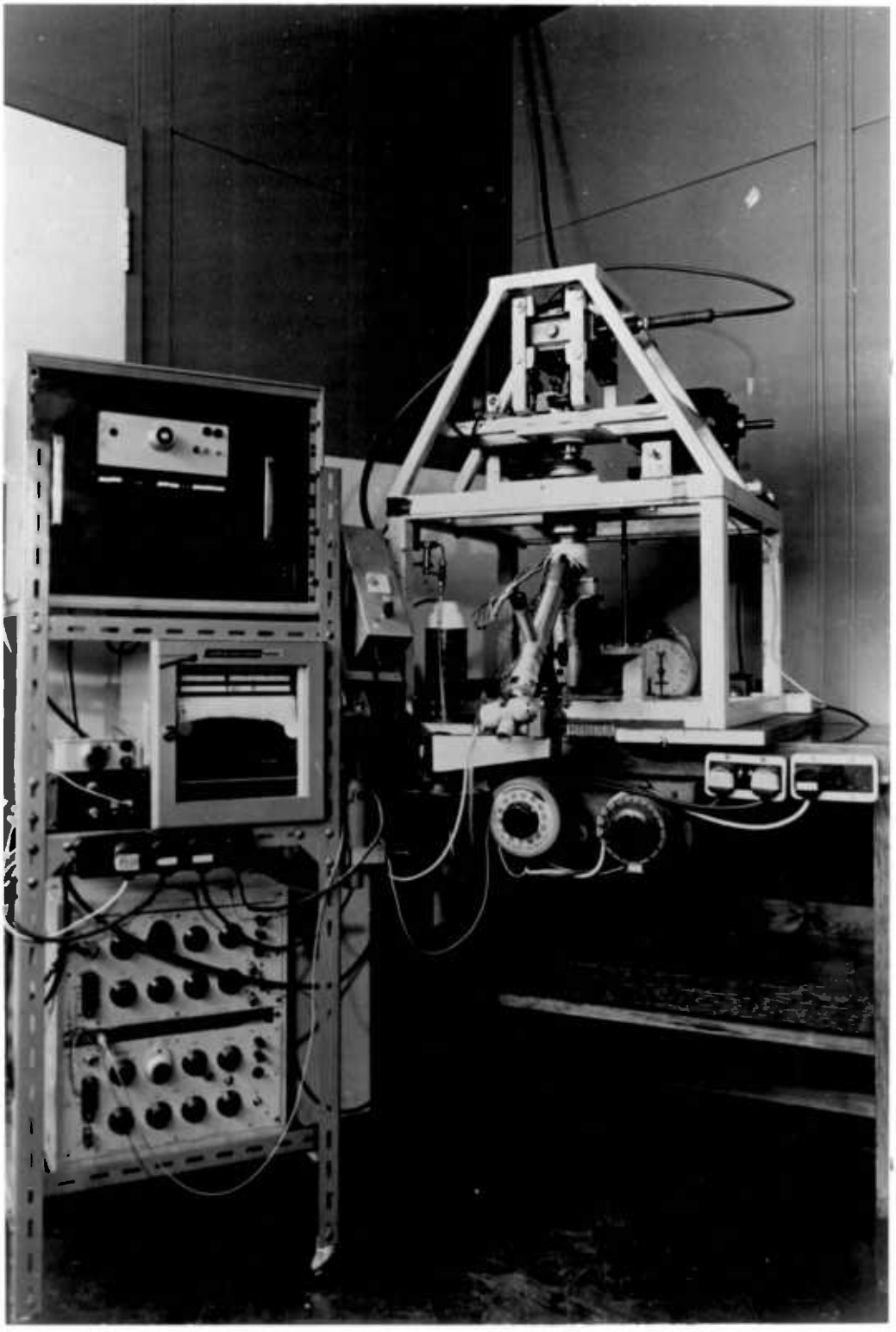


Figure 3.1 The Triplane Apparatus.

Peg	Angle to vertical	Circumferential angle
A	45°	0°
B	$55^{\circ}\ 45'$	$+137^{\circ}\ 42'$
C	$34^{\circ}\ 15'$	$-99^{\circ}\ 36'$

Table 3.2 Geometric arrangement of the rollers for Ball on Triplane apparatus.

The pegs are held in a stainless steel carrier. During the manufacture of the peg carrier, a 6.35 mm (1/4") hole was bored in the centre. This hole was normally plugged by an interference fit stainless steel plug. An alternative plug was produced with a very small hole in its centre, such that, if required, a gas could be passed through the lubricant.

The lubricant is retained by a detachable shield which screws onto the peg carrier (fig. 3.2). This is surrounded by an electric heater controlled by a Variac transformer. The assembly is mounted on a cyndanio block which is loaded from beneath by a pivoted loading arm system. A spring balance is used to apply and measure the load. The load acted through a thin walled torque tube fitted with strain gauges arranged to measure friction.

Temperature was monitored by a thermocouple in contact with the trailing side of one of the pegs (peg A in table 3.2). The outputs from the strain gauges and thermocouple were recorded by a pen recorder. A computer programme was written to calculate the coefficient of friction from the recorder traces.

The ball is held in a chuck, driven, via a V-belt and pulleys, by

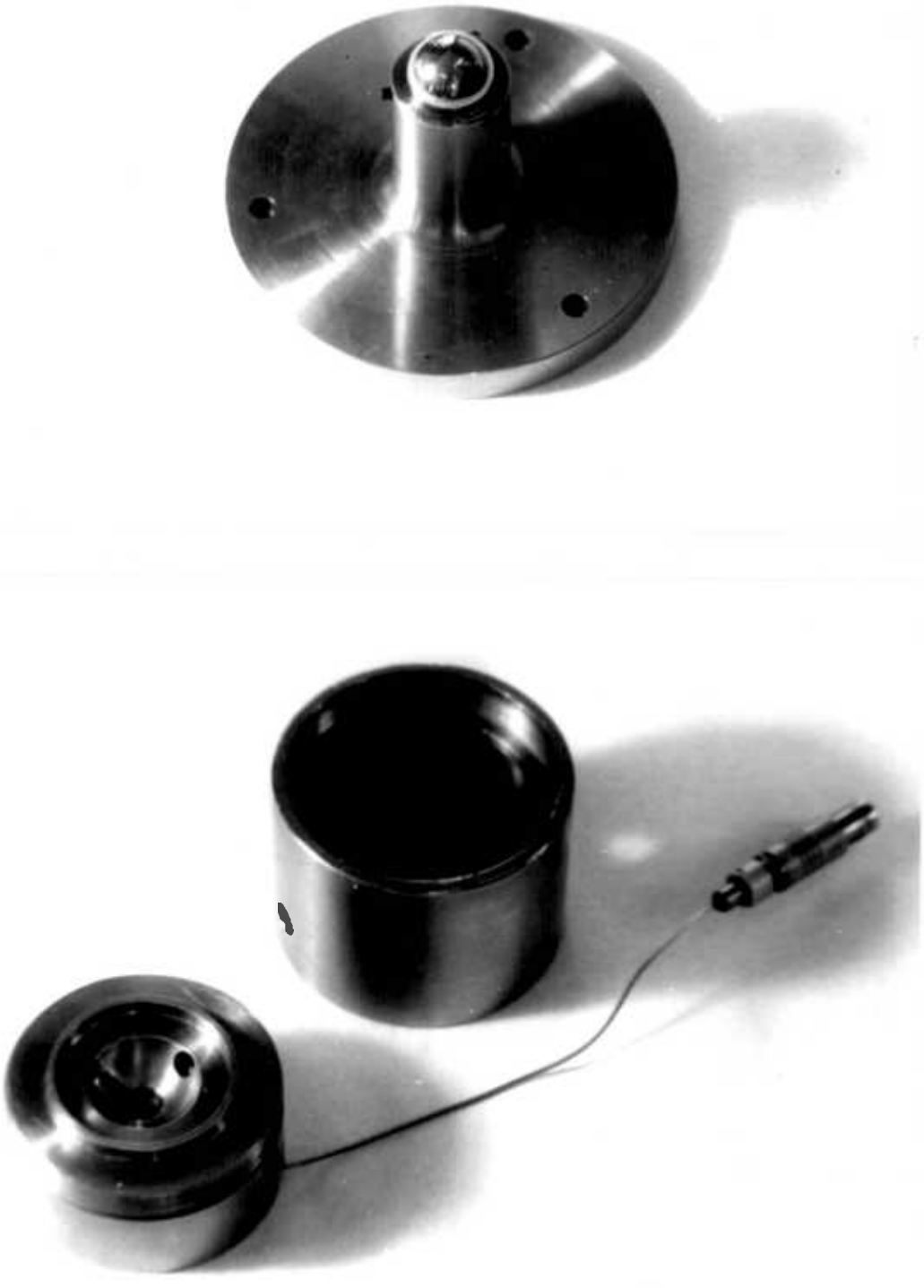


Figure 3.2 The ball chuck, peg carrier and lubricant retaining ring from the triplane apparatus.

an electric motor. Various speeds were obtained by changing the pulleys. Rotational speeds were determined using a hand tachograph. This had a specified error of not greater than 1%. A comparison of the speeds indicated using this device and electronic speed measuring equipment showed the variation to be about 1%.

This apparatus has certain advantages over the four ball rig, but there are disadvantages with regard to the analysis of surface films. Three wear tracks are produced instead of one. This improves the repeatability of results, since any surface inconsistencies are only likely to affect one wear track and thus have a diminished effect. Most spectroscopic analysis techniques require smooth flat surfaces. The four ball machine uses all curved surface specimens whereas the triplane rig uses a ball on a flat. However, since the Hertz stress depends on the reciprocals of the radii of the system in contact, similar stresses to those encountered with the four ball rig can only be obtained on a triplane rig employing 25.4 mm balls, by applying a top ball load some eighteen times greater than for the four ball machine. This would mean that loads of the order of four hundred kilograms would be required. To overcome the necessity for such large loads the diameter of the ball was reduced. A 12.7 mm ball would need a load only four times greater to obtain the same pressure but smaller diameter balls are less amenable to surface analysis using spectroscopic techniques. Therefore a compromise was struck and a 19.06 mm ball was used. For similar pressures this diameter ball requires a load some ten times that used in the four ball machine.

3.3 CLEANING METHODS

3.3.1 Cleaning Balls and Pegs

Since this work was concerned with films formed on surfaces it was considered important to have either a very clean metal surface, or at least a reproducibly 'dirty' surface prior to testing. The probability of obtaining and retaining a chemically clean surface was considered remote, since the ball and pegs had to be cleaned, then transfered to, and assembled in, the triplane apparatus. This meant that the ball and pegs would certainly become contaminated with airborne oil vapours and other debris. The technique adopted was one in which the ball and pegs were well cleaned to remove particularly organic material, then allowed to come into contact with air, which would give an oxide layer.

There were three methods of cleaning available, soxhletting, ultrasonic cleaning and ionic bombardment.

3.3.2 Soxhletting

Soxhletting involves repeatedly washing the specimens in hot solvent. A solvent typically employed is toluene. This has certain disadvantages. It adheres to the surface rather tenaciously, and thus has to be removed using another solvent. Acetone is often used for this purpose. Toluene acts as a radical trap, so it was essential to remove all traces of it, since its presence could inhibit any radical reactions which may occur during the running of the test rig. Experience showed that water tends to collect in toluene used for soxhletting. This has the effect of producing a variable surface composition, since its concentration is not controlled.

3.3.3 Ultrasonic Cleaning

With ultrasonic cleaning the items to be cleaned are subjected to ultrasonic vibrations whilst submerged in a solvent. As with

soxhletting, toluene is often employed as the solvent. It is washed off with clean acetone, and the items cleaned again, but using fresh acetone as the solvent. The cleaner cabinet contains water to ensure good mechanical contact and it is not uncommon to find an increase in the concentration of water in the solvents. This was, as previously noted, undesirable.

3.3.4 Ionic Bombardment Cleaning

The third technique is ionic bombardment, in which the specimens to be cleaned are bombarded with medium energy ions and electrons. By controlling the conditions of ambient pressure and the potential across the discharge path, it is possible to form a plasma in which the ions and electrons have sufficient energy to remove both physisorbed and chemisorbed films from the surface. The method is also capable of eroding the metal itself, so care has to be taken to avoid excessive damage to the substrate metal. The design of the apparatus is such that it was impossible to transfer the cleaned ball and pegs to the test lubricant without exposure to air. Thus, an oxide layer is formed on the surfaces after cleaning. The cleaned specimens become quite hot, ~80°C., so it is unlikely that much water vapour would be picked up on the surfaces. The time taken for transfer, and the path used, were both kept to a minimum. This was the cleaning method used in this study. The actual apparatus is described below.

3.3.5 Ionic Bombardment Cleaning Apparatus

The ionic bombardment cleaning apparatus, fig. 3.3, consists of an all glass vacuum line evacuated by a rotary pump, and a relatively small glass discharge chamber, energised from a high voltage transformer (fig. 3.4). Under the influence of high energy ions and electrons any oil or grease in the system could be polymerised on the

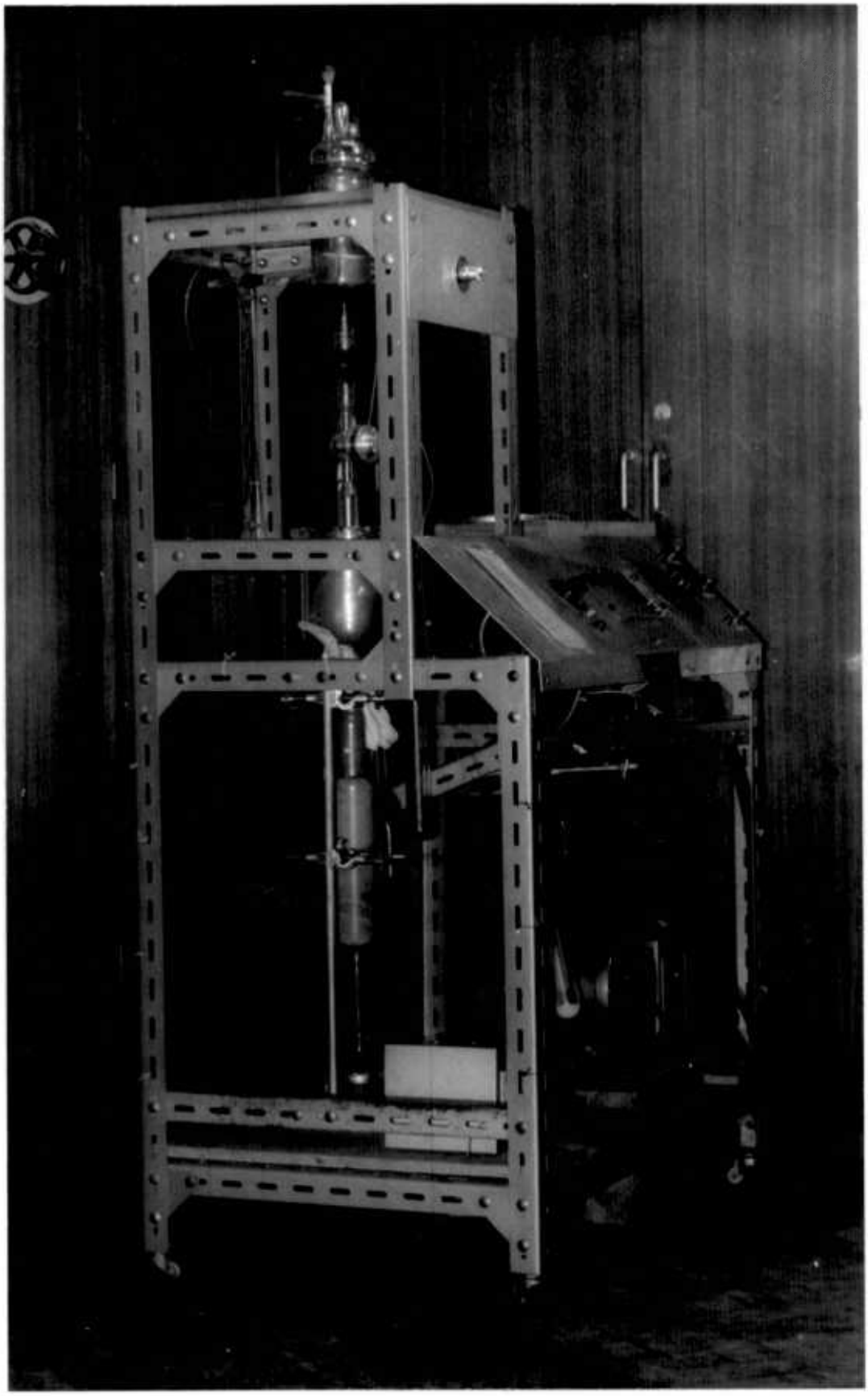


Figure 3.3 The Ionic Bombardment Apparatus.

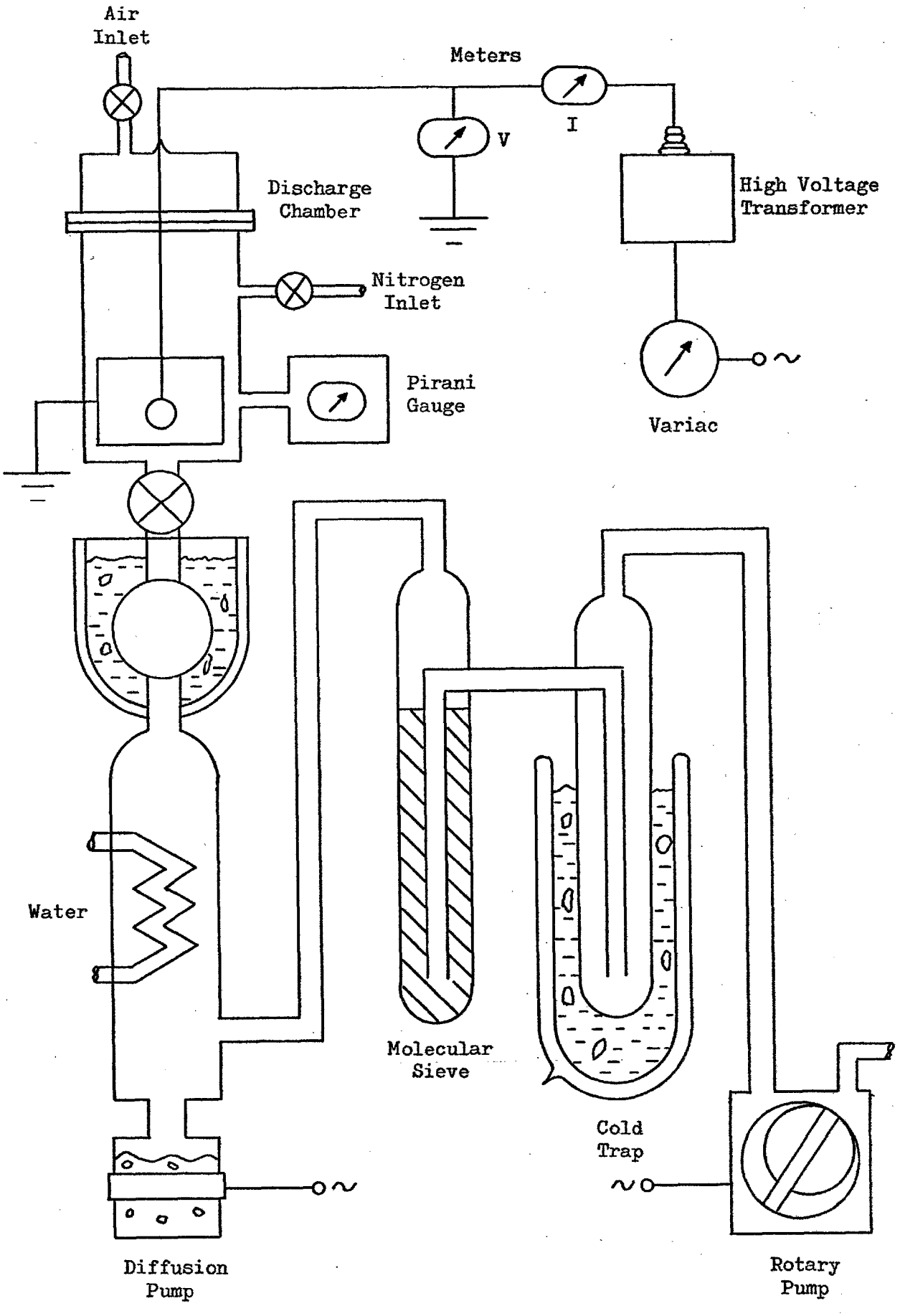


Fig. 3.4 Diagram of the Ionic Bombardment Cleaning Apparatus.

ball's surface[72] to produce highly persistent films. For this reason all joints and valves were greaseless, the only oil present being the high vacuum oil in the rotary pump. This was purged regularly to remove any impurities which may have collected in it. Cones and sockets were sealed with pycene wax.

The discharge chamber was evacuated through a high vacuum valve. The lower part of the chamber contained a cylindrical aluminium electrode maintained at earth potential, and a needle valve to leak air or any other gas into the chamber. The top cover of the chamber was fitted with a PTFE valve for air admittance and a sealed in metal conductor to energise the high voltage electrode. Attached to this electrode was a horizontal wire loop of internal diameter 18 mm, its height arranged so that a ball resting in it would be held at the centre of the cylindrical aluminium electrode.

The electrical system consisted of a 'Variac' transformer supplying a high reactance step up transformer capable of supplying 50 mA at 5kV. Meters were provided to monitor the voltage and current of the discharge.

The cleaning procedure involved first wiping any preservative oil off the ball and pegs using a tissue. This was followed by a preliminary cleaning in the ultrasonic cleaner using toluene and acetone successively as solvents. The degreased ball was then placed in the ring attached to the chamber cover and the chamber evacuated, pumping continuing for about ten minutes. Further pumping produces a pressure which was too low to obtain a discharge. Air was normally used as the bombarding gas but experiments were carried out in which 'oxygen free' nitrogen (white spot quality) was used. There was no difference in the friction values obtained whether the balls were cleaned in a nitrogen or an air atmosphere, so for the sake of convenience air was normally

used. Discharge was initiated at 1.7 kV and 30 - 40 mA. These conditions gave a well developed cathode glow discharge which completely surrounded the ball. This area of the discharge path is the most well supplied with energetic ions. Cleaning was achieved by ionic bombardment on one half-cycle of the current wave form, and by energetic electron bombardment on the other half-cycle. Exposure to the discharge was limited to 25 seconds. Exposure times greater than 30 seconds tended to cause damage to the metal substrate. This showed itself as small pits on the surface. Even so, after about 50 cleanings a thin metal film was found to be deposited on the inside of the glass chamber. The efficiency of the cleaning process was related not only to the rate of removal of contamination from the ball, but also to the rate at which this contamination was removed from the chamber once it had passed into the vapour phase. This was particularly rapid if there was a flow of clean gas through the chamber. On termination of the discharge the high vacuum valve was closed and the pressure in the discharge chamber rapidly brought up to atmospheric using air filtered through Whatman 542 filter paper. The ball was transfered quickly into a beaker containing test lubricant. The pegs were cleaned in an identical manner, except that they were held in an aluminium holder in such a way that the end faces were freely exposed to bombardment by the ions (fig. 3.5).

3.3.6 Comparison of Cleaning Methods

An experiment was conducted to compare the results of cleaning the specimens by the three different methods. It was assumed that the cleaner the metal surfaces, the higher the friction[73]. Therefore a ball and pegs were cleaned by each method, assembled into the triplane rig and run at a sliding speed of $9.4\ 10^{-5}$ ms^{-1} using purified hexadecane as the lubricant. The values of the coefficient of friction

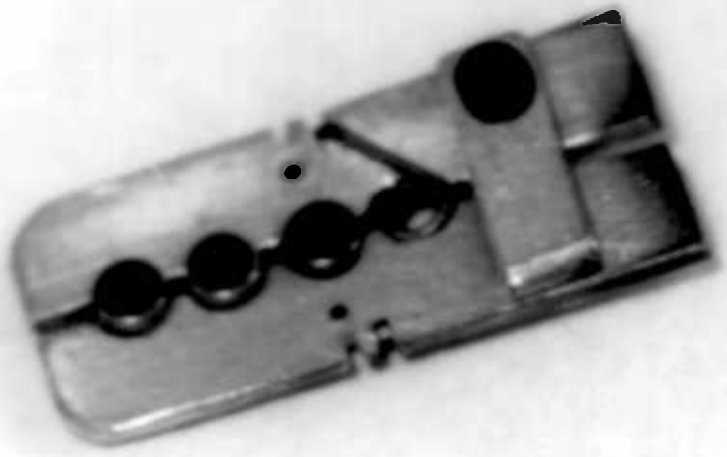


Figure 3.5 The device for holding the pegs in the ionic bombardment apparatus in such a way that the faces of the pegs were exposed to bombardment.

given by balls and pegs cleaned using the ultrasonic cleaner and by soxhletting in toluene were both 0.7, whereas the value for balls and pegs cleaned in the ionic bombardment apparatus was 0.8. This clearly indicates that the ionic bombardment method gives a cleaner surface than do the other cleaning methods.

3.3.7 Cleaning Chuck and Peg Carrier

The physical dimensions of the ionic bombardment apparatus rendered its use impossible for cleaning the chuck and peg carrier. Therefore one of the less efficient methods had to be employed. Comparison of soxhletting and ultrasonic cleaning when used to clean balls and pegs showed that there was no detectable difference in cleanliness. Thus the quicker and easier ultrasonic method was used.

As received from manufacture the chuck, peg carrier and lubricant retaining ring were contaminated with cutting fluids and general workshop oils and dirt. Initially they were ultrasonically cleaned using toluene as the solvent followed by acetone. All the surfaces, except for the threads, were abraded using 400 grade wet and dry paper. They were ultrasonically cleaned as before. This produced shiny surfaces from which acetone evaporated quickly and evenly. This is a useful indication of cleanliness. Any dirt or grease causes 'islands' of acetone to form as it evaporates less quickly from the dirty areas.

During the ensuing work the following cleaning procedure was adopted:

(1) Any lubricant remaining from a previous test was washed off using toluene and acetone.

(2) The parts were ultrasonically cleaned using Analar toluene as the solvent followed, after rinsing in Analar acetone, by Analar acetone.

(3) The components were stored under fresh Analar acetone until

required for use. This time was only a few minutes.

(4) The parts were removed from the acetone, allowed to dry naturally, and assembled, together with the pegs, ball and test lubricant.

During drying care was taken to ensure that the acetone evaporated quickly and evenly. If this were not the case the cleaning procedure was repeated from stage (2). The thread between the peg carrier and lubricant retaining ring was sealed using PTFE tape.

Each lubricant system was studied in two stages, the determination of the load bearing capacity and the surface analysis. Between the two stages the abrasion method of cleaning was used. It was similarly employed when the lubricant composition was changed.

3.4 LUBRICANT

The preliminary requirement in this programme was to run a system which would produce some friction polymer. This would enable the various experimental and analytical techniques to be tested. Subsequently a more systematic study could be made. To do this initial work a lubricant was required which had the following properties:

(i) It must be obtainable pure.

(ii) It must be a liquid at room temperature.

(iii) It must be easy to analyse for.

(iv) It must be able to undergo chemical reactions with the liklihood of a polymeric product being formed.

The first and third of the criteria suggest a fairly small molecule containing only a few carbon atoms. Generally the smaller a molecule the more data there is available concerning it. There are also fewer possible reaction mechanisms in which it can take part. Its behaviour is therefore more easily predicted. The fourth requirement implies

that the lubricant should not be an alkane, since these are chemically fairly inert, but it should contain reactive functional groups, such as double bonds, hydroxyl groups or a halogen. If any analysis is to be done the lubricant should be obtainable preferably in a very pure state, but, if this is not possible, with a known purity, the impurities being identified.

Consideration of these four factors led to the initial choice of lubricant being a mixture consisting of hexane (C_6H_{14}), 1-hexene (C_6H_{12}) and 1,5-hexadiene (C_6H_{10}) in the ratio 2:2:1. They were supplied as puriss grade by Messrs Koch Light Laboratories Ltd. Further purification was not considered important at this point, since the priority was to obtain some polymeric material. If any impurity were present which initiated polymerisation then so much the better.

3.5 TESTS USING C_6 COMPOUNDS

3.5.1 Experimental Procedure

The ball and pegs were manufactured by Messrs R.H.P. and made from EN31 steel. This is a standard bearing steel which is readily available in the form of balls and rollers. The composition of this alloy is shown in table 3.3.

	C	Si	Mn	S	P	Ni	Cr	Mo
min.	0.90	0.10	0.30	0.00	0.00	0	1.00	0
max.	1.20	0.35	0.75	0.050	0.050	0	1.60	0

Table 3.3 Percentage composition of EN31 steel. Balance is iron.

The steel specimens were cleaned by first washing in toluene and acetone, then by ionic bombardment as previously described. The chuck, cup and lubricant retaining ring were cleaned in an ultrasonic cleaner using analar toluene as solvent, and repeated, after rinsing in acetone, with analar acetone. These components were immediately assembled, using PTFE tape to seal the threads of the cup and retaining ring against lubricant leakage. The pegs were removed from the mixture of hexane,hexene and 1,5-hexadiene (2:2:1) into which they were placed after ionic bombardment and fitted into the cup. Fresh lubricant was introduced into the cup. The ball was inserted in the chuck and quickly placed in the lubricant. The whole unit was assembled into the triplane apparatus, the ball and pegs brought into contact and the gauge bridge balanced. The pen recorder was started and the ball rotated at the required speed of 0.43 ms^{-1}. The load was quickly applied. Values of friction and temperature were recorded.

3.5.2 Results and Discussion

First attempts to operate the apparatus with a single high load failed. Scuffing invariably occurred during the application of the load. This resulted in a ball with badly scored wear tracks and pegs with torn faces. Following this experience a load of 2.5 kg was applied initially and the apparatus allowed to run for three minutes in order to run-in the ball and pegs. The load was subsequently increased every three minutes in units of 1 kg until the onset of scuffing. This occurred at a load of 5.5 kg.

To obtain a reasonable yield of reaction products previous workers found that the running time of an apparatus must be of the order of hours[45]. To determine whether or not extended operation was feasible with this lubricant system, after a run-in period of three minutes at 2.5 kg a load of 4 kg was applied, and the apparatus allowed to run

until scuffing occurred. Operation only lasted for thirty minutes. On dismantling, it was found that all the lubricant had evaporated. Other running-in loads and times were tried, but these did not appear to affect the onset of scuffing. The continuous running load was varied between 2 kg and 5 kg, but loss of lubricant due to evaporation caused failure, generally within an hour.

It became clear then that this lubricant mixture was unsuitable for the purpose of producing polymeric material. Although it may be a chemically reactive system, it would not support a high enough load, and its boiling point was too low for extended runs to be contemplated. It is well known that the load carrying capacity of a hydrocarbon increases with increasing chain length. The boiling point of alkanes also increases with increasing molecular weight. However the solubility of alkane derivatives in hydrocarbon solvents tends to decrease with increasing molecular weight. The alkane which is required must therefore have

(i) a large enough molecule to a) support a reasonable load, and b) have a high boiling point (~250°C), but

(ii) a small enough molecule for its derivatives, such as the alcohol and acid, to be soluble in simple hydrocarbon solvents.

To meet these requirements hexadecane ($C_{16}H_{34}$) was selected. It is a well used 'model' lubricant base stock for research. Its boiling point is high (286 - 293°C/760 mm Hg)[74]. The derived alcohol and acid, hexadecan-1-ol and hexadecanoic acid, are both soluble in hexadecane. Hexadecane was used as the basic lubricant for all further work.

CHAPTER 4

HEXADECANE

4.1 INTRODUCTION

Preliminary investigations showed that short chain alkanes were unsuitable as a base stock. Hexadecane was chosen because it fulfilled the requirements of load carrying capacity, boiling point and purity. Several derivatives were also reasonably freely available. It is a straight chain alkane of molecular formula $C_{16}H_{34}$ which has often been employed as a model lubricant base stock for research purposes. Its use in this study is more readily comparable with that of other published data. As far as could be ascertained, no one had closely studied the effect of the purity of hexadecane. This work was concerned with the formation of films, one aspect being their source. It was therefore considered important that any impurities present should be detected and identified. Ideally such impurities should be removed altogether. With this in mind considerable effort was expended in the purification and analysis of this material.

4.2 PURIFICATION

4.2.1 Procedure

Hexadecane was supplied as puriss grade by Messrs Koch Light Laboratories Ltd. As received it possessed an odour. Pure hexadecane is odourless. In previous research in this laboratory[75,76]

hexadecane had been purified by standing over an activated mixture of silica gel and alumina. This produces an odourless product but no chemical analysis was attempted.

The high melting point of hexadecane, 18.13°C[74], means that it will readily solidify in a cool laboratory. This property was utilised in the purification process. The procedure used is described below.

(1) Impure hexadecane was allowed to stand over a mixture of activated silica gel and alumina in a dark bottle for one week, after which time there was no detectable smell.

(2) The odourless product was cooled in a water bath until it was just crystallising. The crystals were filtered off in apparatus at 18°C.

(3) Step (2) was repeated three times, each time using the previously filtered crystals as the starting material for the next crystallisation.

(4) The 'pure' crystals were recrystallised from 'analar' acetone and dried in vacuum.

The melting point of a sample was determined after each stage of the process. The refractive index of the molten crystals was also recorded.

4.2.2 Determination of the Purity of Hexadecane

A sample was heated to determine whether or not it yellowed. This is a sensitive test for impurities. Very pure hexadecane does not discolour even after heating for three days at a temperature close to its boiling point of 290°C. Unpurified puriss grade decomposes and yellows at similar temperatures after just a few hours[77].

No yellowing was observed after three days at 250°C. This is in contrast to Spikes[76] who observed yellowing with hexadecane purified only by standing over silica gel/alumina.

A sample of purified hexadecane was analysed by GLC. The only impurities were $C_{14}H_{30}$, $C_{12}H_{26}$ and possibly a minute trace of C_8H_{10}. These were identified by the use of authentic standards. Since these are alkanes and their concentrations were low (<0.1%) they were not expected to interfere with friction results or polymer formation.

An analysis by mass spectroscopy is shown in fig. 4.1. It can be seen that the peak at m/e 106, the molecular ion for octane, is very small. The intensity of the peak at m/e 194, the parent ion peak of $C_{13}H_{28}$, is also low. It must however be remembered that the mass spectrometer does not have the capability which gas chromatography possesses of detecting very small quantities of one material in another.

Purification Procedure	Melting Point °C	Boiling Point °C	Refractive Index
None	18.0	278	n_D^{21} 1.4324
Standing over alumina/ silica gel	18.15 - 18.25	280 - 6	n_D^{20} 1.4337
Once filtered crystals	18.2	283 - 6	n_D^{22} 1.4330
Twice filtered crystals	18.2	283 - 6	n_D^{22} 1.4330
Thrice filtered crystals	18.2	283 - 6	n_D^{22} 1.4330
Recrystallised from acetone	18.2	284 - 6	n_D^{19} 1.4348
Literature[74]	18.13	286 - 93	n_D^{20} 1.4345 n_D^{25} 1.43230

Table 4.1 The effect of purification on the melting point, boiling point and refractive index of hexadecane $C_{16}H_{34}$.

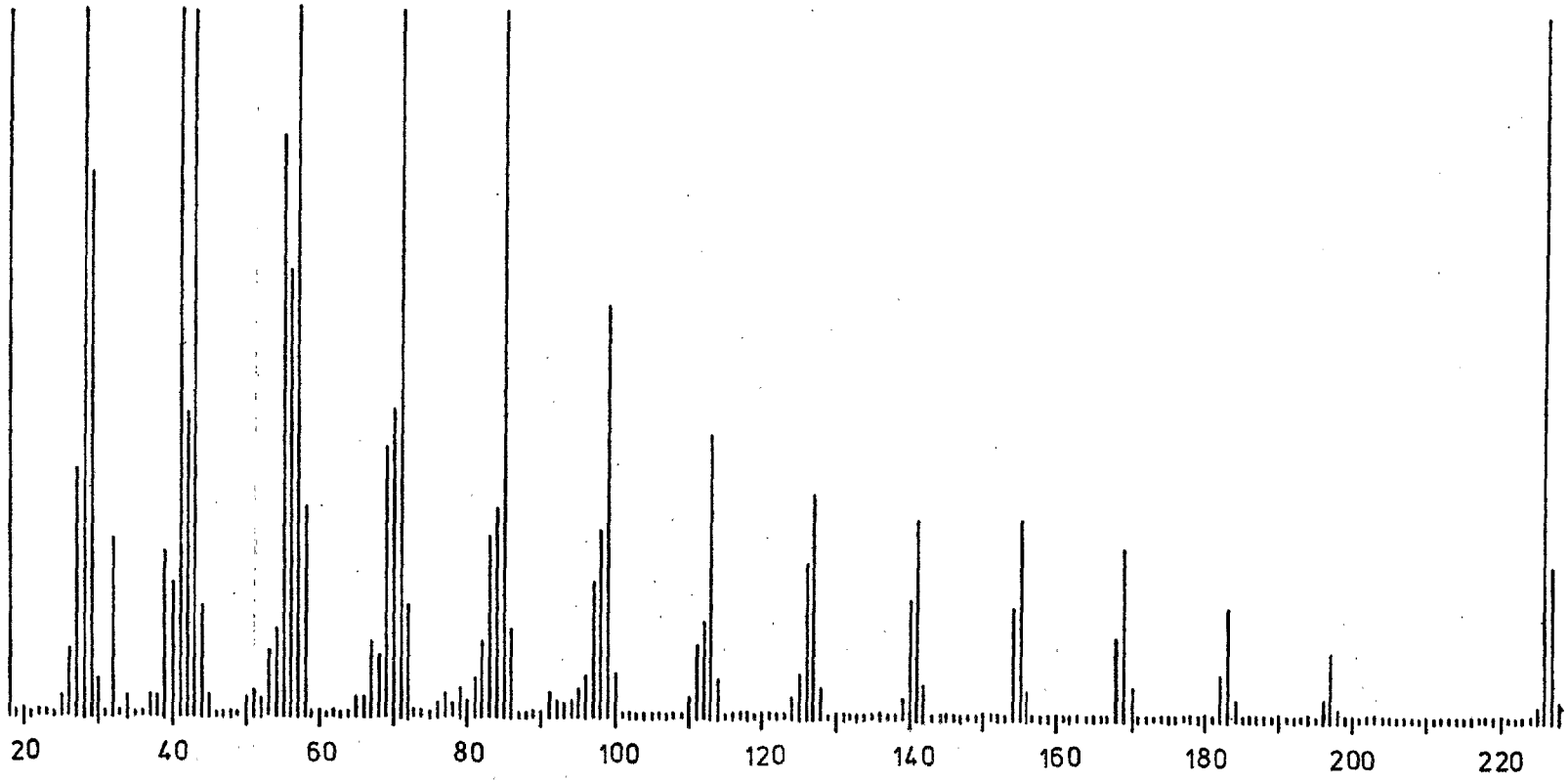


Fig 4.1 The mass spectrum of purified hexadecane.

As can be seen from table 4.1 there was no detectable change in either the melting point or the refractive index after standing over a silica gel/alumina mixture and filtering the crystals once at their melting point. GLC showed that a sample so purified was identical to one which had received the full treatment. As a result of this, all the hexadecane used in this work was subjected to this standardised purification. The purified alkane was stored over freshly activated silica gel/alumina, but for only up to two weeks after which it was repurified.

4.3 DETERMINATION OF LOAD CARRYING CAPACITY

4.3.1 Procedure

The ball and pegs were cleaned using the ionic bombardment method. The ball chuck, peg carrier and shield were ultrasonically cleaned. These parts were assembled, the cup filled with lubricant, and the assembly installed in the rig. The loading arm was adjusted so that there was zero load on the pegs. The strain gauge bridge was balanced and the drive motor switched on. The load was immediately set at 6.9 kg top ball load. After running for three minutes the load was increased by 6.9 kg. This was repeated until scuffing occurred. Scuffing was defined as a disproportionate increase in friction. The load applied when this occurs is the scuffing or failure load.

It was noted during this type of determination that sometimes scuffing occurred at an unexpectedly and irreproducibly low load. Such events seemed to have associated with them a greater than average noise emanating from the apparatus prior to scuffing. Closer examination revealed that the scuffing load depended on the run out of the ball chuck as measured at the ball. If the ball rotates concentrically then the load on the pegs would be as expected. However

any eccentricity would cause a sideways component of the load on the pegs. The pegs would then be subjected to a greater load. With a large eccentricity (about 0.26 mm) this added component could precipitate scuffing. To overcome this the ball chuck was marked for repeatable assembly and then the drive system to which it was attached was shimmed to attain minimum run out at the ball. It was found that a run out of less than 0.08 mm was repeatably attainable.

4.4 EFFECT OF THE PURITY OF HEXADECANE ON LOAD CARRYING CAPACITY

4.4.1 Introduction

It is now becoming acknowledged that many tribochemical reactions may not be due directly to an additive, but to impurities in the additive. Most technical grade chemicals are about 85% pure; many are almost equimolar mixtures of two or more substances. 'Analar' grade materials are usually better than 99.9% pure. When dealing with surface chemistry very small quantities of materials can have a profound effect on the chemical nature of a surface. The concentrations envisaged are of the order of 10^{-3} mole per cent. If friction values and scuffing loads are dependent on the chemical nature of the surfaces involved, it would be expected that friction and scuffing load would be very sensitive to the purity of a lubricant.

4.4.2 Procedure

Two load carrying capacity determinations were conducted at a sliding speed of 1.09 ms^{-1} using ionic bombardment cleaning for the balls and pegs, and abrasion and ultrasonic cleaning for the chuck, peg carrier and lubricant retaining ring. The applied load was increased in increments of 2.7 kg until scuffing occurred. In one run hexadecane had been allowed to stand over activated silica gel/alumina

until there was no detectable smell, but was otherwise unpurified. In the other the hexadecane had been subjected to the full purification sequence of standing over activated silica gel/alumina, filtering crystals from the mother liquor at its melting point three times and recrystallising these crystals from acetone. The tests were duplicated, alternately using 'unpurified' and purified hexadecane.

4.4.3 Results and Discussion

The results were quite repeatable. The purified lubricant had a scuffing load of 21 kg. The unpurified material gave a scuffing load of 69 kg (top ball). This shows that the load bearing capacity of 'unpurified' puriss hexadecane is some three and a half times that of the carefully purified material. The effect of purity was also shown by the value of the coefficient of friction recorded during the runs. These are shown in table 4.2.

Considering the highly purified material first; it would be

Top ball load (kg)	Fully purified hexadecane		Partially purified hexadecane	
	μ	T ^{o}C	μ	T ^{o}C
6.8	0.088	20	0.088	20
13.8	0.088	24	0.044	24
20.6	0.088	32	0.043	28

Table 4.2 Comparison of the coefficient of friction, μ, using fully purified and partially purified hexadecane at a sliding speed of 1.09 ms^{-1}.

expected that increasing the load would cause an increase in friction because more of the load would be carried by boundary contact and less by the hydrodynamic component. This was not observed here, but the loads are quite small and only vary by a factor of three. The coefficient of friction did not vary with time at a given load.

When using the unpurified hexadecane the friction coefficient decreased with increasing load. This indicates that there are substances present which react with the surface. If it is assumed that the reaction of these impurities with the surface is time dependent, the coefficient of friction would decrease with increasing time at a given load. This was found to be the case. μ was the same at the beginning of running at the lowest load for both the purified and unpurified hexadecane, its value only dropping after some sliding had occurred. This suggests that sliding is necessary for the impurities to affect the surface.

4.5 EFFECT OF SLIDING SPEED ON LOAD CARRYING CAPACITY

4.5.1 Introduction

A sliding speed of about 0.4 ms^{-1} seemed from previous investigations to be suitable for the production of polymeric materials (table 3.1). The triplane rig could be readily geared to give a rotational rate of 610 revs min^{-1} which gives a mean sliding speed of 0.43 ms^{-1}. This was the speed used for the surface analytical investigations. However a higher speed 1540 revs min^{-1}, corresponding to a sliding speed of 1.09 ms^{-1}, was tried to see if changing the speed had any effect on the scuffing load or friction.

4.5.2 Results and Discussion

The results obtained are summarised in table 4.3.

Top ball load (kg)	Sliding speed			
	0.43 ms^{-1}		1.09 ms^{-1}	
	μ	T °C	μ	T °C
7	0.088	20	0.088	20
14	0.09	25	0.088	24
21	0.115*	35	0.088	32
28	0.132*	45		
34	0.14 *	55		
41	0.146*	70		
48	0.15 *	76		
55	0.153*	100		
62	0.156	111		
69	0.158	125		
76	0.16	140		
83	0.16	150		

Table 4.3 Comparison of coefficients of friction at two sliding speeds using hexadecane. *denotes minor scuffing which recovered during running.

Sliding speed has a very marked effect on the load at which scuffing occurs. At the higher sliding speed the load carrying capacity has been much reduced - from 83 kg to 21 kg.

The values of the coefficient of friction for the two speeds overlap over such a small number of loads that it is impossible to draw any definite conclusions. It was shown in the previous section that

unpurified hexadecane gave a much higher scuffing load than purified hexadecane. Therefore using unpurified hexadecane would give a larger number of comparable figures, but it was also shown that the coefficient of friction was lower for the unpurified than for the purified material. Thus the use of the impure alkane would yield no meaningful data. It could be tentatively agreed that the higher speed gave a lower value of friction. This could be explained by assuming that there is a much greater hydrodynamic component in the lubrication régime at the higher sliding speeds. The frictional force would then be due more to the viscosity of the hydrocarbon than to actual metal-metal contact. There is a considerable hydrodynamic component at both sliding speeds. This is shown by the difference in the coefficient of friction with a load of 32 kg at sliding speeds of 0.43 ms^{-1} and 9.4 10^{-5} ms^{-1}. The latter is an almost pure boundary regime. The respective values are 0.14 and 0.8, both being measured at ambient temperature and using purified hexadecane as lubricant. Similarly, the increase in friction with increasing load can be explained by proportionately less of the load being taken by the lubricant film and more by boundary contact. This is confirmed by the greater surface damage of the ball when higher loads were used.

4.6 EFFECT OF OXYGEN CONTENT ON SCUFFING LOAD

4.6.1 Introduction

It has been shown that molecular oxygen acts as an extreme pressure agent. Since most liquids contain dissolved oxygen it was considered necessary to determine whether or not this oxygen had an effect on the behaviour of hexadecane as a lubricant. Friction and the load at which scuffing occurs are both sensitive to impurities. Three tests were conducted using purified hexadecane in its 'normal' state,

enriched with oxygen and depleted in oxygen.

4.6.2 Method.

Load bearing capacity tests were conducted as before, at ambient temperature with a sliding speed of 1.09 ms^{-1}, and using top ball load increments of 2.7 kg (6 lbs). The lubricant was hexadecane purified by the standard method. In the first test the alkane was used directly from storage over an activated silica gel/alumina mixture. This is the hydrocarbon in its 'normal' state of oxygen content.

To increase the oxygen content the triplane rig was set up as previously described, but using the peg carrier fitted with the alternative plug through which gas can be introduced into the lubricant. Immediately before the drive motor was switched on, air was passed through the lubricant. Air was passed throughout the duration of the test. The bubbling of air was commenced only immediately before the test was begun so that no appreciable oxidation of the hydrocarbon would occur. This ensures that the observed results were not due to hexadecane oxidation products, but to either gases dissolved in the alkane or possibly substances produced during the sliding process.

Ideally, completely oxygen free hexadecane should be used for comparison. It is impossible to attain this state without using an ultra high vacuum. Vacuum techniques are impossible with the triplane apparatus, so a compromise was struck in that as low a lubricant oxygen concentration as possible was obtained, then efforts were made to prevent subsequent solution of oxygen. This was achieved by outgassing purified hexadecane in a vacuum chamber. The chamber was filled with nitrogen (white spot quality), and, whilst still in the chamber, nitrogen was bubbled through the liquid via a sintered gas diffuser. The lubricant was again outgassed and the procedure repeated. The 'low oxygen' hydrocarbon was carefully transfered to the assembled ball

chuck/peg carrier via a siphon tube to reduce contact with the atmosphere. Nitrogen was constantly bubbled through the fluid in the peg carrier. The drive motor was started and the load increased stepwise as before.

4.6.3 Results and Discussion

In all three tests scuffing occurred at a top ball load of 21 kg (45 lbs). The friction values were also the same (table 4.3).

In the first test hexadecane was used without passing any gases through it. The oxygen content of this lubricant was unknown, but since it was stored over silica gel and alumina and under nitrogen, it probably contained slightly less oxygen than if it had stood in the atmosphere. Passing air through the alkane would ensure a saturated solution of oxygen, but again its concentration was unknown and not determined. The third test used hexadecane with very little oxygen dissolved in it. The amount of oxygen was determined by the quality of the nitrogen passed through it. The nitrogen used was 'white spot' quality 'oxygen free' nitrogen. Although called 'oxygen free' the suppliers, The British Oxygen Company, state the oxygen content as approximately 6ppm. It is clear, therefore, that the lubricant used in each test contains oxygen, but its concentration was different.

One of two conclusions can be drawn from the results obtained. Either changing the oxygen content of a pure lubricant has no effect on its lubricating behaviour, or, the amount of oxygen required to react in some way, either with the lubricant or the metal surface, is very small, and in this experiment this critical concentration was always exceeded. Which of these two possible explanations is the correct one can only be determined by using a friction machine mounted in an oxygen free vacuum chamber and using vapour phase lubrication, or alternatively using liquid lubrication in a closed system with an inert atmosphere

such as one of the noble gases. This type of apparatus was unavailable, so confirmation was impossible. However the results of the investigation into the effect of purity on lubricating behaviour showed that very low concentrations of impurities have a marked effect. It is thus very likely that the second explanation of not attaining a low enough oxygen concentration is the correct one.

4.7 EFFECT OF DIFFERENT METALLURGY ON SCUFFING LOADS

4.7.1 Introduction

The ball and peg material used in this study was EN31. This is a standard bearing steel. However a limited number of chilled EN39 B balls and chilled and unchilled EN39 B pegs were available. The specification of EN39 B, a gear steel, is given in table 4.4.

4.7.2 Procedure

The scuffing load was determined in the normal way but using a load increment of 2.75 kg. The lubricant used was purified hexadecane and a chilled ball was rubbed against both chilled and unchilled pegs with a sliding speed of 1.09 ms^{-1}.

4.7.3 Results and Discussion

The first combination of ball and pegs examined was a chilled ball

	C	Si	Mn	S	P	Ni	Cr	Mo
min.	0.12	0.10	--	---	---	3.8	1.0	0.15
max.	0.18	0.35	0.50	0.050	0.050	4.5	1.4	0.35

Table 4.4 Percentage composition of EN39 B steel. Balance is iron.

and chilled pegs. This combination proved quite difficult to lubricate, mild scuffing, which recovered, occurring at loads as low as 6.9 kg. Complete failure occurred at loads above 13.8 kg.

The second combination was chilled ball and unchilled pegs. This system supported a similar load before similar scuffing occurred. The minor scuffing which occurred during the run suggested that this system was slightly more difficult to lubricate than that using similar metallurgies. The friction in the contact was not measureably different from that using both chilled ball and pegs.

EN39 B would be expected to be more difficult to lubricate than EN31 because it is a nickel steel rather than a chrome steel. It has been shown[78] that similar metals sliding against each other are easier to lubricate than dissimilar metals sliding together. This would explain the difference in the nature of the minor scuffing occurring during sliding. The surface structures of unchilled and chilled EN39 B are different owing to the different heat treatments received.

4.8 ANALYSIS OF WEAR DEBRIS

4.8.1 Introduction

During runs at sliding speeds of 1.09 ms^{-1} using very pure hexadecane as the lubricant a brown material was observed to form on each side of the wear tracks produced on the ball. In order to discover more about this material an extended test was conducted, the idea being to produce as much as possible, since the more one has, the easier it is to analyse.

4.8.2 Method

The sliding speed chosen was 1.09 ms^{-1}, using an EN31 ball and pegs and purified hexadecane at room temperature. The load on the top

of the ball was 8.3 kg. This load was chosen as being the maximum permissible before scuffing caused problems of gross metal tearing. If this were to occur the debris would contain a good deal of steel which would complicate the analysis of inorganic matter. The duration of the test was one hour.

The debris was readily removed from the surface by wiping with a tissue. It was insoluble in toluene, acetone, ethanol, carbon tetrachloride and dichloromethane. Toluene and acetone were used to wash the debris. It was fairly readily soluble in warm dilute hydrochloric acid. This information suggested that in all probability the debris was not organic but inorganic in nature. The only two possibilities of inorganic compounds are the metal itself or oxides of the metal. Iron oxides have a characteristic X-ray powder pattern. X-ray analysis of the wear debris was therefore attempted.

4.8.3 X-Ray Analysis of Wear Debris

Procedure. The wear debris obtained as described in the previous section was carefully washed in toluene and acetone to remove any residual hexadecane. The powder remaining was dried in vacuo and transfered to an X-ray powder analysis frame for transmission powder analysis. The frame is a metal plate with apertures called windows (fig. 4.2). The powder is held in the windows by first attaching

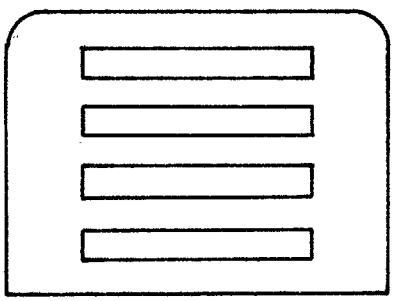


Fig. 4.2 X-ray powder analysis frame.

'Sellotape' to the reverse side of the frame, then sprinkling powder onto the sticky tape, and finally sealing the window with another piece of 'Sellotape' on the face side. This ensures that the whole window contains sample. The frame contains four windows. One is normally left empty but covered with 'Sellotape'. 'Sellotape' has a crystal structure so it produces a powder pattern which is superimposed on that produced by a sample. The blank makes designation of the source of the pattern easier. In this instance an authentic sample of iron (III) oxide was used in one of the windows. It was produced chemically from iron (II) sulphate by precipitation of the carbonate which is readily oxidised to red iron (III) carbonate, which, on heating, decomposes to give pure iron (III) oxide. Complete conversion from carbonate to oxide was confirmed by the lack of effervescence with dilute hydrochloric acid.

Results and discussion. Examination of the developed film showed that the prepared iron (III) oxide was authentic. The wear debris gave no pattern, indicating that it was amorphous, i.e. it consisted of crystals with two few atoms to cause any appreciable diffraction.

4.8.4 Wet Chemical Analysis of Wear Debris

Introduction. Only a very small sample, of the order of milligrams, was available, therefore titrimetric analysis was prefered to gravimetric. The ideal situation would be to be able to analyse for iron selectively. Iron (III) oxide contains 69.94% iron, so if the analysis showed this proportion of iron, it would be reasonable to assume that the debris was in fact iron (III) oxide. (The chances of another compound or a mixture of compounds having this composition of iron is very small.)

The method used was as described by Welcher[79]. Ethylenediaminetetraacetic acid (EDTA) forms a yellow complex with iron (III) ions.

Iron forms a violet complex with salicylic acid at pH 2 - 4. The strength of this complex is less than that of the EDTA complex, so addition of EDTA to the salicylic acid complex causes a colour change from violet to yellow.

Procedure. Wear debris was collected from balls from several different runs. It was washed in toluene and acetone and dried in vacuo. A weighed quantity was dissolved in dilute hydrochloric acid. Sodium acetate was added to obtain pH~3. At this pH the analysis is selective to iron. Using more basic conditions the analysis becomes less selective. An aliquot was titrated with EDTA using salicylic acid as indicator to a violet to almost colourless end point. The rather pale final colour was due to the very small quantity of iron present.

Results. The results of several determinations showed that the amount of iron in the initial sample was between 67% and 73%. Considering the small quantities involved, and the subsequently large errors, this is in good agreement with the 69.9% for pure iron (III) oxide. However iron (II) di-iron (III) oxide (Fe_3O_4) contains 72.4% iron, so it is conceivable that the debris could be Fe_3O_4. This oxide is magnetic, the wear debris was not. It can therefore be concluded that the wear debris was iron (III) oxide.

4.9 ELECTRON PROBE MICROANALYSIS OF WEAR TRACKS

4.9.1 Introduction

Having established that the wear debris was iron (III) oxide, electron probe microanalysis was used to determine whether the surface of a wear track contained more iron oxide than the non worn areas of a ball. If this were so it may be that the wear debris was produced as iron oxide on the surface which is then rubbed off, rather than as abraded iron which oxidises outside the contact area.

4.9.2 Method

A ball was obtained using conditions identical to those described at the beginning of this section with purified hexadecane as the lubricant. The ball was washed using analar toluene followed by analar acetone. Loose wear debris was removed using a soft tissue rather than chemically. The ball was sectioned on an elastic wheel and a section containing a wear track was subjected to probe analysis. The wear track was compared to the non worn areas as standards.

4.9.3 Results and Discussion

No sulphur or carbon were present. A scan for chromium showed its concentration to be variable, but on average it was about the same both inside and outside the wear track. A line scan for iron showed a decrease in iron content over the worn areas as compared to the unworn areas. A similar line scan for oxygen showed its concentration to be higher in the wear track than outside. The concentration also varied across the track, being higher at the edges than in the centre.

These variations were not quantified, but if the oxygen concentration is taken as a measure of the amount of iron oxide present, there is more oxide at the edges of the wear track than in the centre. This could be explained by assuming a greater accessibility of disolved oxygen to the periphery of the contact. This would lead to an increase in the amount of oxide just behind the contact as compared to the contact point itself. During the next cycle the greater pressure at the centre of the contact might push the newly formed oxide to the edges of the wear track where it would remain. The thickness of the oxide layer at the edges of the track would then be greater than along the centre.

It might be argued that Fe_3O_4 is present in the centre of the wear track whilst Fe_2O_3 is present at the edges. Fe_3O_4 is normally

produced at high temperatures whilst Fe_2O_3 is the main product at lower temperatures. The conditions of sliding used to produce the wear debris for this examination would be expected to be very similar across the whole width of a wear track, thus only Fe_2O_3 would be expected, or possibly a more or less homogeneous mixture of Fe_2O_3 and Fe_3O_4, the former predominating. The difference in oxygen content between these two oxides is about 2.5%. The probe showed the change of oxygen concentration to be much greater than this. It must therefore be the thickness of the oxide which is the significant variable, and not its composition.

4.10 REMOVAL OF FILMS FROM SURFACES OF BALLS AND PEGS

4.10.1 Introduction

Since it was found impossible to satisfactorily examine the ball surface directly for organic materials, the possibility of removing any polymeric film which had formed by dissolving it off in a soxhlet was considered. In selecting a suitable solvent due regard was paid to its ability to dissolve high molecular weight substances which might or might not contain polar groups. It also needed to be fairly inert so that it would not effect the materials it dissolved. It had also to be easy to handle. Ease of handling here implied a liquid which is not very volatile, i.e. one having a boiling point approaching 100°C. However the higher the boiling point, the hotter the mixture has to be heated to remove the solvent. This carries with it a greater liklihood of chemical reactions occurring. Evaluation of several solvents including pentane (b.p. 36.3°C), acetone (b.p. 56.2°C), trichloromethane (b.p. 61.2°C), hexane (b.p. 68.7°C), ethanol (b.p. 78.5°C), and toluene (b.p. 111°C) led to the selection of dichloromethane (b.p. 40.2°C) as being suitable. Dichloromethane fulfils all the above

conditions and is also readily available in various purities. It is commonly used for the extraction of spots from TLC plates in preparation for injection into a GLC instrument[80].

4.10.2 Procedure

An EN31 ball was rubbed against three EN31 pegs at a sliding speed of 0.43 ms^{-1} using purified hexadecane as the lubricant for two hours at a constant load of 41.3 kg. Running in was achieved by increasing the load in units of 6.9 kg at one minute intervals. The experiment was started at ambient temperature, the only heating being frictional heating which caused the temperature to rise to about 125°C.

The ball and pegs were taken hot from the ball chuck and peg carrier after running and immediately put into an extraction thimble in a soxhlet containing dichloromethane. In this way the surfaces of the ball and pegs were always covered by a layer of hexadecane solution, and not exposed directly to the air. The soxhlet employed had a capacity of six balls, so six runs were conducted and all the balls and pegs put in the same soxhlet. This should have the effect of giving a more concentrated end product. This was important since only very small quantities of materials were expected to be formed on the surfaces. Soxhletting was continued for a minimum of twenty four hours. The resultant solution was vacuum distilled to remove the dichloromethane leaving only a few drops of liquid. This was analysed using mass spectrometry.

As a check on the extraction procedure, 'blank' experiments were conducted. To determine whether there were any impurities in the dichloromethane, two litres were reduced in volume to concentrate impurities, and the resultant liquid was subjected to mass spectrographic analysis. No impurities were detectable. Complete evaporation left no residues. By refluxing dichloromethane and purified hexadecane

together for twenty four hours, removing the dichloromethane and examining the product, it was shown that there was no chemical reaction taking place. There was similarly no chemical reaction when either EN31 steel or a thimble or both were present. It was therefore concluded that any products come only from the metal surfaces, or from the small amount of lubricant transfered with the balls and pegs.

4.10.3 Results

The mass spectrum for the extracted material was found to have no significant differences from that of the pure hexadecane (fig. 4.1). The mass spectrum of a sample of the used lubricant was also obtained. This too showed no differences from the pure hexadecane.

It was concluded therefore that there were no chemical reactions occurring such that the lubricant was changed. During the two hour running period the coefficient of friction did not alter. This further suggests that no chemical reactions were occurring after the initial running in.

4.11 ANALYSIS OF IRON IN A DICHLOROMETHANE EXTRACT

4.11.1 Introduction

A sample of the dichloromethane extract was examined for its iron content. Because of the smallness of the sample X ray fluorescence (XRF) could not be used. (XRF needs about 20 cm^3.) Therefore atomic emission spectrometry was employed.

4.11.2 Procedure

The sample was washed into a tared platinum crucible using analar benzene. The benzene was evaporated off on a water bath until the crucible and contents reached constant weight. The sample was redissolved in a minimum quantity of analar benzene and Ringsdorf

graphite added to the crucible to absorb the sample solution. The benzene was evaporated and the graphite packed into a graphite electrode cup. An arc was struck between the graphite containing the sample and a second electrode. The resultant spectrum was examined quantitatively.

4.11.3 Results

The concentration of iron was found to be 20±5 ppm. This was probably wear debris transfered with the small amount of lubricant adhering to the surfaces of the balls and pegs.

4.12 EFFECT OF SLIDING SPEED ON DICHLOROMETHANE EXTRACT

4.12.1 Procedure

A similar series of experiments was conducted to determine whether or not operating under conditions where a greater hydrodynamic component and a lesser boundary component were present had any effect on the nature of the dichloromethane extract. The experimental procedure was exactly as described in the previous section except that the sliding speed was 1.09 ms^{-1} and the top ball load was 14 kg. (Running in consisted of operation at a load of 6.9 kg for one minute after which the load was increased to 14 kg.)

4.12.2 Results and Discussion

No detectable differences between the mass spectra of the extracted material, used lubricant and purified hexadecane were observed. It was therefore concluded that no chemical reactions involving the hexadecane had occurred. As further evidence for this, the coefficient of friction did not decrease during the running period. These results are not directly comparable with those from runs using a sliding speed of 0.43 ms^{-1} because the applied load is less. This was

necessary because pure hexadecane does not support a load of 41.3 kg at a sliding speed of 1.09 ms^{-1} whereas it does so at 0.43 ms^{-1}.

4.13 RUSTING OF BALLS AND PEGS AFTER SOXHLETTING IN DICHLOROMETHANE

4.13.1 Observations

If balls and pegs which had been refluxed in dichloromethane were allowed to stand undisturbed in the atmosphere, they were found to corrode within two or three days. The rust was examined in more detail using an optical microscope.

Pegs. The ends of the pegs were generally rusty, the rust appearing as a background of red-tan coloured oxide, very fine in texture. There were also 'trees' of oxide growing randomly over the surface. In all cases, however, the wear spot appeared black with darker lines running across it in a single direction. This was assumed to have been the direction of sliding. Little or no fine rust covered the wear spot, but there were 'trees' of oxide growing on it. These were orientated in straight lines parallel to the dark lines.

Balls. The appearance of the balls was very similar to that of the pegs. The wear tracks had little or no fine rust on them, but where it was present it occurred in lines running round the ball in the direction of sliding. Small 'trees' of rust grew over the ball's surface, but their population was much less on the wear tracks than on the unworn part of the ball. Where these growths occurred on a wear track they were orientated in lines along the wear track.

4.13.2 Discussion

The difference in rust formation over the different areas was probably due to the strains set up in the material during running. The areas which had been strained could already have formed an oxide

coating, probably of Fe_3O_4. No further oxide would be expected to be formed on top of this. This straining effect is further demonstrated by the alignment of the red oxide 'tree' formation on the wear tracks. Strains would be set up in the material in the direction of sliding as the ball rotated against a peg, thus the oxide would be expected to occur in circumferential lines. This was found to be the case.

4.14 EXAMINATION OF USED HEXADECANE

4.14.1 Infra Red Spectroscopy

A sample of hexadecane which had been used as the lubricant in an extended duration test at a sliding speed of 0.43 ms^{-1} with a top ball load of 41.3 kg was examined using infra red spectroscopy. The spectrum obtained was compared to that produced by purified hexadecane. The spectra were found to be identical.

This indicated that no new functional groups had been produced by any tribochemical processes. Interpretation of the spectra showed that the only groups present were those which would be expected from a straight chain alkane.

4.14.2 Iron Analysis

A similar sample of used hexadecane was examined for iron using X ray fluorescence (XRF). The concentration was found to be less than 15 ppm. This is at the limit of detectability of iron using XRF so no great significance should be attached to this figure. (Purified hexadecane gave a similar result.)

The porous cup method for emission spectroscopy is more sensitive. This method gave a concentration of 20 ppm. This figure is the same as that determined from the dichloromethane extract. This confirms that the iron content of the extract emanated from the small amount of used

lubricant transfered on the surfaces of the balls and pegs.

4.15 CONCLUSIONS

1. Hexadecane was to be used as the base stock for all subsequent tests. As received it contained impurities which were detectable by smell. A technique of purification was developed which involved standing the hexadecane over an activated silica gel/alumina mixture, filtering the crystals from the mother liquor at its melting point, and storing over fresh activated silica gel/alumina. The only detectable impurities in the product were traces of C_8 and C_{13} alkanes.

2. Friction and load bearing capacity tests were carried out using the lubrication laboratory ball on triplane apparatus. Care was taken in the cleaning of the ball, rollers and all parts which come into contact with the lubricant. Ionic bombardment, being the most effective method of obtaining a molecularly clean surface, was chosen for the ball and pegs, whilst ultrasonic cleaning in toluene followed by acetone was selected for the chuck and peg carrier assembly.

3. The load bearing capacity of hexadecane was determined. It was found to decrease with increasing sliding speed, but increase if the hexadecane were not carefully purified. The coefficient of friction at a given load was constant for the purified hydrocarbon, whereas the impure material gave a decreasing value of μ. Reduction of the oxygen content of the lubricant had no effect on the load bearing capacity; however it was probable that the oxygen concentrations were much greater than the critical concentration at which the lubrication processes change.

4. X-ray powder analysis of wear debris showed it to be amorphous, but wet chemical analysis using EDTA indicated that it consisted of Fe_2O_3.

5. Electron probe microanalysis of the wear tracks on the balls showed no sulphur and little or no carbon. There was an increase in the oxygen concentration and a decrease in the iron concentration confirming the presence of iron oxide.

6. Soxhletting of the ball and rollers using dichloromethane followed by mass spectrographic analysis of the extract showed there was no organic material present on the surfaces. This was verified by electron probe microanalysis. A very small amount of iron (about 20 ppm) was found in the extract. This almost certainly emanated from the small amount of used lubricant transfered to the soxhlet on the surfaces of the balls and rollers. The used lubricant contained a similar concentration.

7. Mass spectroscopy and infra red spectroscopy proved that there was no decomposition of the bulk lubricant.

It can be concluded that iron oxides are formed on the surfaces of the balls and rollers, but that purified hexadecane does not itself take part in any chemical reactions during sliding. It can therefore be used as a base stock in future friction experiments with no problems of its contributing to the effects of any additives.

CHAPTER 5

1-HEXADECENE

5.1 INTRODUCTION

1-Hexadecene is an unsaturated hydrocarbon of semi-structural formula $C_{14}H_{29}CH=CH_2$. Compounds containing terminal double bonds are known for their formation of dimers and polymers, viz. ethene which gives polyethene.

The dimerisation of alkenes takes place in the presence of concentrated sulphuric acid and proceeds via a carbonium ion. Alkylation is also acid catalysed with a carbonium ion intermediate. Both these reactions produce higher molecular weight products, but neither would be expected to take place in a lubrication system, since suitably concentrated acid should not be present.

Polymerisation is a free radical reaction requiring an initiator. This is often a peroxide (i.e. a compound containing the -O-O- linkage). Peroxides are found as impurities an many compounds as a result of reaction with atmospheric oxygen. It would therefore be expected that when hexadecene is used as a lubricant in the presence of oxygen polymerisation would occur. However free radical reactions are often chain reactions. The rate of a chain reaction is very much reduced by the presence of chain terminators, or altered by chain transfer agents. An effective chain terminator is molecular oxygen. It reacts with a radical R• to give R-O-O•, which is generally much less reactive than R•. The reaction is thus slowed down, or, if sufficient oxygen is

present, stopped completely.

In this work the reactions of pure hexadecene, rather than of peroxides, in a lubrication system were of interest. Care was taken to remove any peroxides, radicals or other compounds which may have already formed via peroxide impurities. It has previously been shown for hexadecane that it is impossible to remove all oxygen from a liquid, so some peroxides may be produced during running. The relatively high concentration of molecular oxygen should effectively stop any free radical chain reactions occurring in the bulk lubricant.

5.2 PURIFICATION OF 1-HEXADECENE

1-Hexadecene is a colourless mobile liquid manufactured by the vapour phase dehydrogenation of the alcohol hexadecan-1-ol. It was supplied as puriss grade by Messrs. Koch Light Laboratories Ltd. The supplier's analysis of the particular batch used is shown in table 5.1.

This material could have been purified using a chemical technique. An example of this would be reacting the alkene with bromine. This gives the dibromide. The 1,2-dibromide could be separated from the

α-olefin	95%
C_{16} olefin	98%
Main impurity	~3% non α-olefin, also <1% non C_{16} α-olefin
GLC analysis	Two peaks; one >99%, one <1%
Infra-red spectrum	Comparable with reference

Table 5.1 The supplier's analysis of 1-hexadecene.

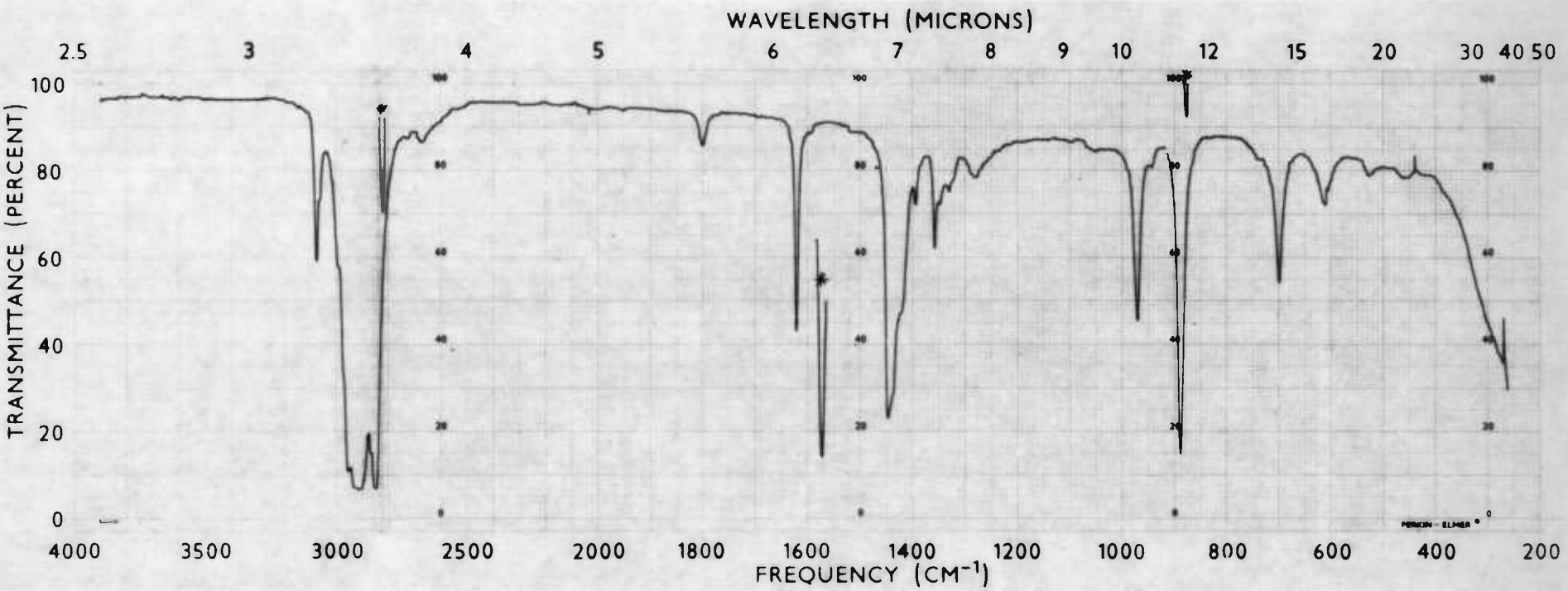


Fig. 5.1 The infra red spectrum of 1-hexadecene.

non 1,2-dibromides and the double bond regenerated by reaction with zinc. However, since the infra-red spectrum (fig. 5.1) showed no peaks from functional groups other than those expected for an α-olefin, and gas liquid chromatography showed that at least 99% of the material was 1-hexadecene, a physical method of purification was adopted.

Addition across the double bond is the most likely reaction to occur. It was thus considered expedient to remove any materials which might add on, then remove the products of any such reactions which might have already occurred. To this end 1-hexadecene was stood in a nitrogen atmosphere over an activated alumina-silica gel mixture for one week. It was then fractionally distilled at reduced pressure under nitrogen. The middle cut was collected. This was allowed to stand over a freshly activated alumina-silica gel mixture. No sample was used more than four weeks after distillation.

Table 5.2 shows the physical properties of hexadecene, both as supplied and after purification.

The mass spectrum of a sample (fig. 5.2) shows that there are no substances present with a molecular weight greater than that of

Property	As supplied	After Purification	Literature[74]
Refractive index	n_D^{22} 1.4377	n_D^{20} 1.4418	n_D^{20} 1.4410 n_D^{25} 1.43907
Boiling Point	274/760 mm	120-2/3 mm	284-7/760 mm 157.5/15 mm 152-4/13 mm
Melting Point	---	---	2.2 °C.

Table 5.2 The properties of 1-hexadecene before and after purification.

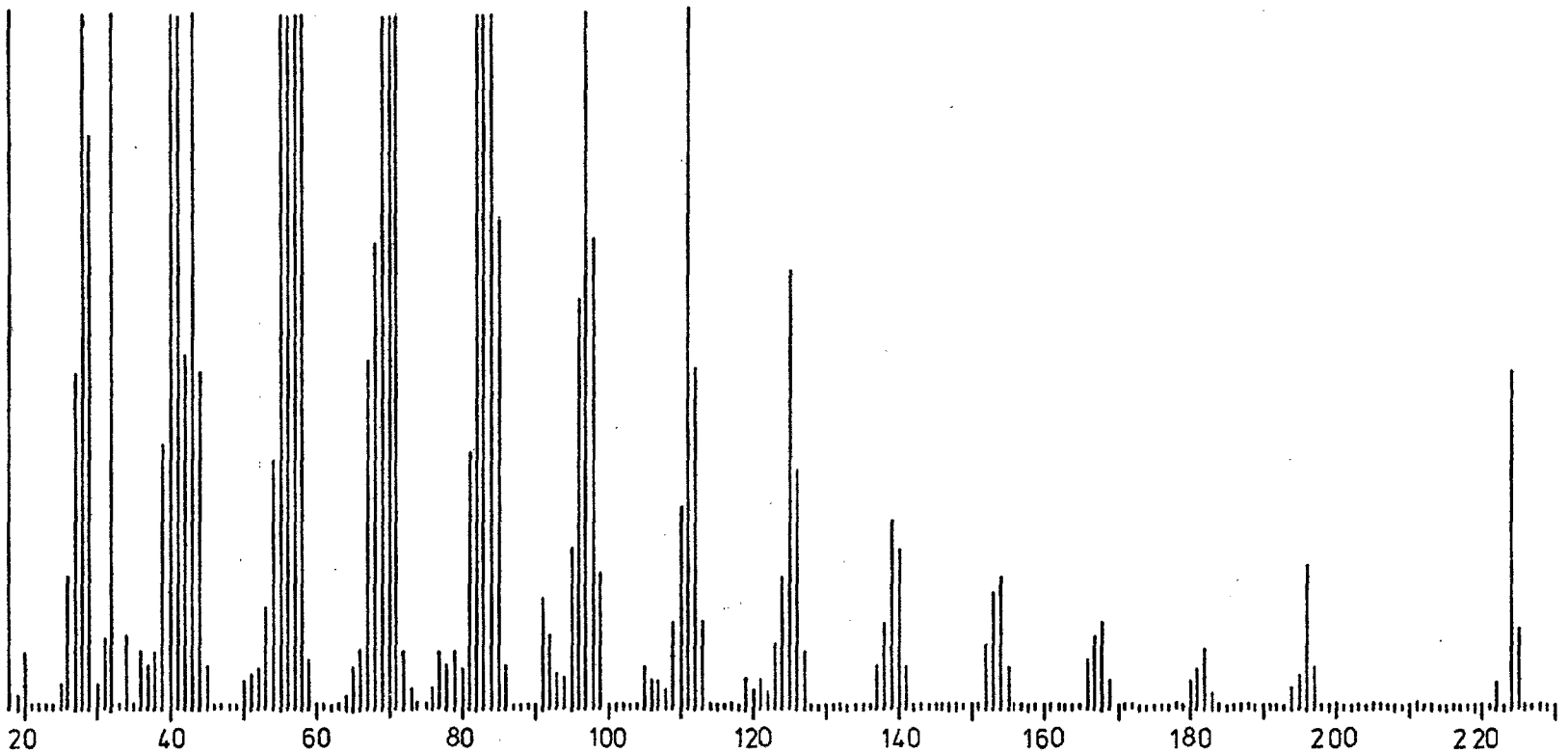


Fig. 5.2 The mass spectrum of purified 1-hexadecene.

hexadecene (224), neither are there any peaks other than those which would be expected from the specification of the material.

5.3 DETERMINATION OF THE LOAD CARRYING CAPACITY

5.3.1 Experimental Details

The load carrying capacity was determined in the same manner as for hexadecane. As with the alkane two sliding speeds were employed, 0.43 ms^{-1} and 1.09 ms^{-1}, to study the effect of speed. Three lubricant compositions were tested at each sliding speed. They were;

(a) neat purified hexadecene,

(b) a one per cent solution of hexadecene in hexadecane and

(c) a two per cent solution of hexadecene in hexadecane.

Friction and temperature were monitored throughout a test.

Concentration of 1-hexadecene	Load carrying capacity (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
100%	103	55
1%	96	34
2%	96	34

Table 5.3 The load carrying capacities of purified 1-hexadecene and one and two per cent solutions of 1-hexadecene in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

5.3.2 Results and Discussion

The results are summarised in table 5.3.

The Effect of Speed. Failure occurred much sooner at the higher sliding speed than at the lower speed. This was observed for both solutions of hexadecene in hexadecane and for the purified alkene used alone. This is a well known phenomenon. Although at higher speeds a thicker hydrodynamic film is built up, any asperity contacts will be much more severe. The heat generated, being very localised, probably causes desorption of adsorbed films, and may even result in the removal of protective layers chemisorbed on the surface. Metal to metal contact occurs and scuffing takes place.

It was noted that hexadecane and 1-hexadecene qualitatively showed the same trend in the effect of speed on failure load. The effect was much less marked for the alkene as shown in the table below. The difference was probably due to the chemical natures of the two substances. The alkane would be less likely to adsorb onto a metal

Lubricant	Load carrying capacity (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
Hexadecane	83	21
1-Hexadecene	103	55

Table 5.4 A comparison of the load carrying capacities of hexadecane and 1-hexadecene at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

surface because a dipole would have to be induced, whereas the alkene already possesses a dipole because of the presence of the terminal double bond. This is electron rich so it would readily attach itself to a metal surface, a surface which is normally regarded as effectively being positive. A sorbed film of the alkene would offer slightly more resistance to metal-to-metal contact than the weakly sorbed alkane molecules, thus being able to support a greater load. The resistive effect of the sorbed molecules would be expected to be more pronounced at higher speeds where this film may cause a thicker hydrodynamic film to be formed, or it might even behave in a similar manner to 'extreme-pressure' additives.

The Effect of Solution Concentration. Two concentrations of 1-hexadecene in hexadecane were tested. They were one per cent and two per cent solutions. Both gave the same load carrying capacity. This might indicate that concentration has no effect. The failure load of these solutions was, however, considerably greater than that of purified hexadecane used on its own (tables 5.3 and 5.4). The presence of hexadecene in hexadecane must then have an effect, albeit not a very large one at the lower sliding speed. At 1.09 ms^{-1} the effect is much more marked, the alkene solutions supporting a load some sixty seven per cent greater than the pure alkane. As discussed in the previous section this is explicable by the preferential sorption of the polar hexadecene molecules onto the metal surface, thereby preventing metal-to-metal contact. This then leads one to suspect that the amount of alkene present has an effect. The minimum quantity required to increase the load carrying capacity of hexadecane was not disclosed by these experiments due to the relatively high concentrations used. It would nevertheless be quite a simple matter to make up more dilute solutions and determine their scuffing loads. Such solutions

containing a very small quantity of alkene (about 10^{-3} mole per cent) are particularly difficult to analyse chemically, and since this work was primarily concerned with chemical analysis these very dilute solutions were not investigated.

Pure 1-hexadecene itself has a higher scuffing load than its solutions in hexadecane. For pure alkene the limiting factor for the concentration of sorbed hexadecene molecules is probably a geometric one, whereas, if hexadecane is present, it also physisorbs onto the surface, thus reducing the number of surface sites available to the hexadecene. The closeness of the values of scuffing load for pure hexadecene and a one per cent solution in hexadecane shows the much greater surface activity of the alkene.

5.4 THE ANALYSIS OF USED HEXADECENE

5.4.1 Introduction

After use in the triplane apparatus the hexadecene had a cloudy yellow appearance. The cloudiness settled on standing showing that it was either insoluble wear debris or insoluble decomposition products.

5.4.2 Method

In order to ascertain whether or not the supernatant liquid contained any decomposition products, it was decanted and filtered to remove any remaining insoluble material, then its infra-red spectrum was compared to that of a sample of unused pure hexadecene.

To discover whether the insoluble material was organic or inorganic samples were separately shaken with acetone, ethanol, ether, dichloromethane and dilute hydrochloric acid.

5.4.3 Results and Discussion

The Supernatant Liquid. The infra-red spectra of unused purified

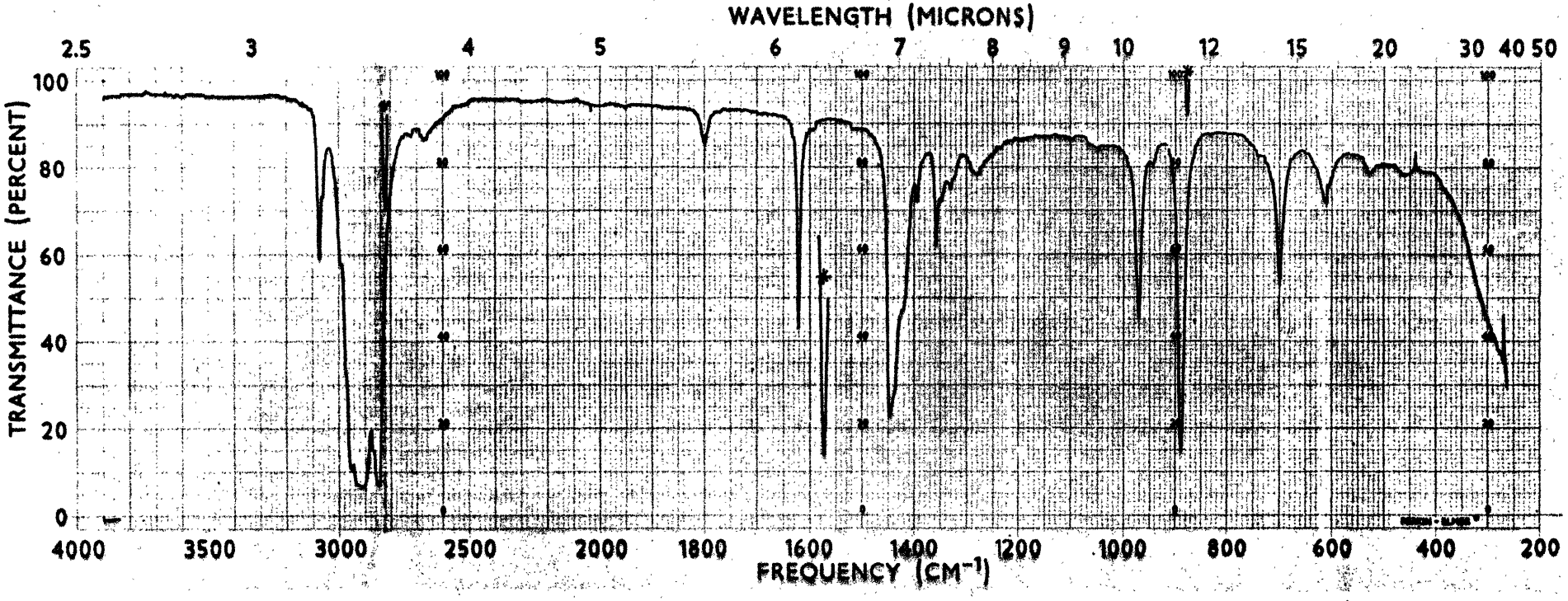


Fig. 5.3 The infra red spectrum of pure unused 1-hexadecene.

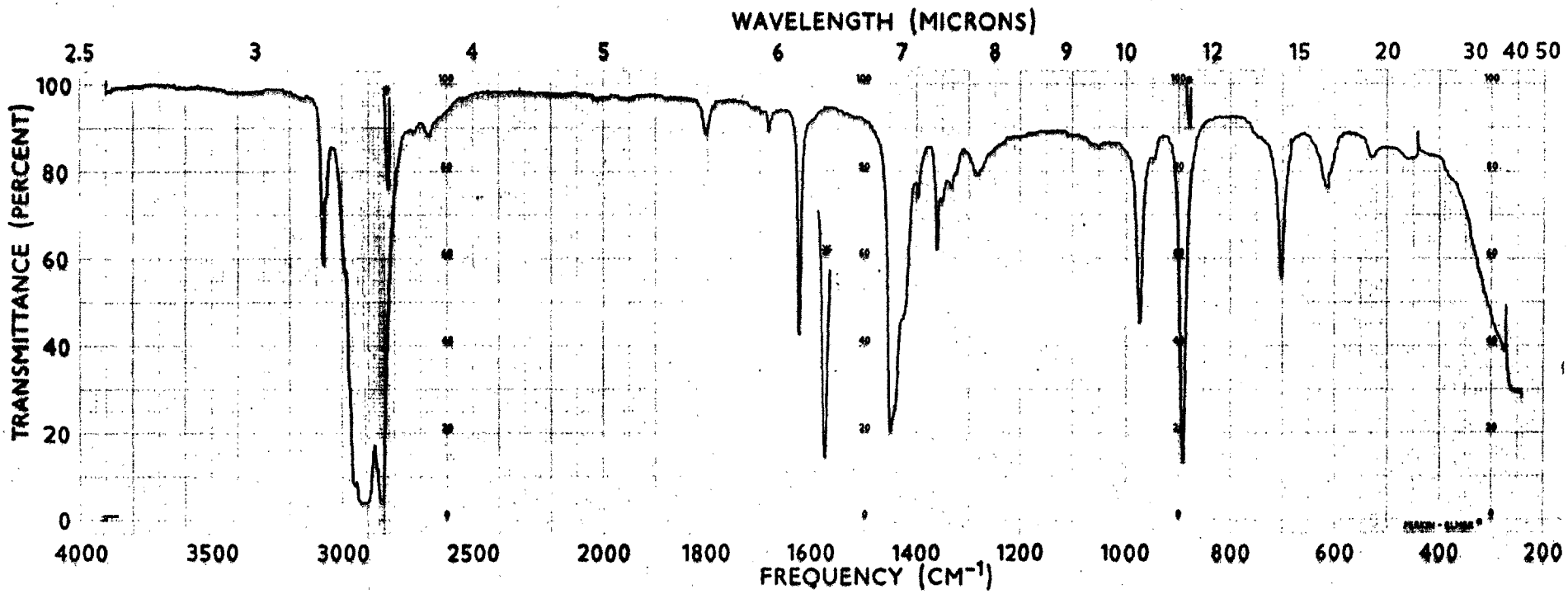


Fig. 5.4 The infra red spectrum of used 1-hexadecene.

hexadecene and of filtered used hexadecene are shown in figs. 5.3 and 5.4 respectively. The spectra are identical apart from a peak at 5.85 μm which is present in the used lubricant spectrum, but absent in the spectrum of the unused material. It may result from the presence of a small amount of either

(a) hexadecan-2-one, $C_{14}H_{29}C(=O)CH_3$,

(b) the aldehyde, $C_{15}H_{31}C(=O)H$ or

(c) the acid, $C_{15}H_{31}C(=O)OH$.

The infra-red data is not conclusive, but results from tests on used two per cent solutions of hexadecene suggest that it is the ketone which is responsible.

The used lubricant was not subjected to further analysis since it was not of prime interest.

The Precipitate. This was found to be insoluble in acetone, ether, ethanol and dichloromethane, but soluble in dilute hydrochloric acid. This suggests that it was inorganic in nature. Such a result was not unexpected since the surfaces of the ball and pegs were scored. Iron and chromium analyses were carried out to see if the ratio of iron to chromium was the same as in bulk EN31 (Fe:Cr approx. 97:1). The porous cup method was employed.

The ratio found was 4:3. This is a surprisingly high proportion of chromium if one assumed that the debris originated from bulk ball and peg material as a result of scoring. It has been reported that the composition of oxide layers on the surface of an alloy depends on the enthalpy of formation of each oxide [81]. The higher the enthalpy, the greater is the proportion of that oxide on the surface. Chromium

oxide has a higher enthalpy of formation than iron oxide (FeO -266 kJ $mole^{-1}$, Fe_2O_3 -822 kJ $mole^{-1}$, Cr_2O_3 -1128kJ $mole^{-1}$ [82]). Chromium would therefore be expected to be in a greater concentration at the surface than analysis of bulk EN31 would suggest. Mild abrasion of the surface would then result in chromium rich debris. Another factor may be involved in the increase of chromium at the surface; namely migration. It has been shown in this laboratory[83] that under conditions of sliding, alloying metals can migrate to the surface. This might occur under the conditions used here, resulting in a further increase in the availability of chromium at the surface.

Summarising, it appears that pure hexadecene, when used as a lubricant, undergoes some slight oxidation to form a ketone. An insoluble inorganic wear debris is produced which is richer in chromium than would be expected from the composition of the EN31 steel used.

No dichloromethane extraction studies were undertaken with pure hexadecene. There were two reasons for this.

(1) 1-Aminohexadecane, hexadecan-1-ol and hexadecanoic acid are solids, so they could not be used by themselves as lubricants at room temperature. Work involving these compounds was undertaken using their solutions in hexadecane. Information gleamed from the use of hexadecene alone would not be directly comparable with that obtained using these solution systems.

(2) The results of load bearing capacity determinations of solutions of hexadecene in hexadecane showed that the alkene is preferentially sorbed onto the metal surfaces. A solution of hexadecene would therefore be expected to give reasonably similar results to those obtained if the pure alkene were used by itself.

5.5 DICHLOROMETHANE EXTRACTION STUDIES

5.5.1 Introduction

A two per cent solution of 1-hexadecene in hexadecane was used. This concentration was chosen because the more alkene present the easier the chemical analysis. Both the one and two per cent solutions had the same load carrying capacity so would be expected to behave in a chemically similar manner.

If it is assumed that the extent of any reactions is proportional to time, from an analytical point of view the greater the duration of the test, the better. Bearing this in mind, the slower 0.43 ms^{-1} sliding speed was selected. This, together with a top ball load of 70% of the scuffing load, gave conditions, after running in, suitable for extended runs of the order of four hours.

5.5.2 Procedure

The peg carrier, lubricant retaining ring and ball chuck were cleaned in an ultrasonic cleaner, first using toluene as the solvent, then acetone. An EN31 ball and EN31 pegs were cleaned by the ionic bombardment method. They were assembled into the triplane apparatus together with a two mole per cent solution of purified 1-hexadecene in purified hexadecane as the lubricant. The sliding speed was set at 0.43 ms^{-1} and the top ball load increased from zero to 69 kg in increments of 6.9 kg. Each load was maintained for 30 seconds. Having attained an applied load of 69 kg, the apparatus was left to run for four hours. Both temperature and friction were monitored throughout. Constant watch was kept to ensure that the load remained steady, since any wear of the ball or pegs would cause a decrease in the load applied. The only heating was frictional heating, the test beginning at room temperature.

After four hours had elapsed the ball chuck and peg carrier assembly were removed from the triplane apparatus. The lubricant was transfered to a sample tube, and the ball and pegs to an extraction thimble in a soxhlet containing dichloromethane. Care was taken to minimise contact with the atmosphere by performing transfer operations quickly, by immediately sealing any sample tubes and by keeping the ball and pegs submerged in dichloromethane once in the soxhlet. The extraction thimble had a capacity of six balls and eighteen pegs; so six runs were performed and all the balls and pegs put together into the same soxhlet. This should have the effect of giving a six fold increase in the quantity of any reaction products.

Soxhletting was continued for a minimum of twenty four hours. The resultant solution was vacuum distilled to remove the dichloromethane. This left a few drops of liquid. These were subjected to infra-red and mass spectroscopy. The used lubricant was also examined using these techniques. The spectra were compared to that of an unused freshly prepared two per cent alkene solution. The dimensions of the wear scars on the pegs were recorded. Blank experiments were performed to ascertain the source of any new products generated.

5.5.3 Results and Discussion

The Used Lubricant. The mass spectrum of an unused two per cent solution of purified 1-hexadecene in pure hexadecane is shown in fig. 5.5. Fig. 5.6 shows the mass spectrum of a sample from the same batch, but which had been used in the triplane apparatus. Comparison of these spectra revealed no differences below a mass to charge ratio of 224 (the molecular weight of 1-hexadecene). However, there is an additional peak at m/e 240 in the spectrum of the used lubricant. Also the peak at 255 is of greater intensity. A structure with a mass of 240 is $C_{14}H_{29}CO.CH_3$, though of course any other ketonic structure

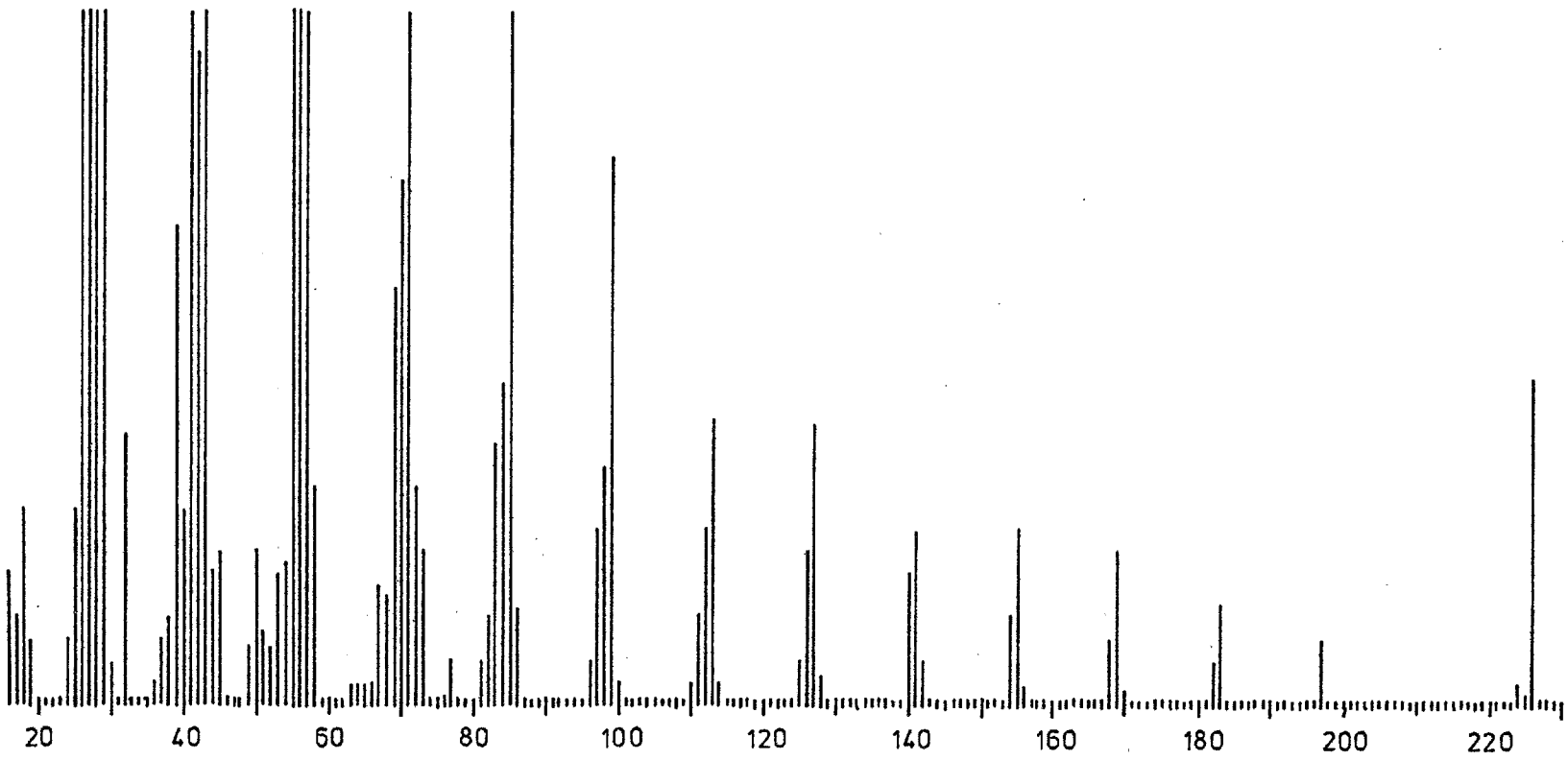


Fig. 5.5 The mass spectrum of a pure unused 2% solution of 1-hexadecene in hexadecane.

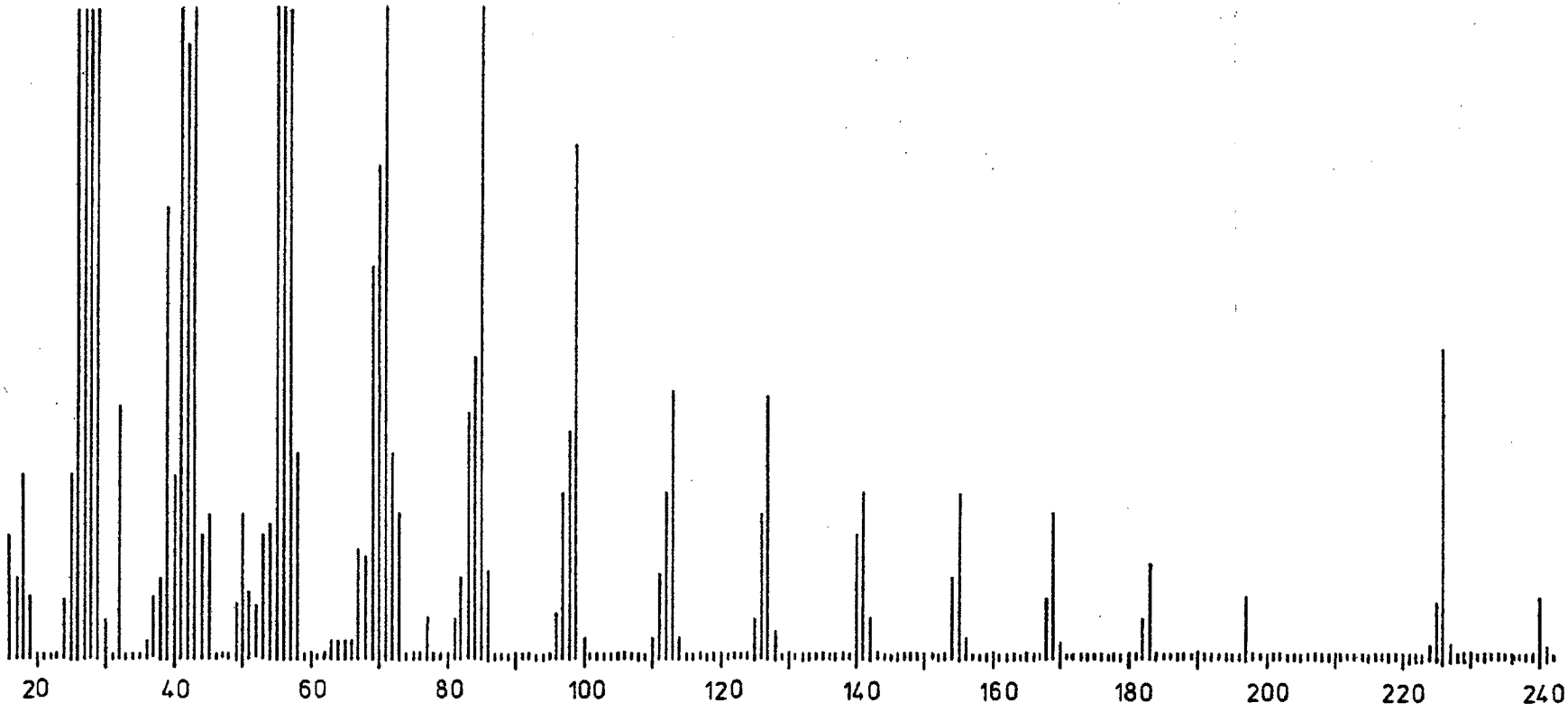


Fig. 5.6 The mass spectrum of a used 2% solution of 1-hexadecene in hexadecane.

containing sixteen carbon atoms would fit. This structure was selected for two main reasons.

(a) The infra-red spectrum showed a peak at 5.85 μm. A peak in this position normally arises from the presence of a carbonyl group (>C=O).

(b) The intensity of the peak at 255 is increased.

A peak at 225 initially results from the presence of the carbon isotope ^{13}C in the C_{16} carbon chains. Ketones fragment at the C-C bond adjacent to the carbonyl group, so $C_{14}H_{29}CO.CH_3$ would cleave to give $CH_3\overset{+}{C}=O$ and $C_{14}H_{29}\overset{+}{C}=O$. These fragments have molecular weights of 43 and 225. The peak at 43 was so large in any case (due to the presence of $\overset{+}{C}_3H_7$ from the fragmentation of both hexadecane and 1-hexadecene) that the contribution from $CH_3\overset{+}{C}O$ was not observable. The contribution from the $C_{14}H_{29}\overset{+}{C}=O$ fragment would be significant when compared with that from the presence of ^{13}C, giving an observable increase in the intensity of the 225 peak. Ketones also undergo rearrangement in the mass spectrometer to form lower molecular weight ketones. The intensity of these peaks is normally quite high, so it would be expected that peaks at m/e ratios corresponding to the series (240 - 14n), where n is an integer, would be observable. Unfortunately the concentration of the ketone can only be very small, so the contribution from these ions would be particularly small when compared to those arising from the hexadecane fragmentation. This illustrates one of the problems associated with the detection and identification of very low concentrations of one material in a large excess of another.

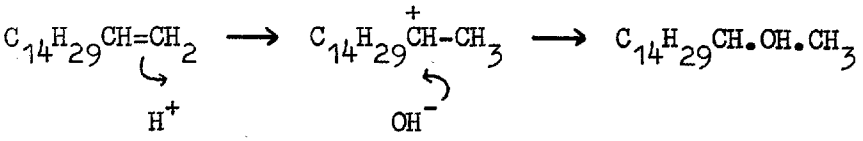
Gas liquid chromatography using carbowax 6000 on Chromosorb W column separated a sample of the used lubricant into six components. Using known standards five of these were indentified as 1-hexadecene, hexadecane and the three impurities in hexadecane; octane, dodecane and

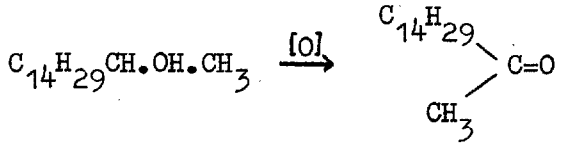
tetradecane. It was assumed that the sixth was hexadecan-2-one (from the information given by the infra-red and mass spectra).

As far as could be discovered, no authentic sample of hexadecan-2-one was available, neither was there sufficient information to enable a prepared sample to be characterised. Thus the infra-red and mass spectra could not be compared to those of known samples as would be the ideal situation, but were taken as sufficient in their own right.

'Blank' Tests. A blank experiment was performed to decide whether rubbing was necessary for the production of hexadecan-2-one. The cleaning of the apparatus, its assembly and dismantling were duplicated exactly. The ball was not, however, rubbed against the pegs. To take into account the temperature rise resulting from sliding, the external heater was employed. The heating rate and final temperature were as near as possible the same. There is clearly a difference here in that during sliding the heat was generated at an EN31 steel-EN31 steel interface, whereas in the blank test the heat emanates from the stainless steel lubricant retaining ring. No way of overcoming this difference was possible without considerable modification of the triplane apparatus.

A sample of the alkene solution from the blank test was subjected to mass spectroscopy. It gave a spectrum identical to that of the used lubricant, showing that rubbing was not required for the production of the ketone. Simply heating a pure unused solution in a glass test tube, in the absence of steel for four hours at 120°C. gave traces of hexadecan-2-one. This proved that metal need not be present for the formation of the ketone. Hexadecan-2-one might be formed from hexadecene by the mechanism shown overleaf.



followed by 

hexadecan-2-one

The alkene reacts with water from the surrounding atmosphere to give a secondary alcohol. The addition of water across the double bond is a Markownikoff type of reaction, i.e. the OH adds onto the more highly substitued carbon atom. The alcohol is subsequently oxidised to the hexadecan-2-one.

This scheme requires the presence of water. If it is correct, heating the alkene solution in the absence of water would give no ketone. This was put to the test using the apparatus shown in fig. 5.7.

A two per cent solution of 1-hexadecene in hexadecane was prepared by adding the requisite amount of freshly distilled alkene at about 150°C. to purified hexadecane at a similar temperature. The object of the elevated temperature was to eliminate the presence of water. Dry white spot quality oxygen free nitrogen was passed through the solution at 130°C. (The gas was dried by passing it first through activated silica gel, then over molecular sieve 4A.) This encourages any water still present to pass into the vapour and out of the apparatus. Nitrogen was chosen rather than air to reduce the possibility of unexpected oxidation. A 'natural', but water free, atmosphere, was created by drawing dried air into the apparatus. The solution temperature was held at 150°C. for four hours. It was cooled to a solid to prevent further reaction. One sample was injected into the mass spectrometer, and another examined by infra-red spectroscopy.

No mass peak at 240 was observed. There was no infra-red

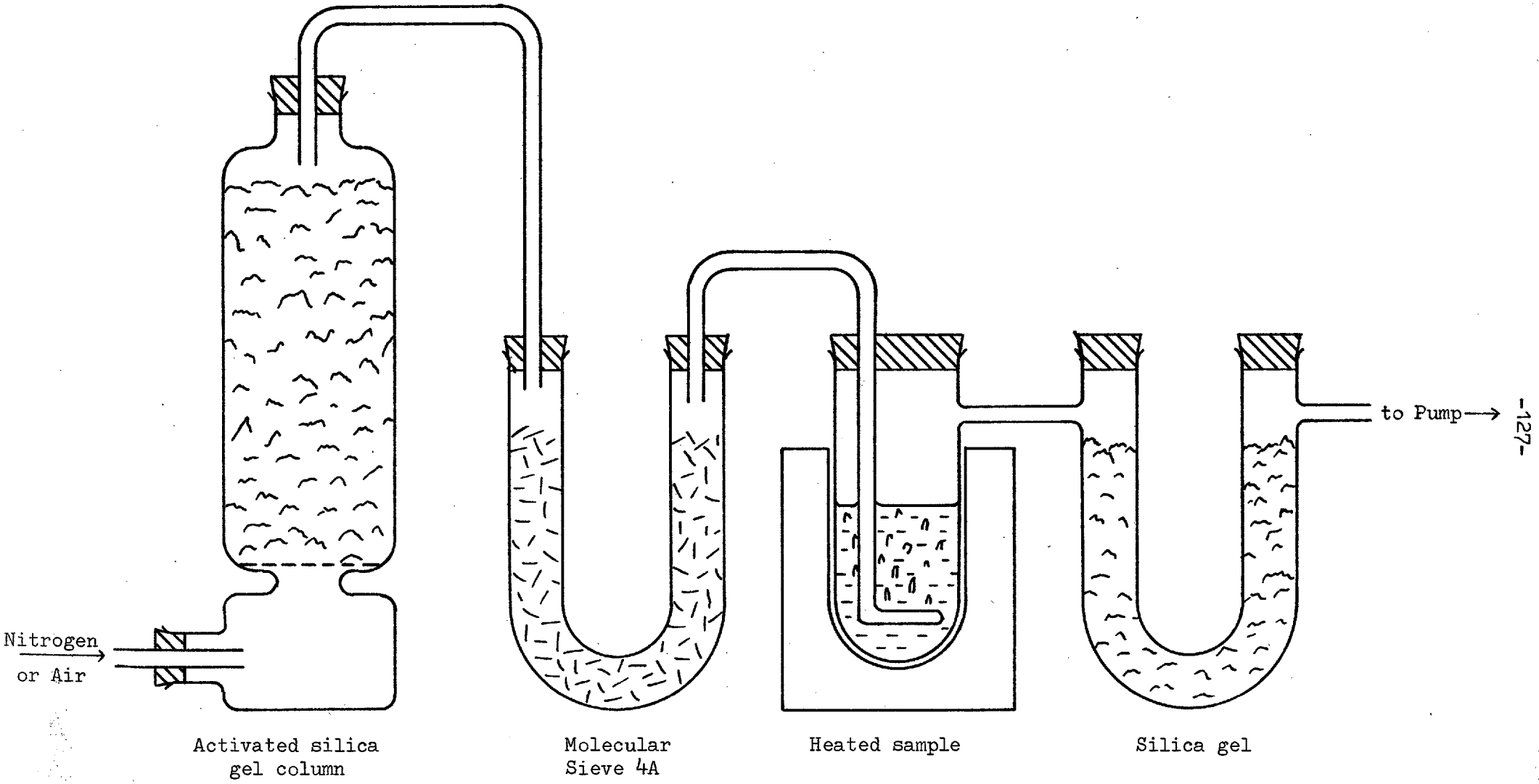


Fig. 5.7 Apparatus to determine the effect of heat on a solution of hexadecene in hexadecane in a water free environment.

absorption in the 5.9 μm region. It was concluded that no ketone was present.

These results lend credence to the suggested reaction mechanism. No tests were conducted to establish the effect of temperature. (If the temperature were reduced to room temperature it would have taken nearly four years to conduct an equivalent experiment.)

In conclusion, when a solution of 1-hexadecene in hexadecane was used as a lubricant in the ball on triplane apparatus, some oxidation occurred to form hexadecan-2-one. Blank tests showed that neither sliding nor metal were necessary for the reaction to occur. Providing water is present, simply heating the solution generated the ketone.

The Dichloromethane Extract. Fig. 5.8 shows the mass spectrum of the dichloromethane extract. It is identical to that of the used lubricant shown in fig. 5.6. (When the spectra were arranged in tabular form with the intensity of each peak expressed as a percentage of the most abundant peak, small differences were noted. These differences however, came within the limits of variation of the spectrometer.)

Not surprisingly gas-liquid chromatography separation and infra-red spectroscopy gave results identical to those from the used lubricant. This can be explained by a small amount of used lubricant being transfered into the soxhlet on the surfaces of the balls and pegs. This would be present in the residue which was analysed.

No new substances detected in the residue showed that either there was no film on the ball or peg surfaces, or the soxhletting process had been unsuccessful. If the extraction method does work, then the balls' surfaces should be free from carbon. An electron probe microanalysis scan of the surface, and particularly the wear scars, showed carbon to be absent. It was concluded that no chemical film

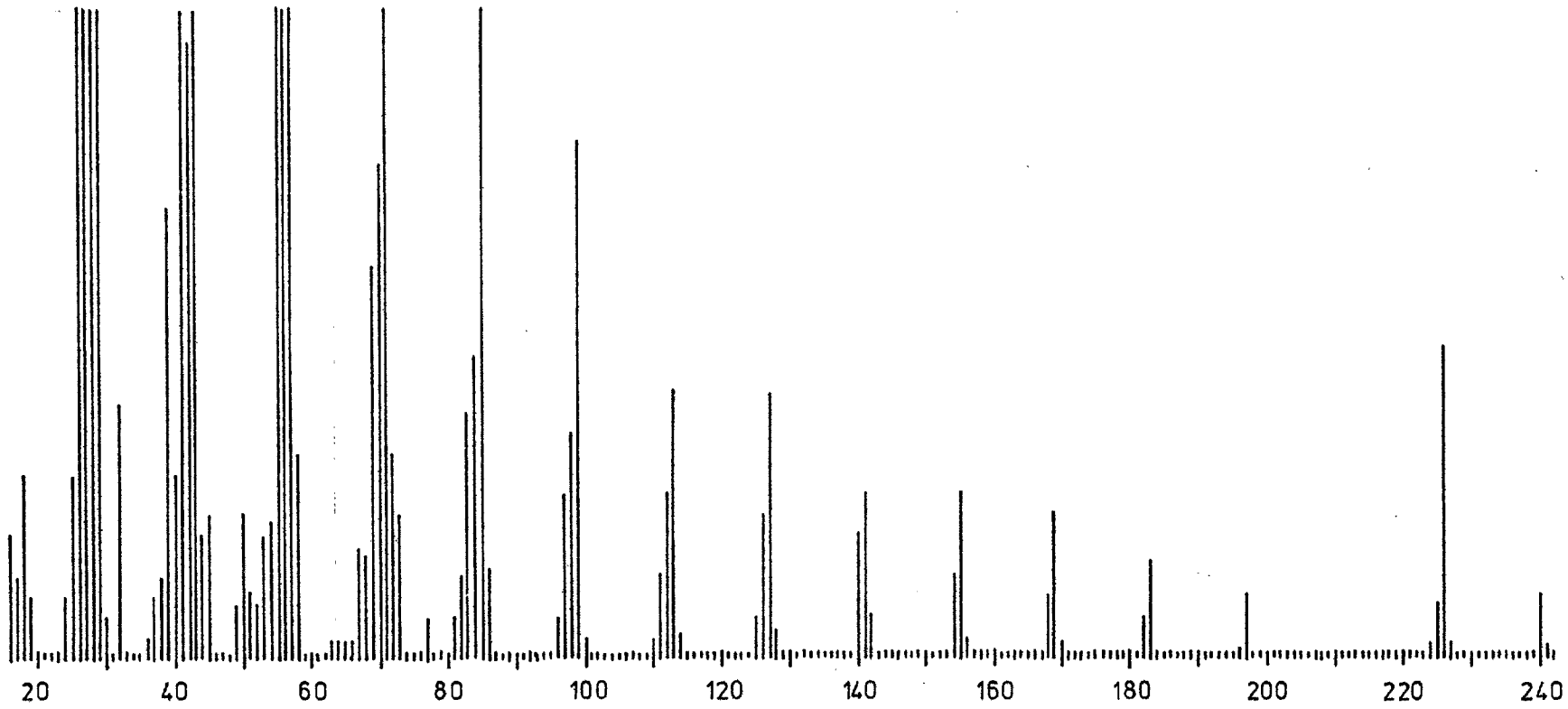


Fig. 5.8 The mass spectrum of the dichloromethane extract when using a 2% solution of 1-hexadecene in hexadecane.

had been formed in the contact regions during sliding.

At this juncture it was decided that electron probe microanalysis of each ball and peg after extraction in dichloromethane was going to be both costly and time consuming. It also carried with it a great risk of surface contamination. Contamination would arise from cutting a ball to get a sufficiently small segment to insert into the analyser, or from general handling and transfer from the triplane apparatus to the site of the EPMA equipement. A quick, cheap and reliable alternative method for checking surface cleanliness was required. The technique developed utilised the ability of copper to plate out from aqueous solutions of its salts onto an iron surface. It is now described in more detail.

5.6 COPPER PLATING TO DETERMINE THE CLEANLINESS OF A STEEL SURFACE

5.6.1 The Technique

It is well known that when a steel object is placed in a concentrated copper sulphate solution a brown layer of copper is deposited on the surface. This coating does not usually adhere very strongly to the steel substrate. If, however, a very dilute solution of copper sulphate is used, plating is either very slow, or, if the surface has not been freshly abraded, the copper may not be deposited at all. This property was studied to see whether or not it could detect an organic film on a metal surface.

A series of experiments showed that a freshly prepared 0.02 M solution of 'Analar' copper sulphate in distilled water gave good results. The solution is dilute enough to give a firmly adhering deposit of copper, but the reaction occurs quickly enough to prevent electrolytic stripping.

The reaction which gives copper on an iron surface is:

$$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$$

In electrolytic stripping the substrate metal is removed leaving the required film to fall off into the solution. This is undesirable for our purposes since if the film were removed a clean surface remains on which the copper would plate out. The presence of the film would not then be disclosed.

5.6.2 Results

Tests with known systems gave the hoped for results (fig. 5.9).

(1) An ionically bombarded ball gave a matt brown colour.

(2) A ball which had been run in a solution of hexadecan-1-ol in hexadecane, a system which gives an organic film in the wear tracks, was allowed to stand in the copper sulphate solution. No copper was deposited on the wear tracks, but the remainder of the ball had a uniform coverage.

(3) A similarly run ball was ionically bombarded, then tested. A film of copper was present over the whole surface of the ball.

(4) Another similar ball was soxhletted in dichloromethane according to standard practice. After standing in the plating solution, a uniform film was observed over the whole surface of the ball, including the wear scars.

It was further observed that this technique disclosed the position in which a ball was held in the ring in the ionic bombardment chamber. Consequently a ring was then adopted with a diameter such that it could not completely cover any wear track. Obviously this less well cleaned area would probably cross at least one track. It was unfortunately impossible to determine where this mark was until after a run was terminated.

This copper plating technique also detects finger prints on a

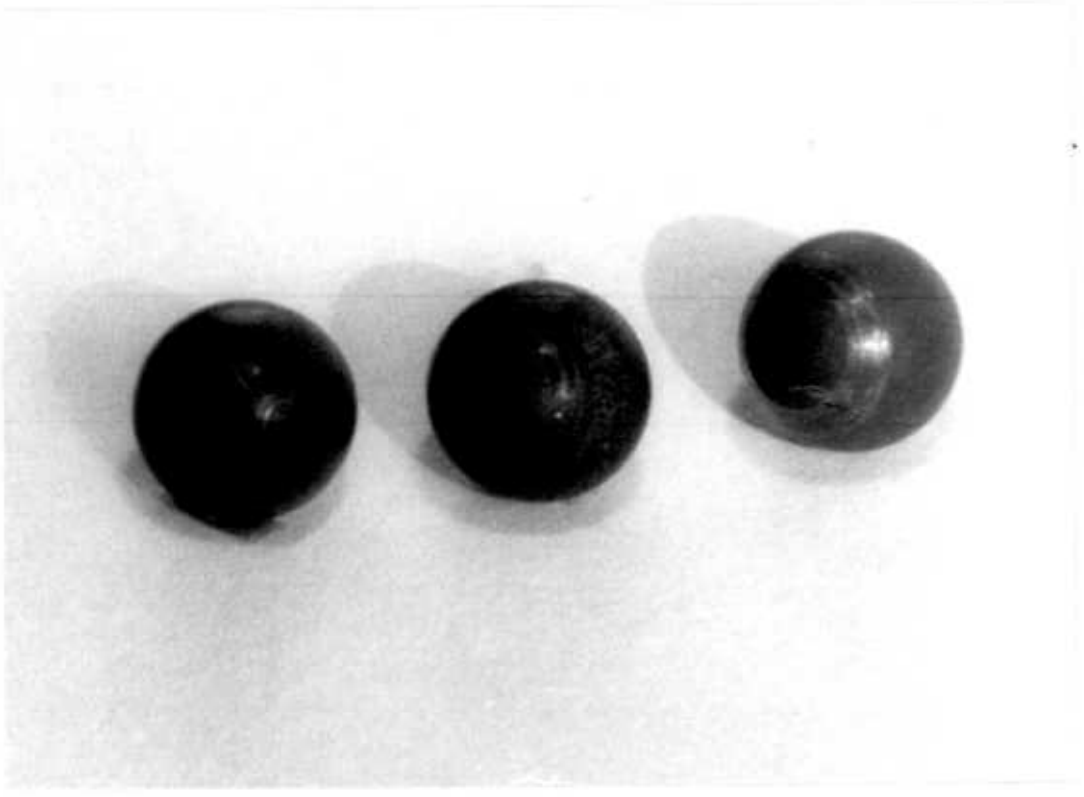


Figure 5.9 Copper plated steel balls. The one on the left has been cleaned by ionic bombardment, then imersed in the plating solution. This gave a uniform deposit of copper. The middle ball has been run in a 2% 1-hexadecanol solution, then soxhletted in dichloromethane. Again there is a uniform copper coating. The third ball has been run in a 2% 1-hexadecanol solution, rinsed with ether, then placed in the plating solution. Note how the copper has not plated out on the wear scars where there is an organic film sorbed.

clean ball, giving quite a clear pattern.

5.7 CONCLUSIONS

The following conclusions were drawn from the experimental results.

1. (a) The load bearing capacity of pure 1-hexadecene was considerably greater than that of hexadecane.

   (b) Increasing the sliding speed decreases the load carrying capacity.

2. (a) The addition of small amounts (1-2%) of 1-hexadecene significantly improves the load carrying capacity of hexadecane. Its value closely approaches that of the pure alkene.

   (b) Both one per cent and two per cent solutions exhibited the same scuffing load.

3. (a) 1-Hexadecene, being polar, was more strongly sorbed onto the steel surfaces, so more effectively kept them apart.

   (b) The bulk concentration of alkene necessary to give maximum surface coverage was less than one per cent.

4. (a) The hexadecene solutions remaining after running the triplane apparatus were found to contain traces of the oxidation product hexadecan-2-one. Its identity was confirmed using mass and infra-red spectroscopy.

   (b) A mechanism proposed to explain the formation of the ketone required the presence of water. This was confirmed by experiment.

   (c) The oxidation was independent of sliding and the presence of metals.

5. No chemical films were formed on the ball or peg surfaces

during sliding. This was verified by electron probe microanalysis.

6. A copper plating technique for detecting organic films on steel surfaces was developed.

Table 5.5 Table of analyses carried out on materials used in chapter 5.

Sample	Analysis						
	Refractive index	Boiling point	Mass spectroscopy	infra red	GLC	Wet chemistry	Fe/Cr analysis
Hexadecene as supplied	*	*					
Purified hexadecene	*	*	*	*	*		
Used hexadecene (100%)			*	*		*	*
Pure unused 2% solution of hexadecene in hexadecane			*	*	*		
Used 2% solution of hexadecene in hexadecane			*	*	*		
Dichloromethane extract			*	*	*		
Blank dichloromethane extraction process			*				
Blank, 2% hexadecene solution heated in triplane apparatus			*				

continued . . .

Table 5.5 (continued)

Sample	Analysis						
	R fractive index	Boiling point	Mass spectroscopy	infra red	GLC	Wet chemistry	Fe/Cr analysis
2% solution of hexadecene in hexadecane heated at 120°C for 4 hours without steel			*				
2% solution of hexadecene in hexadecane heated at 150°C for 4 hours in dry atmosphere			*	*			

CHAPTER 6

1-AMINOHEXADECANE

6.1 INTRODUCTION

The fatty amines are now no longer in general use as additives. At one time, during the late nineteen forties, they were used to maintain basicity - particularly in marine oils. However their caustic nature led to their disuse. Nowadays certain aromatic amines are used as oxidation inhibitors. Tetraethylene pentamine is a good ashless dispersant which also maintains the basicity of an oil. Amines are not added to crankcase oils because they cause gumming of pistons and ring sticking - a characteristic which is far from desirable.

Nitrogen separates carbon and oxygen in the periodic table. Since carbon and oxygen containing compounds, hexadecane and hexadecan-1-ol, were examined in this work, it was decided to include the nitrogen containing compound, 1-aminohexadecane, for the sake of completeness, despite the lack of commercial use of amines.

Hexadecane has already been found to be unreactive under the conditions of testing to which it has been subjected. The next chapter shows how hexadecan-1-ol undergoes change under similar test conditions. Nitrogen is more like oxygen than carbon in that it, like oxygen, possesses a lone pair of electrons. On this basis 1-aminohexadecane would be expected to behave more like hexadecan-1-ol. This was found to be the case, the amine did undergo chemical changes. The nature of these changes is described in this chapter. The determination of the

load carrying capacity, under varying conditions of sliding speed and solution concentration, is also presented. Solutions in hexadecane were employed since the amine is a solid at room temperature.

6.2 PURIFICATION

1-Aminohexadecane could only be obtained as technical grade. It was supplied by Messrs. Koch Light Laboratories Ltd.. The manufacturers analysis by GLC gave an overall purity of 87%, the major impurities being the C_{14} and C_{18} homologues, together with traces of the C_{15} and C_{17} homologues.

1-Aminohexadecane readily absorbs carbon dioxide from the atmosphere to give the carbonate salt:

$$2\ C_{16}H_{33} - NH_2 + CO_2 + H_2O \longrightarrow (C_{16}H_{33}NH_3^+)_2\ CO_3^{2-}$$

First attempts to recrystallise the amine from any of the normally used solvents failed. In each case a crystalline product of melting point 93°C. was obtained, whereas the melting point of the freshly prepared amine has been cited in the literature as either 46°C.[84] or 78°C.[85]. The lower melting point is generally taken as the correct one. The failure of a physical purification led to a chemical method having to be adopted.

Amines are basic materials so they dissolve in dilute aqueous acid to form the corresponding salt. Since a strong acid displaces a weaker acid, any salts of weak acids already present will be converted to the salt of the strong acid. The amine is regenerated by making the resultant solution alkaline. The actual purification consisted of intimately grinding the amine with 50% aqueous hydrochloric acid. This liberates carbon dioxide from any carbonate present to form the chloride:

$$(C_{16}H_{33}NH_3^+)_2\ CO_3^{2-} + 2HCl \longrightarrow 2\ C_{16}H_{33}NH_3^+Cl^-$$

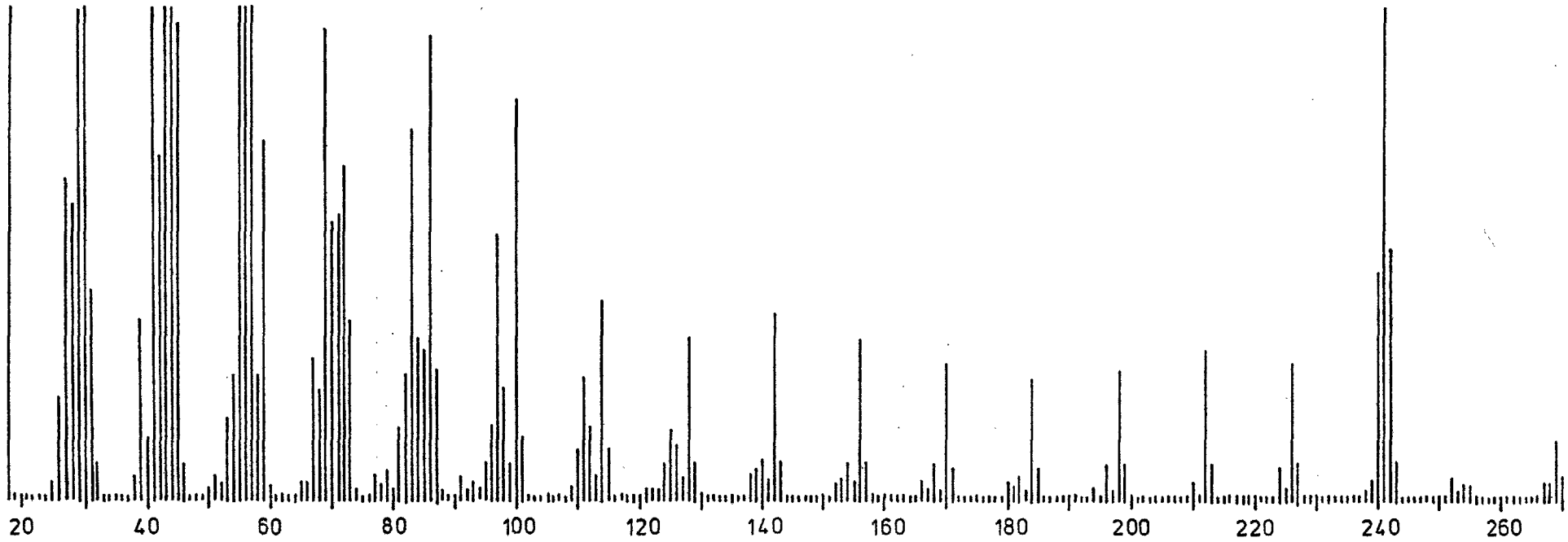


Fig. 6.1 The mass spectrum of purified 1-aminohexadecane.

Any amine is also converted to the chloride salt:

$$C_{16}H_{33}NH_2 + HCl \longrightarrow C_{16}H_{33}NH_3^+Cl^-$$

The chloride was mixed with solid potassium hydroxide and the mixture distilled under vacuum. The middle cut of the distillate was collected and found to have a melting point of 45 - 46.5°C.. This was considered an acceptably narrow melting range. The refined product was stored under nitrogen. Fuller data is given in table 6.1.

At all times great care was taken to avoid unnecessary contact with air, with its associated risk of absorption of carbon dioxide. Mass spectroscopy showed that even in the purified product there was still some 1-aminooctadecane present (mass peak 269 in fig. 6.1). The peak at 252 is due to loss of the NH_3 fragment, and that at 253, to the loss of NH_2. The peak at 227 arises from the presence of $C_{15}H_{31}NH_2$. This may be derived from an impurity or from fragmentation and rearrangement of a longer carbon chain amine. This type of rearrangement is very common in amine spectra. The remaining peaks are what one would expect from a long straight chain primary amine.

Property	As supplied	After purification	Literature
Melting point	42 - 83°C.	45 - 46.5°C.	46°C.[84]
Boiling point	---	165/3 mm	330/760 mm[74] 197/12 mm[74] 170-5/12 mm[84]

Table 6.1 The properties of 1-aminohexadecane before and after purification.

6.3 DETERMINATION OF THE LOAD CARRYING CAPACITY

6.3.1 Procedure

The load carrying capacity was determined in the same manner as previously described in chapter 4 for hexadecane. Two sliding speeds were employed to ascertain the effect of speed. They were 1.09 ms^{-1} and 0.43 ms^{-1}. Two lubricant compositions were tested, a one per cent solution of 1-aminohexadecane in hexadecane and a two per cent solution in hexadecane. All the materials involved were carefully purified before use. The amine is a solid at room temperature so it could not be used by itself as a lubricant at room temperature. It would have been possible to heat the triplane apparatus to a temperature above the amine's melting point of 46°C. to determine its load carrying capacity. This would not, however, have been directly comparable with data obtained both previously and subsequently. For this reason such a test was not undertaken.

During operation of the test equipement, temperature and friction

Concentration of 1-aminohexadecane	Load carrying capacity (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
1%	105	48
2%	135	69

Table 6.2 The load carrying capacity of one and two per cent solutions of 1-aminohexadecane in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

were monitored continuously. A mass spectrum of the lubricant remaining after scuffing was obtained. Used balls and pegs were subjected to the copper plating test.

6.3.2 Results and Discussion

The results obtained are summarised in table 6.2.

The Effect of Speed. Increasing the sliding speed decreased the load carrying capacity. This was demonstrated for both solution concentrations. These results are similar to those obtained when testing hexadecane, hexadecene and solutions of hexadecene. This is in fact a common type of behaviour. Although the higher sliding speed produces a thicker hydrodynamic film, there is still an element of boundary lubrication with asperity contacts. Because of the high speed there is large localised heat generation. These flash temperatures can denude the surface of any sorbed films thus allowing metal to metal contact and scuffing.

The Effect of Solution Concentration. Increasing the concentration of the amine improved the load carrying capacity. It was envisaged as a result of greater reaction with the surface at higher concentrations. The actual reaction with the surface will not be considered in detail here, but is described in a following section. The general scheme appears to be as shown in fig. 6.2 overleaf.

An 'altered organic layer' is formed on the ball or peg surface. This surface may be metal or metal oxide, though the presence of oxygen would favour the latter. The 'altered organic layer', once formed, remains bound to the surface and is not removed by rubbing. It is reasonable to assume that the amine, possessing an inherent dipole, orientates itself, to a greater or lesser extent, perpendicularly to this layer. Amine and alkane molecules would lack any systematic

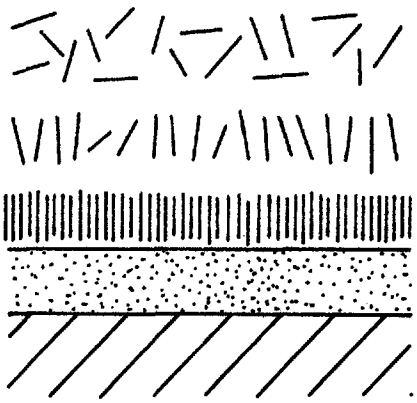


Fig. 6.2 The suggested surface structure produced when a solution of 1-aminohexadecane in hexadecane is used as the lubricant.

arrangement in the bulk liquid.

Accepting that it is the amine molecules which are responsible for the 'altered organic layer', and therefore for the increased load carrying capacity as compared to hexadecane, then the greater their concentration, the greater their potential rate of reaction with the surface. (This can be envisaged from a consideration of simple Collision Theory.) This infers that, taking simple figures, if one halves the concentration, the rate of reaction is halved, so twice the time is required to attain the same extent of reaction.

It was hoped that some information regarding rates of reaction might be obtained from the friction traces. The friction between two clean steel surfaces is exceedingly high. (Very clean metal surfaces cold weld together.) Once some surface contamination is introduced, friction begins to decrease, and, leaving complex surface activity

aside, the more 'contaminant' present, the more the friction drops. Thus, if a variation in the value of the coefficient of friction, μ, is noted, one must be observing the effect of a change in either the metal surfaces, or the lubricant, or both. It would be anticipated that the rate of change of μ would give some idea of the rate of such changes. As far as solutions of 1-aminohexadecane in hexadecane are concerned, it was found that friction decreased very slightly with increasing time at a given load. The variations were very small. Unfortunately no difference in slope between one and two per cent solutions could be positively identified. As a check the rate of drift of the pen recorder was ascertained. It was of such a magnitude that it could not have been responsible for the observed slopes.

The rate of reaction may, of course, not be determined by the rate of collision of molecules with the surface, but by a reaction occurring on the surface. A direct study could not be undertaken because of the design of the triplane apparatus, but the similarity in the slopes of the friction traces for both one and two per cent solutions may indicate this to be the case. If this is so, the reaction must still be dependent on the concentration of the amine to account for the difference in the load carrying capacities. The system is further complicated by the effects of amine and alkane molecules sorbed on top of the 'altered organic layer'. Here the greater the concentration of amine, the greater the surface coverage, which itself could explain the observed results.

On removing the ball and pegs from their locations in the test machine, it was noted that the rubbing surfaces were severely torn. During tearing, bare metal surfaces are exposed. This is a chemically very reactive system, so the chances are that any organic materials which may have been present on the surfaces of the ball and pegs before

scuffing would be either removed or altered in some way. The surrounding bulk lubricant is also likely to undergo changes. To investigate this possibility the mass spectrum of a sample of the bulk lubricant taken after failure was obtained. The spectrum is presented in fig. 6.3. For comparison fig. 6.4 shows that of a sample of a pure unused two per cent solution of 1-aminohexadecane in hexadecane. Although the spectrum of the failed lubricant is fairly complex and difficult to analyse because isotope peaks are often masked by other peaks, several general observations can be made. They are:

(1) Considerable chemical reaction occurs at the moment of failure. A sample of the bulk lubricant taken before failure was indistinguishable from a freshly prepared unused solution.

(2) The 'altered organic layer' mentioned earlier is lost from the metal surfaces.

(3) The amine solution is oxidised. This involves both the uptake of oxygen and the loss of hydrogen.

A comparison of figs. 6.3 and 6.4 shows which peaks are due to fragmentation of hexadecane and 1-aminohexadecane. Once the amine has lost the CH_2NH_2 fragment it is isobaric with the alkane after loss of CH_3. This is why the spectrum of a pure solution is fairly simple. The remaining peaks are a result of the fragmentation of new species. The peaks at $(95 \pm 14n)$ are probably due to presence of dienes, 95 itself corresponding to C_7H_{11}. The peaks corresponding to $(151 + 14n)$ probably contain oxygen or possibly a benzene ring. A peak at m/e 77 is evidence for the presence of the aromatic group.

The other series of peaks $(205 - 14n)$ are almost certainly oxygen containing. The fragment responsible for the peak at 205 also contains four double bond equivalents, so it may be aromatic. The series does seem to stop at 79 so it is quite probable that a benzene ring is

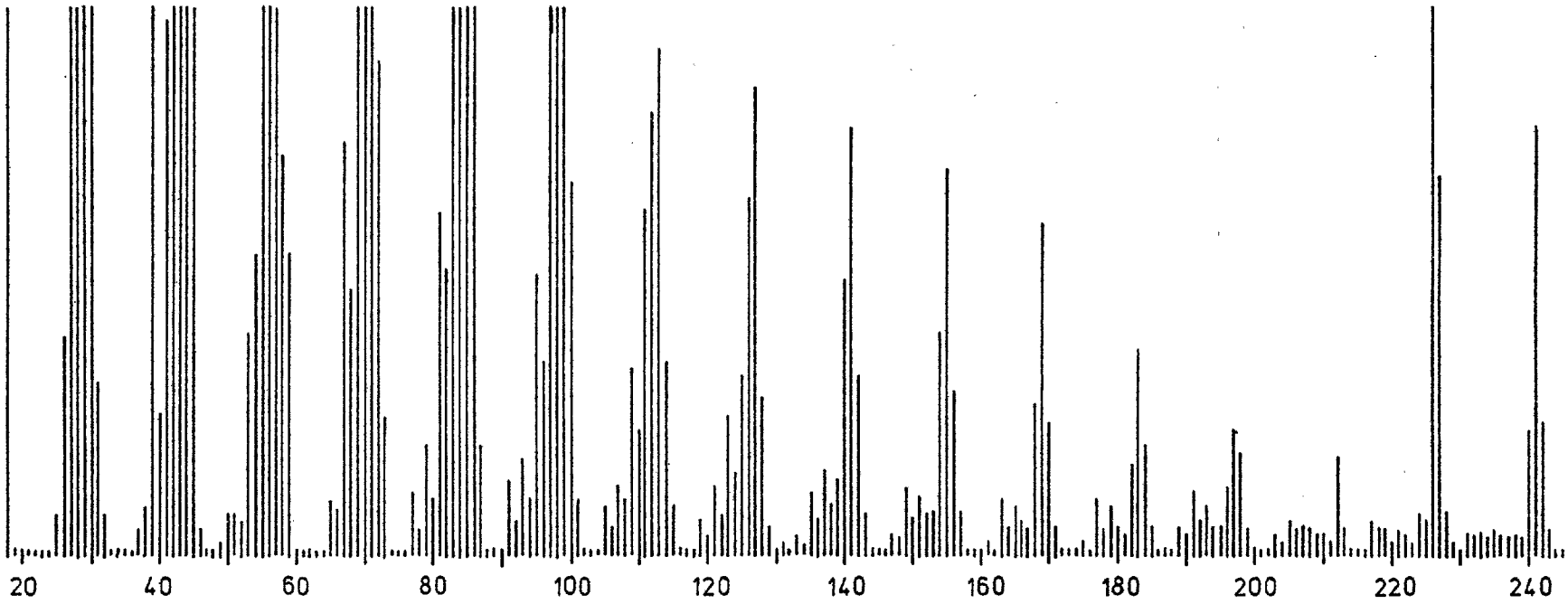


Fig. 6.3 The mass spectrum of a 2% solution of 1-aminohexadecane in hexadecane remaining after scuffing in the triplane apparatus.

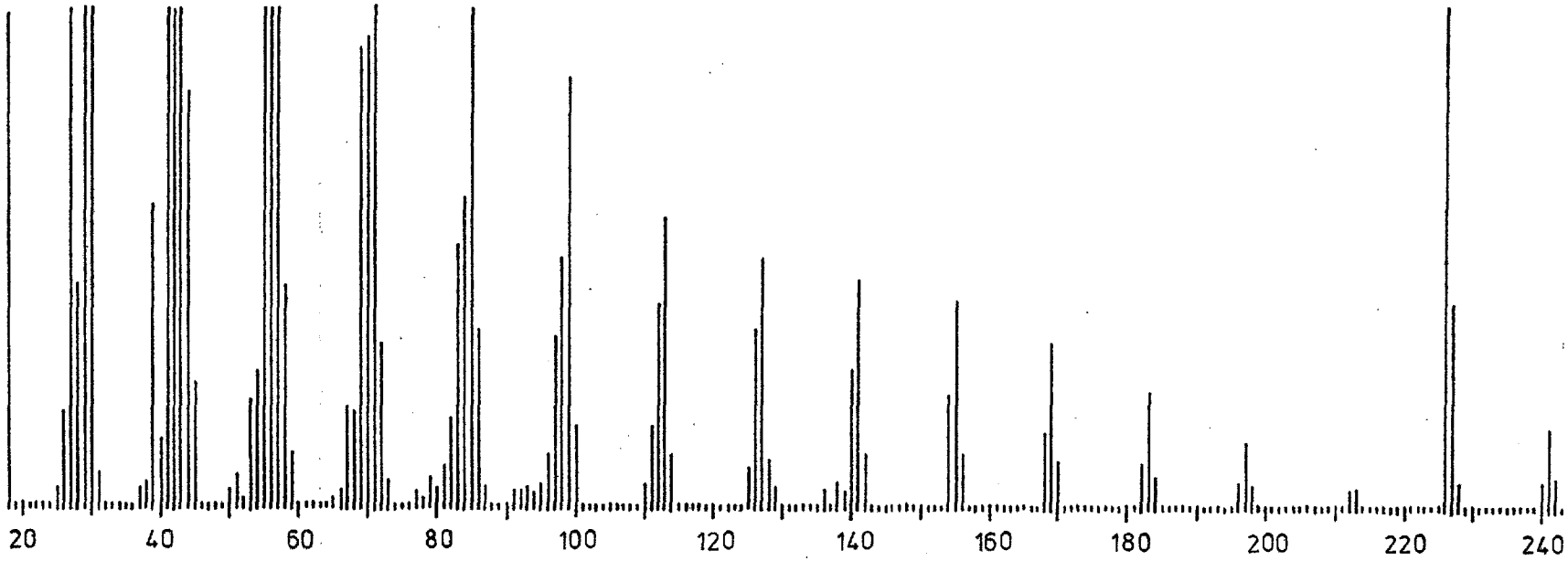


Fig 6.4 The mass spectrum of a pure unused 2% solution of 1-aminohexadecane in hexadecane.

present.

Although chemical reactions at freshly formed metal surfaces have not been greatly investigated, the formation of unsaturated molecules at scuffing would not be unexpected. It is possible to form double bonds and aromatics by the dehydrogenation of alkanes over chromium (III) oxide (Cr_2O_3). This process is used industrially, the extent of unsaturation being controlled by the temperature and the residence time of the reactants. As already explained, an EN31 steel surface has a considerable amount of chromium oxide on it which may cause the dehydrogenation reaction to occur. During scuffing a chemically clean chromium surface is produced. This could be quickly converted to chromium oxide by oxygen dissolved in the lubricant. It is generally accepted that many materials are more reactive when freshly prepared. At the same time as considering the chromium oxide, one must not neglect the nascent iron, chromium and small amount of manganese. The incidence of either chromium or manganese at the surface is probably small, but may be increased by migration.

Reactions are often initiated by rubbing a metal surface. This has been attributed to what are sometimes known as 'exo-electrons' or the 'Kramer effect'[86] after the physicist who studied the phenomenon. Most recent work has suggested that it is not in fact electrons but positive ions which are released from the surface[40, 87]. Whichever is correct, a highly reactive system is generated which could lead to many different products.

Some of the products contain oxygen. This could be available dissolved in the bulk lubricant. The mechanism of incorporation of the oxygen may be a 'direct' reaction between molecular oxygen and the organic molecules concerned, probably via a peroxide intermediate, or may involve a reaction on, and catalysed by, a metal or metal oxide

surface.

Closer investigation of the mechanisms involved in the chemical reactions undergone at scuffing was not undertaken because of its complexity and its considerable deviation from the intended course of the study.

If a scuffed ball and pegs were put into copper plating solution without washing, no copper was deposited. On rinsing with ether a uniform layer of copper was formed. This indicated that any organic material was totally removed from the wear track by the scuffing process. (If no scuffing occurred, copper would not deposit on the wear tracks even after rinsing in ether. The plating process nevertheless took place on other parts of the ball.)

Summarising then, increasing the concentration of 1-aminohexadecane in hexadecane increases the load carrying capacity, whereas increasing the sliding speed causes it to decrease. Until the onset of scuffing the bulk lubricant remains unchanged, but at scuffing it undergoes oxidation and hydrogenation, resulting in compounds containing oxygen and double bonds, probably even benzene rings. This was attributed to the formation of nascent metal surfaces.

6.4 DICHLOROMETHANE EXTRACTION STUDIES

6.4.1 Introduction

In the previous section reference was made to an 'altered organic layer' on the surface of the ball and pegs. The evidence for the presence of this film will now be presented.

To facilitate analysis, a two per cent solution of 1-aminohexadecane was employed initially. A one per cent solution was also tried to see whether or not changing the solution concentration gave different

products. The operating parameters of the test equipment were selected so that these tests were comparable with those using similar solutions of other materials in hexadecane.

6.4.2 Procedure

The peg carrier, lubricant retaining ring and ball chuck were ultrasonically cleaned in toluene and then acetone. Ionic bombardment was employed for cleaning the 3/4 inch (19.06 mm) EN31 ball and pegs. These were assembled with the lubricant solution and fitted into the triplane test apparatus. The sliding speed selected was 0.43 ms^{-1}. Run in was achieved by increasing the top ball load in increments of 6.9 kg, each load being maintained for thirty seconds. The final load was 69 kg. Constant observation ensured that the load did not fluctuate significantly. Friction and temperature were monitored throughout. No external heating was provided, any temperature rise being due to frictional heating alone.

After four hours running, the apparatus was dismantled and the ball and pegs transfered quickly to a soxhlet containing dichloromethane. Care was taken to minimise contact with the atmosphere. A little of the used lubricant was transfered to a sample tube and sealed. The balls and pegs from six runs were put together in one thimble to increase the quantity of the reaction products. After soxhletting for twenty four hours, the dichloromethane was removed under vacuo. The few drops of product remaining were examined using mass spectroscopy. The resulting spectrum, together with that of the used lubricant, were compared to the spectrum of an unused sample of the same solution. Blank tests were conducted to ensure that the observed results were due to running and not to the extraction procedure.

After soxhletting the balls and pegs were each subjected to the

copper plating test to ensure that there was no residual organic material present. Several balls and pegs were taken after running in the triplane apparatus but not soxhletted. Instead they were quickly rinsed with ether and allowed to stand in copper plating solution. This should indicate whether or not there was any organic film on the ball or pegs, and, if there was, where it was.

The diameters of the wear scars on the pegs were recorded.

6.4.3 Results and Discussion

The Copper Plating Tests. A ball taken from the triplane apparatus, after rinsing with ether, did not show a copper colour on the wear scars. The remainder of the ball was uniformly covered. This showed the presence of an organic film only on the worn areas. It also indicated that quickly rinsing with ether removed adherent liquid lubricant but left the chemically bound organic layer. When subjected to similar treatment the pegs displayed the same behaviour. This leads to the conclusion that the organic film was generated in the actual contact. If contact with the bulk lubricant were required, a film would be produced on the ball but not on the pegs, since the ball is in cyclic contact with a peg and the liquid lubricant whereas each peg is in constant contact with the ball, so is not freely exposed to the bulk fluid. This is in contrast to Bayles's findings[88], that the reaction between dibenzyl disulphide, an extreme pressure additive, and an EN31 steel surface depends on the length of time for which the ball is in contact with the bulk lubricant infering that reaction occurs between a previously rubbed surface and the lubricant.

The Used Lubricant. Fig. 6.5 shows the mass spectrum of the used lubricant. It is identical to that of the unused two per cent amine solution (fig. 6.4). No change in the bulk lubricant had taken place.

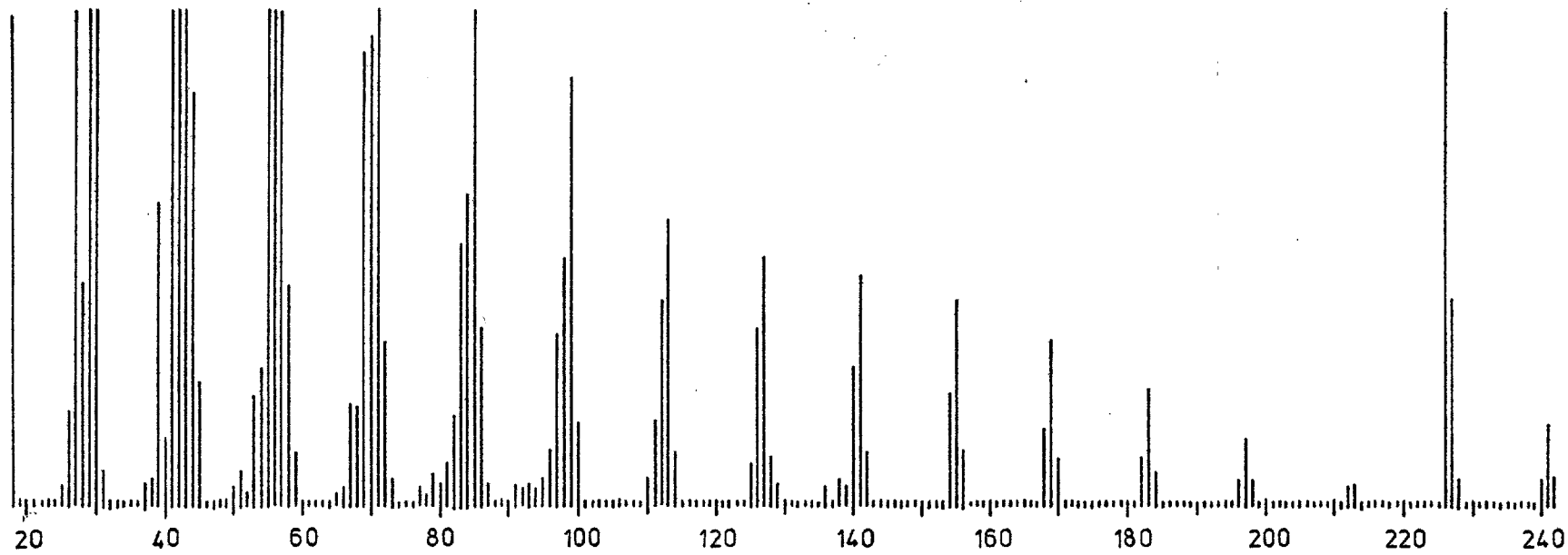


Fig. 6.5 The mass spectrum of a used 2% solution of 1-aminohexadecane in hexadecane.

The significance of this will become apparent when the dichloromethane extract results are discussed. Suffice to say, at this point, that any products which may be formed on the ball or peg surfaces remain there and do not resolve in the bulk liquid. This contrasts with results obtained by Fein[46] who found that organic films produced by cyclohexane on metal surfaces were resolved if flooded liquid lubrication was used. This finding probably influenced later workers who employed vapour phase lubrication to preclude film stripping.

The Dichloromethane Extract. When a solution of 1-aminohexadecane in hexadecane was used as a liquid lubricant, a reaction occurred in the contact which produced new species which were firmly bound to the metal surface. The mass spectrum of this organic layer is shown in fig. 6.6. An interpretation is now presented.

Comparison with fig. 6.4 will facilitate an understanding of the argument. 1-Aminohexadecane, with a m/e ratio of 241, fragments by losing $-NH_2$ to give $C_{16}H_{33}^+$ of m/e 225. Further breakdown is isobaric with hexadecane after loss of $\overset{+}{C}H_3$ leaving $C_{15}H_{31}^+$ (m/e 211). This leads to the series (211 - 14n) together with the isotope peaks and hydrogen loss equivalent peaks at m/e (211 - 14n)+1 and (211 - 14n)-1 respectively. If reaction of the amino group had occurred, the molecular structure $C_{16}H_{33}$ - (G), where (G) is the reaction product grouping, would be expected. This would give a peak, or series of peaks, at m/e ratio greater than 225. Once loss of (G) had occurred, however, the (211 - 14n) series would be expected to dominate. This did not appear to be so as additional peaks below m/e 211, and not corresponding to the above series, occurred. These must contain functional groups. The absence of peaks at 239, 253, 267 etc. indicates that the carbon skeleton has not been increased in length. Neither has there been any chain branching (shown by the unchanged

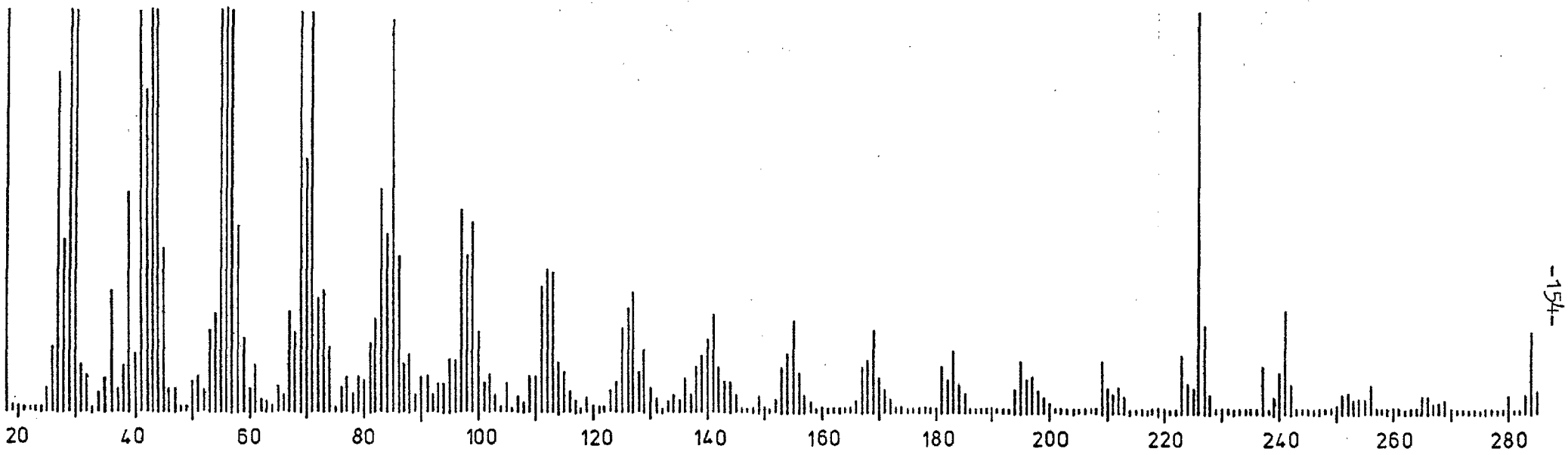


Fig. 6.6 The mass spectrum of the dichloromethane extract when using a 2% solution of 1-aminohexadecane in hexadecane as lubricant.

intensity of the peak at m/e 56 corresponding to $-CH_2-\overset{CH_3}{\underset{|}{CH}}-\overset{+}{C}H_2$, and 70, corresponding to $-\overset{+}{C}H_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2$).

The most interesting peak in the spectrum must be the one at m/e 284. This is by no stretch of the imagination a polymer, nevertheless it shows an unexpected increase in molecular weight. It does not arise from the absorption of carbon dioxide which would give a peak at 303. No peak was found at this m/e ratio. (If the carbonate were formed it would be more likely to be formed in the used lubricant. It was not.)

Alkanes have the general formula C_nH_{2n+2}. The mass of 284 does not correspond to this formula. This, together with the absence of peaks at (269 - 14n), is conclusive evidence that an alkane is not responsible. (The small peak at 269 is due to the impurity $C_{18}H_{39}NH_2$ in the aminohexadecane.)

There are three types of structure which have a molecular weight of 284. They are an alcohol, an acid and an ester. The alcohol is unlikely. There are several reasons for this. They are:

(1) The higher the molecular weight of an alcohol, the less prominent the parent ion peak. Here the peak at 284 is quite intense.

(2) Alcohols fragment in one of two ways, depending on whether the cause is ion bombardment or thermal decomposition. The former gives rise to peaks at m/e ratios of p - 18 resulting from the loss of H_2O, then at (p - 18)-14n from the further loss of CH_2 units. The latter shows a peak at p - 20. This is due to the loss of H_2O, followed by the loss of pairs of hydrogen atoms, and accompanied by ring formation and double bond formation within the rings.

In the extract spectrum no peaks corresponding to either fragmentation mechanism were present. It can be concluded then that an alcohol is not responsible for this peak.

It is improbable that an ester is the source of this peak since esters also have very small parent ion peaks. An ester of formula RCO.OR' fragments to give R^+, $(RCO)^+$, $(CO.OR')^+$ and $(OR')^+$. R^+ and $(RCO)^+$ give peaks isobaric with the corresponding hydrocarbons and so are not easily differentiable. Oxygenated fragments of formula $(OR')^+$ are not prominent in heavy esters but are usually strong in methyl, ethyl and propyl esters. These give peaks at m/e 31, 45 and 59 respectively. In the spectrum under examination there is no peak at 31, but there are already peaks at 45 and 59. There is, however, no difference in the relative intensity between 45 and 59 in the spectra from the extracted and pure samples. Assuming the proportion of each ester is not the same, these possibilities are ruled out. Thus an ester is not the source of the 284 peak.

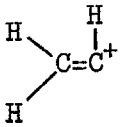
The remaining possibility is an acid. Acids normally do not have large parent ion peaks, but the intensity does increase with increasing molecular weight, a maximum occurring at stearic acid ($C_{17}H_{35}CO.OH$). With heavier molecules the intensity begins to decline. Stearic acid has a molecular weight of 284 which corresponds to the peak of concern here, so it would be expected to be of a fairly large intensity. Carboxylic acids normally fragment by loss of $(OH)^+$ and $(CO.OH)^+$ giving peaks at (p - 17) and (p - 45) respectively. However, the loss of $(OH)^+$ and $(CO.OH)^+$ is much less likely in long chain compounds and the peaks corresponding to this mode of fragmentation are not usually observable. Their absence is compensated for by the anomalously large parent ion peak. In the spectrum being studied here, there are only very small peaks at 267 (p - 17) and 239 (p - 45). Further

fragmentation is by loss of methyl groups to give a series of peaks at (225 - 14n). These are isobaric with hexadecane fragments.

It appears then that the peak at 284 is due to the presence of stearic acid. To check that this interpretation was not incorrect, a simple wet chemical test was applied. A sample obtained in the same manner as the one subjected to the above tests was mixed with dilute aqueous sodium hydroxide solution. The mixture was warmed to effect solution, then cooled to room temperature to eliminate solubility effects. The mixture was filtered, and the filtrate acidified with dilute hydrochloric acid. Opalescence was evident. This is indicative of the presence of acidic groups. Carboxylic acids normally liberate carbon dioxide from sodium bicarbonate solution. Exceptions to this are the long chain fatty acids, of which stearic acid is one. Some difficulty is encountered if only a small amount of acid is used, because then the little carbon dioxide which is liberated may dissolve in the solution so no effervescence is observable. Because of the uncertainty in interpretation of results from this test, it was not attempted.

The small peak at 256 is also probably due to an acid, in this case hexadecanoic acid ($C_{15}H_{31}CO.OH$).

There is a series of peaks, beginning at the upper end with a small peak at m/e 265, and decreasing in multiples of fourteen as far as m/e 27. A structure corresponding to a m/e ratio of 27 is



It seems that this series arises from the presence of a compound, or, because of the increasing intensity with decreasing mass, a series of compounds, containing a terminal double bond. The terminal position was chosen because the peaks go down to 27. If the bond were in the

2- position, the smallest peak would be at m/e 41 from $H_3C-\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}^{+}$. For a double bond in the 3- position the smallest peak would be 55, and so on. There was no evidence from the mass spectrum that the molecule/s contained any other functional groups. A solution of bromine (1%) in tetrachloromethane added dropwise to the extract dissolved in tetrachloromethane was decolourised. This indicates unsaturation and so confirms the presence of double bonds.

As far as could be ascertained, there is a series of peaks at (185 - 14n) due to lower amines. Although fragmentation and rearrangement to form lower amines often occurs in the mass spectrometer, it would be expected that this phenomenon would have been observable in the spectrum of the pure unused material. It was not, so it must be assumed that these amines are generated during sliding.

There are additional peaks at m/e 144, 102, 88 and 74. It is not possible to give exact designations to these peaks. They may be the parent ions of either alcohols or acids. If acids are responsible the mass peak at 60, which corresponds to the following rearrangement,

$$HO.OCCH_2\!\sim\!R\!\sim\!H \longrightarrow HO.OCCH_2H ,$$

would be expected to be more intense than it is. It is more likely that these peaks are due to the presence of alcohols. There is a fragmentation process from an amino-alcohol which gives a peak at 60 corresponding to the unit $H_2NCH_2CH(OH)\!\sim\!R$. This sort of molecule may be the source of these peaks. It is unfortunate that the large intensities of the hexadecane and 1-aminohexadecane fragmentation peaks tend to mask any peaks which might point to which structure is the correct one.

There is one mass peak not yet accounted for, that at 61. The only possible structure which could give this is $HO{:}CH_2-\overset{+}{C}HOH$. It is not at all clear where this fragment could have come from.

From the mass spectrum, then, it seems that there has been a slight increase in molecular weight, associated with oxidation. General oxidation appears to have occurred with the formation of alcohols and acids. At the same time dehydrogenation has also taken place.

An infra-red spectrum confirmed the presence of acid groups, double bonds and alcohols - the latter rather masking the peak expected from the amine which is known to be present.

It is impossible to begin to give reaction mechanisms for all the reactions which must have occurred. Reactions catalysed by solid catalysts are notoriously difficult to explain. The chemical system here is particularly complex in that several metals and metal oxides are present as the solid 'catalyst'. The rubbing of metal surfaces is known to cause the release of electrons[86] or ions[40, 87] from the surface. Free electrons colliding with anything have quite a devastating effect. The one thing which is clear is that the action of sliding is necessary to produce these new chemical species, and they are produced only on the abraded surface and not in the bulk liquid lubricant.

This leads one to expect that the formation of these materials would occur very soon after the commencement of sliding. They must also not be rubbed off, otherwise they would be present in the bulk lubricant. To test this idea balls were removed from the test apparatus at varying intervals after start up and soxhletted. The shortest running time was thirty seconds. It was found that about three minutes was sufficient to produce the quantities obtained in the extended runs. Shorter sliding times gave amounts which were barely discernable. How much had been produced was estimated from the height of the peak at 284 with respect to that at 241. This is a

rather crude criterion since relative peak heights tend to vary from sample injection to sample injection. That the extracted material came from different sets of runs might give rise to some variation in relative intensities. This method was nevertheless selected because of its simplicity.

When balls and pegs were separately analysed for surface coatings, using the extraction method, similar organic materials were found in the wear scars of both. These new substances must be formed by reactions occurring in the contact itself and not by reactions between an abraded surface and the bulk lubricant.

All the previous experiments were repeated using a one per cent solution of the amine. The results were indistinguishable from those obtained using a two per cent solution. The variation in load carrying capacity with concentration observed in earlier tests must therefore be due to the sorption of amine molecules on this 'altered organic layer' and not to the organic layer itself.

6.5 CONCLUSIONS

When using solutions of 1-aminohexadecane in hexadecane as the lubricant in the ball on triplane apparatus, it was found that:

1. The load carrying capacity was higher than for hexadecane used by itself. Increasing the concentration of the amine from one to two per cent increased the scuffing load, whilst increasing the sliding speed led to a decrease in the load carrying capacity.
2. The bulk liquid lubricant underwent no change when used in the test apparatus.
3. There were chemically altered materials formed on both the ball and pegs. This points to reactions occurring at the point of contact during sliding.

4. Sliding was necessary to produce these substances.
5. The film contains acids, alcohols, unsaturated molecules and lower amines. There was only a slight increase in molecular weight from that of the amine (MW 241), to an acid (MW 284). This involved a lengthening of the carbon chain with loss of nitrogen.

No mechanisms for the formation of these new compounds were proposed since the system was so complex and there is little or no reliable data relating to reactions occurring under these sorts of conditions.

Table 6.3 Table of analyses carried out on materials used in chapter 6.

Sample	Analysis				
	Mass spectroscopy	Infra red	Wet chemistry	Melting point	Boiling point
1-aminohexadecane as supplied				*	
Purified 1-aminohexadecane	*			*	*
Pure unused 2% solution of 1-aminohexadecane in hexadecane	*	*			
2% solution of 1-aminohexadecane taken before failure	*				
2% solution of 1-aminohexadecane taken after failure	*				
Used 2% solution of 1-amino-hexadecane	*	*			
Dichloromethane extract of balls and pegs with 2% solution of 1-aminohexadecane	*	*	*		

continued . . .

Table 6.3 (continued)

Sample	Analysis		
	Mass spectroscopy	Infra red	Wet chemistry
Dichloromethane extract of balls only using 2% amine solution	*	*	*
Dichloromethane extract of pegs only using 2% amine solution	*	*	*
Dichloromethane extract blank with 2% amine solution	*	*	
Used 1% amine solution	*	*	*
Dichloromethane extract of balls and pegs using 1% amine solution	*	*	*
Dichloromethane extract of balls only using 1% amine solution	*	*	*
Dichloromethane extract of pegs only using 1% amine solution	*	*	*
Dichloromethane extract blank with 1% amine solution	*	*	

CHAPTER 7

HEXADECAN-1-OL

7.1 INTRODUCTION

Alcohols are common impurities in many hydrocarbons. They may be formed via a peroxide by the reaction of a hydrocarbon with atmospheric oxygen. There are three types of alcohol; primary, secondary and tertiary. Tertiary alcohols are very difficult indeed to oxidise. Secondary and primary alcohols are fairly readily oxidised, secondary alcohols forming ketones, whilst primary alcohols give acids. The latter are of more interest since acids can form soaps with metals and the formation of such soaps is alleged to be responsible for the lubrication behaviour of many acids such as stearic acid.

Because of this interest in the sequence, primary alcohol to acid to soap, it was decided to examine the alcohol, in the absence of any acid, to see if an acid is formed during running, then later to separately look at the corresponding acid.

Hexadecan-1-ol was chosen for study. This consists of the C_{16} straight chain backbone of hexadecane with one of the hydrogens on a terminal carbon replaced by an -OH group.

As with the compound already investigated, the load carrying capacity was determined, followed by tests of extended duration to see if any surface films were formed. The nature of any such films was studied as far as was possible.

7.2 PURIFICATION

The hexadecan-1-ol used was supplied as puriss grade by Messrs. Koch Light Laboratories Ltd.. It appeared as small white spheres of melting point 49 - 50°C.. Purification by repeated recrystallisation from ether yielded a product with a constant melting point of 48.5 - 49°C. (Lit. 49°C.[74]) after two recrystallisations. The purified alcohol appeared as white plates which had a greasy texture. Data concerning the alcohol before and after purification is presented in table 7.1.

Thin layer chromatography using silica gel GF_{254} as absorbent and 40-60 petroleum ether as eluent gave only one spot on the plate, confirming the presence of only one alcohol. Similarly gas liquid chromatography showed one peak.

The mass spectrum, shown in fig. 7.1, gave no evidence for impurities with a molecular weight greater than that of the alcohol. The absence of the parent ion peak, at m/e 242, is quite common for long chain alcohols.

Sample	Property	
	Appearance	Melting Point
As supplied	White spheres	49 - 50°C
After two recrystallisations	White plates	48.5 - 49°C
Literature[74]	White platelets	49°C

Table 7.1 Data on hexadecan-1-ol as supplied and after recrystallisation from diethyl ether.

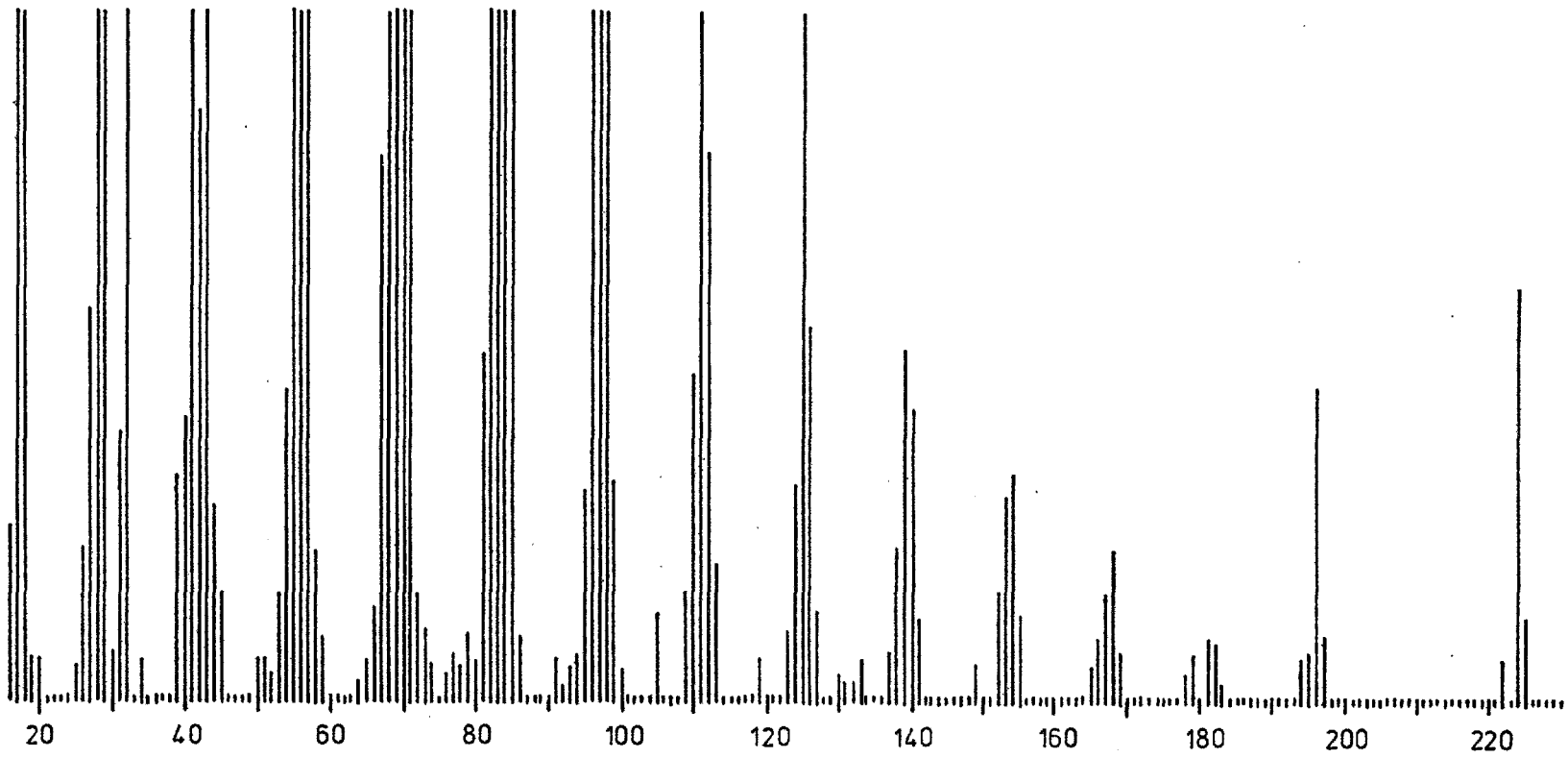


Fig. 7.1 The mass spectrum of purified hexadecan-1-ol.

7.3 DETERMINATION OF THE LOAD CARRYING CAPACITY

7.3.1 Procedure

The method for obtaining the load carrying capacity of a lubricant has been described in some detail already so it will not be repeated here. As with the compounds previously studied, tests were conducted with one and two per cent solutions in hexadecane. All the materials used were carefully purified. Care was taken to avoid any contamination of solutions, balls, pegs and those parts of the triplane apparatus in contact with the lubricant. Copper plating was used to check random samples of balls and pegs to ensure that cleaning had been carried out to the required standard.

7.3.2 Results and Discussion

The results are summarised in table 7.2. Both one and two per cent solutions had the same load carrying capacity at each of the two sliding speeds selected.

Alcohol concentration	Load carrying capacity (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
1%	96	48
2%	96	48

Table 7.2 The load carrying capacity of one and two per cent solutions of hexadecan-1-ol in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

The addition of the alcohol led to a great improvement in the scuffing load as compared to hexadecane used alone, an improvement almost certainly due to the more facile, and stronger, sorption of alcohol molecules onto the steel surfaces. That the failure loads were the same for both solution concentrations indicates that saturation of the surface by alcohol molecules occurs at, or, more likely, below a liquid phase concentration of one per cent. Later studies show that a new species was formed on the surface of the ball and pegs, so the actual system, shown in fig. 7.2, is not unlike the one proposed for 1-aminohexadecane.

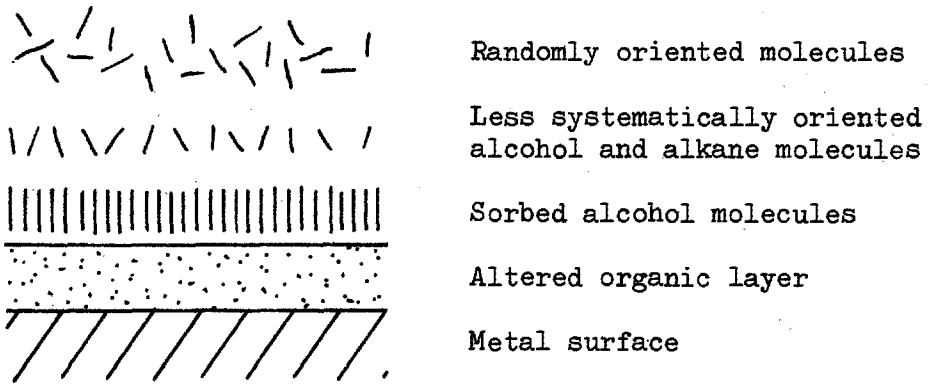


Fig. 7.2 The suggested surface structure produced when a solution of hexadecan-1-ol in hexadecane is used as the lubricant.

The decrease in failure load with increasing speed was attributed to the more violent asperity contacts causing the denudation of sorbed films from the metal surfaces and allowing metal to metal contact and scuffing.

The scuffing load at a sliding speed of 1.09 ms^{-1} is half that at 0.43 ms^{-1}. This ratio was observed for solutions of 1-aminohexadecane but not for 1-hexadecene or hexadecanoic acid. This was considered to be a coincidence and no significance was attached to it.

In all cases the lubricant remaining after failure appeared very pale yellow to colourless. A sample was taken from one of the tests conducted with a two per cent solution at a sliding speed of 0.43 ms^{-1}. This particular sample was chosen because it contained a relatively high concentration of alcohol, and it had been heated, by friction, to 100°C.. It was hoped that it had gone through more change than any other sample so the quantity of new products would be maximised. When its mass spectrum was compared to that of an unused two per cent solution an interesting fact emerged. The intensities of peaks attributable to the alcohol were increased, suggesting the generation of more alcohol in the bulk liquid lubricant during testing. This is confirmed in the next section.

7.4 DICHLOROMETHANE EXTRACTION STUDIES

7.4.1 Introduction

Dichloromethane extraction studies were carried out in the same way as already described for each of the compounds so far investigated. Hexadecanol was found to be particularly reactive, and for this reason great care was taken in the execution of blank experiments to ascertain the source of any new materials formed. For ease of analysis a two per cent solution was used throughout.

7.4.2 Blank Tests

A series of experiments was devised to discover what factors could be responsible for the formation of new chemical species. The

tests, and their results, were as follows.

(1) A few drops of a two per cent solution of hexadecan-1-ol in hexadecane at around 120°C. were added to about 250 ml of dichloromethane and the mixture refluxed for twenty four hours. The dichloromethane was vacuum stripped and the remaining liquid analysed using mass spectroscopy.

The mass spectrum was indistinguishable from that of a sample of unused alcohol solution, showing that the dichloromethane is unreactive towards the alcohol. (It has already been shown that it does not react with hexadecane.) It may also be concluded that heating the alcohol solution to the boiling point of dichloromethane (40.2°C.) has no noticeable effect. The presence of steel may alter the situation so the following experiment was performed.

(2) The soxhlet apparatus was set up with dichloromethane as the solvent. Six hot clean balls and eighteen hot clean pegs were each dipped into a pure two per cent hexadecanol solution and then placed in the soxhlet. Soxhletting was continued for twenty four hours after which time the solvent was removed by vacuum distillation and the mass spectrum of the remaining few drops of liquid obtained.

No change had occurred. This is strong evidence that the soxhlet extraction procedure in no way alters the hexadecanol solution. Any new products detected after running in the triplane apparatus must result from the test conditions used.

(3) A solution of hexadecan-1-ol in hexadecane (2%) was heated to 125°C. and held at that temperature for eight hours. The solution was then rapidly cooled to prevent further reactions and a mass spectrum obtained.

The temperature selected, 125°C., was the equilibrium running temperature of the triplane apparatus. The solution, after such

treatment, was pale yellow. The intensity of colour was about the same as that of a sample of used lubricant taken after the conclusion of a load carrying capacity test. The mass spectrum was interesting in that the peaks due to the alcohol, notably the one at m/e 224 (due to loss of water), were all of considerably greater intensity than in the spectrum of pure unused solutions. The mass spectrometer had not, up till now at least, shown behaviour to suggest that this change was a machine effect. It must be concluded that there was more alcohol present after heating than in the original solution. This implies that once some alcohol is present as an impurity in an alkane, heating causes generation of more alcohol. (Heating carefully purified hexadecane by itself did not show any signs of alcohol formation.)

This observation is of importance from a practical point of view since it suggests that if an alcohol free system is required, great care must be taken to ensure that there is absolutely no alcohol present to begin with, otherwise significant quantities of alcohol may be produced. It may be that previous workers who have taken hexadecane as a base stock, but who have not taken considerable care in its purification, may have been observing the effects of very dilute solutions of hexadecanol in the alkane.

(4) The above experiment was repeated, but a number of EN31 steel balls and pegs were introduced into the solution during heating.

The physical appearance of the solution was the same as in the previous test. The mass spectrum was also similar. It seems therefore that the presence of the steel had no effect.

Conclusions. These blank tests indicated that

(i) The soxhlet extraction procedure did not have any effect on solutions of hexadecan-1-ol in hexadecane.

(ii) There was a change caused by heating the alcohol solution

whether or not steel was present. The effect appears to be the generation of more alcohol. As far as operation of the triplane apparatus is concerned, the heat generated by friction could well cause the production of more alcohol, so that its concentration at any time is unknown.

(iii) There were no new compounds formed. This considerably simplifies interpretation of the dichloromethane extraction studies.

7.4.3 Procedure

The triplane test apparatus was operated at a sliding speed of 0.43 ms^{-1} with a two per cent solution of hexadecan-1-ol in hexadecane as the test lubricant. After running-in in the normal manner, the top ball load was set and maintained at 69 kg. The test was continued for four hours. The balls and pegs from six runs were soxhletted together in dichloromethane for twenty four hours. The residue after vacuum distillation of the dichloromethane, together with samples of the unused and used lubricant, were subjected to mass spectroscopy. A separation of the components of the extract was attempted using gas liquid chromatography. This was later modified by using a mass spectrometer as the detector.

All the normal precautions for avoiding contamination were taken. Copper plating was used to check that the extraction process had been efficient.

The diameters of the wear scars on the pegs were recorded.

7.4.4 Results and Discussion

Copper plating tests. The ball and pegs were taken from the triplane apparatus after extended running but were not soxhletted. Instead they were rinsed quickly with ether and submerged in the copper

plating solution. Copper was observed to be evenly deposited over the whole of the surfaces except for the wear scars. No copper was deposited on these worn regions. From this preliminary test it would be expected that some material, possibly newly formed, will be detected in the dichloromethane extract.

After soxhlet extraction using another ball and pegs, the whole surface of the ball and pegs was evenly plated with copper. Soxhletting must have removed the films from the wear scars.

The used lubricant. The mass spectrum of a sample of the used lubricant is shown in fig. 7.3. Fig. 7.4 shows the spectrum given by an unused freshly prepared sample of the alcohol solution. It is from the same batch as used in the triplane tests.

No new peaks are present, but the peaks which arise from the alcohol are more intense. This behaviour was observed when a sample of unused hexadecanol solution was heated by itself; infact the spectrum given by both were almost indistinguishable.

It can be concluded that running in the triplane apparatus generated no new products in the bulk lubricant, but it did increase the concentration of the alcohol in the bulk lubricant, the latter being a result of frictional heating. Any products formed on the surfaces of the balls or pegs must not be resolved in the bulk liquid lubricant but must remain firmly bound to the metal surfaces.

The dichloromethane extract. The copper plating tests indicated that the residue after extraction might well show new products. This is confirmed by the mass spectrum of fig. 7.5. This is clearly a very complex spectrum. Interpretation would be simpler if the number of components could be determined. It would be even better if the molecular weights of each component could also be ascertained. To this end a sample was initially subjected to gas liquid chromatography to

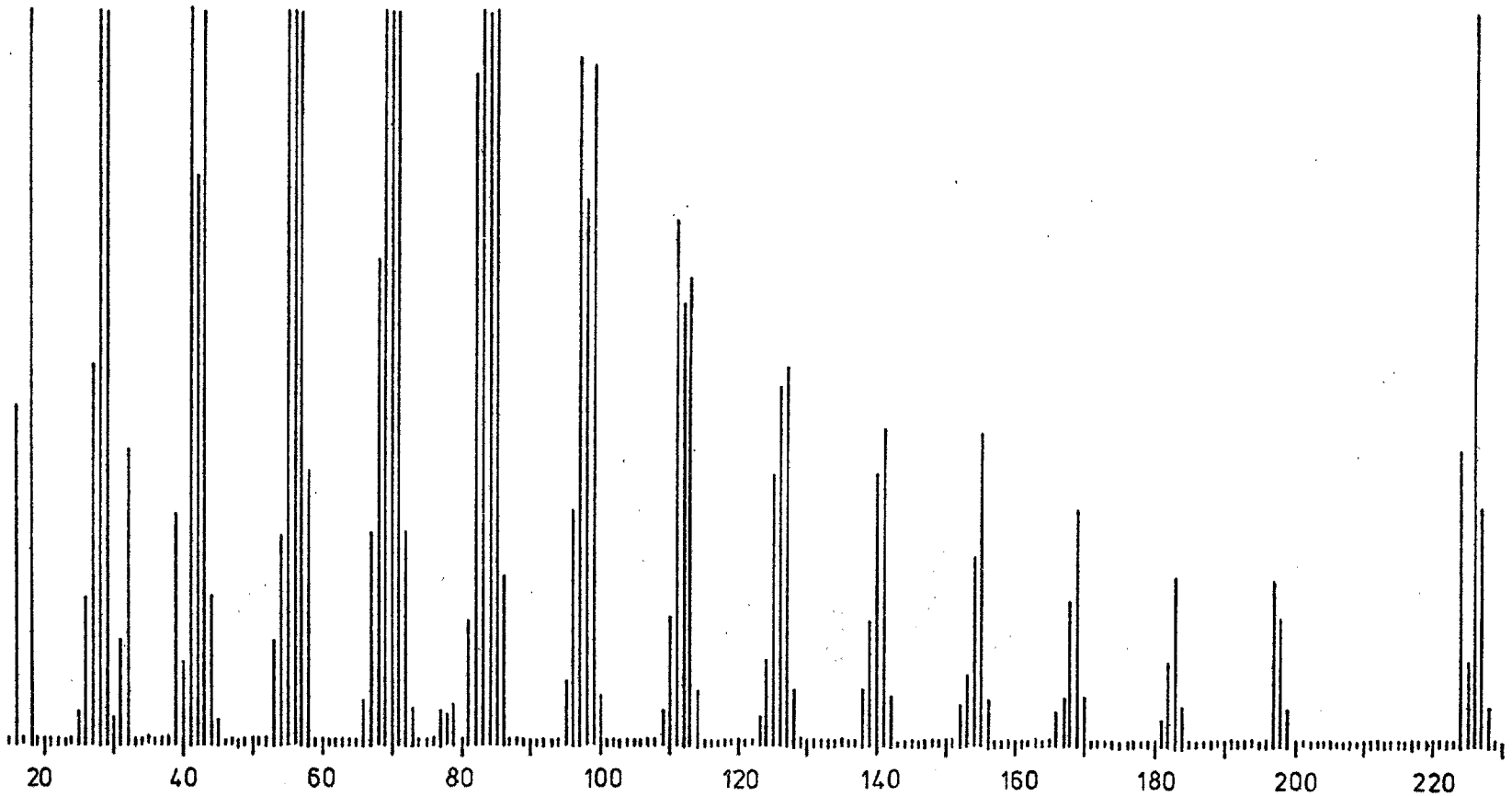


Fig. 7.3 The mass spectrum of a used 2% solution of hexadecan-1-ol in hexadecane.

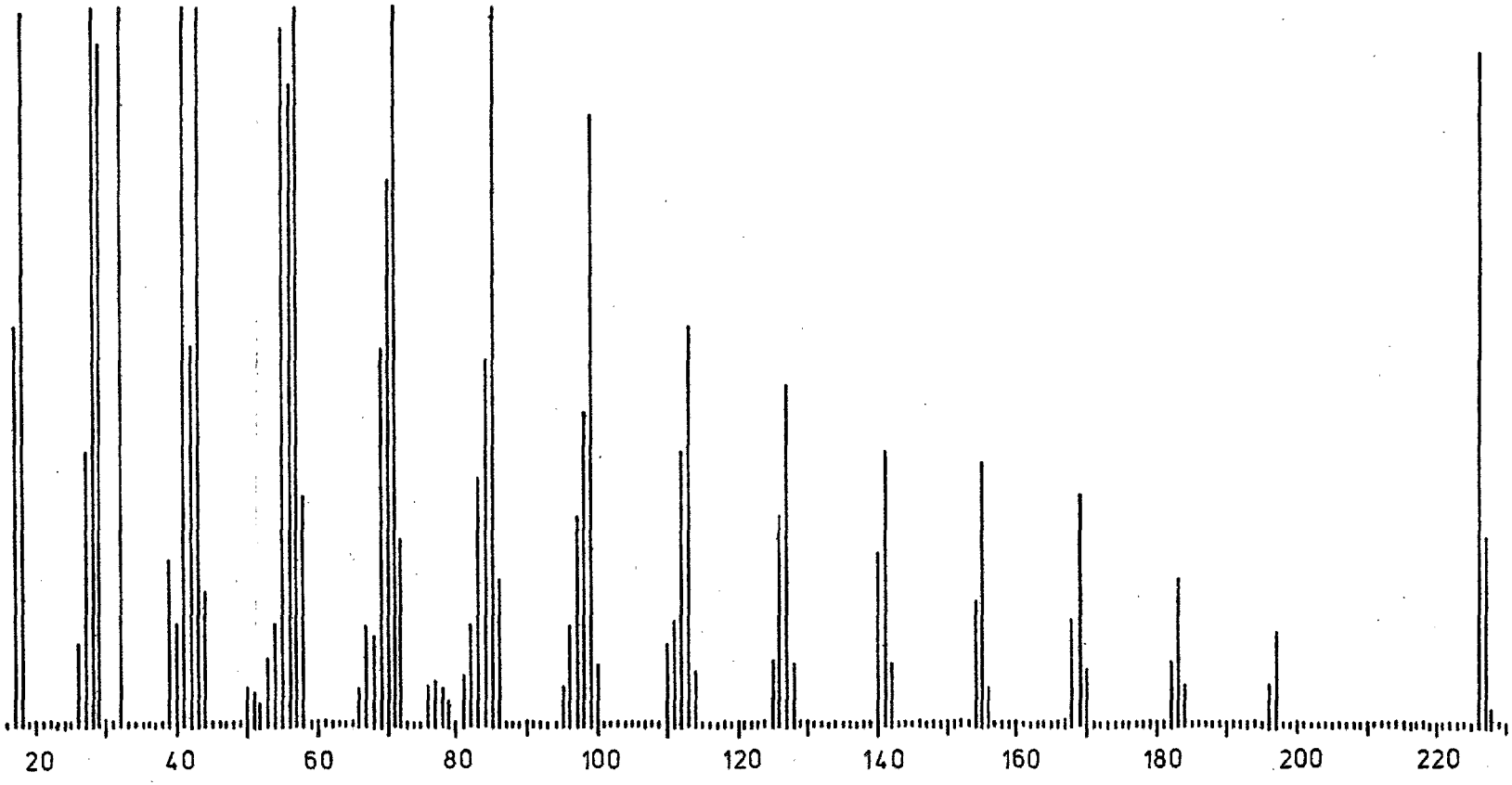


Fig. 7.4 The mass spectrum of a pure unused 2% solution of hexadecan-1-ol in hexadecane.

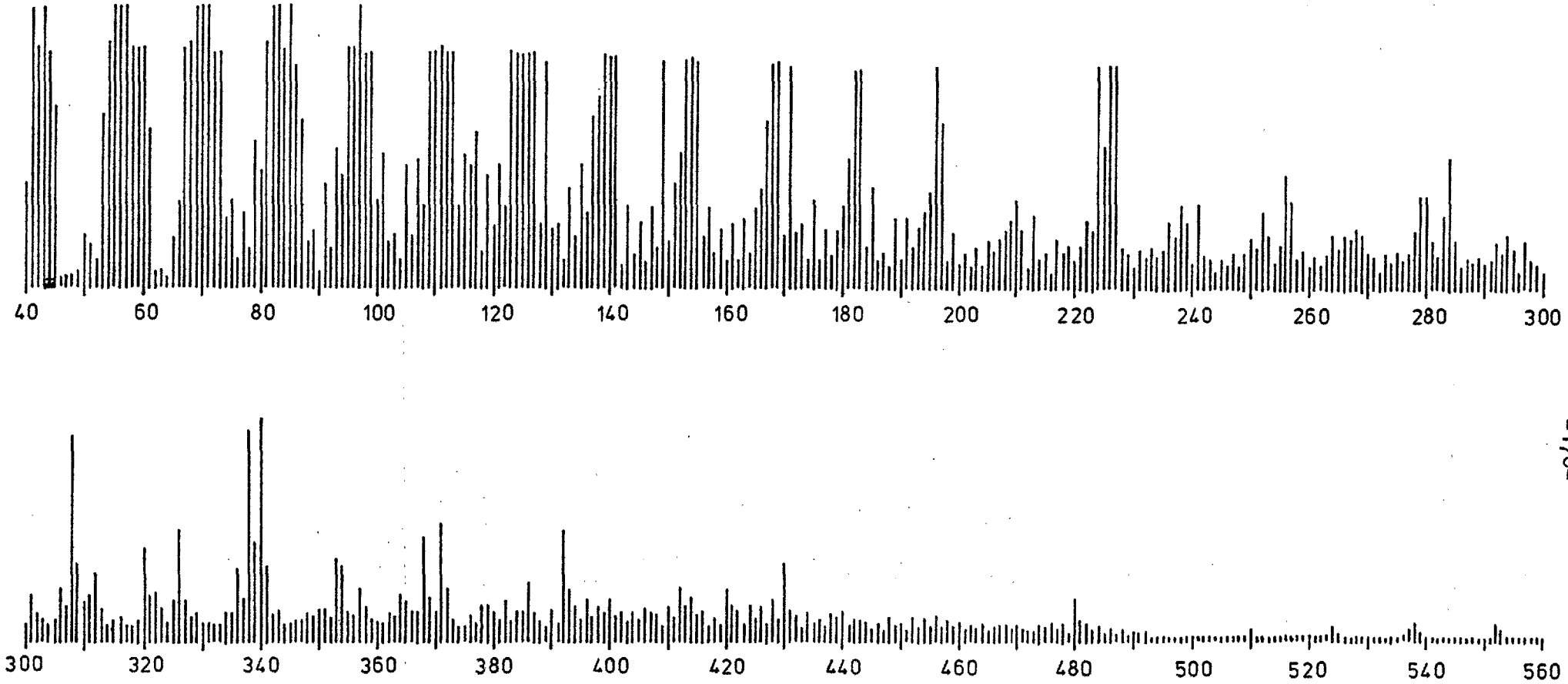


Fig. 7.5 The mass spectrum of the dichloromethane extract when using a 2% solution of hexadecan-1-ol in hexadecane as lubricant.

try to find out how many components were present. This was later modified by interfacing a GLC unit with a mass spectrometer. Chromatography separates the components of a mixture but the detector, commonly a hot wire or flame ionisation detector, destroys the product after separation. By using a mass spectrometer as the detector the molecular weight of each component can be discovered.

The ideal system of GLC/mass spectrometry proved unproductive of useful information. Many metres of photosensitive paper yielded only a handful of rather small peaks to which no meaning could be given.

Gas liquid chromatography used by itself did produce some information. Separation was attempted on two different column materials. One was Carbowax 6000 supported on Chromosorb W, a column which separates components according to polarity. The other column was packed with Apiezon L on Chromosorb P which gives a molecular weight separation. (Details of the conditions used are given in Appendix I.) The use of both columns provides information about how many compounds have molecular weights above or below that of hexadecanol, and the number of compounds more or less polar than the alcohol. (Hexadecanol was used as a known datum point.) Unfortunately no relationship between polarity and molecular weight is indicated. The results using the Carbowax column suggested that there were no materials present in the extract which were not present in the pure unused solution. This was not borne out by the mass spectroscopy data. It can only be assumed that either the conditions were such that elution did not occur, i.e. the products were very polar indeed, or the conditions selected for separation were not suitable. Many combinations of oven temperature programmes, gas flow rates and injection temperatures were tried, but still no separation was achieved.

The Apiezon column did effect a separation, but only one new

product was detected. The separation was found to be possible only under one set of conditions, those described in appendix I. Despite the use of other combinations of carrier gas flow rate and oven temperature programmes, the hexadecanol could not be eluted so no estimation of the concentration of this new material could be made.

In an attempt to elute hexadecanol a different column material, Silicone fluid 550 plus Bentone 34 on Chromosorb W, was tried (Appendix I). This sorbent tends to separate components according to their molecular weight. This column gave results which confirmed the findings when using the Apiezon column; but again the hexadecanol was not eluted.

If the gas chromatography experiments are to be taken at face value, only one new product has been formed and its concentration is unknown. The mass spectrum argues strongly against this.

Although an attempt was made to elucidate the nature of the individual species giving rise to the mass spectrum, it was found to be impossible. In trying to associate the various peaks with each other it was concluded that there are probably at least ten new species formed. This represents the higher molecular weight materials, there may be even more if lower homologues were to be taken into account. The smaller molecules could not be detected because of the almost continuous spectrum of high intensity peaks resulting from the higher molecular weight products. Machine variations would also become more significant when very small differences in peak height need to be determined.

It was however concluded that the following types of compounds were present.

Alkynes. These may be formed by the catalytic effect of chromium (III) oxide on a carbon chain. The triple bonds are probably

in the terminal position.

Di-alkynes. These are compounds of the form H-C≡C-C≡R. It is known that they are formed when a copper alkyde is oxidised by atmospheric oxygen. Although copper is supposedly absent, there may be enough present for this reaction to occur or it may proceed via another transition metal alkyde. Alternatively the di-alkyne might be formed directly by catalytic effects of the chromium in the EN31 steel.

Alkenes. The double bond is present in the terminal position. It may also occur in other positions in the carbon chain. There were so many peaks that fragmentation processes from non 1,2 unsaturated compounds, although suspected, could not be conclusively proven. The alkenes may be formed by the catalytic effect of the steel surfaces.

Dienes. These may be produced by the same type of reaction as the alkenes.

Aromatic rings. Again these may be formed by the catalytic effects of the EN31 steel surface.

Alcohols. Both primary and secondary alcohols were detected. Clearly since hexadecan-1-ol is known to be present, the occurrence of primary alcohol fragments would not be unexpected. However this does show that not all the alcohol is oxidised. The secondary alcohols were possibly formed by the effect of water on alkenes, though they may also result from oxidation by molecular oxygen.

Diols. There was evidence for species of the form $HO\text{-}C_2H_4.OH\sim R$. These must be formed by general oxidation of the lubricant solution.

Acids. Acids are readily formed by the oxidation of primary alcohols. The acids detected were all long chain acids, the molecular weights apparently increasing to around 500.

Esters. The presence of both acids and alcohols would be expected to lead to esters. The ester between hexadecan-1-ol and its

corresponding acid, hexadecanoic acid, was formed. It has a molecular weight of 480. Other esters of both shorter and longer chain alcohols and acids were also present.

The presence of the above groupings was confirmed by infra-red spectroscopy.

Many different reactions must have occurred to have produced this range of compounds. Since the products were only detected on the worn surfaces of the balls and pegs, the reactions must have been catalysed by sliding.

Balls and pegs were run in the triplane apparatus but subjected to soxhlet extraction separately. The mass spectra of the extract residues were much the same as the one discussed here, suggesting that very similar products were formed on the wear scars of both the balls and pegs.

7.5 CONCLUSIONS

On the basis of the experimental results obtained using the triplane apparatus, the following conclusions were reached.

1. (a) The addition of small amounts (1% - 2%) of hexadecan-1-ol to hexadecane significantly improved its load carrying capacity.
   (b) Increasing the sliding speed caused a decrease in the scuffing load.
   (c) The quantity of hexadecanol required to improve the load carrying capacity was less than one per cent.
   (d) A model for the 'structure' of the contact was described which involved a metal surface on which was formed an 'altered organic layer'. Hexadecanol and hexadecane molecules were sorbed on top of this film, the order decreasing with increasing distance from the surface.

2. Copper plating tests showed that the 'altered organic layer' was present on both the ball and pegs, but only in the wear scars, and it could be removed by soxhlet extraction.

3. No new compounds were formed in the bulk liquid lubricant, though the concentration of the alcohol was probably increased.

4. (a) Dichloromethane extraction studies showed that the 'altered organic layer' contained compounds with molecular weights up to 550.

   (b) The actual compounds present were not elucidated, but there were at least ten, including alkynes, di-alkynes, alkenes, dienes, aromatic compounds, alcohols, diols, acids and esters.

   (c) Gas liquid chromatography failed to satisfactorily separate the mixture.

5. Blank tests indicated the following;

   (a) The increase in alcohol concentration in the bulk lubricant was due entirely to the effect of heat.

   (b) Sliding was necessary for the production of the material detected in the extraction studies.

6. Similar organic films were produced on the wear scars of both balls and pegs.

Table 7.3 Analyses carried out on materials used in chapter 7.

Sample	Analysis		
	Mass spectroscopy	Infra red	Melting point
Hexadecan-1-ol as supplied	*		*
Purified hexadecan-1-ol	*		*
Pure unused 2% solution of hexadecanol in hexadecane	*	*	
2% solution of hexadecanol after scuffing	*		
2% solution of hexadecanol before scuffing	*		
Used 2% solution of hexadecanol in hexadecane	*	*	
Dichloromethane extract using 2% solution of hexadecanol in hexadecane	*	*	
2% solution of hexadecanol heated alone to 125°C	*		
2% solution of hexadecanol heated with EN31 steel	*		
Hot 2% hexadecanol solution added to dichloromethane	*		
Blank dichloromethane extraction	*	*	

CHAPTER 8

HEXADECANOIC ACID

8.1 INTRODUCTION

Hexadecanoic acid, $C_{15}H_{31}CO.OH$, is the oxidation product of hexadecan-1-ol. When hexadecanol solutions were used as the lubricant in the triplane apparatus, this acid was found on the wear scars of the balls and pegs. It was considered interesting to find out whether the multitude of products obtained when using the alcohol were similarly produced by the acid. Acids such as stearic acid, $C_{17}H_{35}CO.OH$, are often used as additives in research work, so from this point of view also, it was thought useful to study the solutions of hexadecanoic acid.

This particular acid was chosen because it is a C_{16} molecule, which facilitates the interpretation of mass spectra. As with the materials already examined, the load carrying capacity of one and two per cent solutions in hexadecane were determined at two sliding speeds, 0.43 ms^{-1} and 1.09 ms^{-1}. Dichloromethane extraction was carried out on balls and pegs removed from the triplane rig after tests of extended duration.

8.2 PURIFICATION

1-Hexadecanoic acid, supplied by Koch Light Laboratories Ltd., was purified by recrystallisation from 60/80 petroleum ether, until a constant melting point of 62.5° - 63°C (Lit. 63° - 4°C [74]) was

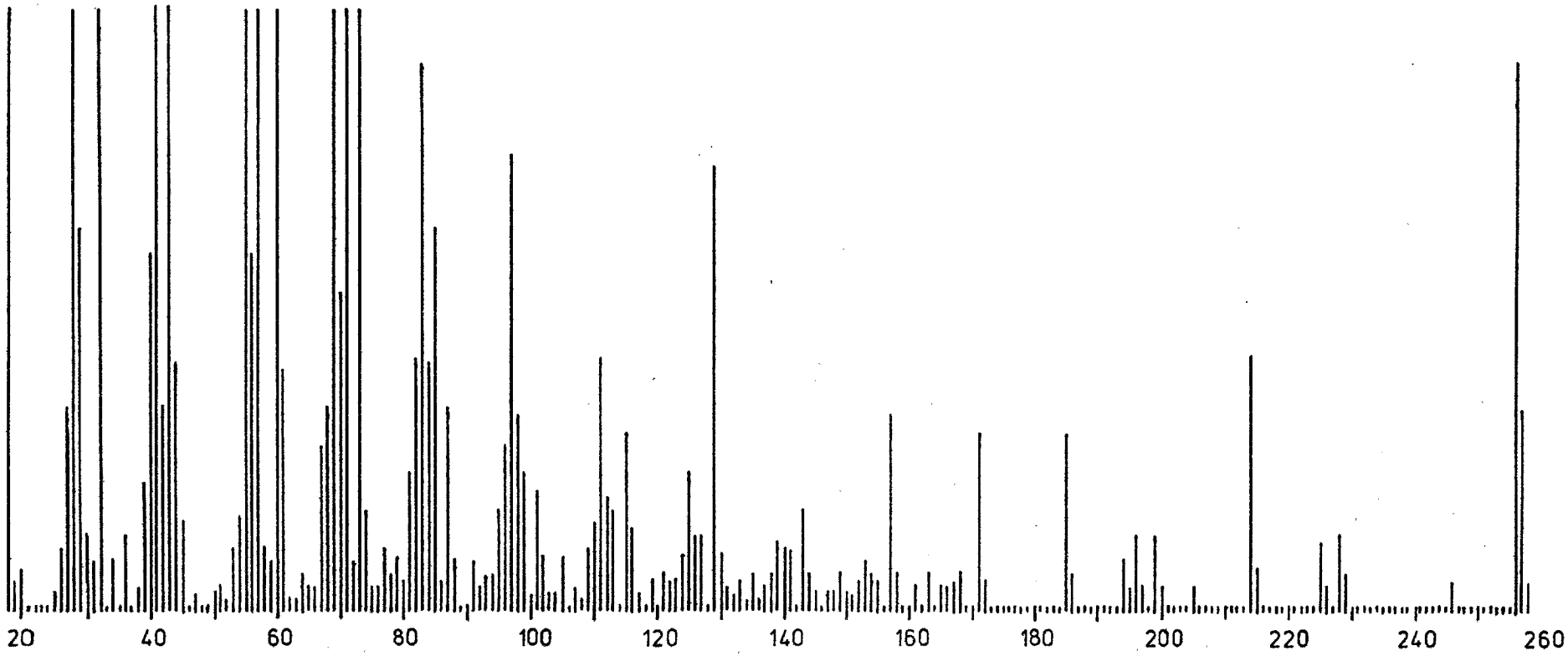


Fig. 8.1 The mass spectrum of purified hexadecanoic acid.

obtained. The purified product appeared as white platelets with a greasy texture. The mass spectrum of the purified material (fig. 8.1) showed the fragment peaks expected. There were no peaks of m/e ratio greater than 256, the molecular weight of the acid (except peaks caused by heavier isotopes of the elements present). Purified acid was used to make up all the solutions tested in this study.

8.3 THE DETERMINATION OF THE LOAD CARRYING CAPACITY

8.3.1 Results and Discussion

The load carrying capacity of one and two mole per cent solutions of the acid in purified hexadecane were determined using the triplane apparatus in the normal manner. Two sliding speeds were employed, 0.43 ms^{-1} and 1.09 ms^{-1}. The results are shown in table 8.1.

The load carrying capacity of both solution concentrations was the same. In each case increasing the sliding speed caused scuffing to occur at a lower load. The latter has been observed for all the

Acid Concentration	Load carrying capacity (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
1%	83 (117)*	41
2%	83 (124)*	41

* see text.

Table 8.1 The load carrying capacities of 1% and 2% solutions of hexadecanoic acid in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

solutions so far studied and has been attributed to earlier rupture of boundary films with the more violent asperity contacts at higher sliding speeds.

Table 8.1 shows two scuffing loads for each solution concentration at the lower sliding speed, but just one at the higher speed. When the sliding rate was 1.09 ms^{-1} failure occurred on increasing the applied load, in other words the coefficient of friction went up and remained high (0.09 to 0.3). Failure had clearly occurred. However when operating at the lower speed mild scuffing was detected at applied loads of 83 kg and above, but recovery was fairly rapid, usually in less than fifteen seconds. The coefficient of friction before any scuffing occurred was typically 0.07, but after an initial increase on scuffing it decreased to about 0.1 and thereafter remained constant. Any further increase in load was again accompanied by mild scuffing but recovery was fairly rapid. The value for the top ball load shown in brackets was the applied load at which recovery no longer occurred.

This behaviour is very different from that of solutions of hexadecanol which exhibited well defined scuffing loads. Hexadecanol was shown to form an organic layer at the metal - metal contact, so scuffing might be expected to occur when this film was ruptured, but on the other hand, as will be shown later, hexadecanoic acid did not form such a layer. It is quite likely therefore that the behaviour of the acid was controlled by its physisorption onto the metal surfaces. The higher total failure load given by the more concentrated solution might result from the more rapid adsorption of the acid to renew any breaks in the adsorbed film caused by mild metal - metal contact.

8.4 COPPER PLATING TESTS

8.4.1 Procedure

The triplane apparatus was operated, after running in, for four hours using EN 31 pegs and ball with a top ball load of 69 kg and a sliding speed of 0.43 ms^{-1}. The lubricant was a two per cent solution of hexadecanoic acid in hexadecane. At the end of the test the apparatus was allowed to cool, then the ball and pegs were removed, and after quickly rinsing in ether were immersed in the copper plating solution.

A blank test was also conducted to show that copper would not plate out even if hexadecanoic acid were present on the surface. A clean ball was dipped in a pure two per cent acid solution, and after allowing excess solution to drip off was submerged in the plating solution.

8.4.2 Results and Discussion

The balls and pegs taken from the triplane apparatus had an even film of copper deposited over the whole of their surfaces - including the wear scars. This would lead one to expect that the dichloromethane extract would contain no new compounds. (The ether washings did not contain any new substances.)

The ball which was merely dipped in the acid solution did not show any evidence of copper plating on the surface. This rules out the possibility of a soluble copper salt being formed, which would, once it had dissolved, allow copper to plate onto the substrate steel surface. (Hexadecanoic acid itself is insoluble in water.)

8.5 DICHLOROMETHANE EXTRACTION STUDIES

8.5.1 Procedure

The operating conditions for the triplane apparatus were as described above. After four hours running the ball and pegs were taken hot from the rig, and, together with the balls and pegs from five other runs, were soxhletted in dichloromethane for twenty four hours. The residue after removal of the dichloromethane was subjected to mass spectroscopy. The mass spectrum of a sample of the used lubricant was also obtained, together with that of the pure unused two per cent acid solution for reference purposes.

8.5.2 Results and Discussion

The Used Lubricant. The used lubricant was colourless. Its mass spectrum is shown in fig. 8.2. It is identical to that of the pure unused two per cent hexadecanoic acid solution (fig. 8.3). It appears that the acid solution underwent no change as the bulk lubricant.

The Dichloromethane Extract. There were no new compounds detected in the dichloromethane extract, but it did appear to contain more acid than the pure unused solution. This was deduced from the increased intensity of the mass peaks attributable to the acid (fig. 8.4). The hexadecanoic acid must have been physisorbed on the steel surfaces during running in the triplane apparatus, and then have been stripped off by the dichloromethane, resulting in an increase in its concentration in the extract.

It was impossible to determine exactly where on the ball and peg surfaces the acid was sorbed, since, after rinsing with ether, copper plated out over the whole surface of the ball and pegs. Simply wiping the ball and pegs with a tissue also enabled copper to plate out over the whole surface. Electron probe microanalysis was not tried since as soon as a ball were handled the acid would be removed and probably

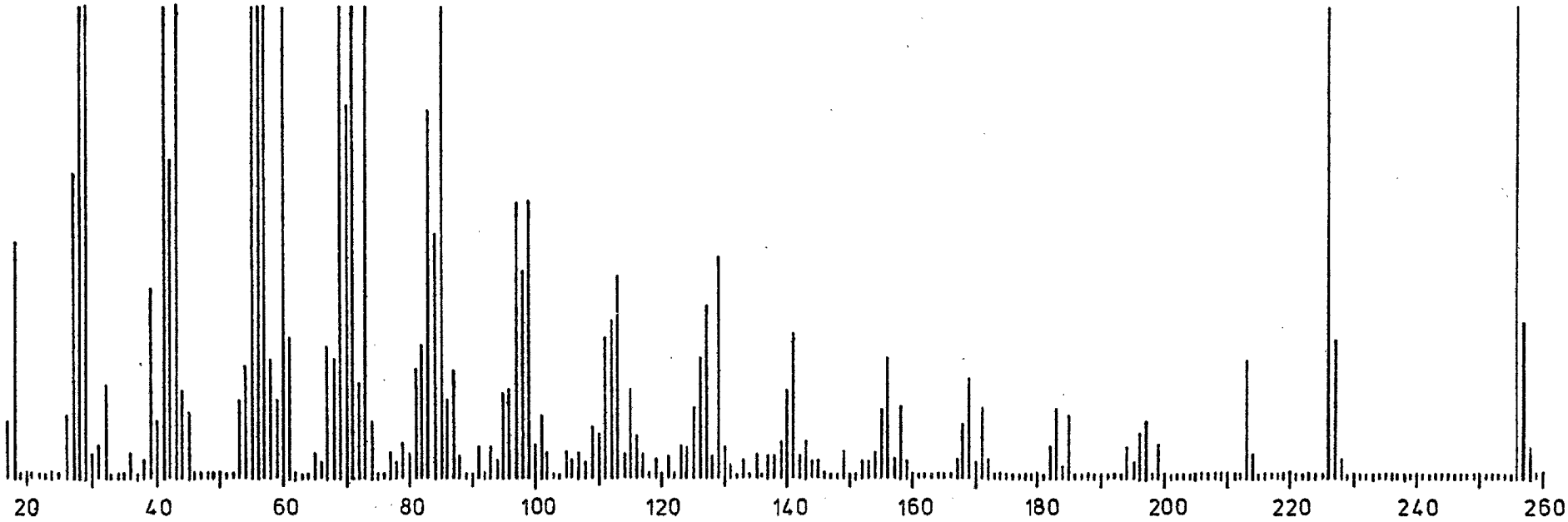


Fig. 8.2 The mass spectrum of a used 2% solution of hexadecanoic acid in hexadecane.

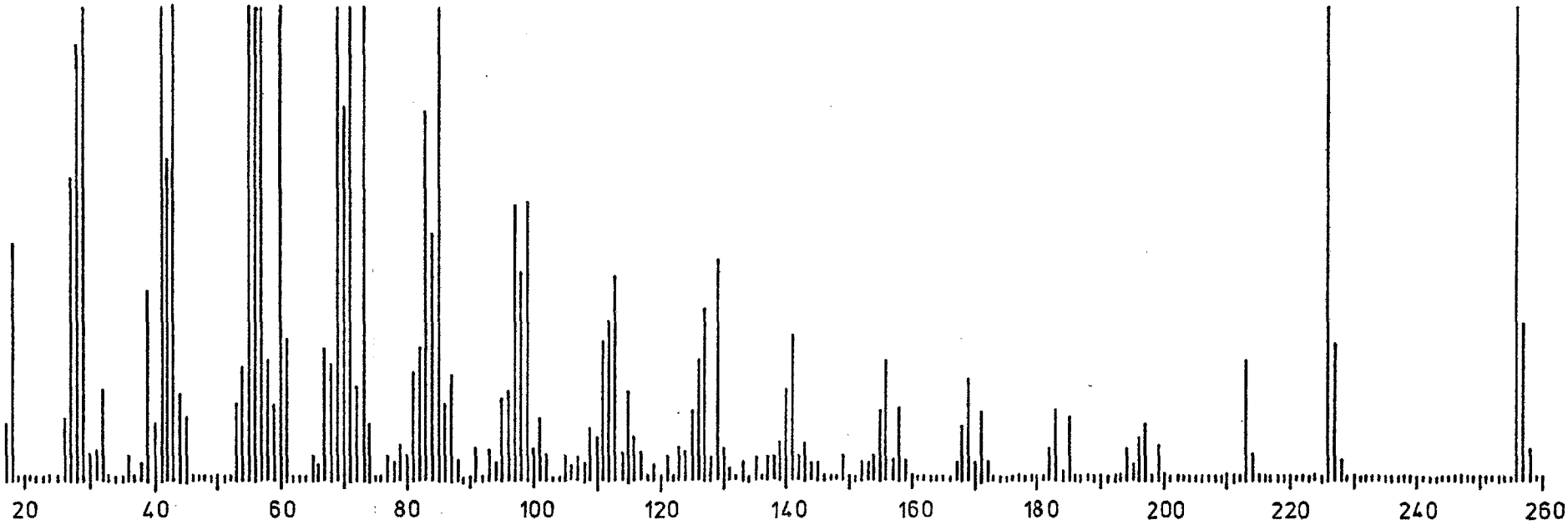


Fig. 8.3 The mass spectrum of a pure unused 2% solution of hexadecanoic acid in hexadecane.

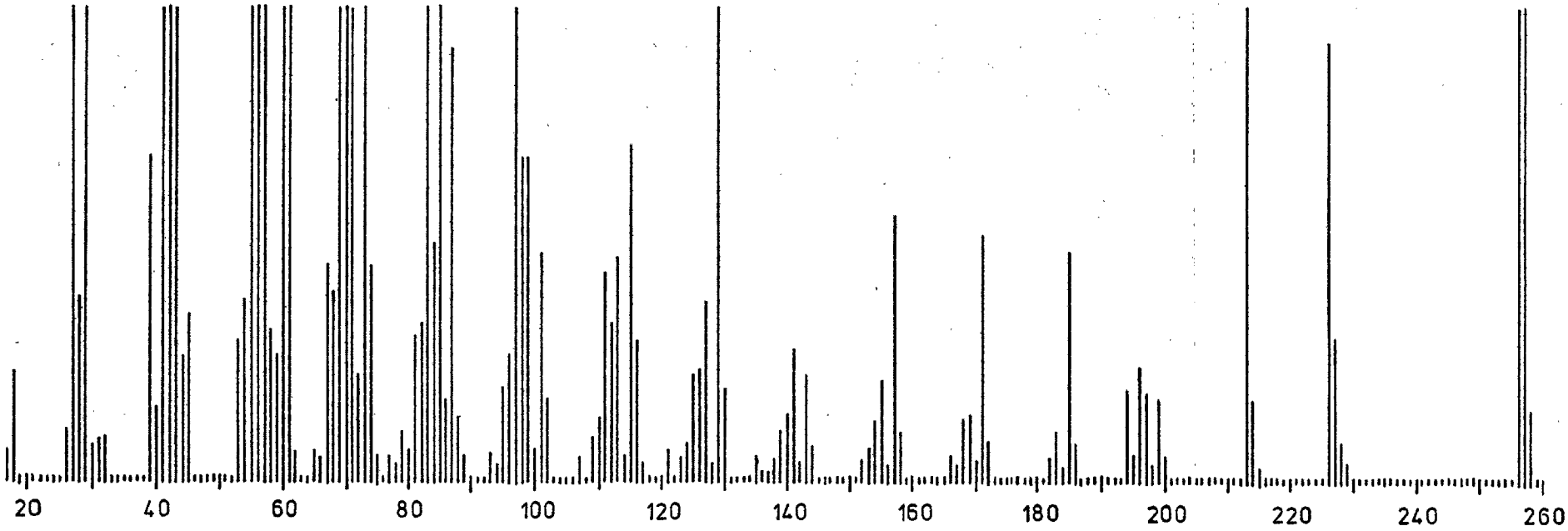


Fig. 8.4 The mass spectrum of the dichloromethane extract when using a 2% solution of hexadecanoic acid in hexadecane as lubricant.

be replaced by amino acids from the skin.

8.6 CONCLUSIONS

The following conclusions were reached.

1. (a) The addition of small quantities of hexadecanoic acid to hexadecane increased its load carrying capacity.
   (b) The improvement was due to the adsorption of acid molecules onto the metal surfaces.
   (c) Increasing the sliding speed decreased the load carrying capacity.
2. Copper plating tests showed that there was no chemisorbed film anywhere on the ball or peg surfaces.
3. A sample of the bulk lubricant taken after extended running was found to be unchanged.
4. Dichloromethane extraction showed that hexadecanoic acid was preferentially adsorbed onto the metal surfaces - no new compounds were formed.

Table 8.2 Analyses carried out on materials used in chapter 8.

Sample	Analysis	
	Mass spectroscopy	Melting point
Hexadecanoic acid as supplied		*
Purified hexadecanoic acid	*	*
Pure unused 2% solution of hexadecanoic acid in hexadecane	*	
Used 2% solution of hexadecanoic acid in hexadecane	*	
Dichloromethane extract blank	*	
Dichloromethane extract using 2% solution of hexadecanoic acid in hexadecane	*	
Ether washings after rinsing used ball and pegs prior to copper plating test	*	

CHAPTER 9

HEXADECYL HEXADECANOATE

9.1 INTRODUCTION

Esters have found considerable use as base stocks for gas turbine lubricants, and now for automotive oils because of their low viscosity and subsequent lower power losses. Unfortunately they tend to have low scuffing loads so have to be considerably bolstered up by the addition of various additives. Because of the importance of esters it was decided to test an ester to see if any change in molecular weight occurred. The ester chosen, hexadecyl hexadecanoate, was selected because information was already available concerning the alcohol and acid from which it was prepared.

9.2 THE PREPARATION OF PURE HEXADECYL HEXADECANOATE

9.2.1 Method

Hexadecyl hexadecanoate was prepared by the esterification of an equimolar mixture of puriss hexadecan-1-ol and hexadecanoic acid in the presence of p-toluene sulphonic acid as a catalyst. The acid and alcohol were refluxed in xylene for four hours, the water produced being removed as the reaction proceeded. The xylene was stripped off under vacuum leaving a brown liquid. A little anhydrous calcium chloride was added to remove any unreacted alcohol. After filtration the liquid was allowed to cool to give a white solid. This was

recrystallised from diethyl ether until a constant melting point of 53.5 - 54°C. was obtained (Lit. 51-2°C.[74]). The purified product consisted of white plates.

To check that the purified ester contained no residual acid it was titrated with alcoholic potassium hydroxide in accordance with ASTM standard D 974 - 64 (IP 139/65). No acid was found to be present.

The mass spectrum (fig. 9.1) showed only those peaks expected from hexadecyl hexadecanoate. The largest m/e ratio, 480, is the molecular weight of the ester.

9.3 DETERMINATION OF THE LOAD CARRYING CAPACITY

9.3.1 Results and Discussion

The load carrying capacity of one and two per cent solutions of hexadecyl hexadecanoate in purified hexadecane were determined using the triplane test apparatus at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

Ester Concentration	Scuffing load (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
1%	55 (85)*	34
2%	55 (92)*	34

* see text

Table 9.1 The load at which scuffing occurred when using one and two per cent solutions of hexadecyl hexadecanoate in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

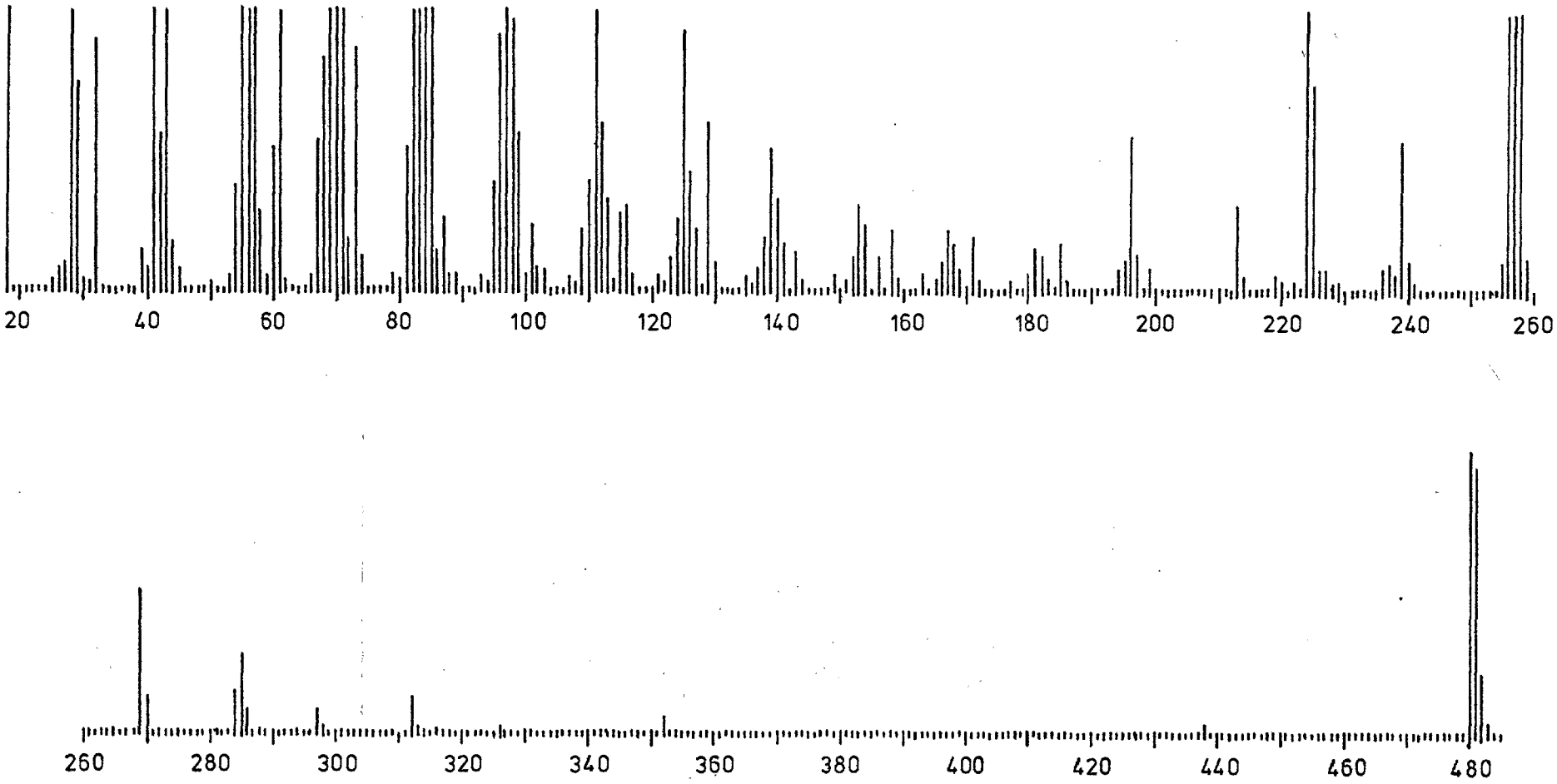


Fig. 9.1 The mass spectrum of purified hexadecyl hexadecanoate.

The ball and pegs were EN31 steel.

Table 9.1 summarises the results. Both the one and two per cent solutions behaved in the same way. The higher sliding speed resulted in scuffing occurring at a lower applied load. At this speed failure occurred suddenly on increasing the load. However at the lower sliding speed failure was not so well defined. With a top ball load of 55 kg mild scuffing occurred, i.e. $\mu \sim 0.3$, but recovery was rapid, within 15 seconds, if not complete. Before the onset of any scuffing the coefficient of friction was about 0.08, rising to 0.3 on scuffing, but on recovery it assumed a value of about 0.1. The load shown in brackets was the load at which no recovery occurred.

It will be shown later that hexadecyl hexadecanoate was probably physisorbed rather than chemisorbed onto the steel surfaces. Metal to metal contact would occur when the adsorbed film was penetrated, but would be prevented once more ester had adsorbed. The higher total failure load of the more concentrated solution might result from the more rapid adsorption of ester to renew any breaks in the sorbed film.

9.4 COPPER PLATING TESTS

In earlier work in this thesis, the ball and peg samples for the copper plating tests were obtained from runs of extended duration using an applied load of 69 kg, and a sliding speed of 0.43 ms^{-1} with a two per cent additive solution. Reference to table 9.1 shows that these conditions are unsuitable for hexadecyl hexadecanoate solutions since the scuffing load was less than 69 kg. Tests of extended duration were therefore conducted with a load of 50 kg. The sliding speed and solution concentrations were as before.

The ball and pegs taken from the triplane apparatus after such a run were rinsed quickly in ether and submerged in the copper plating

solution. Copper was found to plate over the whole surface - including the wear scars, of both the ball and pegs. It was concluded that anything sorbed on the metal surfaces was probably physisorbed.

A mass spectrum showed the presence of only hexadecane and hexadecyl hexadecanoate in the ether used for rinsing. It is therefore very likely that no new substances were formed during running. To confirm, or reject, this, dichloromethane extraction of the ball and pegs was carried out.

9.5 DICHLOROMETHANE EXTRACTION STUDIES

9.5.1 Procedure

The triplane apparatus was operated continuosly for four hours at a sliding speed of 0.43 ms^{-1} and with a load of 50 kg using EN31 steel ball and pegs. A two per cent solution of hexadecyl hexadecanoate in hexadecane was used as the lubricant. The ball and pegs were removed hot from the apparatus and soxhletted in dichloromethane together with the ball and pegs from five other similar runs. The residue after removal of the dichloromethane was examined using mass spectroscopy. The resultant spectrum, together with that of a sample of the used lubricant, were compared to the spectrum of a pure unused two per cent ester solution.

9.5.2 Results and Discussion

The spectra of the unused ester solution, the used lubricant and the dichloromethane extract were identical. The mass spectrum of the extract is shown in fig. 9.2. No increase in the concentration of the ester could be detected in the extract.

A possible explanation is that there was so little ester on the metal surfaces that, after dilution by the small quantity of the liquid

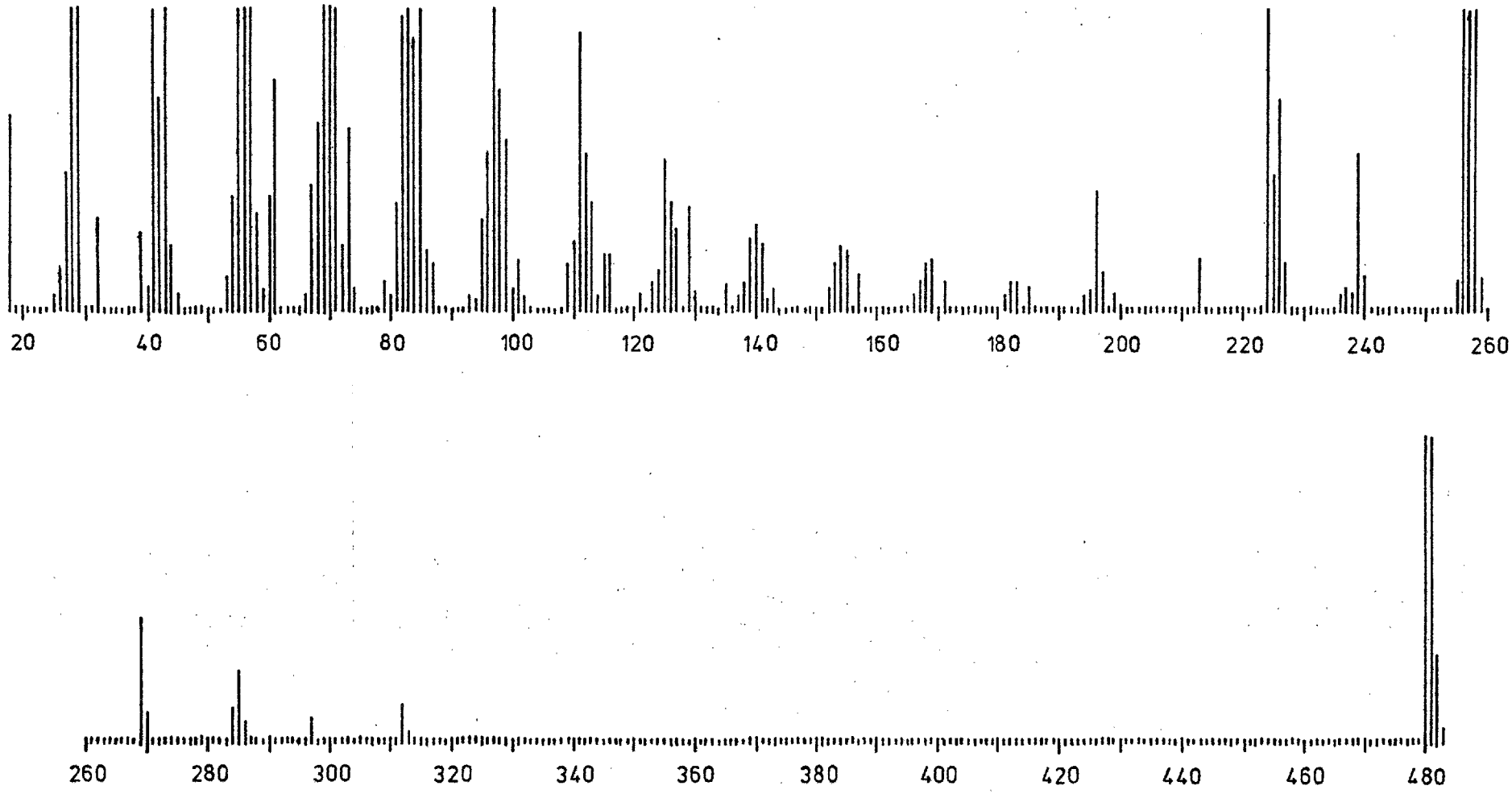


Fig. 9.2 The mass spectrum of the dichloromethane extract when using a 2% solution of hexadecyl hexadecanoate in hexadecane as lubricant.

lubricant transfered into the soxhlet on the surfaces of the ball and pegs, there was virtually no change in the ester's concentration. It might be that there was a greater concentration of ester in the wear scars due to increased adsorption resulting from activation of the metal by rubbing. However the results do not favour this possibility and unfortunately there was no direct method of confirmation.

One deduction that could definitely be drawn was that during running in the triplane apparatus the bulk lubricant underwent no change and no new materials were formed on the surfaces of the ball or pegs. Both the unused solution, the used lubricant and the extract were all neutral as tested using the ASTM standard D 974 - 64 (IP 139/65).

9.6 CONCLUSIONS

The following conclusions were reached.

1. (a) The load carrying capacity of hexadecane is only very slightly improved by the addition of one or two per cent of hexadecyl hexadecanoate.
   (b) The load carrying capacity decreased with increasing sliding speed.
   (c) Concentration appeared to have no effect on the load at which initial scuffing occurred.
   (d) The ester appeared to be weakly physisorbed rather than chemisorbed.
2. No new compounds were formed in the bulk lubricant or on the surfaces of the ball and pegs.
3. Preferential adsorption of the ester on the wear scars was considered, but not proven, unlikely.

Table 9.2 Analyses carried out on materials used in chapter 9.

Sample	Analysis		
	Mass spectroscopy	Titration	Melting point
Purified hexadecyl hexadecanoate	*	*	*
Ether washings prior to copper plating tests	*		
Pure unused 2% solution of hexadecyl hexadecanoate in hexadecane	*	*	
Used 2% solution of hexadecyl hexadecanoate in hexadecane	*	*	
Dichloromethane extract using 2% solution of hexadecyl hexadecanoate in hexadecane	*	*	

CHAPTER 10

AN EQUIMOLAR MIXTURE OF HEXADECAN-1-OL AND HEXADECANOIC ACID

10.1 INTRODUCTION

The addition of small quantities of hexadecan-1-ol or hexadecanoic acid has been shown to improve the load carrying capacity of hexadecane quite considerably. On the other hand, hexadecyl hexadecanoate gave little improvement. It was therefore of interest to see if an equimolar mixture of hexadecan-1-ol and hexadecanoic acid would exhibit the behaviour of the alcohol or the acid, or whether they would react together to form the ester, and give low scuffing loads.

10.2 DETERMINATION OF LOAD CARRYING CAPACITY

10.2.1 Results and Discussion

The load carrying capacity of one and two per cent solutions of an equimolar mixture of hexadecanol and hexadecanoic acid in hexadecane were determined in the usual manner using the triplane apparatus. All the materials were purified before use. The results are summarised in table 10.1 overleaf. The load carrying capacity was the same for both solution concentrations and both sliding speeds. At 1.09 ms^{-1} some very slight scuffing was evident at an applied load of 28 kg, but total failure did not occur until a load of 41 kg was applied.

If the scuffing loads for the mixture are compared to those of hexadecanol, hexadecanoic acid and hexadecyl hexadecanoate, some

interesting facts emerge.

Considering firstly the lower sliding speed. The mixture exhibited behaviour in between that of the alcohol and the acid in that its scuffing load was higher than the alcohol's but lower than the acid's. This implies that the addition of hexadecanoic acid to a hexadecanol solution improves the alcohol solution's lubricating properties, but adding the alcohol to an acid solution leads to a decrease in the scuffing load of the hexadecanoic acid solution. This might be explained by competitive sorption onto the ball and peg surfaces. If the ball were completely covered with sorbed acid molecules the load carrying capacity is good. If the surface were covered entirely by alcohol molecules the load carrying capacity is not so good. Competitive sorption would lead to a mixture of molecules on the surface and an intermediate scuffing load.

At the higher sliding speed the mixture gave a scuffing load which

Concentration of alcohol - acid mixture	Scuffing load (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
1%	103	41
2%	103	41

Table 10.1 The load carrying capacity of one and two per cent solutions of an equimolar mixture of hexadecan-1-ol and hexadecanoic acid in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

was the same as that given by the acid, which would indicate that sorption of the acid was the dominant factor. The acid has been shown to be physisorbed on the ball and peg surfaces, whereas the alcohol formed a complex mixture of new materials attached to the steel surfaces. It will be shown later that an organic film was formed on the wear scars whose nature was very similar to that produced by hexadecane solutions of hexadecan-1-ol alone. It might therefore be concluded that the scuffing load was determined by a layer of acid molecules physisorbed on top of the organic film due to the alcohol.

It might be argued that the scuffing load of the mixture at the lower sliding speed ought to be the same as that of the acid solution rather than intermediate between those of the acid and alcohol solutions. However, at the higher temperatures generated by the higher sliding speed one would expect the generation of more ester. This would effectively decrease the concentration of acid and would introduce the presence of ester as another element determining the scuffing load. The ester has been shown to be a poor additive, so the more ester present the lower the scuffing load because of surface dilution of the acid and alcohol by ester molecules.

This idea was confirmed by the results of titrating the acid in a sample of the bulk lubricant taken just before failure, with alcoholic potassium hydroxide according to the ASTM standard D 974 - 64 (IP 139/65). There was some twenty five per cent more acid remaining after the slower speed runs than after the higher speed tests.

10.3 COPPER PLATING TESTS

10.3.1 Procedure

Tests of extended duration were conducted using both one and two

per cent solutions of the alcohol - acid mixture in hexadecane. The sliding speed was 0.43 ms^{-1} and the load 69 kg. The ball and pegs were both of EN31 steel. The tests were commenced at room temperature, the only source of heat being frictional heating. After four hours running the apparatus was allowed to cool to room temperature. The ball and pegs were removed, rinsed quickly in ether and then immersed in the copper plating solution. A mass spectrum of the ether washings was obtained to check whether anything other than used alcohol - acid solution had been removed.

10.3.2 Results and Discussion

With both solution concentrations copper plated out over the whole of the ball and peg surfaces except for the wear scars, implying the presence of an organic film. The ether washings did not show anything not found in the used lubricant. (The latter is discussed in the next section.)

These results show that the alcohol present in the mixture was probably reacting with the worn surfaces, just as it did when no acid was present. Thus it would be anticipated that the dichloromethane extract would contain compounds similar to those present in the extract using pure hexadecanol solutions, though possibly the quantities might be different, e.g. more ester from the presence of the acid.

10.4 DICHLOROMETHANE EXTRACTION STUDIES

10.4.1 Blank Test

Before the actual extraction process was carried out three blank tests were conducted. Taken together they cover all possibilities of reactions not caused directly by the running conditions occurring in the triplane apparatus.

(1) The soxhlet apparatus was set up with dichloromethane as the solvent. Six cleaned balls and eighteen cleaned pegs were dipped in a freshly prepared two per cent alcohol - acid solution at room temperature and then quickly transfered to the soxhlet thimble. Soxhletting was continued for twenty four hours after which the solvent was stripped off and the residue analysed in a mass spectrometer.

The resulting mass spectrum was identical to that of the original alcohol - acid solution (fig. 10.1). No ester had been produced. Clearly then the conditions existing in the soxhlet were not favourable for the formation of hexadecyl hexadecanoate or any other new compounds. Any ester found in the extract must be introduced into the soxhlet on the surfaces of the balls or pegs.

(2) A two per cent solution of the alcohol - acid mixture in hexadecane was heated alone at 120°C. for four hours in a glass tube. These temperature conditions are fairly close to those existing during extended running of the triplane apparatus. The solution was cooled rapidly and the mass spectrum of a sample obtained.

No ester was detected, neither were any other new materials. To explain the absence of any ester one must consider the mechanistics of esterification. Normally for esterification to occur there are four criteria which must be fulfilled. They are:

(i) all steps must be significantly reversible;

(ii) acyl-oxygen bond breakage must occur;

(iii) the transition state must consist of a molecule of alcohol, a molecule of acid and an H^+ ion, and

(iv) the reaction must pass through an intermediate that can survive long enough to allow oxygen exchange with the solvent.

(i) and (ii) must be fulfillable since the ester has been prepared from the acid and alcohol. Little can be said of (iii) except that

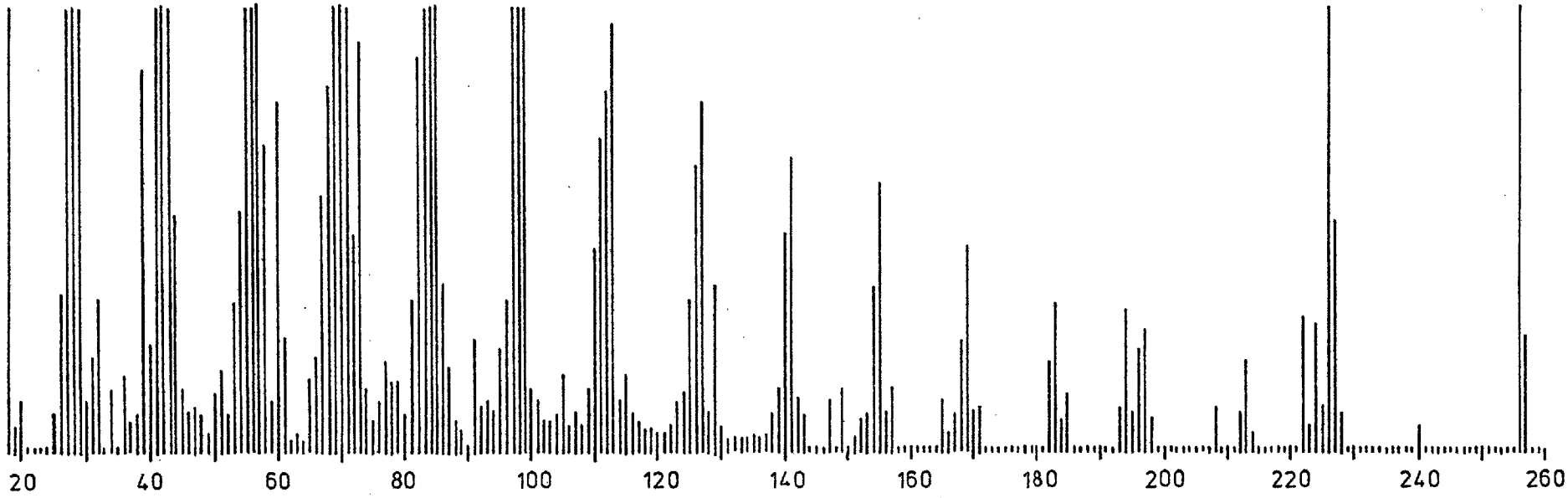


Fig. 10.1 The mass spectrum of an unused 2% solution of an equimolar mixture of hexadecan-1-ol and hexadecanoic acid in hexadecane.

because no water was initially present the concentration of H^+ would be extremely low, so the chances of forming the transition intermediate would be correspondingly low. As far as (iv) is concerned, the solvent, hexadecane, does not contain any oxygen at all, so oxygen exchange between the intermediate and the solvent would be impossible. Esterification must therefore not be a favoured reaction, so the absence of ester after heating the dry acid and dry alcohol in dry hexadecane was no surprise.

(3) The triplane apparatus was assembled as if for a test with a two per cent solution of an equimolar mixture of hexadecanol and hexadecanoic acid in hexadecane as the lubricant. Meticulous care was taken to ensure that all parts of the apparatus in contact with the lubricant were as dry as possible. The ball, ball chuck, pegs, peg carrier and lubricant retaining ring were heated, using the external heater, to 120°C.. This temperature was maintained for four hours, after which time a sample of the liquid was removed, cooled, and subjected to mass spectroscopy.

The mass spectrum was identical to the one obtained in the last test. No new compound had been generated. The presence of steel can not have had any catalytic effects.

Conclusions. Taken together the results of these three experiments showed that soxhletting did not affect the alcohol - acid solution, neither did simply heating the solution, whether steel was present or not. It was therefore safe to assume that any new products which might be detected in the used lubricant or the dichloromethane extract were a result of the effects of sliding.

10.4.2 Soxhlet Extraction: Procedure

An ionically bombarded EN31 steel ball and three pegs were assembled into the clean triplane apparatus with a two per cent solution

of an equimolar mixture of hexadecanol and hexadecanoic acid in hexadecane as the lubricant. Great care was taken to ensure that no part of the apparatus in contact with the lubricant had any appreciable quantities of water assoiciated with it. To do this, after cleaning, all the metal components were stored in analar acetone dried by molecular sieve 4A.

A sliding speed of 0.43 ms^{-1} was chosen. After running in, a load of 69 kg was applied and the apparatus allowed to run for four hours. The ball and pegs were quickly removed and placed in the soxhlet together with the balls and pegs from five other similar runs. These were soxhletted for twenty four hours after which the dichloromethane was vacuum distilled off leaving a few drops of liquid whose mass spectrum was obtained. This was compared to that of a freshly prepared pure unused two per cent alcohol - acid solution. A sample of the liquid lubricant remaining after the test was also analysed by mass spectroscopy. The pure unused solution, the used lubricant and the extract were also examined by infra-red spectroscopy.

10.4.3 Results and Discussion

The used lubricant. The used lubricant was found to contain traces of hexadecyl hexadecanoate but no other changes were evident from the mass spectrum (fig. 10.2). The quantity of ester formed was so small that the loss of acid could not be quantified by titration with alcoholic potassium hydroxide.

It is difficult to say just how the ester was formed. A blank test showed that the triplane apparatus could be assembled, heated, and a sample of the used lubricant removed and subjected to mass spectroscopy without any ester being formed. The ester must have been produced either on the worn areas during sliding and was subsequently

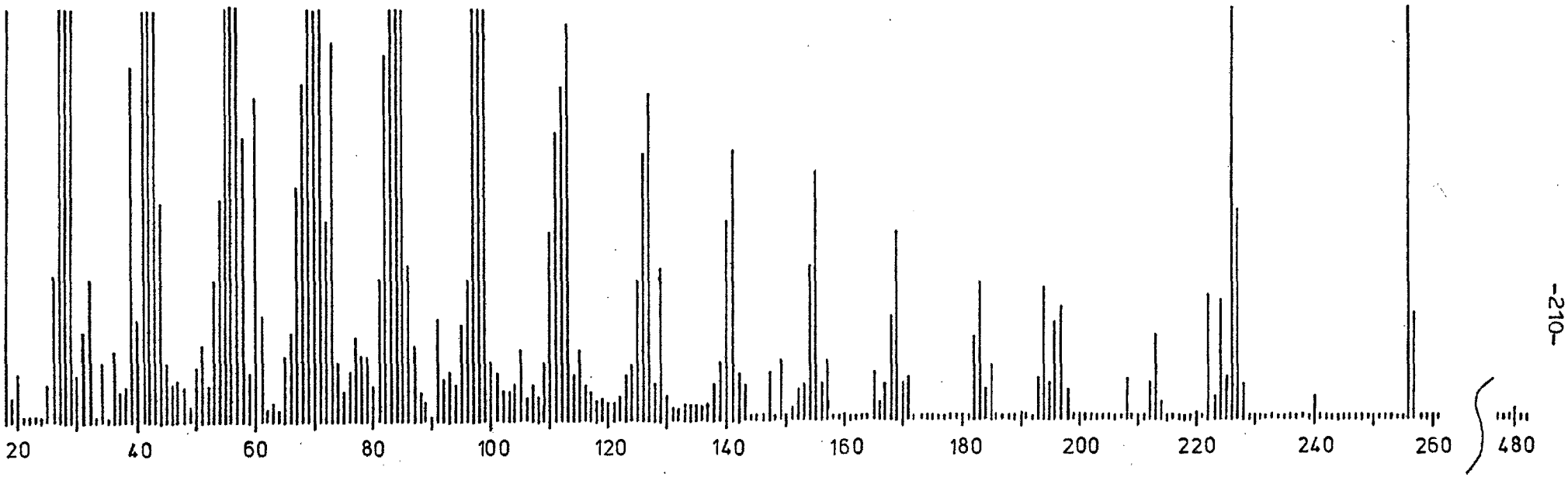
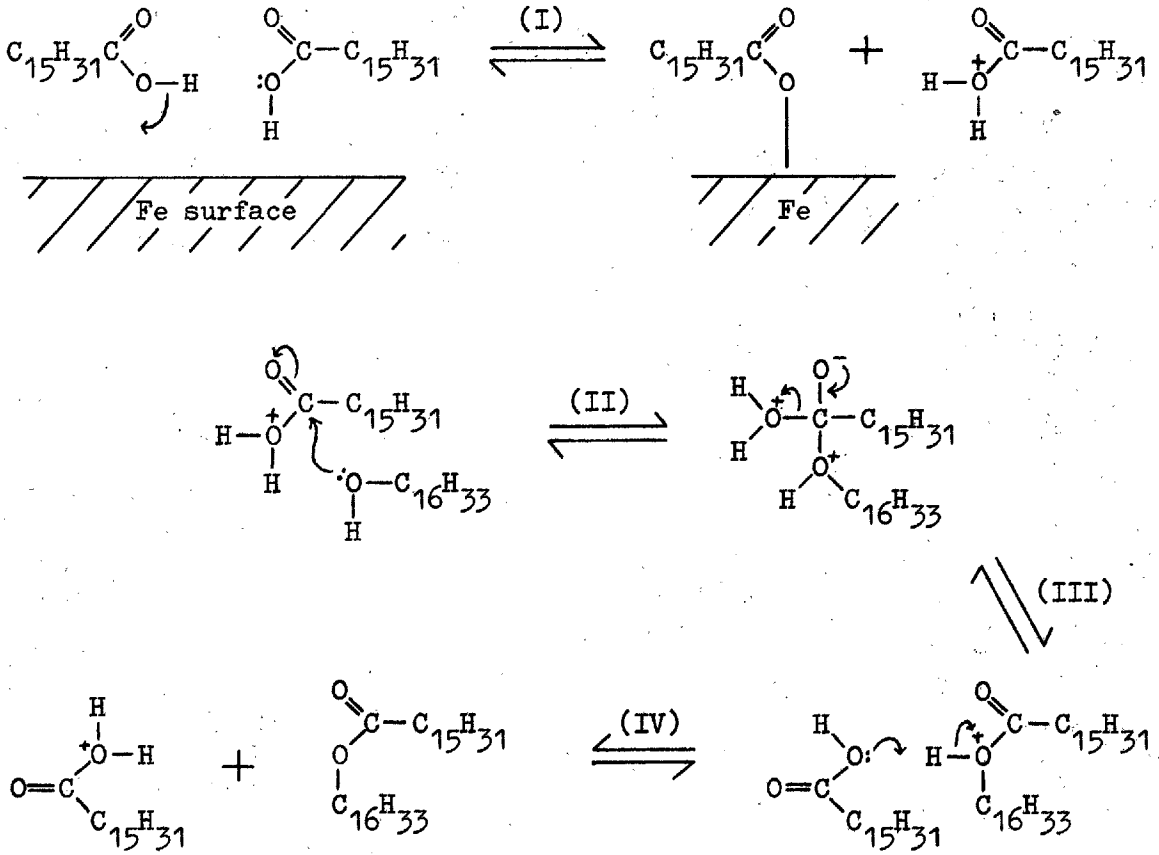


Fig. 10.2 The mass spectrum of a used 2% solution of an equimolar mixture of hexadecan-1-ol and hexadecanoic acid in hexadecane.

rubbed off, or in the contact but not directly on the steel surfaces, the combination of nascent steel and rubbing acting as a catalyst. The dichloromethane extract showed that the 'rubbing off' idea was incorrect since many other compounds were formed on the wear scars but none of these appeared in the bulk lubricant. The ester must have been generated in, or very close to, the contact. A possible mechanism involves the formation of 'iron hexadecanoate' as an intermediate, and is shown below:



All the reactions involving two molecules combining together are concerted. This must be the case since entities such as H^+ would not be expected to exist freely in a hydrocarbon medium. The first step involves the reaction between two acid molecules so that one becomes protonated whilst the resultant negative charge on the other is

neutralised by the metal surface. This must obviously occur at the metal surface. Such a reaction would be infrequent due to the probable effects of molecular orientation at the surface and the availability of free metal surface - bearing in mind that the alcohol is also reacting with the surface. Steps (II) and (III) are the normal esterification intermediate steps for an acid catalysed reaction. Although step (IV) is shown as a reaction between an intermediate and another acid molecule it might also be a reaction between the intermediate and a water molecule. The latter reaction would considerably slow down the overall rate of production of ester.

The above mechanism requires a metal surface with which an acid molecule can react which probably means that the surface must be a chemically clean one. The only time that this might occur is at the very beginning of sliding before any chemically altered film could be formed. Since this condition is short lived, very little ester would be expected.

An attempt was made to obtain experimental evidence for this idea. An EN31 ball was ground against three pegs submerged in a two per cent alcohol - acid solution to try to produce nascent metal for the esterification to occur. Very little ester was detected. This does not necessarily mean that the mechanism is correct. It must be remembered that the quantities being dealt with were very small indeed, so each individual step could not be investigated in detail, but obtaining a result predicted by the mechanism does mean that at least part of it might be correct.

The Dichloromethane Extract. The mass spectrum of the residue after removal of the dichloromethane solvent is shown in fig. 10.3. It is of greater interest to compare this with fig. 7.5, the mass spectrum of the dichloromethane extract of a two per cent solution of

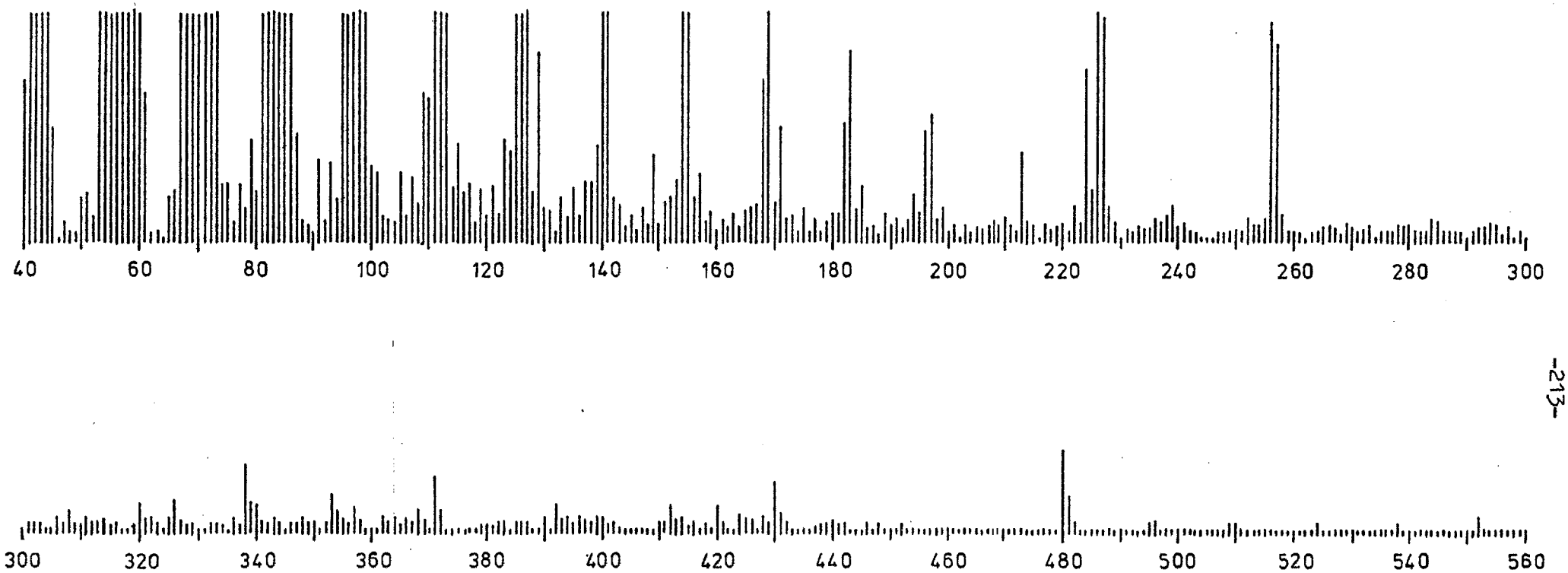


Fig. 10.3 The mass spectrum of the dichloromethane extract when using a 2% solution of an equimolar mixture of hexadecan-1-ol and hexadecanoic acid in hexadecane as lubricant.

hexadecanol in hexadecane, rather than fig. 10.1, the pure unused two per cent alcohol - acid solution. It will be seen that the two spectra (figs. 10.3 and 7.5) are very similar indeed. The differences lie not in the actual materials present, but in their proportions. For example, there is a large peak at 256, due of course to the hexadecanoic acid originally present, and at 480, the molecular weight of hexadecyl hexadecanoate. Clearly if more acid were present, more ester would be expected.

This demonstrates that the hexadecan-1-ol reacted with the surface undergoing the same reactions whether or not hexadecanoic acid was present. The addition of the acid merely altered the extent of the reactions.

When examined separately, balls and pegs gave similar results.

10.5 CONCLUSIONS

The following conclusions were reached.

1. (a) A one or two per cent solution of a purified equimolar mixture of hexadecan-1-ol and hexadecanoic acid in pure hexadecane gave a scuffing load comparable to those of solutions of hexadecanol and hexadecanoic acid of similar concentrations.

   (b) The effect of added acid on the scuffing load of an alcohol solution and of added alcohol on an acid solution depended on the sliding speed, and apparently on the extent of ester formation.

2. (a) The dichloromethane extract showed the presence of materials on the balls and pegs which were the same as those given by solutions of hexadecanol alone.

   (b) The presence of the acid appeared to alter only the quantities of these materials (e.g. more ester was produced).

3. The used lubricant showed the presence of only a little ester, its generation being due to the effects of sliding rather than heating.

4. Heating the alcohol - acid solution in the presence of EN31 steel produced no ester. This was explained by the mechanism of esterification.

Table 10.2 Analyses carried out on materials used in chapter 10.

Sample	Analysis		
	Mass spectroscopy	Titration	Infra red
Pure unused 2% solution of equimalar mixture of hexadecanol and hexadecanoic acid in hexadecane	*	*	*
Used 2% & 1% alcohol - acid solutions from failed runs		*	
Dichloromethane extraction blank	*		
Pure 2% alcohol - acid solution heated alone	*		
Pure 2% alcohol - acid solution heated with steel in triplane apparatus	*		
Used 2% alcohol - acid solution	*	*	*
Dichloromethane extract using 2% alcohol - acid solution	*		*

CHAPTER 11

1,16-HEXADECANEDIOL

11.1 INTRODUCTION

Patents have been taken out covering the use of mixtures of diols and diacids as lubricants[54-61]. Typically the mixture is sprayed onto a clean surface where the diol and acid are expected to react to form high molecular weight polyesters. The latter are thought to be the actual lubricant.

Since the ultimate aim of this work was to examine a diol - diacid mixture, a suitable diol and diacid were first separately investigated. The diol chosen was 1,16-hexadecanediol and the diacid, hexadecanedioic acid. These were both C_{16} compounds so a direct comparison could be made with the alcohol, acid and alcohol - acid mixtures already studied. This chapter deals specifically with hexadecanediol.

11.2 PURIFICATION

1,16-Hexadecanediol was supplied by the Aldrich Chemical Company Ltd. as a 99% pure material as determined by GLC. It was recrystallised from benzene until a constant melting point was obtained. Only two recrystallisations were necessary. The effect of recrystallisation on the melting point is shown in table 11.1 overleaf.

The mass spectrum of the recrystallised diol was recorded (fig. 11.1). There were no peaks at m/e ratios greater than 258, the

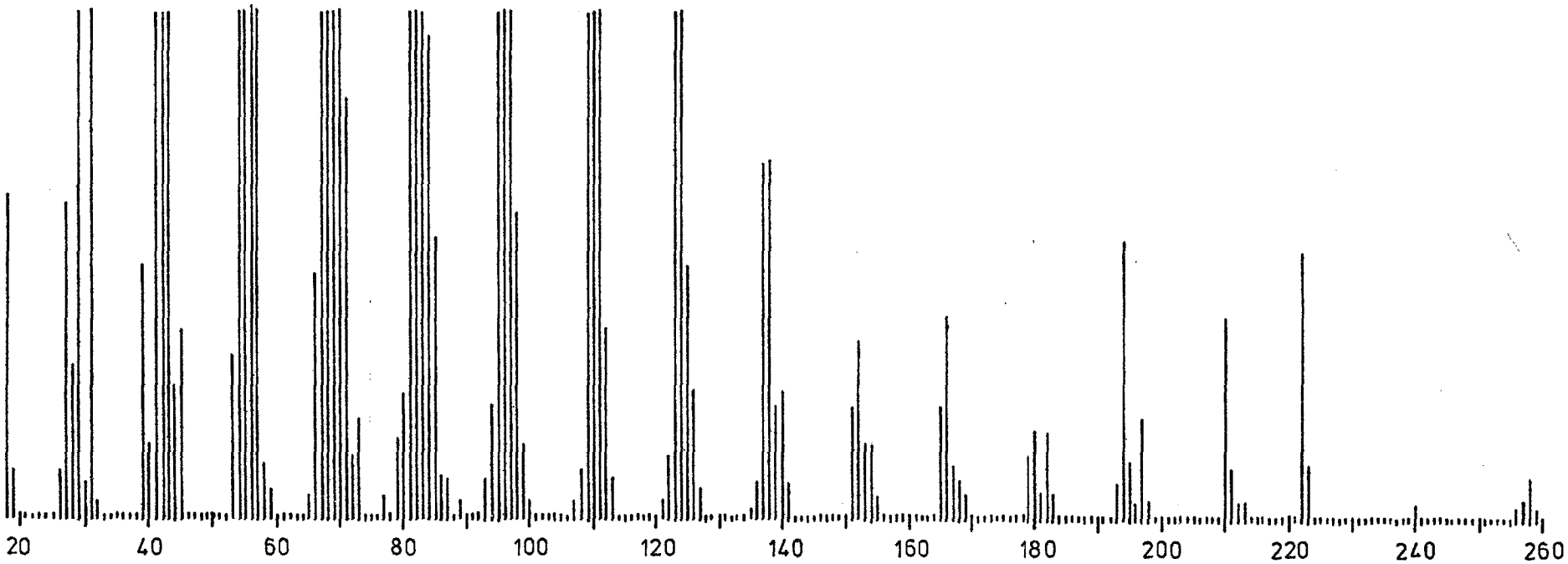


Fig. 11.1 The mass spectrum of purified 1,16-hexadecanediol.

molecular weight of the diol, nor were any impurities detected. An infra-red spectrum showed only absorbances associated with a straight carbon chain and a primary alcohol.

The recrystallised diol was used to make up all the solutions used for testing.

11.3 SOLUTION PREPARATION

1,16-Hexadecanediol is only sparingly soluble in purified hexadecane, a saturated solution at 25°C. containing about 0.5% diol. Increasing the temperature increased the solubility of the diol so that at 70°C. a one per cent solution was readily obtainable. The solution concentrations required were 0.5 and one per cent, since these gave the same concentrations of functional groups as the one and two per cent solutions already studied. To maintain solution of the diol the assembled triplane apparatus was always heated before a test.

11.4 THE MASS SPECTRUM OF 1,16-HEXADECANEDIOL SOLUTIONS

It was found necessary to use temperatures of 130 - 140°C. to get

Purification	Melting point found	Literature melting point
None	91.5 - 92°C. 92 - 93°C. (Manufacturers value)	---
Once from benzene	91 - 91.5°C.	91.2 - 91.5°C.[89]
Twice from benzene	91 - 91.5°C.	91.5°C.[90]

Table 11.1 The effect of recrystallisation from benzene on the melting point of 1,16-hexadecanediol.

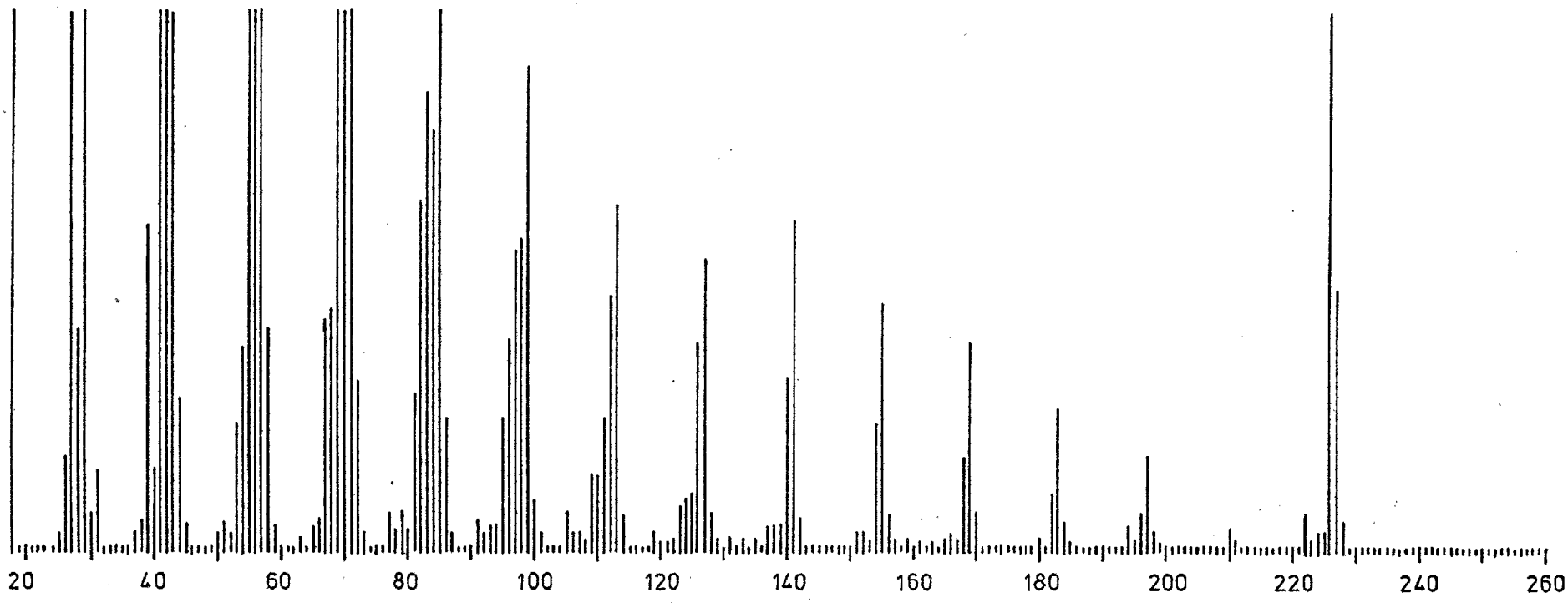


Fig. 11.2 The mass spectrum of an unused 1% solution of 1,16-hexadecanediol in hexadecane.

a good spectrum of a one per cent solution of 1,16-hexadecanediol in hexadecane. At temperatures significantly lower than this only the hexadecane peaks were visible, whereas at higher temperatures thermal fragmentation processes tend to dominate over the electron bombardment processes.

The parent ion, at m/e 258, was not present as would be expected from the general behaviour of alcohols in a mass spectrometer. The largest diol peak was at 222, corresponding to the loss of two molecules of water (fig. 11.2).

11.5 DETERMINATION OF THE LOAD CARRYING CAPACITY

11.5.1 Procedure

The load carrying capacity was determined using the triplane apparatus. The method has already been described in some detail. Previously all tests commenced with the apparatus at room temperature, but because of the limited solubility of hexadecanediol in hexadecane these tests were begun at slightly elevated temperatures. Two initial temperatures were used, 70°C. and 120°C.. The reason for this will be apparent when the results are considered. The solution concentrations used were 0.5 and 1.0 mole per cent. The ball and pegs were of EN31 steel.

11.5.2 Results and Discussion

The results are summarised in table 11.2 overleaf. In every case failure occurred suddenly and completely on increasing the load.

The higher sliding speed led to scuffing occurring at a lower load, a phenomenon observed for all the lubricants so far examined.

The difference in the concentration of the hexadecanediol had no observable effect. This was most probably because the minimum

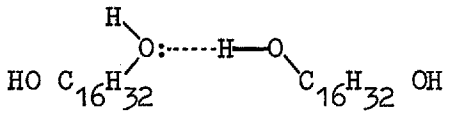
concentration of diol required to give maximum surface coverage and so the highest possible load carrying capacity was less than 0.5 mole per cent. It would not have been very difficult to ascertain just how much diol was necessary, but this was not done since the chemical analysis of very dilute solutions becomes very difficult.

The initial temperature of the apparatus and lubricant had a marked effect on the scuffing load, the higher temperature giving a higher load carrying capacity. The difference at the lower sliding speed was small, but at the higher speed it was quite large. It is sometimes argued that failure occurs when the surface temperature reaches a certain critical value[75]. The temperatures at which scuffing occurred were the same at the lower speed, but at 1.09 ms^{-1} they were 105°C. and 150°C. for the lower and higher initial

Concentration of hexadecanediol	Starting temperature	Load carrying capacity (kg)	
		Sliding speed	
		0.43 ms^{-1}	1.09 ms^{-1}
0.5%	70°C.	83	34
1.0%	70°C.	83	34
0.5%	120°C.	86	50
1.0%	120°C.	86	50

Table 11.2 The load carrying capacity of 0.5 and 1.0 mole per cent solutions of 1,16-hexadecanediol in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1} and initial triplane temperatures of 70°C. and 120°C.

temperatures respectively. This proves that the thermal failure argument does not apply in this case. The differences might be due to the effects of association of the diol. Two or more diol molecules might be joined together by hydrogen bonding:



Because of the presence of an alcohol group at both ends of the molecule, there would appear to be no limit to the number of molecules which might associate. The extent of association in hexadecane could be determined experimentally by cryoscopic measurements. This would only give the degree of association at the temperature of the experiment (about 18°C.). As the temperature is increased, the kinetic energy of individual molecules overcomes the attractive effects of the hydrogen bonding and disassociation occurs. For a one per cent solution at 70°C. there would be a certain degree of association so the concentration of diol 'units' would be less than one per cent. If it is assumed that the diol molecules were responsible for preventing metal to metal contact, then at the higher temperature there is effectively more diol present for sorption onto the steel surfaces, resulting in an increase in the scuffing load.

The system might be further complicated by the shape of the diol molecules in solution. There is a very simple formula relating the 'end to end' distance of a molecule with the number of bonds in it. It is $\langle r^2 \rangle^{\frac{1}{2}} = n^{\frac{1}{2}} l$ where n = number of bonds,

l = length of each bond,

r = end to end distance.

With hexadecanediol $l = 1.54.10^{-10}$ m and n is 15 (for the carbon chain only) whence $\langle r^2 \rangle^{\frac{1}{2}}$ is $5.96.10^{-10}$ m compared to 22.10^{-10} m if the molecule were fully extended. If the above formula were refined, it

would become temperature and solvent sensitive.

The similarity in the failure loads at the lower sliding speed was probably accounted for by the comparable temperatures attained during running. Although the starting temperatures were different, the rate of heating was greater with the lower starting temperature. In both cases failure occurred at between 130°C. and 135°C..

11.6 COPPER PLATING TESTS

11.6.1 Procedure

Tests of extended duration were conducted at an applied load of 69 kg, a sliding speed of 0.43 ms^{-1} and with a one mole per cent solution of purified 1,16-hexadecanediol in purified hexadecane. The ball and pegs were EN31 steel. After twenty four hours running, the apparatus was allowed to cool to room temperature and the ball and pegs removed. They were rinsed quickly with ether, then submerged in the copper plating solution. The ether used for rinsing was examined by mass spectroscopy to ensure that it had removed only adherent used lubricant.

11.6.2 Results and Discussion

Copper did not plate out on the wear scars of either the ball or pegs. It was deposited on the remaining surfaces. The ether did not remove anything other than adherent liquid lubricant.

The results indicated that an organic film was formed on the wear scars, but nowhere else on the steel surfaces. This film ought to be detected in the dichloromethane extract.

11.7 DICHLOROMETHANE EXTRACTION STUDIES

11.7.1 Procedure

Using the triplane apparatus, tests of six hours duration were conducted. The running conditions were as described in the previous section. Mass and infra-red spectra of the used bulk liquid lubricant and the dichloromethane extract, after removal of the dichloromethane, were compared to that of a pure unused one per cent diol solution. Copper plating was used to check that the ball and pegs were clean after soxhletting.

To ensure that the observed results were due to the running conditions existing in the triplane apparatus, three blank tests were performed. They showed that:

(i) heating a pure unused one mole per cent solution of hexadecanediol in hexadecane to 140°C. for twenty four hours caused no change in the solution whether or not EN31 steel was present

(ii) the soxhlet extraction process in no way altered the diol solution.

11.7.2 Results and Discussion

The Used Lubricant. The bulk liquid lubricant was found to be unchanged after use in the triplane apparatus. No traces of any new materials were detected, either by mass spectroscopy or by infra-red spectroscopy. Any chemically altered film formed on the wear scars of the ball and pegs was not dissolved off by the bulk liquid.

The Dichloromethane Extract. The mass spectrum of the residue after soxhletting the balls and pegs from six identical runs is shown in fig. 11.3. The spectrum of a pure unused one per cent solution of the diol has already been presented in fig. 11.2. It is, however, of

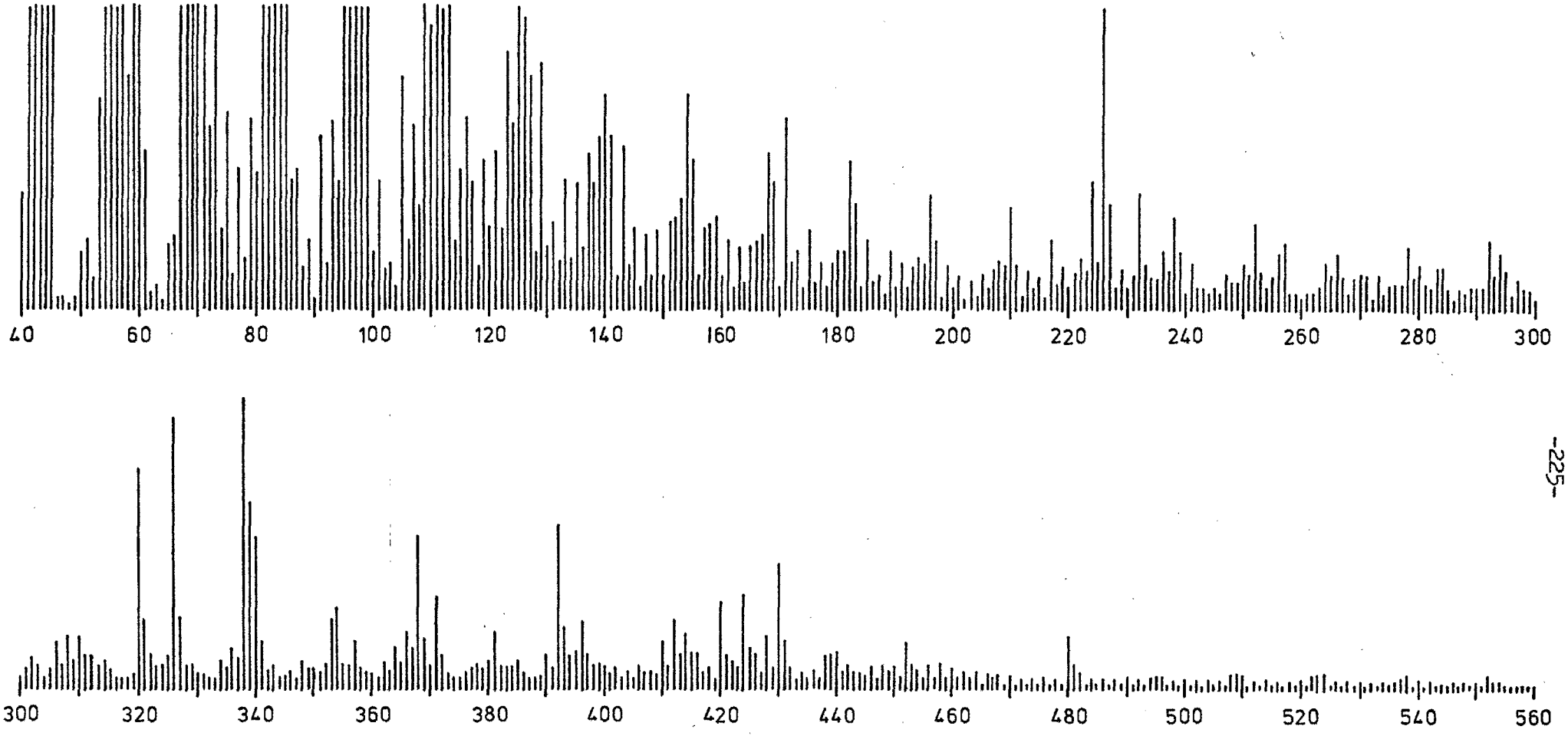


Fig. 11.3 The mass spectrum of the dichloromethane extract when using a 1% solution of 1,16-hexadecanediol in hexadecane as lubricant.

greater interest to compare fig. 11.3 with fig. 7.5 which is the mass spectrum of the dichloromethane extract when the lubricant was a two per cent solution of hexadecan-1-ol. The two spectra are remarkably similar. The infra-red spectrum of the diol extract showed absorbances associated with alcohols, the carbonyl group (probably as the acid and ester) and saturated and unsaturated carbon chains.

If oxidation were to occur, the following reactions would be expected to take place.

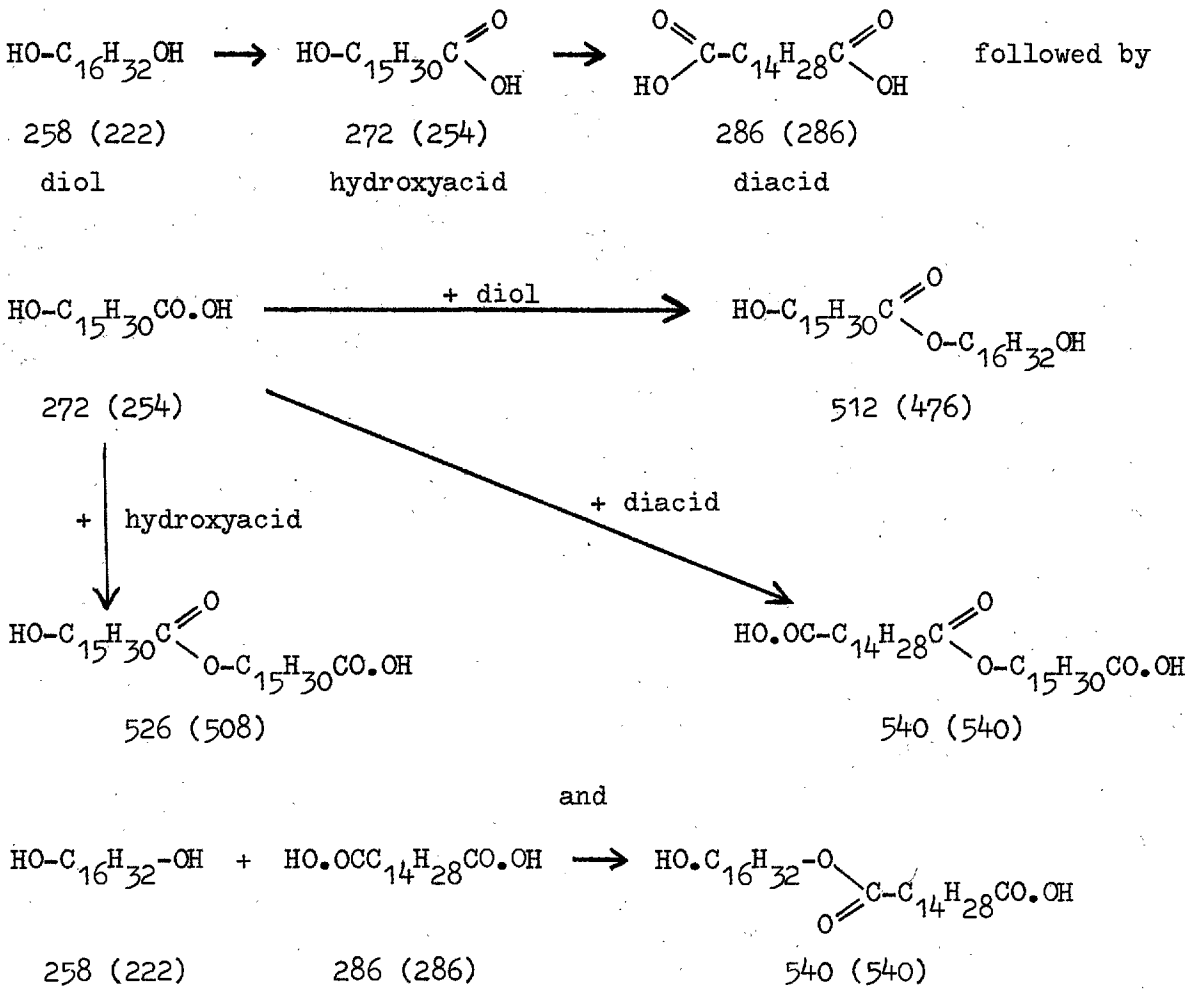


Fig. 11.4 The oxidation and subsequent reactions of 1,16-hexadecanediol. (The first number is the molecular weight, the second, in parenthesis, is the highest m/e ratio expected in a mass spectrum.)

The mass spectrum did not show peaks of suitable intensity at these mass to charge ratios (viz. the very small peak at 286 and relatively small peak at 254). Acids were present as shown by the very large peaks at 45 ($CO.OH^+$) and 60 ($CH_3CO.OH$), and by the infra-red spectrum, so oxidation did occur. Unsaturation was also evident so it is clear that the reactions occurring on the surface were very complex indeed. In view of the similarity between this mass spectrum and that of the hexadecan-1-ol extract, it is possible that the carbon chain might be being broken giving alcohols and acids as well as hydoxyacids and diacids.

Because of the great complexity of the mass spectrum it was impossible to state with any degree of certainty the individual compounds formed. The important fact, from the point of view of lubrication, was that there was an increase in molecular weight, though not as great as might have been expected.

When the ball and pegs were separately soxhletted, the mass spectra of the respective extracts were very similar both to each other and to that presented in fig. 11.3.

11.8 CONCLUSIONS

When using solutions of 1,16-hexadecanediol in hexadecane as the lubricant in the triplane apparatus, the following conclusions were reached.

1. The scuffing load decreased with increasing sliding speed.
2. Both 0.5 and one mole per cent solutions gave similar scuffing loads.
3. The failure load was dependent on the initial temperature of the apparatus, particularly at a sliding speed of 1.09 ms^{-1}. This was attributed to association of the diol.

4. The used lubricant, after extended running times, underwent no changes.
5. Similar organic films were formed on the wear scars of both the ball and the pegs. There were many new materials formed, including oxidation products, but the overall molecular weight was not as high as might be expected. The film was very similar to that formed by solutions of hexadecan-1-ol in hexadecane.
6. The film was not removed by the bulk liquid lubricant.

Table 11.3 Analyses carried out on materials used in chapter 11.

Sample	Analysis		
	Mass spectroscopy	Infra red	Melting point
1,16-hexadecanediol as supplied			*
Purified hexadecanediol	*	*	*
Pure unused 1% solution of hexadecanediol in hexadecane	*	*	
Used 1% solution of hexadecanediol in hexadecane	*	*	
Blank dichloromethane extraction	*		
Dichloromethane extract using 1% hexadecanediol solution	*	*	
Pure 1% diol solution heated at 140°C for 24 hours in presence of EN 31 steel	*		
Pure 1% diol solution heated alone at 140°C for 24 hours	*		

CHAPTER 12

HEXADECANEDIOIC ACID

12.1 INTRODUCTION

The previous chapter dealt with 1,16-hexadecanediol. In this chapter the diacid derived from it, hexadecanedioic acid, is examined. It is a C_{16} straight chain diacid of semistructural formula $HO.OCC_{14}H_{28}CO.OH$. As with the compounds already studied, the load carrying capacities of two solution concentrations in hexadecane were determined at two different sliding speeds. This was followed by dichloromethane extraction studies carried out on the ball and pegs after tests of extended duration.

12.2 PURIFICATION

Hexadecanedioic acid, supplied by the Aldrich Chemical Company Ltd., was purified by recrystallisation from ethyl acetate until a constant melting point of 124.5 - 125°C was obtained (lit. 126°C[74]). The purified diacid was used in the preparation of all the lubricant solutions.

Some difficulty was encountered in obtaining an interpretable mass spectrum. Diacids are often thermally unstable, a common reaction being the loss of carbon dioxide:

$$HO.OC\text{-}R\text{-}CH_2CO.OH \xrightarrow{heat} HO.OC\text{-}R\text{-}CH_3 + CO_2$$

Anhydrides may also be formed with the loss of water. Initially low

temperatures were used to minimise thermal effects, but this resulted in an ill defined spectrum. On increasing the temperature the parent ion peak became observable. However raising the temperature led to an increase in the relative heights of certain other peaks, such as that at m/e 254, which were not attributable to electron bombardment fragmentation of the diacid (fig. 12.1). As far as could be ascertained there were no significant quantities of any impurities initially present in the diacid, certainly there was nothing of molecular weight greater than 286, the molecular weight of the diacid.

12.3 SOLUTION PREPARATION

At room temperature hexadecanedioic acid had a limited solubility in hexadecane. If the temperature were increased to 125°C, the melting point of the diacid, solutions of 0.5 and one mole per cent were readily obtainable. No separation of the diacid was apparent. All tests using the triplane apparatus were commenced at 125°C to ensure solution of the diacid. The mass spectrum of a 0.5 mole per cent solution was easily obtainable.

12.4 DETERMINATION OF LOAD CARRYING CAPACITY

12.4.1 Results and Discussion

The load carrying capacity was determined in the normal manner. Solution concentrations of 0.5 and one mole per cent were tested at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}. All the tests were commenced at 125°C. The results are summarised in table 12.1.

The torque tube on the triplane apparatus could not be used with safety above 250 kg. At the lower sliding speed failure had not occurred by the time this load was reached. The temperature stabilised at about 130°C and running continued smoothly until failure occurred

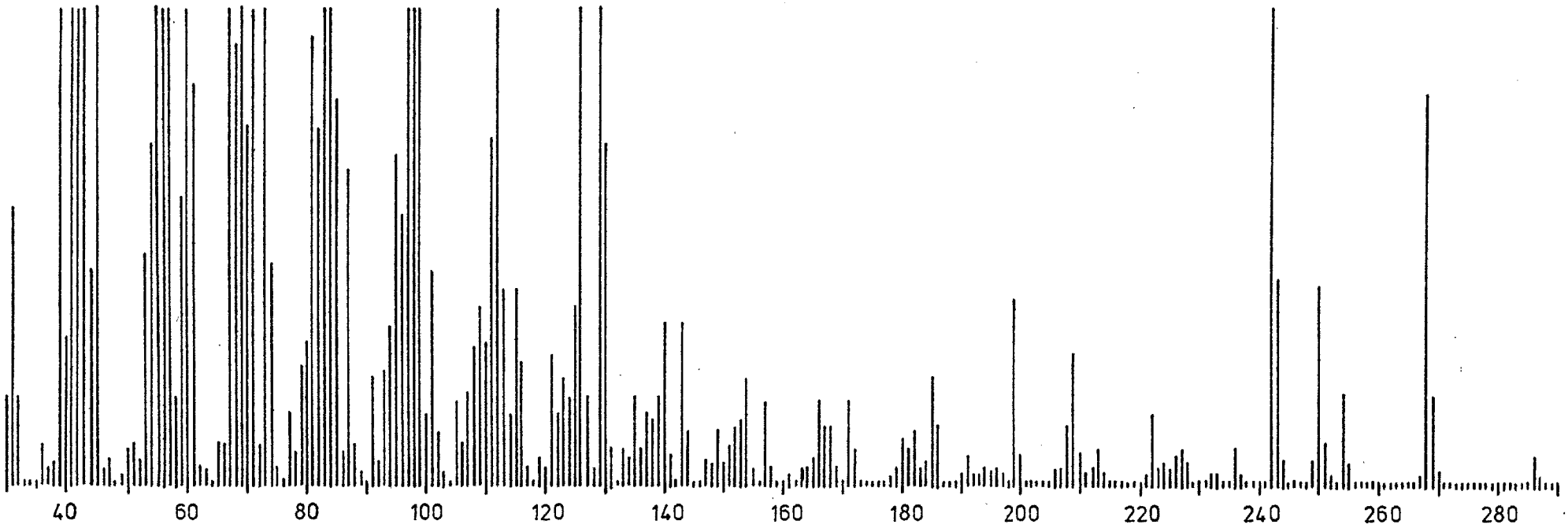


Fig. 12.1 The mass spectrum of purified hexadecanedioic acid.

Solution concentration mole per cent	Scuffing load (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
0.5	>250	103
1.0	>250	117

Table 12.1 Scuffing loads of 0.5 and 1.0 mole per cent solutions of hexadecanedioic acid in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

through loss of the lubricant by evaporation.

At the 1.09 ms^{-1} sliding speed, failure, when it occurred, was quite violent. The shear pin on the drive shaft broke and, on dismantling the apparatus, the ball and pegs were found to be welded together. The lubricant was colourless, but metallic wear debris, not unlike wire wool, was found wrapped round the pegs and at the bottom of the peg carrier. The temperature at which scuffing occurred was the same for both solution concentrations. This is not indicative of a thermal failure process since the temperature fluctuated by less than 5°C once it had reached 150°C which occurred at a load of 35 kg. The difference in the scuffing loads was probably due to the greater sorption of the diacid onto the steel surfaces at the higher concentration.

After a test at a sliding speed of 0.43 ms^{-1} the lubricant was found to be colourless. The pegs had the typical circular wear scar

with a diameter of 1.4 mm but there was also a hard brown deposit on the trailing side of the wear scar (fig. 12.2). It was firmly attached to the peg and could only be scraped off with some difficulty. The worn surface of the ball was smooth with traces of a brown deposit at the edges of the wear marks. Although there was no film visible on the wear scars of either the ball or the pegs, copper plating disclosed its presence.

The brown deposit and the used lubricant were both analysed. The results are discussed later when they can be compared to the dichloromethane extract of the ball and pegs.

12.5 DICHLOROMETHANE EXTRACTION STUDIES

12.5.1 Procedure

Tests of six hours duration were conducted with a sliding speed of 0.43 ms^{-1}. Although a relatively high load could have been used the standard 69 kg was employed. This allowed the results to be compared directly with those of previous tests, and also enabled a comparison to be made between the deposit obtained at this load with that previously obtained with the much higher load. All runs were begun with the apparatus at 125°C to ensure that the one mole per cent of hexadecanedioic acid was in solution in the hexadecane.

Preliminary tests yielded a brown material floating in the used lubricant. The dismantling procedure was therefore modified. At the end of a test the used lubricant was filtered hot to remove the solid wear products. These were washed with ether to remove liquid lubricant, then 'air' dried in a current of nitrogen gas. The ether was examined using mass spectroscopy to ensure that it had removed nothing other than used liquid lubricant. After the removal of any adherent brown deposit the ball and pegs were soxhletted in dichloromethane in the

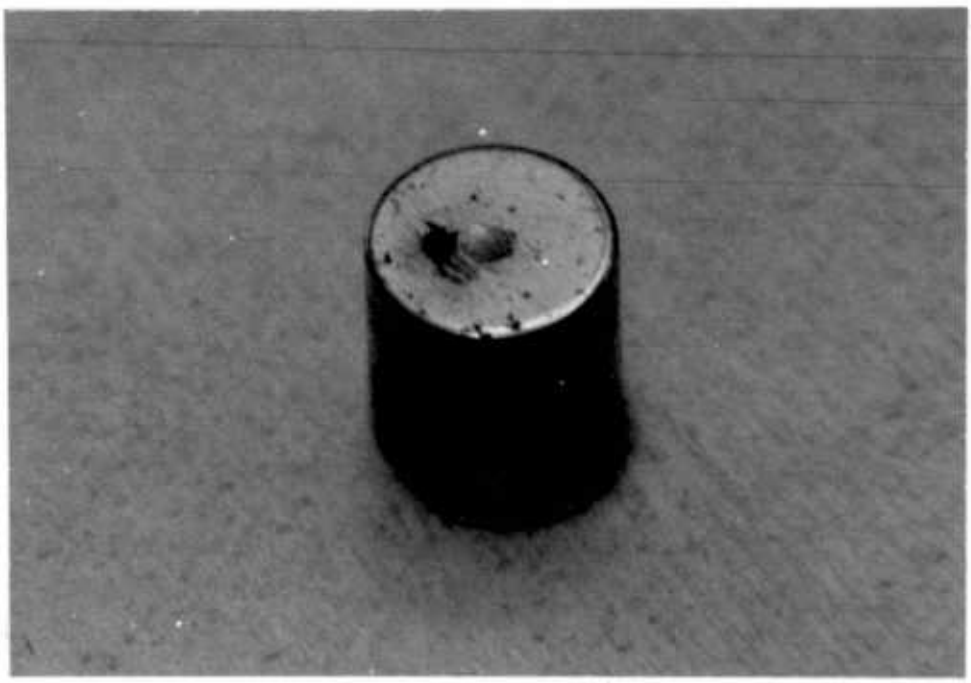


Figure 12.2 A peg after running in a 1% solution of hexadecanedioic acid in hexadecane. The brown deposit can be seen to the left of the round wear scar in the centre of the flat face.

usual manner. The residue, after removal of the solvent, was subjected to mass spectroscopy. The brown material was analysed separately.

Blank tests were performed to ensure that the observed results arose from sliding in the triplane apparatus and not from any other cause.

12.5.2 Results and Discussion

The used lubricant. For the purposes of comparison the mass spectrum of a pure unused one mole per cent solution of hexadecanedioic acid in hexadecane is shown in fig. 12.3. The spectra given by the used lubricant from the tests of extended duration and from the scuffing load determinations were identical to each other and very similar indeed to that of the pure unused diacid solution. One of these spectra is shown in fig. 12.4. It must be concluded that no reactions had occurred in the bulk lubricant. It must also be that the brown deposit found on the surfaces of the ball and pegs, and suspended in the used lubricant, was not soluble in the diacid solution.

The dichloromethane extract. The mass spectrum of the dichloromethane extract, fig. 12.5, was, as far as could be ascertained, the same as that of the used lubricant and the pure unused diacid solution below a mass to charge ratio of 270. It did show peaks at m/e ratios greater than 286 and up to 473. No definite designations could be attached to the individual peaks, but it was concluded that there was more than one compound. All the compounds consisted of polyfunctional molecules, but none of them were straight chain or cyclic anhydrides as might be expected from a purely chemical point of view. The reaction giving an anhydride from two acid groups is shown overleaf.

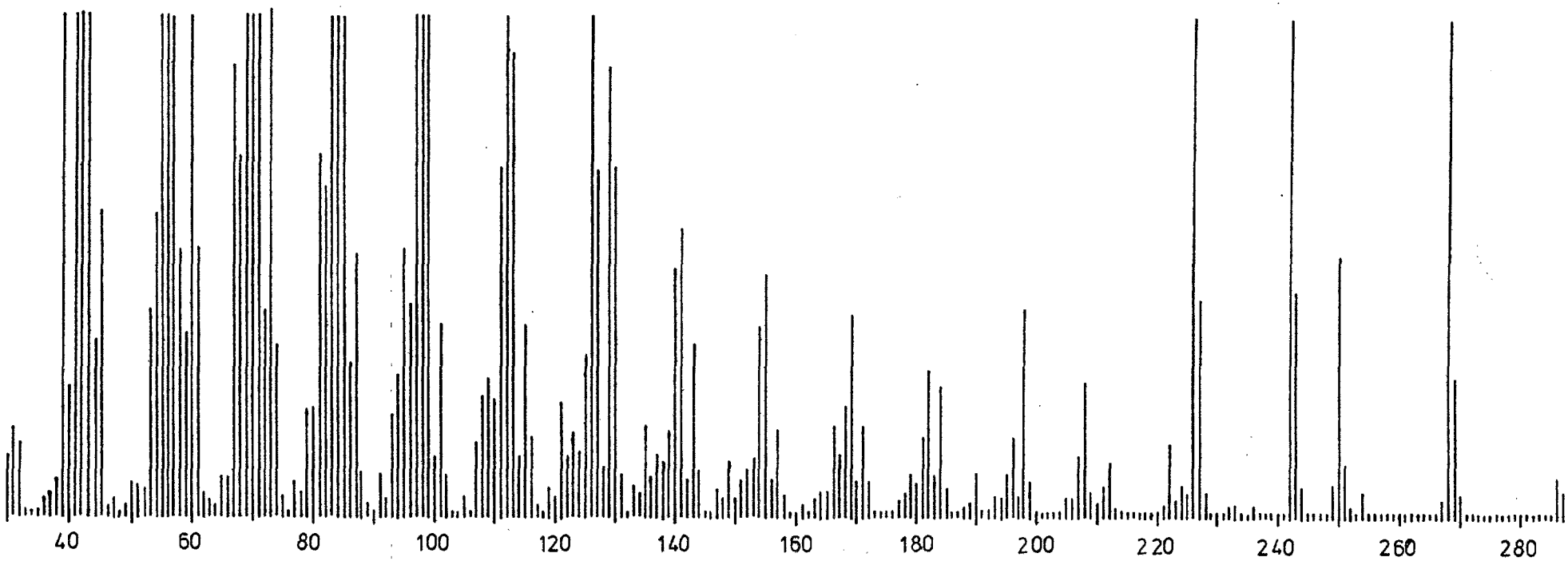


Fig. 12.3 The mass spectrum of a pure unused 1 mole per cent solution of hexadecanedioic acid in hexadecane.

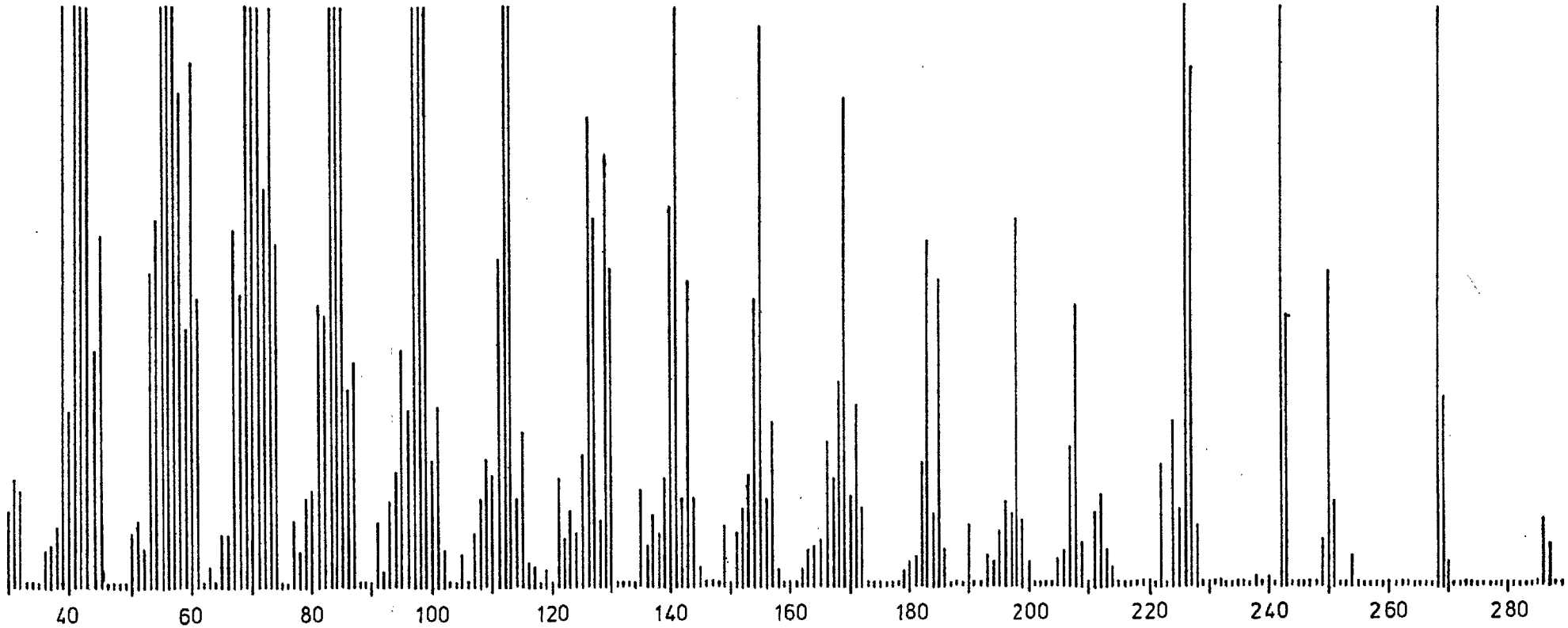


Fig. 12.4 The mass spectrum of a used 1 mole per cent solution of hexadecanedioic acid in hexadecane.

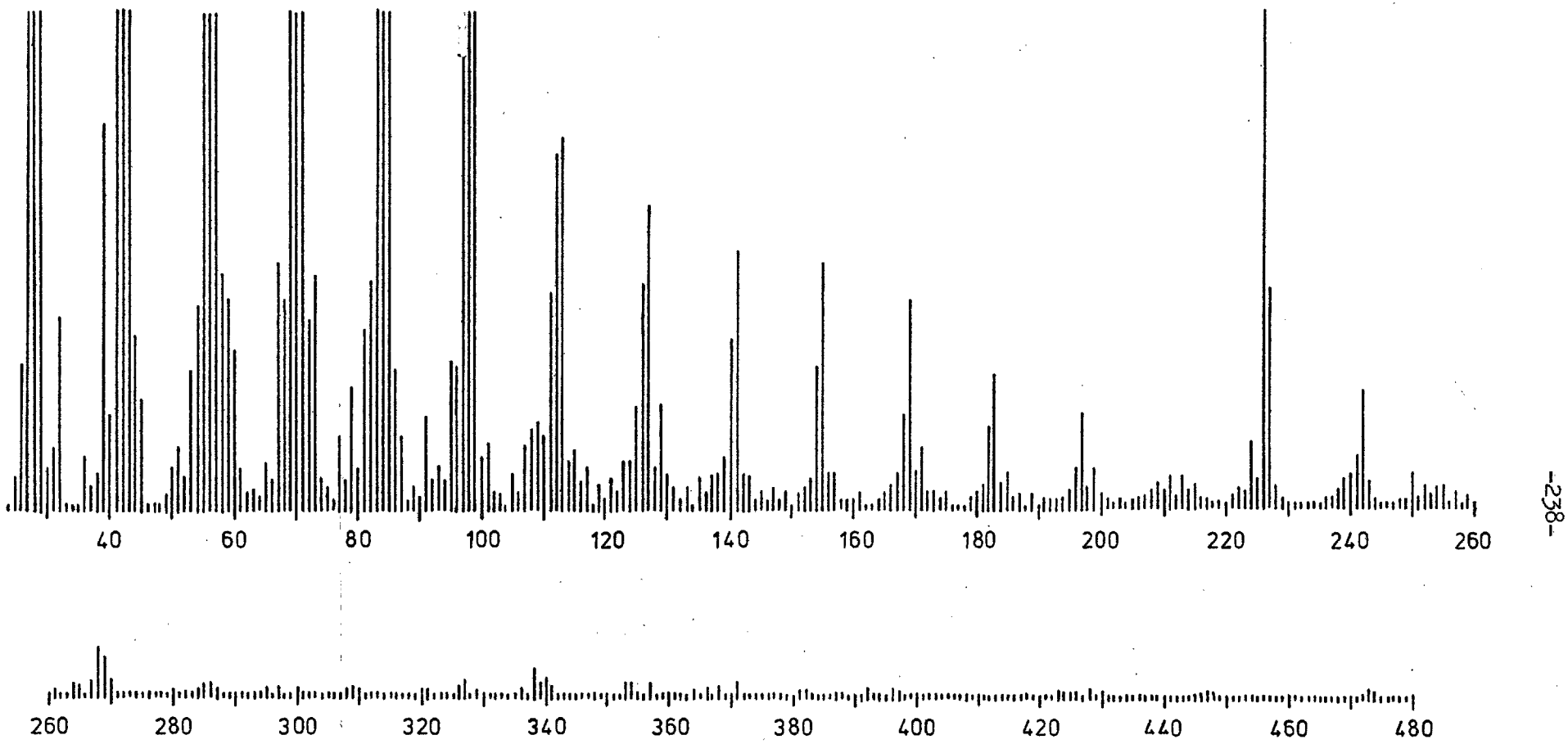
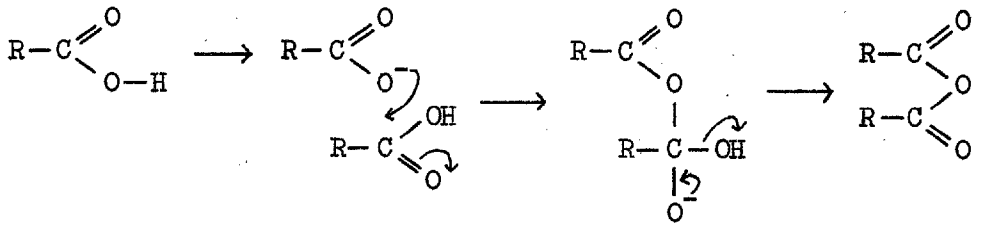


Fig. 12.5 The mass spectrum of the dichloromethane extract when using a 1 mole per cent solution of hexadecanedioic acid in hexadecane.



This could obviously occur at both ends of a molecule resulting in either a chain if several different molecules reacted together, or a ring structure if one molecule reacted with itself. Ring formation would probably not be the prefered reaction because of the low chance of the reacting groups coming into close proximity for reaction to occur. A seventeen membered ring is also not a prefered size.

A belief commonly held is that when an acid is present the lubricating species is an iron soap. No trace was found of any iron salts. Iron is not a strong base, neither are these acids strong acids, so it might be that the Fe—O bond was broken during soxhletting or in the mass spectrometer. The latter is certain to ocurr. If the salt were to dissociate in the spectrometer Fe^{n+} and $RCO.O^{-}$ would be the ions produced. The iron ion would probably be recorded, but the anion, being negatively charged would not be detected. The highest mass peak would then be (p-45) or possibly (p-18) with a very small parent ion peak p. The relative peak heights suggested that free acid was present rather than acid anions.

The maximum increase in molecular weight only amounted to 65%, which by no means produces a polymer in the true sense. (Care was taken to ensure that there were no peaks in the m/e 800—1000 region which would suggest that the peaks at 400+ were due to doubly charged fragments.)

Infra red spectroscopy gave no further information other than that anhydrides were absent. (There were no peaks in the 5.5 and 9.0 μm

area.)

The mass spectrum of the extract was quite different from that of the solid brown material found around the wear scars of the ball and pegs and floating in the used lubricant. This material is now described.

The solid brown deposit. This was subjected to inorganic mass spectroscopy, X ray diffraction, wet chemical analysis and organic mass spectroscopy.

Table 12.2 gives the results of the inorganic mass spectroscopy. The spectrum was obtained by mixing the deposit (5.6 mg) with pure graphite powder (49.7 mg) and using this to tip a pure graphite rod. This was sparked to give a gaseous product which was analysed in exactly the same way as in an organic mass spectrometer. Although table 12.2 shows iron taken as 100, in practice the quantities were compared to the ^{57}Fe isotope which has a natural abundance of 2.19%, a figure closer to those recorded here.

The relative abundances of iron, manganese and chromium were very

Metal	Relative abundance	Metal	Relative abundance
Fe	100	Mn	0.88
Cr	0.71	Ca	0.21
K	0.25	Cl	0.07
S	0.28	P	0.10
Si	1.10	Na	0.96

Table 12.2 Result of inorganic mass spectroscopy on the brown deposit found beside wear scars and in the used lubricant. The abundances are taken relative to iron as 100.

similar indeed to those in the actual EN31 steel used. Sulphur, phosphorous and silicon are high, but this was probably due to adventitious pick up. This was almost certainly the source of the calcium, chlorine, potassium and sodium. Considerable gassing occurred when the graphite rods were sparked, indicating a high oxygen content.

X ray diffraction showed that the oxides or hydrated oxides of iron and the minor elements were absent. Wet chemistry showed that the iron was in the iron (III) state with only a trace in the iron (II) state. Taken together these results pointed to the brown material consisting of a mixture of organic salts of iron and the other metals in EN31 steel. The quantity of each salt was proportional to the occurrence of each metal in the steel.

As far as the organic mass spectroscopy was concerned, spectra obtained at different temperatures were quite dissimilar. A mass spectrum recorded at 150°C showed the presence of a mixture of hexadecanedioic acid and hexadecane. At 240°C the spectrum produced showed the complete absence of diacid, but the presence of species with m/e ratios of up to 740. Careful analysis of the high temperature spectrum showed that the high molecular weight products were probably of the form R-R'-R where R' was bifunctional and R was typically $C_{13}H_{27}$. The occurrence of metastable peaks and correlations made between other peaks suggested that the species responsible for this spectrum were generated in the spectrometer rather than in the triplane apparatus. The spectrum obtained at the lower temperature was therefore taken as the one arising from the products generated during sliding. The peak at m/e 286, the parent ion peak, was very weak, suggesting that very little free diacid was present. The fragmentation peaks were, however, as expected, implying the presence of the anions formed by the diacid.

A sample of iron (III) hexadecanoate was prepared by heating

excess hexadecanedioic acid with sodium hydroxide to 130°C. The resultant mixture was ground in an aqueous iron (III) chloride solution. The product, which was brown, was filtered and washed with water until the washings were chloride free (silver nitrate test). The iron hexadecanoate so prepared, after miximg with a little hexadecane, gave a mass spectrum which was very similar indeed to that of the brown material produced in the triplane apparatus.

It was concluded that the brown substance was a mixture of the hexadecanoates of the metals present in EN31 steel, the amount of each being in the proportion in which the metal occurs in the steel, together with traces of hexadecane. The source of the hexadecane was probably an adherent film not removed by brief washing with ether.

The analysis described above was carried out on the solid brown material generated during the tests of extended duration. An identical analysis was carried out on the brown deposit produced during the load carrying capacity determinations. The results indicated that both products were identical. The formation of the metal hexadecanoates must be independent of pressure in the contact. It did appear, however, to be dependent on the sliding speed, since none was detected when the triplane apparatus was operated at a sliding speed of 1.09 ms^{-1}. Iron is a weak base and hexadecanedioic acid is a weak acid so the Fe-O bond formed between the iron and the organic molecule would probably be relatively weak, and thus fairly easily broken. It might well be that the thermal energy generated in the contact at the higher speed was enough to break the bond, or effectively to prevent its formation.

12.6 WEAR RESULTS

The diameter of the wear marks on the pegs was taken as a guide to

the extent of wear. Although the diacid solutions gave higher scuffing loads than 1,16-hexadecanediol solutions, the wear scar diameters were much larger, typically 1.6 mm as opposed to 1.1 mm after six hours running at a load of 69 kg and a sliding speed of 0.43 ms^{-1}. It might be that the larger diameter scars were caused by reaction of the diacid with the steel, so effectively removing the steel. The improved load carrying capacity may then have been a direct result of the load bearing area being twice as great.

As to whether or not the presence of a diacid is beneficial depends on what aspect of a lubricant is desirable. Hexadecanedioic acid solutions in hexadecane increase the load carrying capacity and reduce friction, but the question is whether or not the wear rate is acceptable.

12.7 CONCLUSIONS

When using hexadecane solutions of hexadecanedioic acid the following conclusions were reached.

1. The addition of 0.5 to 1.0 mole per cent of the diacid to hexadecane increased the load carrying capacity very significantly. At a sliding speed of 0.43 ms^{-1} the failure load was too high to be measured by the triplane apparatus.
2. After failure at a sliding speed of 1.09 ms^{-1} the lubricant was colourless, but contained wire wool like metallic wear debris. This was not so at the lower speed.
3. At a speed of 0.43 ms^{-1} a brown material was found on the trailing edges of the pegs and on the edges of the wear marks on the ball.
4. This brown material consisted of a mixture of metal salts of the diacid, the amount of each salt being in proportion to the occurrence of the metal in the sample of EN31 steel. It was

insoluble in hexadecane. No oxides were present.

5. The generation of this substance was accompanied by relatively high wear rates. It might be that the high scuffing loads resulted from the larger area of the contacts produced during sliding: friction was, however, relatively low.
6. The lubricant remaining after a test was found to be unchanged.
7. The dichloromethane extract contained substances with molecular weights of up to 473. No anhydrides were detected.

Table 12.3 Analyses carried out on materials used in chapter 12.

Sample	Analysis		
	Organic mass spectroscopy	Infra red	Melting point
Hexadecanedioic acid as supplied			*
Purified hexadecanedioic acid	*	*	*
Pure unused 1% solution of hexadecanedioic acid in hexadecane	*	*	
Pure 1% solution of diacid heated alone at 150°C for 24 hours	*	*	
Pure 1% diacid solution heated at 150°C for 24 hours in presence of EN 31 steel	*	*	
Blank dichloromethane extraction	*		
Used 1% diacid solution	*	*	

continued . . .

Table 12.3 (continued)

Sample	Analysis				
	Organic mass spectroscopy	Inorganic mass spectroscopy	Infra red	XRD	Wet chemistry
Dichloromethane extract using 1% diacid solution	*		*		
Brown deposit on ball and pegs after sliding at 0.43 ms^{-1}	*	*	*	*	*
Brown deposit on ball and pegs found after load carrying capacity determinations	*	*	*	*	*
Ether used for washing brown deposit	*		*		
Authentic sample of iron (III) hexadecanoate	*		*		

CHAPTER 13

EQUIMOLAR MIXTURE OF HEXADECANEDIOL AND HEXADECANEDIOIC ACID

13.1 INTRODUCTION

The previous two chapters dealt with the behaviour of hexadecanediol and of hexadecanedioic acid in hexadecane. In this chapter the results when using an equimolar mixture of the diol and diacid are presented. This type of system is being studied as potentially having a commercial use as a lubricant, particularly for forging. In the industrial process diacids, such as linoleic acid dimer, and diols, such as glycols containing about sixteen carbon atoms, are either partially esterified or used as a mixture. The partially esterified mixture is supposed to undergo self polymerisation[54-61], whereas the unesterified mixture is supposed to form a polyester film on contact with a clean metal surface whether or not that surface is generated by rubbing. Although these ideas have been put forward, and patented, no actual proof has been offered for the existence of any polymeric films - their existence has always been implied. In this chapter direct evidence is offered for the size of these 'polymers' when using unesterified diol - diacid mixtures under sliding conditions.

13.2 DETERMINATION OF LOAD CARRYING CAPACITY

13.2.1 Results and Discussion

The load carrying capacities of 0.5 and 1.0 mole per cent solutions

of an equimolar mixture of hexadecanediol and hexadecanedioic acid in hexadecane were determined in the usual manner at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}. All materials were carefully purified before use. Because of solubility problems with the diacid all tests were commenced at 125°C.

The results are presented in table 13.1. At the lower sliding speed the failure load was greater than could be measured without risk of damage to the torque tube. On dismantling the apparatus traces of a brown deposit were noted on the trailing edges of the pegs. This material will be considered in detail when the dichloromethane extraction studies are discussed. The lubricant remaining was pale yellow.

At 1.09 ms^{-1} failure was sudden and complete. The lubricant was however colourless, with no brown wear deposit visible on the metal

Solution concentration mole per cent	Scuffing load (kg)	
	Sliding speed	
	0.43 ms^{-1}	1.09 ms^{-1}
0.5	>250	70
1.0	>250	90

Table 13.1 Scuffing loads of 0.5 and 1.0 mole per cent solutions of an equimolar mixture of hexadecanediol and hexadecanedioic acid in hexadecane at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

surfaces. The 1.0% solution gave a higher scuffing load than the 0.5% solution. This was probably due to greater surface coverage offered by the higher concentration of diol and diacid. Viscosity changes alone were not of sufficient magnitude to explain the difference.

It was previously observed that a solution of a mixture of hexadecanol and hexadecanoic acid gave scuffing loads intermediate between those of the alcohol and acid solutions. (The alcohol gave the lower failure load.) The same behaviour was noted here, and as before, the performance of the mixture was closer to that of the diacid than to that of the diol. The diol, diacid and their mixtures all gave higher failure loads than the monohydric alcohol, mono-acid and a mixture of both. This might be due to the greater chance of a polar group coming close to the metal surface, resulting in sorption or a chemical reaction. The molecular chain lengths are so similar that the differences would have little or no effect.

In determining the load carrying capacity of solutions of the monofunctional compounds the temperatures encountered were lower than those used for the difunctional materials. To see if this was significant, the scuffing loads of the monofunctional compounds were redetermined using the same temperature conditions as employed for the difunctional compounds. The scuffing loads were the same as found previously, showing that temperature effects were not responsible for the observed differences.

13.3 EFFECT OF STARTING TEMPERATURE ON SCUFFING LOAD

It was found that the scuffing load of a solution of hexadecanediol in hexadecane was dependent on the starting temperature of a test. Mixed diol - diacid solutions showed similar behaviour. At temperatures below 125°C the failure load was temperature dependent. At 125°C and

above the scuffing load was independent of temperature. The temperature, 125°C, might be significant in that it is the melting point of the diacid. The diol exhibits much lower failure loads than the diacid, and it might be that at temperatures up to 125°C there is only a little diacid effective in the solution, whereas above 125°C the diacid is fully dissolved so it exerts its maximum possible effect.

13.4 BLANK TESTS

13.4.1 Procedure

It was expected that heating the diol - diacid mixture might produce mono- or polyester. If this reaction were to occur during the preliminary heating of the apparatus, before sliding commenced, the system being studied would be an ester solution rather than a solution of the diol - diacid mixture. To discover the rate of esterification, and whether or not it was important, a freshly prepared diol - diacid solution was heated from room temperature to 130°C over a period of twenty minutes. This is the time typically taken to heat the triplane apparatus prior to the start of a test. The temperature was maintained at 130°C for twenty four hours. At half hourly intervals a sample was removed, cooled rapidly to prevent further reaction, and analysed by mass spectroscopy.

13.4.2 Results

No ester was detected in samples removed up to one and a half hours after the heating up period. After two hours, however, there were traces of the two esters:

$$HO.OC\ C_{14}H_{28}CO.OC_{16}H_{32}OH \qquad (MW\ 526)$$

and

$$C_{14}H_{29}CO.OC_{16}H_{32}OH \qquad (MW\ 482)$$

These are the expected esters. The second is formed either before or after esterification when a carboxyl group on the diacid leaves as carbon dioxide. (The mass spectra were obtained at relatively low temperatures (about 30°C) to avoid thermal effects in the spectrometer.) Even after heating for twenty four hours no polyesters or cyclic esters were found. The heating process was repeated both with and without EN31 steel present, but no differences could be detected.

Soxhletting in dichloromethane for twenty four hours did not appear to change the diol - diacid solution, probably because of the low temperature involved.

13.5 DICHLOROMETHANE EXTRACTION STUDIES

13.5.1 Procedure

Tests of six hours duration were conducted using a 1.0% solution of an equimolar mixture of hexadecanediol and hexadecanedioic acid in hexadecane. The sliding speed was 0.43 ms^{-1} and the applied load 69 kg. Sliding was not begun until the temperature of the lubricant had stabilised at 125°C.

The lubricant remaining after a test, and the residue after the ball and pegs had been soxhletted in dichloromethane were compared to the pure unused diol - diacid solution. The solid brown wear 'debris' found predominantly on the trailing edges of the pegs was carefully scraped off prior to soxhletting. It was then analysed separately.

13.5.2 Results and Discussion

The used lubricant. For reference purposes the mass spectrum of a pure unused one per cent solution of an equimolar mixture of hexadecanediol and hexadecanedioic acid in hexadecane is shown in fig. 13.1. The used lubricant spectrum, fig. 13.2, was similar to the

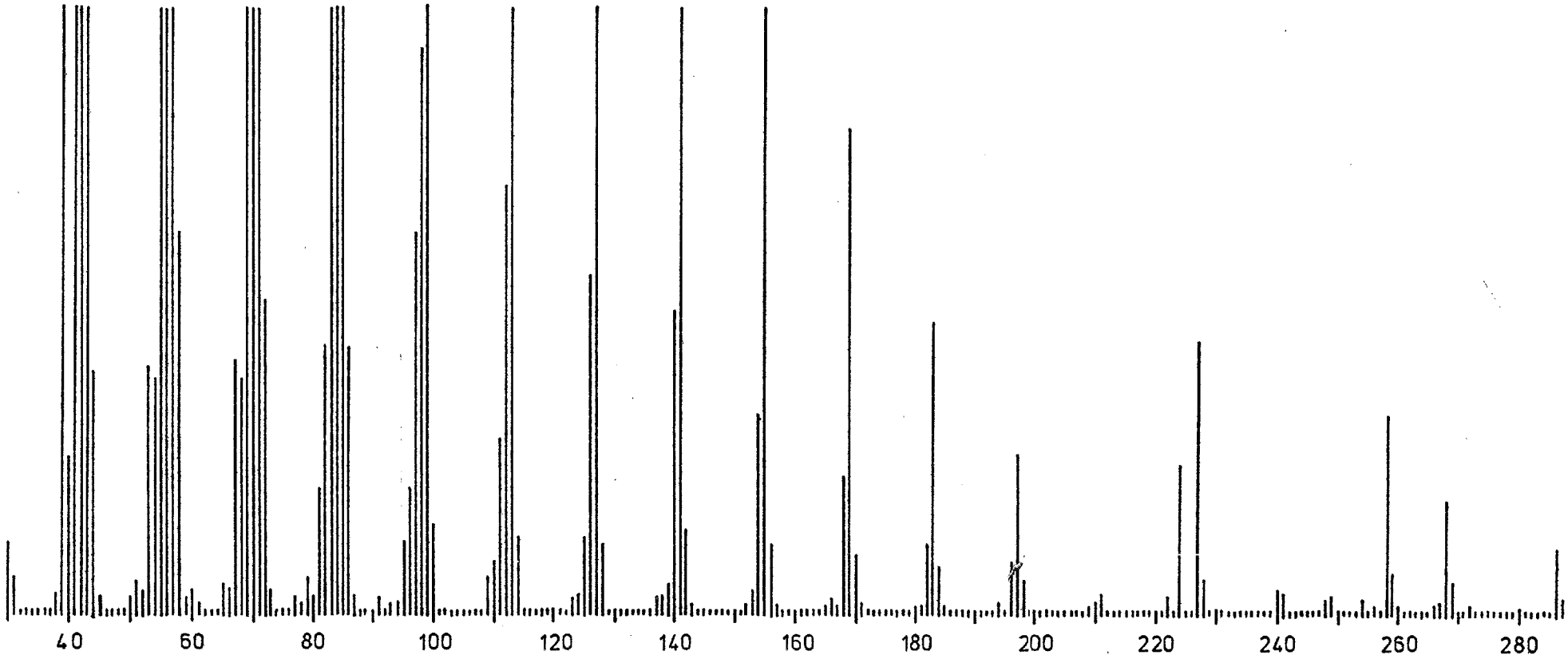


Fig. 13.1 The mass spectrum of a pure unused 1 per cent solution of an equimolar mixture of 1,16-hexadecanediol and hexadecanedioic acid in hexadecane.

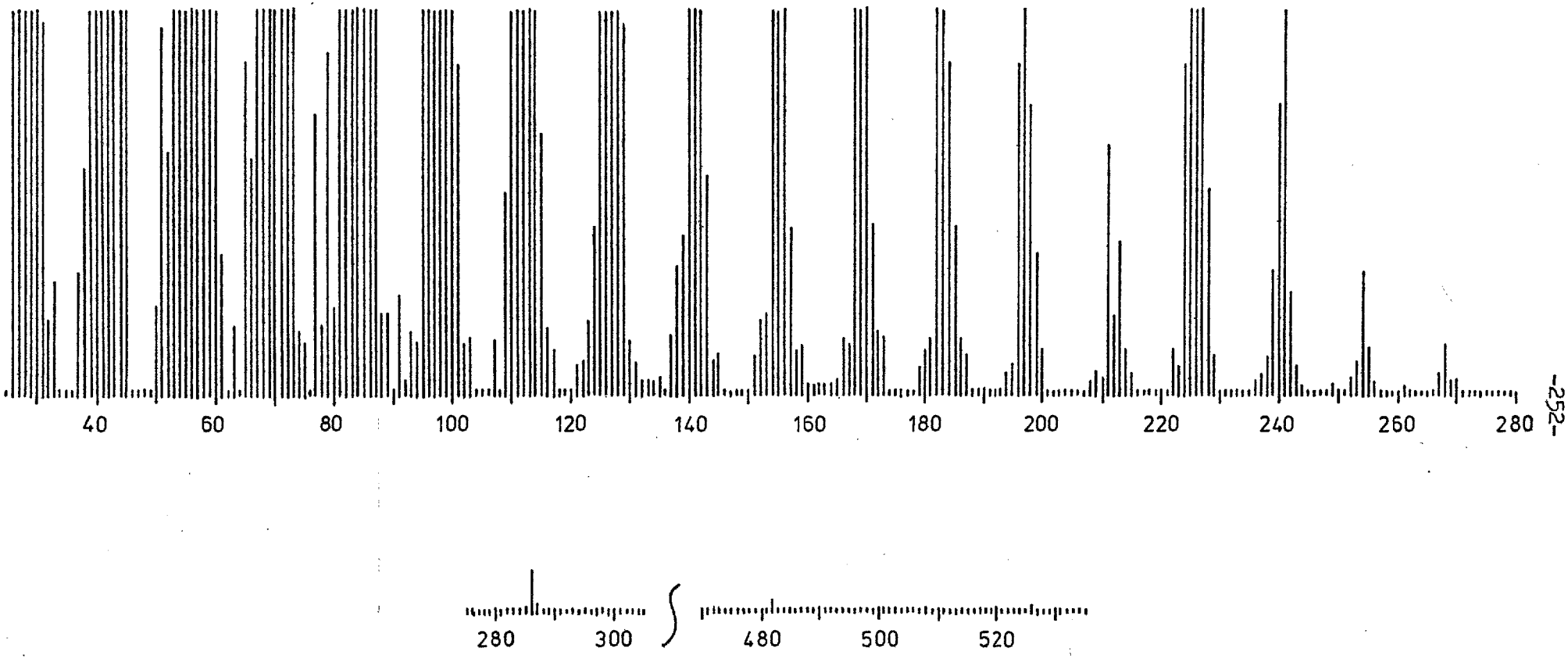


Fig. 13.2 The mass spectrum of a used 1 mole per cent solution of an equimolar mixture of 1,16-hexadecanediol and hexadecanedioic acid in hexadecane.

spectrum of the pure unused solution which had been heated for twenty four hours at 130°C, except that there was relatively less free diacid present. It was concluded that thermal effects had caused esterification to occur, but during sliding another reaction had occurred which had removed some of the diacid. This reaction was thought to be the formation of metal salts. Confirmation of this was given by the analysis of the brown deposit found at the edges of the wear scars on the pegs and, to a lesser extent, on the ball.

The dichloromethane extract. The dichloromethane extract mass spectrum showed the presence of a mixture of esters, apparently the same as detected in the used lubricant, together with metal salts of the diacid. There was very little free acid present, but its fragmentation peaks were quite intense, suggesting the presence of organic anions. The extract probably consisted of transfered used lubricant and traces of the brown deposit which were not removed prior to soxhletting.

Copper plating tests performed on the balls and pegs after soxhletting showed the absence of any organic films. The same test was conducted on a ball and pegs after scraping off the brown deposit, but before soxhletting. Copper did not plate out on the wear scars or on the regions from which the brown material had been scraped. This is further evidence for the suggestion that the extract was a mixture of used lubricant and the brown deposit. The latter is now examined in detail.

The brown deposit. The combined results of inorganic and organic mass spectroscopy showed that the brown deposit was a mixture of esters and organic salts of the elements present in EN31 steel. The relative amount of each metal was in proportion to its occurrence in the EN31 steel used. It would appear therefore that the acid reacts with the

metal during sliding to produce organic salts. At the same time some of the acid reacted with the diol to produce an ester.

In neither the brown deposit, the used lubricant nor the dichloromethane extract were any esters found which consisted of more than one acid and one alcohol molecule. Considering the thermal decomposition reaction of a diacid it would be surprising to find esters formed from more than three units, one diol and two diacid. The results obtained here suggest that the formation of polyesters, as has been supposed by some workers, is unlikely. The extent of reaction must only be relatively slight. It must not be forgotten however that the materials used here were of the highest possible purity. If one were working with technical grade materials whose purity is typically 85%, other reactions would be not only possible but quite likely.

13.6 CONCLUSIONS

When using a 0.5% to 1.0% solution of an equimolar mixture of 1,16-hexadecanediol and hexadecanedioic acid in hexadecane as the lubricant in the triplane apparatus the following conclusions were reached.

1. The scuffing load of the mixture solution was intermediate between those of solutions of diol and diacid alone. Increasing the sliding speed decreased the failure load.
2. The diol - diacid mixture had a higher load carrying capacity than a mixture of the C_{16} mono-alcohol and mono-acid of similar functional group concentration.
3. The scuffing load was temperature dependent below 125°C, but not above this temperature. This was attributed to the limited solubility of the diacid below 125°C.
4. At a sliding speed of 0.43 ms^{-1} a brown deposit was observed at the

edges of the wear scars on the ball and particularly the pegs. The deposit consisted of metal salts of the acid.

5. The bulk liquid lubricant underwent some esterification during sliding - a result of thermal effects alone.
6. In contrast to some previous workers ideas[54-61] no polyesters were detected. There was also no evidence for cyclic esters, or any ester containing more than one alcohol and one acid unit.

Table 13.2 Analyses carried out on materials used in chapter 13.

Sample	Analysis		
	Organic mass spectroscopy	Inorganic mass spectroscopy	XRD
Pure unused 1% diol - diacid solution in hexadecane	*		
Pure 1% diol - diacid solution heated from 25°C to 130°C over a period of 25 minutes	*		
Samples removed from 1% diol - diacid solution held at 130°C for up to 24 hours; steel absent	*		
Samples removed from 1% diol - diacid solution held at 130°C for up to 24 hours in presence of EN 31 steel	*		
Blank soxhlet extraction	*		

continued . . .

Table 13.2 (continued)

Sample	Analysis		
	Organic mass spectroscopy	Inorganic mass spectroscopy	XRD
Used 1% diol - diacid solution	*		
Dichloromethane extract using 1% diol - diacid solution	*		
Brown deposit found on and around wear scars on pegs and ball after running at a sliding speed of 0.43 ms^{-1}	*	*	*

CHAPTER 14

CONCLUSIONS

14.1 ANALYTICAL METHODS

There are no methods currently available for the in situ detection and identification of the type of organic films formed in lubricated systems. Elements such as sulphur and phosphorous can be detected, but these probably only account for a small part of a boundary layer. The techniques of surface analysis fall broadly into two categories, those which have been developed specifically for examining surfaces, and those which are adaptations of other methods.

The purpose-designed group includes field emission microscopy which will detect an atom on an atomically clean surface. This requires an ultra high vacuum which makes it unsuitable for tribochemical systems. A recently developed analytical tool which can be used for examining 'bulk' films on surfaces is ESCA. It gives information on both the type of atoms present and their bonding states. Unfortunately it was not suitable for this study since it was found to be too sensitive in that it detected impurities picked up whilst samples were being transfered from the test apparatus to the ESCA machine.

Amongst the 'adapted' methods are reflection infra red and Raman spectroscopy. Both were found to be unsuitable because the surfaces to be examined were both rough and curved. These conditions caused so much attenuation that no meaningful spectra could be obtained. Certain X-ray techniques suffer from the same problem. They also require a

crystal structure, and since apparently none were present, X-ray analysis proved unfruitful.

It was concluded that the films formed on the surfaces could only be examined after removal from the substrate steel. This was not an altogether satisfactory arrangement since there is no guarantee that the compounds removed are the same as those present on the surface, but it was unfortunately necessary. The method chosen was soxhlet extraction using dichloromethane as the solvent. Blank tests carried out showed that the materials extracted did not undergo any changes during soxhletting. The extracted substances were then analysed using more conventional methods such as mass and infra red spectroscopy.

A new method for the detection of chemisorbed films on EN31 steel surfaces was developed. This involved allowing copper to plate out onto the metal surface from an aqueous 0.2 M copper (II) sulphate solution. Copper did not plate where an organic film was present. It also appeared to give an indication of surface cleanliness in that it would detect whether or not a surface had been ionically bombarded.

14.2 HEXADECANE

Hexadecane was used as the carrier for all the additives examined. It was found to undergo no chemical changes whatsoever when used by itself in the triplane apparatus. This was only true if it had been carefully purified before use. The initial presence of impurities resulted in oxidation occurring quite rapidly. When pure, hexadecane was a very poor lubricant indeed - considerably worse than many researchers have reported. However the purity of their material was generally not stated. Any wear debris produced with hexadecane consisted of oxides - predominantly the iron (III) oxide.

14.3 ADDITIVES

14.3.1 Summary

Solutions of various additives were tested, first to determine their load carrying capacity, then to discover whether or not they gave products with an increased molecular weight. The solution concentrations used were between a half and two per cent. The additives and results are summarised in tables 14.1 and 14.2.

14.3.2 Load Carrying Capacities

In every case the presence of an additive gave a scuffing load considerably higher than that shown by pure hexadecane. This was attributed to the additive molecules' polar end groups allowing more facile sorption onto the steel surfaces. Although the sliding speeds and loads used produced a mixed hydrodynamic - boundary lubrication regime, viscosity changes were not of sufficient magnitude to account for the observed results.

At a sliding speed of 0.43 ms^{-1} the failure load spanned a range of values between 85 kg and 130 kg. There were two exceptions to this. One was hexadecyl hexadecanoate which had a very low scuffing load. This was thought to be due to steric effects preventing the polar oxygen atoms from being freely available for 'bonding' with the metal surface. The other exception was solutions containing hexadecanedioic acid which exhibited very high load carrying capacities. This was associated with the presence of a brown deposit on and around the wear scars of the ball and pegs. This material is described later.

The effect of sliding speed. In every case increasing the sliding speed caused failure to occur at a lower applied load. This was attributed to the more violent asperity contacts at the higher speed causing local heating which resulted in the desorption of adsorbed

Table 14.1 Summary of load carrying capacities, L, coefficients of friction, μ, bulk lubricant temperatures, T_b, and and total temperatures, T_t, at sliding speeds of 0.43 ms^{-1} and 1.09 ms^{-1}.

Additive	Concentration	Sliding speed							
		0.43 ms^{-1}				1.09 ms^{-1}			
		L kg	μ	T_b °C.	T_t °C.	L kg	μ	T_b °C.	T_t °C.
Hexadecene	100%	103	0.11	135	339	55	0.088	112	317
	1%	96	0.15	135	403	34	0.1	120	301
	2%	96	0.1	130	308	34	0.088	115	274
1-Aminohexadecane	1%	105	0.07	105	236	48	0.06	116	246
	2%	135	0.07	130	280	69	0.06	105	263
Hexadecan-1-ol	1%	96	0.11	100	296	48	0.05	60	169
	2%	96	0.11	120	316	48	0.073	65	223
Hexadecanoic acid	1%	83 (117)*	0.1	135	300 (334)*	41	0.088	65	241
	2%	83 (124)*	0.06	118	217 (241)*	41	0.08	78	238
Hexadecyl hexadecanoate	1%	55 (85)*	0.15	125	323 (375)*	34	0.13	86	321

continued . . .

Table 14.1 (continued)

Additive	Concentration	Sliding speed							
		0.43 ms^{-1}				1.09 ms^{-1}			
		L kg	μ	T_b °C.	T_t °C.	L kg	μ	T_b °C.	T_t °C.
Hexadecyl hexadecanoate	2%	55 (92)*	0.14	130	314 (374)*	34	0.11	83	282
Equimolar mixture of hexadecan-1-ol and hexadecanoic acid	1%	103	0.07	88	218	41	0.07	111	251
	2%	103	0.06	102	213	41	0.088	90	266
1,16-hexadecanediol	0.5%	86	0.11	135	320	50	0.11	110	354
	1%	86	0.077	130	259	50	0.073	145	307
Hexadecanedioic acid	0.5%	>250	0.025	142	217	103	0.018	149	208
	1%	>250	0.016	135	183	117	0.029	170	271
Equimolar mixture of 1,16-hexadecanediol and hexadecanedioic acid	0.5%	>250	0.03	150	240	70	0.028	142	216
	1%	>250	0.03	140	230	90	0.03	135	226

* Total failure occured at this load (see relevant chapters).

Additive	Concentration	Percentage increase in molecular weight	
		Used lubricant	Dichloromethane extract
1-Hexadecene	2%	0	0
1-Aminohexadecane	2%	0	~17
Hexadecan-1-ol	2%	0	100
Hexadecanoic acid	2%	0	0
Hexadecyl hexadecanoate	2%	0	0
Equimolar mixture of hexadecan-1-ol and hexadecanoic acid	2%	Trace of ester	~100
1,16-Hexadecanediol	1%	0	~100
Hexadecanedioic acid	1%	0	~65*
Equimolar mixture of hexadecanediol and hexadecanedioic acid	1%	Trace of monoester	Trace of * monoester

Table 14.2 Increase in molecular weight caused by the addition of various additives to hexadecane. *denotes that a brown deposit was found on and beside the wear scars.

layers. If the films were not renewed quickly, the high friction between the metal surfaces caused an acceleration in the temperature rise and total failure rapidly ensued. An examination of the temperatures and coefficients of friction show that there was not a constant desorption temperature.

The effect of additive concentration. In general doubling the concentration from one per cent to two per cent had no effect on the failure load. This was probably because the surface became saturated with additive molecules at a concentration of below one per cent. Exceptions to this were 1-aminohexadecane, hexadecanedioic acid and an equimolar mixture of 1,16-hexadecanediol and hexadecanedioic acid. In these cases the concentration required for surface saturation was greater than one per cent. It is believed that this is a kinetic rather than a pure thermal effect.

Collision Theory predicts a greater rate of reaction with a surface with increased concentration. A higher additive concentration would therefore offer more rapid replacement of any protective organic film removed from the metal surfaces during sliding. Total failure would thus be postponed until a load was reached when the rate of removal of surface layers would be greater than the rate of their formation.

In the case of the amine competitive adsorption with hexadecane was thought to be a contributory factor.

The effect of starting temperature. The starting temperature of a test was only significant for solutions of 1,16-hexadecanediol and hexadecanedioic acid.

Below 120°C the load carrying capacity of the diol was proportional to the starting temperature, but above 120°C it was independent of the temperature. This was probably due to association effectively reducing

the availability of the alcohol to the metal surface to protect it. 120°C was the temperature at which the degree of association was constant and possibly zero.

Hexadecanedioic acid was only slightly soluble in hexadecane below its melting point (125°C). Its scuffing load was considerably higher than that of the diol, so when a mixture of both was tested the starting temperature had to be above 125°C. If this were not the case the concentration of dissolved diacid was very low. The failure load was then nearer to that of the possibly partially associated diol than to the value which would be given by a truly one per cent equimolar mixture.

14.3.3 Used Lubricants

With most of the additives the bulk liquid lubricant underwent no changes. Where changes were observed they were due to thermal rather than sliding effects.

1-Hexadecene yielded traces of the ketone hexadecan-2-one. This was formed by the addition of water to the double bond. A dry system produced no ketone.

When solutions of hexadecan-1-ol were used the concentration of the alcohol increased. It was not clear how this occurred, but it may have involved peroxides generated by reaction with atmospheric oxygen. The presence of a steel surface was not required.

A mixture of hexadecan-1-ol and hexadecanoic acid produced a used lubricant containing traces of ester. A mechanism was proposed which involved sorption onto a freshly formed steel surface. It is theoretically impossible to form the ester by simply heating the mixture in a pure hexadecane solvent. This was confirmed by experiment.

The 1,16-hexadecanediol - hexadecanedioc acid mixture also gave traces of esters. Two were detected, HO.OC $C_{14}H_{28}CO.OC_{16}H_{32}OH$ and

$C_{14}H_{29}CO.OC_{16}H_{32}OH$. The second was generated by the thermal loss of carbon dioxide from the diacid followed by reaction of the resulting pentadecanoic acid with hexadecanediol.

14.3.4 The Brown Deposit Formed By Hexadecanedioic Acid

When hexadecanedioic acid was present, either by itself or with 1,16-hexadecanediol, a brown deposit was formed on and around the wear scars on both the ball and pegs. Relatively large amounts were found on the trailing side of the contact area on the pegs. This material was insoluble in the diacid solution, but particles of it were found floating in the used lubricant.

Organic and inorganic mass spectroscopy and X-ray diffraction showed that it consisted of a mixture of the salts of the metals present in the EN31 steel. The amount of each salt was proportional to the occurrence of each metal in the steel. The iron in the iron salt was almost exclusively in the iron (III) state. This was confirmed by comparison with an authentic sample.

The formation of this deposit was independent of load, but the sliding speed was important. At 0.43 ms^{-1} considerable quantities were formed, but at 1.09 ms^{-1} none was detected. This might be because the salts did not have a high thermal stability so they were decomposed by the higher flash temperatures generated at the higher speed. Alternatively, if the first step in the reaction mechanism involved adsorption onto the steel surface, the reaction would not be favoured by high temperatures.

14.3.5 The Dichloromethane Extracts

The dichloromethane extracts always contained traces of the compounds present in the bulk lubricant since some liquid was always transfered into the soxhlet on the surfaces of the balls and pegs.

No new compounds were detected in the extracts obtained when solutions of 1-hexadecene or hexadecyl hexadecanoate were used as the lubricant.

The 1-aminohexadecane extract showed the presence of stearic acid and other lower acids together with alcohols and possibly amino alcohols. These might have been formed via alkenes, traces of which were also detected. The formation of an alkene from an alkane by the catalytic effect of chromium oxide is a commercially used reaction.

When a two per cent solution of hexadecan-1-ol was used as the lubricant the dichloromethane extract was a complex mixture of organic materials. At least ten new compounds were produced. These included alkenes, dienes, alkynes, diynes, primary and secondary alcohols, acids, diols and esters. Aromatic rings were also detected. An attempt to separate the components of the mixture by gas liquid chromatography so that the compounds could be separately identified proved impossible. The generation of these materials, whose molecular weights ranged up to 580, required sliding and so presumably freshly formed steel surfaces. The mixture formed on the wear scars only of both the ball and pegs. It was not redissolved by the surrounding liquid lubricant.

Hexadecanoic acid did not produce any new compounds on the ball or peg surfaces, but it was physisorbed quite strongly. This resulted in a higher concentration of the acid in the extract.

The dichloromethane extract when the additive was an equimolar mixture of hexadecan-1-ol and hexadecanoic acid was very similar to that given by the alcohol alone. The main difference was in the quantity of each product. There was, as would be expected, more hexadecyl hexadecanoate.

The use of solutions of 1,16-hexadecanediol produced an extract which contained alkenes, dienes, alkynes, hydroxyacids, acids and

traces of esters. Aromatic rings also appeared to be present. The acids were probably formed by the oxidation of the alcohol groups. These then combined with unreacted alcohol to form the esters. The components of the mixture had molecular weights ranging up to 550, and appeared to be similar to those produced when hexadecan-1-ol was the lubricant. They were found only on the wear scars of both the ball and the pegs. Sliding was necessary for their generation.

A solution of hexadecanedioic acid yielded an extract consisting of a mixture of compounds. The effect of heat on the diacid would be expected to give anhydrides, but none were detected. The materials formed had molecular weights up to 473, a sixty five per cent increase over the diacid. The presence, or otherwise, of iron salts or co-ordination compounds with iron was not proven because traces of the brown deposit previously mentioned masked any mass spectral evidence. Sliding was necessary for the generation of these new substances which were found only on the wear scars.

The dichloromethane extract obtained when the additive was a mixture of the diol and diacid contained esters and iron salts of the acid. The source of the iron salts might have been the brown deposit. The esters probably came from the used lubricant and were introduced into the soxhlet on the surfaces of the balls and pegs. The esters were not polyesters as might be expected from a comparison with Furey's results[54-61]. Instead they consisted of one acid and one alcohol molecule condensed together. It could be argued that heating might convert the diacid to the mono acid, pentadecanoic acid. The largest possible ester which could then be formed would be by the reaction of two acid molecules with one diol molecule. This implies that it is necessary to use low temperatures to produce polyesters. Another consideration must be purity. In this work the purest possible

materials were employed. This cannot be definitely said of previous work which was aimed at a commercial market so presumably technical or commercial grade materials were used.

SUGGESTIONS FOR FURTHER WORK

In this thesis the effects of various functional groups in the terminal position of a straight chain alkane have been investigated. It would be useful to know the effect of these groups in non terminal positions and also when attached to branched chain alkanes. This should then enable the behaviour of most additives and base stocks to be predicted. The nature of the sliding metal surfaces is almost certainly a significant factor and should also be examined - in particular the apparently greater efficiency of palladium in producing friction polymer, as noted in the literature survey.

The formation of 'friction polymers' on metal surfaces is possibly more important than is often thought, so the above suggestions would be well worth acting on - at least from a 'purist' point of view. However, considering the complexity of many additive packages, it may not have any direct commercial application. Nevertheless a greater understanding of the chemical reactions occuring in metal-metal contacts during sliding is an important step forward towards a better understanding of the phenomenon of lubrication.

The development of an analytical method to examine rapidly chemical films consisting of low atomic number elements in situ on rough curved metal surfaces would be of great use to lubrication chemists in general. This would ideally involve electronic spectroscopy so that the bonding of the elements could be examined. Perhaps electronic treatment of the results given by the latest generation of ESCA machines might give satisfactory results.

Finally, many misconceptions and misunderstandings would be removed if the name 'friction polymer' ceased to be used to describe chemically altered films generated in sliding contacts. A better term might be 'friction film'.

APPENDIX I

(A) CARBOWAX 6000 ON CHROMOSORB W

Column material:	Both columns Carbowax 6000 on Chromosorb W in ratio 10:90, 60 - 80 mesh packed in 3 mm od stainless steel tube 2 m long
Injection volume:	0.1 μl
Oven programme:	Initially 118°C for 12 minutes, rising at 4°C min^{-1} to 199°C
Injection temperature:	282°C
Carrier gas:	Oxygen free nitrogen (white spot)
Flow rate:	24 ml min^{-1}
Detector:	Flame ionisation detector
Chart speed:	2 mm min^{-1}

(B) APIEZON L ON CHROMOSORB P

Column material:	Both columns Apiezon L on Chromosorb P in ratio 10:90, 60 - 80 mesh packed in 3 mm od stainless steel tube 2 m long
Injection volume:	0.1 μl
Oven programme:	Initially 167°C for 20 minutes, rising at 1.5°C min^{-1} to 200°C
Injection temperature:	378°C
Carrier gas:	Oxygen free nitrogen (white spot)
Flow rate:	14.5 ml min^{-1}
Detector:	Flame ionisation detector
Chart speed:	2 mm min^{-1}

(C) SILICONE FLUID MS 550 + BENTONE 34 ON CHROMOSORB W

Column material:	Sample column; Silicone fluid MS 550 + Bentone 34 on Chromosorb W in ratio 11.5:11.5:77, 80 - 100 mesh packed in 3 mm od stainless steel tube 2 m long Reference column; Apiezon L on Chromosorb P as described above
Injection volume:	0.1 µl
Oven programme:	177°C held constantly
Injection temperature:	273°C
Carrier gas:	Oxygen free nitrogen (white spot)
Flow rate:	15 ml min^{-1}
Detector:	Flame ionisation detector
Chart speed:	2 mm min^{-1}

APPENDIX II

Maximum flash temperature rises at contacts were calculated according to the method of Blok[92]. The basic equation for the ball on triplane apparatus[93] is:

$$\Delta T_{fm} = \frac{2.\mu.P\left[1+\frac{1}{\sqrt{2}}\right]v.a}{4.\alpha.\rho.C\left[1+\left(\frac{\pi.v.a}{8.\alpha}\right)^{\frac{1}{2}}\right]} \quad \ldots \quad \ldots \quad (i)$$

where the symbols have the following meanings and values for EN 31 steel:

μ	coefficient of friction
v	sliding velocity, (m s^{-1})
α	thermal diffusivity, (6.045 10^{-6} W m^{-1} $^{o}C^{-1}$)
ρ	density of steel, (7814.1 kg m^{-3})
C	specific heat of steel, (506.5 kg m^{2} s^{-2} $^{o}C^{-1}$)
a	Hertz radius at the contact, (m)
P	mean Hertz pressure, (kg m^{-2})

The Hertz radius, a, is given by[94]:

$$a = 1.109\left[\frac{W.R}{E}\right]^{\frac{1}{3}} \quad \ldots \quad \ldots \quad \ldots \quad (ii)$$

where:

W is the load perpendicular to the peg's surface (kg),

R is the reduced radius of the contact where $\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$

R_1 and R_2 being the radii of the contacting surfaces and E is Young's modulus (2.10^{10} kg m^{-2}).

Using the appropriate value for R_1, 0.009525 m, the expression for a becomes:

$$a = 6.7402\ 10^{-5}\ L^{\frac{1}{3}}$$

where L is the top ball load in kg.

The mean Hertz pressure, P, is given by:

$$P = \frac{W}{\pi . a^2} . g$$

or

$$P = \frac{L.\sqrt{2}.g}{3.\pi.a^2} \quad \ldots \quad \ldots \quad \ldots \qquad \text{(iii)}$$

Substituting for a and g gives:

$$P = 3.239\ 10^{8}\ L^{\frac{1}{3}}$$

If these values are substituted into equation (i):

$$T_{fm} = \frac{778.87.\mu.L^{\frac{2}{3}}.v}{1 + 2.0925\ v^{\frac{1}{2}}\ L^{\frac{1}{6}}}$$

Experimental values of , L and v were substituted into this equation to obtain the maximum flash temperatures given in the text.

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