SULPHUR LUBRICANT ADDITIVES
FOR OILS AND EMULSIONS

by

YOSHIAKI YAHAGI

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

ABSTRACT

This thesis examines the role of sulphur lubricant additives (extreme pressure additives) in oil and emulsions under boundary lubrication.

Firstly the mechanism of action of sulphur e.p. additives in water-free systems was studied. It was shown that surfactant adsorption occured strongly on sulphurized steel, as well as unreacted steel. These surfactants play an important part in the mechanism of e.p. additives.

Secondly some fundamental studies were made of the lubricating properties of emulsions. It was found that emulsions can lubricate equally as well as paraffin oil in the ball-on-triplane apparatus although they contain water. Three factors were examined, (a) the film formation between sliding surfaces, (b) excess surfactant functioning as friction modifiers and (c) the control of surface temperature by emulsions.

Finally the performance of organo-sulphur extreme pressure additive in emulsions was studied. It was shown that the cooling effect of emulsions can de~~sup~~press the reaction of dibenzyl disulphide and elemental sulphur with steel which inhibits the load-carrying ability of these additives.

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SYMBOLS AND ABBREVIATIONS

B.E.T.	Brunauer, Emett and Teller adsorption model
B.E.T. method	Surface area measurement of solid
cm^{-1}	Wave number, Kayser
D.B.D.S	Dibenzyl Disulphide
E.H.L.	Elastohydrodynamic lubrication
e.p.	Extreme pressure
E.S.	Elemental sulphur
H.L.B.	Hydrophilic (hydrophile) lipophilic (lipophile) balance
J	Joule
mol	Moles
MeSt	Methyl stearate
N	Newton
Pa	Pascal
ppb	Part per billion (10^{-9})
S	Second
HSt	Stearic acid
surfactant	Surface active agent
StOH	Stearyl alcohol
T	Temperature in ^{o}C unless otherwise stated
V	Velocity of sliding
W	Applied load
μ	Coefficient of friction

CHAPTER ONE

GENERAL INTRODUCTION

1.10 BOUNDARY AND EXTREME PRESSURE LUBRICATION

Lubrication is concerned with the study and control of friction and wear in mechanical elements. Lubrication regimes are classified into four groups by the "film thickness" between sliding surfaces. The thickness of film formed between sliding surfaces governs the degree of severity in lubrication.

The coefficient of friction has been shown to depend on film thickness between sliding surfaces as shown in figure (1.1.a) (1). In this figure the following four conditions of lubrication are portrayed.

(A) Hydrodynamic lubrication
(B) Elastohydrodynamic lubrication (EHL)
(C) Boundary lubrication
Extreme Pressure (e.p.) lubrication
(D) Dry Lubrication

(A) Hydrodynamic Lubrication

This condition is the most desirable for the maintenance of mechanical parts. Friction coefficient is usually low (0.001 ~ 0.005) and wear rate is negligible. The film is thicker than the combined surface roughness. The physical properties of the lubricant such as viscosity are far more important than the properties of the sliding surfaces.

(B) Elastohydrodynamic Lubrication (EHL)

With increasing load at the contact, two further effects have to be considered. The viscosity of the fluid in the contact increases, and the contact deforms elastically. This results in the elastohydrodynamic regime. Frictional coefficient is low, but, because films are quite thin, some asperity contact occurs.

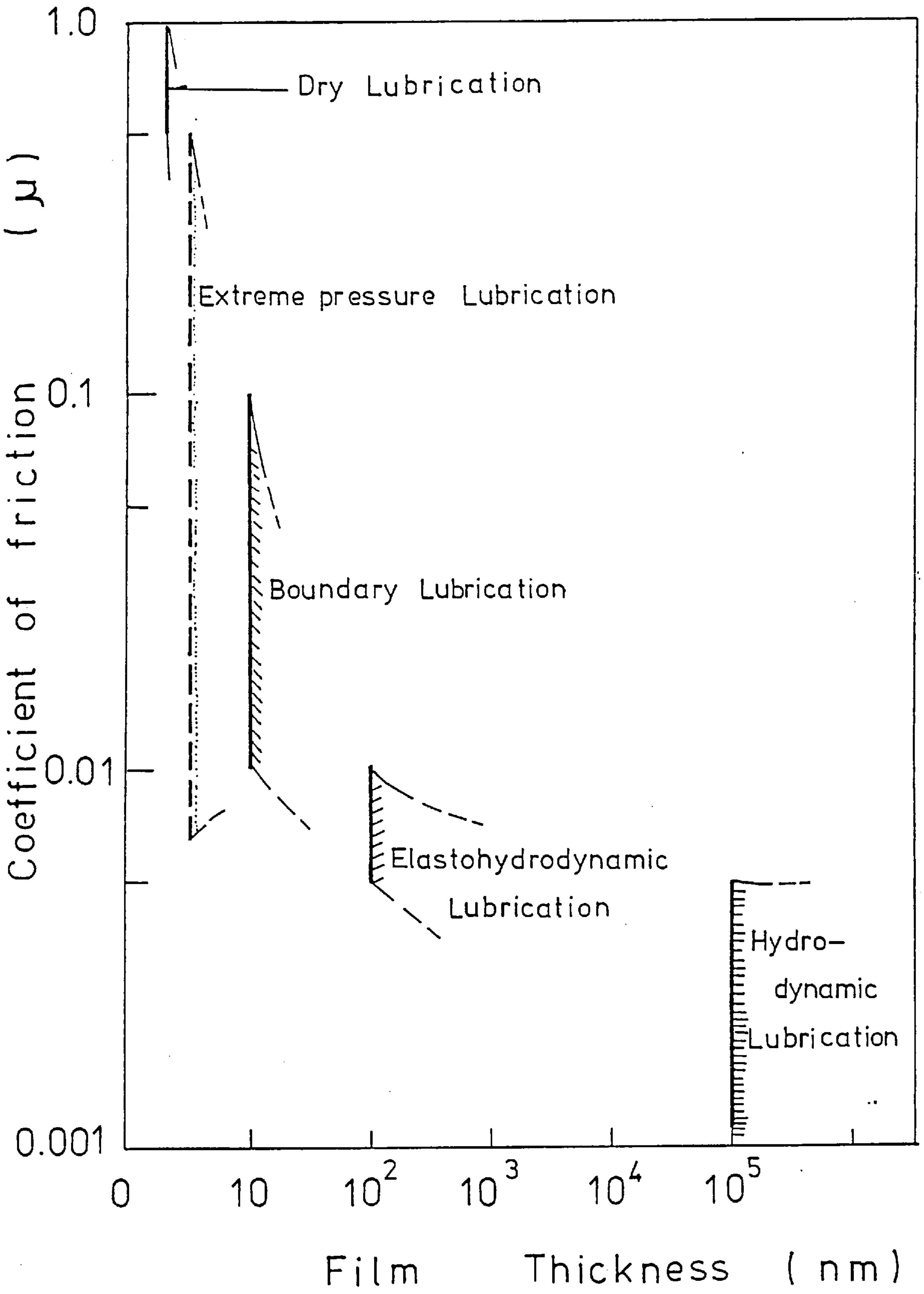


Figure (1.1-a) Coefficient of friction and film thickness

(The average asperity height of unloaded surface : 10^2 - 10^3 (nm))

(C) Boundary and Extreme Pressure Lubrication

With the decrease of film thickness, the properties of the sliding surface become relatively more important. At low speed, EHL films are so thin that large amounts of metal-metal contact occur. Then thin films ($\simeq 10^{-10} \sim 10^{-8}$m) adsorbed on the sliding surfaces become important, and the chemical properties of the adsorbed film and metal surface become more significant than the physical property of the oil. This condition of lubrication is called "boundary lubrication". The frictional coefficient and wear rate are generally higher than the previous two conditions of lubrication.

Heat is inevitably generated in such severe lubricating conditions and increases with the decrease of film thickness between sliding surfaces. The sliding surface, at high temperature, is easily deprived of adsorbed thin films. This is called the "desorption" of the adsorbed film. A new protective film may then form chemically on the naked rubbing surface. This region of lubrication is named "extreme pressure lubrication". The friction coefficient and wear rate are often high.

1.20 SCUFFING

A definition of "scuffing" is given by the Insititution of Mechanical Engineers (2).

> "gross damage characterized by the formation of local welds between sliding surfaces"

"Seizure" is defined as follows,

> "the stopping of a mechanism as the result of interfacial friction"

The scuffing and seizure points, determined by coefficient of friction and severity of running are shown schematically in figure (1.1.b). Two different points of scuffing are observed at the transitions from the less severe lubrication to severe

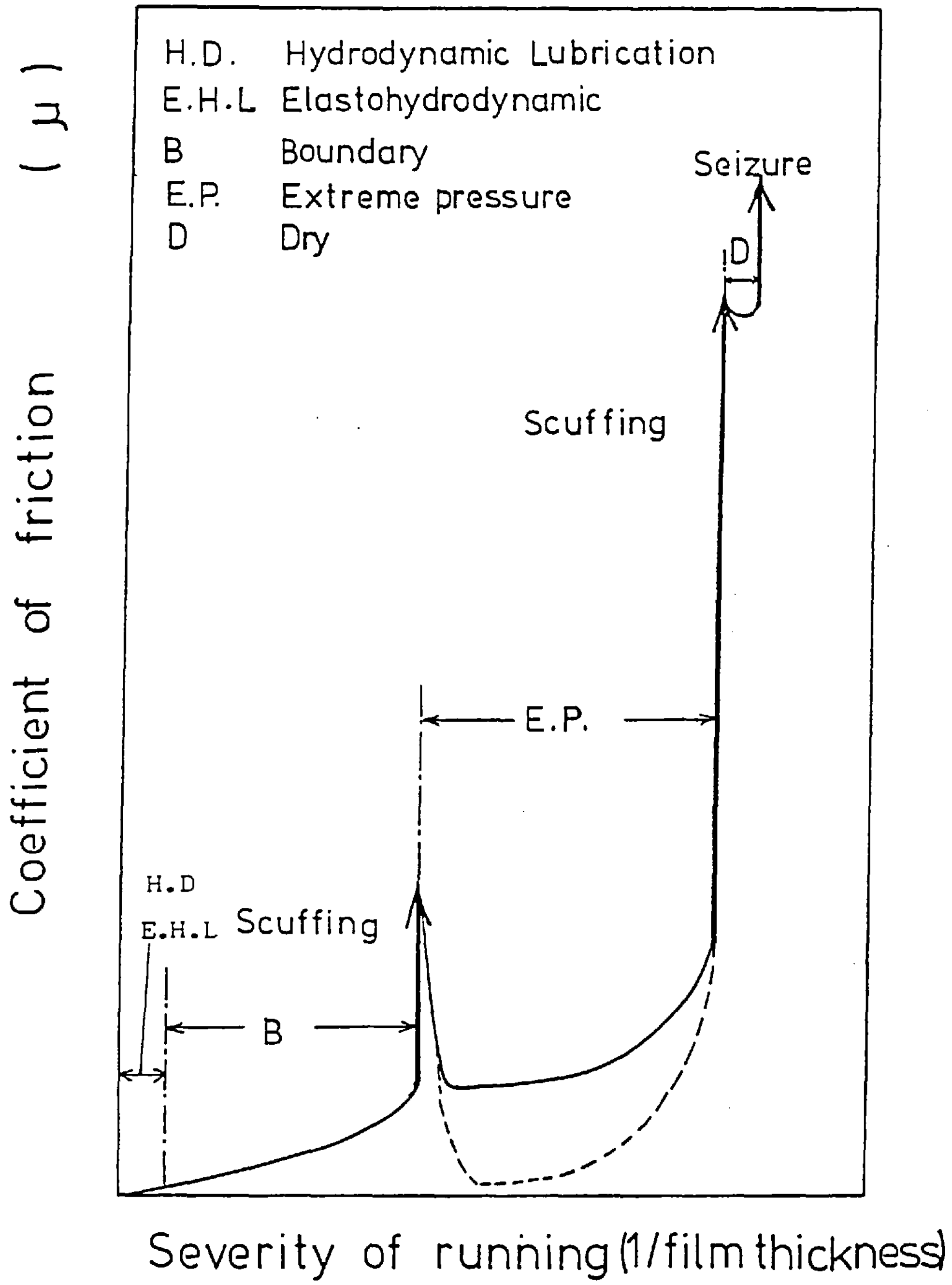


Figure (1.1-b) Scuffing and Seizure point lubrication. One transition occurs from boundary lubrication to extreme pressure lubrication and another is observed from extreme pressure lubrication to dry lubrication. Scuffing is measured by the sudden rise of friction.

Seizure is observed at the end of lubrication. Scuffing is a process of lubrication from one stage to another on the way to seizure.

1.30 EMULSION LUBRICATION

An "emulsion" is a heterogeneous system, which consists of an immiscible liquid, intimately dispersed in another liquid as microdroplets with diameters of 1/10 to 10µm. Microdroplets (emulsions) are usually stabilized by surfactants (3).

The liquid system, emulsion, is not stable thermodynamically and has a time-dependent instability. Quasi-steady emulsions are obtained by the phase inversion temperature (P.I.T.) technique of emulsification (4) (5).

Emulsions are widely used as cutting and rolling oils and as hydraulic fluids. In these applications good lubrication is required. Much research has been carried out on the fatigue and fire resistant properties of emulsions, but by contrast the lubricity of emulions has never (as far as can be found) been studied fundamentally to elucidate the functions of emulsion under boundary lubrication.

1.40 ADDITIVE INTERFERENCE AND EMULSION INTERACTION

Surfactants and other chemical substances are present in lubricating oils. These compounds are called "additives", "chemical additives" or "oiliness and e.p. agents". Chemical reactions of the additives are often initiated at sliding metal surfaces by the thermal energy transformed from mechanical energy in lubrication, when the thermal energy is high enough to overcome the activation energy of reaction,to form a protective film on sliding contacts.

The following factors which control the chemical reaction of an additive are considered important in the lubricity of reacted metal under boundary lubrication.

(1) If one of the additives, which reacts faster with the metal surface, is present in the system, it will be preferentially adsorbed and reacted as the surface film to suppress the chemical reaction of other additives.

(2) If the thermal energy is too low to maintain sufficient reaction rate to form a strong film or relatively lower than the activation energy of reaction, the reaction of an additive will be controlled in the system.

In the first case the adsorption and subsequent reaction of one additive in preference to another is important. This phenomenon is called "additive interference". (6)

The deficiency of the thermal energy for chemical reaction of an additive is important in the second case. Emulsions have been shown to control the surface temperature of sliding metal. (Chapter Five). The chemical reaction of e.p. additives were studied on the metal surface where the surface temperature is controlled by emulsions. (Chapter Seven). The effect of controlled reaction temperature on the reaction of additive due to the interaction of emulsions has been studied in this work.

1.50 OBJECT OF THE RESEARCH

The aim of this work was to elucidate the influence of emulsions on the boundary lubrication regime, and to compare the behaviour of sulphur e.p. additives in oils and emulsions.

A simple lubricating system was considered. Purified paraffin oil was the base oil. Organic acid, ester and alcohol with a long hydrocarbon chain were used in the test of adsorption activity of surfactants on sulphur-reacted surfaces. Nonionic surfactants were used in the emulsion lubrication test. Dibenzyl disulphide and elemental sulphur were used as e.p.

additives in the test of the emulsion interaction in e.p. lubrication. These chemical compounds were examined to measure the lubricating properties using three machines, the ball-on-disc friction apparatus, the ball-on-triplane apparatus and the Bowden-Leben apparatus. The lubricating contacts of a ball and plane were applied in all cases. Analytical and frictional results are compared in this thesis.

This thesis can be conveniently divided into three sections.

(1) The adsorption of surfactants on sulphur-reacted and unreacted steel in oil lubrication.

(2) The boundary lubrication in emulsion.

(3) The effect of emulsions in extreme pressure lubrication.

CHAPTER TWO

ADSORPTION OF SURFACTANTS ON FeS AND α-Fe_2O_3

2.10 INTRODUCTION

The aim of the work described in this chapter was to study the adsorption of long-chain surfactants on FeS and α-Fe_2O_3. It has been suggested several times in the literature (27), (35), (37) that sulphur e.p. additives can act as anti-wear agents by forming a sulphide film on which surfactant molecules adsorb strongly. Definite experiments to test this have not, however, been previously carried out. In this work a flow-micro calorimeter was used to study the adsorption and desorption of fatty acid, alcohol and ester surfactants on both iron sulphide and iron oxide films. The amount of iron taken into solution was also measured.

The conclusions from the work described in this chapter will be relevant to

(a) Lubricity tests of surfactants on oxide and sulphide surfaces (Chapter Three).

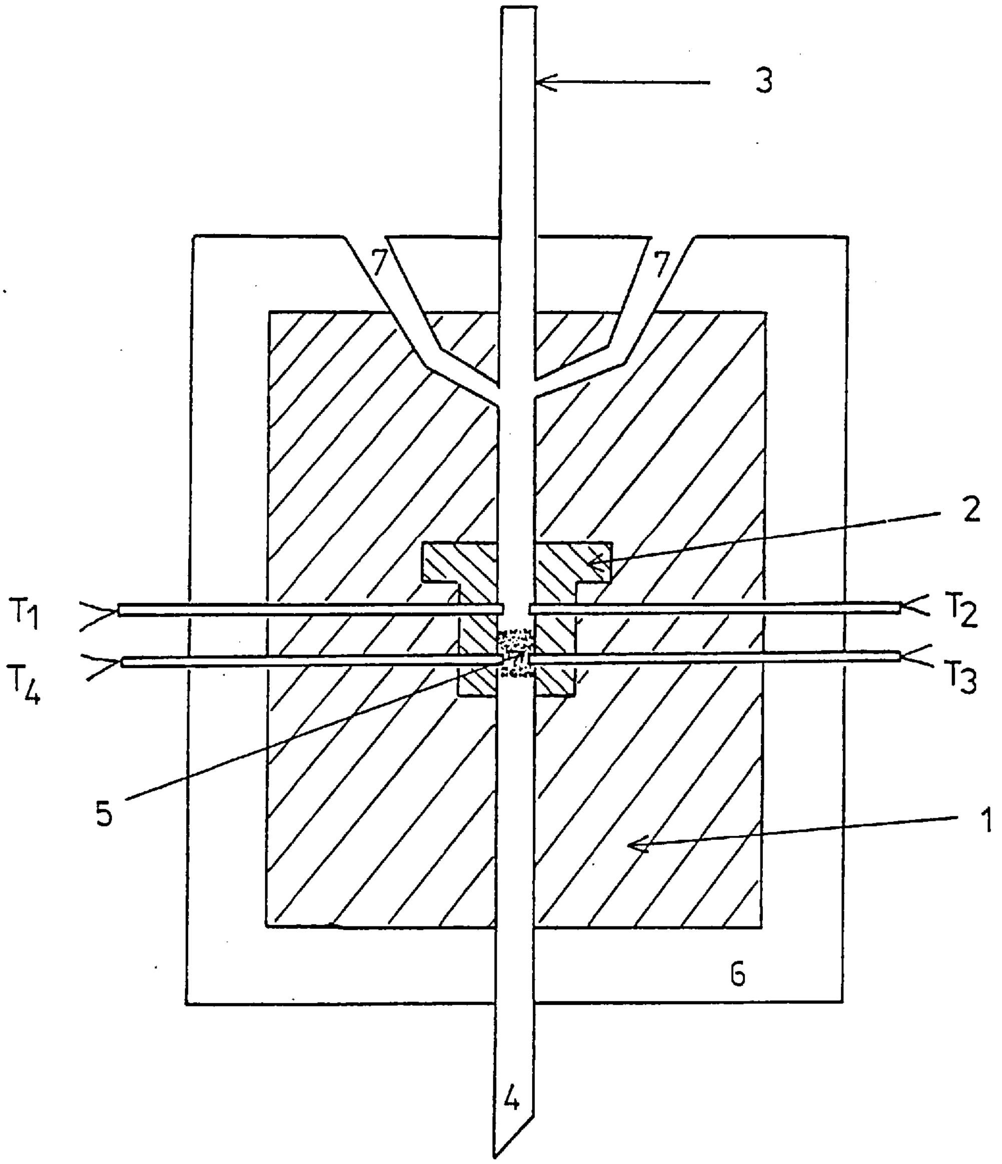
(b) Sulphur e.p. additive tests in the presence of emulsions (Chapter Seven).

2.20 EXPERIMENT

2.21 THE FLOW MICROCALORIMETER APPARATUS

The flow microcalorimeter was developed by Groszek to study the adsorption of surfactants on metal powders. Previous work is found in references (7), (8), (9) and (10).

The schematic diagram of the flow microcalorimeter apparatus is shown in figure (2.1). The apparatus had a metal block surrounded by a cylindrical cavity which contained the calorimeter cell. The cell was connected to a carrier liquid inlet and outlet tube, which was attached by a 200 mesh gauze. The



1. Metal block 2. Teflon calorimeter cell 3. Inlet tube for carrier liquid 4. Outlet tube 5. Adsorbent bed 6. Lagging 7. Cylindrical cavity T_1, T_2,—Reference thermometers T_3, T_4,—Measurement thermometers

Figure (2.1) Diagram of the flow microcalorimeter apparatus powders were placed on this gauze. The temperature sensing elements consisted of four thermometers, two for reference T1, T2 and two for measurement T3, T4. These measurement ones were embedded in the absorbent samples. A constant flow of liquid was obtained by the adjustable dip tube and needle in a flask. A signal worked from the thermometers through an amplifier to a pen recorder.

2.22 MATERIALS

The adsorbents used in this work are shown in Table 2.1.

Table (2.1) Adsorbents

	Purity (%)	Mesh	BET Surface Area (m²/g)
α- Fe_2O_3	99.98	100 ~ 200	3.32
FeS	99.97	100 ~ 200	13.80
Fe_3O_4	99.99	100 ~ 200	5.78

These adsorbents were degassed at 350°C for four hours at 1×10^{-5} mm Hg. (1.33×10^{-3} N/m²) before use. Surfactants were purified as shown in Table (2.2).

Table (2.2) Surfactants

	Purification	Purity Analysis	Purity
Stearic acid	Recrystallization	Elemental analysis	99.7 %
Stearyl alcohol	Recrystallization	Gaschromatography	No impurity detected
Methyl stearate	Column adsorption on copper powder	Gaschromatography	No impurity detected

n-Heptane, the solvent of the adsorption tests, was purified by percolation through a silica gel-alumina column. This was dried in contact with a molecular sieve for two days. The n-Heptane was then distilled in the presence of sodium wire at 98 ~ 98.5°C 760 mmHg.

2.23 EXPERIMENTAL TECHNIQUES

ADSORPTION OF SURFACTANTS ON ADSORBENT

The solvent stream was replaced by the adsorbate solution containing surfactants with the same flow-rate.

The stream of solution continued to flow until an equilibrium between the surfactant and the powder was reached. This caused an evolution of heat and a peak was recorded. A series of tests were run, from low to high concentrations of surfactants. The integrated heat of adsorption in this process is called the cumulative heat.

AMOUNT OF ADSORPTION

The amount of adsorption was calculated from the following equation

$$x = tcf/w \tag{2-1}$$

where x = amount of surfactant adsorbed (mg/g)
t = retention time (min)
c = concentration of solute (mg/ml)
f = flow rate of solution (ml/min)
w = weight of adsorbent in the precolumn (g)

DESORPTION OF SURFACTANTS FROM ADSORBENT

Surfactants were adsorbed previously onto the powder at each concentration. These were desorbed by n-heptane at the same flow rate. The heat of desorption was calculated as the same way as in the adsorption tests.

IRON CONTENT IN THE DESORPTION SOLUTION

Surfactants were adsorbed from the n-heptane solutions onto α-Fe_2O_3 and FeS powders at a flow rate of 0.11 ml/min for four hours. These were desorbed into n-heptane at a flow rate 4.1 ml/min. The iron content in the desorption solution was measured after 1, 10 and 30 minutes by the atomic adsorption analysis. The apparatus was HITACHI - 503 HGA using Fe-Lamp with wave length 2483.3Å. The tests were carried out under the following conditions: drying at 100°C for 30 seconds, ashed at 500°C for 30 seconds and atomizing at 2550°C for 6 seconds.

2.24 REPEATABILITY

The heats of adsorption and desorption and the amount of adsorption were measured by the flow microcalorimeter apparatus with an error of $\pm$ 1.0%.

The iron content in the desorption solution was measured by atomic absorption analysis with a precision of $\pm$ 0.1ppb.

2.30 RESULTS AND DISCUSSIONS

2.31 MEASUREMENTS

The cumulative heats of adsorption of stearic acid onto FeS and Fe_3O_4 powders were much higher than that on α-Fe_2O_3 as shown in figure (2.2). More polar components were shown to adsorb on a sulphide film than a ferric oxide film at the same concentration.

The heats and the amount of adsorption of surfactants from n-heptane onto FeS and α-Fe_2O_3 are shown in figure (2.3) and (2.4) respectively. Stearic acid and stearyl alcohol adsorbed quite actively onto FeS. Even at low concentrations of stearic acid, the heats of adsorption per square meter were remarkably high.

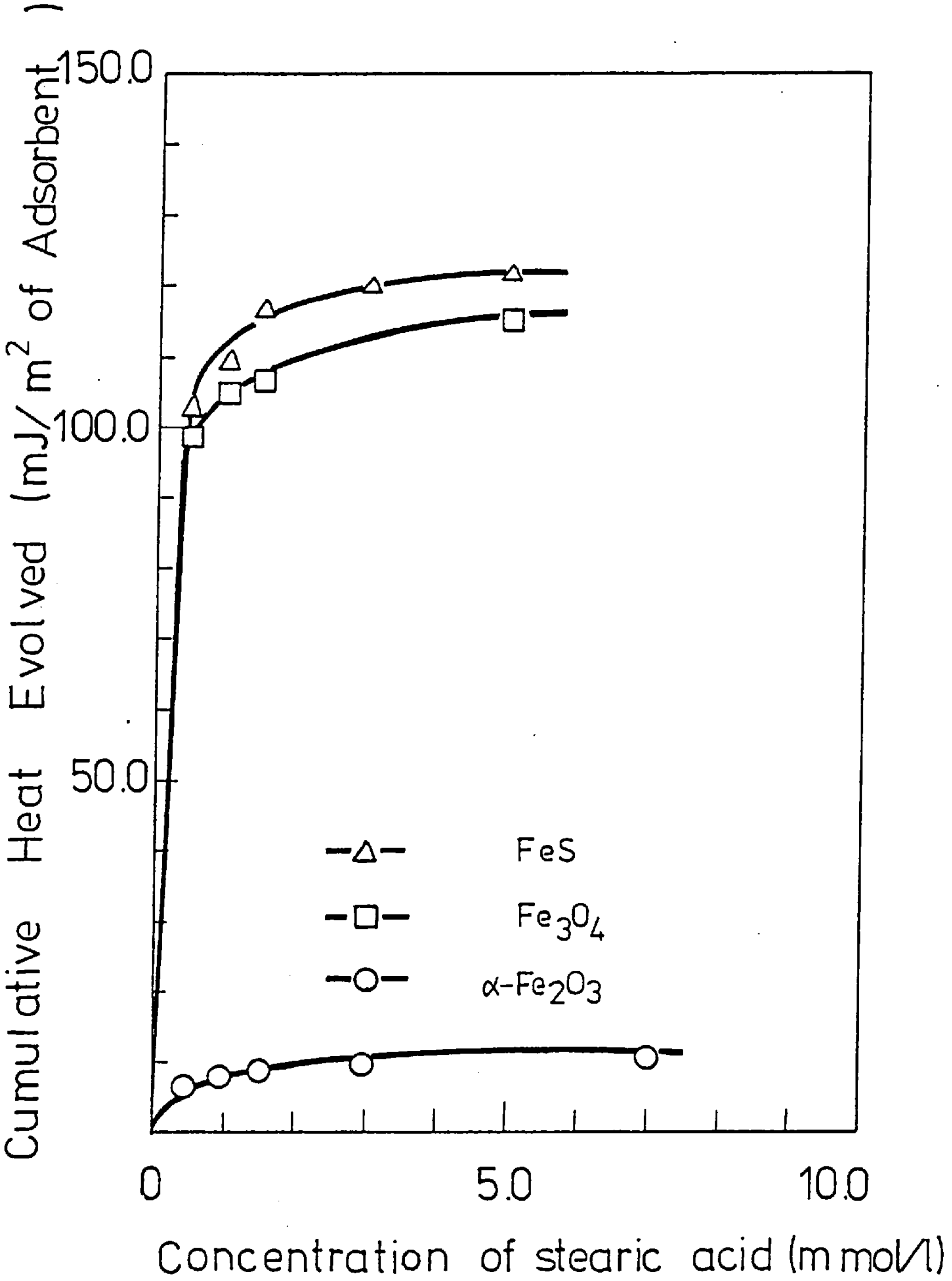


Figure (2.2) Heats of adsorption of stearic acid on FeS and α-Fe_2O_3

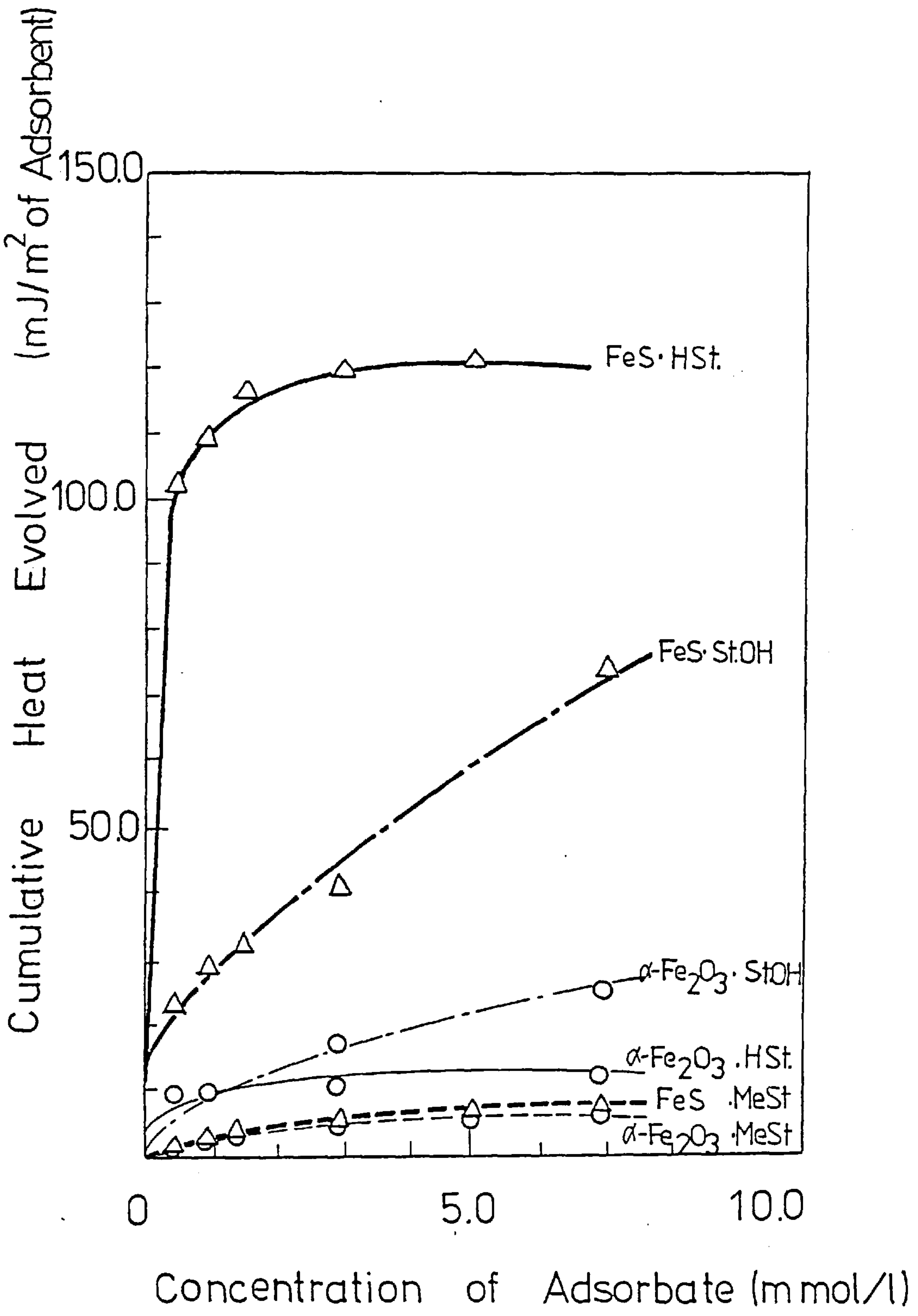


Figure (2.3) Heats of adsorption of surfactants on FeS and αFe_2O_3

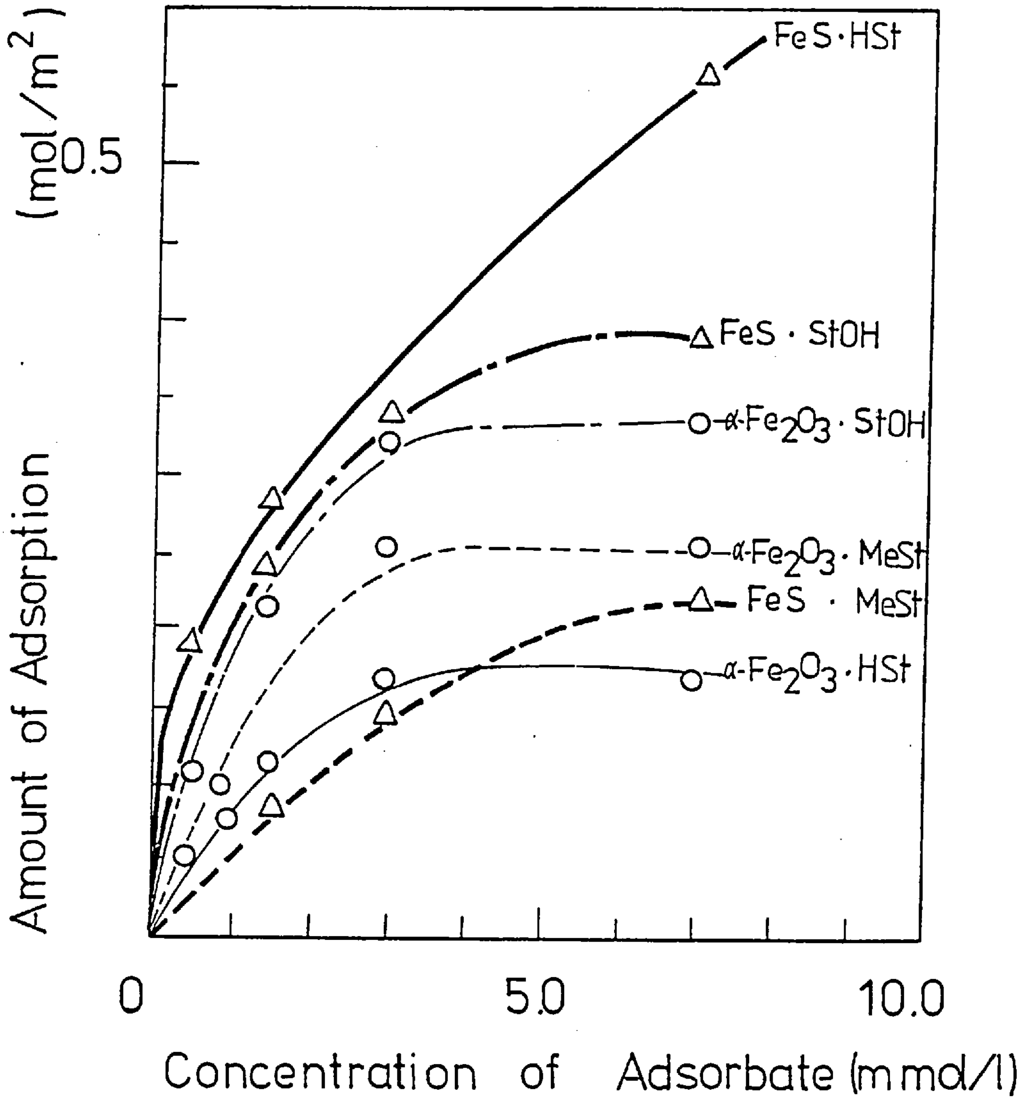


Figure (2.4) Amounts of adsorption of surfactants on FeS and α-Fe_2O_3

The heat of desorption of stearic acid from FeS and α-Fe_2O_3 was lower than that of stearyl alcohol in figure (2.5). The ratio of heats of desorption to adsorption at 7 mmol/l is shown in Table (2.3). Stearic acid adsorbed strongly onto FeS and α-Fe_2O_3 and was difficult to desorb from these powders.

Table (2.3)

Adsorbate	Adsorbent	Ratio
Stearic acid	FeS	0.1
Stearic acid	α-Fe_2O_3	0.2
Stearyl alcohol	FeS	0.5
Stearyl alcohol	α-Fe_2O_3	0.8
Methyl stearate	FeS	0.8
Methyl stearate	α-Fe_2O_3	0.8

The iron content in the desorption solutions is shown in Table (2.4). The highest iron content was observed in the combination between stearic acid and FeS. It may be considered that chemical reactivity of stearic acid with FeS and α-Fe_2O_3 is high in all combinations between surfactants and powders. Methyl stearate may gradually react with iron sulphide with the hydrolysis of methyl stearate. Stearyl alcohol can adsorb on powders due to the strong polar interaction with the powders.

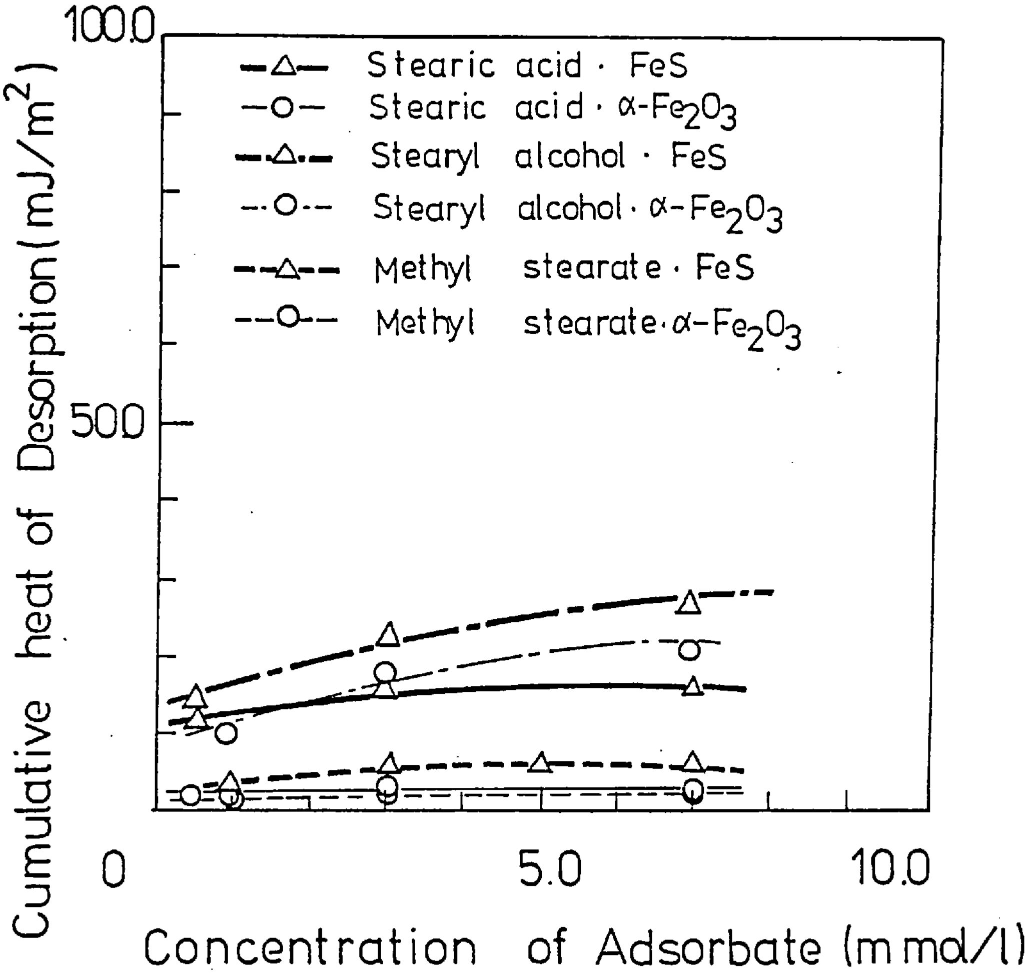


Figure (2.5) Heats of desorption of stearic acid from FeS and αFe_2O_3

Table 2.4

	Fe Content (ppb)		
n-Heptane as an eluent (ml)	4.1	41.0	123.0
Time (min)	1	10	30
FeS - HSt	39.5	-	52.7
α-Fe_2O_3 - HSt	7.9	31.6	39.5
FeS - MeSt	9.2	40.8	48.7
α-Fe_2O_3 - MeSt	13.2	21.1	29.0
FeS - StOH	7.9	13.2	28.9
α-Fe_2O_3 - StOH	7.5	17.6	-

Iron content in desorption solutions by atomic absorption analysis

HSt: stearic acid, MeSt: methyl stearate, StOH: stearyl alcohol

2.32 CALCULATIONS OF LATTICE ENERGY

Surfactants adsorbed on powdered FeS more actively than on α-Fe_2O_3 powders. If a chemical interaction occurs between the adsorbate and the metal ions of the solid surface, this might break the ionic bonding of the solid. If this is so, adsorption should be stronger on solids with weaker bonds and thus more easily disrupted structures. To test this possibility the lattice energies of FeS and Fe_2O_3 were calculated.

The lattice energies of iron sulphide and iron oxide calculated by the Kapustinskii's equation (11).

$$U = \frac{287.2 r Z1\ Z2}{Rc + Ra} \left(1 - \frac{P}{Rc + Ra}\right) \qquad (2.2.1)$$

$$U = \frac{NoAZ1Z2e^{2}}{Ro} \left(1 - \frac{P}{Ro}\right) \qquad (2.2.2)$$

where U = lattice energy

r = the number of irons

Rc,Ra = the formal 6-coordinate radii of the cation and anion in Angstrom units

Z = charge

e = 4.803×10^{-10} esu

A = Madelung constant

Ro = Internuclear distance

No = Avogadro's number

P = parameter 0.345

The results are shown in Table (2.5). The lattice energy of α-Fe_2O_3 was much greater than that of FeS. The surfactants may react with FeS more easily than with α-Fe_2O_3. The surfactants may adsorb onto FeS more strongly than α-Fe_2O_3.

Table (2.5)

	Lattice energy (MJ/mole)
FeS	-0.18
α-Fe_2O_3	-4.82

Lattice energy of iron sulphide and iron oxide

2.40 CONCLUSIONS

The following conclusions were drawn from this work.

(1) Surfactants (stearic acid, stearyl alcohol and methyl stearate) adsorb on FeS powder more actively than on α-Fe_2O_3 powder.

(2) The lattice energy of FeS solid is less than that of α-Fe_2O_3. Surfactants react with FeS more easily than α-Fe_2O_3.

CHAPTER THREE

LUBRICITY OF SURFACTANTS ON SULPHUR-REACTED AND UNREACTED STEEL SURFACES

3.10 INTRODUCTION

The adsorption activity of surfactants on iron sulphide has been studied in the previous chapter. The purpose of the work described now is to examine the effects of adsorption of surfactants, on the wear of sulphur-reacted steel surface.

The wear volume of a sulphur-reacted steel ball in the ball-on-disc friction apparatus was measured in air and argon atmosphere. The wear between the steel plate and the steel ball sulphurized in H_2S was examined in the oil with the same surfactants as in the adsorption tests.

3.20 REVIEW

Chemical reaction on sliding metals is probably the most important way of improving boundary lubrication between the surfaces. (1) (112)

Two different types of surface reaction are relevant to this study, and their literature is briefly reviewed. They are:

(1) Chemical reaction of surfactants with rubbing metals

(2) Chemical reaction of sulphur compounds with rubbed metals.

The former reaction occurs mainly at lower temperature up to about 150°C. The latter reaction occurs mainly at higher temperatures, over 150°C. (Chapter 6).

3.21 CHEMICAL REACTION OF SURFACTANTS IN LUBRICATION

In an early study of lubrication, Sir William Hardy (12) examined the effect of chemical substances on lubricating properties of surfaces. He deduced that the function of a lubricant is to reduce the energy of the surface, and thereby to reduce the capacity for cohesion between sliding surfaces. The chemical reaction to form surface films was studied by Frewing (13) (14). He found frictional properties of the surface films to change with temperature. The transition temperature from good to poor boundary lubrication was explained by the desorption of surfactants from the rubbed surfaces.

The effect of temperature and metal pairs on scuffing was examined by Bailey and Cameron using a ball-on-triplane apparatus, (15) (16). The metallurgy of the rubbing pairs and their positions relative to the contact region were important. The slow-speed friction temperature tests gave results that can be correlated with high speed scuffing runs. The adsorption strength of surfactants in the oil sliding surfaces was studied by Spikes and Cameron (17) with a Bowden-Leben apparatus.

The surface chemistry of adsorbed film of surfactants has also been examined. Bigelow, Pickett and Zisman (18) who found that polar organic molecules are adsorbed from solutions in non-polar solvents to form well-oriented monolayer on polished solid surfaces. Schulman and Waterhouse (19) concluded that the first requirement for an efficient lubricant film in the chemisorption of the long chain compounds as a basic metal soap. The thermal desorption of a lubricant was studied by Kingsbury (20).

Adsorption and desorption phenomena on sliding metal surfaces have been studied by microcalorimetric measurements. Groaszek (7) (8) (9) (10) measured the static heats of adsorption with a flow-microcalorimeter to compare these results with practical wear results.

Determinations of scuffing temperature were made as a function of load and surfactant concentration by Peart and Thorp (21).

Wear products produced by some chemical reactions have been evaluated with respect to the effect of oxygen by Bose, Klaus and Tewkobury (22). A significant reaction between the lubricant, oxygen and the metal appears to play an important role in the mechanism of lubrication.

Oxygen, in either the atmosphere or the lubricant molecule, was suggested to be effective against scuffing by Bjerk (23). He found that steel rollers were difficult to scuff at low sliding speeds in air atmosphere.

Klaus and Bieber (24) concluded that small quantities of less volatile-polar-impurities cause a substantial reduction in wear.

Exoelectron emission was observed at the fatigue sites on the sliding surfaces by March and Rabinowicz (25). This seems to be important for the chemical reaction process on the sliding surface.

Recently a new model of the lubrication mechanism of boundary films was proposed by Georges, Meille, Jacquet, Lamy and Mathia (26). The durability of a deposited monomolecular film of stearic acid on steel surfaces was studied using a pin-on-disc friction apparatus. They found the continuous presence of an agglomerate, composed of the deteriorated and recombined fatty acid molecules, after sliding on the steel surfaces. It was suggested that frictional forces do not result only from friction between the monolayers and the substrates.

3.22 CHEMICAL REACTION OF SULPHUR COMPOUNDS IN LUBRICATION

Sulphur in oil was observed to react strongly with bearing metal at high bearing temperatures in a high-speed machine by Summers-Smith (27).

In an early study of sulphur-reacted sliding metal, Campbell (28) observed an effect of sulphur-reacted film thickness on frictional coefficient. Reacted surfaces were produced by a mixture of hydrogen sulphide and oxygen on steel, copper and brass. Sulphur films reduced the static friction by a constant dependent on the thickness of film.

Greenhill (29) proposed that the most efficient lubricants are the fatty acids with a long hydrocarbon chain, and also sulphur compounds. Disulphide compounds were shown to have superior extreme-pressure properties to monosulphides as assessed with a four-ball apparatus by Davey and Edward (30).

The tertiary disulphides were found to be the most effective lubricant additives using the Falex four-ball apparatus by Dorison and Broman (31).

The adsorption activity of surfactants on the iron sulphide was shown using S^{35} radiosotope technique by Sakurai, Ikeda and Okabe (32).

The chemical composition of reacted films formed on steel by dibenzyl disulphide was examined by electron diffraction, emission spectroscopy, proton scattering and volumetric analysis by Godfrey (33). He obtained FeS in wear scars as well as large amounts of Fe_3O_4 and carbon and hydrogen compounds.

Barcroft and Daniel (34) examined the extreme pressure film formation on hypoid gears with S^{35}. They found three kinds of substances. Iron sulphide, iron sulphate and a substance containing iron and sulphur.

"A controlled corrosion model" of reaction by extreme pressure agents was proposed using the hot wire method by Sakurai and Sato (35). Various e.p. additives composed of sulphur, chlorine, Zn-dithiophosphate and the mixture of sulphur-chlorine types, were used in the work. X-ray analysis of reaction products showed a complex combination of corrosion reaction.

Wheeler (36) studied mild and severe wear conditions in dibenzyl disulphide lubrication by X-ray photo electron spectroscopy. In severe wear scars a sulphide was created instead of the natural oxide by chemical corrosion above 200°C. In mild wear little sulphide occured in the wear scar.

Forkes (37), Coy and Quinn (38) demonstrated that complicated mixtures of iron sulphide and carbon-oxygen compounds are more likely to be the load carrying layer than pure iron sulphide. This has been confirmed by Campbell (28), Greenhill (29) and Bowden and Tabor (1).

Surfaces were examined by Buckley and Pepper (39) using Auger spectroscopy, immediately after exposure to reactive gases, in static and rubbing tests without removing the surfaces from the vacuum chamber. The result of interaction of various gases with the friction and wear surface was monitored. Sulphur dioxide, oxygen, hydrogen sulphide and methyl mercaptan were used in another test to study the chemical interactions of oxygen and sulphur with iron. Sulphide films present on iron surfaces were shown to be displaced by oxygen (40).

The sulphide concentration was shown rapidly to reach an equilibrium value and remain constant throughout the remainder of the break-in and test periods using X-ray photoelectron spectroscopy by Baldmin (41). Sulphur compounds, even at very low concentrations in oil (the order of ppm), were shown effective on a disc apparatus, by Yamamoto and Hirano (42) (43).

Oxygen was shown to be important in forming a smooth surface which maintained mixed lubrication, by Tomaru, Hironaka and Sakurai (44) (45). Elemental sulphur, dibenzyl disulphide, diphenyl disulphide, tricresyl phosphate and dilauryl hydrogen phosphite were used in four-ball tests.

The critical temperature concept was proposed as the major factor of the failure of extreme pressure lubrication by Sethuramiah, Okabe and Sakurai (46). Metallurgical softening of metal surfaces occured at high temperatures. Subsequently microwelding effects caused the failure of a surface layer on the metal leading to scuffing. This has been supported by Bollani (47). The scuffing behaviour of sliding couples was studied as a function of relative sliding speed and bulk oil temperature. The critical temperature concept was shown to be a useful tool in the design of a friction couple under boundary lubrication. Czichos and Kirschke(48). proposed the critical interfacial energy concept for the e.p. lubrication failure. This was composed of thermal and mechanical energy determined by load, velocity and bulk oil temperature.

3.30 EXPERIMENT

3.31 EXPERIMENTAL AIM

The work described in this chapter aims at measuring the wear volume of sulphur-reacted and unreacted steel balls in the oil with the same surfactants as in the adsorption tests of the previous chapter. The amount of wear was to be examined in the ball-on-disc friction under air and argon atmosphere.

3.32 THE BALL-ON-DISC APPARATUS

The wear tests were performed on the ball-on-disc friction apparatus shown in figure (3.1). The rotating disc was made of AISI(SAE) 1055. The diameter was 45mm. The AISI(SAE) 52100 steel balls were 4.76 mm in diameter. The compositions of these materials are shown as follows.

AISI No.	C	Mn	Pmax	Smax	Si	Cr
1055	0.98/ 1.10	0.25/ 0.45	0.025	0.025	0.2/ 0.35	1.30/ 1.60
52100	0.58/ 0.60	0.60/ 0.90	0.040	0.050	-	-

The wear scar diameter was measured by an optical microscope. The wear volume was calculated by the equation proposed by Antler (49).

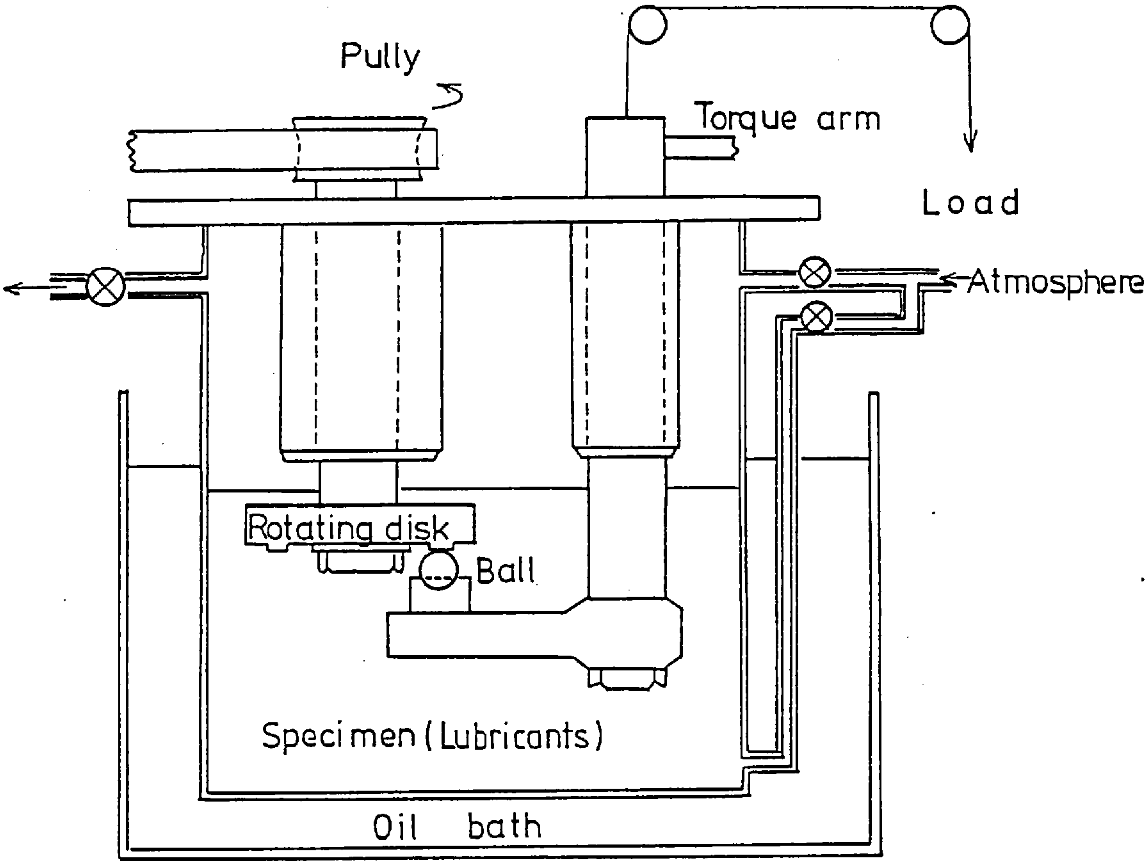


Figure (3.1) Ball-on-dis friction apparatus

$$V = \pi d^4/16D$$

where d = the diameter of the wear scar

D = the diameter of the balls

3.33 MATERIALS

SULPHUR-REACTED STEEL BALL

AISI 52100 steel balls of 4.76 mm (3/16in) diameter were rotated in 100 percent H_2S gas for four hours in a closed vessel. The sulphur-reacted films were examined by X-ray diffraction analysis. The sulphur-reacted steel plate was studied instead of the convex fall which was unsuitable for analysis. The analytical results are shown in Table (3.1). Troilite (FeS) and pyrrhotite ($Fe_{0.88}S$) types of iron sulphide were shown to be formed on the plate.

Table (3.1)

Lattice Spacing d (Å)	Intensity*	Fes Troilite ASTM Index No. 11-151	$Fe_{1-x}S$ (x=0.12) (Pyrrhotite) ASTM Index No 22-1120	α-Fe
5.20	M	5.40	5.27	-
2.99	S	2.98	2.98	-
2.66	M	2.66	2.64	-
2.53	M	2.52	-	-
2.10	M	2.09	-	-
2.03	VS	-	-	2.03
1.93	M	1.92	1.91	-
1.73	VS	1.72	1.72	-
1.43	VS	-	1.43	1.43

* VS : very strong, S : strong, M : medium

Analysis of sulphurized ball by X-ray diffraction

BASE OIL

Hydrofinished oil, purified by passing it through a column of silica gel, alumina and activated carbon, was used in this test. The viscosity was 32.2 cSt ($32.2 \times 10^{-6} m^2/S$) at 37.8°C and 5.3 cSt ($5.3 \times 10^{-6} m^2/S$) at 98.9°C.

SURFACTANTS

Surfactants used in this work were the same materials as in the adsorption tests. (Table (2.2)).

ARGON ATMOSPHERE

The argon gas was passed through pyrogallol to exclude oxygen. It was then passed through silica gel to remove water vapour.

3.34 EXPERIMENTAL TECHNIQUE

Wear tests were carried out in air and argon atmospheres. Oils with 0.1 weight per cent of surfactant were used at 20°C. The tests were run under a load of 10N and a speed of 25 r.p.m. for 60 minutes. The sliding distance was 8.5 m.

All specimens used in this test were purified by a benzene soxhlet for two hours, then dried in a vacuum dessicator.

3.35 REPEATABILITY

The wear volume was measured to an accuracy of $\pm 0.05 \times 10^{-6}$ mm³. Three values of wear scar diameter were measured and an average value given.

3.40 RESULTS

The wear volumes measured on the sulphur-reacted and unreacted balls in the oil with surfactant are shown in Table (3.2). These values allow the air and argon atmospheres to be compared.

Wear volume of the sulphur-reacted balls was shown to be much smaller in oil with surfactants under air, than under an argon atmosphere.

The wear volume of sulphur-reacted steel was shown to be smaller than that of non-reacted steel in air. These results were reversed in an argon atmosphere.

Table (3.2)

	Wear Volume $\times 10^{-6} mm^3$							
Atmosphere	In Air				In Argon			
Additive	None	Stearic Acid	Stearyl Alcohol	Methyl Stearate	None	Stearic Acid	Stearyl Alcohol	Methyl Stearate
Sulphurize ball	19.1	0.2	8.2	11.5	12.5	22.6	22.5	22.5
Steel ball	19.3	5.5	17.3	13.9	15.7	6.6	6.2	10.3

Wear volumes of sulphurized ball in oil with surfactants

3.50 DISCUSSION

The wear test was performed with and without oxygen. The oxygen was shown to have a remarkable role in reducing the wear of sulphur-reacted steel balls in air. On the other hand the reaction between surfactant and sulphur-reacted steel may promote the wear corrosively in the absence of oxygen (35).

Sulphur atoms may be replaced by oxygen atoms after the surfactant reacts with the iron atom of an Fe-S bond. It was found that replacement of sulphur atom by oxygen occurs at sulphurized steel surfaces even under low concentrations of oxygen (40). The replacement of sulphur by oxygen may cause a favourable protection against wear. The protective film may not be formed at the sliding contact in the absence of oxygen. This may cause the increase of wear in the lubricating system.

These lubricating results are clarified by the adsorption test. Strong adsorption of surfactant on the sulphur-reacted steel reduces the wear of sulphur-reacted steel in the oil with surfactants under boundary lubrication. Strong adsorption of surfactant may occur on the less stable lattice of FeS than the α-Fe_2O_3 lattice. (Table (2.5)).

The stronger interaction of stearic acid with the sulphur-reacted and unreacted steel, compared with stearyl alcohol, was observed in both the adsorption test and the lubricity test.

3.60 CONCLUSIONS

The following conclusions can be drawn from this work.

(1) The wear of sulphur-reacted steel was smaller in air than in argon. Oxygen may assist in protecting the sulphurized steel against wear.

(2) The strong adsorption of surfactants causes less severe wear at the sliding contact of sulphurized and unreacted steel.

(3) The wear reducing ability of surfactants on sulphur-reacted and unreacted steel is determined by

(a) the reaction activity of the surfactant

(b) the polar interaction of the surfactant

with sulphurized and unreacted steel surfaces.

CHAPTER FOUR
PROPERTIES OF EMULSIONS

4.10 INTRODUCTION

Emulsions have been used in the food, paint and cosmetic industries for a long time and more recently as lubricants. They have been developed largely by trial and error, and few systematic studies of the properties of emulsion lubricants have been published.

This chapter looks at the particle size distributions and bulk viscosities of several emulsions which are employed in subsequent chapters as lubricants.

4.20 REVIEW

4.21 MECHANISM OF EMULSION STABILITY

(I) Early work on emulsion stability (50) (51).

The importance of interfacial tension of emulsifier was emphasized by Donnan and Potts (52). Adsorption of emulsifiers at the interface between oil and water was studied by Bancroft (53).

Griffin proposed the concept of H.L.B. (hydrophilic lipophilic balance) as a practical determination of the stability of emulsions (54).

The model of emulsions with orientated emulsifiers is generally accepted. This was developed from the micelle model in surfactant solution, studied first by Harkins et al (55).

Sherman (56) examined the effect of phase volume in emulsions. A phase inversion is observed with the increase of dispersed phase in the emulsion. The inversion of phase was considered to be controlled by the changed concentration of emulsifier.

(II) Recent theories of emulsion stability

Boyd, Parkinson and Sherman (57) suggested that emulsion stability is related both to surface elasticity and to surface viscosity. The two-dimensional rheology of surfactant films at interfaces was studied by Boyd and Sherman (58). Rehfeld (59) suggested that hydrocarbon/water emulsion stability is inversely correlated with the spreading coefficient of hydrocarbon on aqueous surfactant solution. Friberg and Jansson (60) considered the enhanced stabilising action of combined emulsifiers. The presence of a liquid crystal structure was shown to reduce the Van der Waals energy for coalescence of emulsions.

Macritchie (61) estimated the stability of emulsions by considering two energy barriers. One was calculated by different critical sizes of holes in colliding emulsion droplets and another was calculated by the kinetics of coalescence of emulsions. The "Marrangoni effect" (Movement of film molecules, caused by interfacial pressure gradients) was also applied to this model.

4.22 TEMPERATURE EFFECT ON EMULSION STABILITY

Sherman and Shinoda have studied the effect of temperature on emulsion stability and have published a series of papers.

Perkinson and Sherman (4) concluded that the phase inversion temperature (PIT) method is the most sensitive technique for stability tests rather than HLB value and particle size analysis.

Shinoda et al (62) (63) (64) concluded the same mechanism of emulsion stability as obtained by Sherman et al. Shinoda and Ogawa (65) found that the solubilization of water in solutions with nonionic surfactants is changed rapidly at an optimum temperature. The optimum temperature is the temperature where the solubilization and cloud point curves meet each other. Therefore the effect of temperature is important in the stability of emulsions. Emulsification at the phase inversion temperature and subsequent cooling to the room temperature was shown to create stable emulsions.

Tamai (66) suggested that the interfacial tension of emulsions is a sensitive technique in determining the stability of emulsions.

4.23 SUMMARY OF REVIEW

Emulsion stability has been reviewed. The stability of emulsions have been observed by Sherman and Shinoda (4) (5) to be dependent on the phase inversion temperature of emulsions. The phase inversion temperature model of emulsion stabiltiy is the most explicable theory of stability.

The effect of temperature on emulsion stability might be important in the elucidation of emulsion lubrication.

4.30 EXPERIMENT

4.31 EXPERIMENTAL OBJECT

The work described in this chapter is mainly concerned with measuring the viscosity of emulsions under shear in order to understand the physical properties of emulsions in lubrication.

Liquids are categorised as (A) Newtonian and (B) Non-Newtonian fluids. Newtonian fluids have a linear relationship between shear rate and shear stress. On the other hand, Non-Newtonian fluids show a non-linear relationship between shear rate and shear stress (67).

4.32 MAKING EMULSIONS

Emulsions were made from distilled water, liquid paraffin and nonionic surfactant (emulsifier) in a Silverson L2R laboratory mixer at 800 rev.min^{-1}. The liquid paraffin was purified before use by percolation through silica gel and alumina. In all cases 10% by weight of surfactant was used.

Water in Oil (w/o) type emulsions were stabilised by a surfactant mixture of HLB 4.5 consisting of 70% sorbitan trioleate (Span 85) and 30% polyoxyethylene (20) sorbitan trioleate (Tween 85). The HLB value of an emulsifier is an experimentally derived measurement. This shows the affinity of the emulsifier for water as opposed to oil at room temperature. (64). The emulsifier mixture and liquid paraffin were mixed at 65°C. This temperature is close to the phase inversion temperature (PIT) of these surfactants (62) (63). Water was added to the stirred mixture which was subsequently cooled down to room temperature. The period of stirring emulsions was 15 min. This technique of emulsification is called the PIT method (62).

Oil in water (o/w) type emulsions were stabilised by mixed surfactants of 50% sorbitan monopalmitate (Span 40) and 50% polyoxyethylene (20) monopalmitate (Tween 40). The HLB value was 11.2. Span 40 was dissolved in liquid paraffin and Tween 40 in water. Both solutions were heated to 60°C. The oil was added to the stirred water solution and cooled down to the room temperature.

Additional emulsifiers were used in frictional tests described in the next chapter. Another w/o type emulsion was made by a mixture of 29% polyoxyethylene tristearate (Tween 65) and 71% sorbitan monostearate (Span 65). The HLB value was 4.5. The o/w type emulsion was made by a mixture of 99% Tween 65 and 1% Span 65. The HLB value was 10.5. The surfactants were obtained from Atlas Chemical Industries Inc. (U.K.) and are part of their standard commercial range.

Polyglycol was used to compare the physical and frictional properties of surfactants (Tween and Span type emulsifiers), which form emulsions. Polyglycol is unable to form emulsions spontaneously when this is mixed with water and oil, since it not an emulsifier . This property of polyglycol may be suitable for understanding the effect of emulsions on the physical and frictional properties of a system, which contains water, oil, sufactants and emulsions. Generally polyglycol with a high fire point (265°C), compared with mineral oil (115°C), is used for hydraulic fluids as well as emulsions. Frictional properties of polyglycol will be described in the next chapter. Polyglycol used in this work was obtained from Hoechst Ltd. (Ger).

4.33 PARTICLE SIZE DISTRIBUTION OF EMULSIONS

Particle size distribution has been shown to be a valid measure of emulsion stability by Harkins and Fisher (68).

The particle size distribution of emulsions was measured by direct measurement from an enlarged photoprint. Thin layers of emulsions were prepared between glass slides. They were photographed in transmitted light. Enlarged magnification was 1000X. The photographs of the w/o type and o/w type emulsions are shown in figure (4.1).

4.34 VISCOSITY OF EMULSIONS UNDER SHEAR

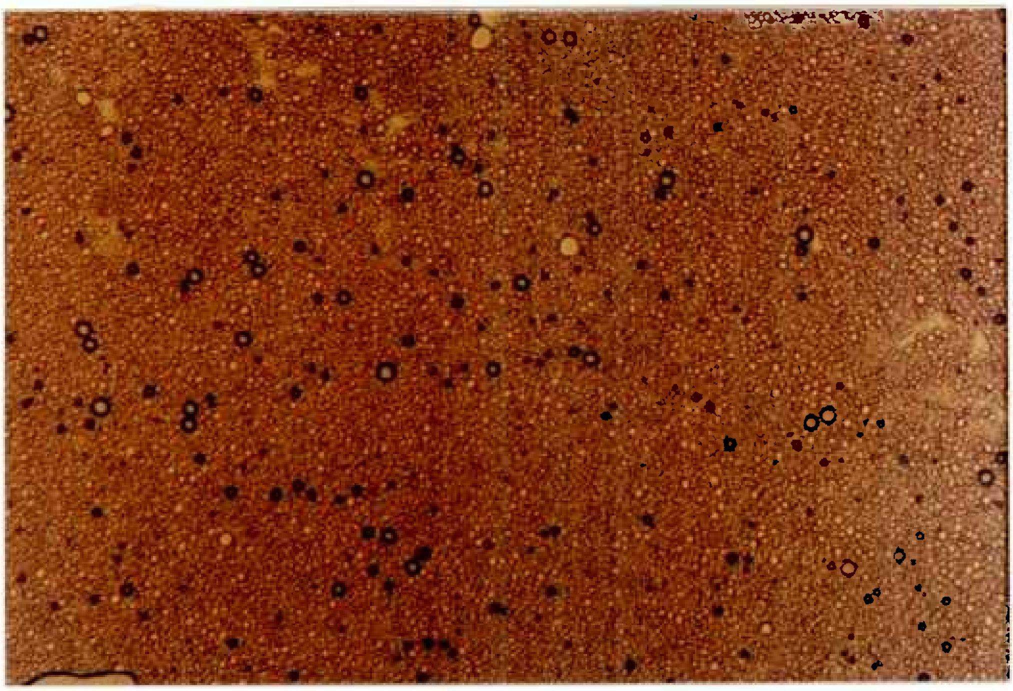
A coaxial cylinder viscometer (Ferranti Ltd., U.K.) was used to measure the viscosity of emulsions under shear in order to understand the lubricant property of emulsions.

This viscometer consists of two rotating cylinders. The outer cylinder is driven by a motor. Another cylinder is situated coxially inside the rotating one. The inner cylinder is free to rotate against a calibrated spring with a pointer. The variation of torque with speed was interpreted to give the relation between shear stress and shear rate. Five different speeds were obtained with different gears. The instrument was placed in a constant temperature bath, and the temperature of emulsions in the bath was checked regularly by a thermometer.

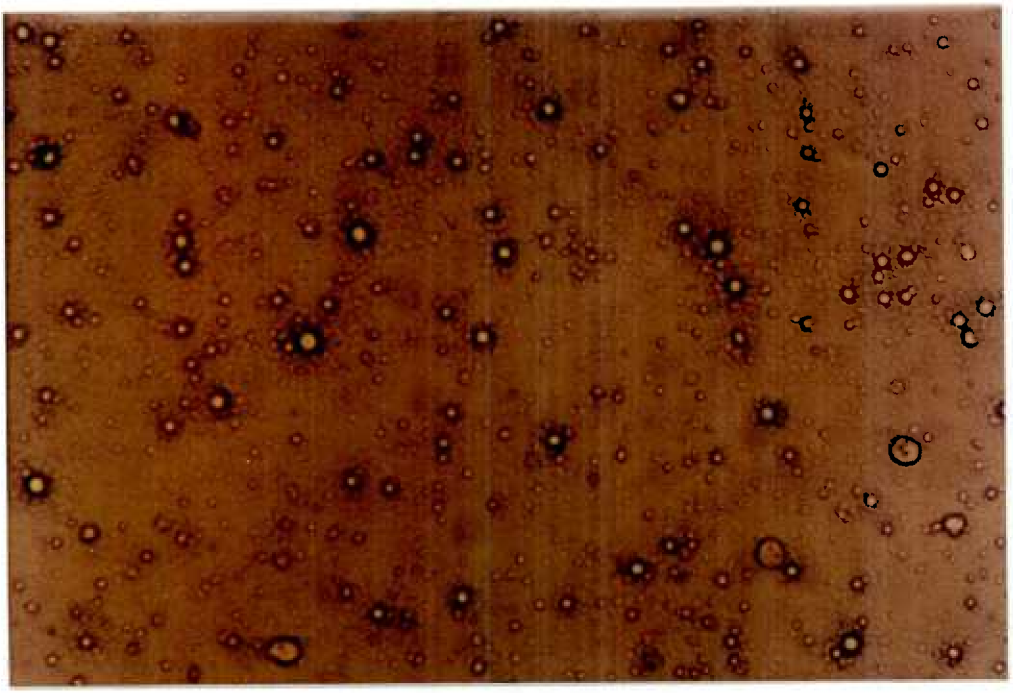
An Ubbelode viscometer is not appropriate for determining the viscosity under shear for Non-Newtonian fluids.

4.35 REPEATABILITY

The error of the viscosity measurement was limited as low as 1.0% by this apparatus.



(a) Water in Oil type emulsions



(b) Oil in water type emulsions

10μm

Figure (4.1) Photographs of W/O and O/W type emulsions(25°C)
(x 1200)

4.40 RESULTS AND DISCUSSION

4.41 PARTICLE SIZE DISTRIBUTION OF EMULSIONS

The particle size distributions of emulsions were shown to be the same (the average diameter was 1.5μm) for different water concentration as shown in figure (4.2).

4.42 SHEAR RATE - SHEAR STRESS RELATIONSHIP

The relationship between shear rate and stress was examined to study the fluid nature of the emulsions. The results are shown in figure (4.3).

Emulsions were shown to change from Newtonian to Non-Newtonian fluids as the dispersed phase volume increased. With 50% dispersed phase, both o/w and w/o, the maximum Non-Newtonian behaviour was observed.

These emulsions with high concentration of dispersed phase have pseudoplastic fluid properties. The pseudoplastic property of fluid is caused by the asymmetric particles aligning with shear rate. (67). Random orientation of emulsions occurs at static conditions. Alignment then occurs in the direction of flow under shear. This results in a constant viscosity of emulsion at higher shear rate.

4.43 SHEAR EFFECT ON VISCOSITY OF EMULSIONS

The viscosity of emulsions was shown in figure (4.4) to decrease noticeably with the increase of shear rate. Higher viscosity was observed with higher concentrations of dispersed phase, but water, oil and polyglycol were shown to decrease in viscosity slightly with shear rate.

The viscosities of emulsions are reported to become the same as that of oil at very high stear rates (69).

4.44 WATER CONCENTRATION EFFECT ON VISCOSITY

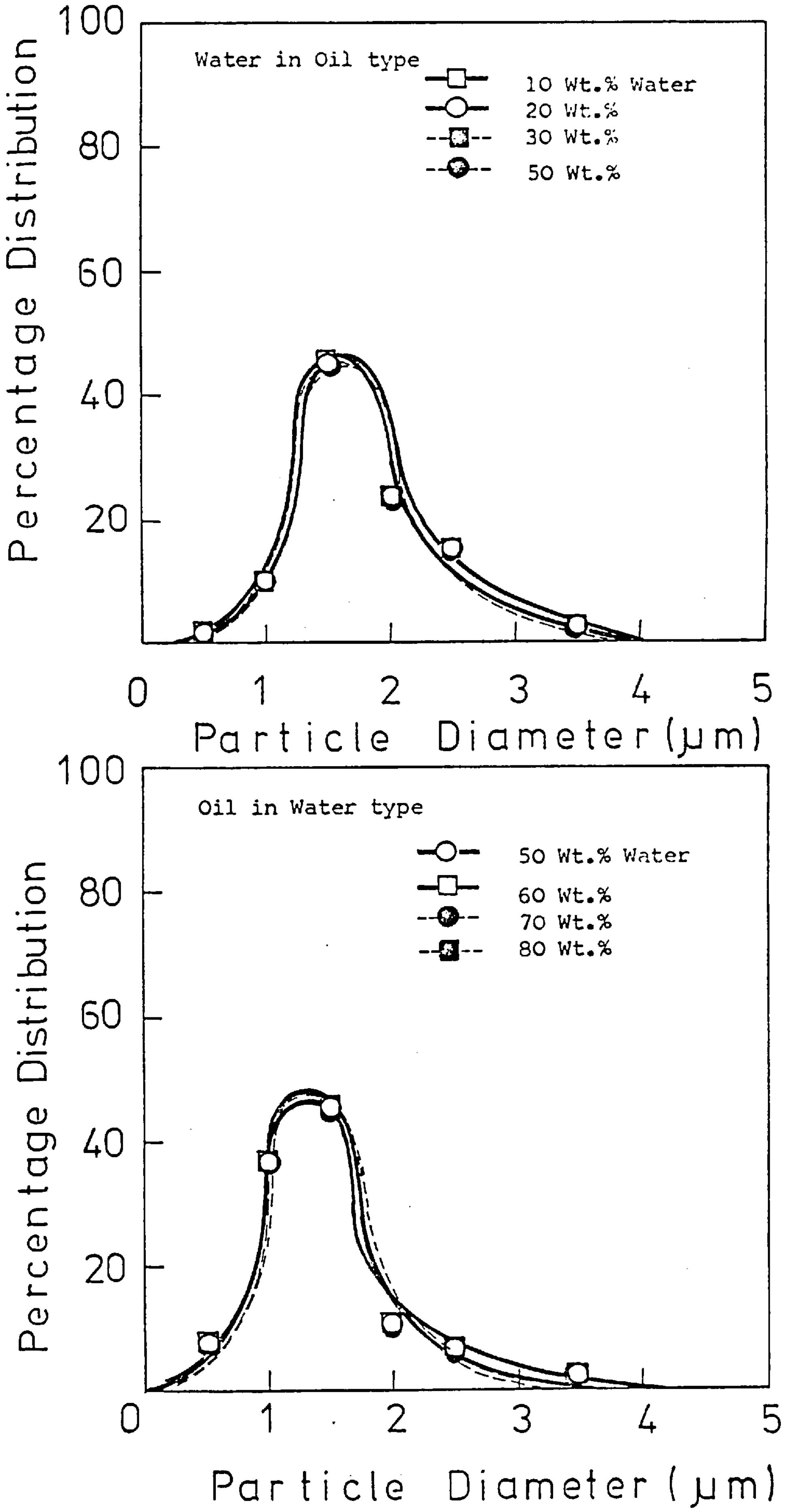


Figure (4.2) Particle size distribution vs. Water in emulsions

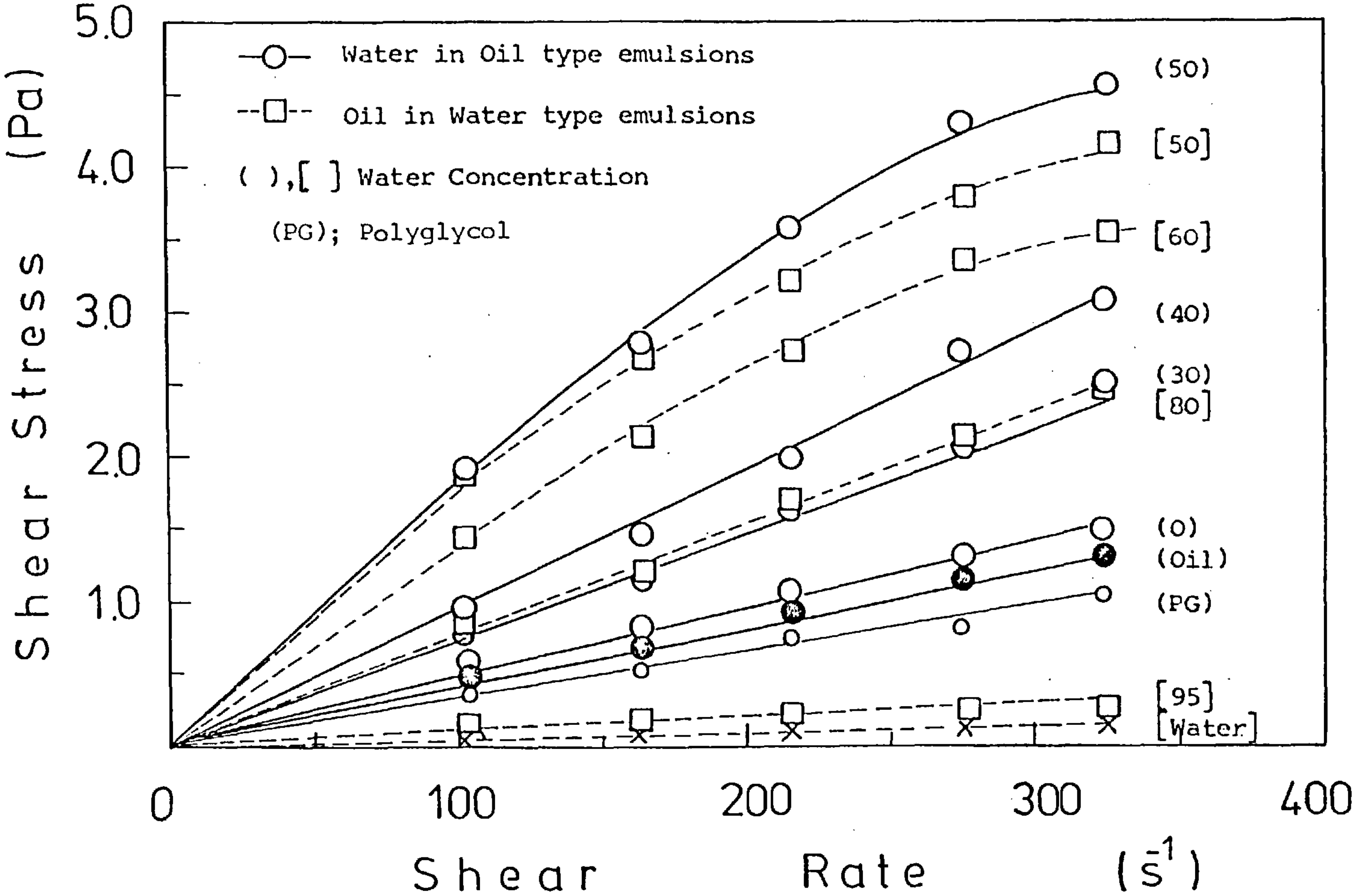


Figure (4.3) Shear stress vs. Shear rate in emulsions

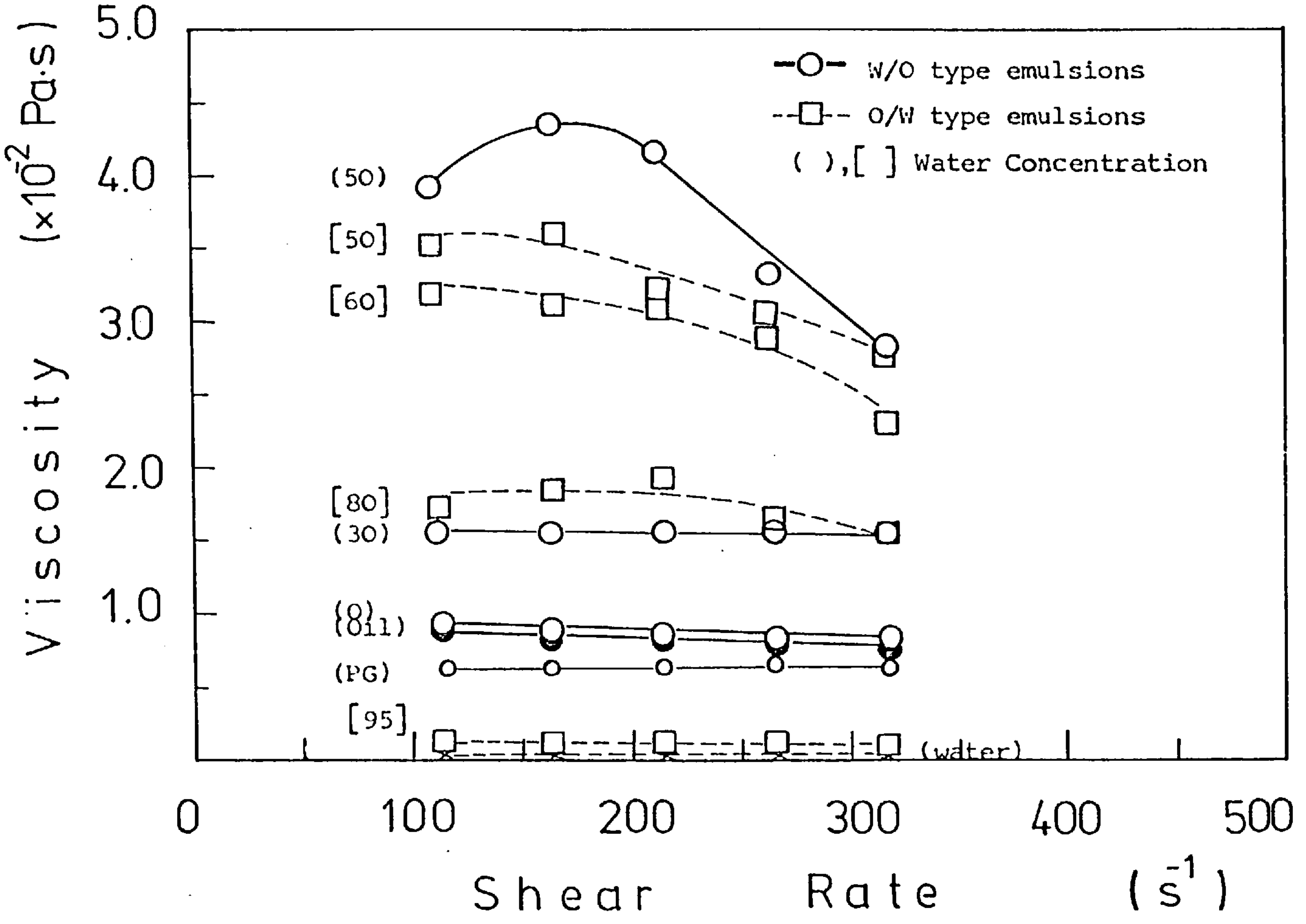


Figure (4.4) Viscosity vs. Shear rate in emulsions

The viscosity of emulsions was shown to increase with dispersed phase volume in figure (4.5).

The viscosity of emulsions increased with water concentration in the w/o type emulsion, and with oil concentration in the o/w type emulsion. The viscosity of a water, oil and polyglycol blend was almost constant with water concentration.

4.45 TEMPERATURE EFFECT ON VISCOSITY OF EMULSIONS

The effect of temperature on emulsion stability has been studied extensively in colloid chemistry (57) (62) (63).

The effect of temperature on viscosity of emulsions under shear is shown in figure (4.6) and figure (4.7). A maximum viscosity was observed at 40°C with the highest shear rate in a w/o type emulsion in figure (4.6). A minimum point was found at 55°C to 60°C. For the o/w type emulsion, a minimum viscosity was observed at 40°C (figure (4.7)).

These viscosity minima can be explained by the phase inversion temperature model of emulsions (4.22) Shinoda et al (63) measured the minimum interfacial tension between oil and water to determine the PIT point. At this temperature Shinoda found some degree of inversion, from w/o to o/w or vice versa. The PIT measured by them was 60°C for the w/o type emulsion, and 40°C for the o/w type emulsion, which agreed well with the minima found in this study.

4.50 CONCLUSIONS

The following conclusions can be drawn from this work.

(1) Particle size distributions of emulsions are independent of water concentration, for the emulsion prepared.

(2) The relationship between shear rate and stress in emulsions was measured. Non-Newtonian pseudoplastic behaviour is observed in emulsions with high concentration of dispersed

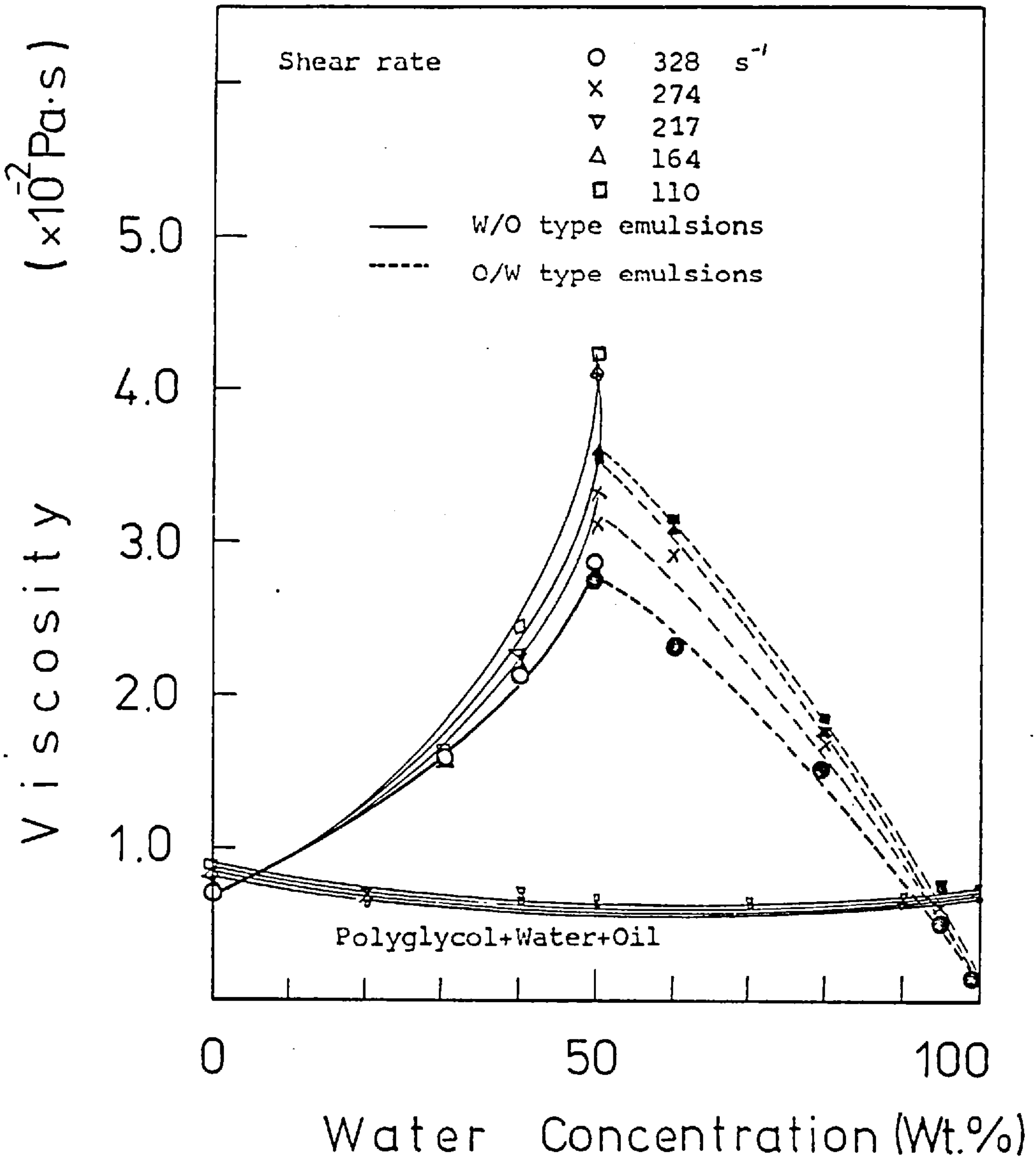


Figure (4.5) Viscosity vs. Water concentration in emulsions

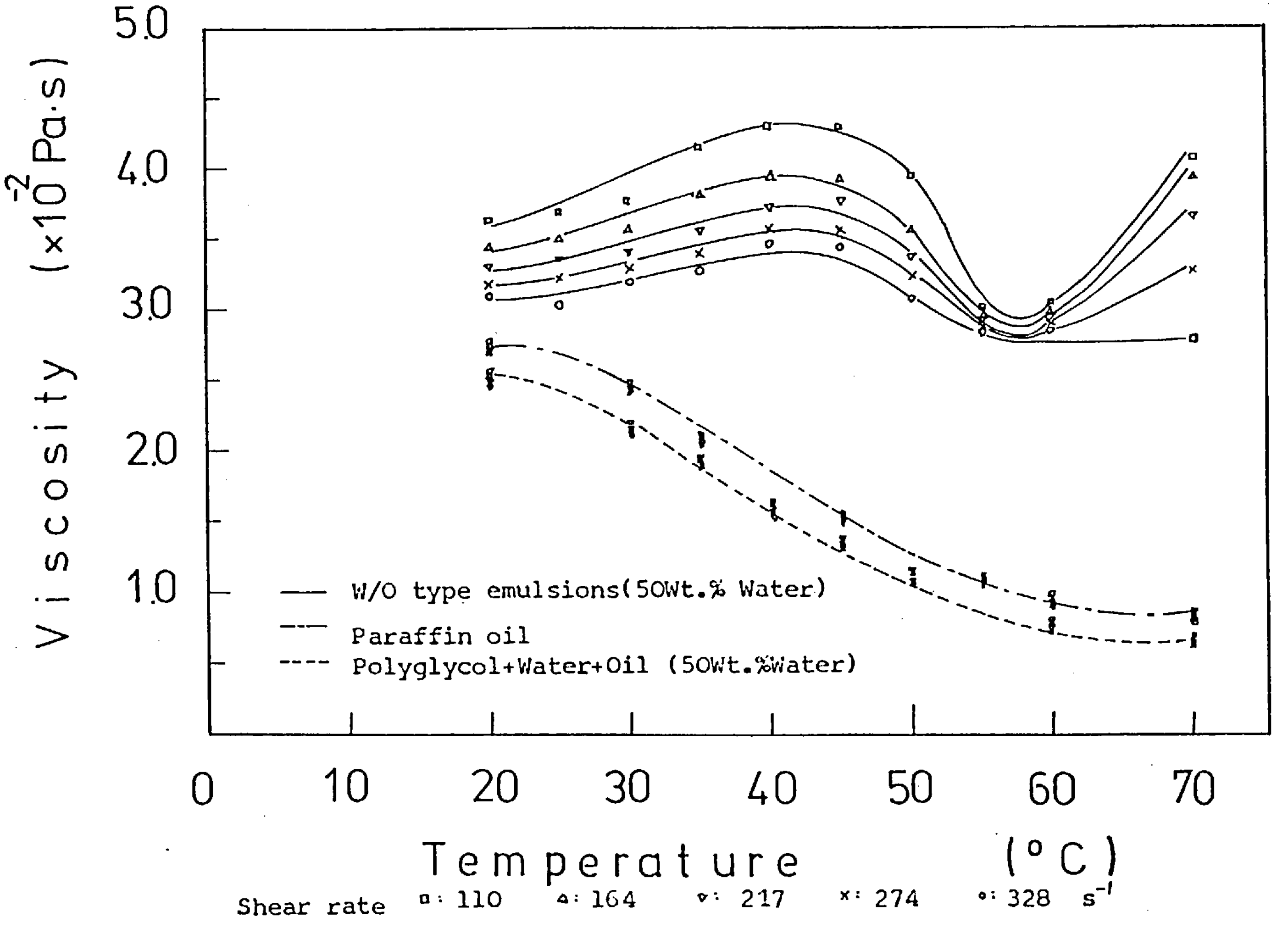


Figure (4.6) Viscosity under shear vs. Tempearture in W/O type emulsions

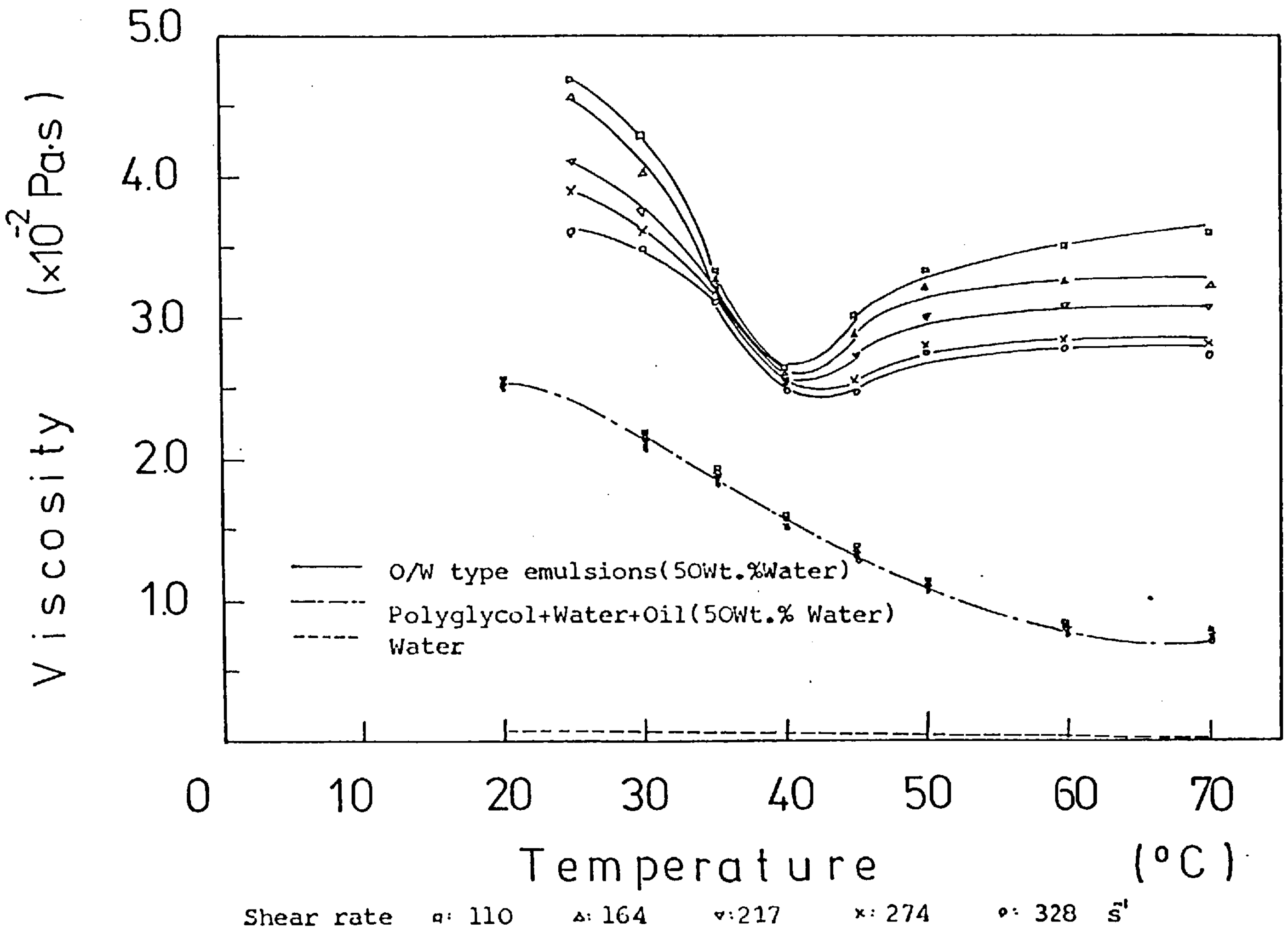


Figure (4.7) Viscosity under shear vs. Temperature in O/W type emulsions phase. Newtonian behaviour is observed in emulsions with low concentrations of dispersed phase. (The dispersed phase of emulsion is water in a w/o type emulsion, and oil in an o/w type. emulsion).

(3) The viscosity of emulsions increased with dispersed phase volume. The viscosity of emulsions decreases with shear rate.

(4) Viscosity minima were observed at particular temperatures in emulsions. At these temperatures, the emulsion may be partly inverted, as has been shown to occur at the PIT.

CHAPTER FIVE
EMULSION LUBRICATION

5.10 INTRODUCTION

The physical properties of emulsions: shear stress with shear rate and viscosity against three factors, shear rate, water concentration and bulk temperature, have been studied in the previous chapter. Two main results from this work are applicable to emulsion lubrication. Firstly the viscosity of emulsions is, where high shear rates are generally encountered, independent of high shear rates due to the pseudoplastic property of emulsions. This is important in lubrication. Secondly emulsions may have partly inverted to the opposite emulsions over the bulk temperature of $50^{\circ}C$ to $60^{\circ}C$, which is called the phase inversion temperature. Emulsions may consist of the similar compositions of water and oil locally on sliding surfaces on the way to scuffing, whatever the type and the water concentration of emulsions.

Hence the emulsions examined may have suitable properties for lubrication, replacing paraffin oils, as well as efficient coolants for grinding, cutting and rolling process. It may be possible that emulsions lubricate between sliding surfaces as pure paraffin oils whatever the compositions, water and oil, of emulsions. However the basic frictional properties of emulsions have not been investigated, although many practical reports on cutting, grinding and rolling have been published (5.20).

Because of decreasing energy sources, oils have become a valuable commodity and need to be used economically in future. It might be possible to dilute the oil with water and make an emulsion lubricant, the mechanical properties of which are similar to that of the oil. As one of the mechanical properties of lubricants, the load carrying properties of emulsions were measured.

The object of the work described in this chapter is to demonstrate the mechanism of boundary lubrication of emulsions.

Stable emulsions, with a constant average diameter of 1.5μm, were employed. Their scuffing loads were measured in a ball-on-triplane apparatus at the slow speed of 100rpm. This speed was chosen in order to prevent the emulsion particles breaking due to high frictional temperatures.

After preliminary work the following three factors were considered likely to influence the lubrication of emulsions, and were investigated.

(1) The film formation between sliding surfaces caused by the viscosity of emulsions under shear.

(2) The adsorption on sliding surfaces of surfactant in excess of that needed to form emulsions.

(3) The surface temperature on sliding surfaces lubricated by emulsions.

5.20 LITERATURE REVIEW

(A) WORK ON PRACTICAL APPLICATIONS

The problems of (1) fatigue and (2) cutting, grinding and rolling by emulsions have been studied by a number of workers and are not considered in detail here other than a brief literature survey.

(A1) FATIGUE PROBLEMS

The effect of hydraulic-fluid lubricant on water-accelerated fatigue has been recently studied. (70) (71) (72).

Hobbs and Mullett (70) estimated using the ball-bearing rig that w/o emulsions reduce a fatigue life of a ball-bearing by over 30 per cent. The life reduction was explained by enhanced crack propagation due to the effect of water on the ball bearing surfaces by Polk and Rowe (71) and Murphy, Polk and Rowe (72). They reported that the cracking rate of fatigue is controlled by stress level, metallurgy and lubricant.

(A2) CUTTING, GRINDING AND ROLLING

A cutting process has been studied by some researchers. (73) (74) (75) (76) (77) (78). They reported that the interactions between the stresses, strains and temperatures generated in cutting are too complex and localized to measure accurately.

A grinding process has been studied in the same way as the cutting process. (77) (79) (80) (81) (82).

Duwell, Hong and McDonald (80) reported that the simple application of water to grinding interface caused an increase of power consumption.

A mechanism of rolling has been studied recently by some researchers. (83) (84) (85) (86) (87).

(B) THEORETICAL WORK

Three main aspects of the lubrication of emulsions are reviewed.

(1) Film formation of emulsion.

(2) Adsorption of water, oil and surfactant*.

(3) Surface temperature of sliding surfaces.

* The adsorption of oil and surfactant on steels has been reviewed in Chapter 2 and 3. The adsorption of water is reviewed in this Chapter.

(B1) FILM FORMATION OF EMULSION

The film formation of emulsions under elastohydrodynamic lubrication has never been studied exhaustively and only a few papers have been published. (69) (88). A programme of work is in progress at the Lubrication Laboratory, Imperial College (118).

The E.H.L. film thickness of emulsions (water in oil type emulsions) has been shown to depend on the E.H.L. properties of pure oil and to be largely independent of water content, by Hamaguchi, Spikes and Cameron (88).

The film thickness at point contact in emulsions was calculated by the viscosity data of emulsions under high shear rate by Dalmaz and Godet (69). They found that the film thickness can be followed by the viscosity of oil under high shear rate.

(B2) ADSORPTION OF WATER

Two compounds of iron, $Fe(OH)_2$ and Fe_3O_4, were found at the iron surface in contact with water vapour in the absence of oxygen at $25^{\circ}C$, by Linnerbom (89). At higher temperature, $60^{\circ}C$ and $300^{\circ}C$ Fe_3O_4 was found and FeO and $Fe(OH)_2$ were not observed at the surface of iron. (90).

The effect of oxide layer induced by stress (the Beilby layer) on boundary lubrication was examined by Moore and McTegart (91), and Tingh (92). A presence of water was found essential for the effective lubrication of metals in fatty acid solution. Krause (93) concluded that hydrated iron oxides decrease the coefficient of friction and wear.

Steel surfaces rolled using emulsions were examined by ATR infrared spectroscopy by Tamai and Sumitomo (94). They found that iron-stearate was formed on the steel surfaces in emulsions containing stearic acid type emulsifier.

(B3) SURFACE TEMPERATURE

Surface temperatures of sliding metals were studied by Blok (95), Bowden (96), Jaeger (97) and Holm (98) (99) in early papers on lubrication.

Archard (100) considered the mechanism of surface temperature of rubbing surfaces. The equation developed by him to calculate surface temperature of rubbing surfaces is generally accepted. The maximum flash temperature is obtained from the equations for different speeds.

(i) for very low speeds ($L < 0.1$)

$$\theta m = 0.5NL$$

(ii) For moderately low speeds ($0.1 < L < 5$)

$$\theta m = 0.5\alpha NL$$

where α is a function of L which can be obtained from Figure 7 of Jaeger's (98) paper.

(iii) for higher speeds ($5 < L$)

$$\theta m = 0.435NL^{\frac{1}{2}}$$

where

$$N = \frac{\mu g \pi Pm}{J\ \rho C}, \qquad L = \frac{W^{\frac{1}{2}}V}{2K(\pi Pm)^{\frac{1}{2}}}$$

C	specific heat
g	the gravity constant
J	the mechanical equivalent of heat
Pm	flow of yield pressure
V	velocity of heat source or speed of sliding
W	normal load
μ	coefficient of friction
ρ	density
K	thermal diffusivity

The average surface temperature was shown to increase with speed and load using the Herbert-Gottwein dynamic thermocouple by Furey (101). The surface temperature was found to be independent of running time.

Quinn (102) (103) (104) studied the effect of surface temperature in a series of tests in the unlubricated wear of steel.

The flash temperature model advanced by Blok (95) for the oil-metal surface was shown to be acceptable as an engineering approximation by Ku and Staph (105) using the sliding-rolling disc and this was shown applicable for EHL contacts by Nazaraj, Sanborn and Winer (106) using the infrared microtemperature detector.

Hsu and Klaus (107) suggested that the surface temperature estimated from a chemical analysis of oxidized oil is higher than the flash temperature calculated by Block-Archard.

5.30 EXPERIMENT

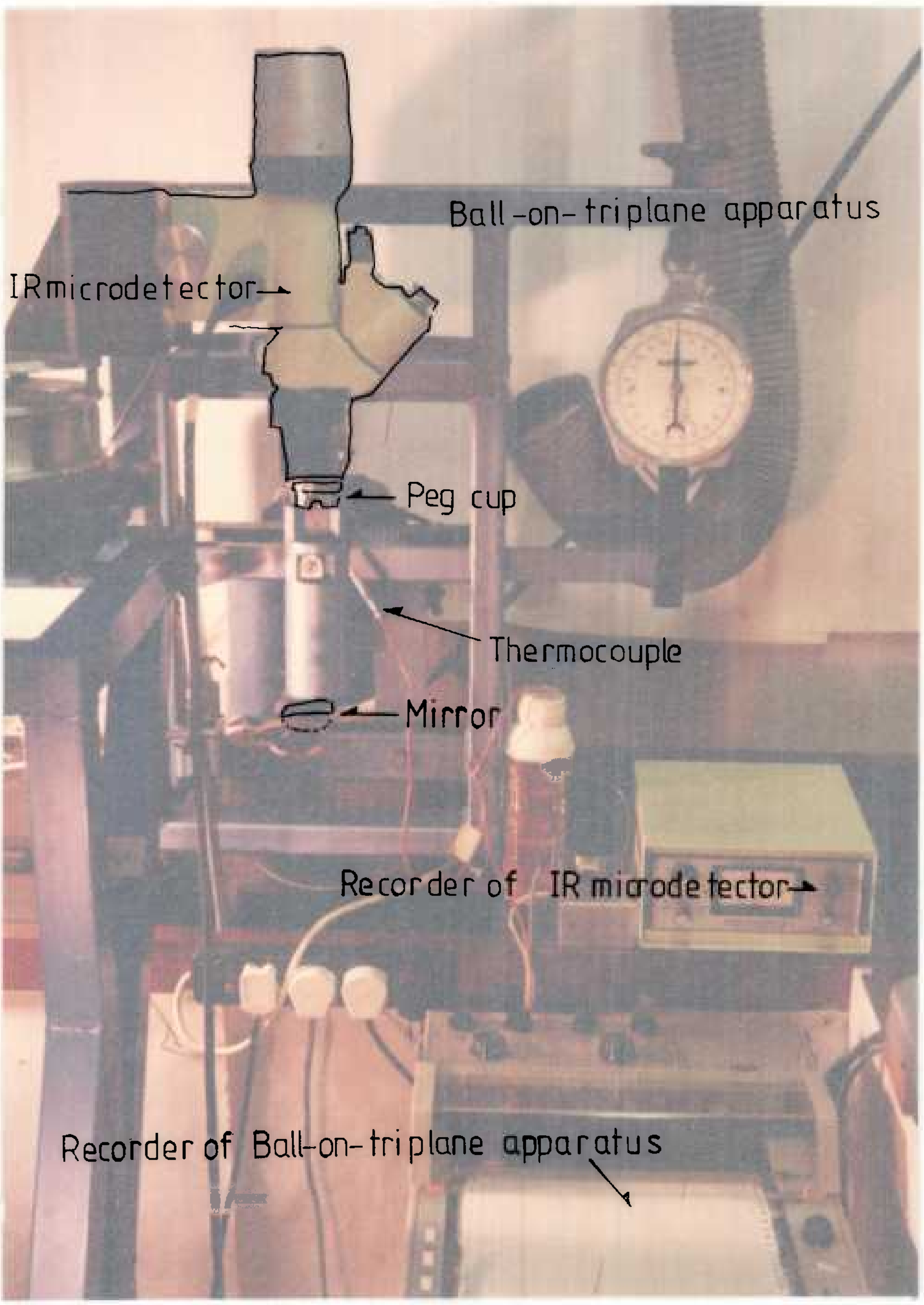
5.31 EXPERIMENTAL AIMS

The object of the work described in this chapter is to demonstrate the mechanism of boundary lubrication in emulsions by analytical and frictional methods.

5.32 BALL-ON-TRIPLANE APPARATUS

The apparatus used is shown in figure (5.1). A 1" diameter EN31 steel ball was held in a chuck driven through the motor. A steel cup was located by three pegs, which were a arranged to make three different tracks on the ball as at 45^{o}, 34^{o} 15' and 55^{o} 45' to the vertical. The second and third pegs were arranged circumferentially at $+137.8^{o}$ and -99.5^{o} to the 45^{o} peg.

The three pegs used in the work were standard EN31 roller bearings with diameter and length of 3/16 in. A thermocouple was mounted on the cup close to one peg, and bulk temperature


Ball-on-triplane apparatus
IRmicrodetector
Peg cup
Thermocouple
Mirror
Recorder of IR microdetector
Recorder of Ball-on-triplane apparatus

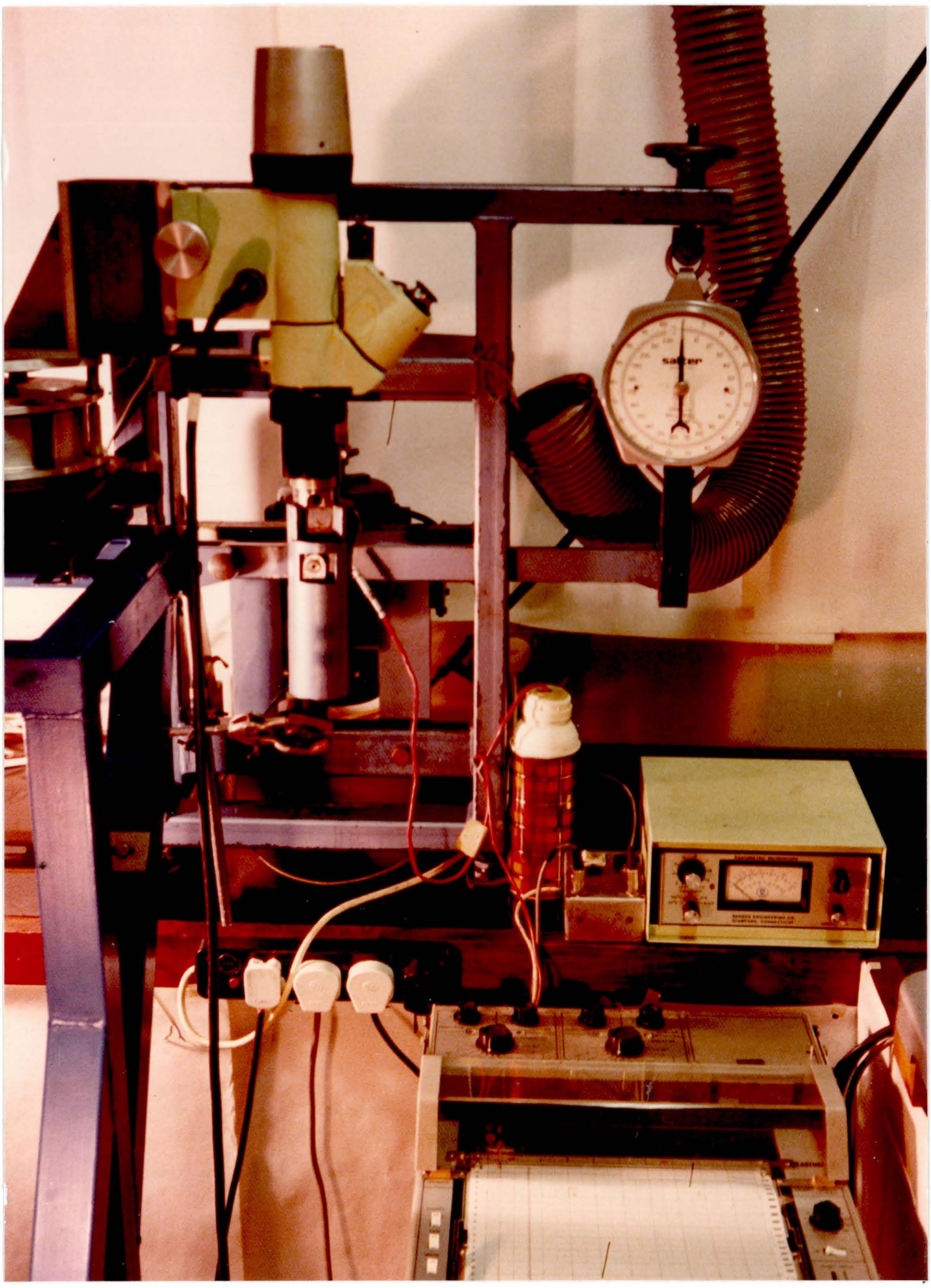


Figure (5.1) Photograph of the IR Microdetector and Ball-on-triplane apparatus

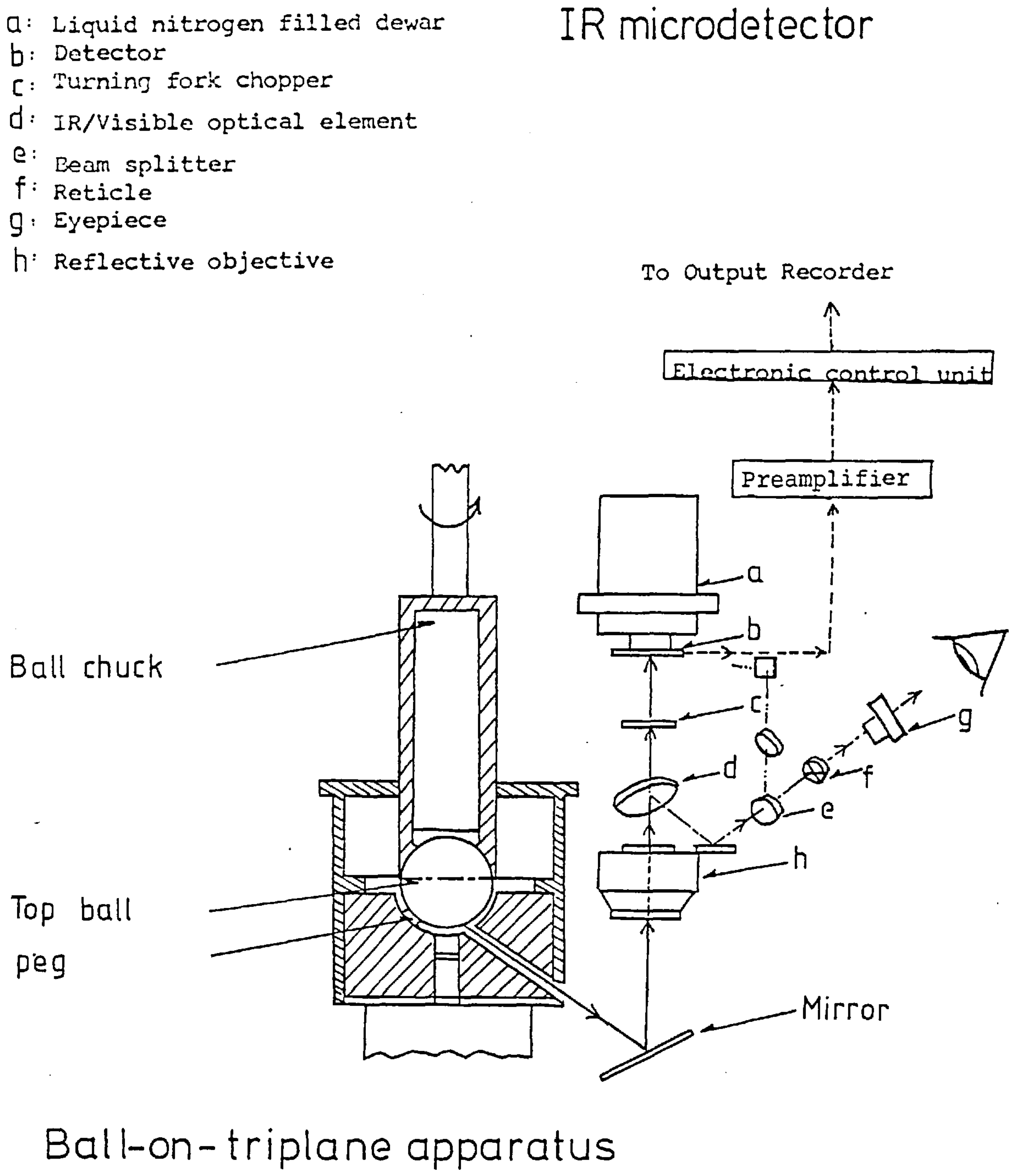


Figure (5.2) Shematic diagram of the combined IR Microdetector-Ball-on-triplane apparatus was monitored using this thermocouple. A window which was made of glass was located in the steel cup so that the track temperature on the steel ball could be monitored using an IR detector.

The ball-on-triplane apparatus was used to measure scuffing loads of emulsions and surface track temperatures of the ball simultaneously. (5.35). Particle size distributions and water concentrations of emulsions were determined from samples removed from the cup of the apparatus after scuffing. The surface of one peg was also examined after scuffing.

5.33 BOWDEN-LEBEN APPARATUS

The apparatus is shown in figure (5.3). This apparatus was used for measuring the coefficient of friction at low speeds and enables the effect of temperature, load and sliding speed on coefficient of friction to be determined independently.

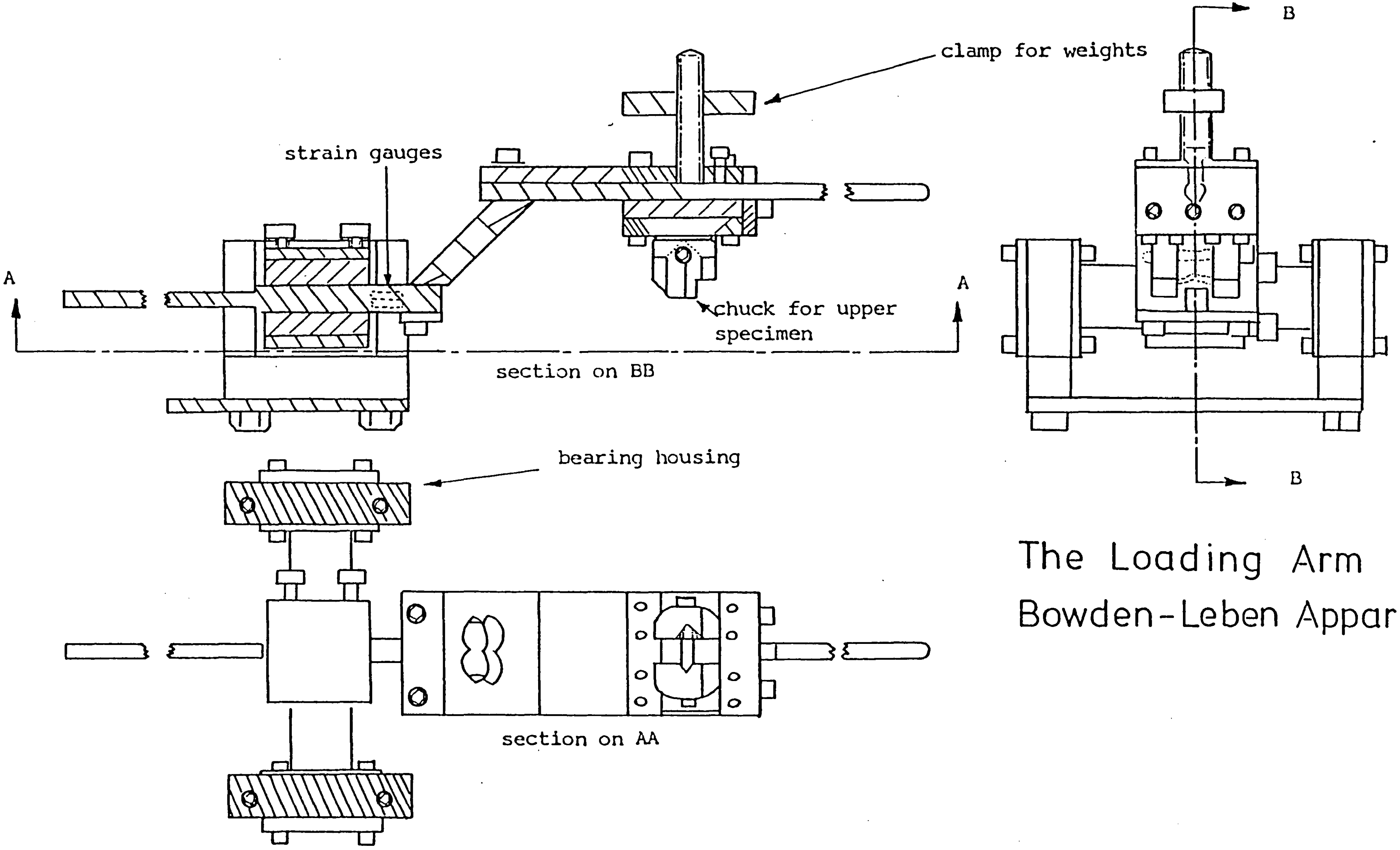
A EN31 steel ball of 15.9mm (5/8 in) diameter rubbed against a flat EN31 steel plate. The steel plate was located in a shallow trough which contained the lubricant. The trough was moved at a constant speed and was externally heated. The ball was loaded against the steel plate.

The steel ball was held in a chuck, and a strain gauge system was attached to the chuck assembly. The strain gauge measured a torsional displacement of the ball-chuck and indicated the frictional force on the ball. A signal was led from the strain gauges through an amplifier to a pen recorder.

The temperature of the lubricant was recorded on a pen recorder by a thermocouple placed close to the rubbing contact.

5.34 MATERIALS

Surfactants, oil and water used in the experiment were the same as in Chapter 4.



The Loading Arm
Bowden-Leben Apparatus

Figure (5.31) Diagram of the Bowden-Leben apparatus

The specification composition of the EN31 steel ball and the EN31 steel plate is shown in Table (5.1).

Table (5.1)

	C	Si	Mn	S	P	Ni	Cr	Mo
EN31	1.0	0.3	0.5	-	-	-	1.0	-

Specification of steel (wt%)

The steel foil used in steel surface analysis (5.36) was ordinary mild steel 0.1mm thick.

5.35 INFRA-RED (IR) MICROTEMPERATURE DETECTOR APPARATUS

A photograph of the combined IR microtemperature detector and ball-on-triplane apparatus is shown in Figure (5.1). The simplified functional diagram of the apparatus is shown in figure (5.2).

Infrared radiation (heat radiation) emitted from the sliding contact in the ball-on-triplane apparatus was measured with an IR radiometric detector. This apparatus had a spot size resolution of 35.6μm. The contact temperatures deduced directly from the reading were mean-time values.

The inherent absorption spectra of window glass, oil, water and surfactants used in the work were checked to measure the absorption ratio before the measurement. The absorption ratio of the system is a measure of the radiation absorbed by the glass window and lubricants over sliding tracks.

$$\text{Absorption ratio} = \frac{\text{Intensity of heat radiation through glass and emulsion}}{\text{Intensity of direct heat radiation}}$$

The direct reading values in a recorder were divided by the absorption ratio to correct to the surface track temperature on the steel ball, under the glass window and emulsions. Otherwise the calibrate temperatures without correction merely show the surface temperature on the glass window of a cup. The absorption ratios are shown in Table (5.2).

The calibration curve between scale of a recorder and actual temperature was determined by a standard black body radiator. A soldering-iron was placed at the same position as the glass window in a ball-on-triplane apparatus. The focus of IR microdetector was on the top of a soldering-iron, where the thermocouple was attached to show the temperature. The calibration curve is shown in figure (5.2.1).

The repeatability of temperature obtained was ± 0.5°C in the direct reading. (± 0.9°C in the corrected values).

Table (5.2) Absorption ratio

	Abosrption ratio
paraffin oil	0.58
water	0.53
surfactants	0.56
emulsion	0.58

5.36 STEEL SURFACE ANALYSIS BY IR AFTER EMULSION TREATMENT

Steel surfaces after reaction with emulsions were studied by IR multiple reflectance spectroscopy to elucidate the mechanism of lubrication, especially the chemical species on steel surfaces. Steel foils were used rather than the actual sliding surface of pegs, which is difficult to examine by IR multiple reflectance spectroscopy.

Two steel foils of different size, 49 x 20 and 51 x 20 (mm x mm), were used to clamp emulsions. These were kept in

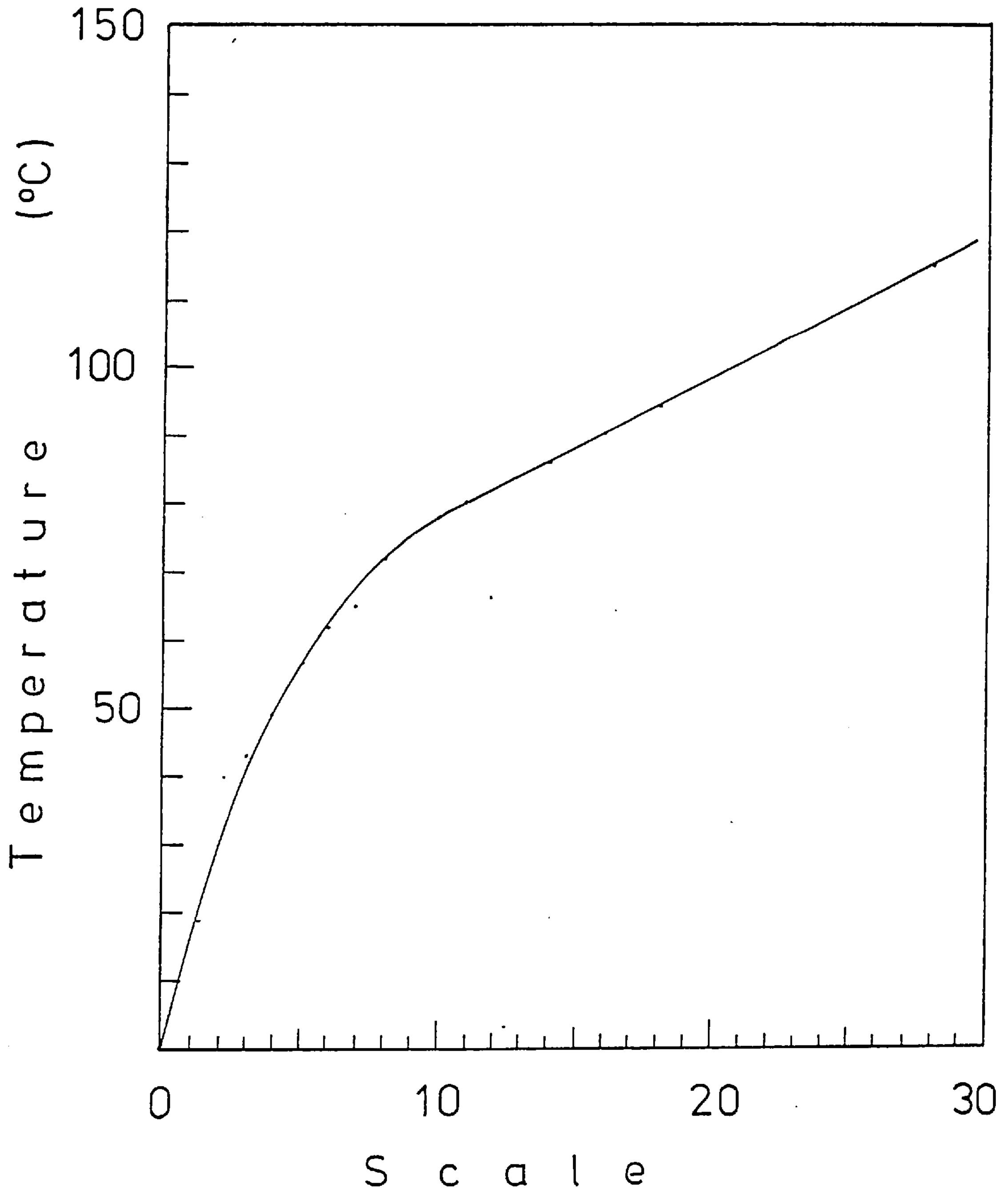


Figure (5.2.1) Calibration curve

the oven at a constant 70^{o}C for 24 hours. They were washed with acetone and soxhletted in toluence for 2 hours.

5.37 INFRARED MULTIPLE REFLECTANCE SPECTROSCOPY

The optical arrangement in infra-red multiple reflectance spectroscopy is shown in figure (5.4). This technique examines the chemical composition of species on metal surfaces. (108) (109) (110).

A multiple reflectance optical accessory was employed to record the spectra of chemical substances deposited on steel foil. (5.36). A optical arrangement with six reflections between the parallel mirror finish steel was employed. The infrared spectrometer used in this test was Parkin-Elmer 45 with specac DS ATR unit modified for multiple spectral reflection.

5.38 EXPERIMENTAL TECHNIQUES

All metal specimens, steel foils, pegs and balls, were cleaned by toluene and acetone, and soxhletted in toluene for three hours before use.

The ball-on-triplane apparatus was used to measure the scuffing load of emulsions. A load of 250N was applied during running-in for five minutes, and then load was increased in 250N step each minute to the scuffing load. The ball speed was 100rpm. (5.41).

The particle size distribution and the water concentration of emulsions were checked before and after scuffing. (5.42) (5.43) (Appendix 1).

The surface of the pegs after a test but without scuffing was observed using optical microscopy. In this case the apparatus was run from the initial load, 250N, by a step load of 250N/min, and stopped at 1.45 GPa, before scuffing. The immediate vicinity of the contact was then washed with acetone and

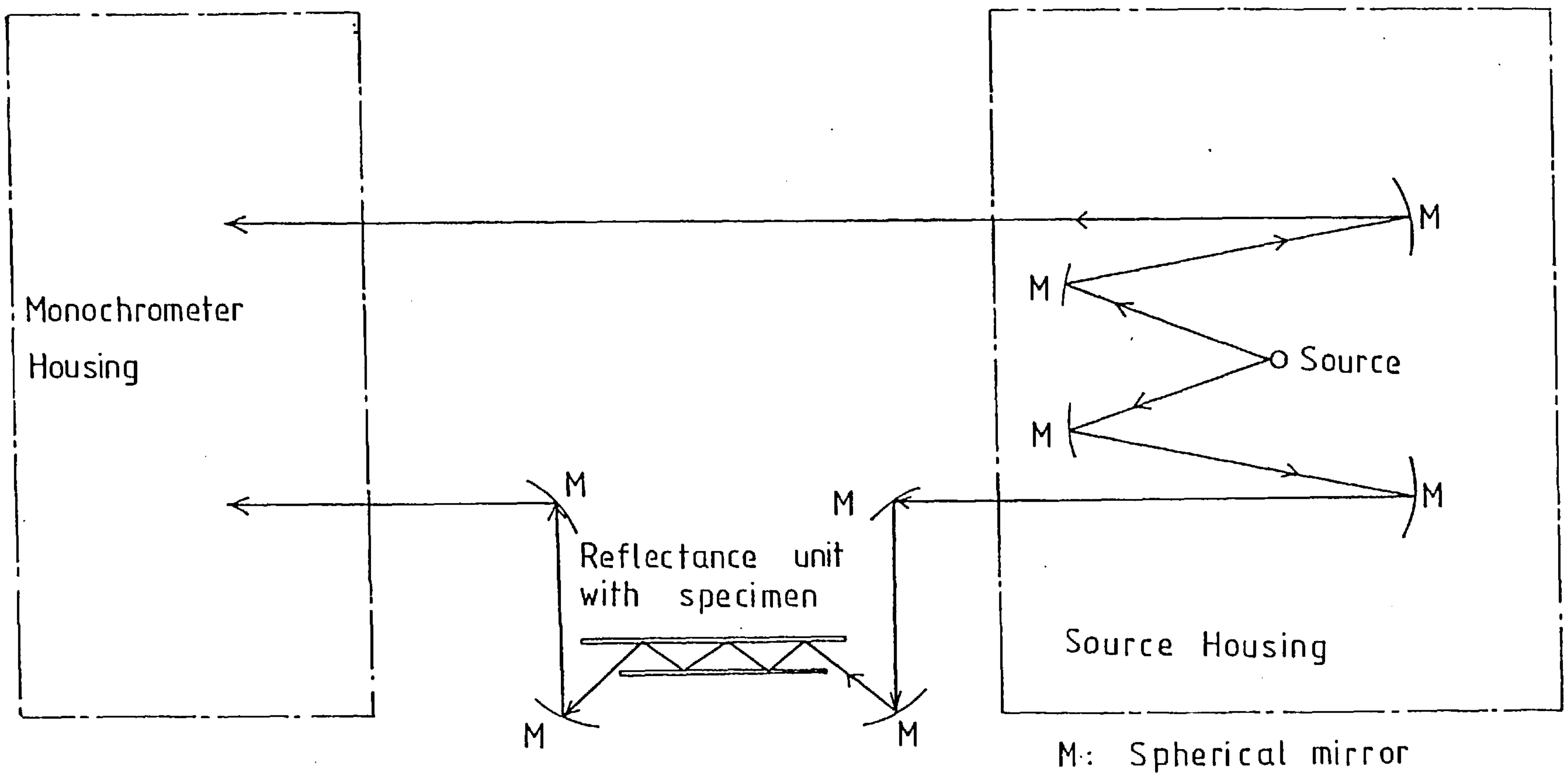


Figure (5.4) Optical arrangement of the IR multiple reflectance spectroscopy toluene without removing the load. The solvents were removed by blown air and absorbent-cotton. The surfaces of the pegs were observed after drying. The magnification of photoprints were x1200. (5.45).

The effect of temperature on frictional coefficients was also studied using the Bowden-Leben apparatus (5.33). Frictional coefficients of emulsions with EN31 steel plate were measured at a slow speed. The tests were carried out under a load of 10N at a sliding speed of 2.5 mm/s. The temperature was raised by $5^{\circ}C$/min. (5.47).

5.39 REPEATABILITY

The repeatability of scuffing load was ± 150N with the same test conditions for three times on the ball-on-triplane apparatus.

The repeatability of particle size of emulsions was ± 0.1µm from the measurement of enlarged photoprints.

The repeatability of water content was ± 0.2wt% by the titration of the Karl Fischer reagent.

5.40 RESULTS

5.41 EMULSION-STAINLESS STEEL LUBRICATION RESULTS

The scuffing loads of emulsions were shown to be nearly constant, 1.50 ~ 1.60 GPa, whatever the water concentration of the emulsions. The scuff load of pure paraffin oil without emulsifier was 1.41 GPa. The scuffing load of emulsions increased slightly with the dispersed phase volume in emulsions, whether water in w/o type emulsions or oil in o/w type emulsions.

The scuffing loads of emulsions, formed by sorbitan tristearate (Span 65) and polyoxyethylene (20) sorbitan tristearate (Tween 65), were observed to be higher than those of emulsions formed by the other surfactants.

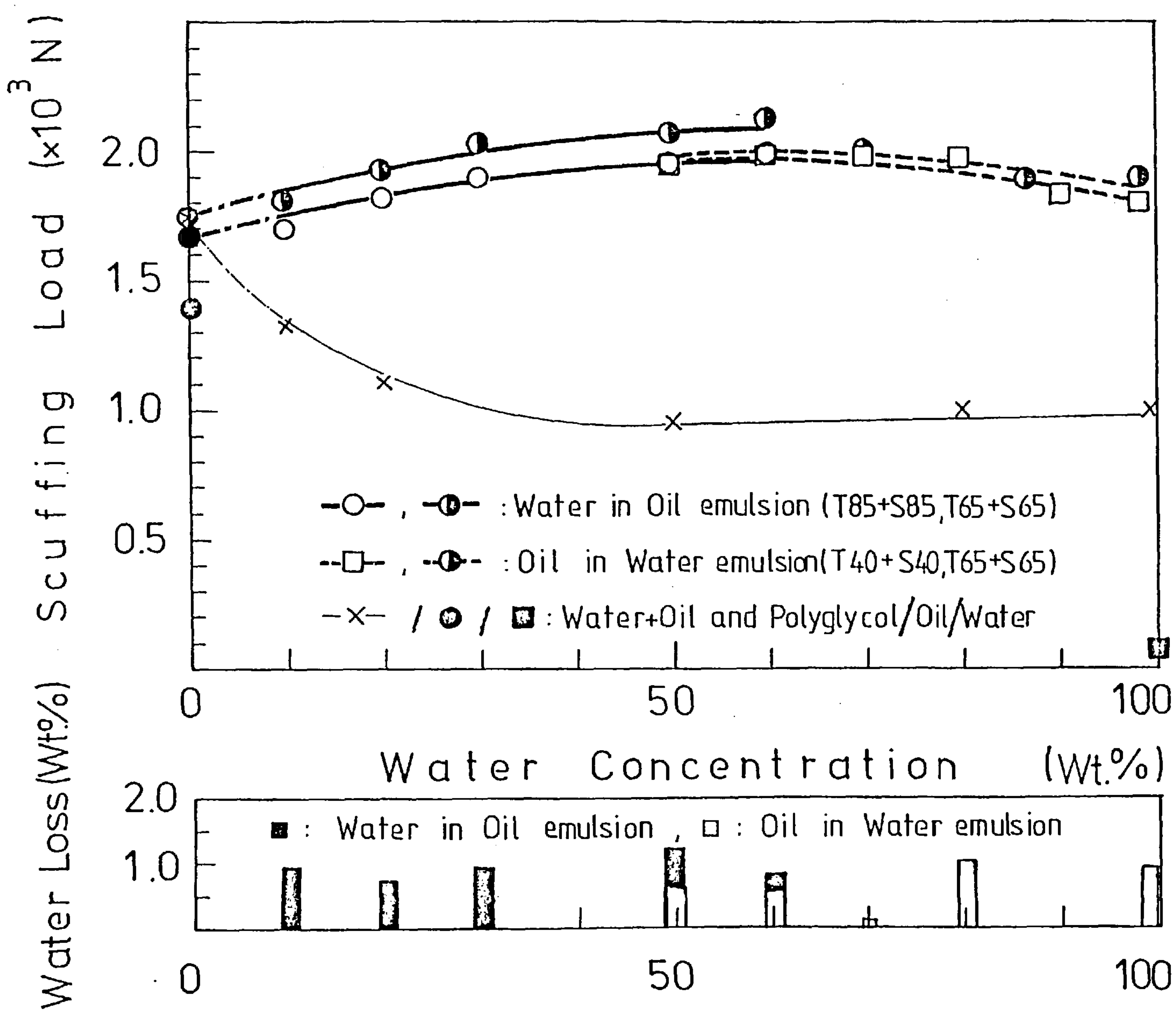


Figure (5.5) Scuffing load vs. Water concentration in emulsions

No detrimental effect of water in emulsions was found on scuffing, examined at a speed of 100rpm in the ball-on-triplane apparatus, although emulsion contains water which, by itself, is a most inferior lubricant.

The effect of water on scuffing was also examined using a mixture of water, oil and polyglycol. Polyglycol is capable of forming mixtures with water of similar properties to those of emulsions, but with single phase solution rather than dispersed phase colloids. (Chapter 4). These simple solutions of water, oil and polyglycol without emulsion particles showed constant viscosity whatever the water concentration of the mixture, although emulsions showed increased viscosity with water concentration. (4.44). The detrimental effect of water in the mixture was found to some extent in figure (5.5), but the scuffing load was maintained above 1×10^3N, which is much higher than that of pure water (0.1×10^3N).

5.42 SLIDING EFFECT ON PARTICLE SIZE DISTRIBUTION

Particle size distribution of emulsions, measured before and after scuffing, are shown in figure (5.6). Only small differences in the particle size distribution were observed.

5.43 SLIDING EFFECT ON WATER CONCENTRATION OF EMULSIONS

Water concentration in emulsions was measured before and after scuffing. The results are shown in Table (5.3) and figure (5.5). Only a small change in the water concentration was observed.

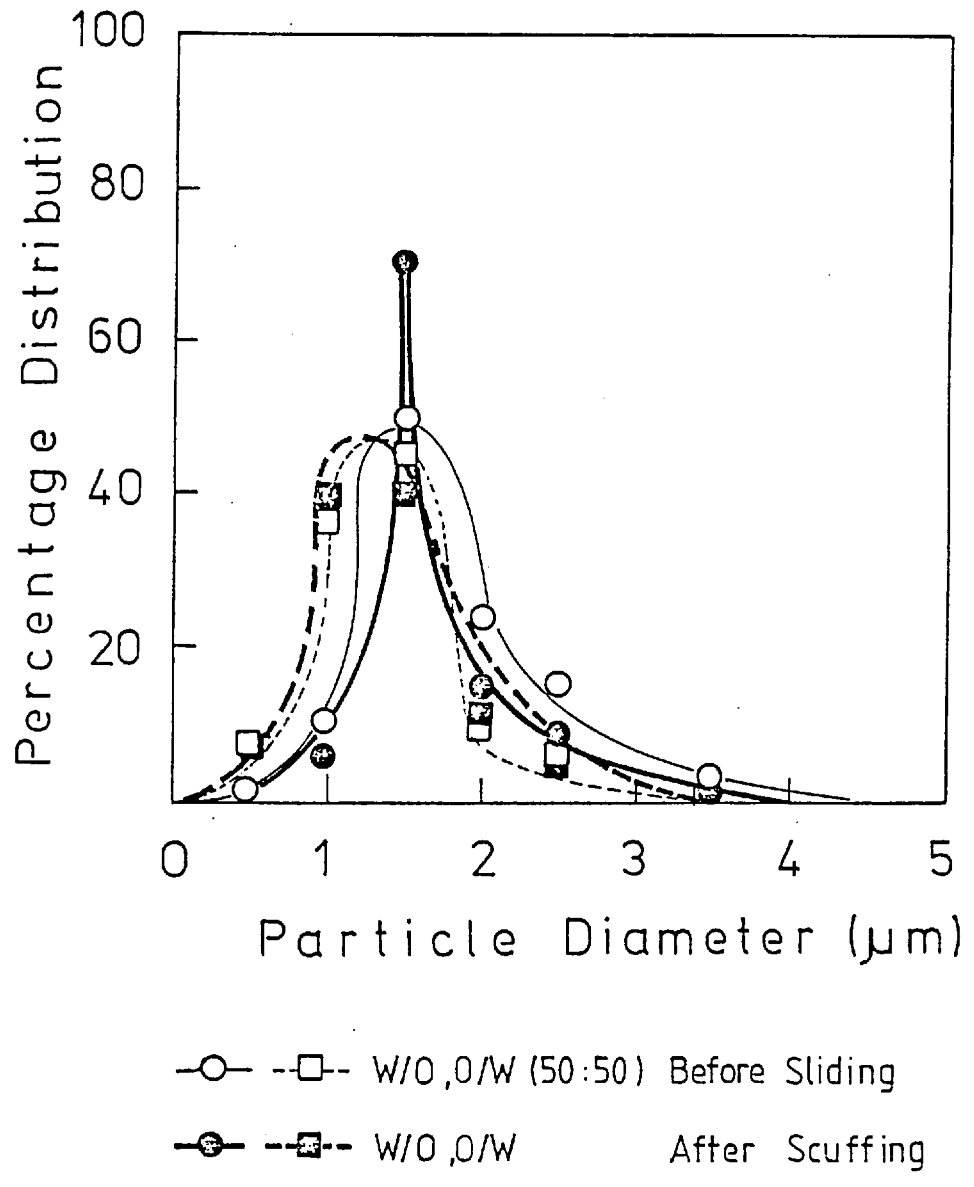


Figure (5.6) Particle size distributions before and after scuffing

Table (5.3) Water Concentration

Type	Water Conc. (wt%)	Water concentration in emulsion after scuffing (wt%)
w/o	10.0	9.2
	20.0	19.4
	30.0	29.2
	50.0	48.9
	60.0	59.3
o/w	50.0	49.5
	70.0	70.0
	80.0	79.1
	99.5	99.2

5.44 VISCOSITY OF EMULSIONS

The viscosity of emulsions under low shear rates was shown to increase slightly with the dispersed phase volume in emulsions, but decreased gradually with shear rate. The viscosity of emulsions under higher shear rate was shown to be nearly constant whatever the water concentration of emulsions (4.34).

At the immediate vicinity to the inlet of metal contact, between a ball and a peg in the ball-on-triplane apparatus, emulsions, with pseudoplastic properties, are considered to be sheared under high shear rates. The shear rates are calculated in the discussion. (5.51). Possible effects by the viscosity of emulsions on emulsion lubrication are then discussed.

5.45 STEEL SURFACE ANALYSIS BY IR AFTER EMULSION TREATMENT

The steel surface in static contacts with emulsions was examined using IR multiple reflectance spectroscopy to elucidate the reaction of water, oil and surfactant with steel surfaces. (5.36) (5.37).

Results of this are shown in figure (5.7). The absorption of surfactant was observed at steel surface even after washing with acetone and the toluene soxhlet. The -CO-Fe- bond (1080 cm^{-1}) was observed on the steel surface in emulsion formed by the nonionic surfactants of stearic acid derivatives, sorbitan tristearate (Span 65) and polyoxyethylene (20) sorbitan tristearate (Tween 65). The -FeO- bond (400 - 600 cm^{-1}) was observed on the steel surface in emulsions.

The same absorption of IR by the metal surface heated with emulsions was observed as was shown by the emulsion surfactants themselves. The oxidized iron was also observed on the steel surface, although the absorption band of -FeO- was negligible on the surface of plain steel foil without treatment.

The wear scar surface of the peg, used in the ball-on-triplane apparatus, was observed after washing the immediate vicinity of the contact by solvents and then drying. (5.38) The photoprints of the peg surface, after removal of the ball, are shown in figures (5.8) and (5.9). A thin oil film with five fringes was observed to cover part of the wear scar. The oil film is considered to be paraffin oil, containing surfactant in emulsions, as deduced from the results of steel foil analysis by IR multiple reflectance spectroscopy.

5.46 SURFACE TRACK TEMPERATURE IN EMULSION LUBRICATION

Surface track temperatures of the ball in the ball-on-triplane apparatus were measured under boundary lubrication using emulsions. Surface temperatures of the ball were measured by the IR microdetector. (5.35). The bulk temperatures of water, oil and emulsions were also measured by a thermocouple installed in the cup of the apparatus respectively. (5.32). Later in this chapter the difference between these two

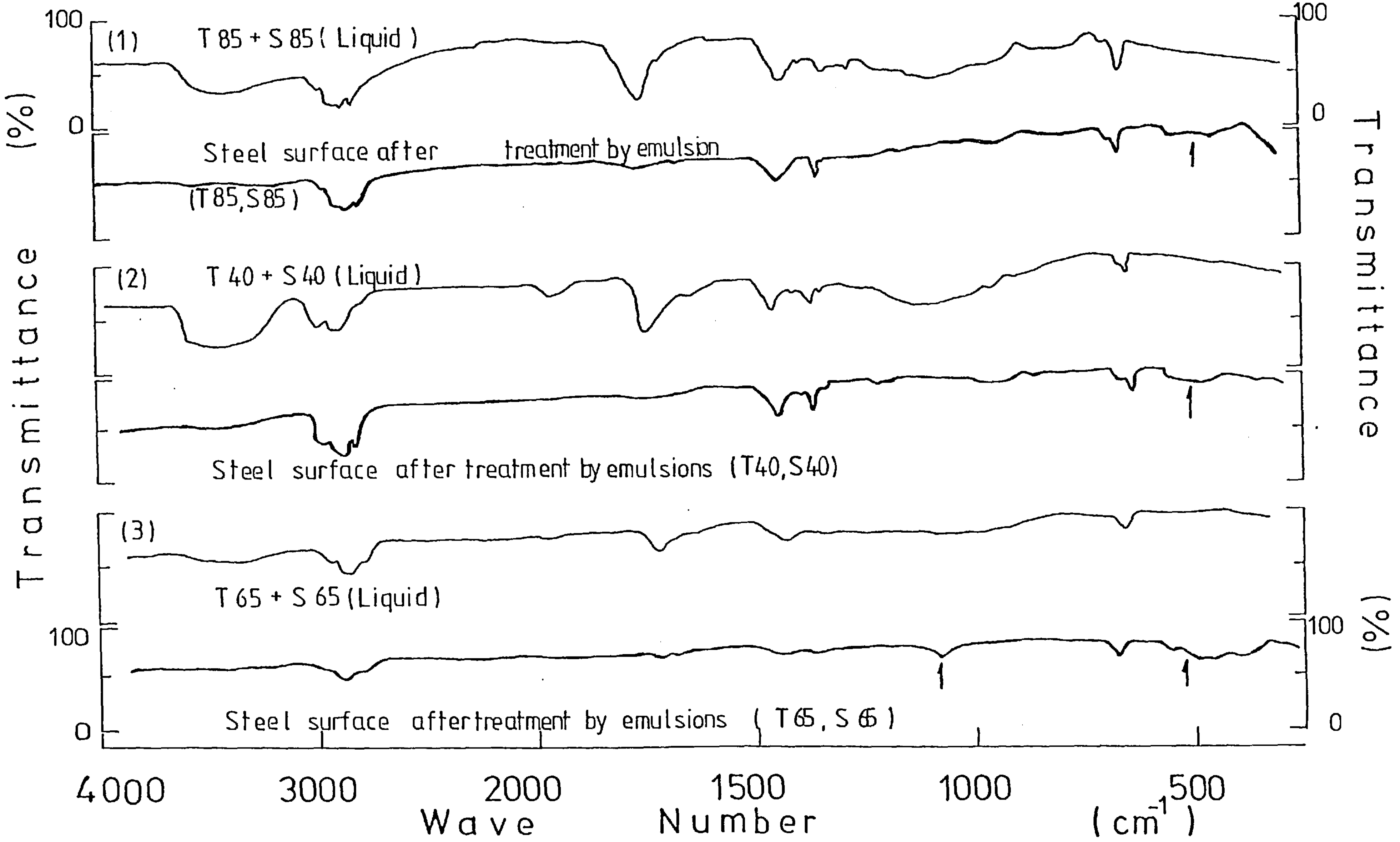


Figure (5.7) Steel surface analysis by IR after the treatment of emulsions

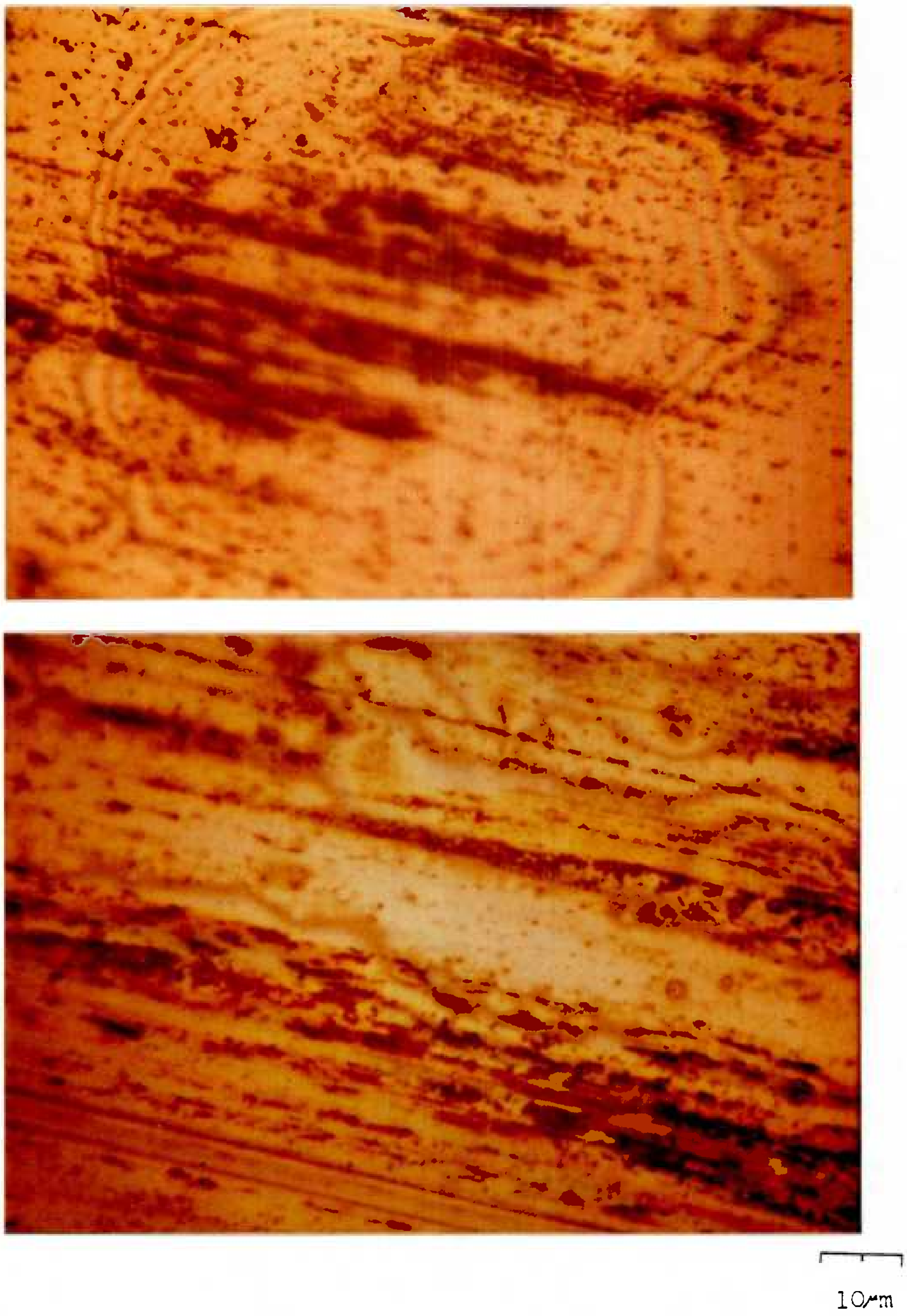


Figure (5.8) Photograph of sliding surface in W/O type emulsions (x1200)

Figure (5.9) Photograph of sliding surface in O/W type emulsions (X 300) temperatures, surface and bulk,is used to define equilibrium skin temperature, ΔT. Equilibrium skin temperature, ΔT, is then used to calculate heat transfer coefficients from the steel surface in emulsions. (5.53).

Surface track temperatures of the ball were measured against sliding distance or running time as shown in figure (5.10). Preliminary tests of surface track temperature showed no difference among the temperatures on three tracks of the ball. The first track from the above was usually studied by the IR microdetector. This track measured has the shortest distance from the contact to the IR spot (≅ 0.9cm) of the three tracks on the ball. The track temperatures were found to increase with sliding distance at a slower rate for emulsions than for paraffin oil. The temperatures in oil-free water were shown to icnrease quite rapidly with sliding time.

Surface track temperatures and bulk temperatures at scuffing were measured against water concentrations of emulsions as shown in figure (5.11). The surface temperatures using emulsions were lower than in paraffin oil and were nearly constant whatever the water concentration of emulsions. Equilibrium skin temperatures, ΔT, are used to calculate heat transfer coefficient of oil, water and emulsions. (5.53).

5.47 FRICTIONAL COEFFICIENT OF EMULSIONS WITH TEMPERATURE

The surface track temperatures of emulsions were lower than those in paraffin oil. (5.46). The frictional coefficients of emulsions were measured against temperature using the Bowden-Leben apparatus and compared with paraffin oil and water.

The results of w/o and o/w type emulsions are shown in figures (5.12.1) and (5.12.2) respectively. The temperatures where frictional coefficient rises are shown to be higher in emulsions that in paraffin oil. The temperatures of friction-rise were 140°C to 150°C in w/o type emulsions and about 120°C in o/w type emulsions. Emulsions, in a shallow trough heated

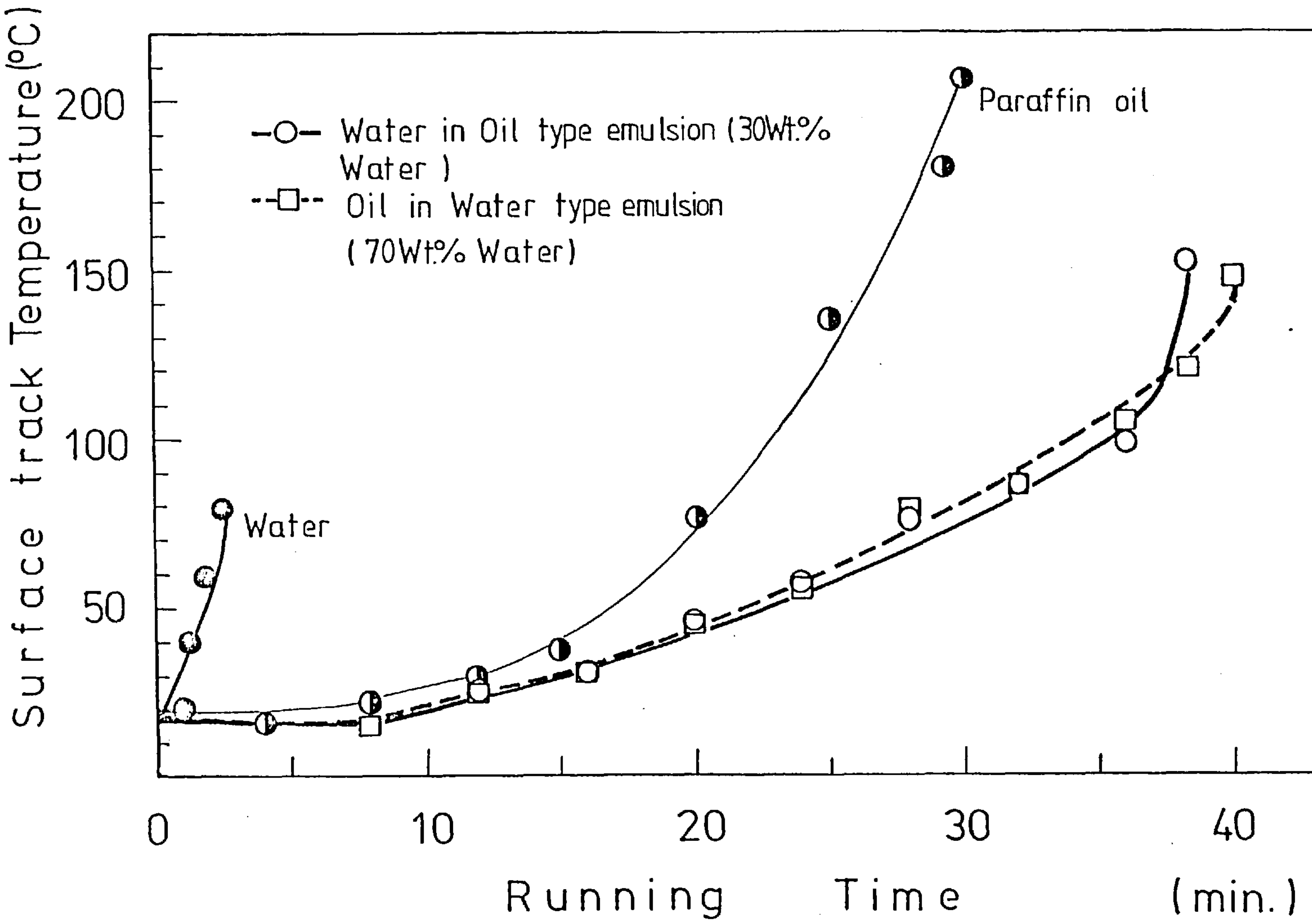


Figure (5.10) Surface track temperature vs. Running time

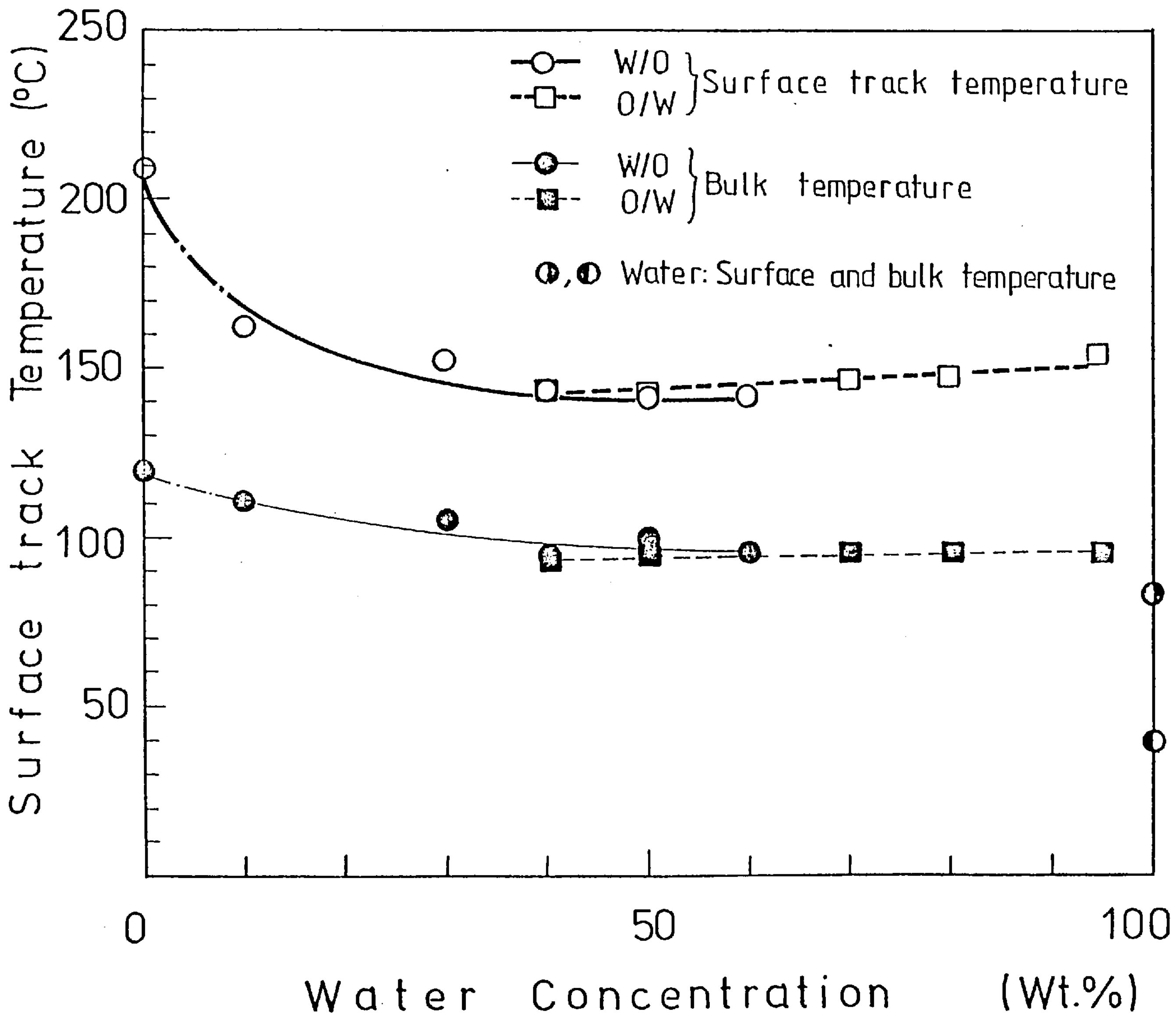


Figure (5.11) Surface track temperature vs. Water concetration

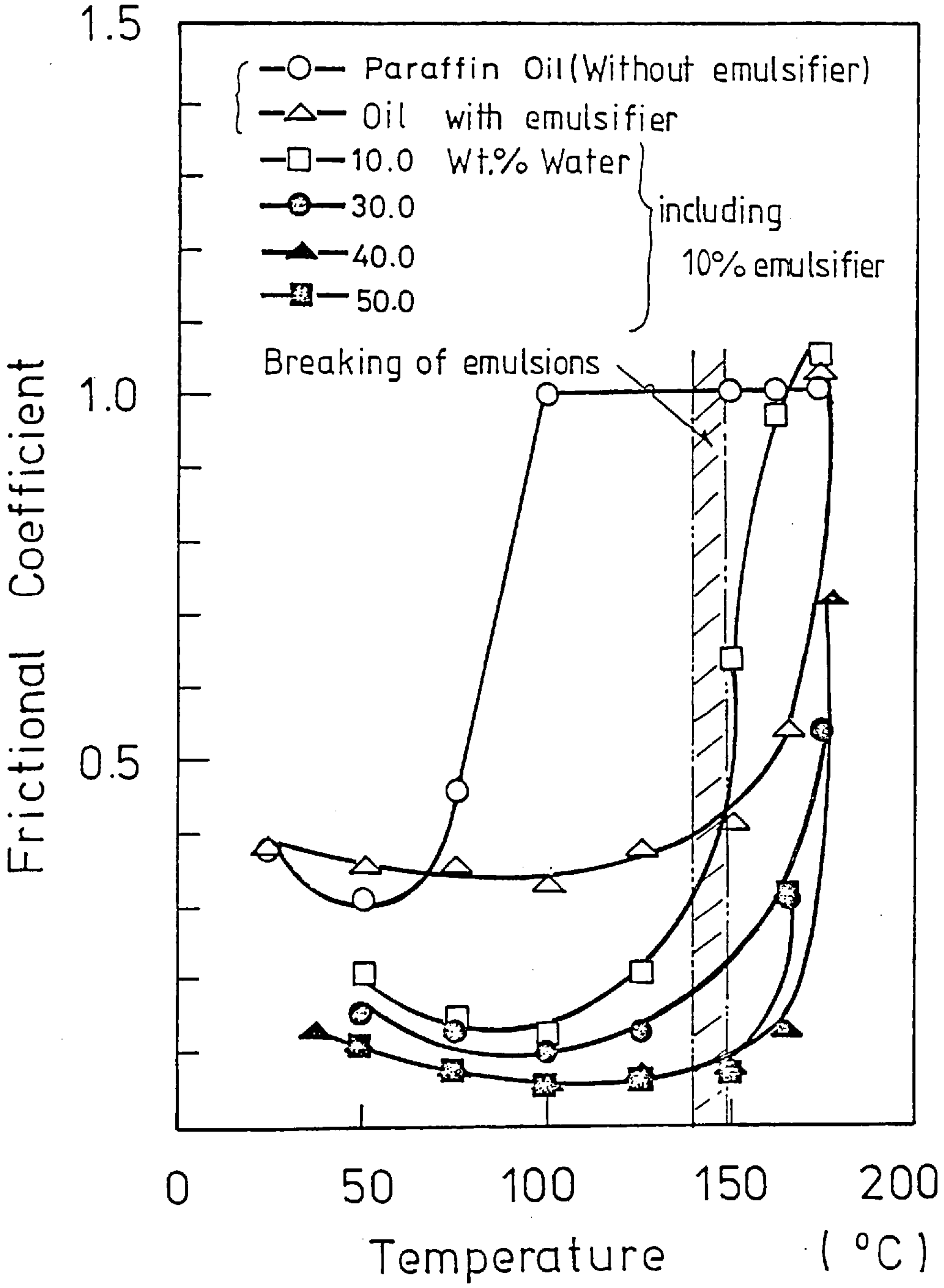


Fig (5.12.1) Frictional coefficient of emulsions with temperatures (W/O type emulsions)

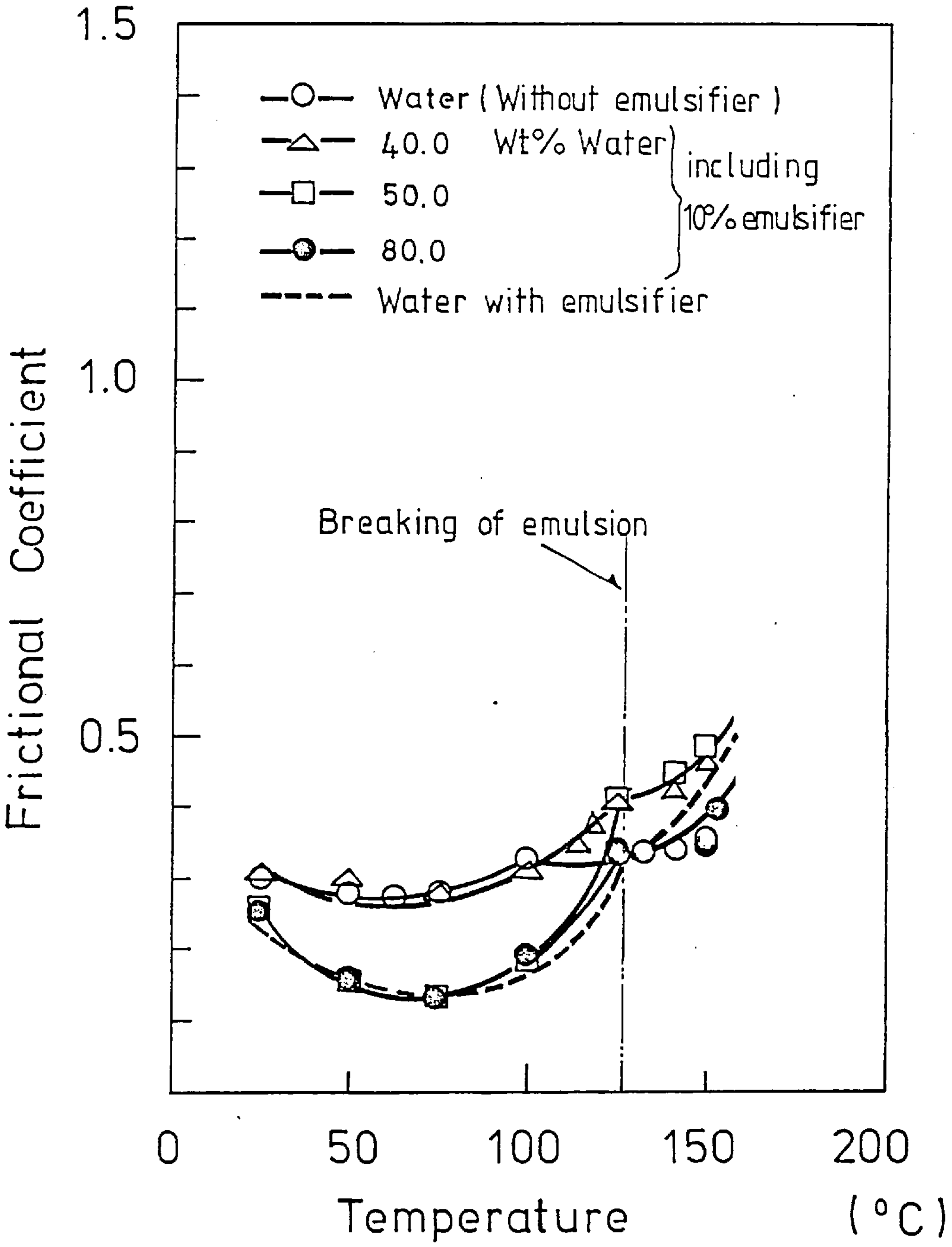


Fig (5.12.2) Frictional coefficient of emulsions with Temperature (O/W type emulsions) externally, were broken at high temperatures. The water of emulsions may be easy to evaporate in an open-air heater. The temperatures where emulsions started to be broken were 140°C to 150°C in w/o type emulsions and 120°C to 130°C in o/w type emulsions. By contrast, in the ball-on-triplane apparatus with vigorous stirring in a half closed cup emulsions were stable even up to scuffing temperatures, 150°C to 160°C.

The pure paraffin oil without emulsifier was found to give increased friction suddenly at 75°C as shown in figure (5.12.1), while the oil with emulsifier maintained constant friction up to 160°C ~ 170°C. The hydrocarbons or weaker surfactants are considered to desorb from the sliding surface at about 75°C, although more polar substances adsorb on the surface up to around 160°C and only later desorb completely. (Chapter 6).

The w/o type emulsions were found to increase friction from about 140°C to 150°C, whereas the water-free oil with surfactant maintained low friction up to 160°C. The friction-rises in the emulsions are considered to be caused by the breaking of emulsions due to the elevated boiling point of water, 140 ~ 150°C for w/o type emulsions. When emulsions are broken, the adsorbed layers of surfactant, formed on sliding surfaces, may desorb at lower temperatures than in water-free oil. The boiling water may disorder the adsorbed layers and the friction thus rises earlier than the water-free oil. The o/w type emulsions were found to increase the friction from the temperature of 120°C, which is also considered to be caused by the breaking of emulsions. The pure water without surfactant was shown to maintain the friction as low as the water with surfactant, when the temperature is over 100°C. The lower friction of water with steel may be caused by hydroxide layer on the sliding surfaces. (93).

It was shown here that emulsifier and emulsions decrease the friction to lower values than in pure paraffin oil and water, until the emulsions break at higher temperatures than the boiling point of water.

5.50 DISCUSSION

5.51 VISCOSITY OF EMULSIONS

Although a great deal of metal-metal contact took place at the speed in this work (100rpm), it is likely that the presence of some kind of EHL film is still an important contributing factor to performance in the ball-on-triplane apparatus. The calculated EHL film thickness of oil was of the same order of surface roughness of the wear scar under the experimental conditions used in this work. ($\cong 0.1\mu m$).

The empirical formula of EHL film thickness has been proposed under the EHL condition, which is fairly accurate for the film thickness in the flat central area of the contact. (111) (112).

$$\frac{hmin}{R} = 0.86\left(\frac{\eta U}{ER}\right)^{0.70}(\alpha E)^{0.60}\left(\frac{ER^2}{W}\right)^{0.05}$$

where

hmin	the minimum film thickness
R	ball radius
η	absolute viscosity (or dynamic viscosity)
U	surface velocity in x direction
E	Young's modulus
α	pressure-viscosity coefficient ($\eta = \eta_o \exp \alpha P$)
W	total load

In this equation the most important factor of film thickness at constant speed is the base viscosity of lubricant, having the biggest index 0.7. The other factors are not likely to contribute to the formation significantly under similar running conditions.

It is obviously necessary to measure the viscosity of water, oil and emulsions at the immediate vicinity of the contact, between a ball and a peg in the ball-on-triplane apparatus, in order to discuss EHL film formation. However the pseudoplastic property of emulsions, as measured in the previous chapter, seems to explain their viscous behaviour at very high shear rates found in EHL contacts. Emulsion particles with random movements in a static condition are forced to align in the same direction of shear. (4.42). The viscosity of emulsions decreases to that of paraffin oil with shear rate whatever the dispersed phase volume of the contact, shear rates by sliding surfaces are likely to increase rapidly, attaining the value of shear rate (112).

$$\text{Shear rate} = 3U/4L$$

where

U surface velocity in x direction

L. the mean oil film thickness up to the midpoint

Under the speed used in this work and the estimated film thickness, calculated from the equation of oil film thickness,

$$\text{Shear rate} = \frac{3 \times 8.5 \times 10^{-2} \text{ m/s}}{4 \times 0.1 \times 10^{-6} \text{ m}}$$

$$= 10^{5}/\text{s}$$

A low shear rate was required (10^2/S) in order to understand the physical properties of emulsions in this work, although the shear rate estimated in the contact, 10^5/S, is much higher than the measured shear rates. But it might be possible to estimate the similar shear stress of emulsions to paraffin oil under high shear rates, as the shear stress was shown to become independent of shear rate with increasing the rate. The similar value of viscosity between emulsions and oil may contribute to the similar value of film thickness between them.

5.52 SURFACTANTS IN EMULSIONS

It is generally accepted that surfactant monolayers at sliding contacts, adsorbed from oil, are very effective in preventing scuffing under boundary lubrication. (1) (112). The effect of surfactants in emulsions was also observed on the frictional behaviour of emulsions in this work. (5.47). The frictional coefficient of surfactants was lower than the pure paraffin oil but higher than the emulsions, containing the surfactants, oil and water.

A thin film of oily substance was observed at the wear scar of washed pegs which had been lubricated with emulsions. (5.45). The film was also found on the steel surface of the foils, treated by emulsions in the static contact. The adsorbed film was examined by IR multiple reflectance spectroscopy and found tobe composed of the same chemical species of surfactants and hydrocarbon as in emulsions.

Hence the surfactant of emulsions was found to contribute to lower frictional coefficients than pure oil and water but the scuffing loads of emulsions increased slightly with the volume of dispersed phase, oil in o/w and water in w/o type emulsions. (5.41) The constant concentration of surfactants was dissolved in the solution of water and oil. The solubility of surfactants is different in oil as compared to water but it may be possible that the surfactants, dissolved in oil and water, adsorb and react with sliding steel surfaces to form a thin film with the similar composition of surfactants on the surfaces whatever the volume of dispersed phase in emulsions.

There seems to be another contributing factor, which is the most important in emulsion lubrication. This is dealt with in the next section.

5.53 SURFACE TEMPERATURE WITH EMULSION LUBRICANTS

Emulsions, containing water which has a high specific heat (4.2J/$^{\circ}$C.g), is likely to remove the frictional heat from sliding surfaces and prevent the microscale welding between them.

The temperature of rubbing parts is an important criterion of scuffing. (112). Scuffing has been found to occur independently of the oil film thickness between sliding parts, and dependent on the critical temperature a film of adsorbed molecules desorbs from the surface. (16) (112) (113).

The effect of temperature on scuffing in emulsion lubrication has been considered in this work. Surface temperatures on the sliding track of a ball were measured in emulsions to understand the thermal properties of emulsion in the boundary lubrication. The temperatures were measured by IR microdetector apparatus. (5.46).

A thermal quantity, which shows how much of the frictional heat is removed from sliding surfaces, is the heat transfer coefficient from the steel surfaces. The relationship of thermal exchange between sliding surfaces and lubricant is understood mathematically and shown as follows. (113) (114).

$$\Delta T = \frac{q}{2Lhc} \qquad (5\text{-}1)$$

where

ΔT the equilibrium skin temperature (^{o}C)

q the heat source strength/unit width feeding into one surface (Joule/s.cm)

L the distance between coefficients (cm)

hc the heat transfer coefficient (Joule/s.cm^2.^{o}C)

This equation was obtained from a series of computations undertaken to see how the temperature grows with finite number of revolutions. (114).

The equilibrium skin temperature is the difference between surface track temperature measured by the IR microdetector and bulk temperature measured by the thermocouple.

$$\Delta T = Tsurf - Tbulk = q/2.\pi D.hc \qquad (5\text{-}2)$$

where

D the diameter of sliding track on a ball (cm)

The skin temperature of emulsions is shown to be nearly constant and of intermediate value between paraffin oil and water, as shown in figure (5.13). The minimum skin temperature was found when the volume of dispersed phase, oil in o/w and water in w/o type emulsion, was a maximum. The optimum temperature found in the figure might be considered as follows: Skin temperatures of sliding surface in emulsions are determined by not only the frictional performance of emulsions but also the cooling effect of emulsions. The emulsions with high water concentration, say, o/w type emulsion with 95% of water has high specific heat, but the lubricating performance is not desirable. On the other hand, the emulsions with low water (high oil) concentration, say, w/o type emulsion with 10% of water should have the good lubricant of oil but the specific heat is low.

The heat source strength in equation (5-1) was obtained from the equation of

$$q = \frac{\text{Total heat generated}}{3} \times \frac{1}{\ell}$$

$$= \frac{\mu W U/J}{3\ell} \qquad (5\text{-}3)$$

where

μ	the frictional coefficient
W	the load on three pegs (g.cm/sec^2)
U	the sliding speed (cm/sec)
J	the mechanical equivalent heat 1×10^7 (erg/Joule)
ℓ	the axial width of sliding track (cm)

As the resolved load per peg is $W/3 = \overline{W}g$ and the sliding speed is written as $U \fallingdotseq \omega \times D/2 = (100\text{rpm} \times 2\pi/60) \times D/2$, the equation (5-3) becomes

$$q = \frac{\mu \times \overline{W}g \times \omega.D/2}{\ell J} \qquad (5\text{-}4)$$

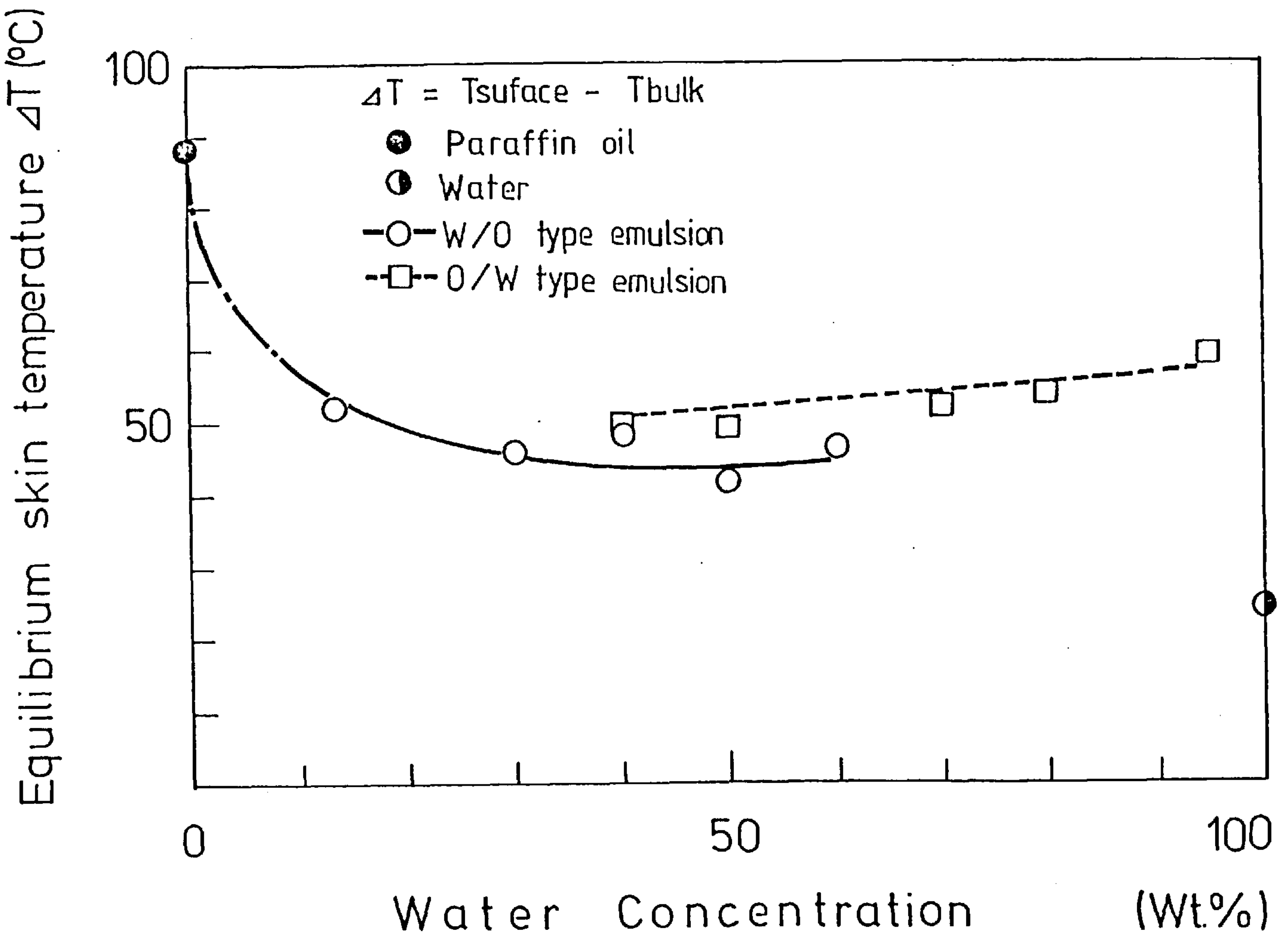


Figure (5.13) Equilibrium skin temperature vs water concentration in emulsions where

$\overline{W}$	the resolved load per peg	(g)
g	the gravitational constant 981	(cm/sec^2)
ω	the angular speed	(rad/sec)

The equation (5-1) becomes

$$T = \frac{\mu \times \overline{W}g \times \omega D/2}{2 \times \pi D \times hc \times \ell \times J}$$

$$= \frac{\omega g}{4\pi J} \times \left(\frac{\mu \overline{W}}{\ell hc} \right) \qquad (5\text{-}5)$$

where the axial width of a sliding track is measured from the average diameter of wear scar on a peg.

Therefore heat transfer coefficient is obtained as

$$hc = \frac{\omega g}{4\pi J} \times \left(\frac{\mu \overline{W}}{\ell . \Delta T} \right) \qquad (5\text{-}6)$$

The results of heat transfer coefficients are shown in figure (5.14). The maximum value of coefficient is found at high concentrations of the dispersed phase in emulsions, water in w/o and oil in o/w type emulsions. The heat transfer coefficient of oil from sliding surfaces was found to be lower than in emulsions and water. The heat transfer coefficient of water obtained is shown to be similar to emulsions.

The higher heat transfer coefficient is found with higher concentrations of the dispersed phase in emulsions. Heat transfer coefficient is the function of frictional coefficient, resolved load per peg, axial width of sliding track and skin temperature in equation (5-6). These factors in emulsions were shown to be superior to paraffin oil. The lower skin temperature and smaller wear scar, and the higher scuffing load were found at higher values of heat transfer coefficient. Superior performances of friction $\mu\overline{W}/\ell$ and better cooling

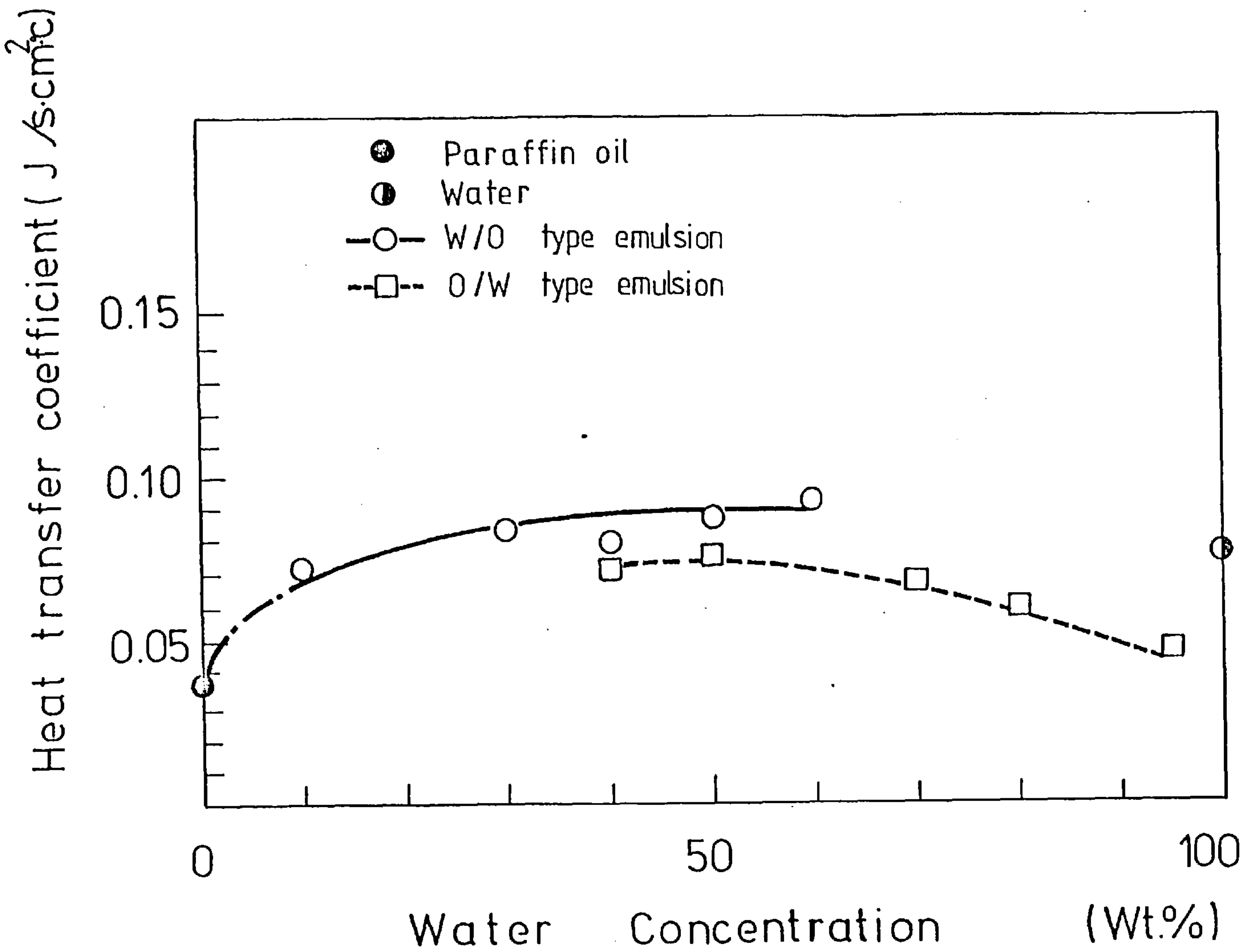


Figure (5.14) Heat transfer coefficient vs water concentration in emulsions effects on sliding surfaces $1/\Delta T$ were found at higher concentrations of the dispersed phase in emulsions.

The value of water was lower than expected and this may be caused mainly by the inferior lubricating property of water, forming severe corrosive wear on steel surfaces. On the steel surface in water at a static condition, the stress and wear of steel are not considered to be serious and the better thermal dissipation than in lubrication is likely to occur from the steel surfaces.

In equation (5-6) the wider wear scar, ℓ, reduces the value of heat transfer coefficient, hc, when frictional coefficient, skin temperature and resolved load are constant. The scuffing load of water was very low (41N/peg) while emulsions had high loads (800N ~ 950N/peg) as shown in figure (5-4). The wear scar of a steel peg in water was wider although the scuffing load was low. The lower value of $\overline{W}/\ell$ in water is considered to make the smaller value of heat transfer coefficient than in a static condition. The axial width of sliding track ℓ, defined from the average diameter of wear scar is shown in Table (5-4).

Table 5.4

Type	Water (wt%)	The average wear scar diameter (cm)	
Paraffin oil	0	0.17	(0.07)
Water	100	0.03	(0.02)
w/o type emulsion	10	0.16	(0.08)
	30	0.16	(0.09)
	40	0.16	(0.09)
	50	0.16	(0.09)
	60	0.16	(0.08)
o/w type emulsion	40	0.17	(0.08)
	50	0.17	(0.09)
	70	0.17	(0.09)
	80	0.18	(0.09)
	95	0.19	(0.09)

( ): elastic contact diameter

The axial width of track ℓ

High heat transfer coefficients were formed with the same concentration of oil and water in emulsions. Although o/w and w/o type emulsions are defined separately at the room temperature, bulk temperatures of emulsions around scuffing are high enough to have inverse emulsions (90 ~ 110°C). It has been observed in the previous chapter that emulsions are likely to invert partly from one type to another type of emulsion at a temperature of approximately 60°C. The similar composition of emulsions might be found between in the o/w and w/o type emulsions, containing high concentrations of the dispersed phase.

The emulsions, which have the same volume of oil and water, were shown to have the desirable property of both lubricant and coolant. This may suggest that a desirable coolant should be composed half from a hydrophobic substance, with a good lubricating property, and half of a hydrophilic substance, with an efficient cooling property.

Three contributing factors to scuffing performances of emulsions have been considered in the discussion of this work. Under the same conditions of oil film thickness and adsorption of substances against the different composition of emulsions, the cooling property of emulsions, supported by good lubricating properties, is quite likely to influence the scuffing properties of emulsions.

5.60 CONCLUSIONS

The water in oil type emulsions were found to be suitable lubricants as far as the load carrying capacity is concerned, despite the fact that emulsions are generally considered to be poor lubricants. The scuffing loads of both types of emulsions were shown to be nearly constant, 1.50 ~ 1.60 GPa, independent of the water concentration in the emulsions, while paraffin oil showed 1.41 GPa. The scuff loads increased slightly with the dispersed phase volume in emulsions, although the water concentration and particle size were constant. Three contributing factors to the scuffing were considered: (1) the formation of oil film, (2) the adsorption of surfactants and (3) the thermal property of emulsions.

Although scuffing loads of emulsions increased slightly with the dispersed phase of emulsions, the thickness of oil film, formed between sliding surfaces,is probably independent of the proportion of dispersed phase to dispersing phase. A constant film thickness is to be considered under high shear rates, because the pseudoplastic property of emulsions may cause a constant viscosity, which is the most influential factor in film formation. The proportion of dissolved phase is also unlikely to alter the effect of surfactant on friction and scuffing, since a constant concentration of surfactant was dissolved in emulsions.

Heat transfer coefficients of emulsions were found to be higher than in paraffin oil and increase with the dispersed phase volume of emulsions. The cooling property of emulsions, supported by the lubricating property, is quite likely to influence the scuffing performance of emulsions. The oil in water type emulsions, which have a small quantity of oil, was found to be suitable as coolant.

CHAPTER SIX

LUBRICATION OF STEEL WITH DIBENZYL DISULPHIDE AND ELEMENTAL SULPHUR

6.10 INTRODUCTION

The purpose of the experiments described in this chapter is to measure the coefficient of friction and the scuffing load of steel with dibenzyl disulphide (DBDS) and elemental sulphur (ES).

The coefficient of friction and the scuffing load in the oil, containing DBDS and ES, were measured using the Bowden-Leben and the ball-on-triplane apparatus, respectively.

The frictional results of e.p. additives obtained in this chapter were compared with those of an e.p. additive-emulsion blend in the following chapter.

6.20 EXPERIMENTS

6.21 MATERIALS

EN31 steel balls and plates were used in the test.

DBDS and ES were purified by recrystallization from carbon disulphide and methanol before use.

6.22 EXPERIMENTAL TECHNIQUE

The Bowden-Leben apparatus was used to examine the frictional coefficient between EN31 steel balls and plate in the oil, containing DBDS and ES. (5.33). The tests were carried out with a load of 10N (0.1 GPa) and a sliding speed of 2.5 mm S^{-1}. The temperature was raised by 5°C per min.

The scuffing was examined with a sliding speed of 100 rpm and by a step load method with 50N/min. using the ball-on-triplane apparatus.

All steel specimens were cleaned in the toluene soxhlet for three hours and dried before use.

6.30 RESULTS

6.31 DIBENZYL DISULPHIDE AND ELEMENTAL SULPHUR - STAINLESS STEEL LUBRICATION RESULTS

The scuffing loads of dibenzyl disulphide and elemental sulphur by the ball-on-triplane apparatus are shown in Table (6.1).

Table (6.1)

Additive	Conc. (Wt/%)	Scuffing load ($X10^3N$)	Mean Contact Pressure (GPa)
DBDS	0.30	4.0	2.0
ES	0.05	4.2	2.0
—	Paraffin oil	1.4	1.4

Scuffing load of DBDS and ES

The frictional coefficients between EN31 steel ball and plate in the paraffin oil with DBDS and ES are shown in figure (6.1). The frictional coefficient is plotted against temperature. The average value of frictional coefficient is plotted for the same test repeated three times.

The frictional coefficient was shown to decrease at the following two temperature: 75°C for both DBDS and ES, and 150°C for ES , 165°C for DBDS. The coefficient of friction in the oil with ES was shown to be lower than with DBDS.

6.32 REPEATABILITY

The scuffing load in the ball-on-triplane apparatus was

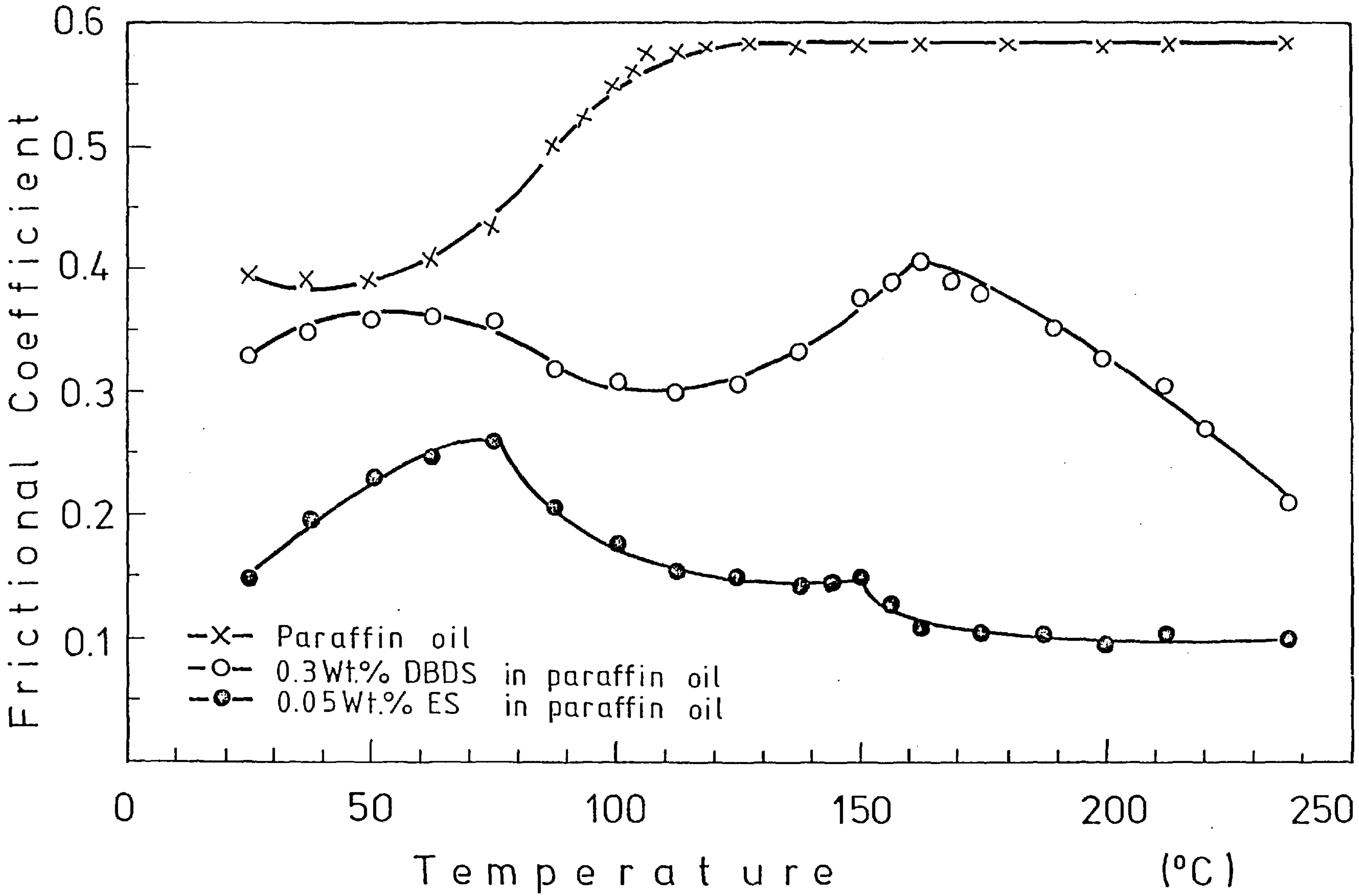


Figure (6.1) Coefficient of friction vs. Temperature for DBDS and ES measured with a repeatability of ± 30N with the same test repeated three times. The variation of frictional coefficient in the Bowden-Leben apparatus was less than ± 15% for good lubrication with the same test run three times.

6.40 DISCUSSION

The frictional coefficient of steel with the paraffin oil, containing DBDS and ES, was shown to change with temperature and decrease at two specific temperatures. A lower frictional coefficient and a higher scuffing load were found in the paraffin oil with ES, than with DBDS. These results are studied here to understand the role of temperature in boundary and e.p. lubrication.

Lubricant molecules, adsorbed on sliding surfaces, are forced to desorb when the surface temperature reaches a certain critical value, this is called the critical temperature. (112) The mechanism of desorption of molecules has been analysed by the Langmuir model, (115), and is generally accepted as the interpretation of "oiliness failure". (7) (12) (13) (14) (17) (20).

The following equation has been obtained, (13) (14), and was originally used to estimate the heat of adsorption of the molecules, $\Delta H^{\ominus}$.

$$\Delta S^{\ominus} - \frac{\Delta H^{\ominus}}{T} = R \ln \frac{\Theta}{(1 - \Theta)} \cdot C$$

where

$\Delta S^{\ominus}$	the standard change in entropy	(115) (116)
$\Delta H^{\ominus}$	the corresponding change in enthalpy	
R	the gas constant	
T	the surface temperature	
Θ	the fraction of sites covered by the molecules	
C	the concentration of the molecules	

When the concentration (and therefore $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$) of additive molecules is constant, the adsorption state of the molecules $\theta/(1 - \theta)$ is shown to be dependent on temperature. The coverage of molecules θ is assumed to reach a maximum value at the critical temperature, where the friction rises sharply. Hence the results obtained in this chapter may be explained by the adsorption and desorption of additive molecules on sliding surfaces.

There were two specific temperatures, where the friction decreased. One was 75°C for both DBDS and ES, the other was 150°C for ES and 165°C for DBDS. Hydrocarbon molecules, in the paraffin oil containing e.p. additives, may start to adsorb onto sliding surfaces and form a thin film on the surfaces. The new film can reduce friction and wear. However this film becomes oxidized by moisture and air, which are dissolved in the oil. (1) (112). The oxidized hydrocarbons may weaken the strength of the adsorbed film. The frictional coefficient in the paraffin oil without e.p. additives was shown to increase gradually with temperature, although the two specific temperatures were found in the oil containing e.p. additives. On the other hand, sulphur e.p. additives are reported to be oxidation inhibitors (117). DBDS and and ES may protect the hydrocarbon molecules, which form the smooth surfaces, while the paraffin oil without e.p. additives may be oxidized and increase the friction.

The adsorbed films of hydrocarbons, protected by DBDS and ES, are then forced to desorb from the sliding surfaces when the surface temperature reaches to about 150°C. (1) (37) (112). Chemical reactivities of DBDS and ES increase simultaneously with the desorption of hydrocarbons. (Chapter 7). The sites, from which the hydrocarbon has desorbed due to increased temperature, may be covered by DBDS and ES to form the sulphurised film on steel. After the formation of the sulphurized film, surfactants were found to adsorb and react strongly with the sulphurized surface and reduce the wear effectively. (Chapter 2 and 3). Desorbed surfactants might adsorb and react again with the sliding surface, which has been then sulphurized by e.p. additives, and reduce the friction around 150°C. The chemical reactivity of ES with steel is higher than that of DBDS at the same temperature. (Chapter 7). A lower frictional coefficient and a higher scuffing load of ES is quite likely to be caused by the higher chemical reactivity of ES.

6.50 CONCULSIONS

The following conculsions were drawn from this chapter.

(1) The frictional coefficient of steel with the paraffin oil, containing DBDS and ES, changed with temperature and decreased at the following two temperatures: $75^{o}C$ for both DBDS and ES, and $150^{o}C$ for ES and $165^{o}C$ for DBDS.

(2) A lower frictional coefficient and a higher scuffing load were found in the paraffin oil with ES, than with DBDS.

CHAPTER SEVEN

THE PERFORMANCE OF DIBENZYL DISULPHIDE AND ELEMENTAL SULPHUR EP ADDITIVES IN EMULSIONS

7.10 INTRODUCTION

The work described in this chapter examines the interaction of emulsions with sulphur lubricant additives in the extreme pressure regime. Adsorption activity of surfactants on a sulphur-reacted surface has already been demonstrated by adsorption tests and friction tests (Chapter 2 and 3). The low surface temperature on sliding surfaces with a high heat transfer coefficient has been shown to be effective against scuffing (Chapter 5).

Mixed lubricants, with sulphur e.p. additives in the emulsion, which are often used for grinding, cutting and rolling, have never been studied to see how such lubricants behave at sliding surfaces. Likewise the effect of an emulsion, containing water, oil and surfactants on the chemical reaction of extreme pressure additives has never been examined.

In Chapter 5, scuffing loads of emulsions were found to be nearly constant, higher than in paraffin oil, but changing slightly with the dispersed phase volume. Also, in Chapter 6, scuffing loads of e.p. additives in pure oils were found to be much higher than e.p. free emulsions and e.p. free paraffin oil. It could be possible that if the results of these lubricant tests are combined, it might be expected that mixed lubricants of emulsions and e.p. additives would have greatly improved scuffing properties since they combine both favourable factors, emulsion and e.p. activity. In this chapter the scuffing loads of the such mixed lubricants are examined, it will be seen that, on the contrary, emulsions are unfavourable for e.p. activity.

The scuffing load of an emulsion - e.p. additive blend was examined in the following ways.

Dibenzyl disulphide and elemental sulphur were dissolved in the oil phase of an emulsion. The scuffing load was measured by the ball-on-triplane apparatus. The maximum sulphur content on the surface of steel pegs was measured by electron probe microanalysis (EPMA) and the surface track temperatures on a ball were measured, using an IR microdetector, through a window in the ball-on-triplane apparatus. Water concentration and particle size distributions were verified before and after scuffing, by the Karl Fischer technique and the optical microscope respectively to confirm the stability of the emulsions.

The following three factors were anticipated as being important in the scuffing behaviour of emulsions with an e.p. additive, and were specifically examined.

(1) The surface temperature necessary for an e.p. additive to react with sliding steel surface: The amount of sulphur reaction product on the steel surface was measured as a function of temperature using IR multiple reflectance spectroscopy.

(2) Emulsion adsorption onto oxidized steel surfaces which were then reacted with an e.p. additive: the steel specimen pretreated by emulsion, oil, water and surfactants were reacted with dibenzyl disulphide.

(3) The solubility of the e.p. additive and sulphurized film in water after the reaction of an e.p. additive: solubility tests of DBDS and the sulphurized product formed on sliding surface were carried out.

7.20 LITERATURE REVIEW

The interactions of emulsions with e.p. lubrication have only recently been studied, and few papers have been published (119). However the interaction of friction modifiers, oxidation inhibitors and detergents have been extensively studied in boundary and extreme pressure lubrication. (120) (121) (122) (123).

The frictional characteristic of oil, containing some additives was shown by Rounds (121) to be dependent on three components of the blend:

(i) Friction modifier,
(ii) Oxidation inhibitor and
(iii) Base oil.

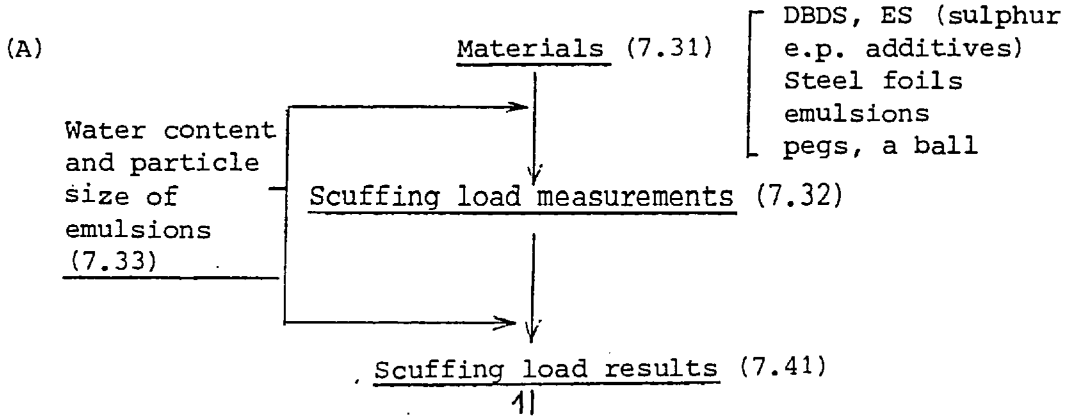
It was found that a little oxidation may be necessary for the maximum additive response but that too much oxidation was detrimental.

Additive interference in e.p. lubrication was studied with radio chemical tests by Spikes and Cameron (122). n-Octadecylamine and calcium sulphonate in n-hexadecane were found to hinder the reaction of dibenzyl disulphide tagged with S^{35}. The effects found in reaction tests were mirrored in friction tests.

Rounds (123) studied the additive interaction in the anti-wear performance of zinc dialkyl dithiophosphate with different types of second additive. Detrimental effects on wear were observed with primary alkyl amine friction modifiers, metallic dithiocarbonate oxidation inhibitors, sulphur and sulphonate detergent-rust inhibitor. On the other hand, detergent-dispersants, VI improvers, oxidation inhibitors and e.p. agents were found to have little or no effect on wear.

7.30 EXPERIMENTAL DETAILS

Figure presents a summary of the various procedures which were used to measure and analyse the scuffing loads of emulsion - e.p. blends. Each is then described in brief, while all the results are deferred until the next section.



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(B)

Sliding surfaces
- Maximum sulphur content on pegs (7.34)
  by Electron probe microanalysis (7.36)
- Surface track temperature measurement (7.36)

(C)

Fundamental analysis
- Sulphur reaction with temperature (7.37)
- Surface pretreatment effects by emulsions on sulphur reaction (7.38)
- Solubility tests of DBDS and sulphur-reacted film (7.39)

( ) : the number of section described

(A) INTERACTION OF EMULSION IN FRICTION TESTS

7.31 MATERIALS

Elemental sulphur (ES) and dibenzyl disulphide (DBDS) (m.p. 69^{o}C) were obtained from B.D.H. chemicals Ltd. (U.K.). These substances were purified by recrystallization(carbon disulphide and methanol) and confirmed by infrared spectroscopy.

The steel foil used for the sulphur reaction tests was ordinary mild steel with a thickness of 0.1mm.

Other materials: The same water, oil and surfactants in this work were used as in the work of emulsion lubrication. (Chapter 5).

7.32 SCUFFING LOAD MEASUREMENTS

(Load carrying capacities of the emulsion - e.p. additive blend).

The scuffing loads of sulphur lubricant additive - emulsion blends were measured by the ball-on-triplane apparatus. The oil-soluble e.p. additives, dibenzyl disulphide and elemental sulphur, were incorporated into the oil phase. The concentration of additives was 0.30 wt% and 0.05 wt% in oil for DBDS and elemental sulphur respectively. The tests were carried our at a speed of 100 r.p.m. (8.5 cm/s) and a load increased by 250N/min, using a step load method.

7.33 WATER CONTENT AND PARTICLE SIZE DISTRIBUTIONS

The water content of emulsions was measured by Karl Fischer technique before and after scuffing. (Appendix 1).

Particle size distribution of emulsions were determined by direct measurement from photographs printed to 1000X magnification.

(B) SULPHUR CONTENT AND SURFACE TEMPERATURE ON SLIDING SURFACES

7.34 MAXIMUM SULPHUR CONTENT ON THE PEGS MEASURED BY EPMA

(Sulphur reaction of e.p. additives on sliding steel surfaces).

Maximum sulphur contents on the EN31 steel surface of pegs were measured by the electron probe microanalysis (EPMA). This technique is described in the next section (7.35).

An unused EN31 peg was taken as a standard to establish a datum level for sulphur in the steel surface. The specimens were removed from the ball-on-triplane apparatus after scuffing. They were washed by acetone and then toluene soxhlet for two hours. The specimens were mounted in plasticene in a brass holder, and earthed to the holder by a painted strip of silver. Two spectrometers in the EPMA apparatus were tuned to the sulphur K-α emission and calibrated to maximum count intensity against a cadmium sulphide standard. Traces for sulphur ran across the middle of the mark. ("Line-scans"). This is perpendicular to the direction of wear as shown by scratches. (Appendix 2).

7.35 ELECTRON PROBE MICROANALYSIS (EPMA)

In electron probe microanalysis, electrons are used to bombard a surface. These excite electrons in the surface and sub-surface into higher energy levels. Excited electrons tend to return to their normal lower level, and in this process these electrons emit X-rays with characteristic wavelength of the elements.

The X-rays emitted are diffracted on a spectrometer crystal in the apparatus. The lattice spacing, d, is known to measure the wavelength according to the Bragg's equation.

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

The intensity of the diffracted X-rays is counted in an ionisation chamber. EPMA thus detects elements in a sample and gives a measure of their concentration, but provides no information about chemical environment.

The instrument used in the test was the Japanese Electron Optics Laboratory (J.E.O.L.). JXA-3A electron probe microanalyser. A diagram is shown in figure (7.1).

The electron beam ("probe") is provided by a tungsten filament electron gun operated at 25KV. This is focused at the specimen surface by two magnetic lenses. Electrons bombard vertically on the surface. The X-rays emitted from the specimen are diffracted at an angle of 20°. Two spectrometers analyse two elements simultaneously. Both spectrometers were used for sulphur in this test. The specimen was scanned linearly by the electron beam at constant speed to determine the element distribution, this technique is called "line-scan". The intensity of count is obtained against distance.

7.36 SURFACE TRACK TEMPERATURE MEASUREMENTS

(Surface temperature on sliding steel surfaces)

The surface temperature is important in e.p. reaction on sliding metal surface. The controlling temperature on sliding

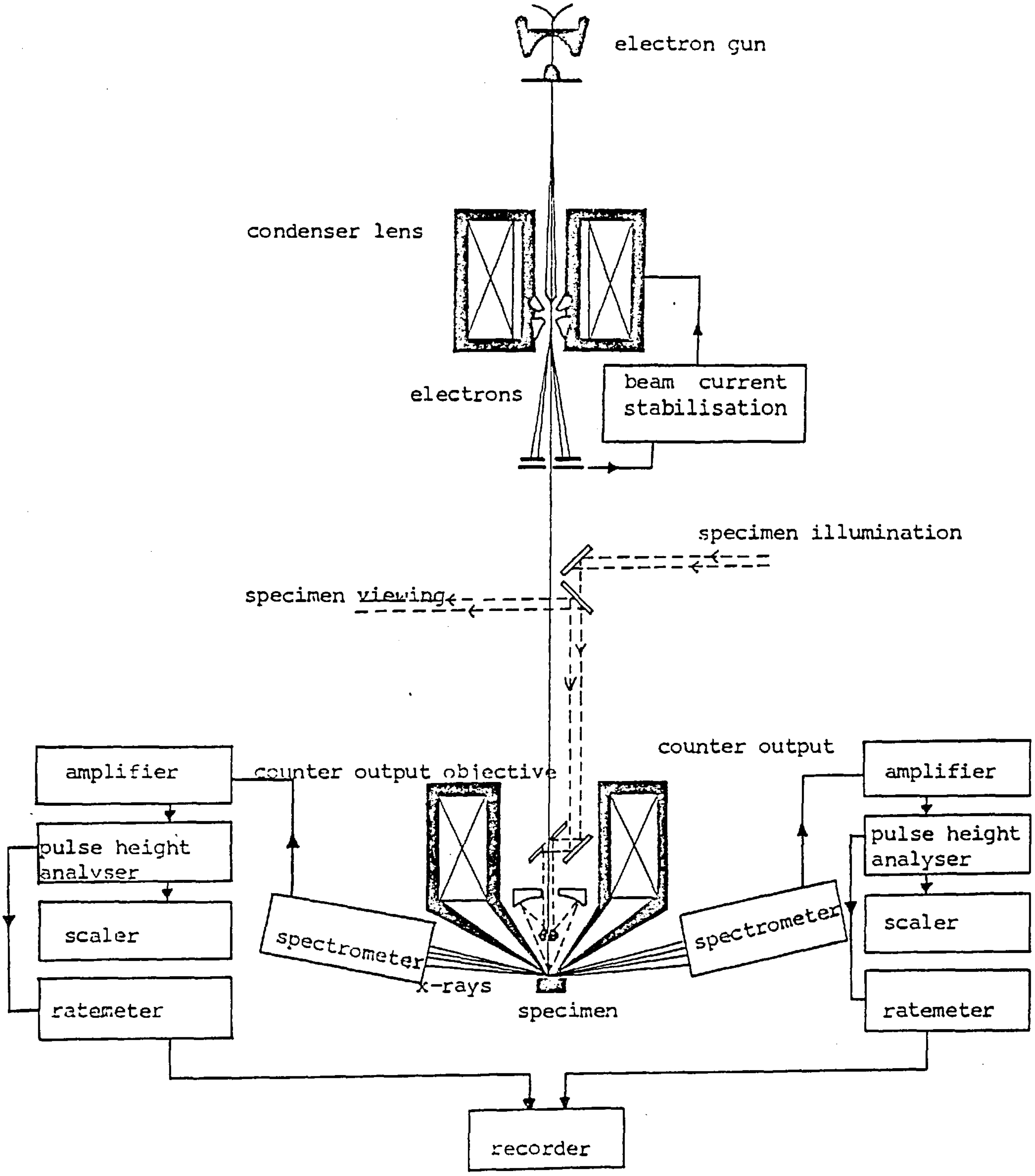


Figure (7.1) Electron probe microanalyser (E.P.M.A.)

metal contacts by emulsions may influence the chemical reaction of e.p. additive in the e.p. - emulsion lubrication. The surface track temperature of a ball in the ball-on-triplane apparatus was measured by the IR microtemperature detector.

The procedure was as described in Chapter Five. The surface track temperature was measured with a load applied on the ball. The scuffing surface temperature was measured and compared with the results of sulphur-reaction test. (7.37).

(C) FUNDAMENTAL TESTS FOR INTERACTION OF EMULSION WITH REACTION

7.37 SULPHUR REACTION WITH TEMPERATURE

(Fundamental analysis for 7.34 and 7.36)

The load-carrying-capacity of e.p. additive at sliding metal contacts was dependent on the chemical reaction of e.p. additive at rubbing metal surfaces, (1) (112) (125) (126) (127).

The reaction temperature is considered to be very important for the chemical reaction of e.p. additive with steel. In the lubrication of an emulsion-e.p. additive blend, the control of temperature of rubbing metal surfaces by emulsions may be important in an e.p. reaction.

Analytical tests were carried out for comparison with friction test. Steel foils were heated in two oils for one hour. One oil contained 0.30wt% of DBDS at different temperatures. The other contained 0.03wt% ES. The specimens were washed with acetone and placed in a toluene soxhlet for two hours before and after the reaction.

The specimens were examined by IR multiple reflectance spectroscopy. Ferrous sulphate $FeSO_4.7H_2O$ and DBDS were used as the standard specimens for quantitative analysis of sulphur-reacted steel surface. Absorption band area (integrated absorption intensities) were evaluated by weighing paper profiles of the bands. Tracing paper was used in the test. The amounts of sulphur reaction on the specific area (mm^2) of steel were calculated on the assumption that the whole area of steel foil was examined completely by IR multiple reflectance spectroscopy. (128).

7.38 SURFACE PRETREATMENT EFFECTS ON SULPHUR REACTION

(Fundamental analysis for 7.34)

The scuffing loads of an emulsion-e.p. additive blend might be influenced by the e.p. reaction with the surface-pretreated steel by emulsions. The surface of sulphur-reacted steel with different surface treatments was examined by the IR multiple reflectance spectroscopy.

Five steel foils were placed in different environments: air, emulsions, water,oil and surfactants. These foils were heated in the oven at 60°C for 24 hours. The specimens were washed by acetone and the toluene soxhlet for two hours before and after treatment.

The specimens were immersed in oil containing 0.3wt% DBDS at 130°C for 30 minutes. After reaction they were washed again by acetone and the toluene soxhlet for two hours.

The surface of specimens was examined by the IR multiple reflectance spectroscopy using the same technique as described in Chapter Five.

7.39 SOLUBILITY TESTS OF DBDS AND SULPHUR-REACTED FILM

(Fundamental analysis for 7.34)

The scuffing load of a DBDS-emulsion blend might be influenced by the following solubility phenomena of DBDS and its reacted sulphurized film from sliding surfaces. The possible phenomena of solubility are as follows.

(1) Before the DBDS reaction with steel
  (1a) DBDS in the oil phase might partition between the water and oil phases in emulsions

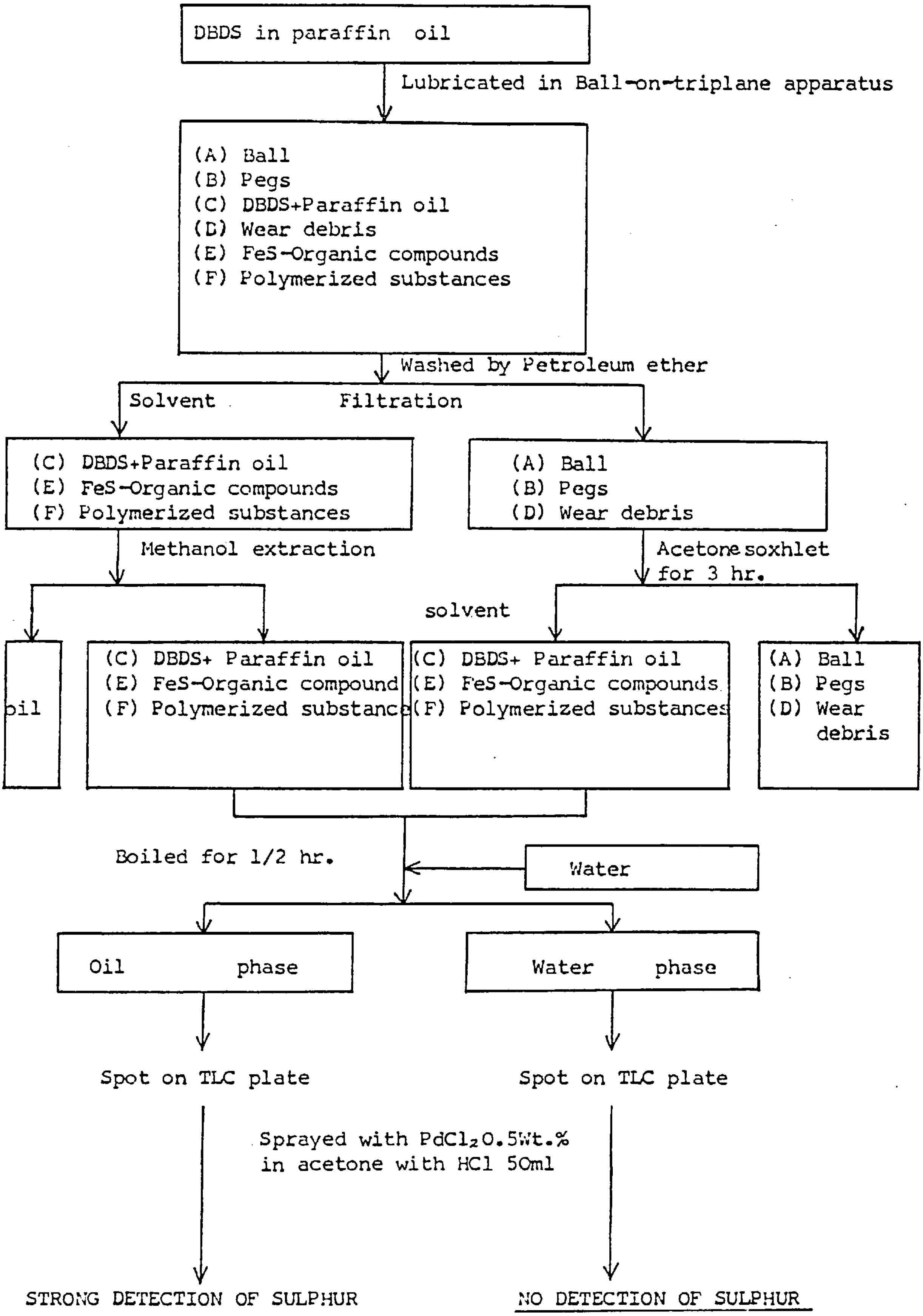


Figure (7.2) Solubility test of the sulphurized substances formed by DBDS in water

(1b) Excess surfactants, not forming emulsions, might extract DBDS from the oil phase to the water phase of emulsions

(II) After the DBDS reaction with steel

(IIa) Water might dissolve the reacted film from the steel surface

(IIb) Excess surfactants might dissolve the reacted film from the steel surface

These dissolving factors were determined by the following solubility tests using the technique of thin layer chromatography (TLC). The principle of TLC is the separation of substances which are absorbed differently on a thin layer of inorganic material due to their absorption intensities on the layer. The details of procedures were as follows.

(I) Before the DBDS reaction with steel.

Mixture of oil, water, DBDS and surfactants were boiled for 30 minutes at 100°C. A drop of water was spotted on the thin layer chromatography (TLC) plate. The silica gel plate was placed in a glass tank containing a few cc's of methanol at the bottom and the solvent allowed to rise up the absorbent plate. If the water phase contains sulphur compound, this should result in a sulphur additive spot, being moved up the plate surface. The plate was sprayed with 0.5wt% $PdCl_2$ in acetone dissolved in HCl 50ml to clarify these sulphur-containing spots. (125).

(II) After the DBDS reaction with steel.

organo-sulphur reacted substances were separated from the residue of an oil-DBDS blend, lubricated in the ball-on-triplane apparatus.

The separation procedures are described in figure (7.2), and the main procedures were as follows:

(1) Residue of the paraffin oil with DBDS (0.30wt%), lubricated

in a ball-on-triplane apparatus: the oil was lubricated under a load of 150N and a speed of 100 r.p.m. for one hour。 The residue of lubricated oil was collected with the same procedure for ten times。 {(A) (B) (C) (D) (E) (F)}.

(2) Filtration after washing with petroleum ether: the residue of lubricated oil was filtered through the fine filtration paper, washing with petroleum ether. The solid and solvent components of the residue were separated each other. {(A)(B) (D) and (C) (E) (F)}。

(3) Extraction by methanol: the solid component (A)(B) (D) on the filtration paper was further washed by acetone soxhlet for three hours. The solvent component (C) (E) (F) in petroleum ether was extracted by methanol in order to separate the paraffin oil in the solvent.

(4) The orango-sulphur reacted substances were thus obtained from the lubricant residue. (C) (E) (F)

The solubility of organo-sulphur substances in water was examined by the same procedure described previously((I) Before the DBDS reaction with steel).

7.3 REPEATABILITY

SCUFFING LOAD (7.32)

The scuffing load in the ball-on-triplane apparatus was measured with a repeatability of ±30N. This value was obtained with the same test three times.

WATER CONCENTRATION AND PARTICLE SIZE DISTRIBUTIONS (7.33)

The repeatability of the Karl Fischer method was ± 0.2wt% of water.

The direct measurement from photoprints of emulsions showed that a difference of length of 0.1μm could be distinguished.

MAXIMUM SULPHUR CONTENT ON THE PEGS MEASURED BY EPMA (7.34)

The probe penetrates the sample surface to a depth of up to 2µm. This depth is dependent on the density of the specimen material. Therefore sulphur distributions recorded are the average values of sulphur content over the depth of penetration. The unit of sulphur concentration was expressed as "weight percent" of sulphur involved in the weight examined by the EPMA.

SURFACE TRACK TEMPERATURE MEASUREMENT (7.36)

The surface track temperature was measured by the IR micro-detector within $\pm 1^{\circ}C$.

SULPHUR REACTION MEASURED BY IR-MULTIPLE REFLECTANCE SPECTROSCOPY (7.37)

Sulphur oxides and the -CSSC- bond were observed on the steel surface reacted with dibenzyl disulphide using the IR multiple reflectance spectroscopy. Amounts of sulphur reaction were determined by the ratio of absorption band area with the calibrated area by $FeSO_4.7H_2O$ and DBDS. A repeated run on the same sample showed little difference in IR absorbencies. ($\pm 0.05 \times 10^{-10}$ mol /mm²).

SOLUBILITY TESTS OF DBDS AND SULPHUR-REACTED FILM (7.39)

The thin layer chromatography (TLC) has been developed for the quantitative analysis of lubricant. (125). The technique of spraying with the $PdCl_2$ - acetone - HCl solution for sulphur is precise enough to distinguish the existence of sulphur with the order of ppm.

7.40 RESULTS

(A) INTERACTION OF EMULSION IN FRICTION TESTS

7.41 SCUFFING LOAD OF EMULSION - E.P. ADDITIVE BLENDS

The scuffing loads of emulsion - e.p. additives (DBDS, ES) mixtures (1.69 ~ 2.00 GPa) were found to be lower than paraffin oil - e.p. additive blends. (2.00, 2.01 GPa), as shown in figure (7.3). The scuffing loads of the blends were nearly constant whatever the water concentration of emulsions, although the total amounts of additives present were increased with the oil volume of emulsions. Even at a quite low concentration of oil (0.5wt%) a similar scuff load to those at higher concentrations of oil was found. (7.52).

Higher scuffing loads were found in the blends with ES than in DBDS. The chemical reactivity of ES was found to be higher than DBDS (7.46), and the results of scuffing loads obtained are suitable for being analysed in terms of chemical reaction of e.p. additives in emulsions (7.37) (7.38) (7.39).

The mixed lubricants, composed of emulsions and e.p. additive, were in a sense considered to have a frictional performance similar to that of mixed lubricants of frictional modifier and e.p. additive. The e.p. additive reacts on sliding surfaces, when friction modifier desorbs by frictional heating, and is found to form an e.p. film whereas, by contrast, friction modifier forms an adsorbed film. Constant smooth lubrication is maintained without any failures over a wide range of temperature. (1) (112). The mixed lubricant of emulsion and e.p. additive was considered to behave similarly up to high surface temperatures on sliding steel although water is contained in the lubricant.

The reduction in concentration of water in emulsions, due to evaporation up to scuffing, is shown in the scuffing load-water concentration diagram in figure (7.3) and was found to be generally less than 1.0wt%. The emulsions were found to have the similar values of water concentration and particle size between before running and after scuffing. (7.42) (7.43).

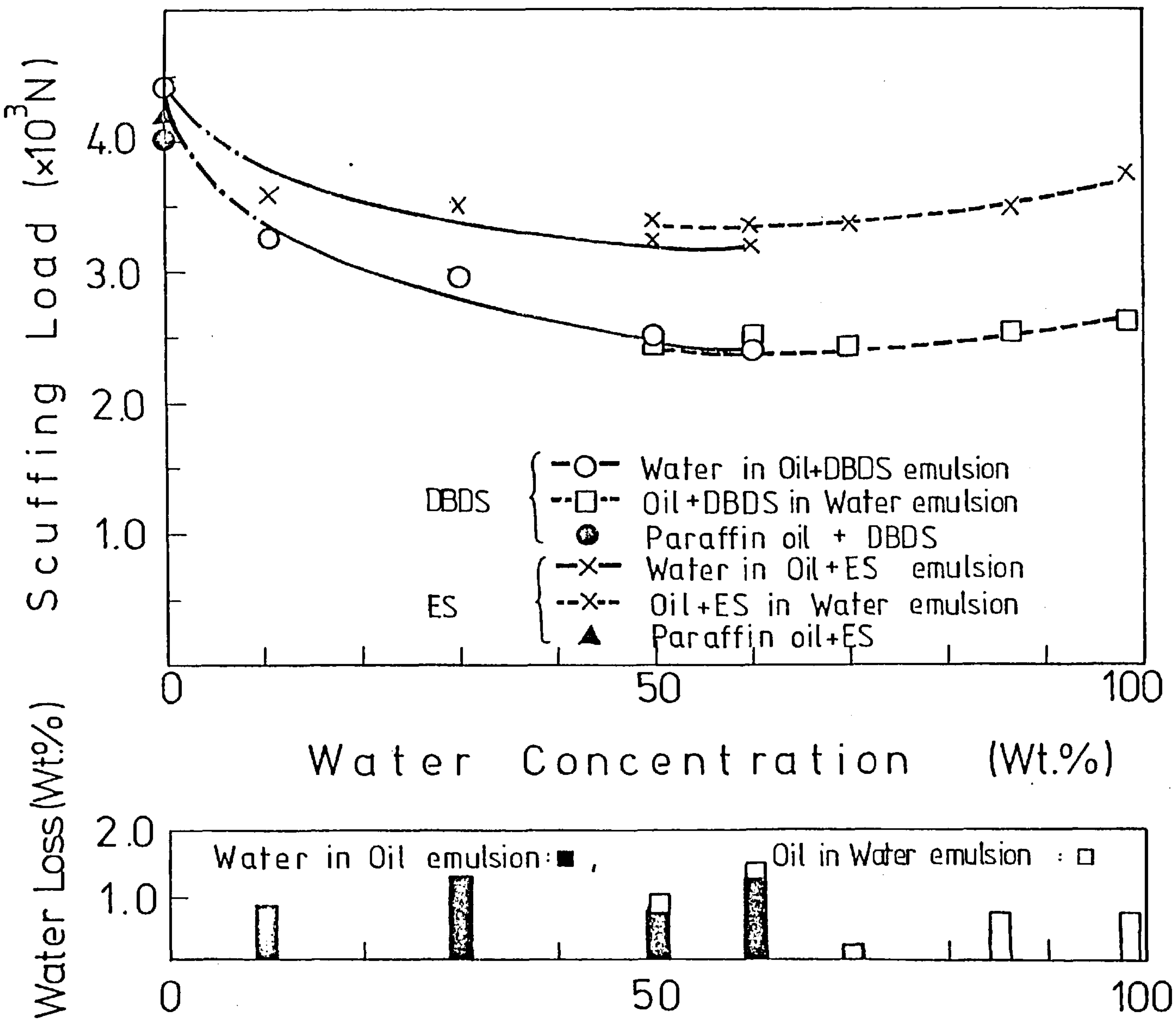


Figure (7.3) Scuffing load vs. Water concentration in an emulsion-e.p. additive blend

7.42 PARTICLE SIZE DISTRIBUTION OF EMULSIONS

(Checking of emulsion particles)

The particle size distributions of emulisons with e.p. additive showed little difference between sliding and after scuffing as shown in figure (7.4a) and (7.4b).

7.43 WATER CONCENTRATION IN EMULSION

(Checking of emulsions)

The water concentration in emulsions with e.p. additive showed little difference between before sliding and after scuffing as shown in table (7.1). The water concentration lost up to scuffing is shown with the scuffing loads - water concentration diagram in figure (7.3).

Table (7.1)

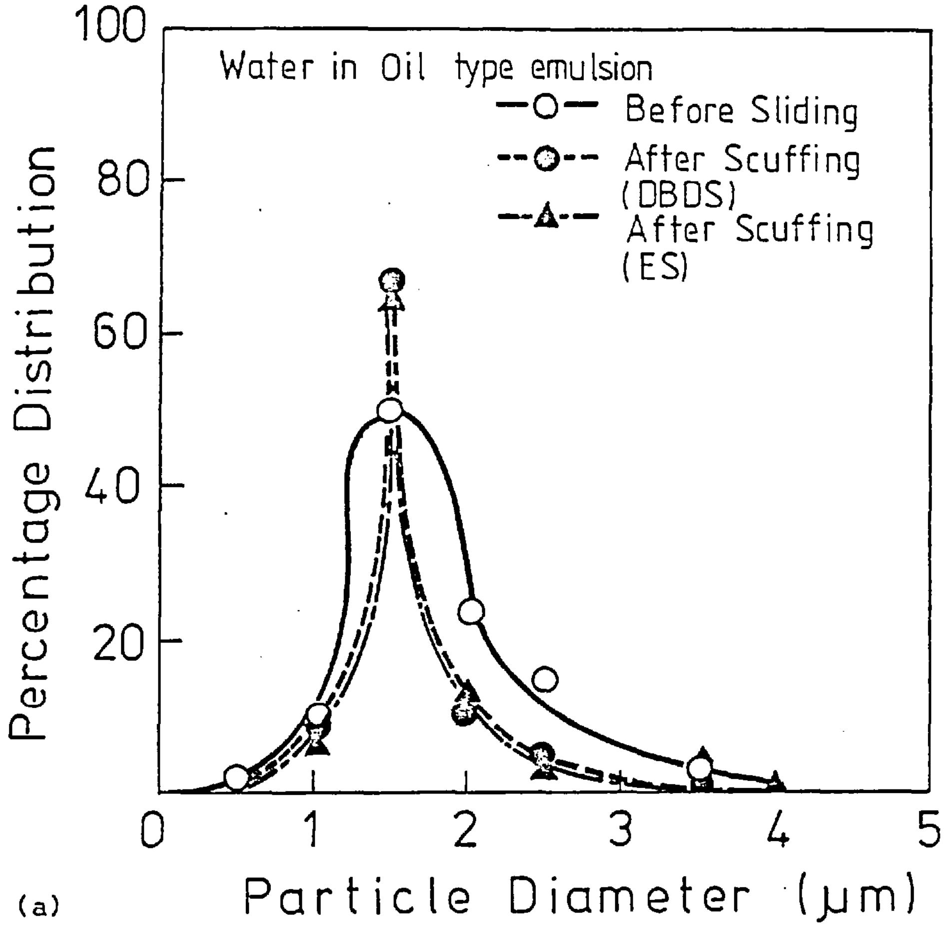
Type	Water Conc. (wt%)	Water concentration in emulsion after scuffing (wt%)
w/o	30.0	28.9
	50.0	49.3
	70.0	70.0
o/w	50.0	49.1
	60.0	58.7
	70.0	70.0
	85.0	84.5
	99.5	99.5

Water concentration before and after scuffing

(B) SULPHUR CONTENT AND SURFACE TEMPERATURE ON SLIDING SURFACES

7.44 MAXIMUM SULPHUR CONTENT ON THE PEGS

(Sulphur reaction of e.p. additives on sliding steel surfaces)



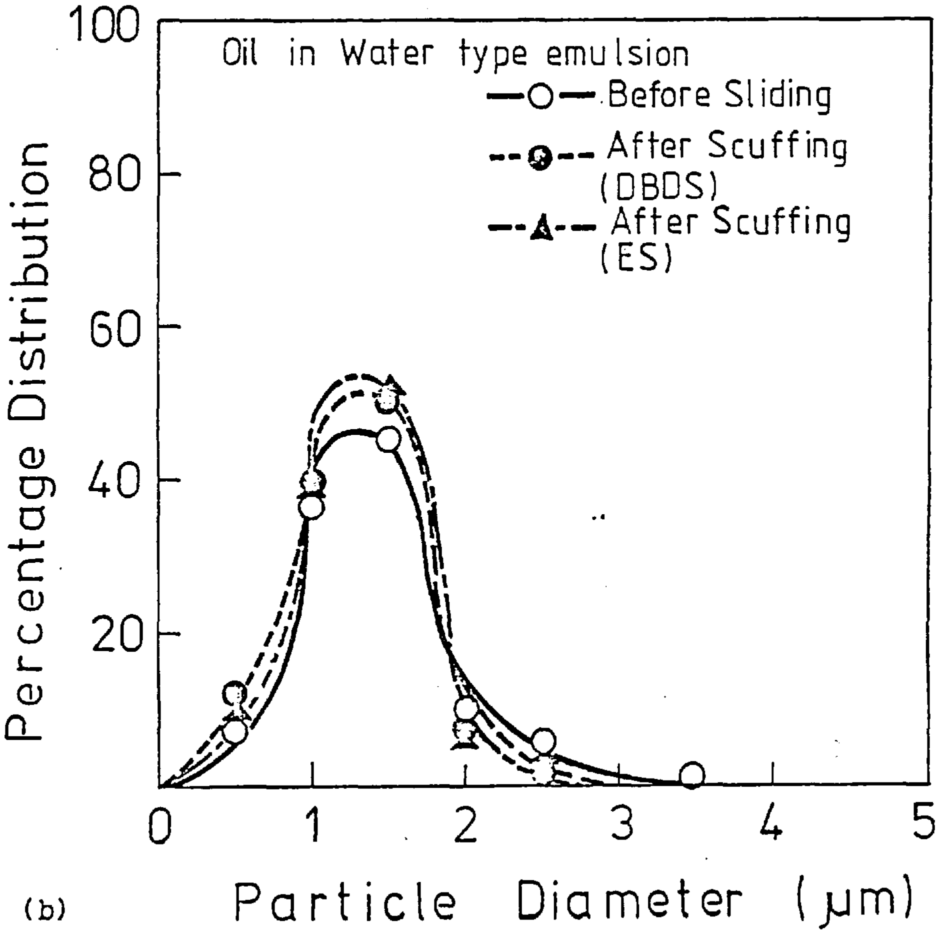


Figure (7.4) Particle size distribution before and after scuffing

The maximum sulphur content in the wear scar of pegs, taken from the apparatus just before scuffing, were determined by EPMA. The sulphur content on the peg surface was shown to be lower in the emulsion - e.p. additive blend (1.8 ~ 4.3wt% for DBDS blends and 4.2 ~ 6.2wt%). The sulphur content on steel surfaces in emulsions with DBDS was lower than with ES. The results are shown in figure (7.5).

The sulphur content on the pegs was found to be nearly independent of the water concentration of emulsions, although the total amounts of e.p. additive were varied to maintain constant oil concentration. The sulphur products reacted on sliding surfaces are generally accepted to be the major function of load-carrying capacity of e.p. additive. (1) (31) (33) (37) (112) (126). The insufficient contents of sulphur on the pegs are considered to cause the inferior scuffing loads of the emulsion blends.

Three possible factors which might cause the insufficient content are examined in separated basic tests. (7.37) (7.38) (7.39).

7.45 SURFACE TRACK TEMPERATURE

(Surface temperature on sliding steel surfaces)

Another property of sliding surfaces, surface temperature was measured and compared with the results of sulphur content on sliding surfaces. (7.44). Skin temperature which is the difference between surface and bulk temperature was also obtained and used to calculate heat transfer coefficient of the emulsion - e.p. additive blends. (7.52).

The surface track temperatures on the ball in the ball-on-triplane apparatus were measured with the IR microdetector apparatus. Various systems were studied against two factors, load and water concentration of emulsions. The systems employed were (1) Water, (2) Oil with and without DBDS and (3) An emulsion - DBDS blend as shown in figure (7.6) and (7.7).

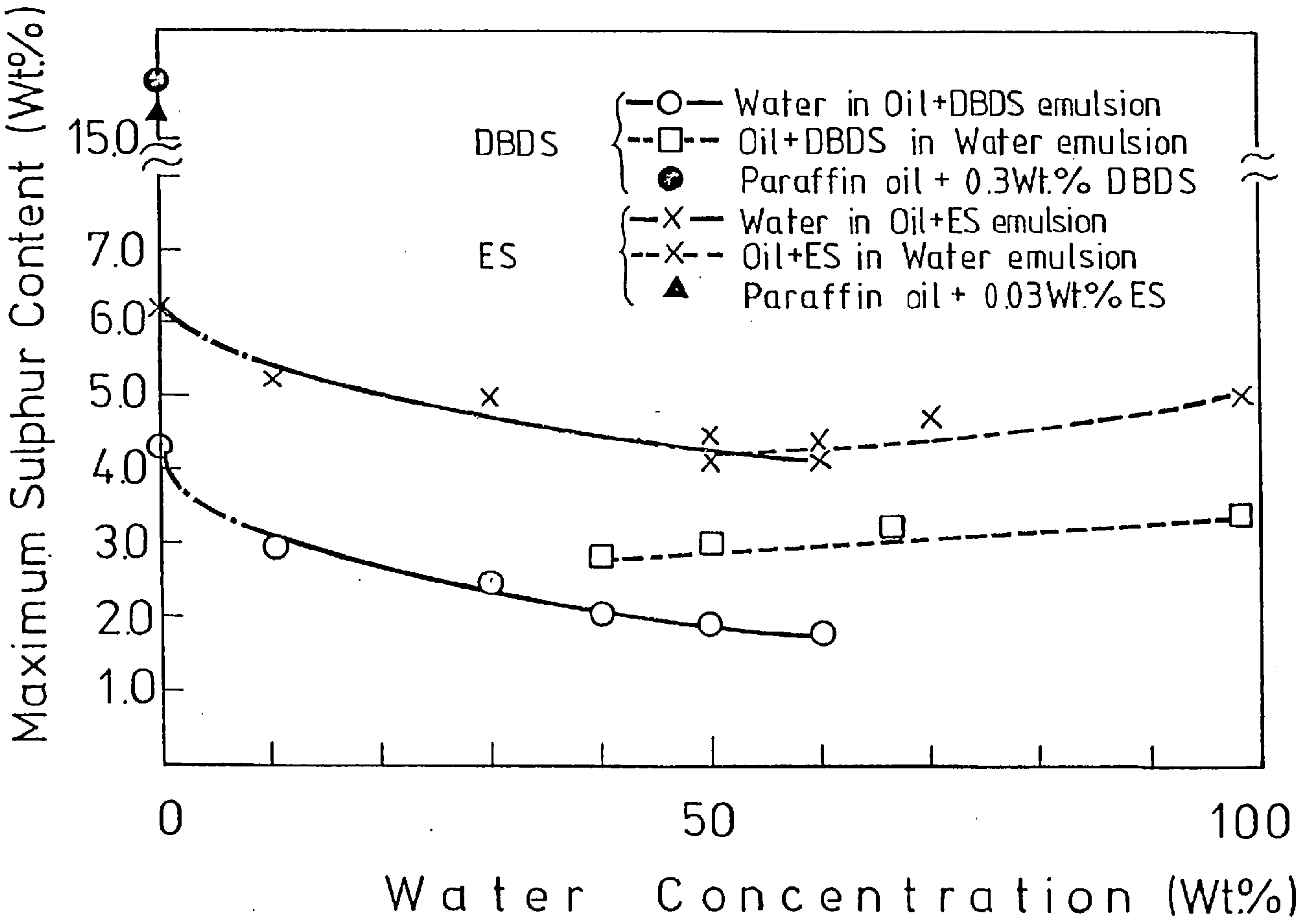


Figure (7.5) Maximum sulphur content on the pegs by the E.P.M.A.

The temperatures in emulsion - DBDS blends were shown in figure (7.6) to increase with load less than in water, oil and the oil containing DBDS, though the mixtures scuffed earlier than oil with DBDS. Emulsion was found to have higher heat transfer coefficient than oil. The lubricant with a high heat transfer coefficient is considered to have the desirable properties of both friction modifier and coolant. (Chapter 5). The inferior load carrying capacities of the blends were found with lower surface temperatures than in the oil with e.p. additive and this is discussed in terms of the thermal property of heat transfer. (7.52).

The surface track temperatures at scuffing in emulsion - e.p. additive blends are further shown in figure (7.7). The temperatures in the blends (≅ 140°C) were much lower than in water free oil with e.p. additive (291°C) and were equal to in the pure emulsions, (figure (5.11)). The surface temperatures in the blends were found to be determined by the thermal properties of pure emulsions. (Chapter 5).

There was little difference of temperature observed in the blends with different e.p. additives, DBDS and ES, although a difference in scuffing loads was observed. (7.41). Higher reactivity of ES than DBDS is found at the same reaction temperature. (7.46). The surface temperature at sliding surfaces in the blends was found to be determined by emulsions and contribute the same temperature for e.p. reactions of DBDS and ES.

(C) FUNDAMENTAL TESTS FOR INTERACTION OF EMULSION WITH E.P. REACTION

The scuffing loads of the emulsion - e.p. additive blends were lower than in the oil with e.p. additive and independent of water concentration. (7.41). The sulphur contents and surface temperatures on sliding surfaces were lower than in the oil with e.p. additive and independent of water (oil) concentration

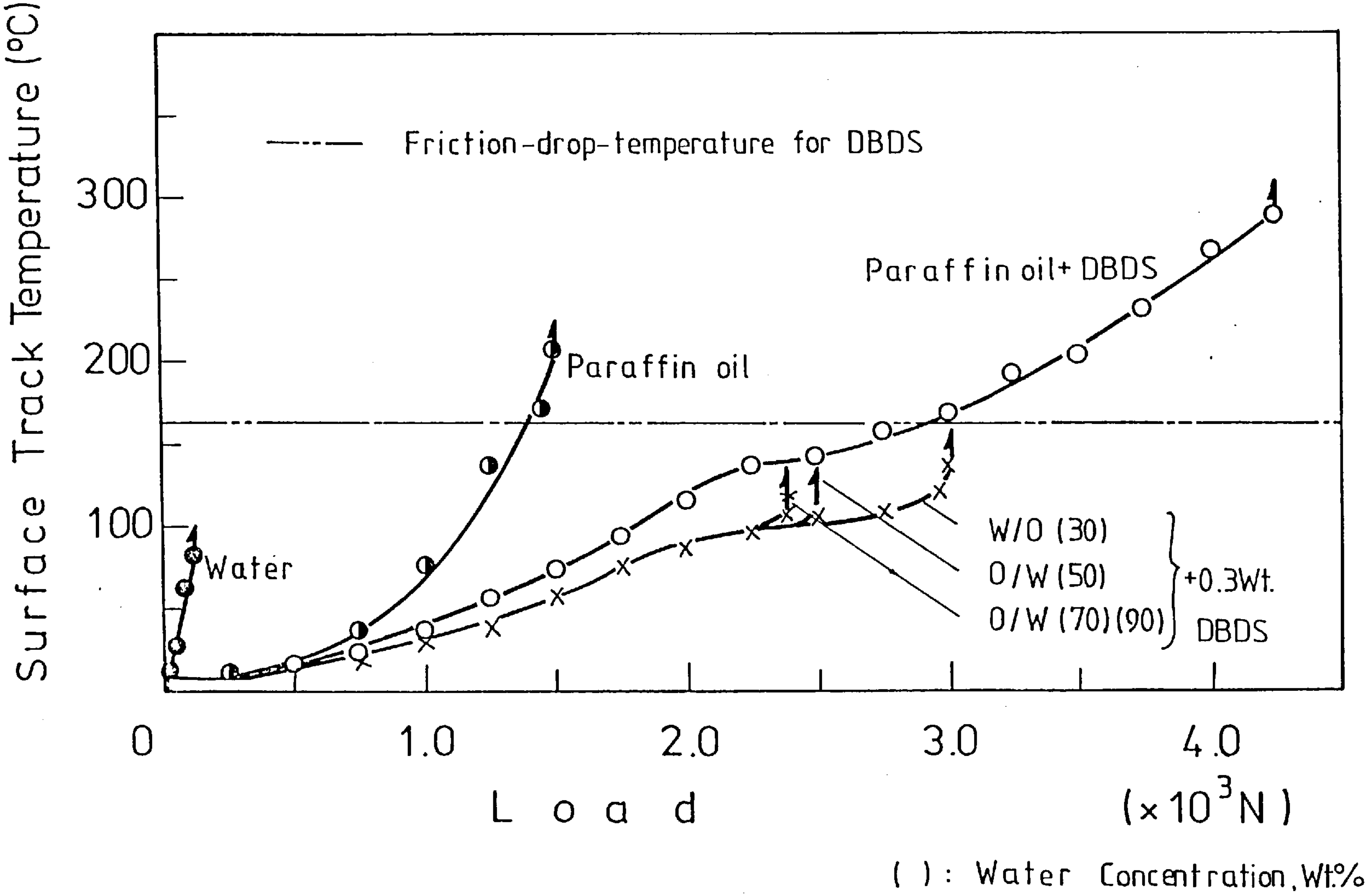


Figure (7.6) Surface track temperature vs. Load in an emulsion-e.p. additive blend

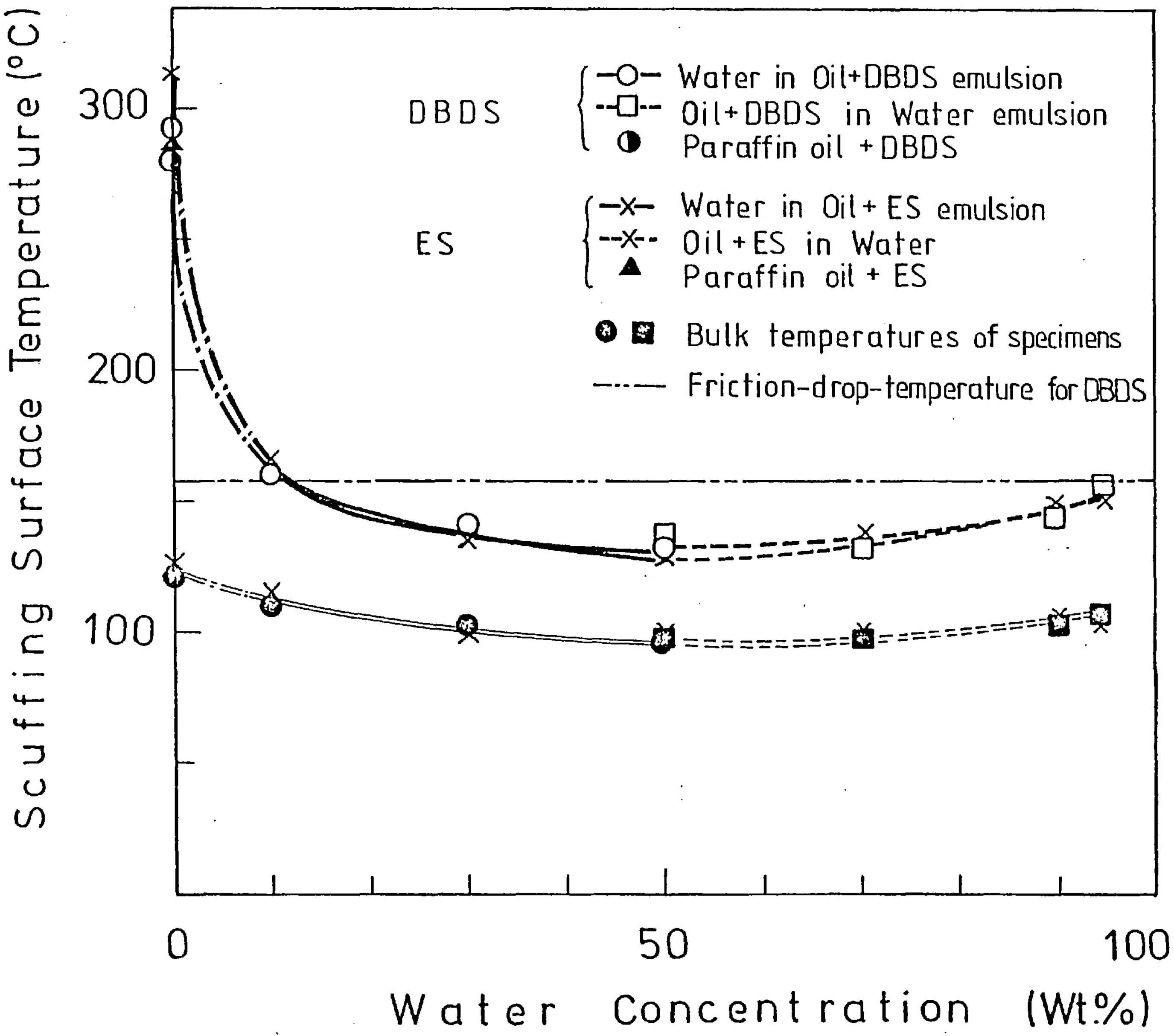


Figure (7.7) Surface track temperatures vs. Water concentration

(7.44) (7.45), although the emulsions were stable and showed little difference between before sliding and after scuffing. (7.42) (7.43).

The inferior scuffing loads of the blends are considered to be caused by insufficient reaction of e.p. additive on sliding surfaces in the emulsion - e.p. blends. The cause of the insufficient reactions is studied in the following basic tests: (7.46) Sulphur reaction with temperature, (7.47) Surface pretreatment effect on sulphur reaction and (7.48) Solubility tests of DBDS and sulphur-reacted film.

7.46 SULPHUR REACTION WITH TEMPERATURE

Adsorption bands of specimens, examined by IR multiple reflectance spectroscopy used to determine the amounts of sulphur reaction on the steel with different reaction temperature, are shown in figure (7.8). Specimens are as follows: the standard specimens of $FeS0_4.7H_20$ (A) and DBDS (B) and the reacted specimens with DBDS at different temperatures, 25°C (C), 50°C (D), 70°C (E), 100°C (F), 130°C (G), 150°C (H) and 200°C (I). All specimens were reacted in n-hexadecane for an hour.

Intensities of IR absorption were shown to increase with the reaction temperature at two regions of wave number, one for -CSSC- bond from 600 to $740cm^{-1}$ and another for sulphur oxides of iron (mainly ferrous sulphate) from 1000 to $1200cm^{-1}$. The -CSSC- and sulphur oxides of iron bond on the static steel surface increased with reaction temperature.

The band areas of absorbtion were then calibrated to determine the amount of sulphur reaction on the steel. (128). The reaction curve with temperature is shown in figure (7.9).

The reacted amounts of DBDS itself and sulphur in DBDS were found to increase with temperature and especially the sulphur of DBDS was shown to react more rapidly than DBDS at 130°C, where the C-S bond of DBDS reacted on the steel may be broken and the separated sulphur may be oxidized to produce

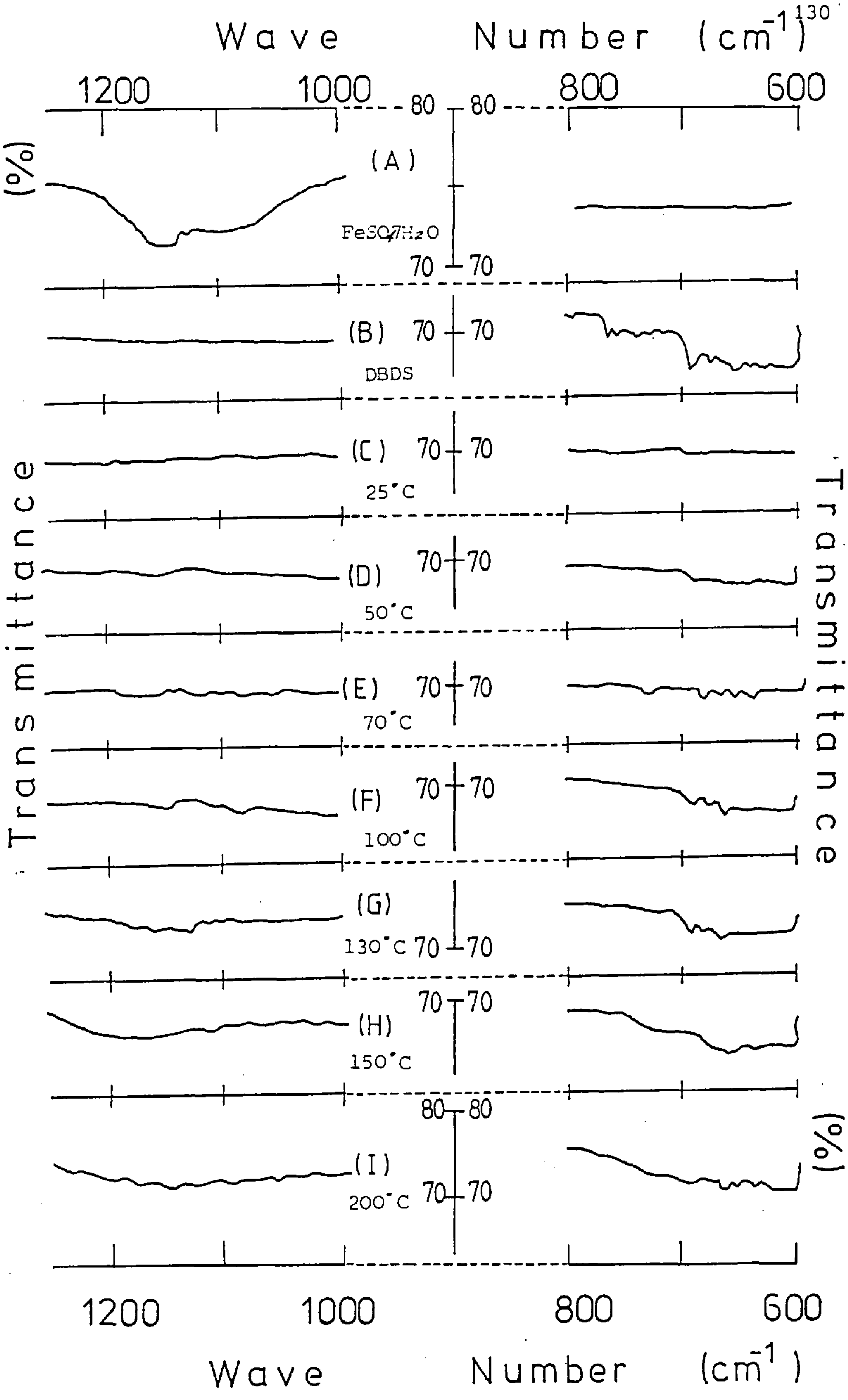


Figure (7.8) IR absorption band on sulphur-reacted steel

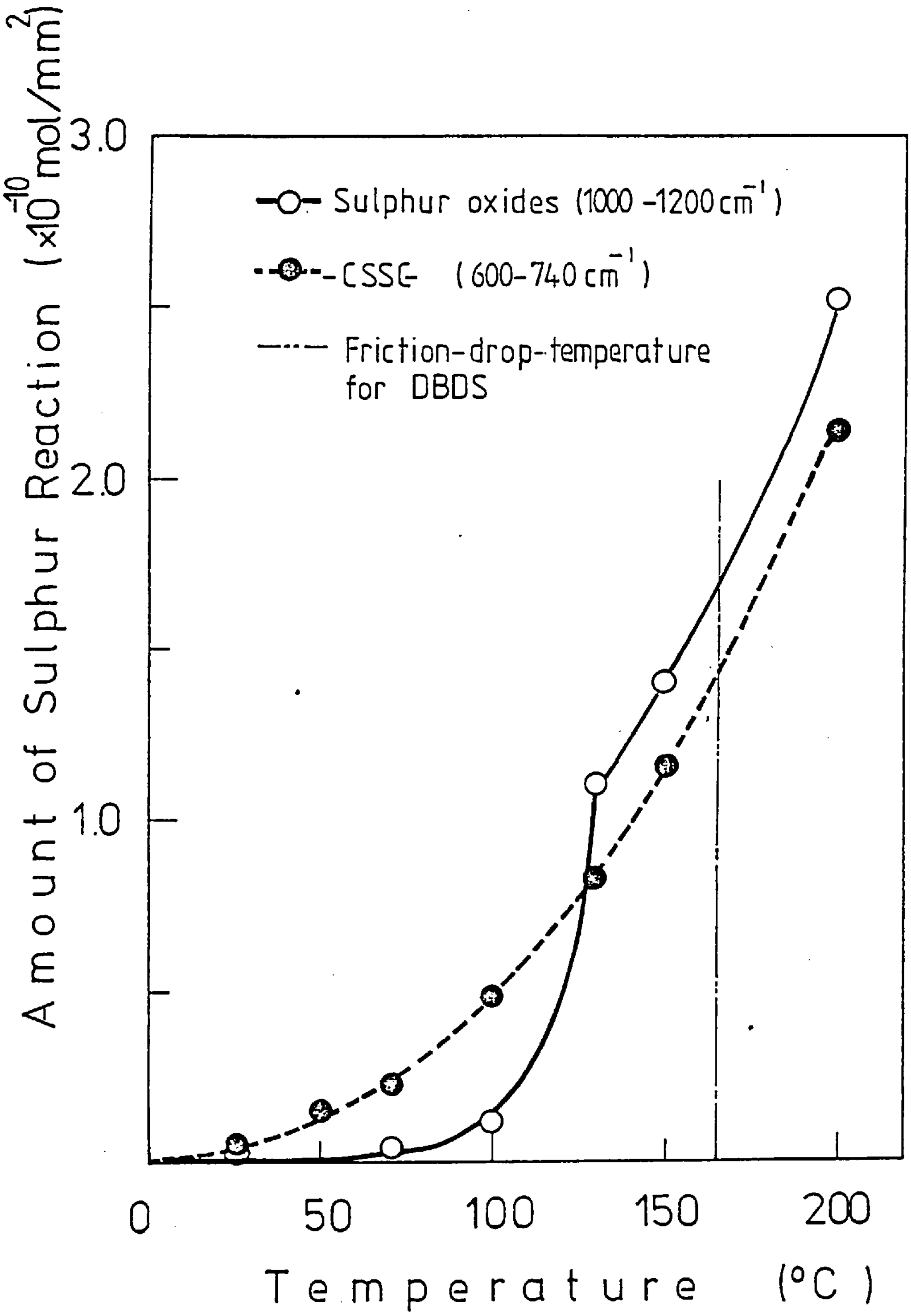


Figure (7.9) Amounts of sulphur reaction product vs. Temperature the sulphur oxide. DBDS is considered to start chemical reaction with steel at 130°C. The frictional coefficient of DBDS with steel decreased from 165°C to higher temperatures (Chapter 6) but the reaction of DBDS is considered to start to activate at lower temperature, 130°C, than the temperature where friction droppedin the tests carried out, i.e. at 165°C. (figure (6.1)).

On the sliding surfaces of the pegs the maximum sulphur content in the emulsion blend with ES was higher than with a corresponding blend of DBDS at the same surface temperature. (7.44). The reacted amount of sulphur from ES was compared with that from DBDS at 130°C and compared with the results on sliding surfaces. The amounts of reacted sulphur from ES were higher than from DBDS at the same reaction temperature as shown in table (7.2).

Table (7.2)

e.p. additive	Amount of sulphur reaction ($X10^{-10}$mol /mm²)
Elemental sulphur	1.4
Dibenzyl disulphide	0.8

Sulphur reaction of DBDS and ES

7.47 SURFACE PRETREATMENT EFFECT ON SULPHUR REACTION

The effect of reaction temperature on sulphur reaction of e.p. additive was examined and the sulphur reaction shown to be quite dependent on reaction temperature in the previous section (7.46). The effect of surfactants in emulsions on sulphur reaction was examined and the possibility of additive interference in sulphur reaction was studied in this section.

Two chemical compositions on sulphurized steels, pretreated by different environments, were observed by IR multiple reflectance spectroscopy. One is the -FeO- (Fe_2O_3) bond, from 400cm^{-1}

to $500cm^{-1}$, and another is the -CSSC- bond, from $600cm^{-1}$ to $700cm^{-1}$, in figure (7.10). The wave numbers were obtained from Cross and Jones (128).

The same absorption intensity of -CSSC- bond was found on steel surfaces, pretreated by air (A), emulsions (B) and emulsifier (E). The intensity resulting from these three environments was weaker than those from water (C) and oil (D). The same absorption intensity of -FeO- bond was found on the steel surface, pretreated by emulsions (B) and water (C). The intensity was stronger than those by air (A), oil(D) and emulsifier (E).

Higher amounts of DBDS reaction on the surface, pretreated by water and oil, were shown in the figure and may be considered as follows: The steel surface pretreated by water may have larger surface area than the others, because water may adsorb on the steel surface to form a hydrated film and partly oxidize the film due to the heat externally added. The larger surface area, on the steel pretreated by water, may thus cause the higher amounts of the reaction. Hydrocarbon molecules may adsorb on the steel surface pretreated by oil. The hydrocarbons with no polar group may desorb from the steel surface more easily by the heat than polar substances. The accumulated reacted layers may be formed step by step on the steel surface while hydrocarbons repeat to adsorb and desorb at the surface.

The steel surface pretreated by emulsions was also shown to have the amount of iron oxide layers as high as by water, but the adsorbed surfactants may disturb DBDS molecules to adsorb on the surface to some extent. It was thus considered that there was little difference of sulphur reaction between the steel surfaces pretreated by emulsions and air. The effect of emulsifier on the reaction of DBDS was, however, quite small as shown in the result of (E) emulsifier. Additive interference of emulsifier was not found significant on the sulphur reacted surface. The possible causes are discussed later. (7.51).

7.48 SOLUBILITY TESTS OF DBDS AND SULPHUR-REACTED FILM

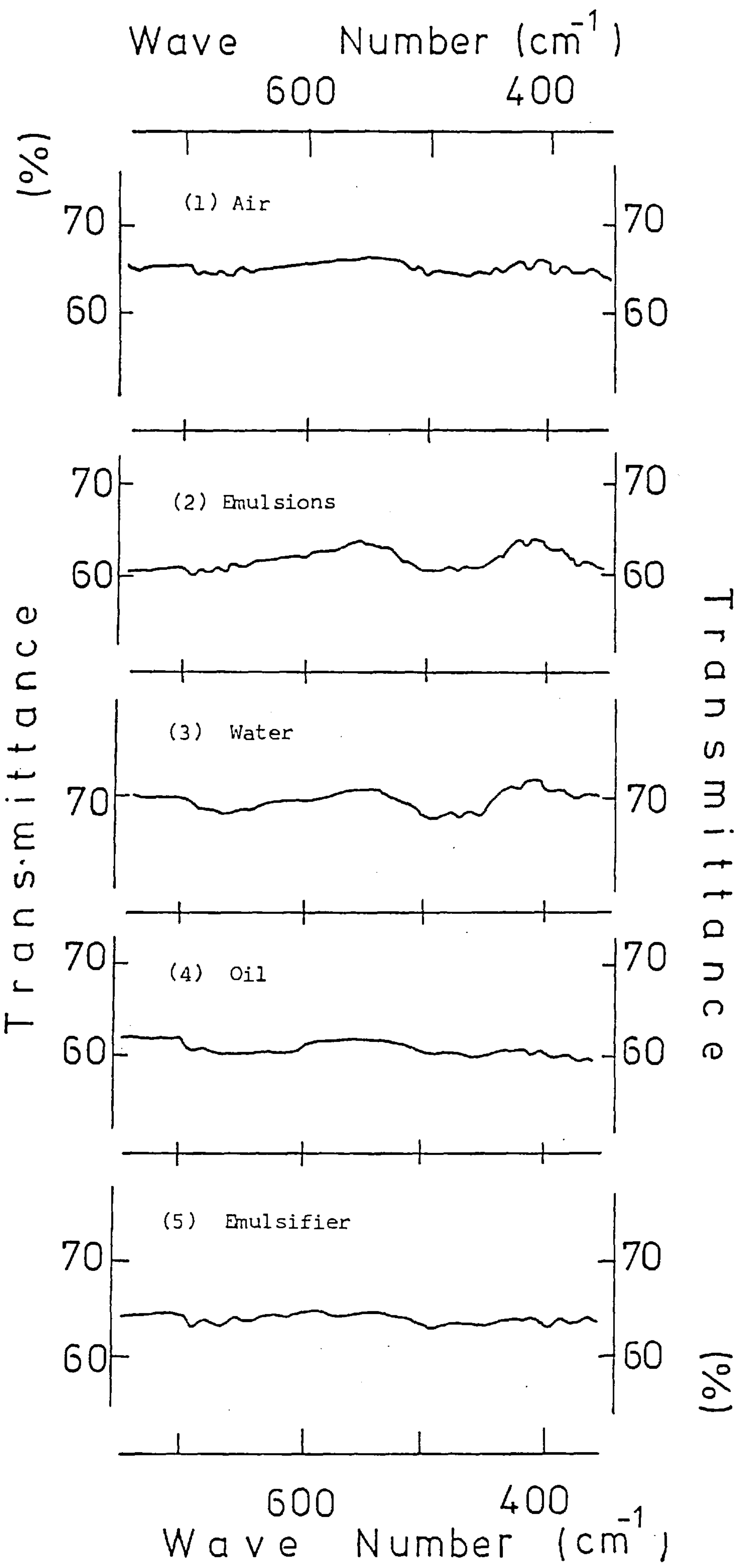


Figure (7.10) IR absorption band of sulphur-reacted steel after pretreatment by emulsions

The last factor which might result in the low sulphur content on sliding surfaces is examined in this section. The e.p. additives might be dissolved in water and prevent the normal reaction of sulphur, or sulphur reacted film formed on sliding surfaces might be removed by solution in water.

Water did not dissolve the e.p. additives (DBDS, ES) but the water with emulsifiers dissolved them. A faint spot of sulphur on the TLC plate was observed from the extracted water with emulsifier, after stirring with e.p. additive. The results are shown in table (7.3). The emulsifier was shown to dissolve the sulphur type of e.p. additive only very weakly (the order of ppm).

Table (7.3)

	Oil	Oil + Emulsifier	Water	Water + emulsifier
DBDS	S	S	No	W
ES	S	S	No	W

S : Strong detection by TLC
W : Weak detection
No : No detection by TLC

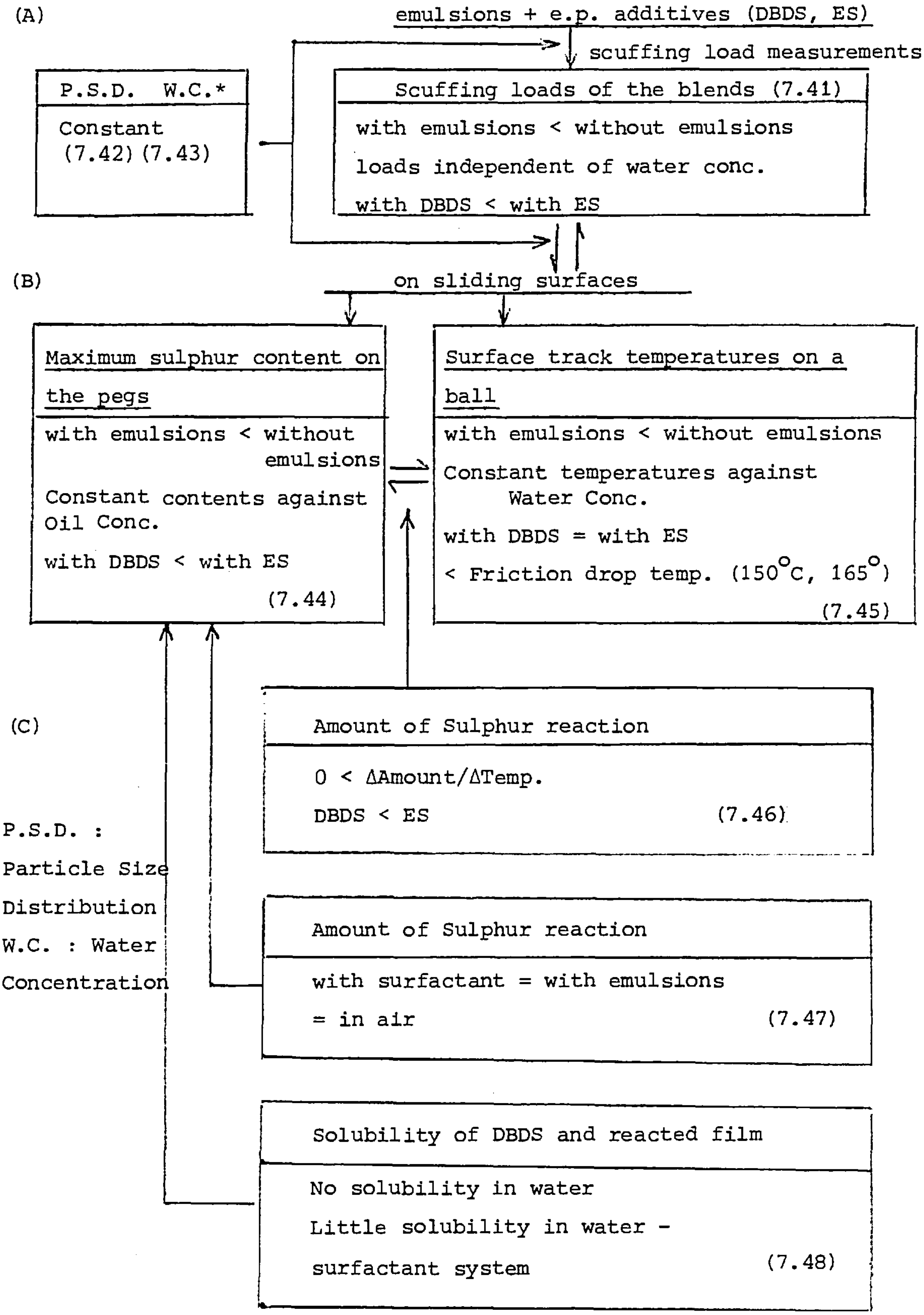
Solubility test of e.p. additive by TLC

The sulphur reacted substances on sliding surfaces were collected by several steps described in 7.39 and in figure (7.2). At the final stage water, oil and the sulphur reacted substances were stirred and boiled for ½ hour and separated into two phases. A strong sulphur spot was found in the oil phase although no spot was detected from the water phase.

It was shown in figure (7.2) that the sulphur-reacted substances were not dissolved by water but dissolved slightly by emulsifier. Sulphur e.p. additive was shown to be non-polar and low solubility in water and water with emulsifier.

7.50 DISCUSSION

The results obtained in this work are summarized as follows before discussing in detail the measured values and the interaction of emulsion with sulphur reaction and frictional tests.



(A)

emulsions + e.p. additives (DBDS, ES)

scuffing load measurements

P.S.D. W.C.*

Constant (7.42) (7.43)

Scuffing loads of the blends (7.41)

with emulsions < without emulsions

loads independent of water conc.

with DBDS < with ES

(B)

on sliding surfaces

Maximum sulphur content on the pegs

with emulsions < without emulsions

Constant contents against Oil Conc.

with DBDS < with ES

(7.44)

Surface track temperatures on a ball

with emulsions < without emulsions

Constant temperatures against Water Conc.

with DBDS = with ES

< Friction drop temp. (150°C, 165°)

(7.45)

(C)

Amount of Sulphur reaction

0 < ΔAmount/ΔTemp.

DBDS < ES (7.46)

Amount of Sulphur reaction

with surfactant = with emulsions

= in air (7.47)

Solubility of DBDS and reacted film

No solubility in water

Little solubility in water - surfactant system (7.48)

* P.S.D. : Particle Size Distribution

W.C. : Water Concentration

7.51 INTERACTION OF EMULSION WITH SULPHUR REACTION

Sulphur contents on the pegs and surface track temperatures on the ball in the emulsion - e.p. additive blends were lower than without emulsions.

The load carrying capacity of e.p. additive is determined by the reactivity with steel, which increases with temperature. (1) (31) (33) (35) (37) (112). Reaction rates of additive are dependent on the activation energy of Arrhenius, and are normally exponential with temperature. This amount of sulphur produced during a certian period should be a function of temperature and increase rapidly with temperature, and was confirmed in this work. (7.46). Hence the reaction temperature is a major factor in determining the amount of sulphur in the surface, which then seems to be a function of the load carrying capacity of additive. The relationship between reaction and temperature refers to small amounts of reaction when the temperature for reaction is low.

Although the quantitative analysis of reaction amount for load carrying capacity of additive has not fully understood, the reaction amount is definitely a major function of the load carrying capacity, (37) and the inferior load carrying capacity is considered to be caused by the low reaction temperature on sliding surfaces. The surface temperature measured in this work were lower than the friction drop temperatures of DBDS and ES (165°C and 150°C).

Other factors apart from temperature which might cause the inferior load carrying capacity of sulphur e.p. additive- emulsion blends are additive interference in the sulphur reaction and solubility of e.p. additive or sulphur reacted film formed on the surface into the water phase in emulsion. However these two possible factors were shown to contribute negligibly to the lower load carrying capacity. (7.47) (7.48).

An additive interference in sulphur reaction may have occured on the steel surface before the reaction of e.p. additive occurs. Surplus surfactants, not needed to form emulsion, may have adsorbed preferentially on the surface. However the amount of sulphur reaction on the steel pretreated by surfactant was found to be equal to the amount on steel pretreated in air. ($\cong 0.5 \times 10^{-10}$ mol /mm²). The nonionic surfactant used in the work was not shown to suppress the e.p. reaction on steel.

The polarity of nonionic surfactant may be too weak to adsorb and react with steel faster than dibenzyl disulphide, although the surfactant with strong polarity is very active on the sulphurized steel surface. (Chapter 2 and 3). The nonionic surfactant with three long hydrocarbon chains may be difficult to adsorb and react to form a coherent layer on steel due to the steric hindrance of the molecular structure.

Solution of e.p. additive and sulphur reacted film may have occured before and after the sulphur reaction on sliding surfaces. However DBDS and the sulphur reacted substances (films), separated from the paraffin oil containing DBDS used in the friction apparatus, were found to be insoluble in water. Although DBDS and the sulphur reacted substances are composed of sulphur, which occupies the same group as oxygen in the elemental table, the aromatic and hydrocarbon part of the molecules may be quite hydrophobic and prevent the molecules solving in water. Hence the area of reaction on sliding surfaces might be restricted and the amount of reaction might be lower than in the oil without water. However, the sulphur contents on the pegs measured in this work were found to be independent of the water volume of emulsions. (7.44). It seems unlikely that the effects of solubility of DBDS and sulphur reacted film are important on the sulphur contents of the pegs and load carrying capacities of the emulsion - e.p. additive blends.

When it was initially observed that the sulphur e.p. additives used were less effective in emulsions than water free systems, three main possible reasons were considered. These were:

(1) Sulphur compounds were being sequestered by water from the oil phase, or were being dissolved off the rubbed surface as they reacted.

(2) The surfactant or the surfactant-water inhibited the reaction of sulphur compounds on steel surfaces by competition.

(3) The emulsion acted as a sufficiently effective coolant to prevent the surfaces reacting at the temperatures of e.p. reaction.

The solubility and direct reaction tests (7.46) (7.47) (7.48) have made the first and the second factor extremely unlikely, whereas the low surface temperature measured may be the cause. The thermal effect of the blends is discussed in the next section.

7.52 INTERACTION OF EMULSION IN FRICTIONAL TESTS

The thermal control by the blends of reaction temperature is quite likely to occur on sliding surfaces. The surface temperatures on sliding surfaces in the blends were lower than without water and nearly constant except at lower concentrations of oil, where temperatures were slightly higher than the other values (7.45).

Heat transfer coefficients have been calculated to understand how much of the frictional heat is removed from sliding surfaces and to determine how much of the e.p. reaction is prevented by the emulsion - e.p. additive blends. (5.50). To begin with, equilibrium skin temperatures were calculated and are shown in figure (7.11).

The skin temperatures, the differences between surface and bulk temperatures, were shown to be nearly constant except at low oil concentrations of emulsions, where the temperatures were slightly higher than the other values. It was shown here that the lower temperatures of sliding surfaces are not always

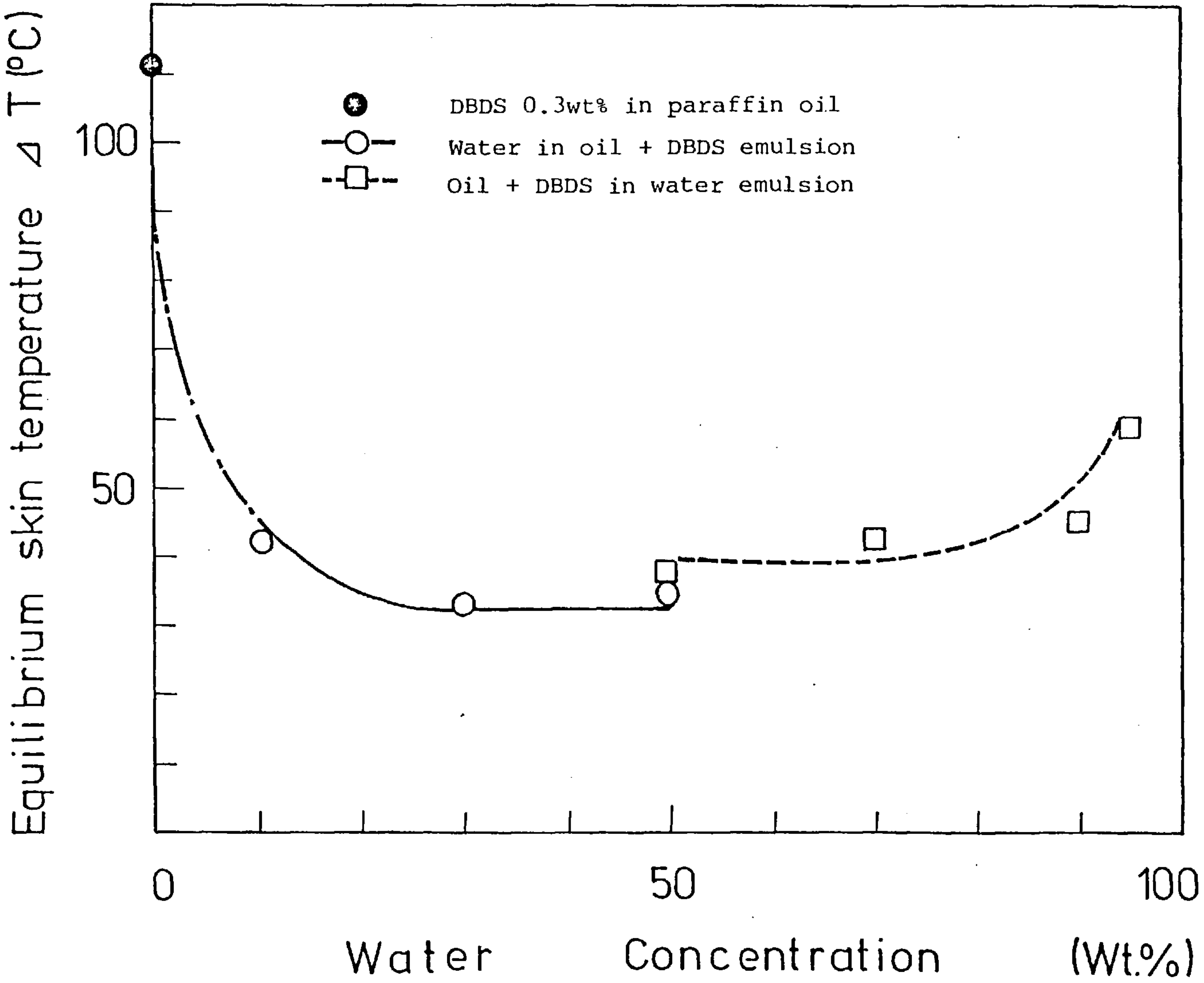


Figure (7.11) Equilibrium skin temperature vs water concentration in emulsions obtained because the lubricant has a high concentration of water and thus a high specific heat. Good lubricating property must be accompanied by cooling property to obtain the lower temperatures (Chapter 5).

Heat transfer coefficients were calculated from the following equation obtained in 5.53.

$$hc = \frac{\omega g}{4\pi J} \times \left(\frac{\mu \overline{W}}{\ell . \Delta T} \right) \qquad (\text{Joule/s.cm}^2 . {}^{o}\text{C}) \qquad (5\text{-}6)$$

ω	the angular speed (rad/sec)
g	the gravitational constant 981 (cm/sec^2)
J	the mechanical equivalent heat 1.0×10^{-7} (eng/Joule)
μ	the frictional coefficient
$\overline{W}$	the resolved load per peg (g)
ℓ	the axial width of sliding track (cm)
ΔT	the equilibrium skin temperature (^{o}C)

The results are shown in figure (7.12). High values of the coefficient is found at high concentrations of the dispersed phase, both water in w/o and oil in o/w type emulsions. Similar results were obtained with the pure emulsions. (Figure (5.14)). The heat transfer coefficient of oil from sliding surfaces was found to be lower than in emulsions.

The lower skin temperature and small wear scar, and the higher scuffing loads were found to cause heat transfer coefficient to increase, which is considered from equation (5-6). At higher concentrations of water, say, 95% water in o/w type emulsions, the measured values of skin temperature and wear scar were higher than at lower concentrations of water, although the scuffing loads were nearly constant. The average diameters of wear scar, defined the axial width of sliding track, are shown in Table (7.4). The severe conditions of wear, which may increase the skin temperature, are considered to decrease the coefficient, hc.

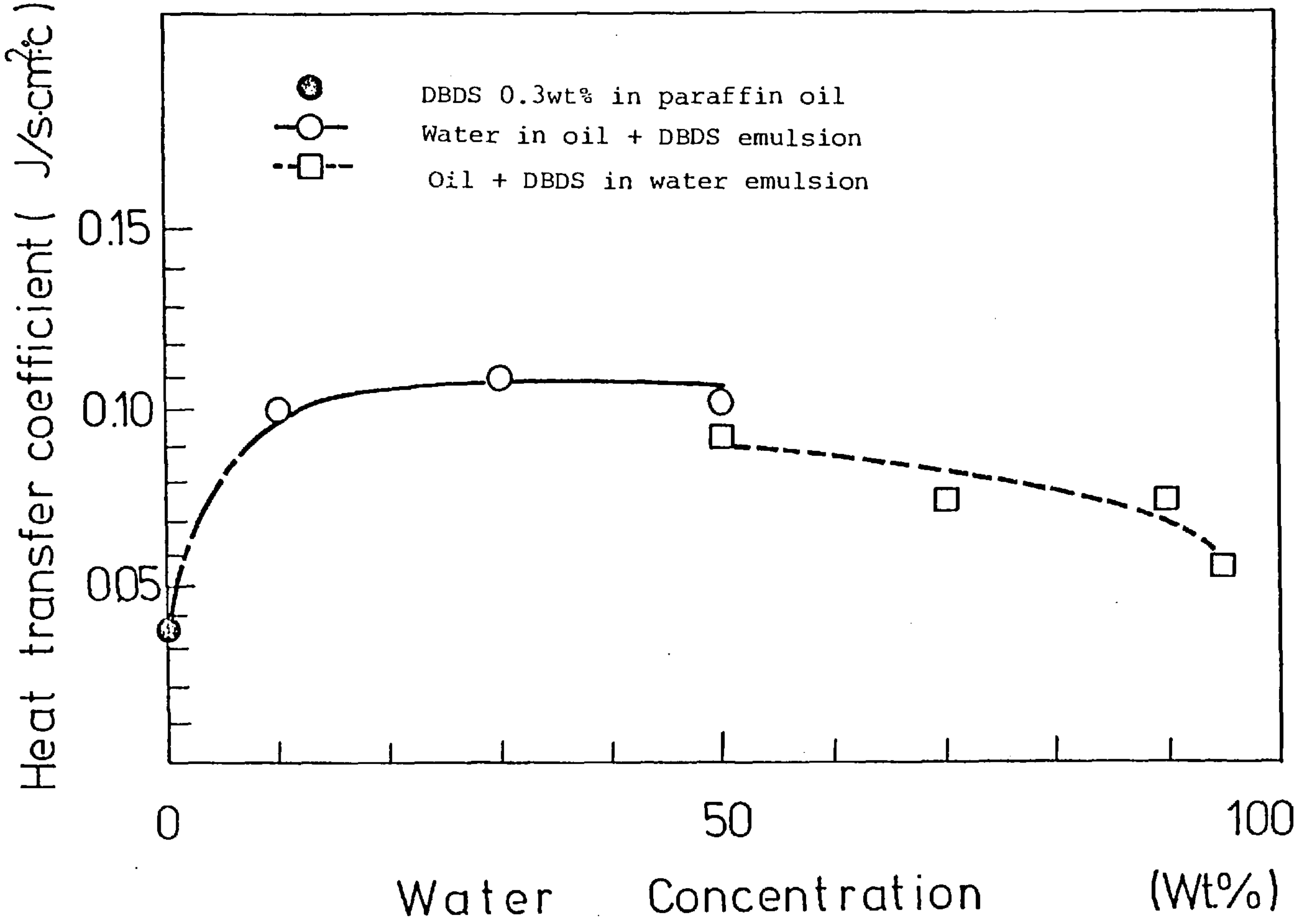


Figure (7.12) Heat Transfer coefficient vs water concentration in emulsions

Table (7.4)

Type	Water (Wt%)	The average wear scar diameter (cm)
Paraffin + DBDS	0	0.20 (0.11)
w/o type emulsion + DBDS	10	0.18 (0.10)
	30	0.18 (0.10)
	50	0.18 (0.10)
o/w type emulsion + DBDS	70	0.18 (0.10)
	90	0.19 (0.10)
	99.5	0.19 (0.10)

( ): elastic contact diameter

Axial track width ℓ

The low values of heat transfer coefficient, at high concentrations of water in o/w water emulsions, are mainly considered to be caused by the wider width of sliding track, that is, wider wear scar, which was also observed on the surface in the pure emulsions. (5.53). The high concentration of water may be corrosive to steel surfaces under severe running conditions. The hydroxide layers produced on the steel in water is reported to reduce friction but increase wear. (93). The sulphur contents on the pegs were shown to increase with water concentration. (7.44) The higher sulphur contents are considered to be caused by the higher temperature on the surface, where the heat transfer coefficient is lower.

The constant values of coefficient were found in w/o type emulsions, and shown to be independent of water and oil concentrations. While the coefficient was shown to increase with water concentration in the pure w/o type emulsion (5.53), the coefficient was independent of water concentration in the emulsion-e.p. additive blend. Heat transfer coefficient is determined by both mechanical property $\mu\overline{W}/\ell$ and cooling property $1/\Delta T$ of the lubricant, and these properties of the blends are considered to be equal on the sulphurized steel whatever the water concentration of the blends.

Mixtures of emulsion and e.p. additives are quite likely to have inferior load carrying capacities due to higher heat transfer coefficients than oil, resulting in lower surface temperature. The low surface temperature is considered to suppress the e.p. reaction on sliding surface and leads to the deterioration of load carrying capacity of an e.p. additive.

It was also recognised in this work that the estimation of mechanical properties, such as load carrying capacity, of mixed lubricants should be based on the chemical reactivity of the lubricants with sliding surfaces, rather than solely on the mechanical properties of each lubricant. Finally it may be an unnecessary procedure in grinding, drilling and rolling processes to mix emulsions with e.p. additives, although the mixed lubricant of emulsion and e.p. additive is often used for the steel products (124).

7.60 CONCLUSIONS

The mixed lubricants of e.p. additive with emulsions were found to have the inferior load carrying capacity, compared with those of the water-free oil with e.p. additive, and thus to be unsatisfactory lubricants. The sliding steel with a high heat transfer coefficient of the blends is quite likely to prevent the e.p. additive reacting at the suitable temperatures, 130°C ~ 165°C, for e.p. reaction, with the emulsions acting as a sufficient coolant.

The other possible factors, which might habe contributed to the inferior chemical property of the blend, were discounted after solubility and direct reaction tests,

(A) Sulphur compounds were not sequestered by water from the oil phase, nor were being dissolved off the rubbed surface as it favored.

(B) The surfactants and the surfactant-water system did not inhibit the reaction of sulphur compounds on metal surfaces by competition.

CHAPTER EIGHT

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

8.10 CONCLUSION

The load carrying capacities of emulsions alone and emulsions containing e.p. additives have been studied. The cause of the results was studied and analysed using basic physical and chemical tests.

E.p. activity increased considerably with temperature and an e.p. agent ideally formed films on metals around the desorption temperature of adsorbed surfactant layers. (150 ~ 165°C). A surfactant film was formed on the sulphur reacted surfaces, where sulphur e.p. additives had reacted with steel at a sufficient high temperature for e.p. formation. The surfactant film on the sulphur reacted surfaces was found to be protective against wear, thus contributing to the good lubrication.

Combination of emulsions with sulphur e.p. additives did not raise the scuffing load as much as expected though this combination is often used for coolants in such processes as cutting, grinding and rolling. Each of the lubricants, (1) emulsion without e.p. additives and (2) e.p. additives in oil, was found to be suitable for the prevention of scuffing.

Emulsions, which have higher heat transfer coefficients than oils, were found to cool the sliding surfaces from which the frictional heat is dissipated. This may prevent microwelding betweeen the mating surfaces, so increasing scuffing loads above comparable oil systems. However the cooling property of emulsions, which is beneficial for pure emulsion lubrication, becomes undesirable when an e.p. action on sliding surfaces is required. The cooling effect of emulsion reduced the e.p. reaction on the sliding surfaces, but was also effective in preventing desorption of surfactant. Thus the mixed e.p. - emulsion system showed little e.p. behaviour.

The main points in this thesis can be summarized as follows.

8.11 ADSORPTION OF SURFACTANTS IN BOUNDARY AND E.P. LUBRICATION

The results of this section were used to study the load carrying capacity of the mixed lubricants between emulsions and e.p. additives. (8.13).

After the formation of sulphur reacted film on sliding surfaces,

(1) Strong adsorption of surfactants reduces wear at the sliding contact of both sulphurized and unreacted steel in boundary lubrication.

(2) The wear of sulphur-reacted steel is less in air than in argon. Oxygen may be favourable in protecting the sulphurized steel against wear.

(3) The wear-reducing-ability of surfactants on sulphur-reacted and unreacted steel may be determined by

(A) reactivity of surfactants

(B) polar interaction of surfactants with sulphurized and unsulphurized steel surfaces.

8.12 EMULSION LUBRICATION

Emulsions were found to show abnormal physical properties, which are different from oil. Lubricating properties of emulsions may be influenced by the following factors, although the shear rates examined were lower than those estimated in the contact. (10^2/S < 10^5/S).

(4) Shear stress becomes independent of shear rate, with the increased volume of the dispersed phase, oil in o/w and water in w/o type emulsions. The linear

relationship between shear stress and shear rate is not found in the emulsions with high concentrations of the dispersed phase. (50% oil : 50% water). The non-Newtonian (the pseudoplastic) property of emulsions becomes dominant, with the increased volume of the dispersed phase.

(5) The viscosity of emulsions at low shear rates decreases suddenly at 60°C for w/o type and 40°C for o/w type emulsions and increases afterwards with temperature. The minimum values of surface tensions and particle sizes have been reported to occur at the phase inversion temperature, where the dispersing phase is partly inverted to the dispersed phase. Emulsions may consist of the similar compositions of water and oil locally on sliding surfaces on the way to scuffing, whatever the type and the water concentration of emulsions.

The load carrying capacity of emulsions have been studied.

(6) Emulsions were discovered to be lubricants when judged by their load carrying capacity. The scuff loads of emulsions are independent of the water concentration and increase slightly with the dispersed phase volume.

The cause of this was studied and analysed. Under the constant conditions of viscosity of emulsions and concentration of surfactant in emulsions, it is deduced that there is the constant thickness of oil film between sliding surfaces and the same effect of surfactant on scuffing. The thermal properties of emulsions are quite likely to contribute to the good scuffing load of emulsions.

(7) Heat transfer coefficients of emulsion are higher than that of oil and of the same value as water. The

coefficients were found to increase with the dispersed phase of emulsions. Hence the lower surface temperature, on sliding surfaces in emulsions with higher heat transfer coefficients, is considered to result in the improved load carrying capacities of emulsions.

8.13 EMULSION INTERACTION IN E.P. LUBRICATION

The load carrying capacity of the mixed lubricant between emulsion and e.p. additive was studied and the results were analysed with reaction tests.

(8) The scuffing loads of the mixed lubricants are lower than that of the oil with e.p. additive. The sulphur content of the pegs and the surface track temperature on a ball in the blends are lower than in the oil with e.p. additive.

(9) The following possible factors did not result in emulsion interference in extreme pressure lubrication.

(A) The nonionic surfactants used for emulsions prevent e.p. additive reacting on sliding surfaces by competition.

(B) The sulphur reacted film and e.p. additive are dissolved from sliding steel surfaces by water in emulsions.

The last factor of the emulsion cooling property is likely to cause their inferior load carrying capacities.

(10) The lower surface temperatures, on sliding surfaces in the mixed lubricants with higher heat transfer coefficients, result in the lower scuffing loads than the oil with e.p. additive. This undesirable combination was found in two lubricants, between emulsion and e.p. additive.

8.20 SUGGESTION FOR FUTURE WORK

A new type of lubricant is in demand for the future, because of the decreasing fossil fuel, and should be developed simultaneously with improvements in conventional lubricating oils. It is difficult to estimate mechanical properties of the lubricant simply by physical properties of the substances which compose it. As shown , the load carrying capacities of the mixed lubricants between e.p. additive and emulsions are not predictable from data of physical properties. The chemical reactions of additives with sliding surfaces were confirmed as important for the estimation and analysis of the mechanical properties. The chemical approach for the solution is considered to be effective, especially for the development of a new lubricant.

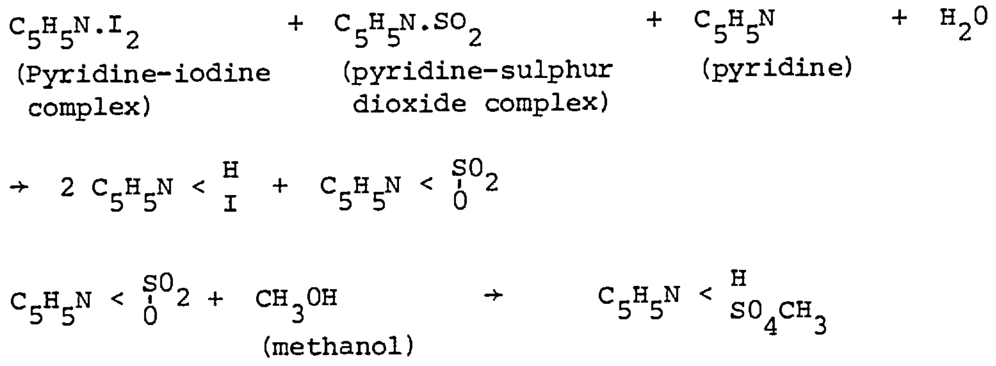
The temperature on sliding surfaces was shown to be a very important factor of chemical reactivity. The more active chemical reaction of lubricating oils with steel improve the load carrying capacity of the oil. Hence the fundamental surveys for chemical reactions of lubricating oils with temperature may be the solution for complicated reactions between lubricating oils and sliding steels.

APPENDIX 1

TITRATION OF KARL FISCHER REAGENT TO MEASURE THE CONCENTRATION OF WATER

There are two basic approaches to measuring the water concentration in the solution categorically, physical and chemical methods. Measurements of physical properties of water such as dielectric constant, electrical conductivity, infrared spectroscopic absorption, density and refractive index are not satisfactory for multiphase systems. Therefore a chemical method - the Karl Fischer method is used for the determination of water in solutions which have two phases such as emulsions.

This simple and precise method was introduced by Karl Fischer in 1935. The basic reaction process is as follows.



$$\underset{\text{(Pyridine-iodine complex)}}{C_5H_5N.I_2} + \underset{\text{(pyridine-sulphur dioxide complex)}}{C_5H_5N.SO_2} + \underset{\text{(pyridine)}}{C_5H_5N} + H_2O$$

$$\rightarrow 2\ C_5H_5N < \genfrac{}{}{0pt}{}{H}{I} + C_5H_5N < \genfrac{}{}{0pt}{}{SO_2}{O}$$

$$C_5H_5N < \genfrac{}{}{0pt}{}{SO_2}{O} + \underset{\text{(methanol)}}{CH_3OH} \rightarrow C_5H_5N < \genfrac{}{}{0pt}{}{H}{SO_4CH_3}$$

The Karl Fischer consists of a mixture of pyridine, sulphur dioxide and iodine in ratio of moles, 10,3 and 1 respectively. The colour of Karl Fischer reagent is dark brown due to the iodine which is changed to the light yellow by reaction with water. At the end of the titration the colour of the solution is changed to reddish brown of unreacted iodine.

Residues of emulsions lubricated rubbing surfaces in a ball-on-triplane machine were weighed and kept in sealed sample tubes for 24 hours and were titrated by Karl Fischer reagent of B.D.H. Chemical Co.

The Karl Fischer reagents were used to titrate emulsion lubricants directly without adding diluent solvents. The reagent easily destroyed the emulsion particles in the direct titration, releasing the water. Weight of water measured by Karl Fischer reagent is divided by the total weight of emulsion residue to calculate the water concentration.

APPENDIX 2

CALIBRATION OF SULPHUR CONTENT ON PEGS BY EPMA

It is not practical to calculate the sulphur content absolutely, because the chemical combination of the S is unknown and the sulphur content is present as a very thin layer. Hence an approximate calibration is made which assume that the S radiation is unaffected by surface impurities and behave as though it were a homogeneous solid. It would be reasonable to assume that the count rate as recorded is proportional to thickness of the layer. The values obtained were not absolute but relative, and were compared under the different conditions.

Cadmium sulphide (CdS) was used as the standard specimen of calibration. The chemical composition has been identified before use. Calibration by CdS was adapted to calculate the sulphur content on all pegs. Allowance was made for the recorded scale as follows: One small division of chart paper corresponds to 0.21wt% of sulphur.

REFERENCES

1. Bowden, F.P. and Tabor, D.
"The Friction and lubrication of solids"
Oxford. The Clarendon Press (1964).

2. Institute of Mechanical Engineers
Memorandum on definitions, Symbols and Units.
I. Mech. E. London.

3. Becher, P.
"Emulsions. Theory and Practice".
Amer. Chem. Soc. Monograph (1957).

4. Parkinson, C. and Sherman, P.
"Phase inversion temperature as an accelerated method for evaluating emulsion stability".
J. Coll. Inter. Sci. 41 (1972) 328.

5. Shinoda, K.
"The correlation between the dissolution state of nonionic surfactant and the type of dispersion stabilized with the surfactant".
J. Coll. Inter. Sci. 24 (1967) 4.

6. Smalheer, C.V. and Mastin, T.V.
"Lubricant additives and their action".
J. Inst. Pet. 42 (1956) 337.

7. Groszek, A.J.
"Heats of preferential adsorption of surfactants on porous solids and its relation to wear of sliding steel surfaces".
ASLE Trans. 5 (1962) 105.

8. Groszek, A.J.
"Heat of adsorption measurements in lubricating oil research".
Chem. Indust. Mar. 20 (1965) 482.

9. Groszek, A.J.
"Determination of surface areas of powders by flow microcalorimetry".
Chem. Indust. Oct 15 (1966) 1754.

10. Groszek, A.J.
"Selection adsorption at graphite/hydrocarbon interfaces".
Proc. Roy. Soc. L. A314 (1970) 473.

11. Kapustinskii, A.F.
"Lattice energy of ionic crystals"
Rev. Chem. Soc. 10 (1956) 283.

12. Hardy, Sir William and Hardy, J.K.
"Note on static friction and on the lubricating properties of certain chemical substances".
Phil. Mag. S. 38 (1919) 32.

13. Frewing, J.J.
"The influence of temperature on boundary lubrication".
Proc. Roy. Soc. L. A181 (1942) 23

14. Frewing, J.J.
"The heat of adsorption of long chain compounds and their effect on boundary lubrication".
Proc. Roy. Soc. L. A182 (1944) 270

15. Bailey, M.W. and Cameron, A.
"The influence of temperature and metal pairs on the scuffing of a commercial oil".
Proc. Inst. Mech. Eng. 187 (1973) 757

16. Bailey, M.W. and Cameron, A.
"The effect of temperature and metal pairs on scuffing".
ASLE Trans. 16 (1973) 121.

17. Spikes, H.A. and Cameron, A.
"A comparison of adsorption and boundary lubricant failure".
Proc. Roy. Soc. L. A336 (1974) 407

18. Bigelow, W.C., Pickett, D.L. and Zisman, W.A.
"Oleopholic monolayers. I. Films adsorbed from solution in non-polar liquids".
J.Coll. Sci. 1 (1946) 513

19. Shulman, J.H., Waterhouse, R.B. and Spink, J.A.
"Adhesion of amphipathic molecules to solid surfaces".
Koll. Zeit. 146 (1956) 77.

20. Kingsbury, E.P.
"Some aspects of the thermal desoprtion of a boundary lubricant".
J.App Phys. 29 (1958) 888

21. Peart, S.D. and Thorp, J.M.
"Boundary lubricant adsorption data from high speed four-ball scuffing temperatures".
Wear, 27 (1974) 209.

22. Bose, A.C., Klaus, E.E., and Tewksbury, E.J.
"Evaluation of wear products produced by some chemical reactions in boundary lubrication".
ASLE Trans. 19 (1976) 287

23. Bjerk, K.O.
"Oxygen - an "Extreme-pressure agent""
ASLE Trans. 16 (1973) 97.

24. Klaus, E.E. and Bieber, H.E.
"Effect of some physical and chemical properties of lubricants on boundary lubrication".
ASLE Trans. 7 (1964) 1.

25. March, P.A. and Rabinowicz, E.
"Exoelectron emission for the study of surface fatigue wear".
ASLE Trans. 20 (1977) 315.

26. Georges, J.M., Meille, G., Jacquet, M., Lamy, B., and Mathia, T.
"A study of the durability of boundary films".
Wear 42 (1977) 217

27. Summers-Smith, D.
"Chemical reactions on bearings in lubricated industrial machines".
Wear 18 (1971) 291

28. Campbell, W.E.
"Studies in boundary lubrication. Variables influencing the coefficient of static friction between clean and lubricated metal surfaces".
ASME Trans. 61 (1939) 633.

29. Greenhill, E.B.
"The lubrication of metals by compounds containing sulphur".
J. Inst. Petrol. 34 (1948) 659.

30. Davey, W. and Edwards, E.D.
"Extreme-pressure lubricating properties of some sulphides and disulphides in mineral oil as assessed by the four-ball machine".
Wear 1 (1957/58) 291.

31. Dorinson, A. and Broman, V.E.
"Extreme pressure lubrication and wear. The chemical reactivity and the extreme pressure action of two aliphatic disulphides".
ASLE Trans. (1962) 75.

32. Sakurai, T., Ikeda, S., and Okabe, H.
"The mechanism of reaction of sulphur compounds with steel surface during boundary lubrication, using S^{35} as a tracer".
ASLE Trans. 5 (1962) 67.

33. Godfrey, D.
"Chemical changes in steel surfaces during extreme pressure lubrication".
ASLE Trans. 5 (1962) 57.

34. Barcroft, F.T.and Daniel, S.G.
"Extreme-pressure film formation on hypoid gears - studies with sulphur - 35"
Proc. Inst. Mech. Eng. 109 (3J) (1964-65) 265

35. Sakurai, T. and Sato, K.
"Study of corrosivity and correlation between chemical reactivity and load-carrying capacity of oils containing extreme pressure agents"
ASLE Tans. 9 (1966) 77

36. Wheeler, D.R.
"X-ray photoelectron spectroscopic study of surface chemistry of dibenzyl disulphide on steel under mild and severe wear conditions"
Wear 47 (1978) 243

37. Forbes, E.S.
"The load-carrying action of organo-sulphur compounds - A review"
Wear 15 (1970) 87

38. Coy, R.C. and Quinn, T.F.J.
"The use of physical methods of analysis to identify surface layers formed by organo-sulphur compounds in wear tests"
ASLE Trans. 18 (1975) 163

39. Buckley, D.H. and Pepper, S.V.
"Elemental analysis of a friction and wear surface during sliding using Auger spectroscopy"
ASLE Trans. 15 (1972) 252

40. Buckley, D.H.
"Oxygen and sulphur interactions with a clean iron surface and the effect of rubbing contact on these interactions"
ASLE Trans. 17 (1974) 206.

41. Baldmin, B.A.
"Relationship between surface composition and wear: an X-ray photoelectron spectroscopy study of surfaces tested with organo-sulphur compounds".
ASLE Trans. 19 (1976) 335

42. Yamamoto, Y. and Hirano, F.
"The effect of sulphur compounds at very low concentration in lubricants on scoring resistance: Part 1".
Wear 42 (1977) 71

43. Yamamoto, Y. and Hirano, F.
"The effect of sulphur compounds at very low concentration in lubricants on scoring resistance: Part2".
Wear 42 (1977) 81

44. Tomaru, M., Hironaka, S. and Sakurai, T.
"Effects of oxygen on the load-carrying action of some additives".
Wear 41 (1977) 117

45. Tomaru, M., Hironaka, S. and Sakurai, T.
"Effects of some chemical factors on film failure under e.p. conditions".
Wear. 41 (1977) 141

46. Sethuramiah, A., Okabe, H. and Sakurai, T.
"Critical temperatures in e.p. lubrication".
Wear, 26 (1973) 187

47. Bollani, G.
"Failure criteria in thin film lubrication with e.p. additives"
Wear 36 (1976) 19

48. Czichos, H and Kirschke
"Investigations into film failure (Transition point) of lubricated concentrated contacts".
Wear 22 (1972) 321

49. Antler, M.
"Preprints of papers presented at the Symposium on Chemistry of friction and wear".
Petrol. Chem. Amer. Chem. Soc. (Chicago meeting) (1958) 153

50. Ostwald, W.O.
"Beträge zur Kenntnis der emulsionen"
(The knowledge of emulsion behaviours)
Koll. Zeit. 6 (1910) 103.

51. Aveyard, R. and Haydon, D.A.
"An introduction to the principles of surface chemistry"
Cambridge. The University Press. (1973)

52. Donnan, F.G. and Potts, H.E.
"Applied Colloid Chemistry" 2nd Edition
N.Y. McGraw-Hill Co. (1926) 359.

53. Bancroft, W.D.
"The theory of emulsification, V"
J. Phys. Chem. 17 (1913) 501

54. Sherman, P.
"Emulsion Science"
140 Academic Press (1968)

55. Harkins, WD., Davies, E.C.H., and Clark, G.L.
"The orientation of molecules in the surface of liquid"
J.Am. Chem. Soc. 39 (1917) 541

56. Becher, P.
"Emulsions. Theory and Practice"
Amer. Chem. Soc. Monograph, 90 (1957)

57. Boyd, J., Parkinson, C. and Sherman, P.
"Factors affecting emulsion stability, and the HLB concept"
J. Coll. Inter. Sci. 41 (1972) 359

58. Boyd, J. and Sherman, E.
"Two-dimensional rheological studies on surfactant films at interfaces"
J. Coll. Inter. Sci. 34 (1970) 76

59. Rehfeld, S.I.
"Stability of hydrocarbon-in-water emulsions during centrifugation. Influence of dispersed phase composition"
J. Coll. Inter. Sci. 46 (1974) 448

60. Friberg, S. and Jansson, P.O.
"Surfactant association structure and emulsion stability"
J. Coll. Inter. Sci. 55 (1976) 614

61. MacRitchie, F.
"Monolayer compression barrier in emulsion and foam stability".
J. Coll. Inter. Sci. 56 (1976) 53

62. Shinoda, K. and Saito, H.
"The stability of o/w type emulsions as a function of temperature and the HLB of emulsions: The emulsification by PIT-method"
J. Coll. Inter. Sci. 30 (1969) 258.

63. Saito, H. and Shinoda, K.
"The stability of w/o type emulsions as a function of temperature and the hydrophilic chain length of the emulsifier"
J. Coll. Inter. Sci. 32 (1970) 647

64. Shinoda, K. and Sagitani, H.
"Emulsifier selection in water/oil type by the hydrophile-lipophilic temperature system"
J. Coll. Inter. Sci. 64 (1978) 68

65. Shinoda, K. and Ogawa, T.
"The stabilization of water in nonaqueous solutions of nonionic surfactants"
J. Coll. Inter. Sci. 24 (1967) 56

66. Tamai, Y., Ebina, S. and Hirai, K.
"Relation of stability of o/w emulsion to interfacial tension and HLB of emulsifier"
International Conference on colloids and surface, 50th.
San Juan. Puerto Rico. Academic Press (1976) 256.

67. Wilkinson, W.L.
"Non-Newtonian fluids"
Pergamon Press (1960)

68. Fischer, E.K. and Harkins, W.D.
"Monomolecular films. The liquid-liquid interface and the stability of emulsions"
J. Phys. Chem. 36 (1932) 98

69. Dalmaz, G. and Godet, M.
"Film thickness and effective viscosity of some fire resistant fluids in sliding point contacts"
ASME 100 (1978) 304

70. Hobbs, R.A. and Mullett, G.W.
"Effects of some hydraulic fluid lubricants on the fatigue lives of rolling bearings"
Proc. Inst. Mech. Eng. 183 Pt3P. (1968) 21

71. Polk, C.J. and Rowe, C.N.
"Crack growth rate: Its measurement and a controlling factor in rolling contact fatigue"
ASLE Trans. 19 (1976) 23

72. Murphy, W.R., Polk, C.J. and Rowe, C.N.
"Effect of lubricant additives on water- accelerated fatigue"
ASLE Trans. 21 (1978) 63

73. Rowe, G.W. and Smart, E.F.
"The importance of oxygen in dry machinery of metal on a lathe"
Brit. J. Appl. Phys. 14 (1963) 924

74. Barlow, P.L.
"Influence of free surface environment on the shear zone in metal cutting"
Proc. Inst. Mech. Eng. 181 Pt 1 (1967) 687

75. Rowe, G.W. and Wolstencroft, F.
"A mechanical approach to the metallurgy of metal cutting"
J. Inst. Metals. 98 (1970) 33

76. Childs, T.H.C. and Rowe, G.W.
"Physics in metal cutting"
Rep. Prog. Phys. 36 (1973) 223

77. Rowe, G.W., Smart, E.F. and Tripathi, K.C.
"Surface adsorption effects in metal cutting and grinding"
ASLE Preprint (1976) No. 76-LC-5A-2

78. Williams, J.A. and Tabor, D.
"The role of lubricants in machinery"
Wear 43 (1977) 275

79. Duwell, E.J. and Hong, L.S.
"The effect of oxygen and water on the dynamics of chip formation during grinding"
ASLE Trans. 12 (1969) 86

80. Graham, D. and Baul, R.M.
"An investigation into the mode of metal removal in the grinding process"
Wear 19 (1972) 301

81. Osman, M. and Malkin, S.
"Lubrication by grinding fluids at normal and high wheel speeds"
ASLE Trans. 15 (1972) 261

82. Kirk, J.A., Cardenas-Garcia, J.F. and Allison, C.R.
"Evaluation of grinding lubricants - simulation testing and grinding performance"
ASLE Trans. 20 (1977) 333

83. Whitton, P.W. and Ford, H.
"Surface friction and lubrication in cold strip rolling"
Proc. Inst. Mech. Engrs. 169 (1955) 123

84. Tsao, Y.H. and Sargent, L.B.
"A mixed lubrication model for cold rolling of metals"
ASLE Trans. 20 (1977) 55

85. Tsao, Y.H. and Sargent, L.B.
"Frictional and slip in the cold rolling of metals"
ASLE Trans. 21 (1978) 20

86. Schatzberg, P. and Felsen, I.M.
"Effects of water and oxygen during rolling contact lubrication"
Wear 12 (1968) 331

87. Tripathi, K.C.
"Development of polymeric films in rolling"
ASLE Lub. Eng. 33 (1977) 630

88. Hamaguchi, H., Spikes, H.A. and Cameron, A.
"Elastohydrodynamic properties of water in oil emulsions"
Wear, 43 (1977) 17

89. Linnenbom, V.J.
"The reaction between iron and water in the absence of oxygen"
J. Electrochem. Soc. 105 (1958) 322

90. Kubaschewski, O. and Hopkins, B.E.
"Oxidation of metals and alloys"
Butterwoths. (London) (1967)

91. Moore, A.J. and Mactagert, W.J.
"Effect of induced oxide film on the structure of the Beilby layer"
Proc. Roy. Soc. L. A212 (1952) 458.

92. Tingle, E.D.
"The importance of surface oxide films in the friction and lubrication of metals"
Trans. Faraday. Soc. 46 (1950) 93

93. Krause, H.
"Tribochemical reactions in the friction and boundary process of iron"
Wear 18 (1971) 403

94. Tamai, Y. and Sumitomo, M.
"On the nature of oil-burn on steel surfaces"
ASLE Lub. Eng. 33 (1975) 81

95. Blok, H.
"Measurement of temperature flashes in gear teeth under extreme pressure conditions"
I Mech. Eng. Gen. Disc. on Lubrication Vol 2 (1937) 14

96. Bowden, F.P., Ridler, K.E.N.
"Physical properties of surfaces III. The surface temperature of sliding metals. The temperature of lubricated surfaces"
Proc. Roy. Soc. L. A154 (1936) 640

97. Jaeger, J.C.
"Moving sources of hear and the temperature at sliding contacts"
Proc. Roy. Soc. N.S.W. 56 (1942) 203

98. Holm, P.
"Calculation of the temperature development in a contact heated in the contact surface, and application to the problem of the temperature rise in a sliding contact"
J. Appl. Phys. 19 (1948) 361

99. Holm, R.
"Temperature development in a heated contact with application to sliding contact"
J. Appl. Mech. 19 (1952) 369

100. Archard, J.F.
"The temperature of rubbing surfaces"
Wear 2 (1959) 438

101. Furey, M.J.
"Surface temperature in sliding contact"
ASLE Trans. 7 (1964) 133

102. Quinn, T.F.J.
"An experimental study of the thermal aspects of sliding contacts and their relation to the unlubricated wear of steel"
Proc. Inst. Mech. Engrs. 183 Pt 3P (1968-69)

103. Quinn, T.F.J.
"Oxidation wear"
Wear 18 (1971) 413

104. Quinn, T.F.J.
"The division of heat and surface temperatures at sliding steel interfaces and their relation to oxidational wear"
ASLE Trans. 21 (1978) 78

105. Ku, P.M., Staph, H.E. and Carper, H.J.
"On the critical contact temperature of lubricated sliding-rolling discs"
ASLE Trans. 21 (1978) 161

106. Nazaraj, H.S., Sanborn, D.M. and Winer, W.O.
"Direct surface temperature measurement by infrared radiation in elastohydrodynamic contacts and the correlation with the Blok flash temperature theory"
Wear 49 (1978) 43

107. Hsu, S.M. and Klaus, E.E.
"Estimation of the molecular junction temperature in four-ball contacts by chemical reaction rate studies"
ASLE Trans. 21 (1978) 201

108. Francis, S.A. and Ellison, A.H.
"Infrared spectra of monolayers on metal mirrors"
J. Optical. Soc. America 49 (1959) 131

109. Poling, G.W. and Leja, J.
"Infrared study of xanthane adsorption on vacuum deposited films of lead sulphide and metallic copper under conditions of controlled oxidation"
J. Phys. Chem. 69 (1965) 2139

110. Poling, G.W.
"Infrared studies of protective films formed by acetylene corrosion inhibitors"
J. Electrochem. Soc. 114 (1967) 1209

111. Dowson, D. and Higginson, G.H.
"A numerical solution to the elastohydrodynamic problem"
J. Mech. Eng. Sci. 1 (1959) 6

112. Cameron, A.
"Basic lubrication theory"
2nd Edition (1976) Ellis Horwood

113. Ling, F.F., Klaus, E.E. and Fein, R.S.
"Boundary lubrication - An appraisal of world literature"
ASME Research committee on lubrication (NY) Chapter 5 (1967)

114. Cameron, A., Gordon, A.N. and Symm, G.T.
"Contact temperatures in rolling/sliding surfaces"
Proc. Roy. Soc. (London) A286 (1965) 45

115. Shaw, D.J.
"Introduction to colloid and surface chemistry"
2nd edition (1972) Butterworths

116. Lewis, G.N. and Randall, M.
"Thermodynamics"
2nd edition (1961) McGraw-Hill

117. Burn, A.J.
"Symposium on reaction of molecular oxygen with organic compounds"
Stanford research institute (1967). San Francisco

118. Seino, Y.
Private Communication

119. Cookson, J.O.
"Cutting fluids: how to work and their form"
Eng. 253 (1970) 557

120. Sprange, S.R. and Cunningham, R.G.
"Frictional characteristics of lubricants"
Indus. Eng. Chem. 51 (1959) 1049

121. Rounds, F.G.
"Effects of additives on the friction of steel on steel II. Additive-base oil interactions"
ASLE Trans. 8 (1965) 21

122. Spikes, H.A. and Cameron, A.
"Additive interference in dibenzyl disulphide extreme pressure lubrication"
ASLE Trans. 17 (1974) 283

123. Rounds, F.G.
"Additive interaction and their effect on the performance of a zinc dibenzyl dithiophosphate"
ASLE Trans. 21 (1978) 91

124. Cookson, J.O.
"An introduction to cutting fluids"
Tribology Feb (1977) 5

125. Hiley, R.W.
"Polysulphides and extreme-pressure lubrication"
Ph.D Thesis University of London (1976)

126. Forbes, E.S. and Reid, A.J.D.
"Liquid phase adsorption/reaction studies of organo-sulphur compounds and their load-carrying mechanism"
ASLE Trans. 16 (1973) 50

127. Spikes, H.A.
"Physical and chemical adsorption in boundary lubrication"
Ph.D Thesis Unversity of London (1971)

128. Cross, A.D. and Jones, R.A.
"An introduction to practical infrared spectroscopy"
Butterworth (London) third edition (1969) 39

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Effects of Adsorption of Some Surfactants on Antiwear Properties

SEIICHIRO HIRONAKA, YOSHIAKI YAHAGI*, and TOSHIO SAKURAI† (Member, ASLE)
Tokyo Institute of Technology, Tokyo, Japan
*Present address: Imperial College, London SW7 2BX, England
†Present address: Tokai University, c/o The Japan Petroleum Institute, Tokyo, Japan

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SEIICHIRO HIRONAKA, YOSHIAKI YAHAGI*, and TOSHIO SAKURAI† (Member, ASLE)
Tokyo Institute of Technology, Tokyo, Japan
*Present address: Imperial College, London SW7 2BX, England
†Present address: Tokai University, c/o The Japan Petroleum Institute, Tokyo, Japan

The adsorption of organic polar compounds onto iron sulfide and onto iron oxide was investigated using a flow microcalorimeter. The effects of a combination of an iron sulfide surface and surfactants on wear were examined in air and argon atmospheres using a ball-on-disk friction machine. The polar interaction and reactivity between organic polar compounds and iron sulfide are important functions for wear reduction. This was shown from the results obtained in the measurement of the heat of adsorption, amount of adsorption, heat of desorption and iron content in the desorption solution. The adsorption of stearic acid on the steel ball sulfidized in H_2S reduced wear significantly in the air atmosphere. Surfactants contribute considerably to wear reduction when used with sulfur EP additives which form an iron sulfide film.

INTRODUCTION

Some sulfur containing EP additives react with the metal surface and the iron sulfide film formed contributes to the partial EHD lubrication and to prevention of wear during severe sliding conditions (*1*), (*2*). Both stearicdibenzyl disulfide molecules were more strongly bound on iron sulfide than on an iron oxide surface, using autoradiograph technique (*3*). Iron sulfide and Fe_3O_4 produced on the rubbing surface were effective in EP lubrication (*4*). Iron sulfate $FeSO_4$ was detected on the steel surfaces, from EP additives during immersion and rubbing tests (*5*). The activity of sulfur EP additives depends both on the formation of sulfide film and on subsequent strong chemisorption of surfactant or EP molecules on top of the film (*6*). Cumulative heat of adsorption of surfactants correlated with their lubricating properties (*7*).

In the present work, the mechanism of the lubricity of surfactants was investigated by the measurements of the adsorption of surfactants on iron sulfide and the iron content in the desorption solution which was determined by atomic absorption analysis. Furthermore, the antiwear property of surfactants was investigated by a ball-on-disk friction machine with the steel ball sulfidized in H_2S.

EXPERIMENTAL

Materials

Adsorbent powders: $\alpha - Fe_2O_3$; purity > 99.98 percent. 100 to 200 mesh, surface area, 3.32 m^2/g, determined by Brunauer-Emmett-Teller (BET) method with nitrogen adsorption. FeS; purity > 99.97 percent. 100 to 200 mesh material, BET surface area 13.80 m^2/g. Fe_3O_4; purity > 99.99 percent, 100 to 200 mesh material, BET surface area 5.78 m^2/g. Prior to the use the adsorbents were degassed at 350°C for 4 hours at $1.33 \times 10^{-3} N/m^2$ (10^{-5}mmHg).

Adsorbates: Commercially available high-purity grade stearic acid (SA) was purified by recrystallization. Its purity was determined by elemental analysis and found to be above 99.7 percent, mp 69 – 70°C, n_D^{80} 1.430. Commercially available high-purity grade stearyl alcohol (SOH) was purified by recrystallization. Methyl stearate (MS) was identified by gas chromatography after column adsorption on copper powder.

Solvent: *n*-heptane as the solvent was of chromatographic grade and further purified by percolation through a silica gel-alumina column. It was dried in contact with a molecular sieve for two days and distilled in the presence of sodium wire (98.0 – 98.5°C/$1.01 \times 10^5 N/m^2$ (760 mmHg)), and then kept in contact with sodium wire.

Base oil: Hydrofinished oil was used which was purified by percolation through silica gel, alumina, and activated carbon columns. Viscosity was $32.2 \times 10^{-6} m^2/s$ (32.2 cSt) at 37.8°C, $5.3 \times 10^{-6} m^2/s$ (5.3 cSt) at 98.9°C.

Adsorption of Surfactants on Adsorbent

The flow microcalorimeter used in this work was reported in the previous paper (*7*).

Saturation method: The whole of the solvent stream is replaced by an adsorbate solution of equal flow-rate. The solution stream is continued until the concentration of adsorbate molecules on the powder bed comes into equilibrium with that in the solution. This results in an evolution of heat and also produces a peak in the recorder chart. By replacing the stream stepwise with solutions of increasing concentration, it is possible to saturate the adsorbent. The cumulative heat in this process is known as the integral heat of adsorption.

Injection method: While the solvent is flowing through the bed of the adsorbent, a steady base line is obtained in the recorder chart. A few microliters of a dilute solution of an adsorbate is suddenly introduced into the stream of the solvent. The adsorbate evolves heat during its contact with the powder bed and produces a peak in the recorder chart. From the area of the peak, the amount of heat evolved is determined.

The amount of adsorption was measured in the same way as that by Groszek (*8*):

$$x = tcf/w \qquad [1]$$

where x = amount of solute adsorbed in milligrams per gram
t = retention time in minutes
c = concentration of solute in milligrams per milliliter
f = flow rate of solution in milliliter per minute
w = weight of adsorbent in the precolumn in grams

Desorption of Surfactants from Adsorbent

The heat of desorption was measured as follows: surfactants which adsorbed sufficiently onto the powder at each concentration were desorbed by *n*-heptane as eluent at the same flow rate. The heat of desorption was calculated in the same way as heat of adsorption.

Iron Content in the Desorption Solution

Stearic acid, stearyl alcohol, and methyl stearate were adsorbed from their *n*-heptane solutions onto $\alpha - Fe_2O_3$ and FeS powders at a flow rate of 0.11 ml/min for 4 hours, and were then desorbed into *n*-heptane at a flow rate of 4.1 ml/min. Iron content in the desorption solution after 1, 10, and 30 minutes was measured by atomic absorption analysis. The analytical condition is shown in the footnote of Table 1.

Effect of Surfactants on Wear of Sulfidized Steel Ball

AISI 52100 steel balls of 4.76 mm (3/16 in) diameter were exposed to 100 percent H_2S for 4 hours during which they were rolled in the vessel. Table 2 shows the results of X-ray analysis of the film on the sulfidized steel ball. A film of troilite and pyrrhotite was formed.

The wear experiments were performed on the ball-on-disk friction machine (Fig. 1). The rotating disk was made of S55C steel (JIS G 3102, SAE 1055) of R_C 63 – 65, and was 45 mm in diameter. The AISI 52100 steel balls were 4.76 mm in diameter. The disk and ball were thoroughly washed in benzene and then cleaned with benzene reflux in a Soxhlet apparatus and finally dried in vacuum for 2 hours. The wear experiment was carried out in air and in argon atmospheres. The oil contained 0.1 weight percent of surfactant at 20°C. The machine load was 1 kg, while the disk was rotated continuously at 25 rpm for 60 minutes, giving a sliding distance of 8.5 m. All experiments were repeated three times and their average values were reported.

TABLE 1—IRON CONTENT IN DESORPTION SOLUTION BY ATOMIC ABSORPTION ANALYSIS.

	Fe CONTENT (ppb)		
n-Heptane as an eluent (ml)	4.1	41.0	123.0
Time (min)	1	10	30
FeS-SA	39.5	——	52.7
α-Fe_2O_3-SA	7.9	31.6	39.5
FeS-MS	9.2	40.8	48.7
α-Fe_2O_3-MS	13.2	21.1	29.0
FeS-SOH	7.9	13.2	28.9
α-Fe_2O_3-SOH	7.5	17.6	——

SA: stearic acid, MS: methyl stearate, SOH: stearyl alcohol.
Analytical condition:
503 HGA (Fe-Lamp)
Wave length 2483.3 Å
Dry 100°C—30s
ashed 500°C—30s
atomizing 2550°C—6s 15mV
All experiments were repeated three times and their average values are shown.

RESULTS AND DISCUSSION

As shown in Fig. 2, the cumulative heats of adsorption of stearic acid onto FeS and Fe_3O_4 powders were much higher than that onto α-Fe_2O_3. From this fact, it seems that a sulfide film adsorbs more polar compounds than a ferric oxide film.

Figures 3 and 4 show the amount of adsorption and heat of adsorption, respectively, of stearic acid, stearyl alcohol, and methyl stearate from *n*-heptane onto FeS and α-Fe_2O_3. These figures show that stearic acid or stearyl alcohol adsorbed more actively onto FeS compared with other compounds. Stearic acid adsorbed strongly on FeS and, even at low concentration, its heat of adsorption per square meter was remarkably high.

The heat of desorption of stearic acid from FeS and α-Fe_2O_3 was smaller than that of stearyl alcohol as shown in Fig. 5. Table 3 shows the ratio of heat of desorption to heat of adsorption at 7 m mol/l. Stearic acid adsorbed intensively onto FeS and α-Fe_2O_3 and might be difficult to desorb.

These results suggest that the polarity and chemical reactivity are important factors in the adsorption of surfactants onto iron sulfide. The authors propose that stearic acid adsorbs intensively on the film such as FeS formed on the metal surface under extreme pressure lubrication and improves the lubricity. Possibly the polar compound reacts tribochemically with iron sulfide to form the effective lubricating film.

Table 1 shows iron content measured in the desorption solutions. In the combination of FeS-SA, the iron content was considerably higher after 1 minute than those of other

TABLE 2—ANALYSIS OF SULFIDIZED BALL BY X-RAY DIFFRACTION

LATTICE SPACING d (Å)	INTENSITY*	FeS (TROILITE) ASTM INDEX NO. 11-151	$Fe_{1-x}S$ (X = 0.12) (PYRRHOTITE) ASTM INDEX NO. 22-1120	α-Fe
5.20	M	5.4	5.27	—
2.99	S	2.98	2.98	—
2.66	M	2.66	2.64	—
2.53	M	2.52	—	—
2.10	M	2.09	—	—
2.03	VS	—	—	2.03
1.93	M	1.92	1.91	—
1.73	VS	1.72	1.72	—
1.43	VS	—	1.43	1.43

*VS = very strong, S = strong, M = medium

combinations regardless of the small ratio of heat of desorption to heat of adsorption. Stearic acid may react with iron sulfide and its chemical reaction product may be dissolved into *n*-hetane. However, the iron content in desorption solution of α-Fe_2O_3-SA combination after 3 minutes was nearly similar to that of FeS-SA combination after 1 minute. With the combination of FeS-SOH and α-Fe_2O_3-SOH, the iron contents were relatively smaller than those of other combinations. Chemical reactivity of stearyl alcohol to FeS and α-Fe_2O_3 was lower compared with that of stearic acid. Methyl stearate may gradually react with iron sulfide as a result of the hydrolysis of methyl stearate.

Since we have established that some surfactants were strongly adsorbed on FeS powder, the wear behavior of sulfidized balls was compared with that of steel balls in air and in argon, using a ball-on-disk friction machine. Table 4 shows the wear test results of sulfidized and unsulfidized steel balls in the oil containing 0.1 weight percent surfactants in air and in argon atmospheres. Wear volume of the sulfidized balls in the oil containing surfactants was much smaller in the air atmosphere than in the argon atmosphere.

The predominant effect of stearic acid on the wear of sulfidized balls could be explained by its strong adsorption and possible reactivity. These results also suggest that oxygen has a pronounced role of reducing the wear of the sulfidized balls with surfactants comparing with that of the unsulfidized balls.

On the other hand, in argon atmosphere, the wear of the sulfidized balls with additives was higher than those without additives and higher than those obtained with the unsulfidized balls. This result shows that oxygen is favorable for the wear reducing abilities of surfatants to FeS, but, in argon atmosphere, the reaction of these compounds with an FeS surface seems to be vigorous which might promote chemical wear. The sulfur atoms released after the reaction between

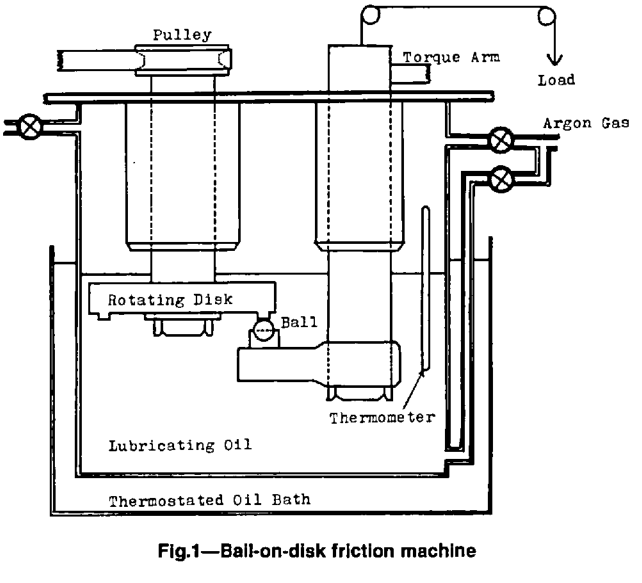

Fig.1—Ball-on-disk friction machine

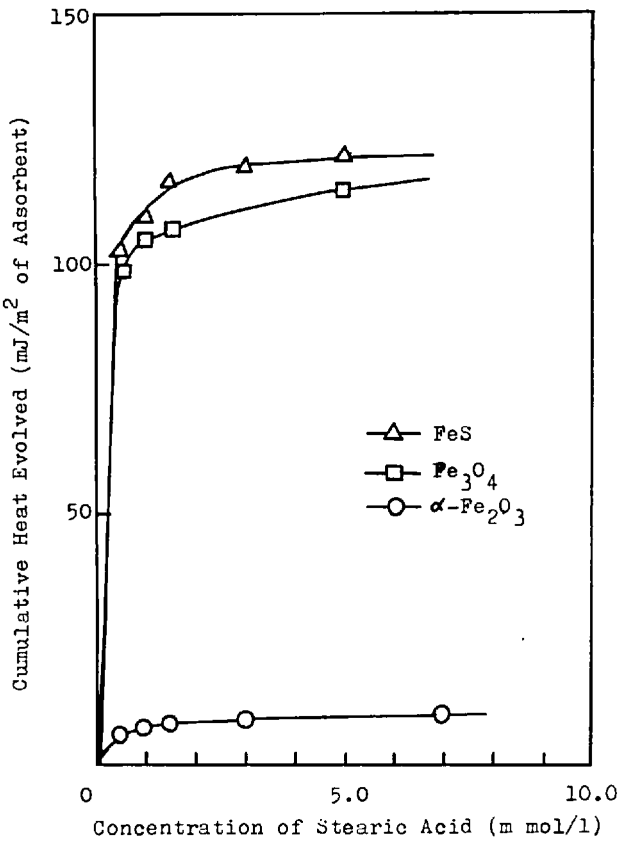

Fig. 2—Cumulative heats of adsorption of stearic acid from *n*-heptane onto FeS, α–Fe_2O_3, and Fe_3O_4 powders.

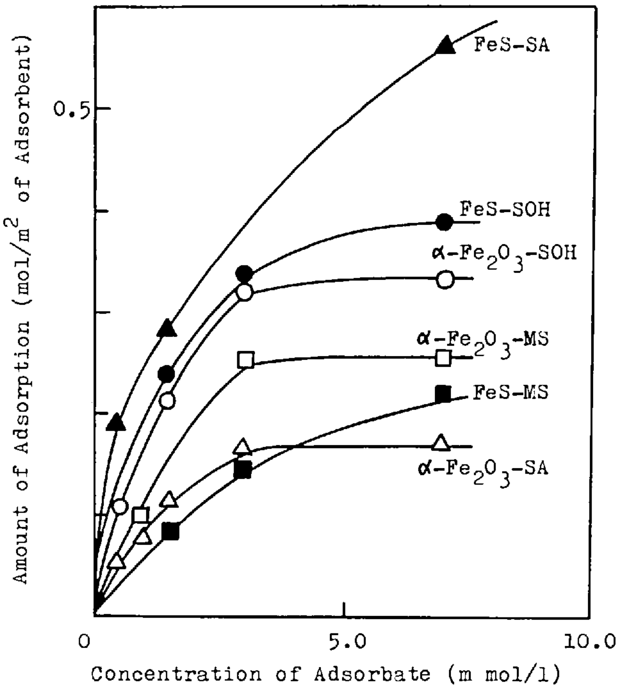

Fig. 3—Amount of adsorption of some polar substances from n-heptane onto FeS and α-Fe$_2$O$_3$ powders.

surfactants and FeS may be replaced with oxygen (9) and may form the iron oxide on the surface to prevent wear. In argon atmosphere, the released surface atoms may act corrosively to the rubbing surface and promote chemical wear.

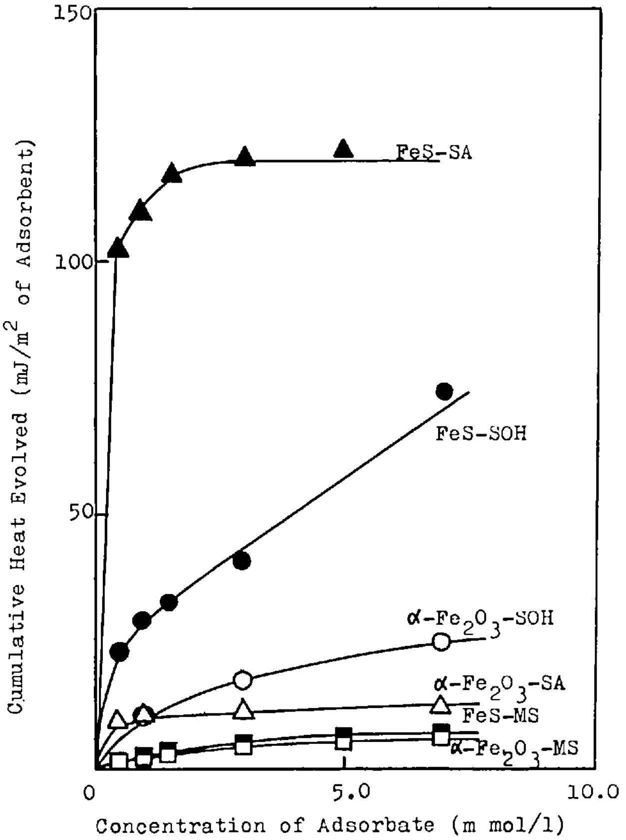

Fig. 4—Cumulative heats of adsorption of some polar substances from n-heptane onto FeS and α-Fe$_2$O$_3$ powders.

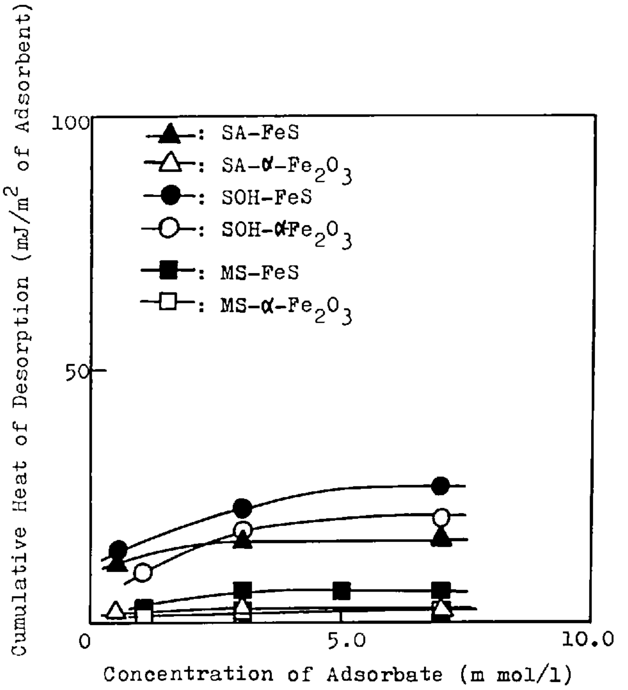

Fig. 5—Heats of desorption of some polar substances at various concentrations from FeS and α-Fe$_2$O$_3$ into n-heptane.

The reactivity of the surfactant with iron may depend on the properties of the surfactant which are generally included in lubricating oils and depend on the strength of bonding between iron atoms and oxygen or sulfur atoms. The lattice energies of FeS and α-Fe$_2$O$_3$ were calculated and estimated by Kapustinskii's equation (10), as shown in the Appendix. The lattice energy (−4.82 MJ/mol) of α-Fe$_2$O$_3$ is much smaller than −0.18 MJ/mol of FeS. This means that the surfactants react more easily with FeS then with α-Fe$_2$O$_3$. The surfactants may adsorb more intensively onto FeS than onto α-Fe$_2$O$_3$. In air, those wear reducing abilities for the sulfidized ball were greater than the steel ball due to the moderate reaction.

CONCLUSION

The results obtained here suggest the mechanism of the adsorption and the reaction of surfactants with sulfidized steel and their antiwear properties.

It was found that the surfactants, stearic acid, stearyl alcohol, and methyl stearate adsorbed more actively on FeS powder than on α-Fe$_2$O$_3$ powder. The authors propose that

TABLE 3—RATIO OF HEAT OF DESORPTION TO HEAT OF ADSORPTION*

ADSORBATE	ADSORBENT	RATIO
Stearic acid	FeS	0.1
Stearic acid	α-Fe$_2$O$_3$	0.2
Stearyl alcohol	FeS	0.5
Stearyl alcohol	α-Fe$_2$O$_3$	0.8
Methyl stearate	FeS	0.8
Methyl stearate	α-Fe$_2$O$_3$	0.8

*at 7 m mol/l

TABLE 4—EFFECTS OF ATMOSPHERE AND SURFACTANT ON WEAR*

	WEAR VOLUME, X 10^{-6}mm^3							
ATMOSPHERE	IN AIR				IN ARGON			
ADDITIVE	NONE†	STEARIC ACID	STEARYL ALCOHOL	METHYL STEARATE	NONE†	STEARIC ACID	STEARYL ALCOHOL	METHYL STEARATE
Sulfidized ball	19.1	0.2	8.2	11.5	12.5	22.6	22.5	22.5
Steel ball	19.8	5.5	17.3	13.9	15.7	6.6	6.2	10.3

*Ball-on-disk friction machine, sliding distance 8.5m, 20°C, 1 kg, 0.1 weight percent additive.
†Base oil: hydrofinished oil, viscosity 32.2 × 10^{-6}m^2/s (32.2 cSt) at 37.8°C, 5.3 × 10^{-6}m^2/s (5.3 cSt) at 98.9°C.
All experiments were repeated three times. The average values are shown.

the polar interaction and chemical reactivity between the surfactants and an iron sulfide film are important for wear reduction during lubrication in air.

The surfactants may react more readily with an FeS surface than with an α-Fe_2O_3 surface because the lattice energy of the former is much higher than that of the latter.

In a sliding system lubricated with the stearic acid solution, the wear of sulfidized balls was much smaller in air than that in argon atmosphere. In argon atmosphere, the released sulfur atoms may act corrosively to the rubbing surface promoting chemical wear. Oxygen may prevent the progressive sulfurization reaction on the ball surface.

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REFERENCES

(1) Tomaru, M., Hironaka, S. and Sakurai, T., "Effects of Oxygen on the Load Carrying Actions of Some Additives," *Wear*, **41**, 117-140 (1977).

(2) Sethuramiah, A., Okabe, H. and Sakurai, T., "Effect of Surface Temperature in Extreme Pressure Lubrication," *Bull. Japan Pet. Inst.*, **14**, 1, 27-39 (1972).

(3) Sakurai, T., Ikeda, S. and Okabe, H., "The Mechanism of Reaction of Sulphur Compounds with Steel Surfaces During Boundary Lubrication using S-35 as a Tracer," *ASLE Trans.*, **5**, 1, 67-74 (1962).

(4) Godfrey, D., "Chemical Changes in Steel Surfaces during Extreme Pressure Lubrication," *ASLE Trans.*, **5**, 1, 57-66 (1962).

(5) Bird, R. J. and Galvin, G. D., "The Application of Photoelectron Spectroscopy to the Study of E. P. Films on Lubricated Surfaces," *Wear*, **37**, 1, 143-167 (1967).

(6) Spikes, H. A. and Cameron, A., "Additive Interference in Dibenzyl Disulfide Extreme Pressure Lubrication," *ASLE Trans.*, **17**, 4, 283-289 (1974).

(7) Hironaka, S., Yahagi, Y. and Sakurai, T., "Heats of Adsorption and Anti-wear Properties of Some Surface Active Substances," *Bull. Japan Pet. Inst.*, **17**, 2, 201-205 (1975).

(8) Andrews, G. I., Groszek, A. H. and Hairs, N., "Measurement of Surface Areas of Basal Plane and Polar Sites in Graphite and MoS_2 Powders," *ASLE Trans.*, **15**, 3, 184-191 (1972).

(9) Buckley, D. H., "Oxygen and Sulfur Interactions with a Clean Iron Surface and the Effect of Rubbing Contact on These Interactions," *ASLE Trans.*, **17**, 3, 206-212 (1974).

(10) Kapustinskii, A. F., "Lattice Energy of Ionic Crystals," *Rev. Chem. Soc.*, **10**, 283-294 (1956).

APPENDIX

	LATTICE ENERGY (X MJ/mol)
FeS	−0.18
α-Fe_2O_3	−4.82

The lattice energies of iron sulfide and iron oxide were calculated by the following equation:

$$U = \frac{287.2\gamma Z_1 Z_2}{R_c + R_a} \left(1 - \frac{0.345}{R_c + R_a} \right)$$

$$U = \frac{N_o A Z_1 Z_2 e^2}{R_o} \left(1 - \frac{P}{R_o} \right)$$

U = lattice energy
γ = the number of ions
R_c, R_a = the formal 6-coordinate radii of the cation and anion in Angstrom units
Z = charge
e = 4.803 × 10^{-10} esu
A = Madelung constant
R_o = internuclear distance
N_o = Avogadro's number
P = parameter, 0.345