Dynamics of dual film formation in boundary lubrication of steels
Part I. Functional nature and mechanical properties

Bülent Çavdar and **Kenneth C. Ludema***

Mechanical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2125 (U.S.A.)

Abstract

Effective "breaking-in" of lubricated steel surfaces has been found to be due primarily to the rate of growth of "protective" films of oxides and compounds derived from the lubricant. The protection afforded by the films is strongly dependent on lubricant chemistry, steel composition, original surface roughness and the load/speed sequence or history in the early stages of sliding. Given the great number of variables involved it is not possible to follow more than a few of the chemical changes on surfaces using the electron, ion and X-ray column analytical instruments at the end of experiments. Ellipsometry was therefore used to monitor the formation and loss of dual protective films in real time, and detailed chemical analysis was done at various stages to calibrate the ellipsometer. This work is reported in three interlinking parts: I, functional nature and mechanical properties; II, chemical analyses; III, real-time monitoring with ellipsometry.

1. Introduction

1.1. General Background

For economic reasons, most lubricated sliding and rolling components operate near the lower limits of adequate lubrication, known as boundary lubrication. During use most components, such as cams/followers, piston rings, wet brakes and clutches, and gears operate momentarily with insufficient lubrication, such as during high loads, during sustained low speeds, at start-up, or with momentary interruption of lubricant. Under these conditions a form of damage known as scuffing may occur on the contacting surfaces.

Scuffing may progress to a more serious form of damage if overload etc. are sustained, but often "heals" if the overload is removed. The most vulnerable stage in the life of tribological surfaces is at the beginning of operation of a newly made surface. The exact reason for this early vulnerability is not known, although several strategies are followed with various mechanical components early in their use to "break them in". Generally, the act of "breaking-in" consists in a low intensity of operation, which prepares a surface to withstand higher intensity than could be sustained without the break-in procedure.

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*Author to whom correspondence should be addressed.

The most widely held notion in mechanical engineering is that break-in consists in smoothing the surfaces so that existing lubrication is adequate to prevent contact between asperities on opposing surfaces. It is generally assumed also that making a surface very smooth in the manufacturing process assures, or perhaps even replaces, adequate break-in. This cannot be an adequate explanation because some surfaces become rougher during break-in, some become smoother and some remain unchanged. Further, the optimum surface roughness for adequate break-in is different for each of several examined microstructures of steel and iron [1].

In the tribology literature break-in and scuff prevention is explained in terms of the formation of a thin "protective" film that forms by adsorption from reactive chemical constituents in the (liquid) lubricant. Over the last 40 years the chemistry of these films has been the subject of much discussion, particularly with a view to formulating the reactive "additives" to be mixed into lubricants. In spite of the great amount of very good research into the chemical aspects of boundary lubrication, and in spite of the great success of the lubricant and additive industries, there are several aspects of break-in that are not well explained, for example the following:

(1) the relative ease of break-in and scuff healing in soft steels compared with hard steels, the difference apparently not being significantly influenced by lubricant chemistry;

(2) the separate effects of overload and speed on the degree of protection provided by various break-in procedures;

(3) the reason why protective films formed in oil containing "antiwear" additives produce a higher coefficient of friction than those without additives;

(4) the mechanical nature and properties of "protective" films, especially for tribological modelling purposes.

1.2. Chemistry of protective films

The composition of protective films, sometimes also called boundary layer films, has been the subject of learned papers for over 40 years. In early days when severe friction tests (e.g. with a four-ball tester) were run with various lubricants (and additives), surface substances were seen and the composition of these films was inferred from the composition of the lubricant. As analytical instruments became available they were applied to analyzing the films, but usually with inconclusive results because the films are thin and composed of many non-stoichiometric compounds. Most papers on the subject report incomplete analyses and conflicting conclusions on the composition of the films. Generally, the film has been proposed to consist of a "friction polymer" [2-4], oxides of various types [5-7] and mixtures of several simple compounds [8-10]. Details of these findings are given in the introduction to Part II [11]. Undoubtedly, the diversity of opinion on film chemistry has at least four causes;

(1) many different methods are used to "clean" specimens before inserting them into the electron, ion or X-ray analytical instruments.

(2) the several detailed analyses reported in the literature were done with different steels, operated in experiments that differed from each other in applied load, sliding speed and specimen geometry, each of these conditions producing different films;

(3) in some cases analyses were done during the progression of a test, by interrupting the test, cleaning the specimen, etc; the investigators assumed that the act of stopping the tests, cleaning, holding for a long time in the analytical instruments and resuming testing was no different than an uninterrupted test;

(4) several analyses such as electron spectroscopy for chemical analysis (ESCA), elastic recoil detection (ERD) and ellipsometry are sensitive to surface roughness.

1.3. Mechanics of protective films

The degree of protection offered by an adsorbed film depends on its mechanical properties (composition) and thickness [12, 13], which in turn depend on the conditions under which it was formed, the condition under which it is maintained, and the nature of overload to which it may eventually be subjected. Previously published papers on film composition reported results of analyses of specimens selected from across a wide range of loads, speeds, steel hardnesses, specimen shapes etc. From these results it has not been possible to connect film composition, film properties and thickness with the conditions of operating the sliding system. Kang and Ludema [1, 13] reviewed many of these papers and concluded that a new method of film measurement would be very useful. They developed a method of ellipsometry for this purpose. They interrupted their sliding tests to make ellipsometry measurements in air, without an oil film. Electron column instruments were used to determine the film composition. The refractive index of the films, now of known composition, was taken from published data and used in ellipsometric calculations of film thickness.

The results of Kang and Ludema were found to be only approximate, for several reasons, but primarily because of changes in surface roughness during some tests. Surface roughness was also found to influence the progression of film growth and protective qualities of films. To continue using ellipsometry it was therefore necessary to control the surface roughness during the sliding tests. Suzuki and Ludema [14] and Lee and Ludema [15] determined the conditions under which the desired surface roughness could be maintained in lubricated sliding tests, which aided considerably the selecting of the test conditions reported in these papers.

1.4. Scope of the present work

A research program was planned to answer the questions posed at the end of Section 1.1. For this purpose the following experimental conditions and materials were used:

(1) a cylinder (non-rotating) on flat plate geometry was used with steel specimens, sliding in lubricants covering a range of reactivities;

(2) a four-Stokes parameter, high speed, computer-controlled ellipsometer was used to monitor changes in film composition and thickness *in situ* under oil;

(3) thorough chemical analyses were done on the films to determine composition and to calibrate the ellipsometric results.

Given the many variables that influence the formation and loss of films, these are relatively few but are adequate for perspective. Further details follow in the next sections.

2. Experimental details

Since this work was primarily done to explore questions raised in previous work [12–14], the same test devices were used. The geometry of the test is the cylinder-on-flat as shown in Fig. 1. The cylinder was taken from a roller bearing and thus is a crowned cylinder. It was 52100 steel, hardness 58 HRC, 6.35 mm long and 6.35 mm diameter. The initial surface roughness in the longitudinal direction was 0.02–0.025 μm R_a.

The flat surfaces were disks 50 mm in diameter and about 4 mm thick. The disks were all made of 4340 steel, oil quenched from 900 °C and tempered to hardnesses in the range 22–60 HRC. The hardnesses are given in Table 1. A range of hardnesses
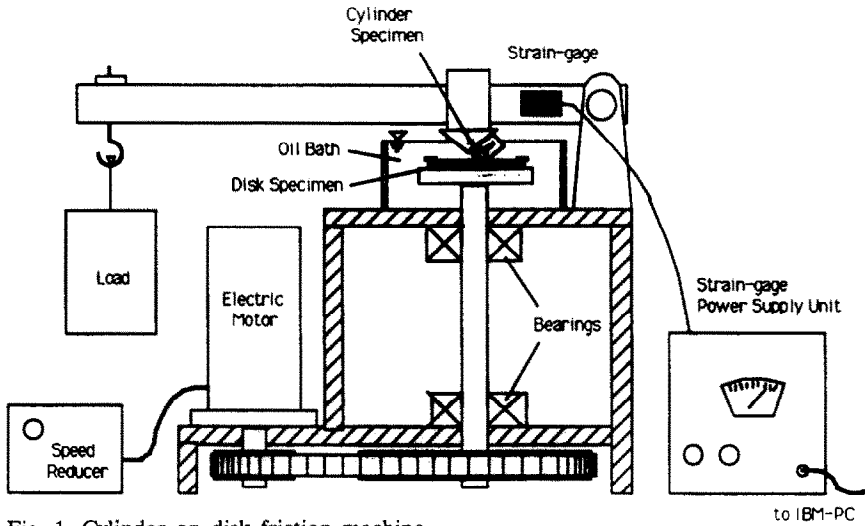
Fig. 1. Cylinder on disk friction machine.

TABLE 1

Specimen notation

Disk hardness (Rockwell C)	Oil type					
	Paraffin oil (code M)	Paraffin oil 0.5% ZDP (code M05Z)	Paraffin oil 1% ZDP (code M1Z)	Paraffin oil 2% ZDP (code M2Z)	Base oil (code B)	Base oil 1% ZDP (code B1Z)
22					22-B	
30			30-M1Z	30-M2Z		
44	44-M			44-M2Z		
45	45-M					
46					46-B	
47				47-M2Z		
48	48-M			48-M2Z		48-B1Z
53	53-M			53-M2Z		
54	54-M			54-M2Z	54-B	
55	55-M				55-B	55-B1Z
57			57-M1Z			
58	58-M				58-B	
59	59-M			59-M2Z		
60	60-M	60-M05Z		60-M2Z		

was used to explore the possibility that much of the ambiguity in the literature on the effectiveness of lubricants and additives arises from different investigators using different hardnesses of steels in their experiments. The steel specimens were prepared by lapping to a roughness of 0.01–0.02 μm R_a. Whereas this roughness is an order of ten less rough than the better commercial surfaces, smooth surfaces reduce ambiguities in the results from analytical instruments. In particular, good results can be achieved with the ellipsometer if the surface roughness is less than 0.13 μm R_a [16].

Two kinds of bulk oil were used as lubricants: white paraffin oil made by Mallinckrodt Company (LOT 6358 KCHB), and base engine oil supplied by the National Institute of Standards and Technology (NIST) having kinematic viscosities of 25.4 cSt and 30.25 cSt respectively. The two oils differ in that the paraffin oil consists of only straight saturated hydrocarbons whereas the base oil includes 32.5% aromatics and 0.49% sulfur. Experiments were done with no additives in the oils, with 0.5% ZDP, 1% ZDP and 2% ZDP as shown in Table 1. ZDP (zinc dialkyldithiophosphate) was also supplied by NIST.

The experiments were done mostly at a sliding speed of 0.06 m s^{-1}. Most of the tests were done with a step loading sequence which considerably shortens the time needed to build up the films of interest. In most cases the steps were 62.5 N in 10 min intervals. In other tests the steps were 25 N in 30 min intervals and 125 N in 10 min intervals. The friction force was measured during the test. Wear of the cylinder was measured with the aid of a microscope, and the surface roughness of each disk was measured at the end of each test.

The chemical composition of the films on the disk surfaces was monitored qualitatively during the tests with an automated Mueller Matrix ellipsometer as shown in Fig. 2. The disk specimens were submerged in oil, and there were submerged windows on tubes in the optical path. Measurements could be made while the disks were rotating, but the most consistent measurements were taken with the disks stopped very briefly at the same point during the tests. Measurements were made at angles of incidence from 50° to 70° to determine both the film thickness and the index of refraction of the film [17, 18].

After the sliding experiments some of the specimens were cut into small pieces for quantitative chemical analysis. The specimens were washed in hexane to remove the liquid lubricant without removing the surface films of interest. The analytical methods used were the following:

(1) ESCA to determine the chemical bonding and elemental identification of the very top surface layers of the films (approximately 1–2 nm);
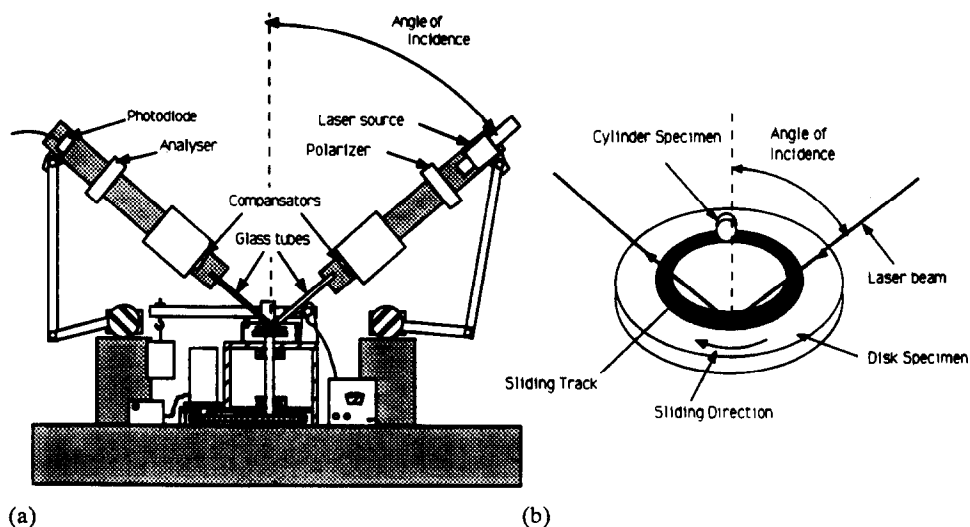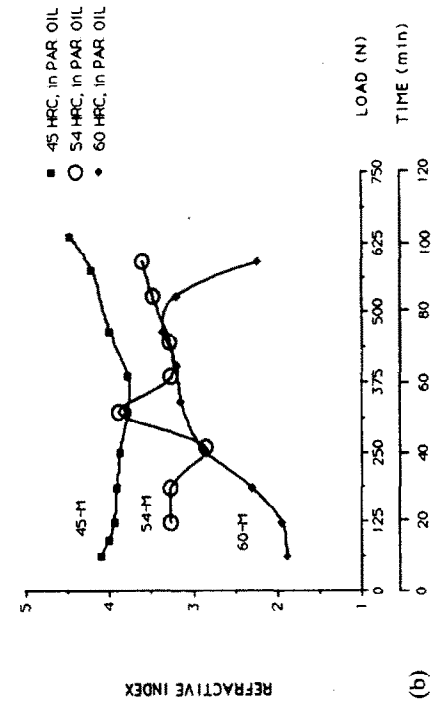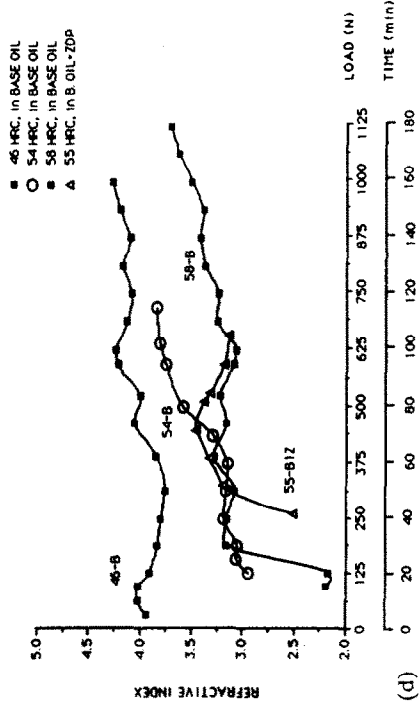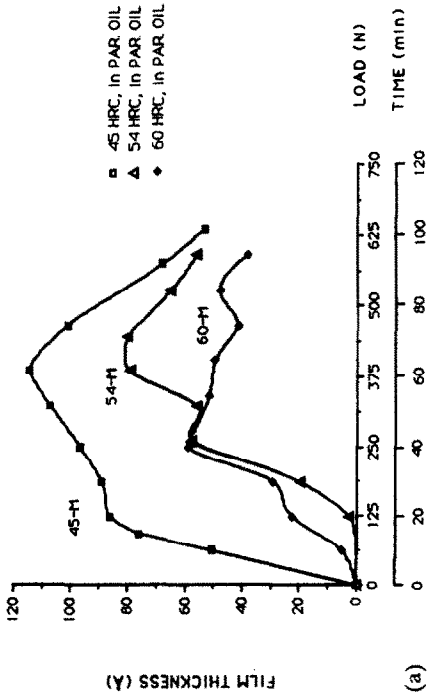

(a) (b)

Fig. 2. Experimental set-up: (a) automated Mueller matrix ellipsometer and friction machine, (b) expanded view of the sliding surface.

(a)

(b)

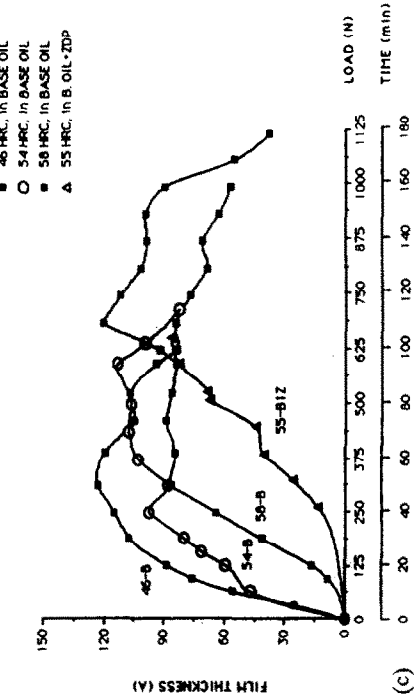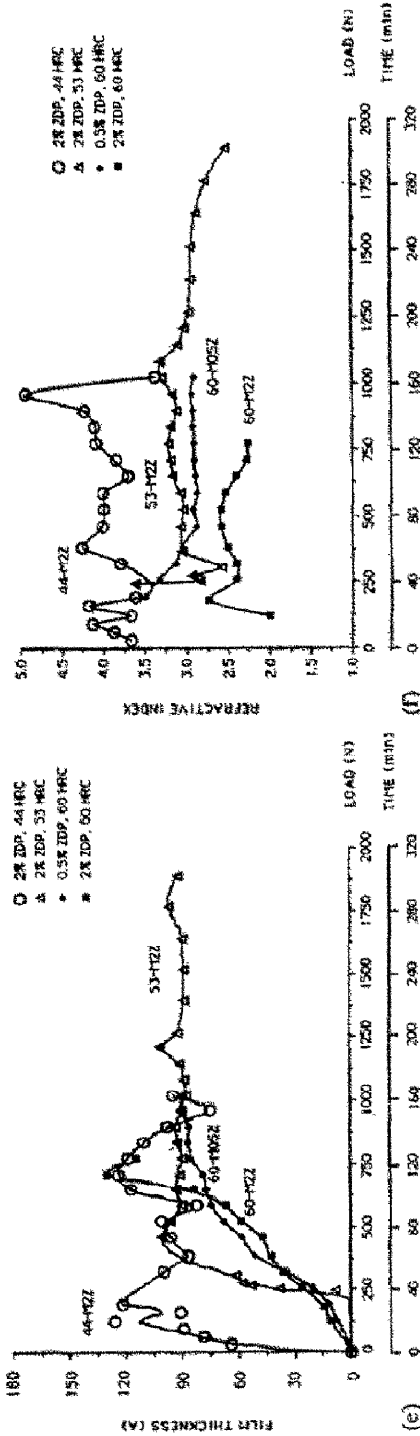(c)

(d)

Fig. 3. The growth of boundary films under increased loads on specimens of a range of hardness and in various lubricants: (a) film growth in paraffin oil, (b) refractive index of the films; (c) film growth in base oil, (d) the refractive index of the films; (e) film growth in paraffin oil with ZDP, (f) refractive index of the films. The load steps were 62.5 N in 10 min intervals.

(2) ERD to determine the hydrogen content of the films;

(3) Fourier transform IR (FTIR) analysis to detect organic compounds.

3. Results

3.1. Physical durability of the films

Figures 3(a), (c) and (e) show changes in film thickness during step loading tests for a range of disk hardnesses and for three lubricants. Differences may be seen in the initial rate of film growth and the maximum film thickness achieved. The films formed in oil containing ZDP were usually thinner than the films formed in oils without ZDP, yet they sustained higher loads before thinning. For example, the 53-M2Z specimen was successfully loaded up to 1890 N (Fig. 3(e)), whereas the non-ZDP films (films formed in paraffin and base oils alone) began to thin with loads of about 400–700 N (Fig. 3(a), (c)). Figure 4 shows that films that become thin owing to high loads can be built up again by decreasing the load although the composition may change. Here, a 54 HRC specimen has been step loaded up to 589 N in paraffin oil. The maximum film thickness was reached at a load of 446 N. Then the thickness began decreasing with increasing load. When the step loading was reversed, fast recovery of the film was observed.

3.2. Appearance and refractive index

The differences in film durability were accompanied by differences in film appearance to the eye and under an optical microscope. Non-ZDP films which formed on soft disks were black but the films formed on hard disks were light colored. Films formed in oil containing ZDP were generally lighter than non-ZDP films for the same hardness of steel. Different appearances were obviously due to the different chemistry of the films. The refractive indices of the films are given in Figs. 3(b), (d) and (f). Darker films formed on softer substrates, and these had higher refractive indices. The refractive index of the films decreased with increasing ZDP content in the oil. The load produced opposite effects: the refractive index of the films which formed in plain mineral oils usually increased under high loads, whereas the refractive index of the ZDP induced films decreased under high load.

3.3. Chemistry

Four of the specimens in Fig. 3 plus a fifth specimen were examined by ESCA and ERD (see Table 2). The films formed in plain mineral oils consist of iron, carbon, oxygen and hydrogen. The films formed in mineral oils containing ZDP contained up to 15% total of zinc, phosphorus and sulfur besides, iron, carbon, oxygen and hydrogen. The coexistence of an iron oxide and another iron compound on all surfaces was shown by ESCA. The presence of a large amount of carbon and oxygen (via ESCA), hydrogen (via ERD) and some organic compounds (via FTIR) suggests that the second iron compound was an organoiron compound (OIC). A small amount of iron–carbon compound was also detected near to the steel substrate. Details of the spectrometric data analysis are presented in Part II [11].

The ESCA data show amounts of oxide relative to OICs in the films. Results are given in Table 3. Data were taken from the "top" of the film and at various depths after ion etching. On 47-M2Z and 54-M specimens, no depth profiling was applied.

The highest OIC fraction is always found at the top of the film, and the lowest is at the bottom. Metallic iron is mixed with the oxide in amounts that often exceed
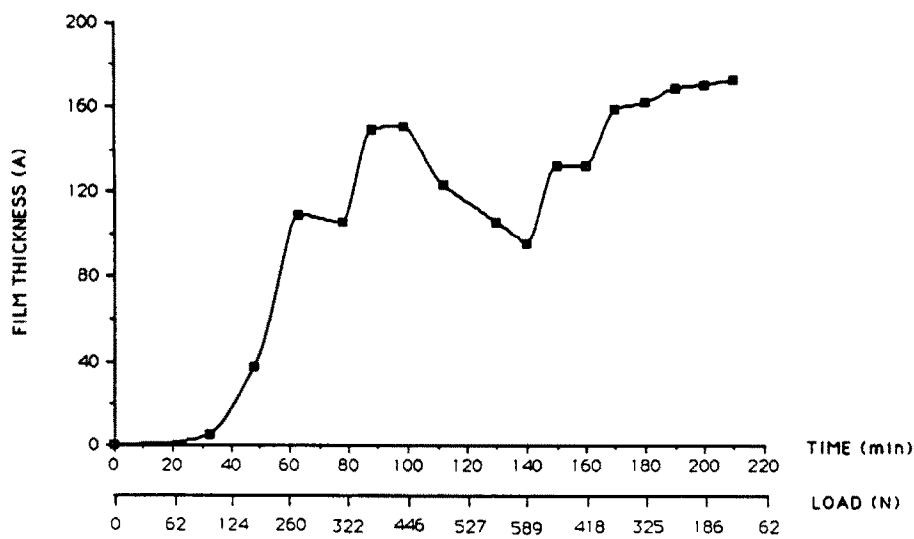
(a)
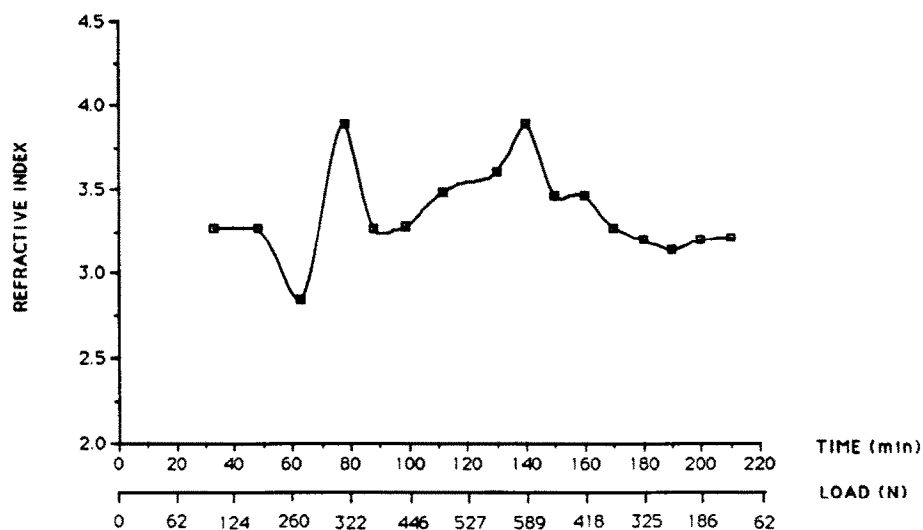
(b)

Fig. 4. An example of film thinning under overload and film recovery when the overload is removed on 54-M specimen. (a) Film thinned exponentially, recovered logarithmically, (b) film refractive index increased when film thinned, decreased when recovered. The load steps were 62.5 N in 10 min intervals.

that of the oxide. The darker films, which had a high refractive index, contained large amounts of oxide; the lighter films formed in oil containing ZDP had less oxide and more OIC. The refractive index of oxide–metal mixture films was found to be about 4.2 and that of OIC was between 1.5 and 2.5, depending mainly on the iron content. The relative amounts of these components in films can be estimated from the refractive index of the films. A measurement of the refractive index of a film containing oxides

TABLE 2

ESCA and ERD specimens

Specimen	Maximum load (N)	Sliding distance	Final film thickness (Å)	Refractive index of film
54-M	589	756	93	3.20
54-B	713	432	82	3.84
47-M2Z	1890	1008	124	3.80
53-M2Z	1890	1008	86	2.52
55-B1Z	527	684	107	3.14

TABLE 3

Film compositions calculated from ESCA data

Specimen	Number of etchings	Ion etching time (min)	Depth (Å) (approximate)	Pure iron (%)	iron oxide (%)	OIC (%)
54-M	1	0.5	20–30	28	33	39
54-B	1	0.3	15–20	0	48	52
	2	1.6	60–90	37	46	17
47-M2Z	1	0.3	15–20	0	0	100
53-M2Z	1	0.5	20–30	39	8	53
	2	1	40–60	56	8	36
	3	1.5	60–80	67	7	26
	4	2	80–100	80	6	14
	5	2.5	100–120	88	4	8
	6	3	120–140	91	3	6
55-B1Z	1	0.15	10–15	1	12	87
	2	0.4	20–30	10	14	76
	3	1.1	45–60	35	16	49
	4	1.8	65–95	52	10	38
	5	2.5	100–120	64	11	25

and OICs will produce an index between those of the single constituent. This connection assured that the use of the ellipsometer was adequate for following the progression of film growth without the need to interrupt the tests for detailed chemical analysis.

Data on the index of refraction are shown in Figs. 3(b), (d), (f) and Fig. 4(b). It should be noted that changes in the ratio of oxide to OIC occur during the tests. Also, it can be seen in Fig. 4 that when the film thickness was decreasing owing to high load the refractive index of the film increased, showing that the iron oxide percentage increased. Then when the film was recovering owing to decreased load the refractive index decreased, indicating an increasing organic content in the film.

3.4. Lubricated friction

Friction coefficient measurements showed a difference between the cases of plain mineral oils and mineral oils with ZDP, as seen in Fig. 5. In plain mineral oils, at the beginning of sliding, the friction coefficient was high, around 0.17. After a short time it decreased to 0.13. In most of the oils containing ZDP, the friction coefficient
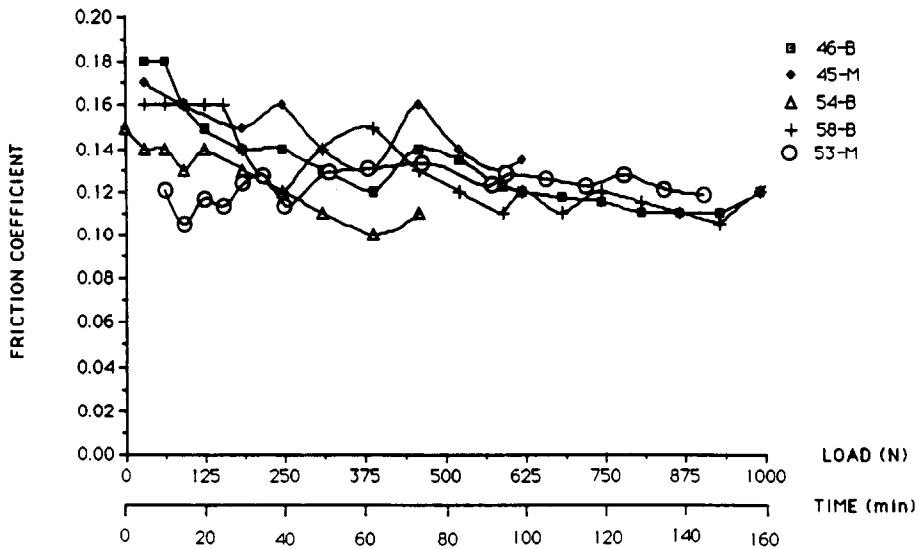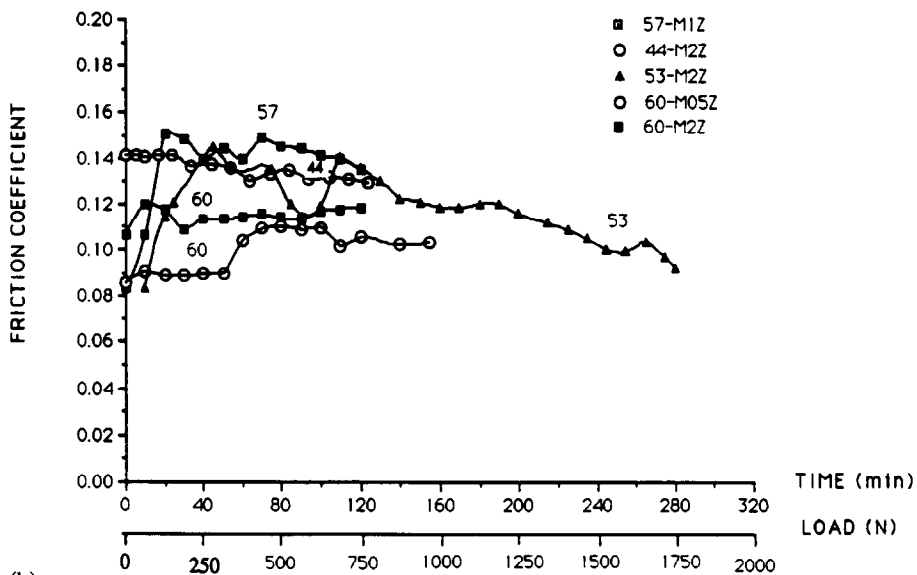
Fig. 5. Change in friction coefficient (a) in plain mineral oils, (b) in minerals with ZDP. The load steps were 62.5 N in 10 min intervals.

was low, 0.13 at the beginning, and did not change. The calculated elastohydrodynamic lubrication minimum lubricant film thickness h_{min} [19] at the start of sliding was 9.5 nm, the composite surface roughness, $\sigma = (R_{a,disk}^2 + R_{a,cyl}^2)^{1/2}$, was 28 nm. Thus the Λ ratio, h_{min}/σ, was 0.34. When the surfaces were roughened under high loads, Λ became still smaller. The value $\Lambda < 1$ indicates that the sliding conditions were in the boundary

lubrication regime, which was confirmed by values of coefficient of friction greater than 0.1.

3.5. Mechanical properties of the observed films

Sliding tests were carried out to determine whether the films by themselves, without a liquid phase present, behave like viscous liquids or soft solids. Films formed during the film durability tests were washed of liquid lubricant by hexane and dried. A new slider was set upon the dried specimen for a friction test. In order not to damage the films, much lower loads and speeds than those which led to their formation were applied. The friction coefficient was measured at 0.0013 m s^{-1}, 0.013 m s^{-1} and 0.13 m s^{-1}. The results are presented in Table 4. There was no consistent increase in friction coefficient with sliding speed except where the surfaces became damaged during the test. Constant friction force over a range of sliding speeds indicates that the films behaved much more like soft solids than like viscous liquids.

For all the films formed in ZDP, the dry friction coefficient was about half of those of non-ZDP cases. However, the dry friction coefficient of films formed in oils containing ZDP was higher on softer steels than on hard steels. Apparently, the higher oxide content in the films on soft steel produces higher friction.

The effect of film ductility on the friction coefficient was important. A corrosion film, identified as Fe_2O_3 and known to be very brittle [13], was formed on the sliding track of a 59 HRC disk specimen by leaving the specimen in a high humidity atmosphere for two days. The dry friction coefficient of corrosion film, 0.63, was three to five times larger than that of other films (Table 4), as also found by Kang and Ludema [13].

3.6. Microhardness

Measurement of the refractive index of films shows that the amount of oxide in the films increases and grows faster on softer substrates than on harder steels. In order to find if there is a connection between oxide formation and plastic deformation on the sliding surface, the microhardness of the disk specimens was measured before and after sliding. As is shown in Table 5, considerably more work hardening occurred on the sliding track of soft steels than on hard steels. On the hardest steels there was no detectable work hardening. Initial and final surface roughness values are also given in the same table. When there was considerable work hardening there was also considerable surface roughening. These data show that there is a good relation between plastic deformation and oxide formation on sliding surfaces, in very good agreement with the existing literature [20–22].

3.7. Wear

Wear scar widths on the cylinders were measured under an optical microscope. The data are presented in Table 5 and shown in Fig. 6. In plain mineral oil, wear of the cylinder was usually higher when sliding against a disk of higher hardness. However, in some cases, softer disks caused higher wear than did the harder disks. In these cases ellipsometric measurements showed a high refractive index on the disk surface, indicating a high fraction of oxide–metal mixture (OMM).

In the case of plain mineral oils, agglomeration and piling up of the oxide particles on the cylinder sliding track was seen under loads larger than 1000 N. Most of the oxide film was removed at these high loads. Oxide agglomeration was not seen with ZDP in oils.

TABLE 4

Dry sliding experiments on already formed boundary films

Specimen		Dry sliding load (N)	Film refractive index	Film thickness (Å)	μ		
					1 rev min^{-1}	10 rev min^{-1}	100 rev min^{-1}
Bare substrate	59 HRC	16			0.26	0.35	
Mineral oils	22-B	6	4.60	122	0.19	0.21	0.20
	44-M	16	4.92	116	0.19	0.15	0.13
	48-M	16	4.05	70	0.32	0.28	0.24
	59-M	16	3.20	45	0.23	0.75	1.23
Mineral oil	44-M2Z	16	3.89	40	0.18	0.32	0.52
and 2% ZDP	48-M2Z	16	3.49	102	0.15	0.16	0.17
	59-M2Z	16	2.77	40	0.14	0.14	0.14
	60-M2Z	6	2.32	111	0.10	0.11	0.10
Fe_2O_3 film	59-CORR.	16	2.97	255	0.63	0.61	0.77

TABLE 5

Microhardness and surface roughness of the disk sliding track before and after sliding, also given wear scar width on cylinders

| Specimen	Maximum load (N)	Sliding distance (m)	Knoop 100 g before	Knoop 100 g after	Roughness R_a (μm) before	Roughness R_a (μm) after	Film refractive index[a]	Film thickness[a] (Å)	Wear width (μm)
45-M	635	432	390	585	0.018	0.117	4.47	53	400
46-B	992	576	381	555	0.010	0.102	4.26	57	410
44-M2Z	1023	591	330	470	0.008	0.257	4.20	79	285
48-B1Z	350	1458	368	435	0.015	0.058	3.63	93	215
53-M	1023	540	460	488	0.020	0.151	2.84	69	520
54-M	589	1512	486	486	0.015	0.053	3.89	50	430
54-B	713	432	465	470	0.013	0.028	3.84	82	450
53-M2Z	1890	1008	452	495	0.013	0.056	2.57	88	414
55-B1Z	527	684	480	516	0.013	0.038	3.14	88	250
58-M	350	2376	568	568	0.015	0.033	2.20	116	N/A
58-B	1116	648	640	650	0.018	0.107	3.71	37	680
60-M	589	360	727	675	0.036	0.036	3.14	41	550
60-M5Z	1023	1026	645	608	0.013	0.037	2.82	93	345
57-M1Z	837	468	478	568	0.014	0.050	3.26	67	230
60-M2Z	837	468	608	590	0.028	0.037	2.32	111	240

[a] At maximum load.
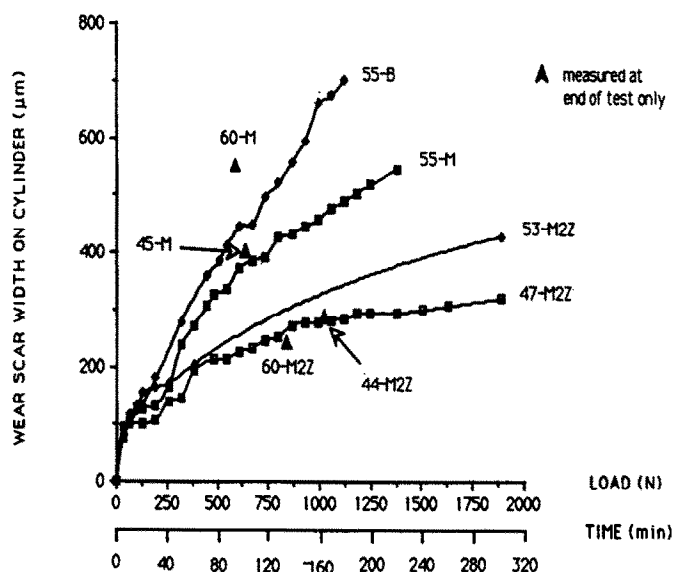
Fig. 6. Wear scar width on the cylinder. On three specimens the wear scar was measured after each load step. On specimen 53-M2Z it was measured twice and on the other specimens at the end of the experiments. More data are available in Table 5. The load steps were 62.5 N in 10 min intervals.

TABLE 6

Thickness and refractive index of films adsorbed during static oil immersion experiments together with their dry friction coefficients

	Immersion temperature (°C)	Film refractive index	Film thickness (Å)	μ	
				1 rev min^{-1}	10 rev min^{-1}
Mineral	25		no film	0.29	0.38
oil	185	2.48	50	0.51	0.57
Mineral oil	25	1.53	55	0.13	0.16
and 2% 2DP	185	2.28	52	0.18	0.29
Engine	25		no film	0.18	0.22
oil	185	1.91	17	0.18	0.22

3.8. Static immersion experiments

In order to see whether sliding in the oils produces a more durable film than does immersion in oil alone, static immersion tests were carried out on 48 HRC disk specimens for 3 h. Since the major effect of sliding is a temperature increase, immersion tests were done at two temperatures: room temperature (25 °C) and 185 °C. Three lubricants were used: paraffin oil, paraffin oil and 2% ZDP, and a fully formulated engine oil (Quaker State SAE 30 motor oil). Data from these tests are shown in Table 6.

After the immersion test the specimens were washed in hexane to remove liquid oil. Ellipsometer measurements showed no residual film on the specimen immersed

in paraffin oil and in engine oil at room temperature. It is possible but not likely that films did form in these cases but the hexane removed them. However, in mineral oil containing ZDP, a 55 Å thick film was detected with a refractive index of 1.53. This was clearly not an oxide film and probably not an organoiron film. The refractive index of bulk liquid ZDP is 1.51. Perhaps ZDP was adsorbed from the oil onto the steel surface at room temperature and hexane was not able to dissolve it. This specimen also produced the overall lowest dry friction. Films were detected on all specimens immersed at 185 °C. The film formed in paraffin oil had the highest refractive index, 2.48, engine oil film had the lowest, 1.91. The film formed in engine oil was also very thin. The results with engine oil, though it contains ZDP, may indicate the effect of competition between several additives.

Friction measurements were made on the immersed specimens after washing and drying and the results are given in Table 6. The adsorbate from plain paraffin oil at high temperature produced a higher friction coefficient than did the adsorbates from paraffin oil and 2% ZDP and from engine oil.

3.9. Boundary films formed in fully formulated oils

Finally, experiments were done with fully formulated diesel engine oil in two states, new and "used". The oil is Amoco 300 15-40 SAE. The "used" oil was taken from a Mack-350 diesel engine after 40 h of unspecified use. These two oils were also used in wear and scuffing experiments, using segments of engine cylinder and piston rings, by another research group. The used oil caused less wear on the piston ring than did the new oil, contrary to common expectations. These oils were tested in the disk and cylinder apparatus using specimen hardnesses corresponding to the hardness combination of cylinder and ring, 48 HRC and 58 HRC respectively. In addition, the final step load was of the same order as the load on an equivalent segment of piston ring, i.e., 326 N. We observed the same phenomenon, namely that the used oil caused less wear on our test cylinder than the new oil did. The ellipsometric measurements of the films showed that the refractive index of the film formed in the new oil was 3.15 and grew up to 155 Å thick. The refractive index of the film formed in used oil was 2.70 and grew up to 85 Å thick. The used oil produced a higher ratio of OIC to oxide than did the new oil. These experiments were also significant from another aspect in that the simulation of boundary lubrication regime in our friction machine was in very good agreement with the real life boundary lubrication regimes.

3.10. Sensitivity of the ellipsometer

The ellipsometer was more sensitive for measurement of the thickness of iron oxide than for organic films because the difference of the refractive indices between iron oxide and the oil medium was greater than that between organic films and the oil medium. These differences would have the greatest effect on the resolution of film thickness measurements of OICs on hard disks. To clear this point experiments were done with a hard substrate (59 HRC), with ZDP and without ZDP, under low loads (up to 188 N, in three steps of 10 min each). Ellipsometric measurements in the oil medium showed no film on the sliding track. After 30 min running, the oil was removed and the specimen was washed with hexane and dried. Then ellipsometric measurements were taken in air, revealing very thin films. In the case of 2% ZDP in paraffin oil, the film thickness was 40 Å with a refractive index of 2.77. In plain paraffin oil, the film thickness was 45 Å and the refractive index was 3.20. Obviously, more iron oxides formed in the absence of ZDP.

4. Discussion

There is general agreement in the literature that protective films prevent adverse asperity interaction in boundary lubrication of iron and steel. There is little agreement, however, on whether these protective films are oxides, or liquid-like polymeric materials, or organometallic substances. Apart from scientific curiosity, the continuing study of these films appears to be motivated by a desire to form protective films on surfaces before they are placed in operation.

Research results are rather complicated and detailed in this field, but it is clear in most cases there are fewer variables being examined than is necessary. The same is true of this research, but it is apparent that some of the confusion in this field arises from the fact that films that form in boundary lubrication experiments contain several constituents, depending on experimental conditions. These constituents are as follows.

(1) Fe_3O_4, iron–carbon and metallic iron mixture (*i.e.* OMM), with small amounts of OIC. The formation of OMM is favored by plastically deforming the steel sliding surfaces. The fraction of metallic iron in the film as shown in Table 3 could be somewhat influenced by the presence of steel below the film, but the escape depth of iron is of the order of 20–30 Å, which is much less than the thickness of the film.

(2) A weak organoiron compound (OIC-M) that forms in plain mineral oils, both high and low aromatic (*i.e.* lower and higher oxygen content).

(3) A strong organoiron compound (OIC-Z) that contains up to 15% phosphorus, sulfur, and zinc, and forms in mineral oils containing ZDP.

The OMM films (plus OIC) reduce friction below that of the original steel surfaces. The OICs generally form above the OMM and reduce the friction still more. The OMM causes more wear of the cylinder than do the OICs. Wear of the cylinders is accompanied by grooving as seen by Suzuki and Ludema [14]. Perhaps there is abrasive action by an iron carbide, or more likely a similar OMM may form on the cylinder and is easily removed.

The identification of the multiconstituent films is a consequence of using several analytical instruments. In papers reporting predominantly oxide or polymer films, only one or two analytical instruments were used, and usually there was inadequate attention to cleaning procedures which would prevent removing the softer OICs.

The experiments performed were of the nature of "breaking-in" of surfaces rather than a study in equilibrium chemistry. Thus, the description of the influence of variables is doubtless strongly dependent on the pre-existence of relatively smooth steel surfaces which are covered with a very thin oxide (among other substances). The results have been reported in terms of mechanical film durability, friction behavior and wear behavior as well as chemical composition.

It is easier to describe the growth of films than to describe how the surfaces survive before the protective films form. The growth and consequent behavior may be divided into three general categories, by hardness of steel in mineral oil alone, and when additives are present in the oil for all steels, as follows.

4.1.1. How films grow in plain mineral oil, on soft steel

The formation of OMM is promoted by plastic deformation of steel, which occurs most with soft steel. This was verified by finding that the surfaces of the soft steels hardened far more than those of the hard steels (Table 5). The presence of metallic iron in the film suggests that the work hardening on the steel surface was carried to the point of fracture or, as previously reported [23], the steel surfaces fail by low

cycle fatigue. We could not determine whether the oxide formed primarily on the metallic particles or on the substrate surface.

The preponderance of OMM over OIC in mineral oil on soft steel may indicate that active iron surfaces do not catalyze the formation of OIC as much as promote corrosion (oxidation etc.). Apparently, some of the metallic iron is available for the formation of OIC above the OMM.

Kang and Ludema's work [13] in which only oxide was reported to have formed on the surface was done with very soft steels, around 10 HRC and less.

4.1.2. How films grow in mineral oil, on hard steel

The formation of OMM is much slower than in the case of soft steel because the hardened steel does not cold work very much. OICs form, but without the OMM below are inadequate for protecting against scuffing failure. This is seen particularly in Fig. 6 where the 60-M disk specimen produced the highest wear of the cylinder. In Fig. 3(a) the predominant OICs grew very slowly and were thinned even under low loads, actually fluctuating between 80 and 120 Å during the test. We therefore classify these OICs as soft and weak, ignoring the question as to whether the weakness lies in the film itself or in a weak attachment to the materials below. Metallic iron debris is seen in this case, but it is not incorporated into the film.

In the literature, in those papers that report the existence of friction polymer and other organic compounds, the experiments were done with hard steel. In the present work there is little evidence that the OIC is polymerized to any great extent.

4.1.3. How films grow in mineral oil containing ZDP, on all steels

OIC-Z was seen to form very quickly (on the residual oxide on the unworn surfaces) in the tests. On hot surfaces of soft steels OMM forms quickly, but on the hard steels OICs formed before a significant amount of OMM formed if any formed at all. The slower formation of OMM probably indicates that ZDP competes for the available oxygen. OIC-Z by itself provides adequate protection of surfaces, producing lower friction than the OMM and preventing wear of the cylinder more effectively than does the OIC-M. We therefore classify OIC-Z as a strong film, again avoiding the question of whether that strength lies in the film itself or in its attachment to the material below. As mentioned before, these films endured loads of more than three times the maximum loads on OMM before thinning occured (Fig. 3(e)).

4.2. Dual film model

A two-layer film model may be used to represent conveniently the relative ratios of OMM and OIC. By assuming a refractive index of 2.1 for OIC and 4.2 for OMM, with zero absorption, the thickness of each fictitious film can be computed. The results are given in Figs. 7–9. In the real films OMM and OIC are not separated as sharply as is shown in the figures, but rather there is a gradual transition as indicated in Table 3. Comparison of Figs. 7–9 shows that the fictitious OMM thickness is higher on softer substrates. Apparently, plastic deformation encourages oxide formation.

On softer steel, OMM forms first and grows thick. Then a thin OIC film forms on the OMM. On harder steels, first the OIC films form then under increased load the oxides start forming. Oxide formation is much slower and the film is thinner in the case of hard steel than in the case of soft steel. During overload the very thin oxide film on 60 HRC steel was completely removed. However, OMM was not removed from softer steels, and metal-to-metal contact was effectively prevented. Figures 7 and 8 shows that when the overload is removed the thickness of the films recovers. The
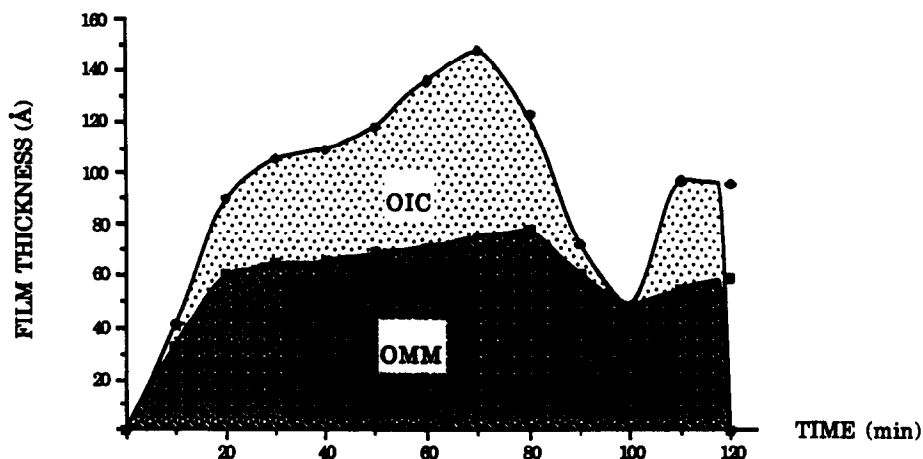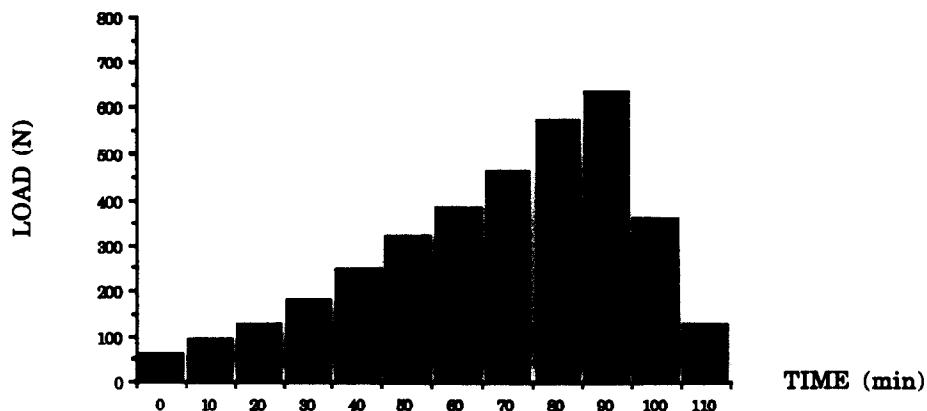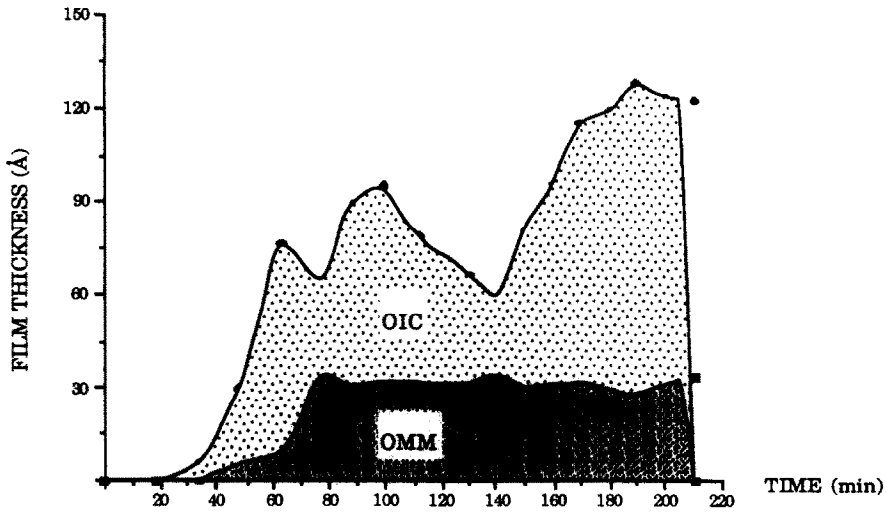
Fig. 7. (a) Film thicknesses obtained from two-layer film model calculations on 45-M disk specimen. The top film is organoiron compound, the bottom film is mixture of iron oxide, metallic iron and iron carbide. (b) Loading history of the specimen.

change in the film thickness due to loading and unloading occurred mainly as changes in the thickness of OIC.

4.3. Initial conditions

The formation of protective films is contingent upon the survival of the surfaces until a film can be formed. The maximum loads and sliding speeds in these tests were deliberately severe, probably more severe than in most engineering practice. Survival of new surfaces in our experiments was assured by starting with low loads. If machinery is always operated at low severity no problems will be seen by beginning with design loads.

If an initial low load is necessary for successful starting, it is likely that a "preformed" protective film would be useful. In the immersion tests, films of various types could have formed. However, only the films formed in ZDP functioned in a helpful way by reducing the initial friction.

(a)
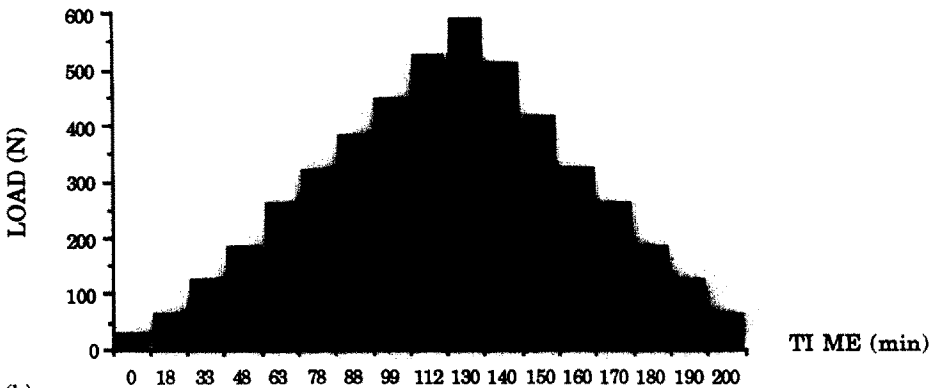
(b)

Fig. 8. (a) Film thicknesses obtained from two-layer film model calculations on 54-M disk specimen. When the load is removed the film thickness recovers. (b) Loading history of the specimen.

4.4. Recommendations on break-in procedures

Optimum break-in prevents early failure of surfaces. From the above results we can see which films are optimum for various materials tested, again in terms of material hardness and oil composition as follows (for the hard cylinder and flat plate configuration).

4.4.1. In mineral oils

On soft steels, the surface temperatures should be kept to a minimum so that OMM will not form to the total exclusion of OIC-M. Some OIC-M mixed with the OMM reduces wear of the countersurface. On medium hardness steels the proper mixture of OIC-M and OMM forms with little precaution.

On hard steels the OMM forms too slowly to be protective in our tests, and the OIC-M is inadequate to protect the surfaces without OMM. If hard steels are required,
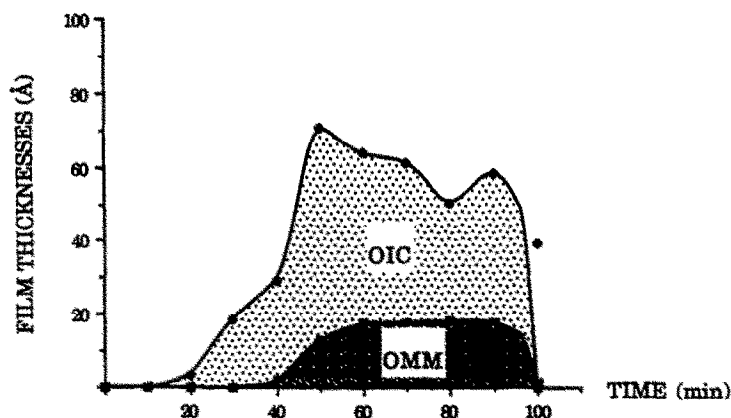
(a)
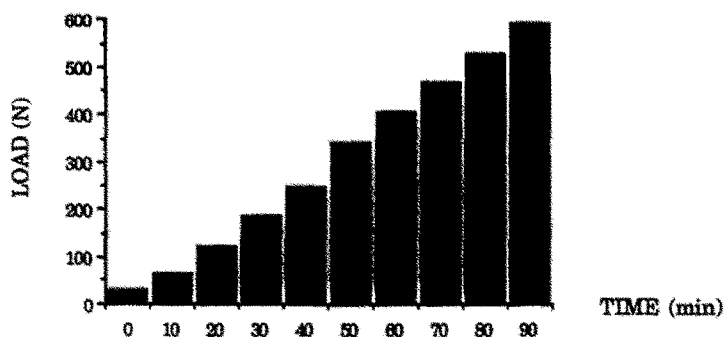
(b)

Fig. 9. (a) Film thicknesses obtained from two-layer film model calculations on 60-M disk specimen. (b) Loading history of the specimen.

adequate OMM formation can be achieved by softening (decarburization or tempering) a thin layer of steel on a hard substrate.

4.4.2. In mineral oils with ZDP

The OIC-Z that forms is adequate by itself. The adsorbed film from ZDP which forms before sliding is helpful but is not an adequate substitute for the OIC-Z that forms later. The formation of OMM is not harmful for scuff prevention, but it does cause more wear than does OIC-Z alone.

These results apply to new (unused) oil. Used oil evidently has a different composition than does new oil as seen in tests described above. Though the composition of the oils was not known, the protection offered by the two oils is clearly connected with the chemistry of the films formed.

5. Conclusions

(1) Ellipsometry is a useful technique for on-line monitoring of thickness and composition of surface films. The technique requires information from chemical analytical

techniques as calibration points. Once calibration is achieved the experiments can be monitored without the need to interrupt experiments for analytical purposes.

(2) The films that form on steel in boundary lubrication are composed of various substances, and each forms under different circumstances. The substances are Fe_3O_4 (forms fastest on soft steel), metallic iron, an iron–carbon compound (these appear to promote wear of the countersurface), and organoiron compounds of two types: a strong and durable compound consisting of up to 15% zinc, sulfur and phosphorus formed from oils containing ZDP, and a weak compound without these elements formed in plain mineral oil.

(3) All boundary films behaved like solids rather than viscous liquids in dry sliding experiments (after being formed under liquid lubrication). The shear strength of these films is considerably lower than that of the substrates, and has implications for modeling of the complete lubricant system.

(4) The ratio of OIC to OMM in the films increases with increasing ZDP content in the oil and increased substrate steel hardness.

(5) OMM forms faster and thicker on the softer substrates owing to the ease of plastic deformation. However, compared with OICs, OMM wears out the counter part faster.

(6) After reaching a maximum, film thicknesses decreased under increased load. When the overload was removed recovery of the films was observed. Films formed in oil containing ZDP had much higher load carrying capacities. They were not thinned even under three times the load that caused thinning of films formed in oils without ZDP. Observation of much less wear on the sliding tracks in oils with ZDP was linked to the durability of the ZDP induced films.

Acknowledgment

References

1 K. C. Ludema, A review of scuffing and running-in of lubricated surfaces, with asperities and oxides in perspective, *Wear, 100* (1984) 315–331.
2 H. W. Hermance and T. F. Egan, Organic deposits on precious metal contacts, *Bell System Tech. J., 37* (1958) 739–776.
3 R. S. Fein and K. L. Kreuz, Chemistry of boundary lubrication of steel by hydrocarbons, *ASLE Trans., 8* (1965) 29–38.
4 M. J. Furey, The formation of polymeric films directly on rubbing surfaces to reduce wear, *Wear, 26* (1973) 369–392.
5 W. Hirst and J. K. Lancaster, Surface film formation and metallic wear, *J. Appl. Phys., 27*(9) (1956) 1057.
6 R. O. Bjerk, Oxygen, an extreme pressure agent, *ASLE Trans., 16*(2) (1972) 97–106.
7 R. S. Montgomery, Run-in and glaze formation on gray cast iron surfaces, *Wear, 14* (1969) 99–105.
8 B. A. Baldwin, Chemical characterization of wear surfaces using X-ray photoelectron spectroscopy, *ASLE Trans., 32*(3) (1975) 125–130.
9 R. J. Bird and D. Galvin, The application of photoelectron spectroscopy to the study of E.P. films on lubricated surfaces, *Wear, 37* (1976) 143–167.

10 A. C. Bose, E. E. Klaus and E. J. Tewksburry, Evaluation of wear products produced by some chemical reactions in boundary lubrication, *ASLE Trans.*, *19*(4) (1975) 287–292.

11 B. Çavdar and K. C. Ludema, Dynamics of dual film formation in boundary lubrication of steels, part II: chemical analyses, *Wear*, *148* (1991) 327.

12 J. K. Lancaster, The formation of surface films at the transition between mild and severe metallic wear, *Proc. R. Soc. London, Ser. A, 273*, 1963, p. 466.

13 S. C. Kang and K. C. Ludema, The breaking-in of lubricated surfaces, *Wear*, *108* (1986) 375–384.

14 M. Suzuki and K. C. Ludema, The wear process during the running-in of steel in lubricated sliding, *ASME paper, 86-Trib-44*, AMSE, New York, 1986.

15 Y.-Z. Lee and K. C. Ludema, The shared-load wear model in lubricated sliding: scuffing criteria and wear coefficients, *Wear*, *138* (1990) 13–22.

16 D. A. Ramsey, Mueller matrix ellipsometry involving extremely rough surfaces, *Ph.D. Thesis*, University of Michigan, Ann Arbor, MI, 1985.

17 A. B. Winterbottom, Increased scope of ellipsometric studies of surface film formation, in E. Passaglia, R. R. Stromberg and J. Kruger (eds.), *Ellipsometry in the Measurement of Surfaces and Thin Films*, National Bureau of Standards, Misc. Pub. 256, 1964.

18 R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light*, North-Holland, Amsterdam, 1977.

19 P. Pan and B. J. Hamrock, Simple formulas for performance parameters used in elasto-hydrodynamicly lubricated line contacts, *ASME Trans.*, *111* (1989) 246–251.

20 F. Hirano, Y. Yamamoto, T. Kawazoe and S. Watanabe, The effect of surface roughness on scoring, part 1: under starved lubricating condition, *Bull Jpn. Soc. Mech. Eng.*, *21* (ISS) (1978) 893–898.

21 Y. Yamamoto, F. Hirano and M. Hashimoto, The effect of surface roughness on scoring, part 2: under flooded lubricating condition, *Bull. Jpn. Soc. Mech. Eng.*, *21* (155) (1978) 893–898.

22 Y. Yamamoto and F. Hirano, Relation between scuffing resistance and the increase in surface hardness during tests under conditions of rolling/sliding, *Wear*, *63* (1980) 165–173.

23 Q. J. Xue and K. C. Ludema, Plastic failure effects in scuffing of soft metals, in K. C. Ludema (ed.), *Proc. Wear of Materials Conf., Riston, VA, 1983*, ASME, 1983, pp. 499–506.