The Influence of Steel Composition on the Formation and Effectiveness of Anti-wear Films in Tribological Contacts

Konstantinos Pagkalis¹ · Hugh Spikes¹ · Jakub Jelita Rydel² · Marc Ingram^{2,3} · Amir Kadiric¹

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Abstract

The effectiveness of antiwear additives in laboratory tests is commonly evaluated using specimens made of AISI 52100 through-hardened bearing steel. However, many lubricated machine components are made of steels with significantly different material compositions, which raises an important practical question of whether the performance of antiwear additives with these other steel types is different from that established with AISI 52100. To help answer this question, this paper investigates the influence of steel composition on the formation and effectiveness of antiwear films. Four steels that are commonly used in tribological applications, namely AISI 52100 through-hardened bearing steel, 16MnCr5 case-carburised gear steel, M2 high speed steel and 440C stainless steel are tested in rolling-sliding, ball-on-disc contacts lubricated with three custom-made oils, one containing ZDDP and two containing different types of ashless antiwear additives. The relative effectiveness of their boundary films was assessed by measuring their thickness and associated wear and friction over 12 h of rubbing at two specimen roughness levels. For ZDDP it was found that the formation of antiwear film was not significantly influenced by steel composition or specimen surface roughness. A similar tribofilm thickness, final tribofilm roughness and friction was observed with all four steels. No measurable wear was observed. By contrast, for the ashless antiwear additives the thickness and effectiveness of their tribofilms was strongly influenced by steel composition, particularly at higher roughness levels. The exact trends in film thickness vs steel relationship depended on the specific chemistry of the ashless additive (ester-based or acid-based) but in general, relative to AISI 52100 steel, M2 steel promoted ashless tribofilm formation whilst 440C retarded ashless tribofilm formation. This behaviour is attributed to the presence of different alloying elements and the ability of the additives to extract metal cations from the rubbing surfaces to support the growth of a tribofilm. In all cases ZDDP films were thicker and rougher, and produced higher friction than those formed by the ashless additives. However, unlike ZDDP, ashless blends generally produced significant wear, particularly with 16MnCr5 and M2 steels. The results indicate that to ensure reliable performance of a given machine component, the chemistry of an ashless antiwear additive should be matched with the types of steel present in the lubricated machine.

Keywords Antiwear additives · Boundary lubrication · Wear · Ashless · ZDDP · Bearing · Gear · Tribofilm

1 Introduction

Boundary and mixed lubrication occur in tribological contacts when the hydrodynamic oil film is not sufficiently thick to fully separate the rubbing surfaces. They are therefore prevalent in machine components where contacts operate at low entrainment speeds or high temperature, and thus low oil viscosity, or which employ start-stop or reciprocating motion. Boundary lubrication occurs when the lambda (λ) ratio (ratio of hydrodynamic film thickness to composite surface roughness) is less than ca 0.3, whilst mixed lubrication occurs when λ lies between ca 0.3 and 3. Under these conditions, lubricants containing antiwear additives react

✉ Amir Kadiric
a.kadiric@imperial.ac.uk

¹ Tribology Group, Imperial College London,
London SW7 2AZ, UK

² Afton Chemical, Bracknell RG12 2UW, UK

³ Present Address: Ingram Tribology, Carmarthen SA31 3RB,
UK

with rubbing solid surfaces to produce solid-like tribofilms that act to protect the surfaces from damage. The protection afforded by such boundary films is important in terms of component reliability since direct metal-to-metal contact causes high surface stresses and temperatures that can lead to a variety of surface damage types, such as scuffing and severe wear. Such damage at best reduces the life of the component, and at worst leads to catastrophic and unexpected failure [1].

To assess the ability of lubricants to provide antiwear and extreme pressure protection, formulations are generally tested in the early stages of development using tribometers such as the four-ball, block on ring, MTM and HFRR. Some of these tribometers, notably the MTM, are also used in research into the mechanisms of lubricant additive action. Other than the block on ring set-up, these test methods almost exclusively use samples made of AISI 52100 (SUJ2, 100Cr6, 535A99) through-hardened bearing steel (see Table 1). The wide-spread use of this specific steel in such tests is likely driven by practical considerations, namely the fact that the ball specimens required in many tribometers are readily and cheaply obtainable in this material owing to the fact that the same balls are used in a vast majority of rolling bearings. However, whilst AISI 52100 through-hardened steel is widely employed in rolling bearings, other machine elements, for example gears and cams, where factors such as toughness or inherent lubricity are important, employ quite different steel compositions. This in turn means that despite the initial research and development of boundary lubrication performance of new lubricant formulations being based on their performance with AISI 52100 steel, they may subsequently be used with quite different steel metallurgies, be it in further component level tests or the actual application. This raises an important practical question of whether the performance of antiwear and extreme pressure additives with

these other steel types is different from that observed with AISI 52100 steel.

In many applications, and internal combustion engines in particular, an additional issue is the current trend towards replacing the zinc-based antiwear additive (ZDDP) with alternative zinc-free ashless additives. It is known that ZDDPs are relatively insensitive to the nature of the substrates on which they form tribofilms [2], probably because zinc ions present in the lubricant itself are available to be incorporated in the phosphate and polyphosphate species that make up much of a ZDDP tribofilm [3]. The ready availability of these ions also ensures that thick ZDDP films form very rapidly. By contrast, ashless antiwear additives such as amine phosphates and dialkyl phosphites form much thinner films, and much more slowly than ZDDP. This has been ascribed to the need for ferrous ions to be released from the rubbing surface to enable stable phosphate glasses [4, 5]. If this is the case, the metallurgy of the rubbing surfaces is likely to be of significance in the formation of the ashless tribofilms so that a better understanding of their relative performance with non-AISI 52100 steels is even more important in this case.

Because of the limited availability of non-AISI 52100 ball specimens, the few studies that have explored other steel metallurgies have tended to use pin-on-disc or block-on-ring set-ups. One class of steels that have received appreciable attention are the high Cr content stainless steels. Dacre et al. [6, 7] compared the adsorption of ZDDP on 52100 steel and a 13% Cr stainless steel and found that, whilst ZDDP chemisorbed on 52100 releasing Zn^{2+} , only physisorption took place on the stainless steel. Rounds [8] compared the reactivity and tribological performance of several steels when lubricated with different ashless additives. He ranked the steels in order of decreasing reactivity as 1018 > 4118 > 52100 > M-50 > 440C > Stellite. This corresponds to the order of increasing Cr content which led Rounds to ascribe the observed trend to ease of Cr oxide formation, i.e. when Cr content was high, as in the case of 440C and stellite, there was increased Cr oxide formation on the steel surfaces which prevented antiwear additive reactions with the surfaces. Hall [9] showed that tricresyl phosphate (TCP) was effective in reducing wear of 52100 steel but ineffective in reducing wear of 440C steel. In contrast, Wei et al. [10] found that ZDDP and the ashless antiwear additives tricresyl phosphate and tributyl phosphate all reduced wear of Cr_2O_3 -coated steel and formed tribofilms on the rubbed surfaces. This apparent discrepancy may be explained by the observations of Suarez [11], who found that the ZDDP film thickness with a 440C tribo-pair eventually reached a similar value to that with a 52100 tribo-pair after 3 h of rubbing but the initial rate of film formation was slower. She attributed

Table 1 Steels used in common lubricant bench tests

	4-ball	HFRR	MTM	Block on ring	
				Block	Ring
	AISI 52100	AISI 52100	AISI 52100	SAE 01	SAE 4620
C (%)	0.95–1.1	0.95–1.1	0.95–1.1	0.85–0.95	0.17–0.22
Mn (%)	0.2–0.5	0.95–1.1	0.95–1.1	1.1–1.3	0.45–0.65
Si (%)	≤0.35	≤0.35	≤0.35	0.2–0.4	0.15–0.35
Cr (%)	1.3–1.6	≤0.35	≤0.35	0.4–0.6	–
Ni (%)	–	–	–	–	1.65–2.0
Mo (%)	–	–	–	–	0.2–0.3
V (%)	–	–	–	≤0.3	–
W (%)	–	–	–	0.4–0.6	–

the difference in the early film growth rates to chromium oxide being initially present on 440C which restricted the early ZDDP film formation; with prolonged rubbing the chromium oxide film was removed allowing faster ZDDP film formation to take place.

Away from 440C, there are very few systematic studies that have explored the effects of other steel types on boundary lubrication. Evans et al. [12] compared the friction behaviour of case-carburized AISI 3310 and through-hardened AISI 52100 in fully formulated commercial wind turbine gearbox oil using a ball-on-disk rolling/sliding contact tribometer. Although tribofilms of similar composition formed on both steels, they had different structures, with that on 52100 being rougher and separated by deep cracks in the film, whilst that on 3310 was smoother and more uniform. Godfrey [13] detected the presence of iron oxides, iron carbide and silicon, in addition to iron sulphide, on the surface of gear teeth made of case-hardened low carbon 4140 steel after lubrication with different extreme pressure additive-containing oils. Oxides, sulphides and silicon were implied to be beneficial for wear and friction reduction. Ueda et al. [14] compared the formation of ZDDP films on AISI 52100 steel to that on a selection of non-ferrous substrates and showed that the presence and concentration of particular metal atoms and ions on non-ferrous surfaces can strongly affect ZDDP film formation and survival. Rydel et al. [15] investigated the influence of steel microstructure on the local thickness of the ZDDP films using four types of bearing and gear steels and found that thinner films were formed locally on carbides than on the surrounding steel matrix.

Despite its practical importance, it is evident from the above that the current understanding of the influence of steel composition on oil performance under boundary lubrication is limited. The aim of the research described in this paper is to investigate systematically the effect of material composition of hard steels used in tribological applications on the formation and effectiveness of antiwear tribofilms in non-conformal tribological contacts. To achieve this, the study employs a selection of steels with widely varying alloying elements and a range of custom-made oils with different additive packages including ZDDP and two ashless based chemistries. Experiments are performed on the mini-traction machine with spacer layer imaging (MTM-SLIM), which allows the rate of tribofilm formation as well as friction and wear to be explored over a range of rolling-sliding conditions. The selected contact pressures and steel types are representative of those commonly found in machine elements such as rolling bearings, gears, cams and cutting tools. The emphasis of this research is on the practical aspects of antiwear film performance namely, tribofilm thickness, rate of film growth, afforded anti-wear protection and resulting friction, rather than the tribofilm chemical composition obtained with different steels. It is hoped that the understanding thus

gained may help in optimizing the lubricant-steel system for a specific machine component.

2 Test Specimens

Test specimens used in this study are 19.05 mm diameter balls and flat discs. Specimens were made of four different types of hard steels and were finished with two different surface roughness levels as outlined below.

2.1 Steel Compositions Tested

The four steels tested in this study are 440C stainless steel, M2 high speed steel, 16MnCr5 low carbon gear steel, and 52100 standard rolling bearing steel. Table 2 shows the nominal composition of these steels [16, 17]. All four are martensitic, tempered steels. 440C, M2 and 52100 steel specimens were through hardened whereas 16MnCr5 specimens were case-carburized. This selection of steels was chosen for two reasons. Firstly, it covers a range of alloying elements which was considered important as the type of alloying elements present on the surface may interact with boundary film formation. The dominant alloying elements in each steel are highlighted in bold italics in Table 2. Secondly, the four steels cover a wide range of practical applications: AISI 52100 is the most common steel used in manufacture of rolling bearings, case-carburized 16MnCr5 steel is commonly used in manufacture of gears, 440C type steel is typically used for rolling bearings where anti-corrosion resistance is required whilst M2 high speed steel is used in manufacture of a variety of cutting tools but is also compositionally similar to M50 which is the main steel used in rolling bearings for aero-engine applications where better high temperature performance than that of AISI 52100 is required.

Table 2 Typical compositions of four steels used for the test specimens in the present study (the figures in bold italics highlight the dominant elements in each composition)

	440C	16MnCr5	M2	52100
C (%)	1.08	0.14–0.19	0.78–1.05	0.95–1.1
Mn (%)	0.50	1.0–1.3	0.15–0.4	0.2–0.5
Si (%)	0.40	0.40	0.20–0.45	≤0.35
Cr (%)	17.0	0.8–1.1	3.75–4.50	1.30–1.60
Ni (%)	–	–	0.3	–
Mo (%)	0.52	–	4.5–5.5	–
Cu (%)	–	–	0.25	≤0.025
W (%)	–	–	5.5–6.75	–
P (%)	–	0.025	0.03	–
V (%)	–	–	1.75–2.20	–
S (%)	–	≤0.035	0.03	≤0.025

Table 3 Surface RMS roughness (R_q) and hardness (HV30) of standard, smooth polished 52100, M2, 16MnCr5 and 440C steel specimens

Material	Disc R_q (nm)	Ball R_q (nm)	R_{qc} composite, $(R_{q_disc}^2 + R_{q_ball}^2)^{1/2}$ (nm)	Disc hardness (HV30)	Ball hardness (HV30)
52100	~ 10	~ 15	~ 18	~ 730	~ 870
M2	~ 10	~ 15	~ 18	~ 790	~ 840
16MnCr5	~ 10	~ 15	~ 18	~ 760	~ 810
440C	~ 15	~ 15	~ 21	~ 630	~ 730

Table 4 Surface RMS roughness (R_q) of *rough* 52100, M2 and 16MnCr5 steel balls

Material	Ball R_q (nm)
52100	~ 47
M2	~ 41
16MnCr5	~ 51

Both MTM balls and discs were obtained in each of the four steels. In all tests shown in this paper, both the ball and the disc were made of the same steel to prevent preferential formation of boundary films on either of the two specimens and/or transfer of material of different metallurgy from one surface to the other, both of which could complicate the interpretation of results.

2.2 Specimen Roughness

MTM tests are typically conducted with highly polished ball and disc specimens with root mean square roughness values, $R_q \sim 10$ nm for discs and $R_q \sim 15$ nm for balls. However, given that the roughness levels in practical applications are usually higher than this, which may be expected to have implications on boundary lubrication, this study used specimens with two different roughness levels: one set of tests employed standard smooth, polished MTM balls ($R_q \sim 15$ nm) and discs ($R_q \sim 10$ nm), whilst the second set of tests used rougher ball specimens with $R_q \sim 40$ – 50 nm against the same smooth, polished discs ($R_q \sim 10$ nm). Rough M2 and 16MnCr5 balls were as supplied, whilst 52100 steel balls were roughened by rotating smooth balls in a tumbler type machine with $0.3 \mu\text{m}$ Al_2O_3 powder for 4 h. Rough 440C balls were not tested.

The roughnesses of the test specimens pre- and post- test were measured with a stylus profilometer. Roughness values were determined using an upper cut-off length of 0.08 mm and a lower cut-off length of 0.0025 mm (equal to stylus diameter). These values were set so that the long wavelength

components of the surface, which significantly impact the measured roughness values but are largely irrelevant to contact operation given the employed contact semi-widths, are filtered out [18]. All roughness values quoted in this paper are averages of at least four measurements in different locations on each specimen made in the direction transverse to the test rolling direction.

Table 3 shows the R_q roughness of the smooth balls and discs whilst Table 4 shows the R_q values for the rough balls. The average surface hardness values of specimens, measured using a Vickers indenter, are also quoted in Table 3. Specimens in all steel compositions have similar hardness in the range of 810 to 870 HV for the balls and 730 to 790 HV for the discs, except in the case of 440C stainless steel, which is somewhat softer, with 730 HV for the balls and 630 HV for the discs.

3 Test Lubricants

All lubricants used in this study are custom blended so that their chemistry is fully known. Their properties are listed in Table 5. All were 150 ISO VG grade and in all cases the base oil was polyalphaolefin (PAO) with a very small quantity of ester added to increase the polarity of the blend to help solubilize the additives.

The ashless additive chemistries tested are either currently used in modern gear oils or being developed for this purpose. The ZDDP, the basic structure of which is shown in Fig. 1, was a mixture of primary and secondary ZDDPs and was used at a typical treat rate which corresponds to 0.08 wt% P. The two ashless dithiophosphate additives, here referred to as 'AW1' and 'AW2' had the generic structure shown in Fig. 2. In the AW1 additive the R' group had an ester structure, whilst that in AW2 contained a carboxylic acid group. The acid-based antiwear additives are

Table 5 Lubricant formulations tested (all are 150 VG, custom blended oils)

Name	Description	P (wt%)
ZDDP	Base oil (PAO and ester) + ZDDP additive	0.08
AW1	Base oil (PAO and ester) + ashless AW1 additive (ester R' group)	0.03
AW2	Base oil (PAO and ester) + ashless AW2 additive (acid R' group)	0.03

Fig. 1 Chemical structure of the ZDDP additive [22]

Fig. 2 Generic structure of the ashless dithiophosphate antiwear additives (in the two specific ashless additives tested here, the R' group contained either ester ('AW1') or carboxylic acid ('AW2'))

Fig. 3 Schematic diagram of the MTM-SLIM setup [25]

reported to be more polar and are expected to have a higher adsorption on polar surfaces than the ester-based additives [19–21]. The treat rates of both AW1 and AW2 correspond to 0.03 wt% P. It should be noted that although the P concentration in the ashless blends is lower than that in the ZDDP blend used here, they were both chosen to be representative of concentrations that may be used with these specific additives in practice.

4 Experimental Methods and Procedures

An MTM ball-on-disc rig with spacer layer imaging system (SLIM) was used in this study as shown schematically in Fig. 3. The rig employs a ball on disc configuration where the two specimens are independently driven so that any slide-roll ratio can be imposed. The disc is immersed in lubricant contained in a temperature-controlled bath. The

load is applied through the ball shaft, the rotational axis of which is inclined to the disc plane to minimize spin in the ball-disc contact. Friction is measured continuously through a force transducer attached to the ball shaft support. The Spacer Layer Imaging Method (SLIM) is used to monitor the development of a boundary film on the test ball during the MTM test. The SLIM measurement on the MTM is made out-of-contact but without removing the test specimens from the rig. The ball is periodically halted, loaded upwards against a coated glass disc and an optical interference image of the contact between the ball and the glass disc is captured. After the image is taken, the ball is lowered, loaded against the steel disc again and the rubbing test is continued. The SLIM method is based on optical interferometry and is widely used for obtaining maps of fluid or boundary film thickness within the contact; for further details the reader is referred to [23, 24].

All tests were conducted at a maximum Hertz contact pressure of $p_0 = 1$ GPa and a temperature of 80 °C. To promote the formation of antiwear films, test speed was chosen so that some solid-to-solid contact occurred, i.e. the contact operated in the mixed lubrication regime. To ensure this, Stribeck curves were first generated at the test load and temperature and based on these results a test entrainment speed of 35 mm/s was chosen. This speed ensures mixed lubrication conditions and is a compromise between the amount of solid to solid rubbing and a reasonable test time required to provide a long sliding distance which is needed to reach steady state boundary film thickness. Similarly, a slide to roll ratio (SRR, ratio of sliding speed to entrainment speed) of 100% was chosen to provide a relatively long sliding distance within a reasonable test time. Following some trial tests, the test duration was set at 12 h. This test duration is significantly longer than the 2 to 4 h commonly employed in MTM boundary film tests (see [5, 26, 27] for example) but it (i) ensures that equilibrium film thickness is reached even with slow-forming antiwear films, (ii) helps to better assess the durability of any boundary films that may be formed and (iii) is more representative of real applications. The chosen MTM test conditions are summarized in Table 6.

Prior to testing, the test ball and disc were cleaned in toluene and isopropanol in an ultrasonic bath (10 min in each solvent) and then mounted in the MTM rig. Before starting the rubbing test, the ball and disc were rotated in pure rolling with no applied load until the oil bath temperature stabilizes at the desired test temperature. The ball was then loaded against the disc and the rubbing test starts. Friction is monitored throughout the test and the thickness of any tribo-film was automatically measured every hour throughout the 12-h test using the SLIM technique described above. Stribeck curves (friction coefficient versus entrainment speed) were also obtained at the beginning and the end of each test. At the end of the test, the ball and disc specimens

Table 6 MTM test conditions used in this study

Test conditions	
Max. Hertz contact pressure (GPa)	1
Hertz contact patch radius (μm)	122
Slide-roll ratio (SRR = sliding speed/entrainment speed), %	100
Temperature ($^{\circ}\text{C}$)	80
Entrainment speed (mm/s)	35
Test duration (h)	12
Max SLIM measurement interval (h)	1
Test oil viscosity at 80 $^{\circ}\text{C}$ (mPas)	28.5
Calculated min. EHL film thickness (nm)	10

were removed, again cleaned in toluene and isopropanol and subjected to post-test analyses such as surface roughness, wear measurements or XPS analysis. Each combination of steel and additive type was tested at least twice and the results were found to be highly repeatable. Boundary film thickness plots presented in this paper include results for two repeat tests and bar charts include error bars indicating the maximum and minimum measured values at each condition.

At the end of each test, wear track profiles of the disc were measured in the transverse direction using a stylus profilometer. The wear depth was taken to be the maximum depth of these profiles. At least four measurements were made at different locations on each disc and the quoted wear depth value is the average of these four measurements. Wear depths are quoted for discs only since the wear on the balls was negligible.

Any tribofilm in the wear track affects wear measurement and therefore tribofilms were removed prior to profilometry measurements. Ethylenediaminetetraacetic acid (EDTA) solution was used to remove of ZDDP tribofilms, whilst oxalic acid solution followed by EDTA solution were used for the removal of ashless tribofilms. Details of the methods employed for removing the ZDDP and ashless based tribofilms are described in [4, 26]. During ZDDP tribofilm removal, a drop of EDTA solution was placed on the wear track for 1 min and then wiped off with a tissue. For ashless film removal, oxalic acid solution was first placed for 20 s on the wear track and then wiped off, followed by EDTA solution for 1 min and then final wiping.

X-Ray Photoelectron Spectroscopy (XPS) was used to identify the main metallic elements present in the tribofilms. XPS gives information of the elemental composition and electronic state of the near surface. The binding energy values of each element corresponding to different states were determined using XPS online data base [28] and other XPS published studies [29–36]. Prior to analysis the specimens were cleaned in toluene and isopropanol in an ultrasonic bath (10 min in each solvent). XPS measurements were performed using a PHI 5000 Versa ProbeTM spectrometer

(Ulvac-PHI Inc, Chanhassen, MN, US) equipped with a monochromatic Al K α X-Ray source (1486.6 eV). The films formed in tracks on 52100, M2, 16MnCr5 and 440C smooth and rough steel ball specimens rubbed with AW1 and AW2 solutions were all analyzed. In addition, the virgin, unrubbed surfaces of ball specimens made of each of the four steels were also analyzed for reference.

5 Results with Smooth Specimens

5.1 Boundary Film Thickness with Different Oil-Steel Combinations

Figure 4 shows mean film thickness and the corresponding typical SLIM images at the start and end of the MTM tests with the blend containing ZDDP antiwear additive. The sliding speed direction is from left to right in all SLIM images. Additional SLIM images for ZDDP as well as the two ashless additive blends and all four steels are shown in Supplementary Information.

It is evident that all four steels formed thick films very rapidly with ZDDP, with thickness stabilizing at its maximum value after about 3 h of testing. M2 formed a slightly thinner film than the other three steels, but in all cases, films were thicker than 100 nm. The film thickness values in tests with the standard AISI 52100 specimens are ca. 120 to 130 nm, which agrees with results reported in the literature [26, 37]. In addition, SLIM images suggest that the observed films have an uneven, pad-like structure, in line with previously reported characteristic of ZDDP films [37–39]. Interestingly, ZDDP was found here to form boundary films on the stainless 440C of more or less the same thickness as those formed on the other three steels, in contrast to some previous reports [11] where ZDDP films on 440C were relatively thin. These observations demonstrate that the film-forming ability of ZDDP is practically independent of steel composition.

Figure 5 shows the equivalent film thickness and initial and final SLIM images for the ester-based ashless antiwear additive (AW1) blend.

Figure 5 shows that for all steels tested, both the film formation rate and the final film thickness with AW1 ashless anti wear additive is considerably lower than those observed with ZDDP blend. The films appear more uniform, without the obvious pad-like structure seen with ZDDP. Nevertheless, the final film thicknesses reached after 12 h of rubbing are still relatively high at around 80 nm for all steels except for 440C stainless steel, where the final film thickness is much thinner at around 20 to 30 nm. Therefore, in contrast to the ZDDP, the film formation with this ashless additive appears to be affected by steel composition.

Fig. 4 MTM-SLIM test results with ZDDP blend for 52100, M2, 16MnCr5 and 440C smooth steel balls rubbed against smooth discs of the same material: **a** Mean boundary film thickness measured over

test time and **b** typical SLIM interference images of the ball wear track at 0 and 12 h

Figure 6 shows typical film thickness measurements and interference images obtained in tests with the acid-based ashless AW2 additive with the same four steels.

It is apparent that after 12 h of rubbing, ashless antiwear additive AW2 forms significant tribofilms, in the range 50 to 60 nm, on all steels except on 440C steel. Like AW1 and unlike ZDDP, the films are relatively uniform. In general, AW2 films are somewhat thinner than those of AW1 and form at a considerably slower rate. Interestingly, owing to this slow growth rate, had only a 2 to 4-h MTM test been carried out as is often done in these types of tests, it would be concluded that AW2 forms films of only 20 to 30 nm. The 12-h long test duration reveals that eventually quite thick films are generated on three of the steels. In fact, for all steels other than 440C, the films appear to be still growing even after 12 h of rubbing.

As a summary of tribofilm thickness results, Fig. 7 compares the measured film thicknesses at the end of the 12-h rubbing tests for the ZDDP, AW1 and AW2 additives with the four different steels. The higher film thicknesses obtained with ZDDP, this additive's insensitivity to steel composition, and the inability of either of the ashless antiwear additives to

form significant films with stainless 440C are immediately apparent.

5.2 Tribofilm Roughness

The final tribofilm roughness was measured on both the ball and disc specimens. Composite R_{qc} roughness value was then calculated, where $R_{qc} = (R_{q, disc}^2 + R_{q, ball}^2)^{1/2}$. Fig. 8 compares the initial roughness of the fresh specimens before rubbing with the measured roughness of the specimens after the 12-h rubbing test for all steels and all three oil formulations.

It is evident that at 70 to 80 nm ZDDP tribofilm roughness is much greater than the roughness of the films generated with either of the ashless additives. It is also significantly higher than the initial specimen roughness, which was about 20 nm composite R_q . By contrast, the roughnesses of the final tribofilms produced with the two ashless additives are very similar to the initial specimen roughness and hence relatively low at around 25 nm composite R_q .

The effectiveness of a tribofilm in reducing wear and friction is not necessarily related to its absolute thickness.

(a)

(b)

Fig. 5 MTM-SLIM test results with ester-based ashless additive blend (AW1) for 52100, M2, 16MnCr5 and 440C smooth steel balls rubbed against smooth discs of the same material: **a** Mean boundary

film thickness measured over test time and **b** Typical SLIM interference images of the ball wear track at 0 and 12 h

To directly assess tribofilm effectiveness, friction and wear results are presented next.

5.3 Friction and Wear

The value of friction coefficient was recorded every 60 s during the 12-h tests. Fig. 9 shows the evolution of friction over the 12-h test for the four oil-steel combinations at the test entrainment speed of 35 mm/s. Average friction values over the 12 h are shown in Supplementary Information.

In all cases, friction shows a slight increase in the first two hours of the test, more pronounced for ZDDP and AW2 than AW1, but is then largely steady for the remaining 10 h. The initial rise in friction is likely to be related to the ongoing development of the tribofilm in the early stage of the test; once the surfaces are well-covered by a tribofilm friction remains steady. In general, friction coefficient was largely unaffected by the steel composition for either ZDDP or ashless additives. However, in all cases, ZDDP-containing oil gave much higher friction than either of the ashless additive solutions, regardless of the steel used. This trend is likely to be caused in large part by the higher roughness of the ZDDP

films as shown earlier, which effectively causes the contact to operate under the lower specific film thickness than in the case of smoother ashless tribofilms [40]. This is supported by the more rapid increase in friction in the first hours of the test for the ZDDP blend than for the two ashless blends—the rapid development of the ZDDP film quickly increases surface roughness and hence friction.

This behaviour is also evident in the Stribeck curves at the start and end of each test shown in Fig. 10. Here it can be seen that ZDDP and AW1 blends show relatively similar friction behaviour at the very start of the test, i.e. before any tribofilm is developed, but ZDDP shows substantially higher friction at the end of the 12-h test, i.e. once the tribofilm covers the surfaces. This ZDDP behaviour results in an effective shift to the right in the Stribeck curve as the test progresses so that higher entrainment speed is needed to move away from the boundary and into the mixed lubrication regime. This behaviour is not seen with the much smoother AW1 films. The Stribeck curves also indicate that prior to tribofilm development, the tests with 440C stainless steel samples had higher friction than the other three steels tested. However, this difference does not persist to the end

Fig. 6 MTM-SLIM test results with acid-based ashless additive blend (AW2) for 52100, M2, 16MnCr5 and 440C smooth steel balls rubbed against smooth discs of the same material: **a** Mean boundary film

thickness measured over test time and **b** Typical SLIM interference images of the ball wear track at 0 and 12 h

Fig. 7 Comparison of the final tribofilm thicknesses on the ball obtained with ZDDP, AW1 and base AW2 blends in tests with smooth 52100, M2, 16MnCr5 and 440C steel balls rubbed against smooth discs of the same material (Error bars indicate max. and min. values obtained in repeat tests)

Fig. 8 Comparison of the final tribofilm roughness obtained with ZDDP, AW1 and AW2 blends with 52100, M2, 16MnCr5 and 440C smooth steel specimens. Composite R_{qc} values shown in all cases (Error bars indicate max. and min. measured values in repeat tests)

of the test, i.e. once the tribofilm is fully developed steel composition has no influence on friction with any of the oil blends and friction is largely determined by the nature of the tribofilm itself rather than the underlying surface material.

With smooth surfaces negligible disc wear was observed for any of the additive/steel combinations tested. It is likely that the additives were all able to form a protective film rapidly enough to prevent significant adhesive wear, whilst the ball, despite being harder than the disc, was so smooth as not to cause abrasive wear.

6 Results with Rough Ball Specimens

In order to assess the effectiveness of the antiwear additives at higher surface roughness levels that are more representative of real engineering surfaces, additional tests were performed with MTM balls of roughness of ca 40 to 50 nm, as described in Table 4. The same polished discs as before were used in these tests, with R_q value of about 10 nm. AISI 52100, M2 and 16MnCr5 steels were studied; 440C stainless steel was not tested here since it was not possible to procure rough MTM balls made in this steel. The same three lubricants (Table 5), and the same test conditions (Table 6) as used in tests with smooth balls were employed.

6.1 Boundary Film Formation with Rough Specimens

Figures 11 and 12 show typical SLIM interference images and a plot of mean tribofilm thickness against time for the tests with AW1- and AW2-containing oils respectively for

the 3 steels tested. Corresponding results with the ZDDP solution were very similar to those from smooth ball tests with ZDDP and are shown in Supplementary Information. Additional SLIM images for all three oil blends and all steels are also shown in Supplementary Information. Fig. 13 compares the final tribofilm thickness after 12 h of testing for rough and smooth MTM balls for the three additives.

Figures 11 and 13b show that the performance of the ashless additive AW1 is strongly dependent on steel composition at these higher roughness levels. AW1 still builds up thick films on M2 steel, as was the case with smooth specimens, but unlike with smooth specimens, the films on 52100 and 16MnCr5 steel are negligible at these higher roughness levels. The final tribofilm thickness with AW2 appears to be relatively less dependent on roughness or steel composition; this additive is able to build substantial films on all three steels even at this higher roughness (Figs. 12 and 13c). However, the rate of growth of the AW2 tribofilm is strongly affected by the steel type, being significantly faster with M2 and case-carburized 16MnCr5 steel than with 52100 steel. These observations indicate that for lubricating oils blended with ashless additives, the type of additive chemistry needs to be carefully matched to the steel being lubricated to ensure adequate antiwear film build up.

The direct comparison of tribofilm thicknesses obtained with rough surfaces presented in Fig. 13d shows that ZDDP builds thicker films with all steels than either of the two ashless additives even at this increased roughness level.

The likely reason behind this strong effect of steel composition on ashless additive performance is the presence of different alloying elements in these steels, with some alloying elements able to promote boundary film growth

Fig. 9 Evolution of friction coefficient over the 12-h MTM test with AISI 52,100, M2, 16MnCr5 and 440C steels with **a** ZDDP blend, **b** Ester-based ashless blend, AW1 and **c** acid-based ashless blend, AW2

Fig. 10 Stribeck curves for the four steels tested with ZDDP and AW1 ashless blends at **a** the beginning of the test and **b** the end of the test (i.e. after 12 h of rubbing). (Note that trends observed with the AW2 ashless blend are similar to those of AW1 so are not shown here for the sake of clarity)

more than others. For example, M2, which was the only steel to show relatively thick films with both ashless anti-wear additives at both roughness levels, has high amounts of molybdenum, tungsten, vanadium and nickel so it is likely that one or more of these metals is reacting with the ashless additives to promote film build up. This process may be similar to that by which Zn cations promote build-up of ZDDP film, but in the case of zinc-free ashless additives suitable metal ions would have to be extracted from the steel during rubbing to form the film, as they are not

present in the additive formulation itself. This is discussed further later in the paper.

6.2 Tribofilm Roughness

Tribofilm roughness at the end of each test was measured and full results are shown in Supplementary Information. In brief, the final composite roughness of ZDDP tribofilms in these tests with rough specimens was ca 85 nm with all three steels; this is similar to that observed with smooth specimens

(a)

(b)

Fig. 11 MTM-SLIM test results with ester-based ashless additive-containing blend (AW1) for 52100, M2 and 16MnCr5 *rough* steel balls rubbed against smooth discs of the same material: **a** Mean

boundary film thickness measured over test time and **b** Typical SLIM interference images of the ball wear track at 0 and 12 h

(a)

(b)

Fig. 12 MTM-SLIM test results with acid-based ashless additive-containing blend (AW2) for 52100, M2 and 16MnCr5 *rough* steel balls rubbed against smooth discs of the same material: **a** Mean

boundary film thickness measured over test time and **b** Typical SLIM interference images of the ball wear track at 0 and 12 h

Fig. 13 Bar charts comparing tribofilm thickness in tests with smooth vs rough specimens for **a** ZDDP, **b** AW1 and **c** AW2 blends. **d** Direct comparisons of tribofilm thickness measured with the three blends in tests with rough specimens

shown above. The composite roughnesses of the two ashless tribofilms were very similar to the initial specimen composite roughness, as was the case for smooth ball tests. This implies that the AW1 and AW2 tribofilms are so uniform in thickness throughout the contact region that final surface roughness is dominated by that of the original substrate.

The fact that the final surface roughness with ZDDP blend was the same regardless of the initial roughness may be of practical significance since it suggests that the widely accepted tendency of ZDDP films to increase the roughness of the original surface may be limited to cases where the initial roughness itself is relatively smooth, as is the case in many laboratory tests. In situations where the initial surface roughness is significantly higher than the typical roughness of the final ZDDP film obtained on a smooth surface (ca 80 nm here) as may be the case in many practical situations, there may well be no roughness increase caused by ZDDP tribofilm growth. This would imply that in many practical situations with moderately

rough virgin surfaces there may be no detrimental effect on the shape of the Stribeck curve and no additional asperity stresses caused directly by the roughness of the ZDDP film itself. This is separate from the well-established mechanism in which ZDDP tribofilms increase severity of asperity stresses through suppression of running-in and in turn, increase the risk of micropitting [41–43].

6.3 Friction and Wear with Rough Specimens

Figure 14a, b compare Stribeck curves at the end of test for rough and smooth disc tests of three steel types lubricated by ZDDP and AW1, respectively. ZDDP produces the same friction coefficient dependence on entrainment speed with both rough and smooth specimens. This is because ZDDP tribofilm roughness is similar for both rough and smooth balls so that contact shows a similar transition from boundary to mixed lubrication as entrainment speed and thus oil film thickness is increased. ZDDP friction is higher than that

Fig. 14 Example Stribeck curves at the end of 12 h tests with rough and smooth specimens for **a** ZDDP blend and **b** AW1 ashless blend

obtained with ashless additive blends regardless of the initial specimen roughness and steel composition.

Ashless additives produced higher friction with rough specimens than with smooth ones. This is because the higher initial roughness of the surfaces, which was shown not to be significantly changed by the formation of ashless boundary films unlike in the case of ZDDP above, simply means that the contact is operating closer to boundary lubrication than is the case for initially smooth surfaces. The steel-additive combinations that produced thicker ashless films in the case

of rough specimens, namely M2 steel with AW1 and all steels with AW2 (not shown in Fig. 14), resulted in considerably higher friction than those that produced thinner films (AW1 with 52100 and 16MnCr5 steels). Interestingly this does not appear to result from a roughness effect since the final composite tribofilm roughness was ca 40 nm for all steels. This also shows that high tribofilm thickness is not necessary for good tribofilm performance, in fact the opposite is true in the case of friction here.

Fig. 15 Measured wear track profiles with 52100, M2 and 16MnCr5 smooth discs after rubbing against rough balls of the same material with ZDDP (a–c), AW1 (d–f) and AW2 (g–i) oil blends (no tribofilm removal prior to measurements)

Figure 15 shows the wear track profiles on the discs for all three steels when rubbed in the presence of ZDDP, AW1 and AW2 blends, respectively. In these profiles any tribofilm formed during the test was not removed prior to measurement. From Fig. 15a–c, it is evident that no observable wear was generated with ZDDP regardless of the steel type used. Instead, a ZDDP tribofilm is clearly present, seen as a ridge on the disc rubbing track in all cases. The corresponding ball profiles showed the same results with no wear and a thick film on the rubbing track.

The wear behaviour of ashless AW1 and AW2 additives with different steels is more interesting. In contrast to ZDDP, wear was observed with ashless additives and this was strongly dependent on the steel type, as evident in Fig. 15. Both AW1 and AW2 produced relatively small amounts of wear on 52100 steel discs (Fig. 15d, g). AW1 produced a very large amount of wear on the 16MnCr5 discs (Fig. 15f). AW2 also produced wear with 16MnCr5 steel but this was significantly less than in the case of AW1 (Fig. 15i). This is of practical significance given that 16MnCr5 is a relatively common case-carburized gear steel. Both additives produced

a significant and relatively similar amount of wear on M2 steel discs (Fig. 15e, h). Together, these results indicate that in the case of ashless antiwear additives, the exact additive chemistry needs to be matched to the steel type of the application to optimize the wear performance of the system.

It should be noted that the observed differences in wear behaviour between different oil-steel combinations cannot be explained in terms of the small differences in roughness and hardness of different steel specimens tested. Although roughness of the counter-face balls was controlled as much as possible, some differences still exist between different materials (Table 4). However, the trends in wear described above are not in line with any roughness differences, see for example difference in wear between AW1 and AW2 with the same 16MnCr5 samples (Fig. 15f, i) or the opposite trend in M2 and 16MnCr5 wear for AW1 and AW2 additive (Fig. 15e, f, h, i). The observed wear trends also do not correlate with the small differences in hardness of different steel specimens. In fact, in many cases, the lower hardness steels suffered less wear than harder ones (compare for example the wear on 52100 steel (730HV)

with either ashless additive to wear on M2 (790 HV) or 16MnCr5 (760 HV)) which were much larger.

It is also noteworthy that although AW1 and AW2 produce thick films on M2 steel, they nevertheless produce high wear on the discs of this material. This means that the films formed on the balls are not effective in protecting the discs from wear and that, as was also observed in relation to trends in friction, the thickness of the boundary films is not in itself an indicator of the practical performance of a given additive.

7 XPS Analysis

XPS analysis indicated that AW1 and AW2 tribofilms have similar components (though different proportions) but the compounds detected vary markedly with steel composition. In the case of 52100 steel, the tribofilms consisted of Fe oxides (Fe_2O_3 , Fe_3O_4 at ≈ 530 eV, 711 eV), Fe phosphates (FePO_4 at 133.7 eV) and Fe sulfates (FeSO_4 at 168.7 eV). M2 tribo-film consisted of Fe, Mo, W oxides (MoO_2 and MoO_3 at 230–234, ≈ 530 eV, WO_2 and WO_3 at 32–34 eV, 530–531 eV), Fe, Mo phosphates ($\text{MoO}_3\text{P}_2\text{O}_5$ at 133.9 eV) and Fe, Mo, W sulfides (FeS and FeS_2 at 706–707 eV, MoS_2 at 232–233 eV, WS_2 at 31–35 eV). 16MnCr5 tribofilms predominantly consisted of Fe, Mn oxides (MnO , Mn_2O_3 , Mn_3O_4 at ≈ 530 eV), Fe, Mn phosphates ($\text{Mn}_3(\text{PO}_4)_2$ at 133.7 eV), Fe, Mn sulfates (MnSO_4 at 169.6 eV) and Fe, Mn sulfides (MnS , MnS_2 at ≈ 162 eV). 440C steel forms tribo-film of Fe, Cr oxides (Cr_2O_3 at 575–580 eV), Cr phosphates (CrPO_4 at 133.4 eV), Fe, Cr sulfates ($\text{Cr}_2(\text{SO}_4)_3$ at 532.10 eV) and Fe, Cr sulfides (Cr_2S_3 at 585.20 eV).

Overall, XPS detected strong phosphorus compound signals when SLIM showed thick tribofilms, and negligible phosphorus compounds and/or high amounts of metal oxides when there was negligible tribofilm. Of particular significance with respect to the current study is the observation that the alloying elements from the steels, namely Mo and W from M2, Mn from 16MnCr5 and Cr from 440C steel, appear to be present in the corresponding tribofilms.

8 General Discussion

This study has investigated the influence of steel composition on the formation and effectiveness of lubricating boundary films in a ball-on-disc tribometer with three oils; one that incorporates the historically widely used ZDDP antiwear additive and two containing more-recently developed, ashless phosphorus/sulphur-based antiwear additives. Most existing studies of boundary film build-up

and the associated friction and wear employ only 52100 steel, most likely because many of these studies are conducted on ball-on disc tribometers and the ball specimens needed are commonly available in 52100 bearing steel. The obvious problem with this approach is that the additive packages designed in this manner may be used in oils that lubricate components where steels have significantly different composition to that of 52100, such as gears or case-hardened bearings, for example, so that their performance in practice may not be as expected. The problem is likely to become more acute as the traditional and relatively well understood zinc-containing, ZDDP antiwear additive is replaced by ashless additives in modern oils.

Results show that the effectiveness of ZDDP is not significantly influenced by steel composition. Thick ZDDP films with similar tribofilm roughness and friction are formed with all four steels and all specimen roughness levels. No measurable wear was observed on any of the specimens. In contrast, the effectiveness of ashless additives was found to be strongly influenced by steel composition. For smooth specimens (ball $R_q \sim 15$ nm), ashless additives were unable to form any appreciable films with 440C stainless steel, even after 12 h of rubbing. The influence of different steel composition becomes further pronounced at higher surface roughness levels tested here (ball $R_q \sim 50$ nm), which are more representative of real machine components. In this case, the ashless additives form substantially thicker films on M2 tool steel compared to other steels tested. Furthermore, the ester-based thiophosphate antiwear additive AW1 is unable to form any significant film with either the 52100 bearing steel or 16MnCr5 case-carburised gear steel in the case of rough specimens. The acid-based AW2 does form films with 52100, 16MnCr5 and M2 steels but the rate of formation varies significantly, being much faster with the 16MnCr5 and slowest with the 52100 steel.

This strong effect of steel composition on ashless additive performance may be attributed to the presence of different alloying elements in these steels, which may act to promote or retard boundary film formation. The participation of these alloying elements is confirmed by XPS analysis of the tribofilms. For example, the M2 steel has high amounts of nickel, molybdenum, tungsten and vanadium, and some of these metals appear to react with the ashless additives to support film growth and survival; XPS shows the presence of both tungsten and molybdenum compounds in the tribofilm. The mechanism of the film growth is thus likely to be driven by the ability of the zinc-free additive to extract the specific cation from the steel surface needed to build up a thick phosphate-based boundary film. In contrast, ZDDP film build up does not rely on extraction of suitable alloying elements from the steel surface because it already contains Zn in its chemical structure and Zn^{2+} cations are effective in promoting phosphate tribofilm growth. Consequently,

ZDDP-containing oil was able to build thick films and at a relatively fast rate regardless of the steel composition.

It follows that the observed differences in the performance of the two tested ashless additives are likely to be related to their respective abilities to extract metal cations from the steel surface. For example, the fact that the acid-based AW2 appears to be less affected by the type of steel is most likely a consequence of the higher reactivity of the acid which is able to extract metal cations from the rubbed surfaces regardless of the type of alloying elements present. The reactivity of a particular additive, and its subsequent ability to extract a cation from the steel surface, is also affected by the prevailing contact conditions; for example, AW2 forms thicker films with rough specimens than smooth ones (see Fig. 13).

No significant films are formed on 440C stainless steel with either of the ashless additives tested. This probably results from the presence of chromium oxide films which limit the release of cations from the surface needed to support film growth. The existence of this oxide layer has been previously linked to relatively poor boundary lubrication performance of stainless steels in general [8, 9, 11] including limited boundary film formation with ZDDP itself [11]. In contrast, present results suggest that ZDDP is able to grow films on stainless steel that are of similar thickness and effectiveness to those formed on the other three steels.

Ashless additives were seen to grow films at a considerably slower rate than ZDDP in almost all oil-steel combinations tested. In many cases this effect was so pronounced that significant final films were only observed because the present study deliberately employed a relatively long test duration of 12 h.

ZDDP produced thicker boundary films than either of the ashless additives in all cases. These films were rougher and resulted in higher friction than the equivalent ashless films. The high tribofilm roughness originates from the well-known pad-like ZDDP film structure [26]. The thinner ashless films were much smoother and resulted in lower friction in mixed lubrication conditions regardless of the steel used. However, ashless additives produced substantial wear on M2 and 16MnCr5 steels when rougher specimens were used, whereas no measurable wear was observed with ZDDP with any of the steels or roughness levels tested. There was no correlation between ashless film thickness and wear performance. For example, AW1 grew a much thicker film on M2 than on 52100 steel but also produced more wear on M2. The acid-based AW2 built films of similar thickness on 52100, 16MnCr5 and M2 steels but produced considerably less wear on 52100 steel. These observations clearly indicate that the film thickness itself is not a good measure of the protection afforded by the boundary film to the rubbing surfaces; wear and friction should be measured in parallel to film thickness to assess tribofilm effectiveness.

9 Conclusions

The present study has investigated the influence of steel composition on boundary lubrication effectiveness of three different antiwear additives, an ester-based and an acid-based di-thiophosphate ashless antiwear additive and a zinc-containing ZDDP additive. Tests covered four common steels used in tribological applications, through-hardened martensitic 52100 bearing steel, M2 tool steel, case-carburized 16MnCr5 gear steel, and 440C stainless steel. An MTM ball-on-disc tribometer with SLIM was employed in this study and tests were conducted with specimens of two roughness levels, standard smooth MTM balls ($R_q \sim 15$ nm) on standard smooth discs ($R_q \sim 10$ nm) and rougher balls ($R_q \sim 50$ nm) on the same smooth discs. The main findings can be summarized as follows:

- The boundary lubrication effectiveness of ashless antiwear additives is strongly affected by steel composition. These additives form tribofilms of varying film thickness depending on the type of steel present. The differences are more pronounced at higher surface roughness levels which are more representative of real applications. The precise influence depends on the chemistry of the ashless additive, but the general trends show that M2 steel promotes ashless antiwear tribofilm formation whilst 440C retards ashless antiwear tribofilm formation. This behaviour is attributed to the presence of different alloying elements in the various steels which appear to promote ashless film formation by providing easily leached metal cations needed to build a metal phosphate film, i.e. these cations play similar role to that provided by Zn in ZDDP but need to be extracted from the rubbing surface itself. Cr in stainless steel forms passivating oxide films on the surface which may prevent metal cation release and hence retard ashless additive film formation.
- In contrast, ZDDP antiwear additive effectiveness is not influenced by steel composition or surface roughness levels. Similar tribofilm thickness, film growth rates, final film roughness and friction were observed in tests with all four steels and no significant wear was measured in any of the ZDDP tests. This behaviour is attributed to the presence of Zn in the additive itself which promotes the growth of stable, thick phosphate boundary films regardless of the composition of the rubbing steel surface.
- With rougher specimens, wear was significantly higher with the ashless antiwear additives than with ZDDP for all steel types. Wear was particularly severe with M2 steels for both ester and acid group containing ashless additives and with 16MnCr5 gear steel with the ester-based additive. The wear of 52100 steel with either

ashless chemistry was less than for other steels but still higher than with ZDDP.

- The observed wear performance does not correlate with the measured boundary film thickness; in many cases, higher amounts of wear occurred when a thicker film was present.
- The final film thickness and the rate of tribofilm growth were lower with ashless additives than with ZDDP for all steels tested. However, ashless tribofilms had much lower final roughness and lower friction than ZDDP films. The lower roughness of ashless films effectively means that the transition from boundary to mixed lubrication is reached at a lower entrainment speed than is the case with ZDDP.
- The relative performance of two ashless additive chemistries is affected not only by steel composition but also surface roughness. At higher roughness levels, acid-based ashless additive is better able to form films on 16MnCr5 gear steel and 52100 bearing steel than the ester-based additive, with film growth rate with 16MnCr5 being particularly fast. This difference is not apparent at the lower roughness level. This may be due to an increased reactivity of the acid-based additive under conditions of high local pressures and shear stresses caused by higher surface roughness.
- These results indicate that to ensure satisfactory performance of mechanical systems lubricated with ashless based oils, it is important to tailor the chemistry of the chosen ashless additive to the specific composition of steel present in the application.

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