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On the role of friction modifier additives in the oil control ring & piston liner contact

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Abstract

In-cylinder internal combustion engine parasitic frictional losses continue to be an area of interest to improve efficiency and reduce emissions. This study investigates the frictional behaviour at the oil control ring-cylinder liner conjunction of lubricants with anti-wear additives, varying dispersant concentration and a range of friction modifiers. Experiments are conducted at a range of temperatures on a cylinder liner with a nickel silicon carbide coating. A novel motored reciprocating tribometer, with a complete three-piece oil control ring and cylinder liner, was used to isolate the friction at the segment-liner interfaces. Four lubricants were tested, three with the same 3% dispersant concentration and 1% ZDDP anti-wear additive: the first with no friction modifier, the second with inorganic friction modifier (molybdenum dithiocarbamates), and the third with organic friction modifier (amide). A fourth lubricant with organic friction modifier with a 9% dispersant concentration was tested to compare the effect of the level of dispersant with the friction modifier. Results indicate that the inorganic friction modifier reduces friction comparatively to the other lubricants, showing the importance of friction modifier selection with anti-wear additives.

Key words: friction, nickel silicon carbide, ZDDP, lubricant, friction modifier

1. Introduction

Despite increasing electrification of powertrain components and systems, reducing frictional losses from internal combustion engines remains a target to improve efficiency and reduce emissions. It is reported by Holmberg et al. [1] that one third of energy usage in passenger cars is used to overcome friction of moving components. Around half of this loss occurs from the friction between the piston assembly and cylinder liner [2,3]. One of the main areas where frictional losses occur is in the sliding contact between the piston ring and cylinder liner. Tribological improvements to these conjunctions have been made over the years through a combination of surface coatings, texturing of the piston ring and cylinder liner [4–6] and improved lubricants.

Cylinder liners are often made of steel, aluminium or cast iron with the addition of wear-resistant coatings, for example in high performance vehicle and motorsport applications nickel silicon carbide coatings are often used. Gore et al. [7] made comparisons of a nickel silicon carbide coated cylinder liner with an uncoated steel liner in a study combining analytical and

experimental results. The liners with the wear-resistant coating had a rougher surface than the steel liners, however this did not result in significantly increased friction.

Lubricants are used within the piston ring/cylinder liner contact to reduce friction and wear. The viscosity of the lubricating oil is important to consider as lower viscosity oils can reduce hydrodynamic friction but can increase boundary friction. Lubricants also provide different functions such as corrosion protection and wear prevention through adsorbed surface films. The additive package of lubricating oils is continually being developed to achieve optimal performance.

Friction modifiers form part of the additive package, and their purpose is to reduce friction when there is boundary or mixed regime lubrication in the contact. Friction modifiers present in a lubricant are classified as either organic or inorganic [8,9]. Inorganic friction modifiers are typically organomolybdenum-type compounds and they reduce friction in sliding contact by being broken down into low shear strength compounds and are activated by temperature [8,10–12]. Organic friction modifiers however, are physisorbed (no chemical change, bonding from intermolecular forces such as Van der Waals) to the surfaces during sliding and form monolayers of molecules which prevent direct contact of the surfaces [8,13,14].

Zinc dialkyl dithiophosphate (ZDDP) is a common additive in engine oils. Introduced over 80 years ago, it is used as an antiwear additive and prevents corrosion and oxidation. ZDDP becomes active in the solution phase, the functionality is dependent on shear stress enhanced thermal degradation, adsorption at metal surfaces, ligand exchange and reaction with peroxide [15]. Mild wear is prevented by the ZDDP forming thin phosphate tribofilms on ferrous surfaces, which can therefore reduce adhesion. ZDDP has been shown to reduce the coefficient of friction when added to bio-lubricants such as mineral oil [16]. The film formed by ZDDP is commonly not uniformly distributed and a roughening of the contacting surfaces can be observed, which has reported to have a negative effect on the friction in ferrous conjunctions under mixed lubrication conditions [17]. The formation of ZDDP tribofilms on non-ferrous surfaces is not fully understood, however, Ueda et al. [18] showed that on silicon nitride surfaces ZDDP tribofilms were formed under boundary lubrication conditions and were thicker than those formed on a steel surface, but less adhesive and could therefore be easily removed.

The specific combination of ZDDP, friction modifier and dispersant must be carefully considered to produce low friction in the contact being considered. This is particularly important when organic friction modifiers are present as both require the formation of an adsorbed layer on the surface [19]. Further study of organic friction modifiers and ZDDP has shown that the interaction of the two additives is dependent on the chemistry and concentration and can result in a positive (lower friction) [20,21] or negative [22] effects (higher friction). Umer et al. [8] conducted experiments on ferrous samples which showed that organic friction modifiers and dispersants interfered with the formation of ZDDP tribofilms which is consistent with other literature [22–26]. Umer et al. also discuss that ZDDP and inorganic friction modifier molybdenum dithiocarbamates (MoDTC) can work together to form a low friction tribofilms [27–30]. They further explored the effect of dispersant level in combination with organic friction modifier, comparing organic friction modifier with a 3% dispersant and a 9%

dispersant at a range of temperatures up to $\sim 150^{\circ}\text{C}$ on a steel cylinder liner. The higher dispersant concentration was shown to reduce the friction at higher temperatures.

Assessing the effectiveness of friction modifiers in lubricants applied to the piston ring/cylinder liner contact is difficult because isolating and measuring the friction between at a component level can be complex multiscale problem. The key dimension of the component is of the order $10^3 \mu\text{m}$, the surface roughness is of the order $10^{-1} \mu\text{m}$, ZDDP tribofilms of the order $10^{-2} \mu\text{m}$ and monolayers of the order $10^{-4} \mu\text{m}$. A successful method was described by Forder et al. [2] in which a motored reciprocating tribometer with a three-piece oil control ring and complete cylinder liner. Forder et al. used the novel test rig to compare the friction in the contact with two different oil grades at a range of speeds at two temperatures. The results demonstrated that the conjunction resides in a mixed regime of lubrication across the conditions tested.

The work presented here shows a novel experiment in which organic and inorganic friction modifiers in combination with ZDDP were tested on a full-size nickel silicon carbide coated cylinder liner. The rig features a three-piece oil control ring where the friction between the ring segments and liner are isolated and measured. The aim of this work was to assess the effect on the frictional behaviour of lubricants with antiwear additives and organic, inorganic or no friction modifier, at a range of temperatures on a cylinder liner with a Nickel Silicon Carbide coating. The motored reciprocating tribometer described by Forder et al. [2] is also used here for the first time to evaluate a selection of lubricants at a range of temperatures from 35°C to 75°C . The results of which can be used to inform the development of lubricants with both antiwear additives and friction modifiers in their additive packages to ultimately reduce frictional losses in the contact when a non-ferrous cylinder liner is present.

2. Experimental Methodology

2.1. Test Apparatus

The tribometer, shown in Figure 1, closely replicates the relative kinematics of a piston ring and cylinder liner system. The reciprocating tribometer, described by Forder et al. [2], comprises of a complete and full-scale three-piece oil control ring and cylinder liner which isolates the friction by using pure rectilinear motion. The oil control ring is held in a stationary position whilst the cylinder liner reciprocates at 90° against it. The tribometer has a 50Hz three-phase 2.24kW motor, mounted centrally to ensure the motor pulley and drive system pulley are aligned. Throughout the stroke, the position of the liner is recorded using a rotary encoder (NI9401 5 V DC), in degrees of rotation. Data is also collected via LabVIEW software from a piezo electric compression and extension load cell.

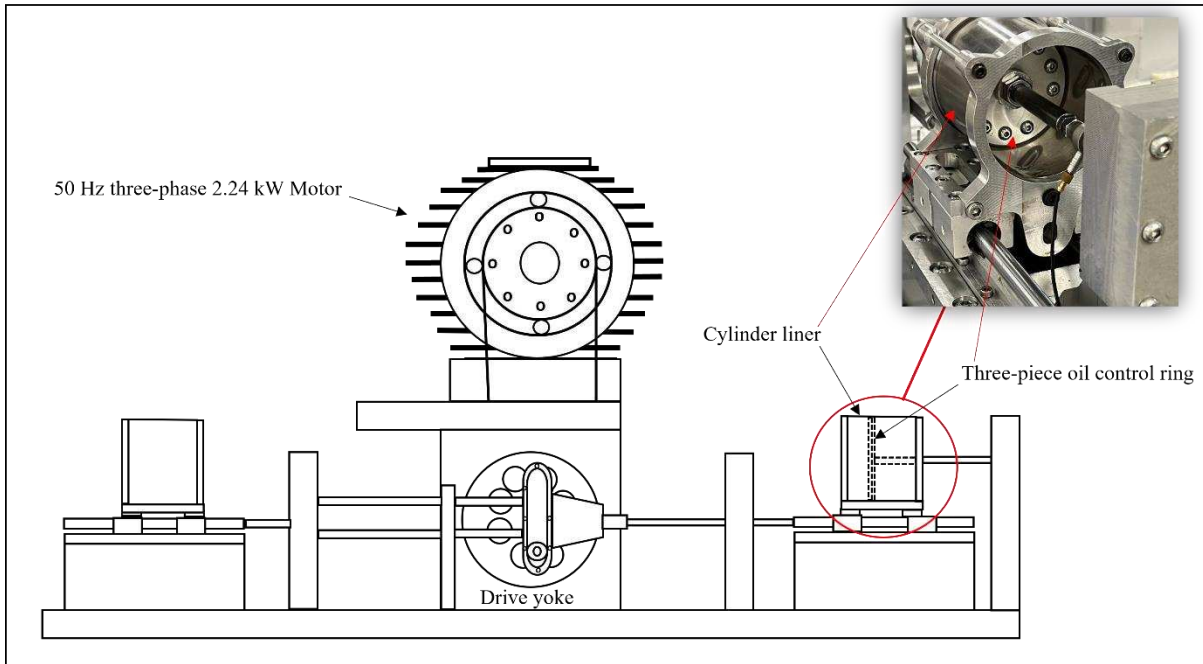


Figure 1: Test apparatus schematic (adapted from Forder et al. [2])

A heater system was used to allow friction to be measured at a range of temperatures. The system consisted of an insulated block, with six 300W pencil heaters inserted around it, controlled by a heater controller, which heated the block by conduction as shown in Figure 2. The insulated block was placed over the cylinder liner and with the contours of the heated block fitting closely over the reciprocating liner, the heat stored in the insulated block was transferred to the reciprocating liner and shuttle passively. Thermocouples were placed on the block and the ring holder to record temperature around the system.

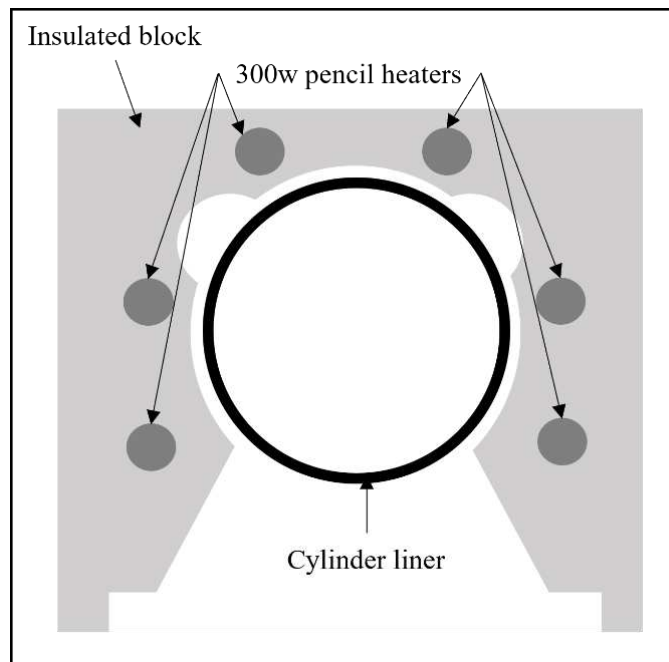


Figure 2: Schematic of heating block

2.2. Test Specimens

Cylinder Liner and Oil Control Rings

The cylinder liners which were selected for testing were manufactured from 19MNV6 stress relieved steel and coated with nickel silicon carbide. Details regarding the coating bath composition and bath operating conditions are described by Ishimori et al. [31] and Howell-Smith [32]. An 80 mm bore diameter with a 60 mm stroke length, representative of a 1200cc four cylinder in-line engine was used for testing. The three-piece oil control ring used in testing was a commercial product produced by Nippon Piston Ring Cup, 6627 type [2], comprising of a waveform expander and two segments with nitride contact faces, with an axial thickness of 0.35mm per segment. The surface roughness of the ring before and after testing is presented in Table 1. The radial force resulting from ring tension was measured at 70N.

Table 1: Surface roughness of ring before and after testing

	Ra (μm)	Rq (μm)
New Ring	0.19 \pm 0.03	0.22 \pm 0.06
Used Ring	0.23 \pm 0.02	0.28 \pm 0.02

Four lubricants were chosen for testing, lubricant A had no friction modifier, lubricant B had inorganic friction modifier (molybdenum dithiocarbamates (MoDTC)), lubricant C had organic friction modifier (amide). and lubricant D with organic friction modifier was tested to evaluate the effect of a higher concentration of dispersant (9 wt%). The lubricants are described in in Table 2:.

Table 2: Lubricant commercial names, friction modifier and dispersant concentration

Lubricant	Friction Modifier	Dispersant concentration (%wt)
A	No Friction Modifier	3
B	0.7 wt% Inorganic Friction Modifier	3
C	0.2 wt% Organic Friction Modifier	3
D	0.2 wt% Organic Friction Modifier	9

The remaining additive package remained consistent across the lubricants as shown in Table 3, the kinematic viscosity for all the candidate lubricants at 40°C is 38.3-40.3 cSt and at 100°C is 7.48-7.55 cSt [8].

Table 3: Lubricant additives present in all lubricants (A, B, C and D)

Lubricant additive	Description
Anti-wear	Zinc primary-secondary alkyl dithiophosphate (1wt%)
Viscosity modifier	Olefin copolymer

Detergents	Mixture of low base number synthetic alkyl benzene calcium sulphonate, and long chain linear alkyl benzene high base synthetic magnesium sulphonate
Dispersant	High molecular weight; polyisobutylene succinimide [2300 Mwt]
Antioxidant	Aminic octyl/butyl diphenylamine and phenolic ester (0.5wt%)

2.3. Test Approach

The three-piece oil control ring and the cylinder liner were cleaned with petroleum ether before installation. Each new liner was then run in for 30 minutes at room temperature at 750 RPM with 1ml of lubricant as suggested by Zhang et al. [33]. This has been shown by Leighton et al [34] to be suitable as the liner surface roughness reached steady state wear behaviour after less than 10 minutes running in. The samples were then rinsed with petroleum ether to remove any debris from the surface.

Friction was measured at 5 different temperatures from an initial temperature of 35°C up to a maximum of 70°C, which was measured using the thermocouple attached to the ring holder. The temperature was selected as a typical engine sump temperature, and it prevents lubricant oxidation in ambient air. It should be noted however that piston, cylinder liner and ring temperatures in application are often significantly higher. Every test was run at an apparatus motor rotational speed of 750 rpm which equates to an average piston speed of approximately 1.5 ± 0.1 m/s. This speed was chosen because it is within the operating parameters of a typical passenger vehicle internal combustion engine. The four lubricants were tested as shown in Table 4, with Lubricant A on cylinder liner 1 initially. The cylinder liner was then cleaned with petroleum ether and Lubricant B was then applied to the same liner. Lubricants C and D were applied in the same manner to cylinder liner 2. A final test on cylinder liner 3 (highlighted in Table 3) was conducted to evaluate the effect of the order the organic friction modifiers were applied and assess whether any of the additives had been absorbed.

Table 4: Test schedule

Lubricant	Liner	Temperature (°C)
A	1	35,45,55,65,70,65,55,45,35
B	1	35,45,55,65,70,65,55,45,35
C	2	35,45,55,65,70,65,55,45,35
D	2	35,45,55,65,70,65,55,45,35
D	3	35,45,55,65,70,65,55,45,35
C	3	35,45,55,65,70,65,55,45,35

In each test after the initial running in, the tribometer was stopped and 1ml of the candidate lubricant applied evenly to the cylinder liner. The tribometer was then run for a minimum of 5 minutes to reach, and then stabilise at, the desired temperature. Once the desired temperature was achieved it was held at that point whilst friction measurements were taken. The friction

was measured continuously for 30 second intervals, at least 30 seconds apart for 5 repeats. Once measurements at the maximum temperature had been recorded the heating block was switched off and further friction measurements were taken as the tribometer cooled to room temperature.

3. Results and discussion

3.1. Friction modifier

The results shown in Figure 3 report the mean friction in the contact of the oil control ring and cylinder liner with lubricants A (no friction modifier, red data markers), B (inorganic friction modifier, blue data markers) and C (organic friction modifier, green data markers) with standard error ($SE = \sigma/\sqrt{n}$, where σ is the standard deviation and n is the sample size). The friction measurements for the initial increase in temperature follow the same trend for all three lubricants, increasing as the temperature rises within the range tested. This is due to the reduced lubricant viscosity and lower hydrodynamic load carrying capacity at the higher temperatures. From these results a comparison between the lubricants with 3% dispersant can be made to observe the effect of the different friction modifiers. The inorganic friction modifier is seen to reduce the friction compared to the lubricant without friction modifier and the lubricant without friction modifier. Notably, friction in the contact with the organic friction modifier is higher than the lubricant with no friction modifier added. The friction increase with temperature indicates that the contact is operating in the mixed lubrication regime.

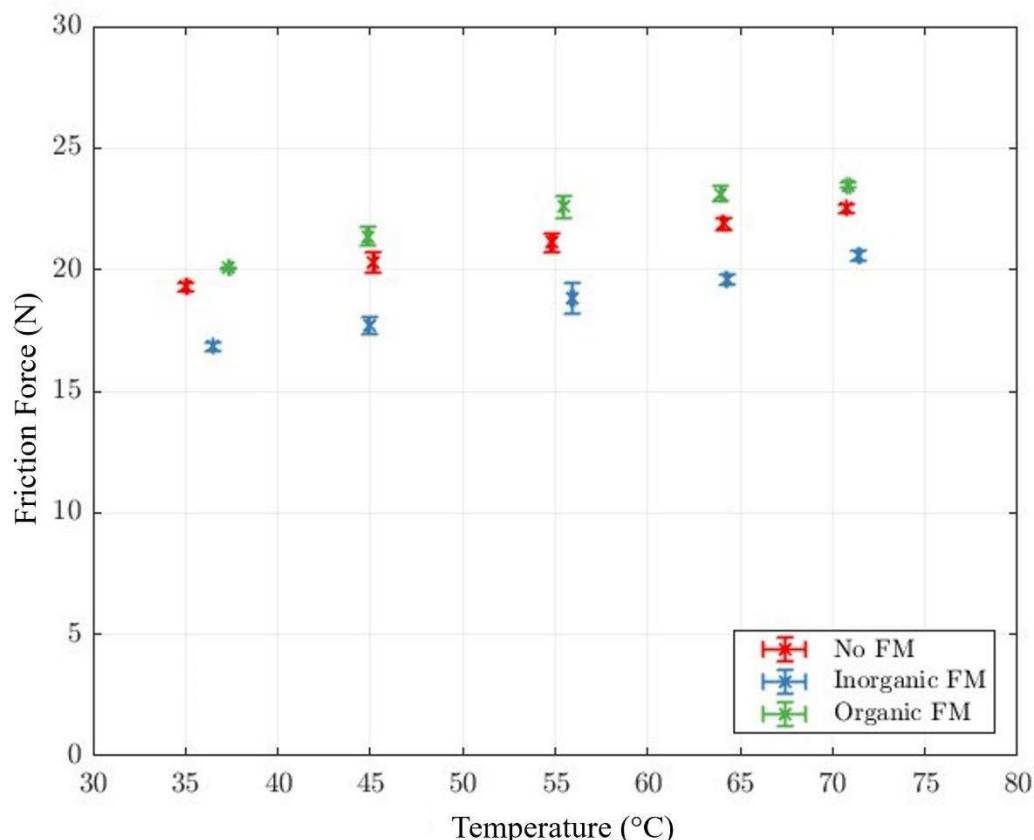


Figure 3: Comparison of mean friction force with standard deviation at the cylinder liner-ring interface with lubricants A with no friction modifier with Liner 1, B inorganic with Liner 1 and C organic friction modifiers with Liner 2 and 3. (Note: Non-zero origin on x-axis.)

3.2. Organic friction modifier dispersant concentration

Umer et al. [8] observed that the presence of an inorganic friction modifier successfully lowered the friction level with both low (3%) and high (9%) dispersant levels. They also similarly observed that the friction did not reduce when organic friction modifier was used with a low level of dispersant (3%) when tested on steel liners, suggesting this to be due to an anti-wear film being formed when a low level of dispersant was present in the lubricant. As part of the investigation of the lubricants on the nickel silicon carbide coated liner, further testing of an organic friction modifier with high (9%) dispersant level was conducted. The results of the friction in the contact with Lubricant C (3% dispersant) and Lubricant D (9% dispersant) are presented in Figure 4.

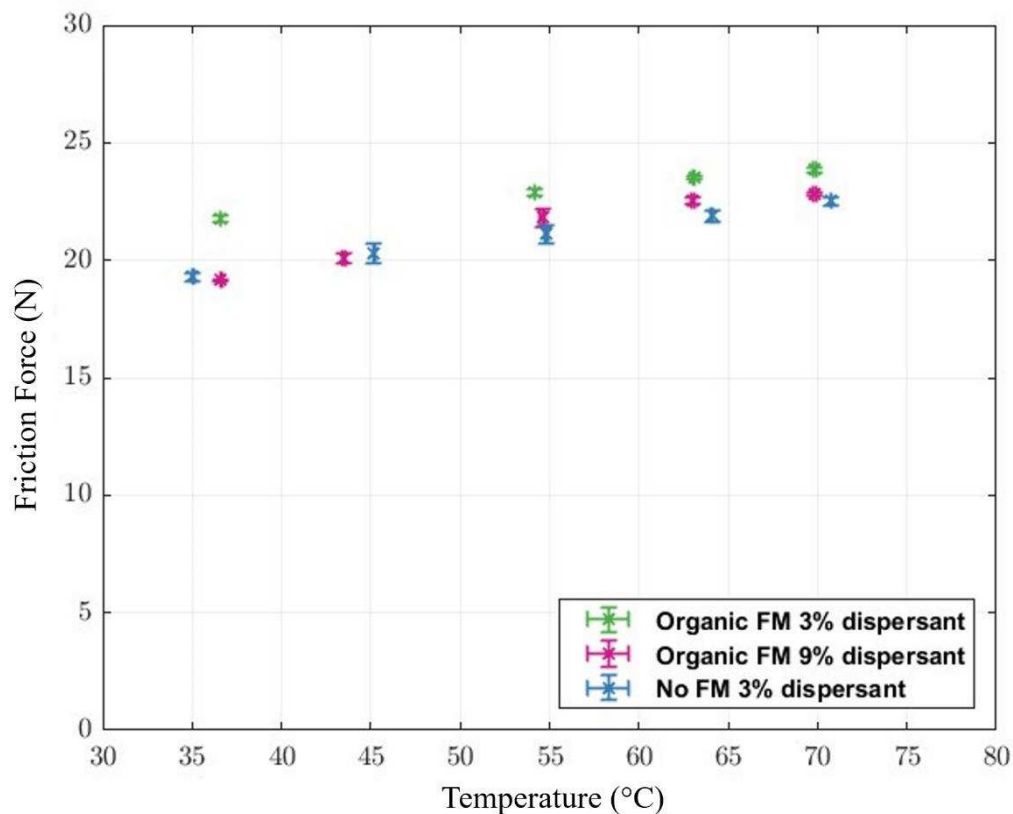


Figure 4: Comparison of the friction force at the cylinder liner-ring interface with Lubricant C (Organic Friction Modifier 3% dispersant) liner 2 and 3 and Lubricant D (Organic Friction Modifier 9% dispersant) on liner 2 with Lubricant A (No Friction Modifier 3% dispersant) on liner 1.

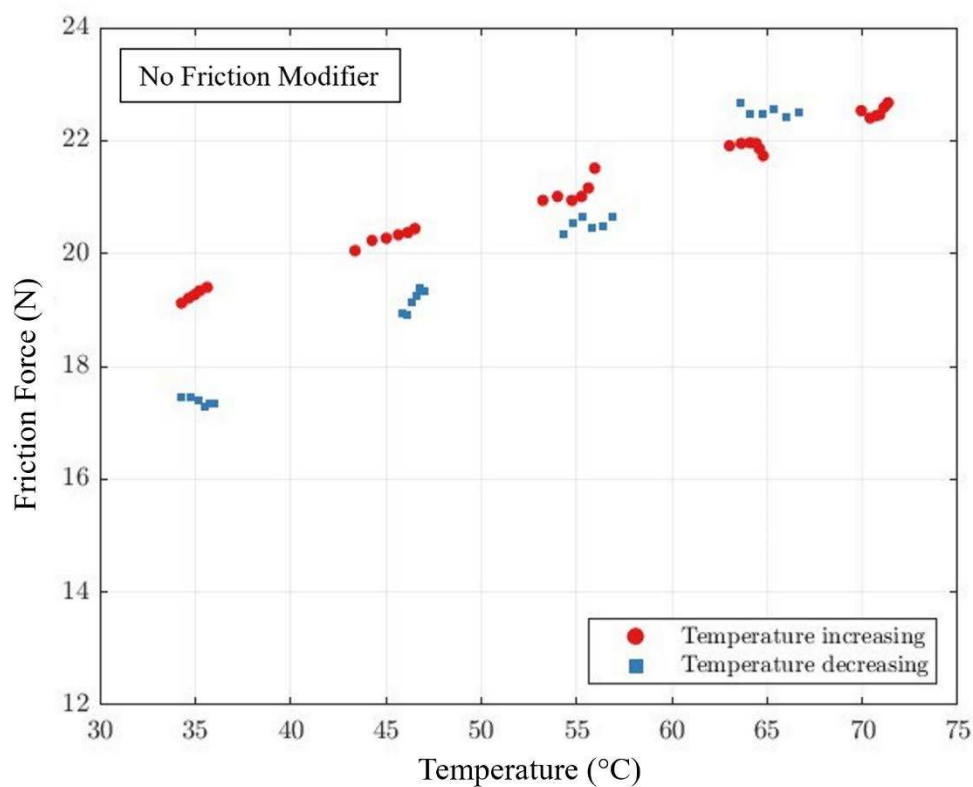
3.3. Heating and cooling

The friction data was recorded during the test both as the temperature increased and decreased. The effect on friction of the heating and cooling of the contact on the different friction modifiers is examined here for lubricants A to C, shown in Figure 5 a-c, respectively. The friction in the contact is generally higher as the temperature increases.

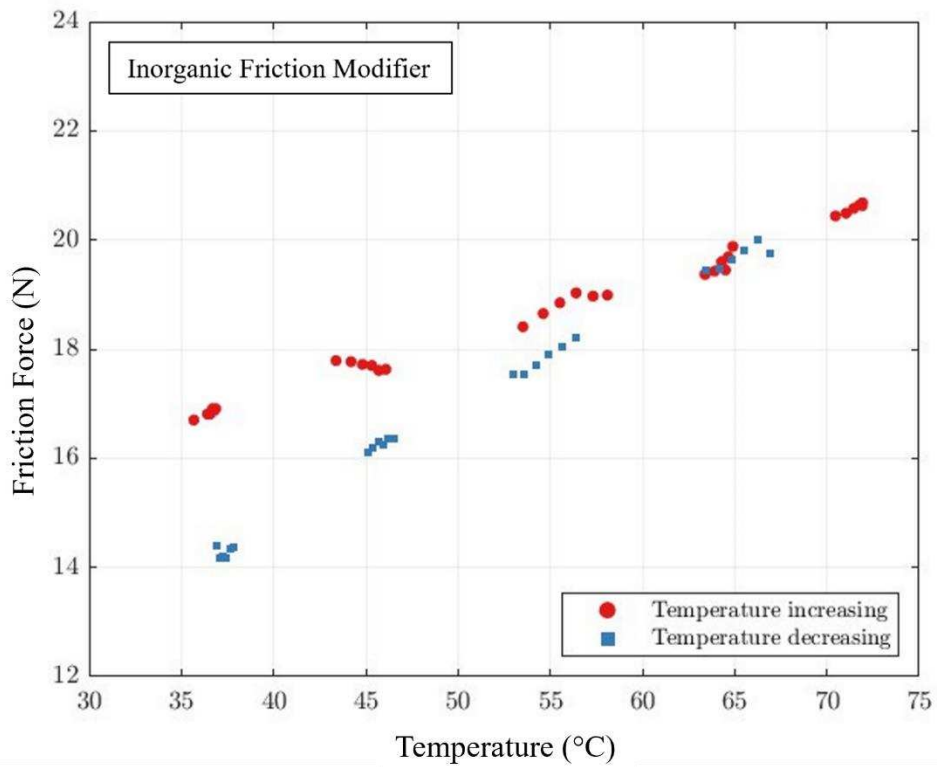
The comparison of friction during the thermal cycle are presented in Figure 5. For the lubricants tested the largest difference in the friction was at the lower temperature, presumably due the establishment of a tribofilm during the prior elevation in temperature. The lubricant with the inorganic friction modifier experienced the biggest difference with a 15% decrease in friction

at $\sim 35^{\circ}\text{C}$ after the temperature had decreased. The lubricant with no friction modifier had a 10% decrease in friction at $\sim 35^{\circ}\text{C}$ after the temperature had decreased and the lubricant with organic friction modifier had a 9% decrease in friction at $\sim 35^{\circ}\text{C}$ after the temperature had decreased. The decrease in friction as the temperature decreases back to the initial temperature is likely to be caused by the thermally and mechanically activated film still residing on the surface during the cooling phase. The effect of (time independent) shear thinning is not considered through post-test viscosity measurements in this work.

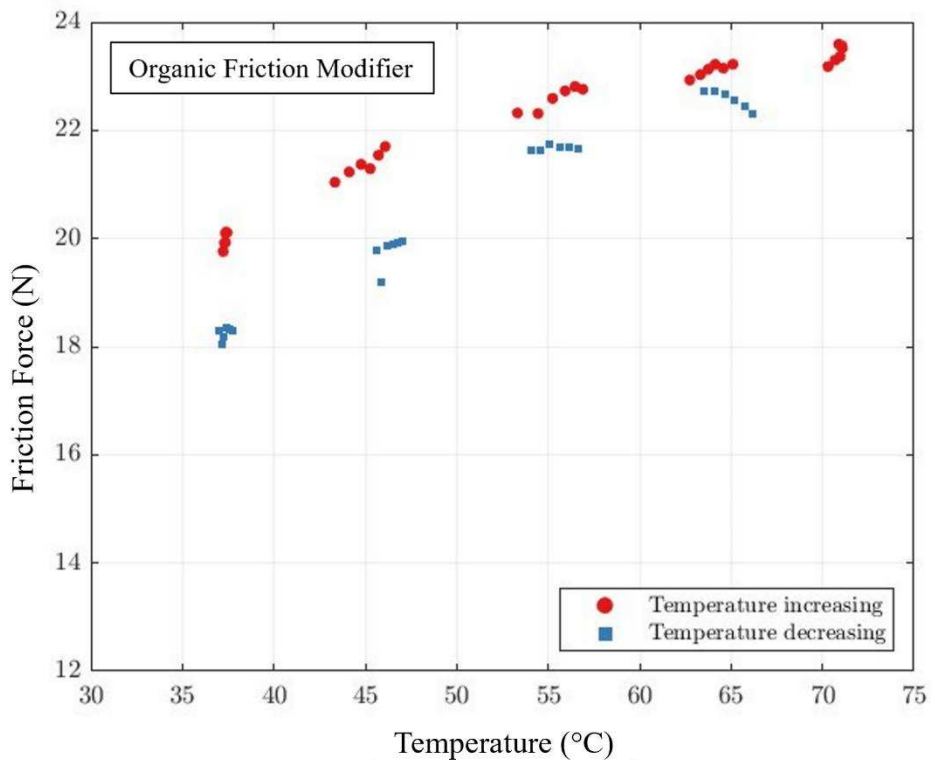
The exception to the friction being lower as the temperature decreases is the lubricant with no friction modifier at $\sim 65^{\circ}\text{C}$, shown in **Error! Reference source not found.a**. The friction was higher as the temperature began to decrease. The time taken to cool from 70°C to 65°C was approximately 18 minutes, which is comparable to the length of time taken for the lubricant with inorganic friction modifier (19 minutes) to cool by the same amount.



a.



b.



c.

Figure 5: Friction force in the contact as the temperature increases and then decreases for lubricants with 3% dispersant concentration and a) no friction modifier, b) inorganic friction modifier and c) organic friction modifier

3.4. Friction measurements across the stroke

The friction force was measured across the full stroke and the data can be examined to provide a mechanistic understanding of differences in frictional performance. In particular the results shown in figure 3 that show the differences of organic and inorganic friction modifiers and non. An example set of data was taken for each of the lubricants at the lower and upper temperatures and is shown in Figure 6a and Figure 6b, respectively. The difference between friction modifiers is greater at the lower temperature ($\sim 35^{\circ}\text{C}$), shown in Figure 6a than ($\sim 70^{\circ}\text{C}$), shown in Figure 6b. However, it should be noted that the results shown here are after exposure to higher temperatures.

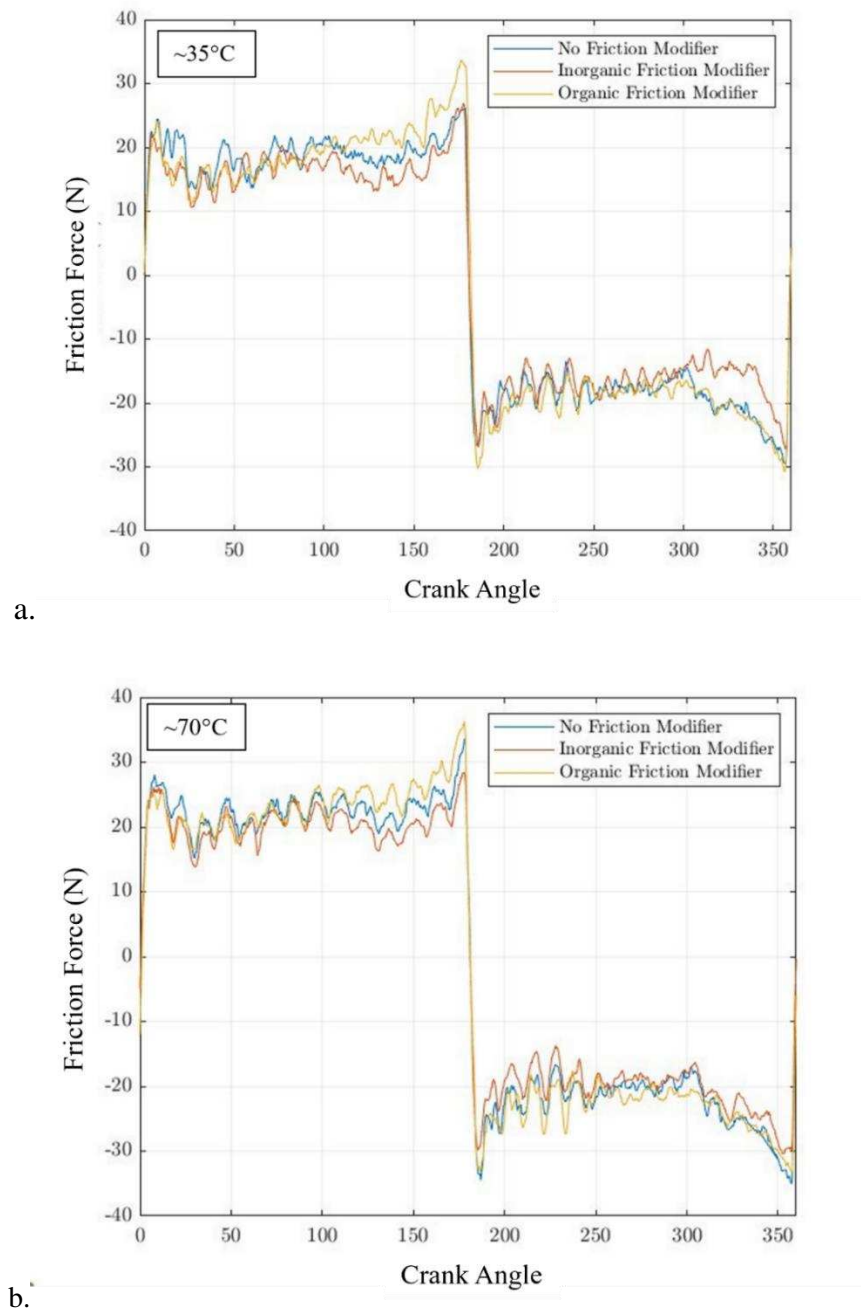


Figure 6: Friction force across the stroke and reversal with the three candidate lubricants in the contact at a) $\sim 35^{\circ}\text{C}$ and b) $\sim 70^{\circ}\text{C}$.

Notably the lack of noise in the frictional signal is a benefit of the dynamical balanced design including isolation of the ring measurement system from the drive system. The post-processing applied to the experimental data consists only of averaging on a crank angle by crank angle basis. There is no other filtering or moving average applied data sets.

The highest friction occurs at reversal due to the cessation of hydrodynamic entrainment. Reversal friction is highest for the conjunction serviced with an organic friction modifier at both temperatures. The inorganic friction modifier is seen to reduce friction more significantly over the second half of the stroke (90-180 degrees and 270-360 degrees) in both directions at the lower temperature. At both temperatures mixed regime lubrication is apparent at mid stroke with boundary lubrication at reversal. Friction force is generally observed to be lower at 35° than at 70°C in the mid stroke. This suggests that asperity contact in the mixed lubrication regime is the dominant effect on friction force, as was observed by Liu et al. [36].

4. Discussion

The results shown from the experimental work conducted in this study indicated the advantageous combination of inorganic friction modifiers on nitride coated oil three-piece oil control rings and nickel silicon carbide cylinder liners. This advantage is shown over a lubricant containing an organic friction modifier and no friction modifier at all. It should be noted that the organic friction modifier tested was an amide and alternate polar groups attached to organic friction modifiers may vary in effectiveness.

The differences shown are clearest as the lubrication regime worsens at top and bottom dead centre reversals indicating differences in interfacial boundary friction responsible for the variation in performance. It has been shown that thick phosphate ZDDP derived tribofilms on steel surfaces increase friction through roughening [37] and increased interfacial boundary shear stress [38,39]. However, it has previously been shown that ZDDP does not form thick tribofilms on Si-C and DLC surfaces, and that these films reduce friction on these non-ferrous surfaces Ueda et al. [18], and Topolovec-Miklozic et al. [40] have shown organic friction modifiers have little effect on friction on some non-ferrous surfaces. This supports the finding of this present study, where the lubricant without a friction modifier outperforms lubricant with an organic friction modifier, and it is suggested this is due to the amide organic friction modifier preventing the formation of the thin low friction ZDDP derived film on the non-ferrous surface. This is supported by the results shown in section 3.3 that show all lubricants cause lowered friction after exposure to higher operating temperatures needed to form a ZDDP tribofilm. The performance of the inorganic friction modifier agrees with findings presented by Haque et al. [41] who showed low friction behaviour of a similar MoDTC additive on non-ferrous surfaces and the synergistic behaviour of MoDTC and ZDDP [25]–[28]. This explains the results shown in section 3.3 where the most significant difference in friction after exposure to elevated temperature is for the lubricant contain inorganic friction modifier.

5. Conclusions

This novel test assesses the effect of different friction modifiers in the contact between a three-piece oil control ring and a nickel silicon carbide coated cylinder liner using a motored reciprocating tribometer. The test rig was seen to be effective for measuring the friction in the contact from ambient temperature to ~70°C. The conclusions that can be drawn from the experiments are:

- 1) the inorganic friction modifier is effective at reducing the friction in the contact at all temperatures on the nickel silicon carbide coated cylinder liner, compared with the lubricant with no friction modifier.
- 2) the organic friction modifier, however, was shown to increase the friction in the contact in comparison with the lubricant with no friction modifier at all temperatures.

It is therefore hypothesised the lubricant performance is a result of the non-ferrous surface lubricant additive system synergies that significantly differ from ferrous systems in the temperature range investigated.

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Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Data Availability Statement

The datasets generated and supporting the findings of this article are obtainable from the corresponding author upon reasonable request.

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