

Simulation of piston ring/cylinder bore system using tribotests – A review focused on the tribochemical aspect

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Abstract

The growing use of tribotest has been helping the researchers to understand the actuation mechanisms of additives on the friction and wear control of engine parts. But, it is common to observe differences between the tribofilms formed in real situation from that obtained using tribotests. Furthermore, the automakers have difficulty to correlate the results obtained using tribotests with that performed using engines in dynamometers. For the piston ring/cylinder bore tribosystem is almost impossible to reproduce its real tribosystem using tribotests. Therefore simplifications are necessary and they affect the tribochemical behavior of the tribosystem. To understand how these simplifications and the test parameters affect the tribochemical behavior of the simplified tribosystem is critical to design a tribotest that correlate well with the real situation.

Introduction

The need to improve the engines efficiency has been leading to lubricants viscosity reduction to minimize the losses in the hydrodynamic lubrication regime. However, this strategy induces the piston ring/cylinder bore system to work more in the mixed and boundary lubrication regimes. In these last two lubrication regimes the strategy adopted to reduce friction and consequently improve efficiency is the use of friction modifiers [1, 2]. The oil viscosity reduction also demands antiwear additives like zinc dialkyldithiophosphate (ZDDP). Therefore the importance of the tribofilm formed from friction modifiers and antiwear additives on friction and wear is increasing. According to Lee [3] this increasing importance of the tribofilms on the piston ring/cylinder bore system performance has been leading to a frequent use of tribotests on the effort of understanding how the tribofilms forms from the additives and behave on the control of friction and wear. Nevertheless, Morina et al. [4] showed that results are far from the objective of reproducing using tribometers the same tribofilm formed in an engine. According to Blau [5] the ultimate challenge in developing reliable tribotests becomes of identifying and controlling the key factors needed to enable materials, lubricants, and coatings to be tested in the laboratory in such a way that directly correlates with their performance in the end application. One of the factors that makes the simulation of piston ring/cylinder bore a great challenge is the behavior changes the tribofilm present when there are changes in the temperature and load for example. Temperature and load are so important that Stachowiak [1] suggest lubrication mechanism classification for boundary lubrication based on load and temperature

severity of the tribosystem. This classification is showed in the table 1.

Table 1. Boundary lubrication mechanisms according to Stachowiak [1].

Temperature	Load	Lubrication mechanisms
Low	Low	Viscosity enhancement close to contacting surface, not specific to lubricant.
	High	Friction minimization by coverage of contacting surfaces with adsorbed monomolecular layers of surfactants.
High	Medium	Irreversible formation of soap layers and other viscous materials on worn surface by chemical reaction between lubricant additives and metal surface. Surface-localized viscosity enhancement specific to lubricant additive and base stock.
	High	Formation of amorphous layers of finely divided debris from reaction between additives and substrate metal surface. Reaction between lubricant additives and metal surface. Formation of sacrificial films of inorganic material on the worn surface preventing metallic contact and severe wear.

The difficult to reproduce the real situation of an engine using a tribotest can be overcome with a carefully parameters selection and with the knowledge about the additives behavior. Therefore the main objective of this work is to review the consolidated knowledge about simulations of piston ring/cylinder bore correlating with the properties of friction modifiers and ZDDP to show the test parameters importance on the tribochemical evaluation of this tribosystem.

Tribotests

Tribotests are simplifications of real systems performed using bench test. The standard DIN 50322 classifies the simplifications in six levels, being the real situation the first. The figure 1 shows schematically this classification.

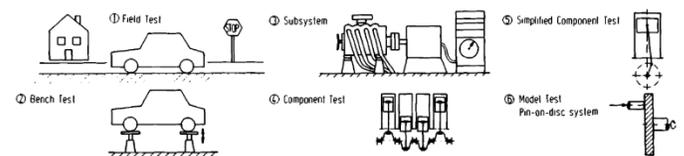


Figure 1. Classification of different types of tribological testing.

Testing of candidate materials for internal combustion engine applications has historically taken several routes: (1) replacement of parts in actual engines subjected to daily use, (2) testing in special, instrumented test engines; (3) and simulative testing in laboratory tribometers using relatively simple specimens [6]. To simulate the piston ring/cylinder bore the tribotests can be performed according to ASTM G181-04 [7] standard. However this standard has important limitations. The main limitation is that this standard does not specify test parameters that could be used as a universal way to compare the performance of materials and oils. ASTM G181-04 [7] recommends the parameters design according to the engine one want to simulate. It makes difficult to compare the results found in the literature. Furthermore there isn't other standardized test with fixed parameters focused on evaluate the piston ring/cylinder bore tribochemical aspect to help researcher to compare their results with the literature. In practice when one needs to simulate piston ring/cylinder bore system the parameters should be designed and this is not a simple task because this system is very complex. The friction between the piston ring and the cylinder varies during the stroke because the relative sliding velocity ranges from zero at top-dead-center of the stroke to over 10–15 m/s at mid-stroke, depending on engine speed and stroke length. Within this range of velocities, several lubrication regimes—from boundary to mixed to hydrodynamic lubrication—can be experienced during the same stroke. The oil film thickness between the ring and cylinder may vary by more than a factor of 10 within a stroke, and likewise, the friction coefficient may vary from 0.001 to >0.10 [8].

The majority of the tribometers have limitations that make impossible the simulation of the entire stroke of a real system. Therefore the tribotests are usually designed to simulate region near the top-dead-center. This region is used because is where the system experiments the most sever conditions of load, temperature and the lubrication regime is boundary. According to Lee [3] the parameters to be considered in designing a tribotest to simulate the piston ring/cylinder bore system can be split into two main groups:

- Components - geometry (surface profile and finish), materials and lubricant.
- System Conditions - speed, load, temperature and, on a reciprocating tribometer, stroke length.

Czichos [9] presented factors that should be considered during the tribotest design. This is showed in the table 2.

Table 2. Some Important Factors Involved in Designing Friction Experiments.

Factor	Considerations
Purpose for friction testing	Simulation; basic research; preliminary screening of material combinations
Type of motion	Can affect the value of friction measured (e.g., unidirectional vs. reciprocating)
Macrocontact geometry	Conformal; nonconformal; affects the regime of lubrication, thermal conditions, and the management of debris
Load, speed, duration of testing	Running-in phenomena; transitional processes; simulation of service history; change of dominant frictional processes
Specimen preparation and cleaning	Simulation of an application; how long during the experiment does the initial surface condition persist?; ambient films and contaminants
State of lubrication	Flow of lubricants; how lubricants are supplied or replenished; thermal effects on lubrication
Number of tests per condition	Unlubricated tests often behave more variably than well lubricated tests requiring more replicates; confidence increases with the number of tests; quality control
Accuracy required	Affects choice of sensor system; method of data recording; how data are treated (statistics)

Furthermore, Blau [6] concluded his review listing some details that deserve special attention such as:

- The contact stress and geometry should replicate the application. Increasing contact stress to accelerate testing may alter the dominant wear mode to one not actually occurring in service.
- Producing the correct type of motion is important in conducting successful simulations (for example, fretting versus reciprocating sliding versus unidirectional sliding, etc).
- Temperature and chemical environments should be duplicated when appropriate. In some cases, the additional testing complications of controlling these factors may not be necessary.
- The state of contamination in the lubricant or environment should be duplicated. For example, it may be better to use contaminated oil than fresh oil when testing cylinder bore materials.
- Specimens should be examined to assure similar modes of wear damage.
- The nature of the wear debris can also be helpful in assessing the effectiveness of simulations.

The importance of selecting test parameters carefully can also be illustrated through the table 3 examination. This table lists a great number of factors that can affect the friction coefficient in a tribotest.

Table 3. Factors that can affect friction depending on contact circumstances. Adapted from [8].

Category	Factor
Mechanical	Contact geometry: macro, micro, nano Load and contact pressure distribution at various scales Loading history System dynamics: vibrations, stiffness, damping, hysteresis Type of motion and velocity profile
Materials	Pairing of materials Composition and purity of materials Adhesive characteristics Microstructure and the sizes of microstructural features relative to the size of the tribocontact Elastic and plastic mechanical properties Property gradients in the near-surface regions Thermophysical properties: thermal conductivity, thermal expansion, etc. Method of creating the surface (finishing, machining artifacts)
Thermal effects	Frictional heating External heat sources Thermoelastic instability Thermally induced phase transformations: softening, melting Tribochemical activation Thermal shock during cycling
Lubrication	Quantity and means of supply Regime of lubrication Properties of the lubricant Lubricant chemistry (tribochemistry) Lubricant "aging" Filtration and cleanliness
Tribochemistry	Relative humidity Cleanliness Composition of the surrounding environment Tribopolymerization Friction polymer formation Oxides and tarnish films
Third bodies	Transfer particle formation Mechanics and lubricity of triboformed layers (tribomaterials) Wear particle concentration and agglomeration Sizes, shapes, and morphology of particles External contaminants Flow of third bodies in and out of the contact

Additives

Friction modifiers

Friction modifiers are the lubricant additives that commonly used in boundary and/or mixed lubrication conditions to adjust friction characteristics and improve the lubricity and energy efficiency [10]. Although in practice many polar organic species and solid particles dissolved or dispersed in base oils produce measurable reductions in boundary friction, there are four main classes of material that have been deliberately developed and applied as additives in liquid lubricants to reduce friction and may thus be formally termed friction modifier additives [2]. These four classes are: organic friction modifiers (OFMs), organo-molybdenum compounds, functionalized polymers and nanoparticles. But this classification is not a consensus. Tang and Li [10] consider just three, excluding the functionalized polymers. The first two are used in automotive oils for a long time and have more importance for this industry. Therefore this work will concentrate on them. Organic friction modifiers and organo-molybdenum compounds are different not only in chemical composition and molecular structure. They are also different in the way they promote boundary lubrication and friction reduction. The tribochemical conditions necessary for each one to act are usually not the same too.

Organic friction modifiers

Organic friction modifiers are generally long chain surfactants with polar end groups, including carboxylic acid, ester, alcohol, amine, amide, imide, borate, phosphate, ionic liquid and their derivatives. Their polar end groups either physically adsorb onto the metal surfaces or chemically react with the surfaces, while the hydrocarbon chains extend into the lubricants [10]. The polar group is one of the governing factors in the effectiveness of the molecule as an organic friction modifier. Chemically, organic friction modifiers can be found within the following categories [11]:

- Carboxylic acids or their derivatives, for example, stearic acid and partial esters
- Amides, imides, amines, and their derivatives, for example, oleylamide
- Phosphoric or phosphonic acid derivatives
- Organic polymers, for example, methacrylates

Currently there are two widely accepted mechanisms to explain the lubrication capacity of organic friction modifiers: monolayer model and thick film model [10]. Rudnick [12] identified action mechanism for some molecules used as organic friction modifiers. This is showed in the table 4.

Table 4. Organic friction modifiers, types and modes of action. Adapted from [12].

Mode of Action	Products
Formation of reacted layers	Saturated fatty acids, phosphoric and thiophosphoric acids, sulfur-containing fatty acids
Formation of adsorbed layers	Long-chain carboxylic acids, esters, ethers, amines, amides, imides

It can be seen that there are differences between the terms used by Tang et al. [10] and Rudnick [12] to identify the lubrication mechanisms related to organic friction modifiers. But, we can consider that “monolayer model” is equivalent to “adsorbed films” and “thick film model” is equivalent to “reacted layers”. This work adopted the denomination used by Rudnick [12].

Briscoe et al. have shown considerable differences between the friction properties of fatty acids when they act as adsorbed films or reacted layers, including quite different friction-speed behavior [13] and, at high speeds much lower friction for the reacted layers than the

absorbed [14]. In the mechanism of adsorbed layer the molecules self-assemble on the surface to form a close-packed monolayer vertically oriented. This reduces friction since there is easy slip between the resultant, opposing methyl end groups [1]. The films are strong and able to withstand high applied pressure because of cumulative van der Waals forces between the methylene groups on the closely packed alkyl chains [1]. The polar end act attaching the molecule to the surface promoting physisorption or chemisorption. The film capacity to withstand contact pressure and temperature is partly determined by the attachment force promoted by the polar group. Chemisorption promotes stronger bind than physisorption and, therefore, are able to withstand greater loads and temperatures before fail. The polar groups generally need an oxide layer to adsorb on metallic surfaces. It happens because the adsorption demands from the surface a determined band of reactivity. If the reactivity is too low the molecules don't fix on the surface. Moreover, if the reactivity is too high the molecule will react with the surface forming a new compound. This means that if the oxide film covering these metals is removed, by severe wear, then a lubrication functioning by adsorption will fail [1].

Stachowiak [1] call soap layer the reacted layer formed from organic friction modifiers. Soap layers are formed by the reaction between a metal hydroxide and a fatty acid which results in soap plus water. If reaction conditions are favorable, there is also a possibility of soap formation between the iron oxide of a steel surface and the stearic acid which is routinely added to lubricating oils [1]. Lubrication by soap layers is a mechanism of some organic friction modifiers that happens when the contact conditions are so severe that the adsorption mechanism became impossible.

Fatty acids constitute a special class of long-chain film-forming additives because they can react with the oxide on metal surfaces in moist ambient air to form soaps. The coefficient of friction observed under such circumstances and the effect of temperature on friction will then be governed by the presence of the soap film [15]. The soap layer formation is illustrated by the figure 2.

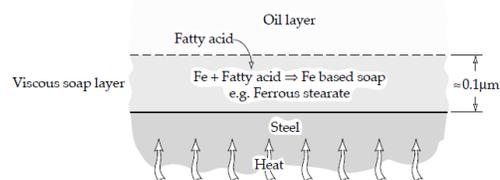


Figure 2. Formation of a viscous soap layer on steel by a reaction between iron and a fatty acid in lubricating oil.

Organo-molybdenum friction modifiers

The two most widely studied and used types of organo-molybdenum friction modifiers are molybdenum dialkyldithiophosphate (MoDDP) and molybdenum dialkyldithiocarbamate (MoDTC) [2]. Because of its greater capacity to reduce friction and the increasing interest of the researches and automotive industries this work will concentrate in discussing MoDTC. In MoDTC the atoms shown as X in the figure 3 can be either O or S. Most commonly the bridging X atoms are S and the double bonded ones O, but the additive is generally more reactive when the latter are S [16].

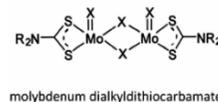


Figure 3. Molybdenum dialkyldithiocarbamate (MoDTC) [2]

It is widely believed that organo-molybdenum compounds act by forming tiny platelets of the low shear strength, layer-lattice compound molybdenum disulphide (MoS₂) on rubbing asperities, and

result in reduced friction [6,7]. But, there is no consensus about the reactions is necessary to transform the molecule of MoDTC in a tribofilm of MoS₂. The most accepted way was proposed by Grossiord et al. [14] and is presented schematically in the figure 2.

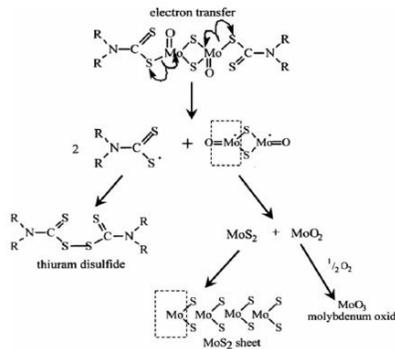


Figure 4. Proposed reaction scheme for the formation of MoS₂ from MoDTC [14].

Recently, Khaemba et al, [17] proposed a new model to explain the formation of MoS₂ from MoDTC. The reaction steps are described below exactly as Khaemba et al. did in their work.

- MoDTC first adsorbs on the tribofilm surfaces.
- In Step 1, shear stress applied on adsorbed MoDTC molecules causes decomposition to occur. The decomposition process begins by rupturing of C–S bonds forming molybdenum intermediate compound which undergoes intramolecular sulphonation forming amorphous MoS_x.
- In Step 2, MoS_x is converted to MoS₂. Since MoS_x is formed at lower temperatures than MoS₂, the activation energy for formation of MoS_x is lower than that for the formation of MoS₂. Therefore, MoS₂ can be formed from MoS_x either through increasing the energy at the contact by increasing temperature or increasing shear stress.
- FeMoO₄ is formed from a reaction of iron oxides on the steel surfaces with MoS_x [17].

The figure 4 shows a graphical representation for this proposed reaction.

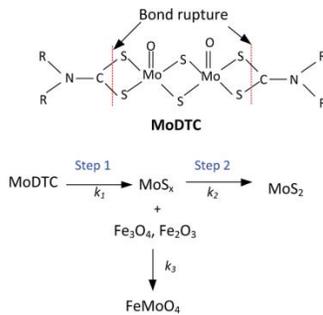


Figure 5. reaction pathway for decomposition of MoDTC within tribocontacts [17].

Khaemba et al. [17] proposed that the reaction initiates with molecule adsorption on the surface. But, analyzing the work of De Feo [18] it is possible to conclude that a thermal breakdown could occur before the molecule to adsorb on the surface, despite he doesn't concluded that. Additionally to the lack of knowledge about the reactions involved in the transformation of MoDTC in MoS₂ almost all of test parameter can affect its tribofilm formation. Formation of MoDTC tribofilms is affected by parameters such as temperature, MoDTC concentration, the presence of antioxidants and other lubricant additives as well as contact parameters such as the stroke length, sliding speed, slide-roll ratio and surface roughness of the sliding

pair which in turn affect the friction performance of the additive [16,18,20,21].

Antiwear additive - Zinc dialkyldithiophosphate (ZDDP)

The most widely used anti-wear additive for lubricants is ZDDP (or ZnDTP) [22]. A simple representation of ZDDP molecule is showed in figure 5.

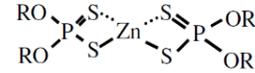


Figure 5. representation of the structural formula of ZDDP [23].

ZDDPs act as an antiwear agent by forming a protective film at the rubbing surfaces preventing excessive wear [24]. From the literature, three main ways that ZDDP acts as an antiwear agent have been proposed; (i) by forming a mechanically protective film; (ii) by removing corrosive peroxides or peroxy-radicals; (iii) by “digesting” hard and thus abrasive iron oxide particles [23], being the last the most controversy mechanism.

Its effectiveness is due to the unique combination of zinc, sulfur and phosphorus chemistry that produces superior tribo-films for protecting machinery of all types [22]. In general ZDDP act decomposing on the metal surface to form complex zinc and iron based polyphosphate films [22]. There are two most accepted models to explain the tribofilm formation from the ZDDP molecule. The first model was proposed by Martin [25] and is based on chemical hardness. This model suggests a reaction with zinc polyphosphate with the iron oxide of the surface to form the tribofilm. These tribochemical reactions would happen based on the chemical hardness model proposed by Pearson [26]. Thus the reaction between the zinc metaphosphate and the iron oxide particles leads to depolymerization of the polyphosphate chains near the metallic surface. This would explain the phosphate chain length gradient observed in the tribofilm and its composition made of mixed Fe/Zn polyphosphates [27].

Another model proposed by Nicholls et al. [47] highlights the role played by the pressure in the formation of the phosphate chains gradient. It is suggested in this model that the pressure and temperature could induce cross-linking of the phosphate chains, leading to the presence at the extreme surface of the tribofilm (where the pressure is higher) of longer zinc polyphosphate chains (metaphosphate composition) than those located in direct contact of the steel surface (orthophosphate composition). Gellman et. al [28] in their review summarized the mechanism of tribofilm formation based in the available knowledge as follow:

- The molecule appears to interact weakly with the steel surface (possibly through the sulphur atoms [29], according to quantum-chemical calculations) at room temperature [30], starting to catalytically decompose around 50°C in the presence of the iron oxide substrate [31]. Upon reaching around 100°C, either through simple thermal treatment or by tribo-induced flash heating, the ZnDTP starts to undergo thermo-oxidative decomposition, due to the presence of either oxygen or peroxide radicals in the oil [25].

The overall results suggest a layered structure for the film consisting of a layer of iron oxide intergrown with a layer of short chain polyphosphate, then covered with a thin layer of long chain polyphosphate [33]. Furthermore, Ito et al. [32] detected the influence of an oxidized layer could have on the friction performance of a tribofilm formed from ZDDP. Their tribosystem reached friction values of 0,06 when the sample surface was previously oxidized in controlled treatment. Accordingly to Spikes [23] the most accepted configuration of a tribofilm formed from ZDDP is showed in the figure 6.

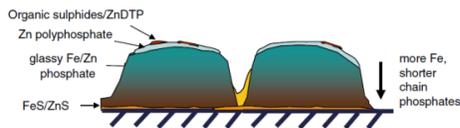


Figure 6. Schematic diagram of pad structure and composition [23].

Despite of the wide acceptance about the tribofilm configuration its structure depends of some factors as temperature, load, roughness, presence of alcohol and additives and many others. Palacios [34] has concluded that the film thickness and antiwear performance are affected by temperature. High temperatures produce thicker films and a worse antiwear performance. Other groups confirmed Palacios [34] conclusion [35, 36]. Furthermore, some investigators [37-40] found that the ratio of Zn:S:P in the surface films varied with temperature. Yin et al. [33] detected that high temperatures changes the kinetics of film formation because increase the rate of ZDDP decomposition. The temperature is a so important factor for film formation from ZDDP that is possible to generate films without contact, just if with temperature. But, the films thermally generated, despite of having similar chemical composition to that generated tribochemically, have different mechanical properties being less effective in wear protection [22,28]. Moreover, if the concentration of ZDDP was less than 0.5 wt%, and it was used at over 200 °C, then it loses its antiwear properties after several hours of rubbing [41]. Yin et al. [33] also identified the concentration influence on the tribochemical behavior of ZDDP. They concluded that the higher the concentration of ZDDP in the solution, the more ZDDP is detected on the surface [33]. Several groups [22, 28] also found that the presence of other additives change the performance of ZDDP, often decreasing its capacity to prevent wear. Other important factor for the tribofilm performance is the applied load. The elastic modulus and load capacity are influenced by the applied load [22]. The load effect was also studied by Palacios [42]. He found that the surface film thickness increased with a load up to 600 N and then decreased. He also reported that surface composition changed with increasing load. When the load increased, the concentration of S was increased and that of P was decreased [33]. High load has a similar effect as high temperature. Under a high load such as 400 N, no unchanged ZDDP is present in the film. When the load is lowered to 40 N, unchanged ZDDP can be detected on the film surface [33]. The tribochemical generated films only form if actual sliding contact occurs—they do not develop in rolling contact or if the hydrodynamic film thickness is significantly greater than the surface roughness [23]. Lin et al. [41] determined that if the contact pressure exceeded 90 MPa, and the surface roughness of a hard surface exceeded 0.3 μm in Ra, then there is no antiwear performance from this ZDDP [41], indicating that contact pressure could be a better parameter to evaluate the tribofilm performance than load. So et al. [43] also reported the effects of roughness on the film formation. The rougher surface required a longer time to form a film. Smoother surfaces help the decomposition of ZDDP and formation of long chain polyphosphate. No unchanged ZDDP was found in the film when a polished surface was used [33]. So et al. also detected the influence of sliding velocity. At higher sliding speed, the film forms quicker. The sliding time is other factor that influences the tribofilm behavior [44]. Rubbing time affects the chemical composition of the antiwear films. At short rubbing times, adsorbed ZDDP on the surface remains unchanged. As the rubbing time proceeds, long chain polyphosphates are formed on the topmost surface and ZDDP is consumed [33]. Other important factor is the additive concentration in the oil. The higher the concentration of ZDDP in the solution, the more ZDDP is detected on the surface [33]. Moreover, if the concentration of ZDDP was less than 0.5 wt%, and it was used at over 200 °C, then it loses its antiwear properties after several hours of rubbing [41]. Costa et al. [45] executing tests in low temperatures detected influence of the

ethanol on tribofilm rate formation, showing that in the tested conditions ethanol affect the ZDDP performance.

Test parameters influence on the additives behavior

Organic friction modifiers:

- **Load and contact pressure distribution:** The researches have been showing that the friction coefficient is proportional to the load. Except for loads excessively lows when the friction coefficient increases. Furthermore, Stachowiak [1] present a critical contact pressure of 1 GPa for additives that lubricates by the adsorption mechanism. In the combustion engines the piston ring/cylinder bore achieve its greatest contact pressure in the top dead center and it is in the MPa order. Therefore, tribotests executed with the objective of accelerate wear can exceed the maximum contact pressure supported by the organic friction modifiers changing the behavior of the tribosystem.
- **Motion and velocity profile:** The tribofilm formed from organic friction modifiers are easily removed from the surface and need to recompose itself during the test. High frequencies can impose a removal rate greater than film formation rate affecting the organic friction modifier performance. The friction coefficient can increase or decrease with the velocity in moderate temperatures [2]. Furthermore, many studies have been showing that organic friction modifiers can lose their effectiveness suddenly when the velocity is increased. It happens because the critical temperature for these additives to work is achieved [2].
- **Piston ring and cylinder bore material:** The critical load and temperature depends on the bond intensity of the molecule with the surface. Because of this, reactive surfaces offers better conditions for this type of additive to operate. On the other hand, the surface can't be so reactive that promote the catalysis of the molecule.
- **Elastic and plastic properties:** For the same load, harder materials offers greatest contact pressures on the top of their asperities. Because of this a hardness improvement of the piston ring and/or cylinder bore can make the organic friction modifiers actuation impossible.
- **Roughness:** The roughness also influences the contact pressure. Increasing roughness the contact pressure will also increase for the same load.
- **Friction heating and external heating:** The heating promoted by the friction or external sources can cause desorption of organic friction modifiers from the surface. Furthermore, if the heating is associated with moderates contact pressures the molecule can react with oxides of the surfaces leading to the formation of soap layers. This reaction changes the lubrication mechanism and consequently the behavior of the tribosystem.
- **Lubricant supply:** The greater is the amount of lubricant for a tested surface the greater is the amount of additive to react with this surface. Furthermore, as mentioned before, the organic friction modifiers tribofilms need to reconstruct during the sliding and it will easier when there is a great quantity of additive available.
- **Lubricant aging:** The organic friction modifiers molecules are consumed during the tribosystem operation. Because of this during the test the amount of molecule available to recompose the tribofilm decreases reducing the lubrication capacity of organic friction modifiers.
- **Oxide layer:** The presence of an oxide layer affects the surface reactivity. According to Stachowiak [1] when this

layer is removed the surface becomes excessively reactive promoting the organic friction modifiers catalysis.

Organo-molybdenum friction modifiers:

- *Load and contact pressure distribution:* Apparently the contact pressure is not a vital parameter for MoDTC when the tribofilm is formed. But, for the MoDTC to activate is necessary a minimal contact pressure. Without this condition is not possible to transform MoDTC in MoS₂ and therefore the friction reduction doesn't happen.
- *Motion and velocity profile:* The tribofilm is removed when the ring slide through the surface. It means that the tribofilm need to form again before the next ring contact. Therefore, high frequencies can remove the tribofilm faster than it is capable to reconstruct. In this situation the MoDTC performance will be affected.
- *Piston ring and cylinder bore material:* The MoDTC activation is possible in the surface of almost any material. But, the activation process includes a step of molecule adsorption on the surface. Thus, reactive surfaces can improve the MoS₂ rate formation.
- *Elastic and plastic properties:* MoDTC activation depends on the contact pressure and, as mentioned before, when the hardness increase the contact pressure also increase.
- *Roughness:* To increase roughness promotes an increasing in contact pressure and it facilitates the MoDTC activation.
- *Friction heating and external heating:* MoDTC activation depends on the temperature. It is necessary to heat to induce the MoDTC transformation in MoS₂. As mentioned before there is strong evidences that the first reaction step is thermal breakdown. If it is true the temperature increasing promotes a thermal breakdown rate increment and it can increase the MoS₂ formation rate. On the other hand, high temperatures induce the MoS₂ and MoDTC oxidation, affecting additive performance.
- *Lubricant supply:* The MoDTC performance also improves when the amount of additive is increased in the lubricant formulation.
- *Lubricant formulation:* As other additives that act forming tribofilms, MoDTC disputes sites on the surface to react. Therefore when there are other additives that also need place on the surface to act a competition occur affecting the MoDTC performance.
- *Lubricant aging:* MoDTC molecules are consumed by the tribosystem to form the MoS_s tribofilme. Thus, over time the MoDTC quantities decreases and it makes the tribofilme reconstruction more difficult.

Zinc dialkyldithiophosphate:

- *Load and contact pressure distribution:* As already mentioned the mechanical properties and wear resistance of the tribofilm formed from ZDDP is strongly influenced by the applied load. Until a limit load which removes completely the tribofilme the load tribofilme load capacity increases with load increments.
- *Motion and velocity profile:* ZDDP tribofilme grows through polymerization reactions forming polyphosphates chains. If the frequency of a reciprocating test is so high that makes the removal rates greater than grow rates the tribofilme performance will be affected. It was also identified that high velocities produces thinner tribofilms [23].
- *Piston ring and cylinder bore material:* The ZDDP tribofilm has a sulfide composition gradient. Near the substrate the amount of ferrous sulfide is maximum and near the surface the zinc sulfide has its greater

concentration. But it happens only under ferrous metals. Furthermore, the tribofilm formation also depends of a molecule adsorption step that is influenced by the surface reactivity.

- *Elastic and plastic properties:* For the same load harder materials provide higher contact pressures and as mentioned before the tribofilm mechanical properties, load capacity and wear resistance depends on the contact pressure.
- *Roughness:* roughness increasing also increases the contact pressure and consequently changes the tribofilm formed performance.
- *Friction heating and external heating:* The tribofilm forms under temperatures slightly above the ambient, around 50 °C [23]. But, its grow rates increase when temperature is also increased because it is based in polymerization. Furthermore, as this tribofilm is a polymeric material high temperatures promote its degradation.
- *Lubricant supply:* The amount of additive available in the tribosystem influences the film grow rates. It is necessary a minimum amount of additive to have an effective wear protection.
- *Lubricant formulation:* ZDDP also demand for surface sites to react. Therefore additives that also need surface sites to react compete with ZDDP affecting the film formation.
- *Lubricant aging:* ZDDP molecules consumption and oxidation make its action less effective over time.

Summary/Conclusions

Tribotests that simulates piston ring/cylinder bore have limitations that makes very difficult to obtain results with good correlation with the real situation. One of the most important limitations is the impossibility to replicate the ring motion exactly as it is in an engine. It affects the shear rate and the flash temperature for example. Furthermore, it implies that is not possible to simulate the entire course of the piston ring using just one set of test parameters. Therefore, researchers usually have been chosen to simulate the cylinder bore top dead center region. This region is of great interest because is where contact pressure and temperature is higher. Moreover, the sliding velocity is too low to provide the necessary conditions for hydrodynamic lubrication to occur. There is a great acceptance that this region presents the most severe operational conditions. Despite of Obara et al. showed that it is possible to find more wear in the bottom dead center [46]. The tribotests limitations drive researches to analyze carefully the test parameters to reply what is possible and control what is not possible. Other great problem of simulating the piston ring/cylinder bore tribochemical phenomena is the lack of references about tribofilm formed in real situations. There is a great amount of information about tribofilm formed in simplified conditions but is not possible to establish if it is close to the reality. The organic friction modifiers have two most accepted boundary lubrication mechanisms. These mechanisms depend mainly on the type of friction modifier, reactivity of the surface, contact pressure and temperature. Furthermore depending on the severity of the tribosystem it can be impossible to friction modifiers to actuate. It means that it can be impossible to detect the actuation of an organic friction modifier if a wrong set of parameters are used or the mechanism of lubrication can be different of the real situation. The same is valid for ZDDP. Its performance is strongly affected by the tested conditions. MoDTC behave different. For this additive there are a band of tribochemical conditions that it activate and promote a great and sudden friction coefficient reduction. The activation is related to the formation of a tribofilm composed of MoS₂. It is unquestionable the importance of tribotests on the knowledge construction about action mechanisms, properties and formation

kinetics of tribofilms formed from additives. In this approach simplifications are necessary and sometimes desired. But, when researchers are trying to simulate the real tribosystems to evaluate oil, materials or surfaces modifications is necessary to replicate the greatest number of parameters is possible taking as reference a real engine. The parameters presented in the section "Test parameters influence on the additives behavior" are not the only ones a researcher needs to take account to have a good piston ring/cylinder bore simulation using tribotests. But, we concluded that if these parameters are not appropriately replicated from the real situation the chances of having good correlation with the real situation are very small.

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Definitions/Abbreviations

ZDDP	Zinc dialkyldithiophosphate
MoDTC	Molybdenum dialkyldithiocarbamate
OFM	Organic friction modifier