

## INFLUENCE OF FRICTION MODIFIER ADDITIVES ON THE TRIBOLOGY OF LUBRICATING OILS

**Ronaldo Nunes de Andrade Ávila**  
FIAT Automóveis S.A.  
ronaldo.avila@fiat.com.br

**Bruno Eduardo de Aguiar Azevedo**  
FIAT Automóveis S.A.  
bruno.azevedo@fiat.com.br

**José Ricardo Sodré**  
PUC Minas  
ricardo@pucminas.br

**Abstract.** Current ambient and technological demands on automotive emissions and oil consumption motivate the development of basic lubricant oils of high thermal and chemical stability and use of highly specified additives. This work evaluates some types of friction modifier additives present in spark ignition and compression ignition engine oils, using a four-balls measuring device. The tribology of conventional lubricating oils were evaluated and compared to those of lubricating oils with friction modifier agents. The test results allowed for determination of the effects of utilization of friction modifiers in automotive lubricating oils.

**Keywords:** Friction Modifier, Additive, Lubricants, Tribology

### 1. Introduction

For close to a century, automobile lubricants have been used to minimize wear, improve efficiency, and hence prolong the life of an engine. The addition of engine oil additives has many purposes. These additives act as defoamers, viscosity improvers, pour-point depressants, anti-wear additives, extreme pressure additives, detergents, and dispersants to name only a few. Such additives have also been extensively developed, with a vast associated literature, to meet different technical as well as environmental requirements for different parts in a car engine. Engine lubricants are intended to work in internal combustion chambers and are subjected to a wide range of fuels. The main problems faced by lubricants include their interactions with the combustion products, which results in their contamination, oxidation, and formation of deposits on contacting and rubbing surfaces. These problems result in serious implications to corrosion and wear (Nicholls et al, 2005).

For years, zinc dialkyl-dithiophosphates (ZDDPs) have been used as the most common and the best anti-wear and antioxidant additive for engine lubricants (Fig. 1); the original ZDDP patents were issued in 1944 (Freuler, 1994). Description of their synthesis can be found elsewhere (Mastin et al, 1945; Yamagushi and Ryason, 1993). It is widely accepted that ZDDPs breakdown in the unforgiving conditions in a combustion engine to create reaction products that, under high temperature and pressure, create sacrificial films that are responsible for minimizing asperity contact which can eventually lead to wear (Sogawa, 2000). This film is commonly referred to as an anti-wear film and has been found to be composed of various amounts of zinc, phosphorus, sulfur, and oxygen (Sheasby et al, 1990; Baldwin, 1976). Its formation and the speed at which it forms are also important in preventing wear. However, despite years of work, the mechanisms of formation and action of the anti-wear films are still poorly understood (Smith, 2000).



Fig. 1- ZDDP - Zinc dialkyl-dithiophosphates molecular structure

According to OICA's (*Organisation Internationale des Constructeurs D'automobiles*) statistical committee, a world production of 60.599.287 vehicles was registered in 2003 ([www.oica.net](http://www.oica.net)). Reduction of CO<sub>2</sub> emissions, as suggested by the conferences of Kyoto, 1997, and Rio, 1992, and by new world regulations for vehicle emissions control, such as CAFE (*Corporate Average Fuel Economy*, [www.nhtsa.dot.gov](http://www.nhtsa.dot.gov)), act like a catalyst to research and development of technologies to minimize the mechanical losses by friction to guarantee reduced fuel consumption, low exhaust emissions and low noise. Friction modifier additives are developed to attend this need, being of superior performance to

guarantee high lubrication efficiency and up to 6% lower fuel consumption when compared to ordinary oil with the same viscosity degree.

This work investigates the utilization of a four-balls testing equipment to evaluate the energy conserving characteristics of high performance lubricating oils used by automotive engines for reduced fuel consumption and lower exhaust emissions. Tests were performed to analyze wear scar in the spheres surface during utilization of lubricating oils with or without friction modifier additives. It is expected that the technique here shown can contribute to reduce costs related to the homologation process of lubricating oils with fuel economy characteristics due to performance evaluation without the need to perform dynamometer tests.

## 2. Classification of Lubricating Oils

Lubricating oils are classified as vegetable or mineral oils and synthetic oils. Mineral oils are obtained from petrol through the refining process, with composition varying from C<sub>24</sub> to C<sub>50</sub>. Synthetic oils are mostly petroleum based, modified through chemical processes, and vegetable oils are originated from extraction and purification of fatty oils (Persson et al, 2002). Mineral or synthetic basic oils are classified by groups according to qualitative characteristics associated to thermal and chemical stability, according to Table 1. Engine oils are also classified according to their viscosity index by the *Society of Automotive Engineers* (SAE), to their performance characteristics by the *American Petroleum Institute* (API) and, for the European market, by the *Association des Constructeurs de L'Automobile* (ACEA).

Table 1 – ATIEL / API basic oils classification (Sogawa et al, 2000).

Group 1	Group 2	Group 3	Group 4	Group 5
Saturated < 90%	Saturated > 90%	Saturated > 90%	Poly- alpha- olefins (PAO)	Others Esters, poly- glycols, etc.
Sulfur > 0,03	Sulfur < 0,03	Sulfur < 0,03		
80 < V.I. < 120	80 < V.I. < 120	V.I. > 120		

Generally speaking, mineral, semi-synthetic and synthetic lubricating oils for internal combustion engines have the following formulation: 70 to 95 % of basic oil + 5 to 20% of additives + 0 to 20% of viscosity index improver + 0 to 15% of pour point depressants.

The group of additives has substances that add properties to improve oil performance. The main additive properties are Persson, 2002): detergent, dispersant, anti-oxidizer, corrosion inhibitor, anti-foam, viscosity index improver, anti-wear, pour point depressants and friction reducer, which is the focus of the present work. Samples of the production lubricating oils used in this work samples were modified in laboratory to analyze the behavior of the friction modifier additive. The specifications are described below in Table 2.

Table 2 – Sample specification.

SAMPLE	SPECIFICATION OIL MOTOR	FRICION MODIFIER
A	5W30 API SL ACEA A1/A5	Yes
B	5W30 API SL ACEA A1/A5	No
C	15W 40 API SL ACEA A3/98	No
D	15W40 API SL ACEA A3/98	Yes
E	Basic oil	0,5%
F	Basic oil	0,75%
G	Basic oil	1,0%
H	Basic oil	2,0%

## 2. Lubricant Role

In sliding metallic systems, when a lubricant is present in the interface, both wear and friction tend to be reduced. However, although these effects are related, the intensity of the lubricant effects is not to the same degree. Different oils affect wear and friction to variable scale. The existence of a lubricating film in the interface results in the insulation of both metallic surfaces and, consequently, the system should show no wear and low friction. Nevertheless, the existence

of a fluid in the interface depends on the contact geometry and on oil viscosity, which affects the hydrodynamic bearing of the oil film. In summary, three typical mechanisms can be considered in the lubricant role to influence wear and friction: surface absorption, chemical alteration and separation.

The physical surface separation results from the lubricant mechanical response to the relative surface movement. During surface sliding, the lubricant can stand the load applied and guarantee surface separation, making a wedge. The minimum lubricant film is a result of the applied load, sliding speed, contact geometry and fluid viscosity.

### 2.1. Lubricant Viscosity

Viscosity is one of the most important parameters to physically characterize lubricants, giving a measure of fluid resistance to shear. A definition of viscosity for Newtonian fluids, in terms of shear stress,  $\tau$ , is mentioned by Hutchings (1992):

$$\tau = \eta \frac{dg}{dt} \tag{1}$$

where  $\tau$  is the shear stress (Pa),  $\eta$  is the dynamic viscosity (Pa.s) and  $dg/dt$  is the shear strain rate ( $s^{-1}$ ) (Maru, 2003).

### 2.2. Film Formation

In a lubricated system where the surfaces are similar, there is an oil wedge formation in the contact interface due to the hydrodynamic flow characteristics. When this phenomenon occurs the minimum film thickness depends on the load, flow speed and fluid viscosity. Enough pressure can be produced in the flow such that the surface can be deformed, resulting in changing geometry in the contact region. There occurs the hydrodynamic lubrication (HD), when the bodies slide in the film without being deformed, or the elastohydrodynamic lubrication (EHL), when the contact bodies are deformed. This is the main type of lubrication that happens in gears and ball bearings, such as in the present work. Figure 2 shows a comparison between spherical surfaces contact in lubricated sliding for systems HD and EHL (Hutchings, 1992).

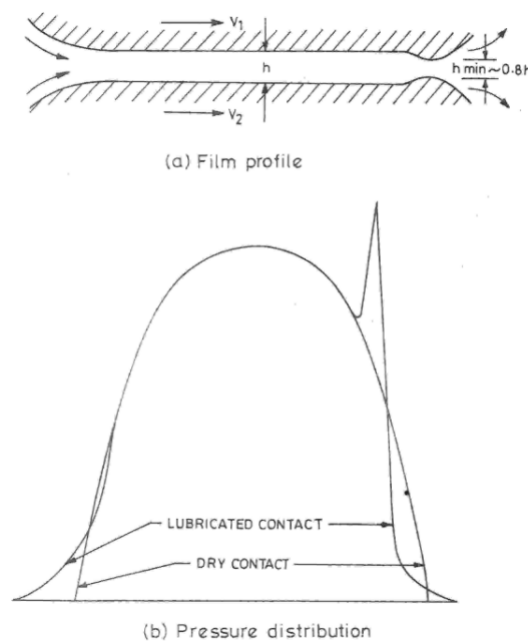


Figure 2- Contact region and film pressure under conditions of elastohydrodynamic lubrication EHL (Hutchings, 1992).

### 2.3. Friction Modifier Additive

Lowering the viscosity of engine oil is effective in reducing the fluid friction. However, it decreases the oil film thickness, and causes the increase in the wear of engine parts. Through engine wear tests using an radioisotope tracer technique, it was clarified that an HTHS viscosity of 2.6mPa was the lower limit to prevent the increasing wear (Dorinson, 1981). It was also found that the influence of the lowering viscosity on the wear of piston rings was larger than that on the wear of the cams and connecting rod bearings. Addition of friction modifiers is effective in reducing the friction under boundary lubricating conditions.

The lubricating fluid used to make easier the movement of sliding surfaces can be more efficient with utilization of friction modifier additives. These additives control friction, preventing scratch and reducing wear and noise. Friction modifiers are organic compounds of long chain with a terminal polar group and a non-polar hydrocarbons chain. The terminal polar group is physically absorbed in the metal surface, while the hydrocarbons chain increases the lubricant film resistance through this association. Friction modifier additives have a limited life due to oxidation and thermal instability (Persson et al, 2002).

## 2.4. Wear Mechanism

There are three conditions that can govern surface wear: contact friction, abrasive materials and corrosive friction. Abrasive wear can be avoided with installation of filter mechanisms. Corrosive wear can be controlled by use of additives that can neutralize the reactive species that attack the surface. An increase in load or reduction in speed can cause contact friction between moving surfaces, increasing the local temperature and, consequently, reducing the fluid viscosity and the ability to form a lubricating film. Under these conditions, the lubricant nature changes from hydrodynamic lubrication to mixed lubrication or even the limiting condition, the thin film (Fig. 3). Anti-wear additives offer protection for mixed film and thin film conditions. Similarly, extreme pressure (EP) additives also protect against mixed and thin films, but there is a need for higher activation temperatures and higher load than for anti-wear additives.

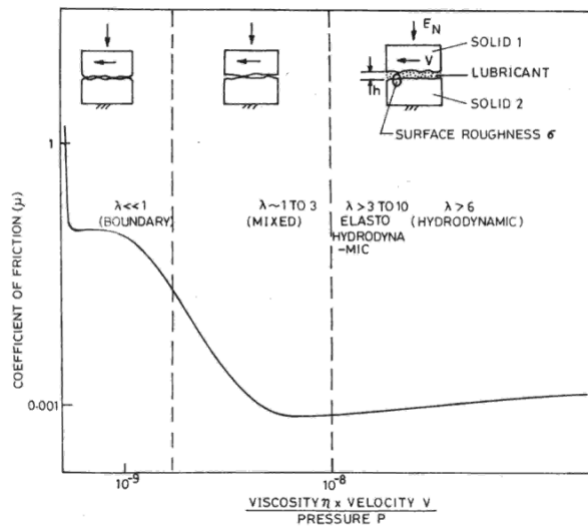


Figure 3 – Stribeck curve (coefficient of friction vs. Viscosity x velocity/pressure (Persson et al, 2002).

Most of the anti-wear and extreme pressure agents contain sulfur, chlorine, phosphorus, boron or a combination thereof. The classes of compounds that inhibit adhesive wear include alkyl and aryl disulfides, molybdenum dithiocarbamates MoDCT, chlorinated hydrocarbons, and phosphorus compounds (phosphites phosphates, phosphonates, and dialkyl dithiophosphates). Anti-wear and extreme pressures additives work with thermal decomposition and formation of products that react with the metal surface to form a solid protection layer that fulfill surface roughness to reduce friction and avoid fusion and wear. Friction modifier additives are different from anti-wear additives and extreme pressure additives due to formation of a film through physical adsorption, instead of a chemical reaction (Persson et al, 2002).

## 3. Experiments

### 3.1. Equipment

Friction modifiers continue to have high interest in the lubricant industry due to the ongoing pressure on fuel economy and energy efficiency. Wear protection is another aspect that is increasingly being considered. There are different rig tests (pin-on-ring, pin-on-disk) to recognized fuel economy efficiency (Kebeck et al, 2000; Buenemamm and Kenbeck, 2002). In this paper, a four-balls instrument was used (Fig. 4), following ASTM D 4172 standard (1988) to measure anti-wear properties, together with FIAT Standard 9.55535. The spheres were constructed on chrome-steel AISI E-5200, with 12.7 mm diameter, degree 25 (extra polished), according to ANSI B3.12, and hardness Rockwell C between 64 and 66. Any oil remaining in the spheres surface was removed by an inert fluid, to guarantee there would be no influence in the wear test results.

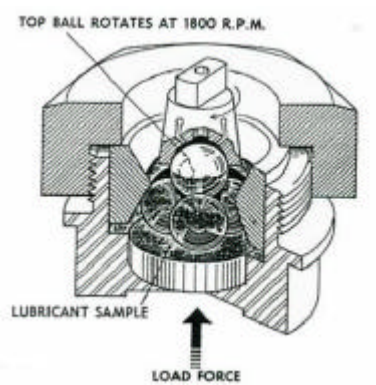


Figure 4 – Four-Balls instrument (Source: Stanhope-Seta).

### 3.2. Experimental Methodology

Many different experimental arrangements have been used to study sliding wear. Use of the four-balls instrument is basically a geometry test. The lower three balls are rotated together in a carrier, and move relative to the upper ball, which is held stationary end pressed downwards under a fixed normal load. This test is often used as a method of evaluating lubricant performance rather than study material behavior (Hutchings, 1992).

The instrument works under a sphere fixed to the bearing of a motor with a rotational speed of  $1700 \pm 60$  rev/min over three other fixed spheres in a metal support with a torque of 67.8 N.m. A load of 600 N was used during 50 min, and the diameter of the weary wheel was measured with an accuracy of 0.01 mm. In these conditions, the hydrodynamic forces cannot keep a lubricating film separating the surfaces, and friction and wear may occur. The samples of lubricants were then added to the spheres surface and tested to verify friction and wear prevention. The test conditions are summarized in Table 3.

Table 3 – Test conditions.

PARAMETER	VALUE
Speed	$1700 \pm 60$ rpm
Test duration	$50 \pm 0,5$ min
Load	$600 \pm 2$ N

### 4. Results and Discussion

The test results showed a wear scar reduction of up to 60% when the friction modifier additive was used (Table 4). When the additive concentration was varied no noticeable changes in the results were observed. The four-ball machine was accurate enough to evaluate the lubricant performance. The results obtained can be used to estimate fuel consumption reduction, reducing the need for dynamometer testing, and to help in the development of lubricants for high performance engines. Figures 5 and 6 shows the wear scar diameter using four-balls instrument for oils with same viscosity classification and the same classification of service with e without friction modifier addition, respectively. With no friction modifier (Fig. 6), the wear scar was almost twice as deeper as when it was used (Fig. 5). However, using friction modifier without ZDDP has produced even deeper wear scar, as shown by Fig. 7. Similar results as those of samples A and B (Figs. 5 and 6) were obtained for samples D and E, for a different lubricating oil (Figs. 8 and 9).

Table 4 – Wear scar for samples A to H.

SAMPLE	WEAR SCAR
A	$0.422 \pm 0.008$ mm
B	$0.73 \pm 0.05$ mm
C	$0.72 \pm 0.04$ mm
D	$0.435 \pm 0.06$ mm
E	$0.40 \pm 0.15$ mm
F	$0.40 \pm 0.05$ mm
G	$0.38 \pm 0.02$ mm
H	$0.35 \pm 0.0$ mm

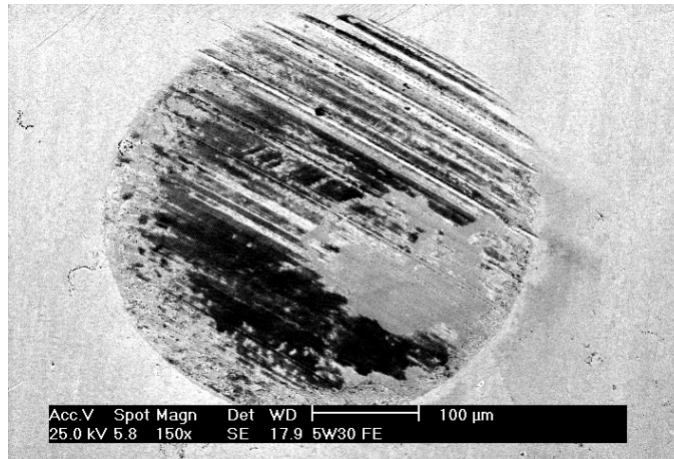


Figure 5 - Detail of the morphology of the wear scar (0,4 mm) for sample A: 5W30 API SL ACEA A1/A5 + FM - oil of normal production with friction modifier addition.

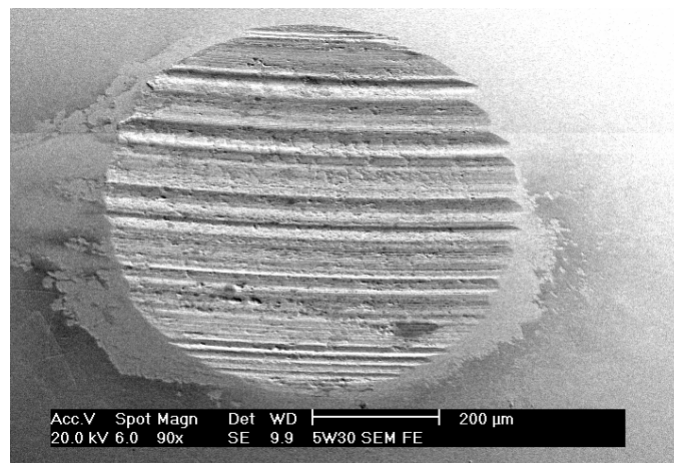


Figure 6 - Detail of the morphology of the wear scar (0,7 mm) for sample B: 5W30 API SL ACEA A1/A5 without friction modifiers.

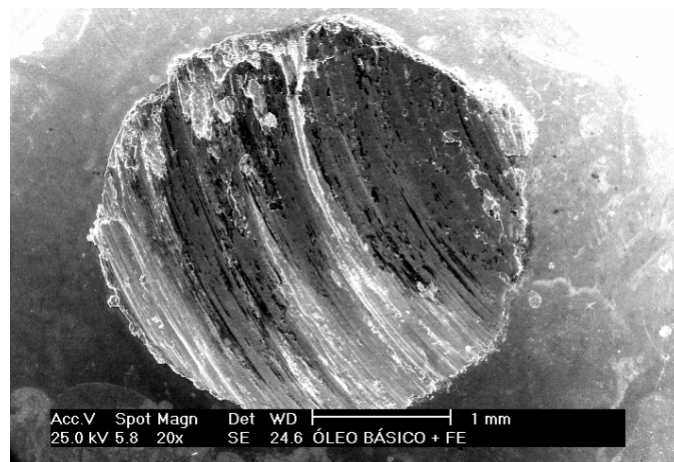


Figure 7 - Detail of the morphology of the wear scar (3,0mm) for sample C: 5W30 API SL ACEA A1/A5 + FM- oil of normal production with friction modifier addition, but without the presence of ZDDP (zinc dialkyl dithiophosphates).

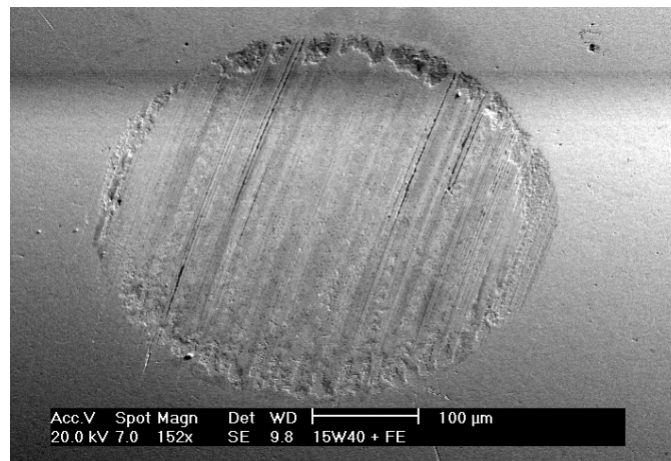


Figure 8 - Detail of the morphology of the wear scar (0,4mm) for the condition of Sample D: 15W 40 API SJ ACEA A3/98 + FM- oil of normal production with friction modifier addition.

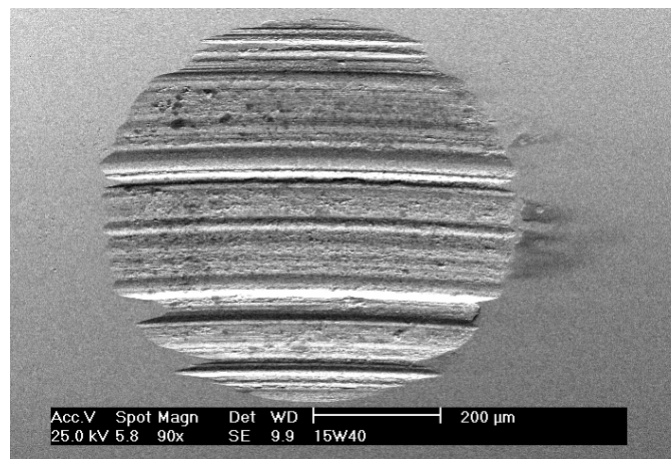


Figure 9 - Detail of the morphology of the wear scar (0,7mm) for the condition of Sample E: 15W40 API SL ACEA A3/98 - oil of normal production without friction modifiers.

## 5. Conclusions

- The results had demonstrated that addition of a high performance friction modifier additive to motor oil smoothes the roughness of the attacked surface.
- The behavior of the wear scar was identified by four-balls tests in motor oils with addition of 0,5% in weight of friction modifier additive. The quantity of ZDDP used associated to the friction modifier had a significant influence in the tribological system of the lubricating oils.
- Through the tests performed it can be concluded that usage of four-balls wear test to evaluate the performance of a lubricant oil with additive friction modifier is viable, reducing the costs of involved in more expensive methods.

## 6. Acknowledgments

The authors thank FAPEMIG and FIAT Automobile S.A. for the financial support to this project.

## 7. References

- ASTM, 1988, D 4172 – Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method), Volume 05.03, Petroleum Products and Lubricants (III), USA, 4p.
- Baldwin, B.A., 1976, Relationship between surface composition and wear: an X-ray photoelectron spectroscopic study of surfaces tested with organosulfur compounds. ASLE Transactions, Vol. 19, N. 4, pp. 335-344.

Buenemann T.F., and Kenbeck D., 2002, Oxidative Stable friction Modifiers for Automotive Applications. STLE Conference.

Freuler, H.C., 1994, Modified lubricating oil. US Patent Office 2-364-2873, United States.

Hutchings, I.M., 1992, Tribology – Friction And Wear of Engineering Materials, Edward Arnold, Great Britain, 273p.

Kenbeck, D., Bunemann T., Rieffe H., 1972, Organic Friction Modifiers – Contribution To Fuel Efficiency, SAE Paper n. 2000-01-1792, Society of Automotive Engineers.

Maru, M.M., 2003, Estudo do Desgaste e Atrito de um Par Metálico sob Deslizamento Lubrificado, Dissertação de Doutorado, Escola Politécnica, Universidade de São Paulo, 254p.

Mastin, T.W., Norman, G.R., and Weilmuenster, E.A. 1945, Chemistry of the aliphatic esters of thiophosphoric acids. I. Journal of the American Chemical Society, Vol.67, pp. 1662-1664.

Nicholls, M.A., Do, T., Norton, P.R., Kasrai, M., and Bancroft G.M., 2005, Review of the lubrication of metallic surfaces by zinc dialkyl-dithiophosphates, Tribology International, Vol. 38, pp. 15-39.

Person, B.N.J, Bucher, F., and Chiaia, B., 2002, Elastic contact between randomly rough surfaces: Comparison of theory with numerical results , Physical Review B, Vol. 65, pp. 184-206.

SETA, 1983, Seta-Shell Four-Ball E.P. Lubricant Testing Machine, Stanhope Seta, England.

Sheasby, J.S., Caughlin, T.A., Blahey, A.G., and Laycock, K.F., 1990, A reciprocating wear test for evaluating boundary lubrication. Tribology International, Vol. 23, N. 5, pp. 301-307.

Smith, G.C., 2000, Surface analytical science and automotive lubrication. Journal of Physics Part D: Applied Physics, Vol. 33, N. 20, pp. 187-197.

Sogawa, Y., Yoshimura N., and Iwasaki, O., 2000, R&D On New Friction Modifier for Lubricant For Fuel Economy Improvement – Group On New Friction Modifier For Fuel Improvement, Petroleum Energy Center, USA.

Yamagushi, E.S., and Ryason, P.R., 1993, Inelastic electron tunneling spectra of lubricant oil additives on native aluminum oxide surfaces. Tribology Transactions, Vol. 36, N. 3, pp. 367-374.

## **5. Responsibility notice**

The authors are the only responsible for the printed material included in this paper.