

CHALMERS



Fatty Amines as Friction Modifiers in Engine Oils

Correlating Adsorbed Amount to Friction and
Wear Performance

Katja Eriksson

Department of Chemical & Biological Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2014

Master's Thesis 2014-06

Fatty Amines as Friction Modifiers in Engine Oils
Correlating Adsorbed Amount to Friction and Wear Performance

A thesis submitted in fulfilment of the requirements for the degree of Master of Science

CHALMERS
UNIVERSITY OF TECHNOLOGY



KATJA ERIKSSON

Department of Chemical & Biological Engineering
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden, 2014

Fatty Amines as Friction Modifiers in Engine Oils
Correlating Adsorbed Amount to Friction and Wear Performance
KATJA ERIKSSON

©Katja Eriksson, 2014

Thesis work completed at:

AKZONOBEL SURFACE CHEMISTRY AB
Hamnvägen 2
SE-444 85 Stenungsund
Sweden

Supervisor:

Sarah Lundgren
Research Chemist
Petroleum and Water applications
sarah.lundgren@akzonobel.com

Examiner:

Martin Andersson
Associate Professor; Chemical and Biological Engineering
Applied Surface Chemistry
Chalmers University of Technology
martin.andersson@chalmers.se

Cover picture: Dashboard signal for oil problems in combustion engines.

Chalmers University of Technology
Department of Chemical & Biological Engineering
Gothenburg, Sweden, June 2014

Abstract

Department of Chemical & Biological Engineering

Master of Science (M.Sc.)

Fatty Amines as Friction Modifiers in Engine Oils Correlating Adsorbed Amount to Friction and Wear Performance

by Katja ERIKSSON

The biggest motivation for having lubricant additives and optimizing them is fuel economy. In the widest sense fuel economy can be explained as the reduction of fuel consumption. This can be achieved by different means but this thesis is focusing on reducing fuel consumption by lowering the friction in the engine with friction modifiers. In the engine oil there are a number of surface active additives which interacts with each other. This can influence the engine oil's performance, so an improved understanding of the relevant systems would be advantageous for future additives and formulations of the engine oils. As friction modifiers two fatty amines from AkzoNobel Surface Chemistry has been studied and the aim was to:

- Find a minimum/maximum treat rate or amount of friction modifiers by correlating adsorbed amount to friction and wear performance.
- If possible find correlation between packing performance and friction.

Quartz crystal microbalance with dissipation (QCM-D) has been used to study adsorption behavior of fatty amines. Friction and wear performance testings was done with a mini-traction machine (MTM) and a high frequency reciprocating rig (HFRR). It has been found that less than a monolayer of friction modifier is needed to get good frictional lubrication. However for the wear protection a monolayer is demanded. A common minimum/maximum treat rate was not found, the treat rate most likely depending on the chemistries of the friction modifiers.

Keywords: Friction, Wear, Adsorption, Fatty amines, ZDDP

Acknowledgements

First of all I would like to thank my supervisor Sarah Lundgren for all the help and support. Also I would like to thank the petroleum group and AkzoNobel. Finally, I would like to thank my examiner Martin Andersson for making this thesis possible.

Katja Eriksson, Göteborg 2014-06-13

*To my mother, who has supported me since the beginning, and
to my boyfriend who has loved and supported me throughout this
thesis.*

Chapter 1

Introduction

The most important driving force for the development of lubricant additives is fuel economy and fuel economy retention. In its broadest sense fuel economy is the reduction of fuel consumption. This can be achieved by different means like increased combustion efficiency as well as reduction of friction in the engine and transmission. Other means can be aerodynamics of the car, usage of lighter materials to decrease the weight, use smaller engines or have different driving pattern and speed.

However this thesis is focused on improving fuel economy with the engine oil. Lubricant formulations each comprise a number of different additives which each have a different role to play in the engine, such as friction modifiers, anti-wear additives, detergents, dispersants, viscosity modifiers, corrosion inhibitors and anti-foam additives. Since the majority of these additives are surface active, there is a high probability that they will interact with one another in solution and/or on the surfaces of the engine, which could influence their performance. An improved understanding of these mechanisms and their relevance in the systems to be studied will undoubtedly aid in the successful development of future additives and formulation of effective additive packs in the base oil.

One way the market is improving the fuel economy in terms of engine oil is lowering the viscosity. Many engine oils used now are 5W30 grade and the market is looking at 0W20. This reduction in viscosity will move the film thickness from full film towards mixed and boundary lubrication. When the lubricant film becomes partial or almost non existing more wear can occur, reduce the durability. This put more stress on the boundary additive like the anti-wear additive and the friction modifiers. Which can be an opportunity if any of AkzoNobels amine chemistries improves both friction and wear performance. The lowering of engine oil viscosity makes it important to understand the interaction of friction modifiers with anti-wear additives such as ZDDP so that oil packages can be effectively designed.

Another requirement from the market is low SAPS (sulphated ash, phosphorus and sulphur). Therefore the chemistries should preferably not contain sulphur or phosphorus, only carbon, hydrogen, oxygen and nitrogen. Friction modifiers like fatty acids, amines and amides work well in low SAPS formulations.

With all the desires of low CO₂ emissions, low SAPS, to get more from every tank of fuel and save the world from the Greenhouse effect, we have come far but still the aim is to keep this improved fuel economy throughout engine oil life time as a next goal.

In a previous study of different products at AkzoNobel Surface Chemistry no clear correlation between adsorbed amount and friction and wear was observed. Figure 1.1 shows the results from this previous study and suggests the purpose for this thesis. To investigate the adsorption behavior of two friction modifiers the quartz crystal microbalance with dissipation (QCM-D) was used. The friction and wear performance was studied with high frequency reciprocating rig (HFRR) and mini-traction machine (MTM).

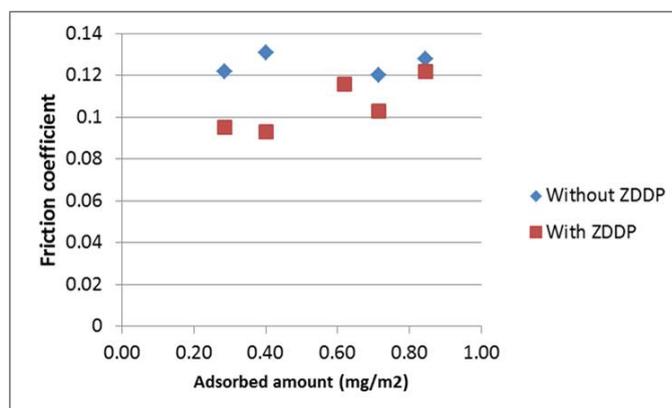


FIGURE 1.1: A previous study done at Akzo Nobel Surface Chemistry showed no clear correlation between adsorbed amount and friction performance between different products.

1.1 Aim and Scope

- Find a minimum/maximum treat rate or amount of friction modifiers by correlating adsorbed amount to friction and wear performance.
- If possible find correlation between packing performance and friction.

Chapter 2

Theoretical Background

2.1 Engines

An engine is a machine that is made to convert energy into mechanical motion. The internal combustion engine is most commonly used today in air crafts, ships to trucks, automobiles and lawn mowers. Apart from size the internal combustion engine can be divided into gasoline and diesel engines. A common characteristic to all of the internal combustion engines is the four-stroke cycle. The first part of the four-stroke cycle is compression of air by a piston, the second part is the ignition, at elevated pressure raising the temperature of the air by the combustion of the fuel. The third part is the expansion to the initial pressure, where the mechanical motion is extracted. The fourth and final part is the exhaust. The piston of the four-stroke engine needs two revolutions around the crankshaft to complete one cycle [1].

The spark-ignition engines works by drawing air and fuel into the cylinder and form a homogeneous mixture of air and fuel vapors by the time it ignites, at the end of the compression stroke. The mixture is ignited by a spark, a discharge between the electrodes in a spark plug. The ignition results in a very rapid expansion and pushes the piston down [2]. The diesel engine has a different approach of igniting the fuel than a spark-ignition engine. Just before the compression stroke is finished, fuel is injected and combusted. The fuel self-ignite because of the high pressure [1].

There is also a two-stroke engine with a similar combustion cycle that only needs one rotation around the crankshaft to be completed. The two-stroke engines are used most widely for smaller engines for smaller units where fuel economy is less important than mechanical simplicity and light weight. But also large engines like the ones on ships also use a two-stroke engine [1], [3].

To function properly the engines need engine oil that has to fulfill a wide range of functions. The tribological duty is to ensure the functional security under all operating conditions. When the engine burns fuel the oil helps to seal the piston and cylinder. On the wall of the cylinder the oil is burned off and should leave no residue. When the fuel is burned the blow-by gases are formed and the by-products created need to be neutralized and held in suspension. Other particles like soot and sludge that are created from incomplete combustion also need to be held in suspension by the engine oil. Furthermore, the engine oil also cools the piston by dissipating heat and transports dirt particles to the oil filter. If any water is formed during combustion the engine oil should emulsify the water and protect against corrosion. Another very important feature of the engine oil is to reduce friction and wear when the distances of the engine parts become limited. During cold start-ups the lubricant should still function and flow well to avoid metal-to-metal contact [4].

To minimize the total engine friction an optimization of rheological and surface chemical properties of the lubricants need to be solved. To solve these obstacles the approach needs to have a wide range of temperatures, pressures and shear stresses. Also a wide range of surface speeds and contact geometries as are encountered in the engine. When the engine is running the components experience various lubrication regimes. If the crankshaft bearings and valve train are both given a good lubrication, since they are sensitive to wear, it can reduce significantly the engine friction [5]. The piston rings are in boundary, partial film and full film lubrication while the piston skirts and cam followers are only in the full film [6], [7]. The engine oil needs to work in all lubrication regimes since it is the same oil that is lubricating the different components.

Gasoline engine has been developed further to continue to optimize the combustion process to increase the efficiency of the engines by direct-injection which can offer fuel savings of about 20 %. However, on the diesel side, direct-injection has become a norm and offers an increase of power up to 50 % with practically constant fuel consumption. The big concern is to further reduce exhaust emissions for diesel trucks and it is done with special exhaust recycling and catalytic converter systems. The fuel consumption has a firm limit and low viscosity engine oils have verified the desired fuel economy effects. The engine based savings can achieve theoretical values of 8 - 10 % but since engine oils cannot defeat all the frictional losses the saving possibilities of 5 % are challenging.

The new generation of engines will demand low-sulphur diesel fuel and also there will be new requirements of the lubricants used. Also surface treatments of pistons and cylinders have lowered the oil consumption and the oil changing intervals have constantly become longer. So the lubricant of the future will be characterized by fuel efficiency, long oil drain intervals and low emissions [4].

2.2 Lubricants

When two surfaces are in contact with each other and are in relative motion a resistance is experienced. This resistance is called friction and it exists in all machinery. At the interface of the contacting surfaces a lubricant can be placed and thus a lower friction and wear scar can be achieved [1].

Lubricants have been used for a long time but it is not known exactly when it first was deliberately or consciously used for the purpose of reducing the friction between the surfaces. Various forms of simple bearings were used in the Middle East several thousand years B.C. and an assumption can be that they also used lubricants. A wheel hub of a chariot has been discovered and it was in use during a later period in Egypt, around 1400 B.C. On the wheel hub they found traces of both chalk and animal fat which suggests that some primitive grease was used. In 1760 the industrial revolution started and the development of the large-scale machinery. The machinery was based on iron and steel and to lubricate all, animal oils were used. Also during this period mineral oils from distillation of coal or shale became available. Later also petroleum oils began to be obtainable and by the 1920's superior lubricants, compared to animal oil, were being produced. The development of petroleum-based oil to be cutting edge became more and more important as the internal combustion engine became more common [8].

The potential of an oil is not an absolute fact but a matter of degree. A certain acceptance of the lubricant and the machine must be taken into account during testing and its limits. The primary function of lubricants is to reduce friction and prevent wear but there are also other functions that the lubricant should fulfill. Lubricants are specialized for the considered area where it is applied. The desired functions of the oil can be friction reduction, wear reduction, cooling, anti-corrosion, cleaning action and sealing, just to mention a few. There are also regulations to what an oil should not do like be too volatile, foam excessively in service, be unstable to oxidation or chemical attack, produce deposits, attack components and so on [8]. An overview of what the fully formulated lubricant contains is shown in figure 2.1 [9].

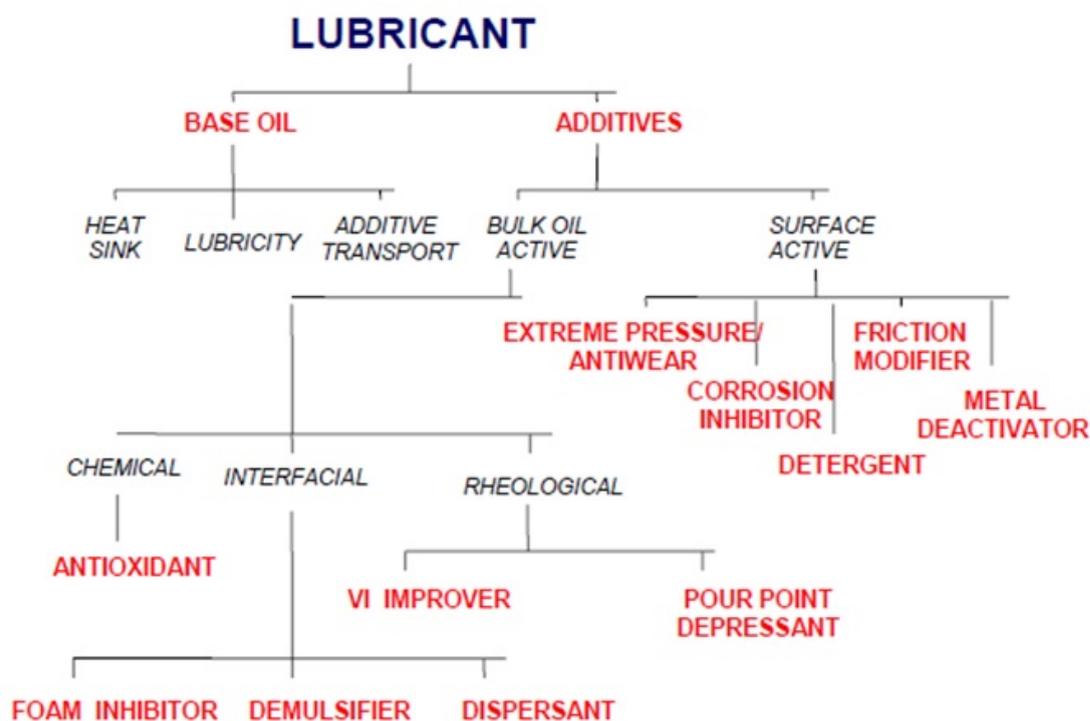


FIGURE 2.1: A fully formulated lubricant and the working areas of the components.

Base Oil

Base oils made from crude petroleum are a complex mixture of organic chemicals. Their composition include small gaseous molecules like methane to large high molecular weight asphaltic components. Undoubtedly some of the components are desired in the base oil for the lubricant but not all of them. Some crude base oil has a low amount of sulphur which makes them flow more easily. While others contain wax which makes them only flow when heated. Although the crudes contain a wide range of hydrocarbons and other organic molecules it is not the types of molecules that define the crude but the relative amounts. To separate the good from the bad a series of physical refining steps are required and chemical reactions may be used to tailor the properties of the oil. The refineries produce different types of oils with distinctive viscosities and chemical properties for certain applications [10].

The oil used in the experimental part of this thesis was a group III base oil for the friction and wear tests. A group III base oil is first hydro-cracked to divide fuels and bottoms residue. After the hydro-cracking the hydrocarbon bottoms residue is refined by catalytic de-waxing which removes wax and controls the low-temperature properties of the base oil. The base oil is refined further by hydro-finishing which removes traces of polar components that improves the color and stability of the oil [10].

Additives

Convoluting machinery has high demands on lubricants. For the moving parts of the engine to be able to come into such close proximity as they do a tailored package of chemical additives needs to be added to the engine oil. The additives do not only make the components able to work closely together but also operate efficiently, they drastically increase the engine's lifetime and reduce maintenance costs [9,3]. Table 2.1 lists the different additives in a common engine oil and their purposes are listed.

TABLE 2.1: Table of additives and their purposes.

Additive	Purpose
Detergents and Dispersants	Prevent sludge deposits and keeps soot in suspension
Antioxidants	Reduces degeneration of the base oil
Viscosity Modifiers	Keeps the viscosity of the oil at high temperatures
Pour Point Depressants	Reduces the viscosity at low temperatures
Anti-foam Agents	Keeps effective lubrication
Corrosion Inhibitors	Reduces oxidation of metal components
Friction Modifiers	Improves the lubricity
Anti-wear	Prevents wear in the engine

Most of the additive classes like pour point depressants, extreme pressure additives, viscosity modifiers, antioxidants, corrosion inhibitors and detergents were presented during the busy decade between 1930 and 1940. They were the response to the problems arising from the fast developing motor car industry [11]. All the additives in the engine oil have different purposes. The detergent and dispersant additives are there to prevent harmful carbon and sludge deposits. If the deposits attach in certain demanding areas of the engine it can lead to engine malfunction and shut-down which leads to repair. Another basic function that detergents and dispersants have is to help maintain the proper oil flow by minimizing oil thickening and suppressing the deposits of carbon sludge. Dispersants are used to suspend harmful soot contaminants while detergents neutralize acids and keep away deposits [12]. Engine oil also becomes exposed to oxidation degradation or aging of the oil and the additive used is antioxidants. The antioxidants are exposed to blow-by gases that are generated in the combustion chamber. The reactive blow-by

gases and high temperatures in the combustion chamber lead to rapid oxidation. Major components that the engine oil is exposed to are free radicals, NO_x , O_2 , partially oxidized fuel etc. The antioxidant has many functions and needs to be made to fulfill all of those functions [13]. Other additives used are the viscosity index improvers and thickeners. At high temperatures oils become non viscous and since it cannot keep the surfaces apart the wear will increase. This additive is mainly made out of polymers and as the name suggests it enhances the viscosity index and thickness. Some structures of viscosity index improvers also combine pour point depressants [14]. The flowability of an engine oil is very important also under start up conditions when the engine is cold. That is where the pour point depressant is used, to improve the low temperature characteristics. Without the pour point depressant there would be excessive wear due to the moving parts wearing the engine. Another challenge for the engine oil is the emulsions and foams that may form under the high shear regime. The emulsions and foams can damage the effective lubrication or block the oil channels and for this reason there is an additive called anti-foams. The engine can also be exposed to corrosion, whereas the engine oil contains corrosion inhibitors. Some additives can help to cope with general corrosion but the corrosion inhibitors are there specifically for the electrochemical process [15].

2.3 Friction Modifiers

Another additive in the engine oil is the friction modifier. From the beginning friction modifiers or friction reducers was used for transmission fluids, gear oil and multipurpose tractor fluids and so on, really anywhere where precise movement was essential. After the Gulf crisis in 1978 the fuel economy became of great importance for all vehicles. This led to the introduction of friction modifiers with the objective to improve fuel efficiency of the motor oil [15]. A general image of the friction modifier can be seen in figure 2.2 from [8]. The friction modifiers improve the lubricity and consequently the energy efficiency by reducing the friction coefficient [16].

Friction modifiers are most efficient in the boundary lubrication, metal-to-metal contacts, since they are attracted to metal surfaces. The friction modifiers are usually long slender molecules and have a straight hydrocarbon chain of at least ten carbon atoms. The dominant factor for the effectiveness of the friction modifiers are the polar head groups. The different head groups can be carboxylic acid, phosphoric or phosphonic acid, amines, amides, imides and all their derivatives. The polar head of the friction modifiers goes to the surface of the metal and the hydrocarbon tail remains solubilized in the oil [15]. The friction modifier can adsorb or chemically react on the oxide covered

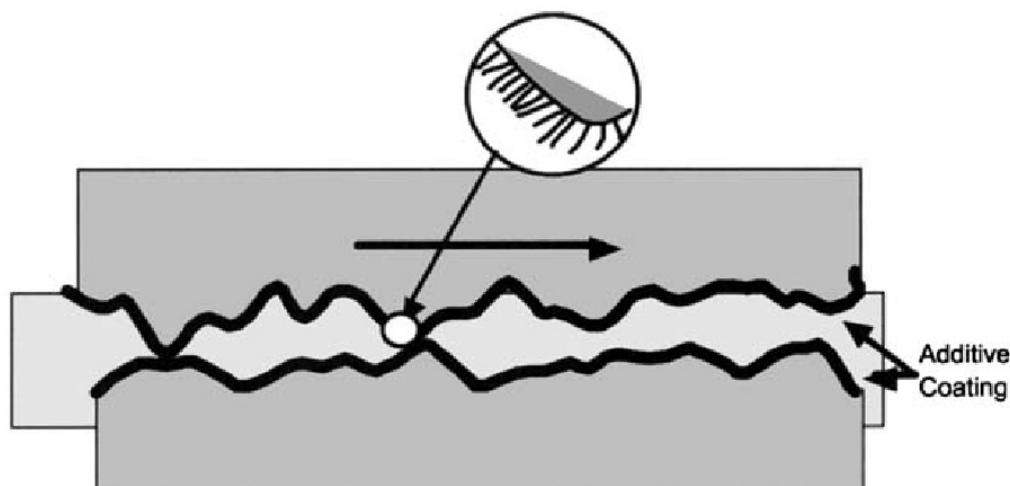


FIGURE 2.2: A comprehensive image of friction modifiers on a metal surface.

metal surfaces of the engine. At certain concentrations the hydrocarbon tail will be perpendicular to the surface and line up with each other. The friction modifiers can form dense monolayers or thick reacted viscous layers. The layer of molecules is easy to shear but not to compress. The easy shearing of the molecules gives the metal surface the slippery nature because of the friction modifier [15], [16].

Except for the organic friction modifiers there are also molybdenum compounds such as molybdenum dithiocarbamate (MoDTC). The MoDTC is not only a friction modifier but also one of the most efficient non-phosphorous anti-wear additives. The additive creates a nanosized single sheet of MoS_2 spread out in a carbon or FeS_2 matrix. The sheet of MoS_2 eases sliding which in turn lowers the friction [16].

2.4 Anti-Wear Additive (ZDDP)

One of the most successful lubricant additives ever invented is Zinc dithiophosphates (ZDDPs), it was presented over 70 years ago and is still in use today [11]. The molecular structure of ZDDP can be seen in figure 2.3. Almost all engine oils use some kind of ZDDP and their survival is remarkable.

Over the last decades numerous companies have made effort to replace them due to the phosphor and sulphur but unsuccessfully. There is no cost-effective alternative that is comparable in anti-wear performance to ZDDPs in engine oils. A lot of research has been performed on ZDDPs as it is very successful and multifunctional. ZDDPs functions include antioxidants, corrosion inhibitors and anti-wear agents [11]. The V8 engines appeared in 1949 with overhead valves and increased compression ratios. This

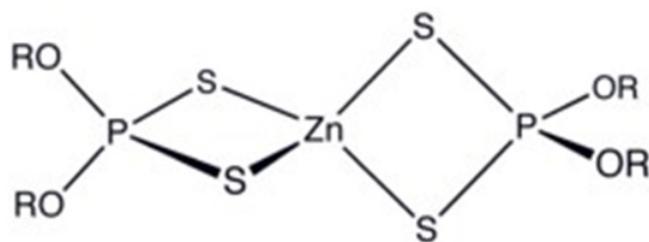


FIGURE 2.3: Molecular structure of ZDDP

caused increased stresses on the valve train components and major wear problems in the cam and followers, resulted in the anti-wear assets was first discovered. ZDDP was further developed to gradually optimize the structure to fit different applications and engine types. In gasoline the more reactive secondary alkyl ZDDPs is being used and the primary ones in oils for the diesel engine because they are more thermally stable. However, in the 1990s with the introduction of exhaust after-treatment catalyst problems arose. Phosphorous oxides, sulphur oxides and ash poisoned the exhaust catalyst which resulted in regulations to limit the amount of ZDDP in engine oils. Commonly the only source of phosphorus in engine oils is ZDDP and this has encouraged research to find phosphorus-free additives. The slow decrease of the phosphorus regulation limit show obvious difficulty of finding a replacement of ZDDP with comparable performance [11]. The current understanding of ZDDP in solution can be seen in figure 2.4 from [11]. As described before ZDDP has a complex behavior and is a multifunctional compound. ZDDP can react in solution and adsorb to a surface to form a film. The reactions in solution include ligand exchange, peroxide decomposition and thermal degradation.

The ligand exchange occurs since the dithiophosphates ligands are labile. The zinc cation can be fairly easily exchanged by a metal ion, this forms a less thermally stable metal dithiophosphates (MDDP). Dithiophosphates are also metal extraction agents. The ZDDPs are known to be antioxidants and it has been shown in the 1950s that it was due to their ability to decompose hydroperoxides. Later it was also found that ZDDP decompose peroxy-radicals and when ZDDP act as the hydroperoxide decomposer the conformation that it forms are not able to create an anti-wear film. If hydrogenperoxides or peroxy-radicals are not present at high temperatures ZDDPs react in solution and thermally degrade. The temperatures depend on the alkyl groups present but is commonly between 130°C to 230°C . For ZDDP to start film formation it must first diffuse and adsorb to the surface. Previous studies have shown that the ZDDP molecules adsorb to iron via the sulphur atom. Above 60°C a loss of Zn ions takes place and the adsorption becomes irreversible. ZDDP can form two kinds of film, the thermal film and

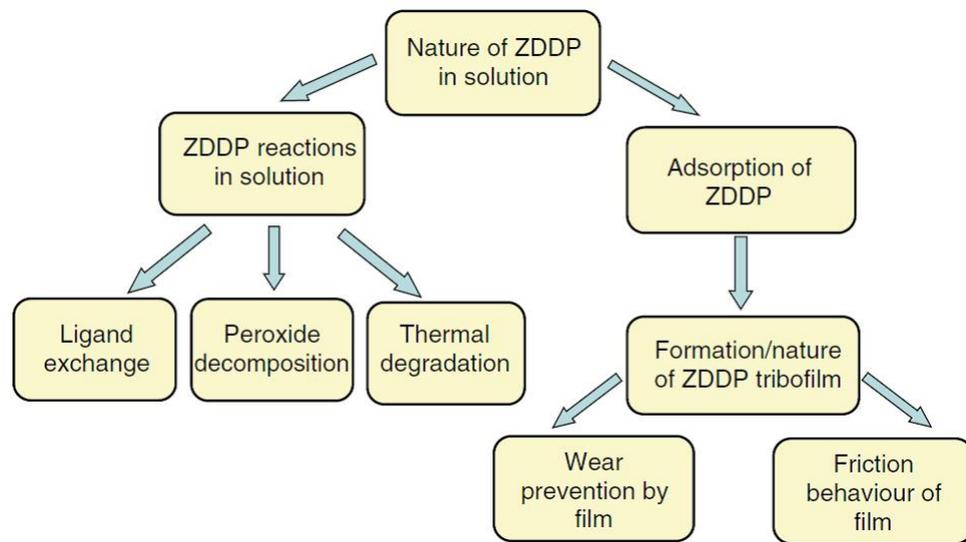


FIGURE 2.4: The behavior of ZDDP in solution.

the tribofilm. They have similar composition and are made up of mainly an outer layer of polyphosphate that is about 10 nm thick. The ZDDP tribofilm however can form at much lower temperatures, even at room temperature but the rate of formation increase with increasing temperature and pressure. They form only on the rubbing tracks and are mechanically stronger than the thermal film. Primary the film form separated patches that develops into an almost continuous structure made out of pads. A representation of the ZDDP film can be seen in figure 2.5 [11].

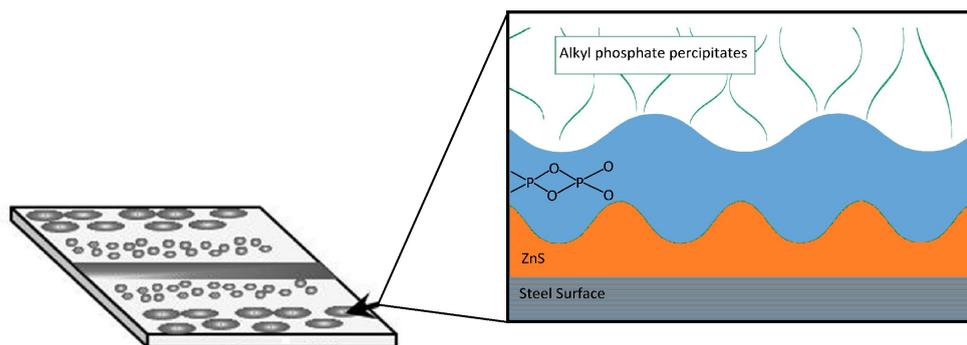


FIGURE 2.5: ZDDP figure of pads and layers

The pads are typically solid-like, $5\ \mu\text{m}$ across and 100 nm thick and they are disconnected by deep valleys. Closest to the metal surface is a rich sulphur coating that consists of zinc or iron sulphide. On top of the rich-sulphur layer there is a glassy phosphate which represents the main part of the pad. The outer layer of the pad consists of zinc polyphosphate or alkylphosphate precipitates. ZDDP is not only an anti-wear additive

but also a mild extreme pressure (EP) additive. The EP additive is there to prevent severe wear. Depending on the severity of the rubbing conditions different compositions of the ZDDP films develop. With mild rubbing conditions the film is mainly a thick phosphate film while with severe rubbing a thinner film with sulphur-rich contents is formed. In broad terms the ZDDP film is a mechanically protective barrier [11].

2.5 Friction Modifiers and ZDDP

To improve the fuel economy friction modifiers are used and a large amount of research has been performed in both base oil and fully formulated engine oils. Generally the fully formulated engine oils contain a lot of surface-active additives including the anti-wear additive ZDDP. ZDDP is recognized to react promptly with the rubbed iron surface to form a thick layer of iron and zinc phosphate based coating. So for the friction modifier to be effective it has to adsorb not only on the metal surface but also on the zinc phosphate pads of ZDDP. Also not all fully formulated lubricants contain the same additive molecules and the selection of optimal additive combinations becomes a trial and error performance [17].

A previous study have showed that on the ZDDP film the amine show an instant reduction in the boundary friction and the friction was considerably reduced after 120 minutes of rubbing. The amine friction modifier also reduced the friction coefficient in the partial film lubrication. The study also observed that the amine created lower boundary friction on the ZDDP film but not on steel surface. Not enough research has been done to establish common rules for which friction modifiers works best with both surfaces and with all the other additives in the fully formulate lubricants. Since the oxidized surfaces of steel have basic properties an additive with acid groups may adsorb better. While an additive with basic groups like the amine may adsorb better on the polyphosphate. They observed that all friction modifiers created a small reduction in the ZDDP film thickness, apart from the amine which generated a striking decrease in the film thickness. The amine did not only decrease the ZDDP film thickness but also slowed down the film formation process. The study suggested that it might be because the additives blocked the film formation. It might be that it formed a complex with ZDDP in solution or that it adsorbed to the surface and was blocking it. It might also be that the friction modifier encourages the removal of the ZDDP film and it became a dynamic process [17].

2.6 Fundamentals of Lubrication

Friction

Friction can be both advantageous and cause problems. We depend on friction to keep the car on the road when driving and braking. However, in lubrication it is an unwanted property that originates from the asperity of surfaces in close contact and in relative motion. *Tribology* is the science relating friction, wear and lubrication. It has taken a long time to develop the understanding of friction. Aristotle around 500 B.C. acknowledged the frictional forces and Leonardo Da Vinci in 1470 was the first to study them scientifically [8].

Mechanisms of Friction

No surface is completely smooth even if it is carefully prepared. The surface will contain large hills and valleys compared to molecular dimensions. On the peaks the solid surfaces will rest and the area of contact is very small. The peaks are exposed to plastic deformation and the surface will flow until the area is large enough to support the load. The friction arises from the small contact area when the sliding takes place. This causes a large surface temperature rise at the rubbing contacts which can cause microstructural changes to the surface and also local melting. At the points of contact there is adhesion and they are welded together. The frictional force experienced is the tearing of these junctions and is directly proportional to the applied load. The frictional force is described in equation 2.1 and it is the energy required to shear the asperities and welded sites for metal-to-metal friction.

$$F_1 = F_A + F_P \quad (2.1)$$

Where

F_A = The force needed to shear the junctions F_A is further on divided into $A_c * S$ where

A_c = The real area of contact taking into account the elasticity of the surface,

S = The effective shear stress of the junction,

F_P = The force required to displace the softer metal of the two.

In most combinations of materials the contribution of F_P is so small that it can be excluded when the friction is calculated. The friction coefficient, μ , is a dimensionless number and given by equation 2.2.

$$\mu = \frac{F_1}{\omega} = \frac{F_A}{\omega} = \frac{S}{H} \quad (2.2)$$

Where

S = Shear strength

H = Effective surface hardness

ω = Applied load

From this equation the material should have low shear strength and high hardness to generate low friction. The requirements can be met if thin layers that have low shear strength form on the hard metal surface. The layers must be thin enough to not increase A_c , the real area of contact [15].

Mechanisms of Wear

As mentioned previously the surfaces are not smooth but have a saw tooth patterns that comes from the machining process and are seldom planar. This makes some areas come in closer contact than others and the asperities, surface roughness will collide. The material is scratched from the surface and becomes wear fragments [8]. There is a number of processes that can cause wear namely adhesion-, abrasion-, corrosion- and contact fatigue-wear. Adhesion wear can occur at the peaks of the surface roughness and it is a bonding or cold-weld formation. In this wear process there is no direct loss of material but it can occur, there is a transfer of material from one surface to the other. The newly exposed surfaces are more reactive and must be pacified by additives. Several wear processes start off as adhesion wear which creates abrasive fragments and transform into abrasive wear. In abrasive wear hard particles scratch the surface like grinding and machining operations of a metal but less efficiently. Abrasive wear stimulates the presence of corrosive wear, which occurs because of a chemical reaction. This type of wear can be influential to service life of the material. The corrosive wear can either be on the whole surface or at selected sites like inclusions or grain boundaries. The selective corrosion can deteriorate the structure of the surface and initiate fatigue. The contact fatigue is predominating in rolling contacts where there are high stresses and low slip, and give rise to pitting or cleavage of the surface. By increasing the film thickness a lower probability of contact fatigue occurs. However, increasing the film thickness may increase the friction[15].

Stribeck Curve

To understand the behavior of different lubrication regions the Stribeck curve gives a good concept. On the vertical axes of the Stribeck curve is the coefficient of friction, μ , under steady state conditions. On the horizontal axes in this case is the Hersey number which is dimensionless and shown in equation 2.3

$$H_S = \frac{\eta * \omega}{P} \quad (2.3)$$

Where

η = Absolute Viscosity [$Pa * s$]

ω = Rotational Speed [rps]

P = Pressure [Pa]

A thick lubricant film gives a relatively high Hersey number and a small number is corresponding to a thin film. The different regions of the film can be concluded from the friction behavior. No real lubricant film can be developed at really low Hersey numbers which give a high friction because of the surface roughness. A Stribeck curve is shown in figure 2.6.

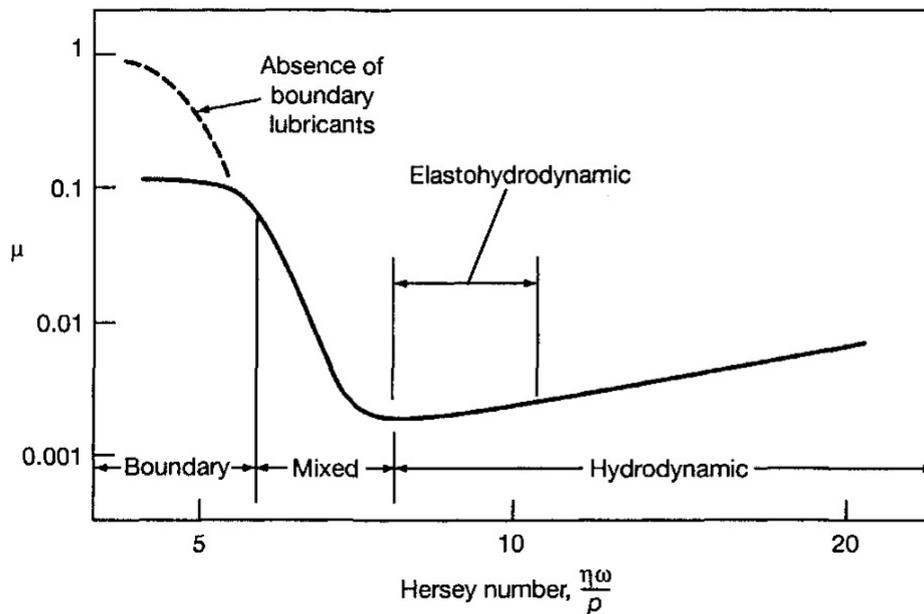


FIGURE 2.6: Shows a Stribeck curve with indications of lubrication regions.

The boundary lubrication represents the first part of the curve where the friction coefficient continues to be high with increasing Hersey number. In this regime the load

transfer and friction between surfaces are determined. With a further increase of the Hersey number a rapid decrease in friction coefficient is noticed and it is described by an increasing lubricant film thickness. The applied load is not only supported by the asperities but also the pressurized liquid lubricant. The friction coefficient can vary a lot in this regime and it is mostly depending on test conditions. The friction coefficient will continue to decrease with increasing Hersey number until a lower plateau is reached. This plateau indicates the beginning of the hydrodynamic lubrication where the lubricant film thickness is sufficient to separate the surfaces and asperity contact has an insignificant influence on load support and friction. Film thickness can also be hindered by geometries of certain bearing which will result in an increase of the friction coefficient at higher Hersey numbers, which also can be seen in figure 2.6. [18].

Two different lubrication regimes can be seen in figure 2.7 namely hydrodynamic lubrication on the left-hand side and boundary lubrication on the right-hand side from article [8].

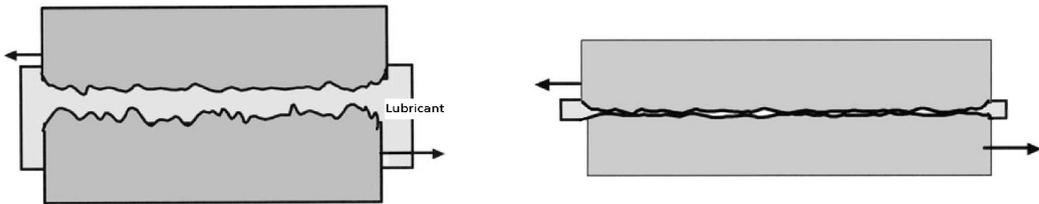


FIGURE 2.7: The left-hand side show hydrodynamic lubrication. On the right-hand side there is boundary lubrication.

Hydrodynamic Lubrication

When a lubricant is presented it separates the surfaces completely, a full film [8]. In hydrodynamic lubrication the viscosity of fluids separates the surfaces. The presence of the positive pressure suggests that a normal applied load can be supported and it is not large enough to cause elastic deformation on the surfaces. The minimum film thickness in hydrodynamic lubrication generally exceeds $1 \mu m$ and this is thick enough for surfaces to not come in contact. This regime offers low friction and high resistance to wear [18]. The friction is much lower due to the only force needed is the one to move the lubricant [8]. The bulk physical properties of the lubricant is steering the lubrication of the solid surface, particularly the viscosity of the fluid. The friction behavior comes from the shearing of the viscous lubricant [18].

Elastohydrodynamic Lubrication

A form of hydrodynamic lubrication is elastohydrodynamic lubrication where the lubricated surfaces become elastically deformed. There are two distinct forms of elastohydrodynamic lubrication (EHL), namely hard EHL and soft EHL. Materials with a high elastic modulus like metals have hard EHL and the lubrication effects of elastic deformation and viscosity-pressure are equally important. Applications where hard elastohydrodynamic lubrication is important include gears, rolling-element bearings and cams. Materials with low elastic modulus like rubber have a soft EHL. Components like seals and tires etc. require soft EHL. The shared characteristics of hard and soft EHL are the local elastic deformation that gives a fluid film and that there are almost no asperity contact. This suggests that the frictional resistance experienced under this condition is due to shearing of the lubricant [18].

Boundary Lubrication

In boundary lubrication a fluid film formation is not possible and there is a significant asperity contact [19],[18]. The physical and chemical properties of thin surface film of molecular proportions manage the contact lubrication. In the boundary regime the bulk properties are of minor importance which results in the friction coefficient being independent of fluid viscosity. The behaviour of the friction depends on the properties at the interfaces between solids and the lubricant film. The film on the surface fluctuates in thickness depending on the size of the molecules, usually between 1 to 10 *nm* [18]. The surface films can either be physically adsorbed (physisorption) or chemically adsorbed (chemisorbed). The physisorption arises under very mild sliding conditions and the bonding interaction with the surface is weak. No additives are needed to generate physisorption on the surface, all lubricants experience the formation of boundary film. Chemisorption on the other hand is a stronger interaction with the surface and actually creates a bond. The molecules in the lubricant can pack efficiently on the surface if they are chemisorbed. Favorable boundary lubricants combine a chemical reaction with the surface and cohesion between the tails of the lubricant.

Mixed or Partial Lubrication

If the running speed of the machine is too low or the pressures in the elastohydrodynamic lubrication regime are too high, the film will be pierced and it will only be a partial film. Both boundary and fluid film effects are present in partial lubrication which creates the behavior of the regime. The film thickness is on average less than 1 μm and larger than

0.01 μm . Another important point is that the shift from elasto-hydrodynamic lubrication does not take place immediately as the magnitude of the load increases. The fluids carry decreasing proportions of the load and larger parts of the load are carried by asperities [18].

2.7 Characterization

QCM-D Technology

Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) is mostly used for the characterization of thin films by looking at multiple harmonics.

QCM has been used for more than 50 years to monitor mass changes on rigid surfaces and most successfully in air and vacuum. The principle of QCM is that a voltage is applied to the quartz crystal which makes it oscillate at a certain frequency. The changes in frequency describe the mass changes on the surface of the quartz. The relationship between change in frequency on the oscillating crystal and mass changes is described by the Sauerbrey relationship 2.4.

$$\Delta m = -C * \Delta f \quad (2.4)$$

Where

Δm = The change in mass

Δf = The change in frequency

C = A constant for the crystal

The equation is only valid for adsorbed layers that are rigid, evenly distributed and sufficiently thin. If the adsorbed layer is soft and viscoelastic the film does not couple to the oscillating crystal and equation 2.4 underestimates the mass on the surface. To be able to analyze such film another method is required namely QCM-D that measures both frequency and dissipation. Figure 2.8 illustrates what changes the instrument experience between a rigid and a soft layer. The dissipation arises when the voltage over the crystal is shut off and the energy from the oscillating crystal dissipates from the structure. The dissipation is defined by equation 2.5.

$$D = \frac{E_{lost}}{2\pi E_{stored}} \quad (2.5)$$

Where

E_{lost} = The energy lost during one oscillation cycle

E_{stored} = The total energy stored in the oscillator

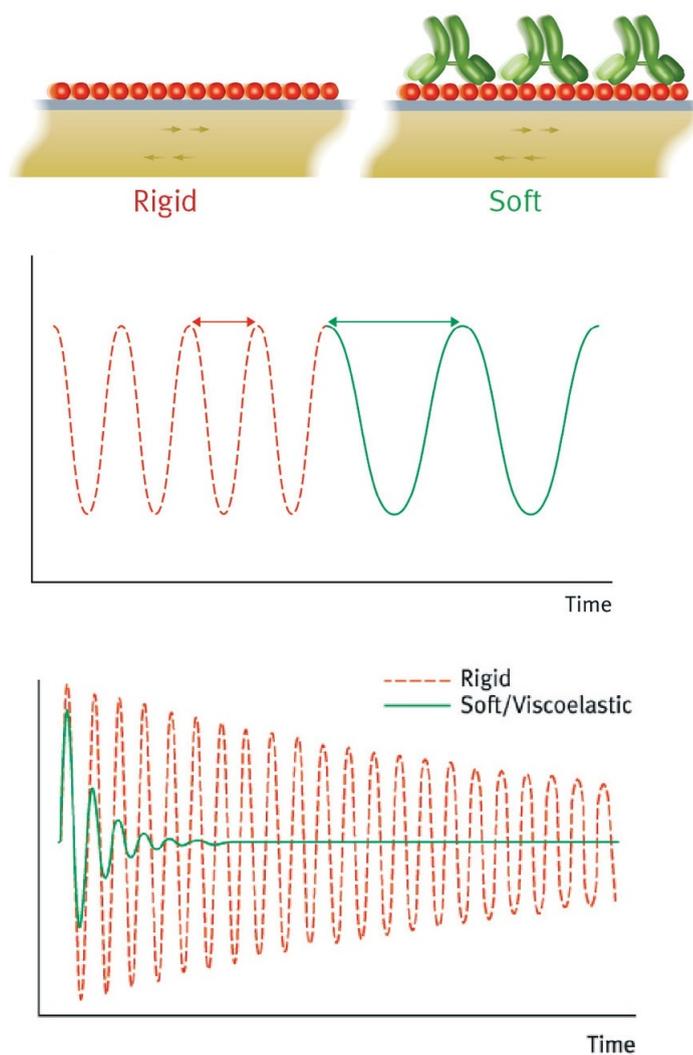


FIGURE 2.8: At the top of the figure two different surfaces can be seen, one rigid and one soft. Underneath the change in frequency can be seen and at the bottom of the figure the change in dissipation.

Water or other liquids can couple to the adsorbed molecules which will generate an additional mass. The measurement of dissipation can determine if the adsorbed layer is hard rigid or soft viscoelastic. Except for this structural analysis that the QCM-D can perform it allows real-time kinetic analysis of both mass and viscoelastic changes [20].

High Frequency Reciprocating Rig (HFRR)

High Frequency Reciprocating Rig (HFRR) is an instrument where friction and wear tests are performed. This method is especially suitable to test poor lubricants and boundary friction [21]. The setup can be seen in figure 3.3 and is based on a steel ball that is loaded against a stationary steel plate. The ball is rubbed on the plate with a certain frequency, other parameters that can be set depending on the profile are load and temperature. A schematic of the sliding action can be seen in figure 2.10.

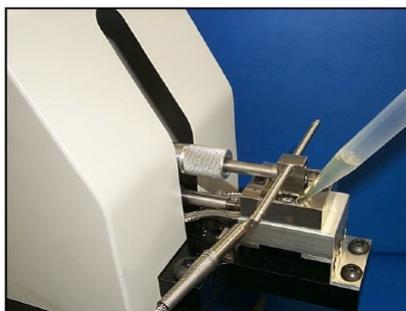


FIGURE 2.9: The set up of the HFRR.

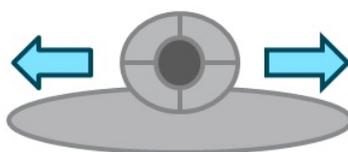


FIGURE 2.10: A schematic representation of the sliding contact in the HFRR.

During the measurement with the help of a computer program the changes in friction coefficient, film formation and temperature can be seen. The film formation is indicated with electrical contact resistance (ECR). The build up of the film acts as an insulator and separates the two surfaces of the test specimens. After the measurement the steel ball can be studied and the wear scar can be evaluated and measured in a microscope [22].

Mini-Traction Machine (MTM)

Mini-Traction Machine (MTM) is an instrument for measuring frictional properties under a wide range of rolling and sliding conditions of lubricated contacts with various additives. One of the most commonly used application of the MTM is the conditions imitating an internal combustion engine and with the MTM the physical resistance mapping is fully automated. In figure 2.11 a general set up of the MTM is shown.



FIGURE 2.11: Set up of MTM

A schematic representation of the MTM surface contacts can be seen in figure 2.12. The test specimens are usually a $3/4$ inch steel ball and a steel disc with a diameter of 46 mm. The ball is lowered on to the disc with a certain load. The test specimens are operated independently of each other to generate a mixed rolling/sliding contact. By a force transducer, force generates a current that is measured, the friction between the ball and the disc is measured. Further sensors measure the applied load, temperature of the lubricant and electrical contact resistance (ECR). ECR gives a hint if there is any contact between the two test specimens. The tests can be run with Stribeck curves where the speed is altered as with a time step where the speed is constant. In the profiles the load and temperatures can be set.

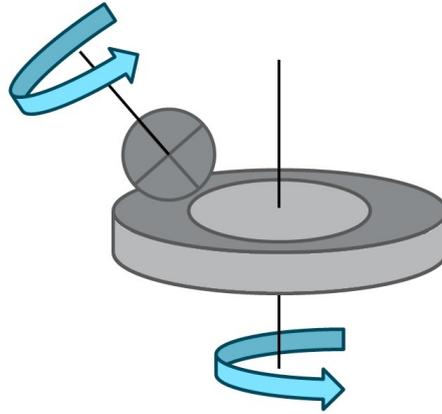


FIGURE 2.12: A schematic representation of the sliding and rolling contacts in the MTM.

3D space layer imaging method (SLIM) makes it possible to measure additive film formation on the test ball during the test. A general set-up is shown in figure 2.13. To measure the film SLIM uses optical interferometry by loading the steel ball against a glass coated with a chromium and silica layer. White light is shone through a microscope and the glass. Parts of the light is reflected from the chrome layer and parts shines through the silica layer and the additive film. When the light reaches the steel ball it is reflected back and by combining the light paths an interference image will be created which can be seen in figure 2.14. The interference image is then focused onto the imager of a camera. The optical interference image can be analyzed with software and determine film thickness [23].



FIGURE 2.13: Set up of MTM with SLIM

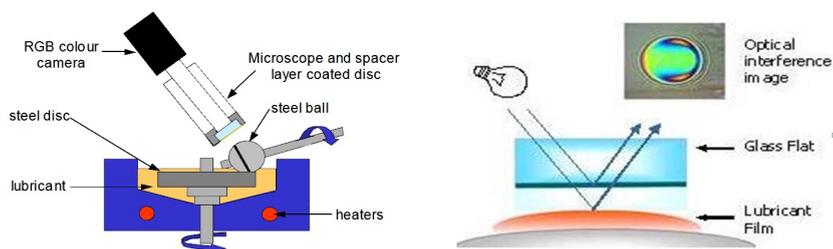


FIGURE 2.14: Shows the practical set-up of the space layer imaging method and a descriptive image of how the it is attained.

Surface Tension Measurements

Surface tension measurements can acquire the adsorbed amount with the help of Gibbs equation 2.6 and by plotting the surface tension versus the logarithmic concentration. Then by studying the slopes of the curves the adsorbed amount can be obtained. Two identical slopes would indicate the same surface area/molecule.

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d(\ln C)} \quad (2.6)$$

Where

Γ = Adsorption [$\mu\text{mol}/\text{m}^2$]

γ = Surface tension [mN/m]

C = Concentration [molar]

By assuming that a monolayer has adsorbed. The adsorbed amount is inverted and proportional to the cross-section of the head of the molecule. The connection is showed in equation 2.7. [24].

$$A = \frac{1000}{6.023\Gamma} \quad (2.7)$$

Where

A = Area/molecule [\AA^2]

Γ = Adsorption [$\mu\text{m}/\text{m}^2$]

The area/molecule can also be calculated from Δf in the QCM-D results and molecular weight (M_w). The unit analysis is shown in equation 2.8.

$$\frac{g/m^2}{g/mol} = \frac{mol}{m^2}, \quad \frac{mol}{m^2} * N_A = \frac{molecules}{m^2},$$
$$\frac{1}{molecules/m^2} = \frac{m^2}{molecule}, \quad \frac{m^2}{molecule} * 10^{20} = \frac{\text{\AA}^2}{molecule} \quad (2.8)$$

Where

$N_A =$ Avogadro's number ($6.022 * 10^{23}$) [mol^{-1}]

Chapter 3

Experimental

3.1 Chemicals

Two different kinds of amines were used to decrease the friction coefficient and prevent wear: Ethomeen O/12 is a tertiary amine ethoxylate which is based on a primary oleyl amine. Armeen O is an Oleylamine. The molecular structures of the two amines can be seen in figure 3.1

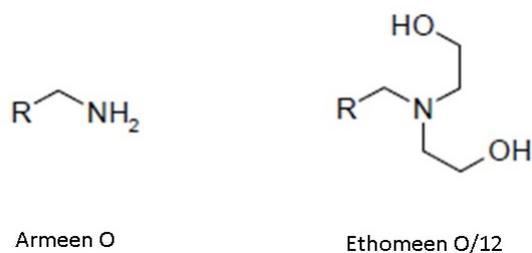


FIGURE 3.1: The molecular structure of the two investigated friction modifiers, where R=18 Carbons.

The anti-wear additive used was a Zinc dialkyl thiophosphate ZDDP (T206) was a primary/secondary blend. The hydrocarbon chains (R) are a blend of C8 and C4. The molecular structure can be seen in figure 2.3.

For the friction and wear performance tests Nexbase was used. Nexbase is a Group III mineral base oil from Neste oil with hydrocarbon chains of C20-C50. The oil was hydrotreated and neutral oil-based.

For the adsorption measurements a thinner oil GreenFlux SD from Total fluides was used. The oil contains hydrocarbon chains of C15 to C20 and aromatics. The aromatics has a hydrocarbon chain of C9.

A heptane extraction with a boiling point range of 94/99 was used for cleaning. The heptane extraction is referred to as SBP.

3.2 Quartz Crystal Microbalance with Dissipation (QCM-D)

Equipment

The sensors used for the experiments in the QCM were quartz discs with a layered structure beginning with chromium, gold, titanium and a top coat of 100 *nm* stainless steel (SS2343). The fundamental frequency of the sensors were 5 *MHz*. The instrument was a Q-sense with an extreme temperature chamber.

The sensor was immersed in a 2 % Hellmanex solution for 30 minutes and then thoroughly rinsed with tap water. The parts of the chamber were first rinsed with SBP and then dried with nitrogen gas. Then the parts were placed in 2 % Hellmanex and run in an ultrasonic bath for 10 minutes. The parts were later cleaned by thoroughly rinsing with tap water. All the parts of the chamber and the sensor were rinsed with ethanol and dried with nitrogen gas. The chamber was put together and placed in the instrument.

Experimental Set-up

The test tubes with the sample and the oil were heated with an oil bath and it was set to 60°C. The test chamber was placed on a heating plate to make the test run at 50°C. A line running from the test tube to the chamber was covered in aluminum foil to isolate. The chamber was then connected to a pump. The program used for the measurements was QSoft401. Before starting the measurement the resonance frequencies were checked for the sensor and then GreenFlux SD was pumped through the system for two minutes and with a flow rate of 0.5 ml/minute. Then the measurement was started to first get a baseline. The instrument was left running for 40 minutes and then flushed with GreenFlux SD with a flow rate of 0.25 ml/minute for one minute. Then the instrument was left running again for 30 minutes to be able to stabilize. When the baseline was stable the measurement was stopped and a new measurement was started. In figure 3.2 below a measurement is shown. The first ten minutes of the measurement was to evaluate if it was a stable baseline and then at exactly ten minutes the sample was pumped in to the system where the first arrow indicates. The sample was pumped with a flow rate of 0.25 ml/minute for two minutes the first time and then stabilizing for 18 minutes. At a total of 30 minutes the sample was pumped into the system for a second time with the same flow rate for one minute. This is indicated with the second arrow. The system was left

to stabilize again for 19 minutes and then the system was flushed with GreenFlux SD for two minutes with the same flow rate. When the system had stabilized the measurement was finished.

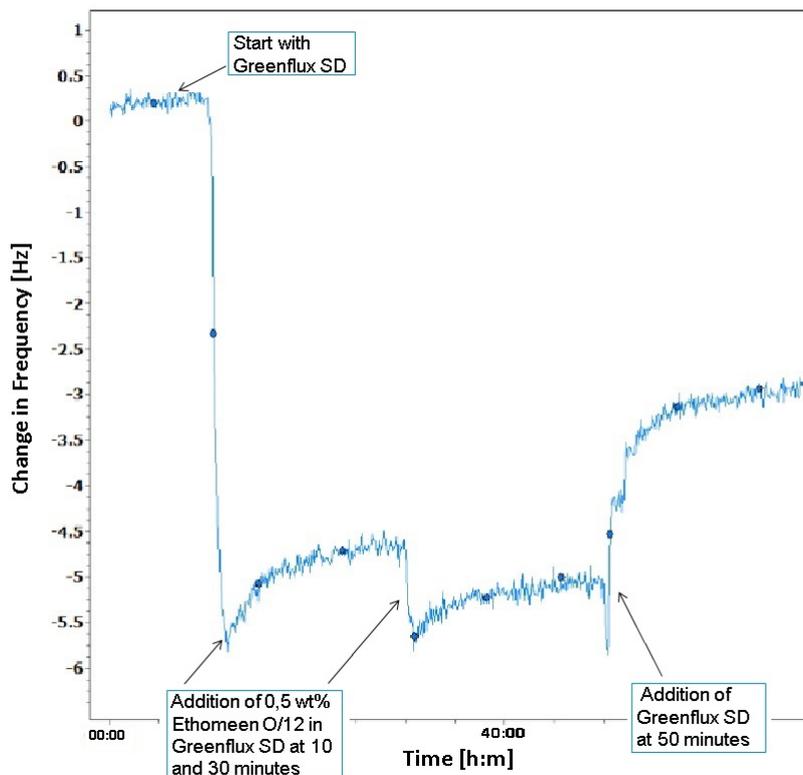


FIGURE 3.2: Shows and describes a measurement performed in the QCM-D.

Data from the experiment was extracted to Qsense own computer program Q-tools and then copied to excel where the adsorbed amounts were calculated with the Sauerbrey equation 2.4.

3.3 High Frequency Reciprocating Rig (HFRR)

Equipment

The ball, the upper specimen was specified to grade 28 (ANSI B3.12), ANSI E-52100 steel, with a Rockwell hardness "C" scale (HRC) number of 58-66 (ISO 6508), and a surface finish of less than $0.05 \mu m R_a$ [21].

The lower specimen, the disc was specified to AISI E-52100 steel machined from annealed rod, with Vickers hardness "HV30" scale number of 190-210 (ISO 6507/1). It was turned lapped and polished to a surface finish of less than $0.02 \mu m R_a$ [21].

The instrument was High Frequency Reciprocating Rig from PCS Instruments.

The test equipment and specimens were cleaned in an ultrasonic bath with SBP for 5 minutes, 10 minutes and another 10 minutes. The clean parts were screwed together. The samples were preheated to 60°C to make sure they were completely soluble. 2 ml of the sample was placed in the HFRR to test. The measurement was run with a load of 600 g and a temperature of 120°C for one hour. The friction coefficient and film thickness were average values during the measurement and the wear scar was measured with a microscope that calculate the diameter. The friction coefficient attained was in the boundary lubrication regime. In figure 3.3 below a measurement is shown and the wear scar after a test.

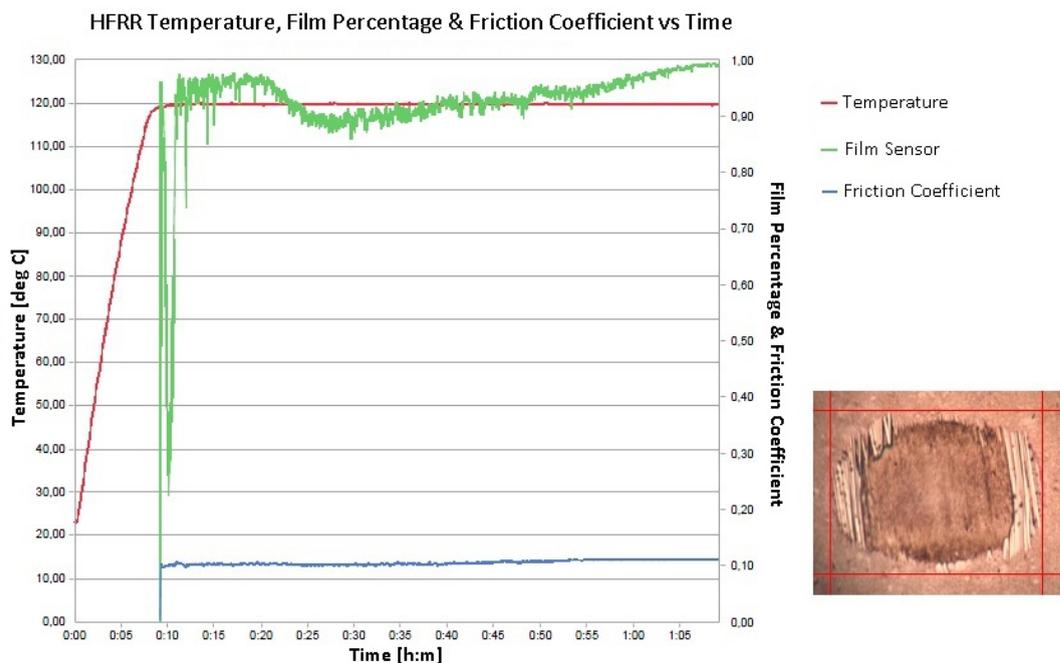


FIGURE 3.3: Shows a HFRR test and the measured wear scar after the test.

3.4 Mini-Traction Machine (MTM)

Equipment

The ball and disc specimens was specified to AISI 52100 (EN31), with a hardness of 720 to 780 HV and a surface roughness of $0.01\ \mu\text{m } R_a$ [23].

The instrument was a Mini-traction machine 2 from PCS Instruments.

The test equipment and specimens for the MTM were cleaned the same way as for the HFRR. The pot that holds and heats the sample is stationary and was cleaned with SBP,

paper towels and nitrogen gas. The samples were preheated before the test to 60 °C and about 35 ml was used. All the test equipment was screwed in place and the sample was poured in the pot. Before the test was started the interference image for SLIM was adjusted. The measurement was started with a profile that first took an initial image of the ball then made a Stribeck curve and then another image. The time step was 120 minutes, to make the film develop then an image was taken. Another Stribeck curve was done and an image was taken.

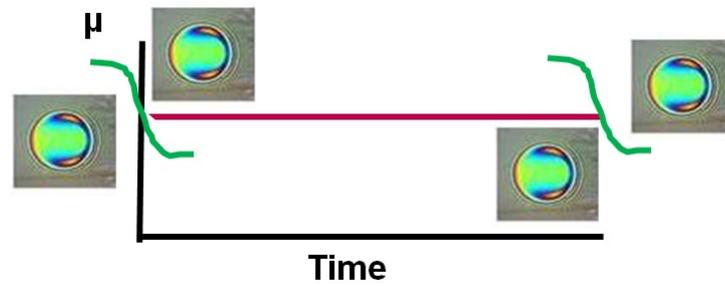


FIGURE 3.4: A schematic representation of the MTM test.

Chapter 4

Results and Discussion

4.1 Without Anti-Wear Additive

From figure 4.1 the adsorbed amount of different concentrations of Ethomeen O/12 can be seen. The adsorbed amount increases with increasing concentration of Ethomeen O/12. The area/molecule have been calculated and are shown in blue. It can be seen that the area/molecule decreases with increasing concentration which suggests that the molecules become more tightly packed. The area/molecule was calculated from the surface tension results performed by John Janiak [25]. The area/molecule from the surface tension results and the area/molecule calculated from the adsorbed amount in the QCM-D can be seen in table 4.1. By comparing figure 4.1 to the surface tension measurements it can be seen that close to a monolayer has been formed at 0.5 wt%.

TABLE 4.1: Results from surface tension measurements [25] and the area/molecule at 0.5 wt% and 1 wt%.

Ethomeen O/12	Surface area [\AA^2]
100 % screening	45
0 % screening	89
0.5 wt%	69
1 wt%	59

0 % screening gave a surface area of 89 \AA^2 and 100 % screening gave a value of 45 \AA^2 , these are extreme values of a monolayer. The average value however is 67 \AA^2 and this

could suggest that close to a monolayer has been formed at 0.5 wt% of Ethomeen O/12. To investigate if this was a plateau higher concentrations were examined. At higher concentrations the adsorbed amount increases which is followed by the area/molecule decreasing and this can be seen in figure 4.2.

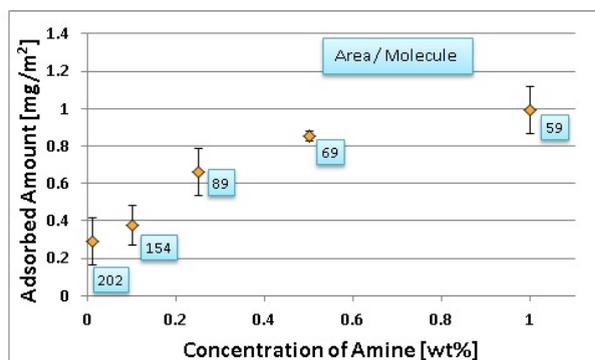


FIGURE 4.1: Adsorbed amount of Ethomeen O/12 and the area/molecule at different concentrations.

However the value given in the blue boxes are lower than the surface area of 100 % screening value which proposes that there is more than a monolayer on the surface. At the higher concentrations the difference between the 3rd and 11th overtone is larger, which indicates a change in bulk viscosity/density meaning that some of the adsorbed amount is due to changes in viscosity/density. Another study suggests that it can be because of loosely physisorbed molecules [26].

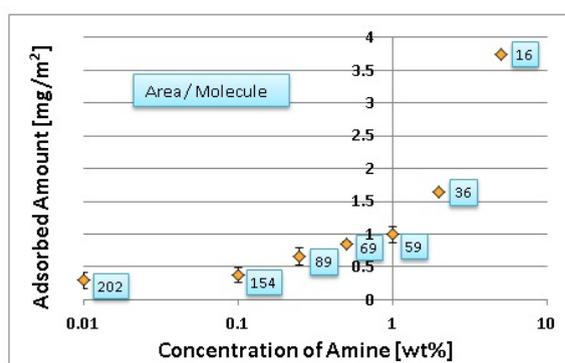


FIGURE 4.2: Adsorbed amount of Ethomeen O/12 and the area/molecule at different concentrations, with the addition of 2 wt% and 5 wt%.

The product Armeen O was also reviewed but since it gave such a low adsorbed amount, 0.27 mg/m^2 at 0.5 wt%, it was not investigated at different concentrations. Also surface tension measurements between the oil-water interface could not be performed since Armeen O is not water soluble. This would have given an indication at which area/molecule a monolayer had been formed. However, when calculated from the adsorbed

amount Armeen O has a area/molecule of 163 \AA^2 . Since the head groups are smaller for Armeen O this would indicate that it is not a closely packed monolayer. The molecules are probably laying on the surface instead of standing up.

Figure 4.3 shows the friction coefficient and wear scar at different concentrations of Ethomeen O/12 from the HFRR measurements. From figure 4.3 it can be seen that upon the first addition of Ethomeen O/12 there is a decrease of the friction coefficient. At 0.25 wt% of the amine concentration a plateau has more or less been reached. The wear scar show no instant decrease at the first addition but start to decrease at a concentration 0.25 wt% and reached a constant value at 0.5 wt%.

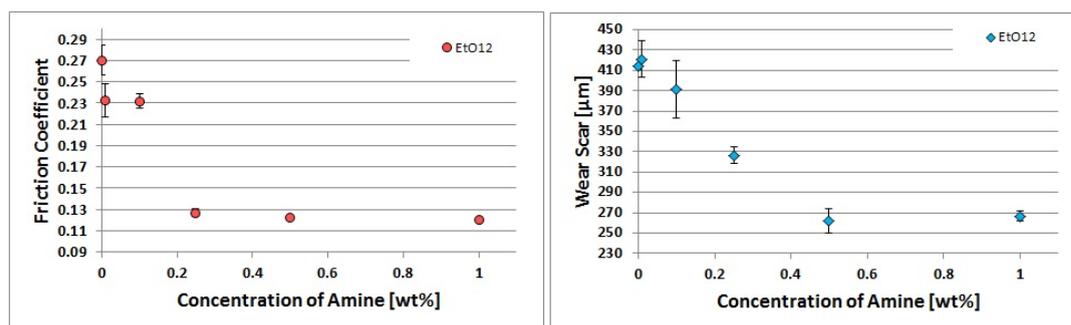


FIGURE 4.3: The friction coefficient and wear scar of Ethomeen O/12 at different concentrations.

The adsorbed amounts from QCM-D, surface tension measurements and the HFRR results of Ethomeen O/12 conclude that less than a monolayer of friction modifier is needed to lower the friction coefficient while for the wear scar close to a monolayer is needed.

Armeen O shows a similar trend in frictional behavior and can be seen in figure 4.4. Upon the first addition there is a decrease in friction and a plateau is reached at 0.1 wt% with a slight inclination at higher concentrations. The wear scar of Armeen O shows a different behavior, here there is an instant decrease with no sign of an additional decrease at higher concentrations. As soon as Armeen O adsorb to the surface it protects the surface slightly. However this is not seen with Ethomeen O/12. It might be a difference between the two chemistries, Armeen O wants to stay in solution while Ethomeen O/12 wants to go to the surface.

If the two products are compared the plateau in friction occurs at similar values of friction coefficient. On the other hand the wear scar diameter for Ethomeen O/12 is much lower than the wear scar value for Armeen O. This might be because of the low amount adsorbed by Armeen O on the surface. It is just not enough to prevent wear.

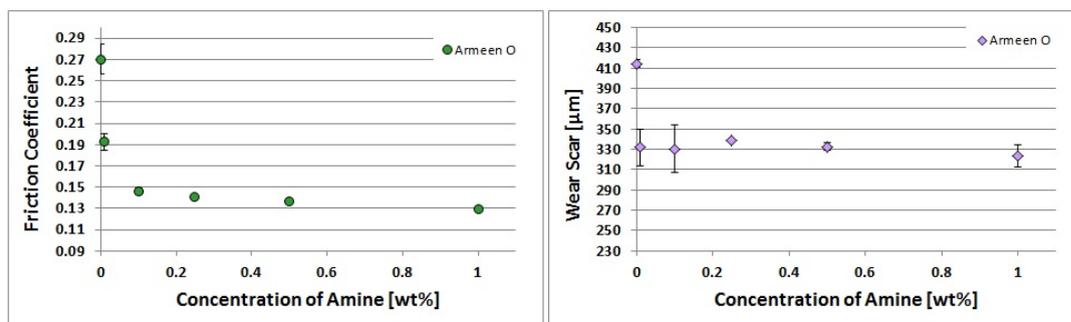


FIGURE 4.4: The friction coefficient and wear scar of Armeen O at different concentrations.

The adsorbed amount of Ethomeen O/12 however is enough to provide better wear protection.

4.2 With Anti-Wear Additive

In figure 4.5 the different measured adsorbed amounts are shown with error bars. By looking at figure 4.5 the error bars show a large variation of the absorbed amount. This means that there is no distinct difference between the adsorbed amount of ZDDP, Ethomeen O/12 and the combination of the two. The summation of 0.5 wt% ZDDP and 0.5 wt% of Ethomeen O/12 would give a higher adsorbed amount than the combination of the two did, which could indicate that there is not enough space on the surface for both. With this test there is no way of knowing which molecules has been adsorbed to the surface.

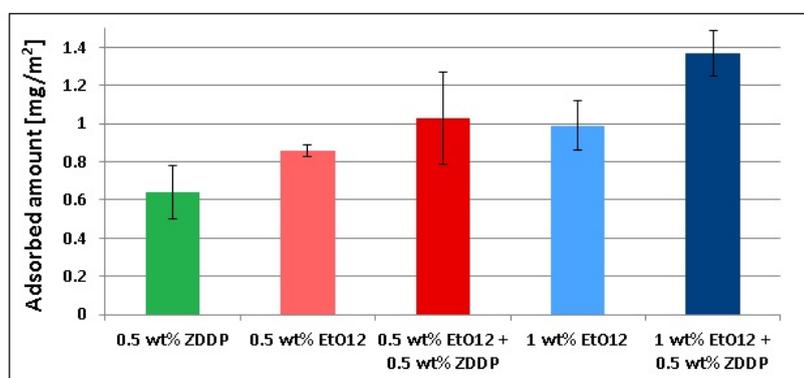


FIGURE 4.5: QCM measurements of adsorbed amounts at different concentrations of Ethomeen O/12 and combinations of the two with a continuous concentration of ZDDP.

We know that both Ethomeen O/12 and ZDDP goes to the surface but the effect of summation of the two on-top of each other is not visible. In figure 4.6 we can see

a difference between the adsorbed amounts. This could indicate that there is enough space on the surface to adsorb both Armeen O and ZDDP. Reference [26] suggests that the functional head group is adjacent to the metal surface. Armeen O has a small head group of only NH_2 while Ethomeen O/12 has a larger head group that covers more space on the surface. Also this could suggest that Armeen O saturates the surface and this leaves enough space for the ZDDP molecule. Ethomeen O/12 on the other hand is very polar and is more attracted to the surface which leaves less space for the ZDDP.

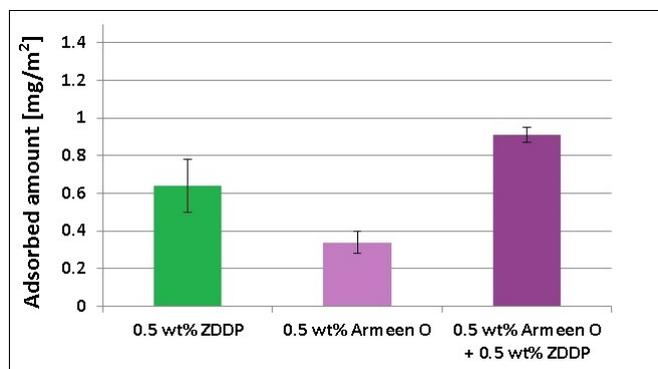


FIGURE 4.6: QCM measurements of adsorbed amounts of ZDDP, Armeen O and the combination of the two with error bars.

Seen in reference [17] that there is evidence that amines can remove ZDDP films from friction tests. To further investigate this QCM-D measurements were performed and the data can be seen in figure 4.7 and 4.8, where the blue squares specifies the adsorbed amounts as an average value. In figure 4.7 two measurements were performed. First there is a 10 minutes baseline. Then addition of 0.5 wt% Armeen O at 10 minutes and then addition of 0.5 wt% ZDDP at 30 minutes. At 50 minutes the system is flushed with GreenFlux SD. This was repeated twice.

Armeen O gave a similar adsorbed amount as previously seen of 0.25 mg/m^2 . Upon the addition of ZDDP an increased adsorbed amount was revealed.

The difference between the adsorbed amounts is 0.2 mg/m^2 . This is much less than the average that ZDDP adsorbs on its own. As a result the total adsorbed amount of the two is 0.55 mg/m^2 and this is less than the adsorbed amount of the combination of the two seen in figure 4.6. Probably Armeen O blocks the surface for ZDDP. The conclusion is that when they are blended together more is adsorbed. In reference [27] they discuss that amines and ZDDP form a complex in bulk. This could also be why they adsorb more in combination.

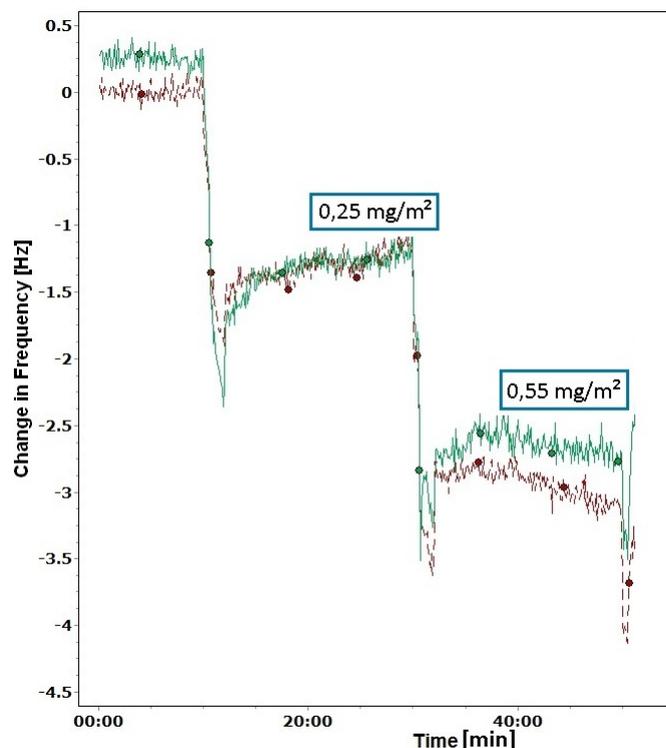


FIGURE 4.7: QCM measurement with 0,5 wt% Armeen O in GreenFlux SD as the first addition and 0,5 wt% ZDDP in GreenFlux SD as the second addition. The system was flushed at 50 minutes.

By switching the order of the additions it can be investigate what Armeen O does to the ZDDP adsorbed on the surface. This can be seen in figure 4.8 where three different measurements were performed. The blue squares specifies the average value apart from the deviating value of 0.34 mg/m^2 which was a single measurement. The addition of ZDDP was similar to that of previous measurements and had a value of 0.79 mg/m^2 . When Armeen O is added we can see that the adsorbed amount decreases and this gave an adsorbed amount of 0.68 mg/m^2 . The multitude of the reduction varied widely. Again the total adsorbed amount is less than when the products are added together. The data confirms the theory in reference [17] about the removal of the ZDDP film with amines. Some future work could be to test this with Ethomeen O/12 instead of Armeen O and also do similar test in the MTM described in reference [17].

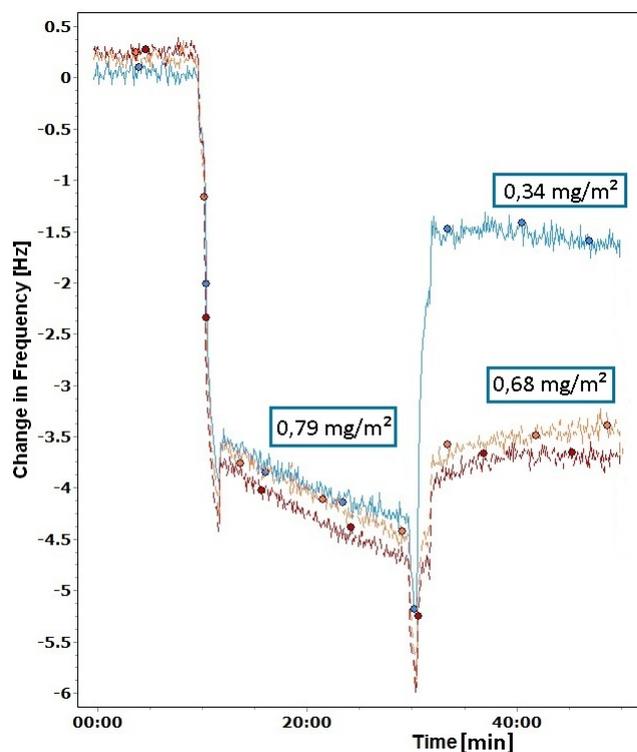


FIGURE 4.8: QCM measurement with 0,5 wt% ZDDP in GreenFlux SD as the first addition and 0,5 wt% Armeen O in GreenFlux SD as the second addition. The system was flushed at 50 minutes.

Friction and wear performance were also reviewed with the anti-wear additive ZDDP. In figure 4.9 we can see the friction coefficient and wear scar measurements of Ethomeen O/12 with and without ZDDP. By looking at the figure we can see that with only the addition of ZDDP both the friction and wear scar decreased. The friction coefficient shows an instant and small decrease upon the first addition of fatty amines to ZDDP. The friction coefficient lies in the same regime as without ZDDP but reached a plateau at a lower concentration. The wear scar needs a slightly higher concentration to reach a plateau but it is still a very low concentration of friction modifier. Probably ZDDP protects the surface and only a small amount of Ethomeen O/12 is needed to get a covering protective film.

Also from figure 4.9 we can see that 0.5 wt% of ZDDP gives a larger wear scar than 0.5 wt% of Ethomeen O/12. Which means that the friction modifier protects the surface better than only ZDDP. Figure 4.10 shows the friction coefficient and wear scar of Armeen O both with and without ZDDP. Both the friction coefficient and wear scar show an instant reduction and continues to decrease until 0.75 wt% where they start to increase. If the wear scar of 0.5 wt% Armeen O and 0.5 wt% ZDDP are compared they show similar values which would indicate that they protect the surface equally.

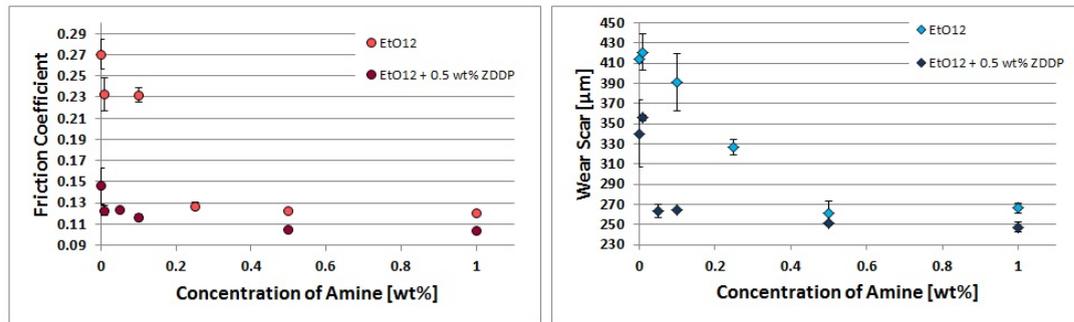


FIGURE 4.9: Shows the data collected from HFRR measurements of Ethomeen O/12 both with and without the anti-wear additive ZDDP. On the left-hand side the friction coefficient can be seen and on the right-hand side the wear scar.

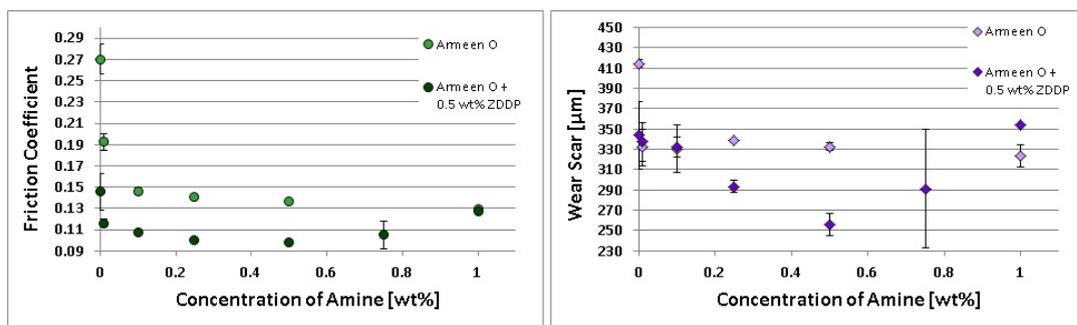


FIGURE 4.10: Shows the data collected from HFRR measurements of Armeen O both with and without the anti-wear additive ZDDP. On the left-hand side the friction coefficient can be seen and on the right-hand side the wear scar.

The ZDDP film is undergoing a constant formulation/removal process. With small amounts of Armeen O this process is not altered. At 0.75 wt% there is enough Armeen O to disturb the formation and removal process. However the large standard deviation suggests that in some cases a film can form. At 1 wt% there is too much Armeen O present and ZDDP can not form a film and as a result the higher friction and wear.

Another method to investigate the frictional behavior and the ZDDP film formation and the friction modifier is the MTM with SLIM. There are however differences between the methods like the point pressures and the contacts between the surfaces. The HFRR gives a calculated point pressure of 1.2 *GPa* while the MTM has 0.8 *GPa*. In the HFRR there is only a sliding contact that reciprocates back and forth 2.10 while in the MTM there is sliding and rolling contact 2.12.

Figure 4.11 shows a series of Stribeck friction curves with different concentrations of Ethomeen O/12 and a constant concentration of 0.5 wt% ZDDP. Also the molar ratios between ZDDP and Ethomeen O/12 are shown in the parentheses.

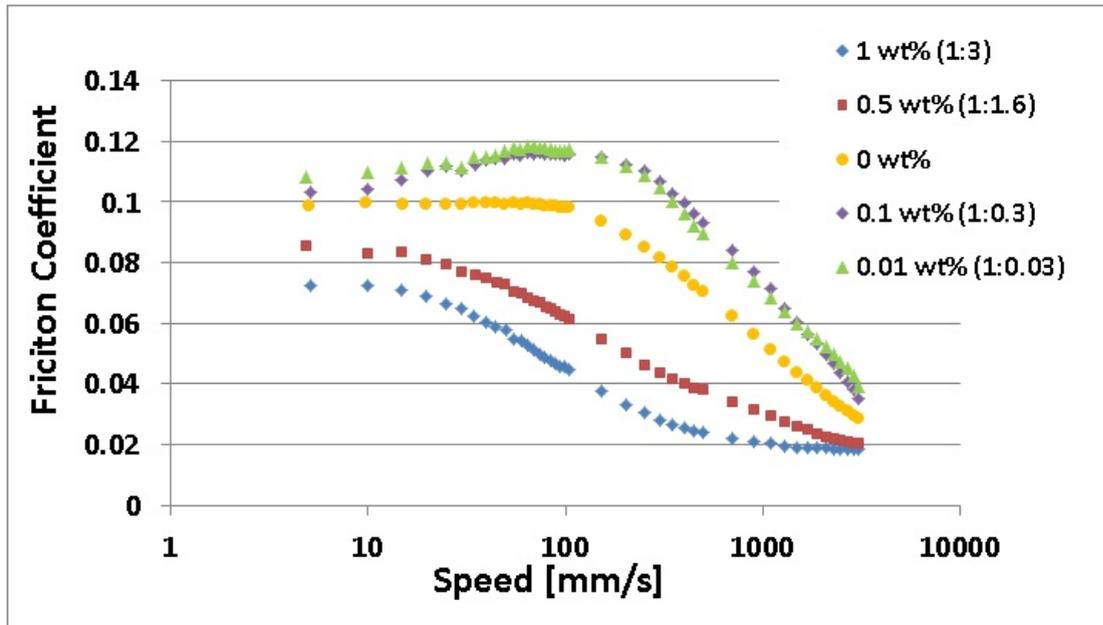


FIGURE 4.11: Stribeck curves at different concentration of Ethomeen O/12 and a constant concentration of 0,5 wt% ZDDP in all samples.

The ZDDP curve lies in between the other curves with friction modifiers. The addition of low amounts of Ethomeen O/12 makes the friction coefficient and boundary lubrication regime increase. An increase of film roughness could give a higher friction coefficient. The larger friction value was not seen in the HFRR measurements.

At the higher concentrations, 0.5 wt% and 1 wt%, the friction coefficient is lower than the ZDDP film without any friction modifiers. Another trend that can be seen is that at 0,5 wt% and at 1 wt% the curves shift earlier into the partial film lubrication, which is good as less wear occur. On the contrary to HFRR no plateau in boundary lubrication is visible in the MTM tests at these concentrations. The ZDDP curve, 0.01 wt% and 0.1 wt% all show the same transition region. By looking at the molar ratio, if the friction modifier has a higher molar ratio than the anti-wear additive a decrease in friction coefficient and an earlier partial film can be observed. For future work more stoichiometric test should be performed between Ethomeen O/12 and ZDDP to know when the friction coefficient shifts below the ZDDP in base oil curve.

The SLIM images are taken right before the Stribeck curve. In the SLIM measurements 4.12 it can be seen that the first film is the thickest, where 0.5 wt% ZDDP and no friction modifier is present. With increasing concentration of Ethomeen O/12 the film becomes thinner as stated in the article, [17]. What also can be seen is that at low concentrations of Ethomeen O/12, 0.01 wt% and 0.1 wt%, the ZDDP film becomes more smooth. Smoother films gives lower friction coefficient [28]. So an increase of film roughness is not the reason why the friction coefficient increases. The reason for the

increase of friction coefficient cannot be explained. However the friction modifier makes the surface more smooth and this might result in an increased contact area between the surfaces. This will in turn raise the friction coefficient.

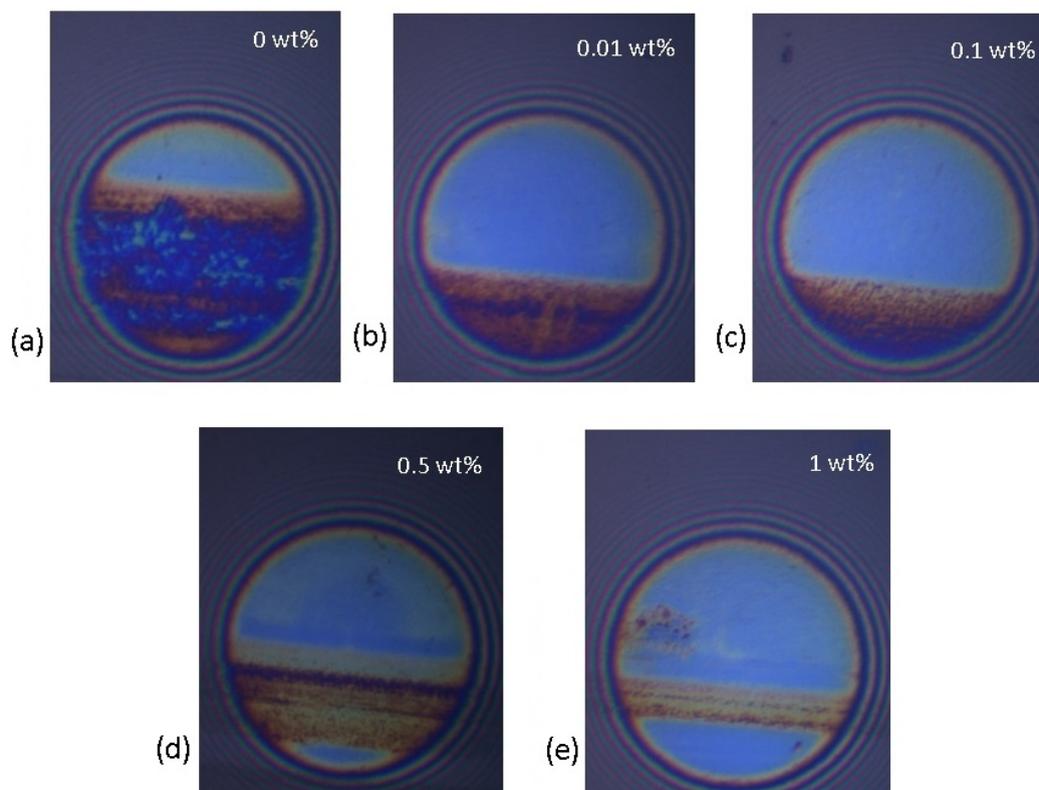


FIGURE 4.12: ZDDP films at 0.5 wt% with different concentrations of Ethomeen O/12, (a) 0 wt%, (b) 0.01 wt%, (c) 0.1 wt%, (d) 0.5 wt% and (e) 1 wt%.

In boundary lubrication Armeen O at 0.1 wt% has a similar Friction coefficient to ZDDP, while the friction coefficient is higher in partial film lubrication. The concentrations of 0.5 wt% and 1 wt% of Armeen O shows a lower boundary friction than ZDDP and in the partial film region the concentrations show a similar frictional behavior to ZDDP. All the Stribeck curves of Armeen O show the same break point into the partial film lubrication regime. To generalize no difference can be seen between the Stribeck curves. With the help of SLIM measurements images of the films could be captured and are shown in figure 4.14.

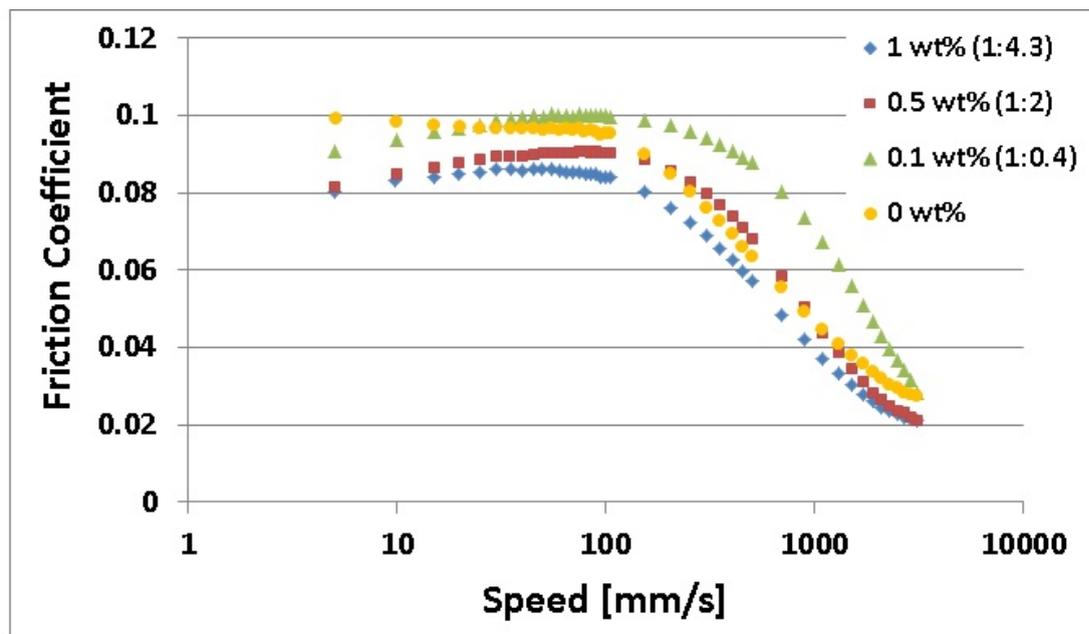


FIGURE 4.13: Stribeck curves at different concentration of Armeen O and a constant concentration of 0.5 wt% ZDDP in all samples.

Also for Armeen O we can see that with increasing concentration the film thickness decreases. From the SLIM images there is no sign of wear, not even at the higher concentration where the anti-wear film is really thin.

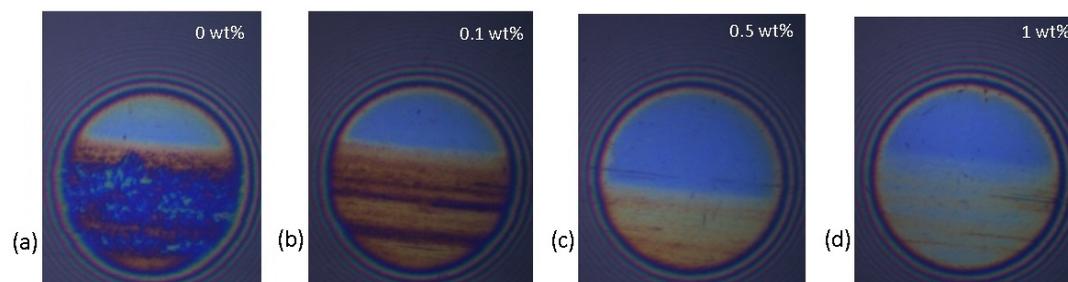


FIGURE 4.14: ZDDP films at 0.5 wt% with different concentrations of Armeen O, (a) 0 wt%, (b) 0.1 wt%, (c) 0.5 wt% and (d) 1 wt%.

From the QCM-D results it could be seen that Armeen O removed the ZDDP film from the surface with a large variation. This is also seen in the SLIM images. Ethomeen O/12 inhibits the ZDDP film formation [28] but not to the same extent as Armeen O even though Ethomeen O/12 adsorb more to the surface. The HFRR measurements of Armeen O above 0.5 wt% showed an increased friction coefficient and wear scar but this cannot be seen in the MTM with SLIM measurements.

The comparison between data obtained from HFRR and MTM are inconclusive.

Chapter 5

Conclusion and Final Remarks

Results from this study suggests that for Ethomeen O/12 less than a monolayer is needed to reach a plateau in the friction coefficient. For the wear scar to reach a plateau a monolayer is needed. Since Armeen O was not soluble in water, surface tension measurements was not possible to perform. Which makes it difficult to determine the area/molecule and discuss in terms of monolayers. At the common treat rate of friction modifiers, 0.5 wt% of the engine oil, Ethomeen O/12 showed a friction coefficient in boundary lubrication of 0.122 and a wear scar of 262 μm . Armeen O had a boundary friction coefficient of 0.137 and a wear scar of 333 μm . This suggests that without any other additives the friction modifier Ethomeen O/12 show better characteristics.

The study with the anti-wear additive gave further insight. No difference could be seen in the adsorbed amounts of Ethomeen O/12, ZDDP and the combination of the two. That could indicate that there is not enough space on the surface for both. However, for Armeen O a difference could be seen. QCM-D tests showed that if Armeen O was first presented to the surface it blocked sites for ZDDP to attach. If ZDDP was first presented to the surface and then Armeen O, Armeen O removed the ZDDP.

By comparing both friction modifiers and the anti-wear additive at 0.5 wt%, Ethomeen O/12 showed the best wear protection. ZDDP and Armeen O gave equal wear scar diameter.

Friction and wear performance with ZDDP gave inconclusive results with the two analysis techniques, HFRR and MTM. The wear scar data from the HFRR measurements showed that an addition of 0.05 wt% Ethomeen O/12 gave a plateau while for Armeen O a minimum was reached at 0.5 wt%. The HFRR results suggests that at a concentration of 0.01 wt% of both friction modifiers a plateau in friction coefficient was reached.

The MTM data however did not show a plateau in friction coefficient for Ethomeen O/12 and all the Stribeck curves for Armeen O was more or less equal to the one of ZDDP.

SLIM images confirm that with increasing concentration of both friction modifiers the thickness of the ZDDP film was decreased. Armeen O more effectively inhibited the ZDDP film formation than Ethomeen O/12. Also HFRR results indicated at 1 wt% of Armeen O an increase in wear and friction would be expected, this is not seen in the Stribeck curves or the SLIM images.

By examining the results a minimum/maximum treat rate cannot be distinguished. The treat rate of friction modifier depends on which product is being used.

For Ethomeen O/12 a packing parameter could be determined and from that less than a monolayer suggests a good frictional lubrication performance.

Bibliography

- [1] *CONCISE ENCYCLOPEDIA OF SCIENCE AND TECHNOLOGY*, McGraw-Hill, 2005 .
- [2] Annand W.J.D. *Internal Combustion Engines*, chap. 2. Gasoline Engines, p., Academic Press Limited, 1988 .
- [3] Henningsen S. *Handbook of Air Pollution from Internal Combustion Engines - Pollutant Formation and Control*, chap. 14. Air Pollution from Large Two-Stroke Diesel Engines and Technologies to Control It, Academic Press, 1998 .
- [4] Harperscheid M. and Omeis J. *Lubricants, 4. Lubricants for Internal Combustion Engines*, Ullmann's Encyclopedia of Industrial Chemistry, Vol. 21, 2012 .
- [5] Korcek S. Bovington C. and Sorab J. *The Importance of the Stribeck Curve in the Minimisation of Engine Friction*, Lubrication at the Frontier, 1999 .
- [6] Taylor I. *Impact of Lubricants on Engine Friction and Durability*, Shell Research Limited, 2011 .
- [7] Talif S. Manolache G., Rakosi E. and Popa F. *Ways to Improve Conditions in Mineral Oil Lubrication of the Internal Combustion Engines*, Ovidius University Press, Vol. 23, 2012 .
- [8] Caines A.J. Haycock R.F. and Hillier J. *Automotive Lubricants Reference Book*, Society of Automotive Engineers, Inc., 2004 .
- [9] Hoey M. *Lubricant Additives*, Advanced Lubrication 301, STLE, 2010 .
- [10] Prince R.J. *Chemistry and Technology of Lubrication*, Springer Science+Business Media Dordrecht, 1997 .
- [11] Spikes H. *The History and Mechanisms of ZDDP*, Tribology Letters, Vol. 17, No 3, 2004 .
- [12] Colyer C.C. and Gergel W.C. *Chemistry and Technology of Lubrication*, Springer Science+Business Media Dordrecht, 1997 .

- [13] Rasberger M. *Chemistry and Technology of Lubrication*, Springer Science+Business Media Dordrecht, 1997 .
- [14] Stambaugh R.L. *Chemistry and Technology of Lubrication*, Springer Science+Business Media Dordrecht, 1997 .
- [15] Psaila A. Crawford J. and Orszulik S.T. *Chemistry and Technology of Lubrication*, Springer Science+Business Media Dordrecht, 1997 .
- [16] Alghawel H. Suen Y.F. Ratoi M., Niste V.B. and Nelson K. *The Impact of Organic Friction Modifiers on Engine oil tribofilms*, RSC Adv., 2013 .
- [17] Topolovec Miklozic K. and Spikes H.A. *Performance of Friction Modifiers on ZDDP-Generated Surfaces*, Society of Tribologists & Lubrication Engineers, 2007 .
- [18] Schmid S.R. Hamrock B.J. and Jacobson B.O. *Fundamentals of Fluid Film Lubrication*, Marcel Dekker, Inc., 2004 .
- [19] Bovington C.H. *Chemistry and Technology of Lubrication*, Springer Science+Business Media Dordrecht, 1997 .
- [20] qsense. *Quartz Crystal Microbalance with Dissipation*, Technology note, www.qsense.com, 2014-05-05 .
- [21] PCS Instruments. *HFRR High Frequency Reciprocating Rig*, www.pcs-instruments.com, 2014-05-05 .
- [22] Kenesey E. Ecker A. Pauschitz A. Werner W.S.M. Kolm R., Gebeshuber I.C. and Störi H. *Tribochemistry of Mono Molecular Additive Films on Metal Surfaces, Investigated by XPS and HFRR*, Life Cycle Tribology, 2005 .
- [23] PCS Instruments. *MTM2 Mini-Traction Machine*, www.pcs-instruments.com, 2014-05-05 .
- [24] Kronberg B. Holmberg K., Jönsson B. and Lindman B. *Surfactants and Polymers in Aqueous Solution*, John Wiley & Sons, Ltd., ISBN: 0-471-49883-1, 2002 .
- [25] Janiak J. *Surface Tension Measurements*, AkzoNobel Surface Chemistry AB, Petroleum and Water Application, Internal Report .
- [26] Cook E.L. and Hackerman N. *Adsorption of Polar Organic Compounds on Steel*, Physical Colloid Chemistry, Vol. 55, 1950 .
- [27] Mansuy H. *Investigation of Interactions Between Antiwear and Dispersant Additives and Their Effect on Surface Activity of ZDDP*, Tribology Series, 1995 .

-
- [28] Garelick K. Guevremont J.M. and Devlin M.T. *Adsorption of Various ZDDP's on Steel: Study of the Initiation of Tribofilm Formation Using Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)*, STLE, Afton Chemicals, 2012-05-07