Department of Physics, Chemistry and Biology

Master's Thesis

Monitoring of Lubricant Degradation with RULER and MPC

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Four engine oils were oxidized using oxygen pressurized vessels and four hydraulic oils were oxidized with turbine oil stability test (TOST). At different stages of oxidation, sample aliquots were withdrawn and analysed. A blend of engine oil and biodiesel was also tested as well as a mixture of hydraulic oil and water. Samples of engine oils were also tested from a rig test running at SCANIA's facilities in Södertälje, Sweden. The samples were evaluated with Remaining Useful Life Evaluation Routine (RULER) and Membrane Patch Colorimetry (MPC). RULER is a voltammetric method that measures the antioxidant level in a lubricant sample and MPC measure the insoluble contaminants by spectrophotometric analysis. Results from these analyses were compared to conventional methods such as acid number, viscosity, and Fourier Transform Infrared spectroscopy (FTIR).

Results from the MPC-analyses showed that this method is dependent on the type of the lubricant tested. RULER performed well for all tested lubricants. It was shown that this analyse method can predict when the lubricant is going to start to degrade due to oxidation. Tests showed that the oxidation of the lubricant starts when there are 20-25% of the antioxidants remaining.

Nyckelord
Keyword
Lubricant oxidation, RULER, MPC

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Sammanfattning

Traditionella metoder så som syratal- och viskositetsmätningar har länge använts för att undersöka en smörjoljas tillstånd. Dessa metoder kan avgöra om en oljas livslängd är över, men kan inte förutspå hur lång tid det är kvar innan den bör bytas ut. Detta försvårar preventiva beslut och gör att det är svårt att bestämma oljebytesintervall. Den vanligaste orsaken till att en olja åldras och bryts ner är oxidation. En smörjolja börjar inte degraderas förrän antioxidanterna, som skyddar mot oxidation, har förbrukas till en viss nivå där de inte längre kan skydda oljan från nedbrytning. Under nedbrytningsprocessen skapas olösliga biprodukter som kan bilda lacker i oljan.

Fyra motoroljor oxiderades i trycksatta kärl och fyra hydrauloljor oxiderades med hjälp av turbine oil stability test (TOST). Vid olika stadium av oxidationen togs delprover som sedan analyserades. En blandning av motorolja och biodiesel testades också, samt en blandning av vatten och hydraulolja. Prover från en cellmotor på SCANIA i Södertälje testades även. De oxiderade proverna analyserades med Remaining Useful Life Evaluation Routine (RULER) och Membrane Patch Colorimetry (MPC). RULER är en metod som med hjälp av voltammetri mäter antioxidantnivåerna i oljan. MPC mäter olösliga kontaminanter i oljan med spektrofotometrisk analys. Resultat från RULER och MPC jämfördes mot sedvanliga metoder som syratal, viskositet och Fourier Transform Infrared Spectroscopy (FTIR).

Resultatet från MPC-analyserna berodde till stor del på vilken typ av smörjolja som analyserades. RULER visade bra resultat för alla testade smörjoljor. Metoden kan förutse när smörjoljan börjar brytas ner av oxidation. Testerna visade att oxidationen börjar när det är 20-25% kvar av de ursprungliga antioxidanterna i oljan.

Acknowledgments

This report is the result of a final thesis project for a Master of Science degree in Engineering Biology at Linköping University. The project was executed at the department of Fuel and Lubricant testing at Exova AB in Linköping, Sweden, between January and June 2010.

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Last but not least my family and friends should be acknowledged for always supporting me.

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Abbreviations and definitions

AN   Acid number; analyses the acidic constituents present in the lubricant.

Additive   A substance added to the lubricant base oil to enhance its performances.

Antioxidant An additive added to the lubricant to protect against oxidation.

ASTM   American Society for Testing and Materials; an organization that develops and publishes technical standards for materials, products, systems, and services.

BN   Base number; analyses the basic constituents present in the lubricant by titration to a specific buffer potential.

BN EP   Base number end point; analyses the basic constituents present in the lubricant. Instead of a specific buffer potential, the inflection point of the titration curve is reported.

Dynamic Viscosity Relates the shear stress, the shearing force acting on the oil per area, and the shear rate, the difference in speed between the two moving surfaces divided by their separation. Measured in units of milliPascal seconds (mPa·s).

FTIR   Fourier transform infrared spectroscopy.

Kinematic Viscosity The dynamic viscosity divided by the fluid density and is measured in mm^2/s or centiStokes. $1\ mm^2$/s = 1 centiStokes

OIT   Oxidation induction time is defined as the time to the onset of oxidation of a test specimen exposed to an oxidizing gas at an elevated test temperature.

SAE   Society of Automotive Engineers

Tribology   The study of rubbing or interacting surfaces, "tribos" means to rub.

Viscosity Index A measure of how kinematic viscosity changes with temperature.

Table of Contents

List of Figures

List of Tables

1   Introduction

A lubricant's two most important functions are to reduce friction and wear. This gives energy savings, protection of resources and also fewer emissions which makes lubricants absolutely indispensable in many fields in society; foremost in industries which uses heavy machinary or engines. But lubricants need to be changed periodically due to the inevitable aging process. Using a lubricant until it is no longer useful can be cost-effective but potentially catastrophic. Oxidation is currently accepted as the major cause of lubricant degradation and ageing. A lubricant consists mainly of two components; base oil which is the backbone of the lubricant and a package of additives used to enhance the good properties of the base oil [1]. Certain additives called antioxidant prevent oxidation and thereby also ageing, but when these have depleted the base oil starts to degrade which generates oxidation by-products. These have delimited solubility in the unoxidized part of the lubricant and can form sludge and laquers called varnish in the system.

The age of a lubricant is therefore strongly associated with antioxidant concentration. Monitoring antioxidant depletion in used lubricants is however still considered a relatively new research area. Another new field is monitoring insoluble contaminants and correlate it to oil degradation. Reamaining Useful Life Evaluation Routine (RULER) is a voltammetric method that measures the antioxidants in a lubricant while Membrane Patch Colorimetry (MPC) detects insolubles with spectral analysis.

1.1   Thesis objectives

The aim of this thesis is:

- To investigate methods to oxidize different types of lubricants in the laboratory.

- To follow oil degradation with RULER and MPC and compare these two against conventional analyses such as acid number and FTIR.

- Evaluate RULER and MPC as methods suitable for condition monitoring of oils in service.

Due to time limitations only two types of lubricants; hydraulic and engine oil, are tested. Furthermore elevated temperatures are needed to speed up the oxidation process and this may cause additional reactions which would not be present at slower oxidation at a lower temperature.

It should also be noted that oxidation methods in this study are not a complete reproduction of the oxidation that happens in machinery systems. For example; soot, contamination, and wear particles which have a great influence on oxidation and ageing are not present in the laboratory methods used for oxidizing the oil samples.

1.2 Methods

A literature study was first performed to get a good insight in current studies and facts on the subject. Focus was on finding methods to oxidize and analyse lubricants. Important was also to gain insight in the chemistry behind lubricant ageing and thereby what to be expected from the tests performed in the experimental part of this project. To get information from the "outside world", contacts were made with the wood-processing industry as well as with SCANIA to get information on what were important subjects to focus on.

The first experimental part of this project was dedicated to find good methods to oxidize different types of oil. In the core study these chosen methods were used to oxidize oil and samples were taken at different degree of oxidation and evaluated with RULER and MPC. The results from these tests were compared to more standard methods such as acid number, viscosity, and FTIR.

1.3 Thesis outline

To properly understand the analysis of lubricants and how to analyse the remaining useful life of lubricants it is not only important to understand how lubricants are composed, but also to understand the mechanism of lubricant oxidation and how antioxidants additives function to stabilize this. The first part of the Theory has the purpose to provide knowledge on this, while the second part explains methods used to analyse the oil condition.

The experimental part of this thesis explains how the laboratory study was performed. Methods used predicate mainly on standards described in the theory section and deviations from these are described.

The Results and Discussion present the most important results and discuss around them. Further results and data from analyses can be found in Appendix A, B, and C. In the last chapters conclusion are presented and further investigations are proposed.

2 Theory

Lubrication oils are used for many applications in today's modern society. Their most obvious use is to reduce friction and wear by interposing a fluid film between rubbing surfaces in motion. In addition to this lubricants serve as coolants or heat transfer mediums, they also help seal at compression rings and suspend materials which help to keep engines clean. Lubricants are commonly divided into two groups; automotive lubricants, which consist of engine and gear oils, and industrial lubricants, were the major classes are working fluids, hydraulic oils, and turbine oils [2]. The focus in this thesis is mainly on engine and hydraulic oils whereby these are described more thoroughly in section 2.4 and 2.5.

2.1 Lubricant base oils

Base oil is the primary ingredient in all lubricants. The backbone structure of the base oil is its hydrocarbon chain, meaning that it is chemically composed of mainly hydrogen and carbon. Typically oils are formulated with 70-99% base oil and the remnant is additives. Base oil derives from three primary sources; crude oil, chemical synthesis, or natural resources such as fat, vegetables, and waxes. [3]

2.1.1 Crude oil lubricants

Crude oil is formed in nature by processes of heat, decomposition, and extreme pressure and contains different types of compounds based mainly on carbon. Which type of refining processes and to which degree each process are carried out decides the properties of the base oil. [3]

API group I, II, and III are categorized based on viscosity index (VI), amount of saturated molecules, and sulphur content. Group IV base oil contains polyalphaolefins, while group V includes base oils not comprised in the other groups such as esters, glycols, and silicones. [4]

Group I base oils are least processed. They are manufactured by a solvent extraction refining technique which separates oil molecule by size and removes some harmful constituents such as heavy metals, wax, and aromatics. Group I base oils consist of three molecule types, paraffinic, naphthenic, and aromatic, as well as a variety of sulphur- and nitrogen-based compounds. They have <90% saturated molecules, consequently ≥ 10% aromatics, and more than 0.03% sulphur. Sulphur compounds and aromatic molecules are highly reactive and tend to react rapidly with oxygen to form various soluble and insoluble degradation by-products. This means a higher risk of oxidation and shorter lubricant lifecycles. Some automotive oils on the market use group I base oils, especially in heavy-duty application and high-viscosity single-grade oil. [4]

Group II oils follow a processing path similar to group I oils, but instead of using solvent extraction they are hydrocracked. This is a process that uses extremely high temperatures and pressures to catalytically react hydrogen with the base stock. This result in a series of molecular rearrangements; including formation of paraffin isomers, breaking of long-chain, and naphthenic molecules and opening and reshaping of aromatic ring formations. In the end

of the process aromatic molecules, sulphur, and nitrogen components are nearly eliminated from the stock. Group III oils are more severely treated with higher pressure, higher temperature, and longer process times then group II which give even better properties. [3]

Group II and III oils are more stable, more resistant to oxidation, experience less temperature-induces viscosity change, and produce less sludge than group I oils. One drawback with group II and III oils is their reduced ability to dissolve or suspend polar additives and polar by-products from lubricant degradation. Hydroprocessing and hydrocracking reduces the natural solubility of the base stock by reducing the concentration of aromatic and naphthenic hydrocarbon. Lubricant stocks with high solvency are able to soak up polar additive compounds and "lock them in place". Stocks with low solvency are unable or less able to soak up these additive compounds or the polar by-products of the oxidation process. [5]

2.1.2 Vegetable oil-based lubricants

Lubricants used today originate mainly from petroleum-based products and are therefore toxic to the environment. Through accidental spillage, volatility, and industrial waste (among others) 50-60% of all lubricants end up in the environment. For hydraulic fluids the loss is estimated to be as high as 70-80% [6]. Lubricants based on vegetable oil are biodegradable and non-toxic, therefore highly preferable in industries such as the wood-processing industry. Public demand, industry concerns, and governmental agency policies will increase the need for renewable and biodegradable lubricants. [7] Today the most important sources for vegetable oil are rapeseed (canola), sunflower, and soybean [8].

Vegetable oils consist primarily of triacylglycerides. Triacylglycerides are glycerol molecules with three long chain fatty acids attached at the hydroxyl groups via ester linkage. Due to high molecule weight triacylglycerides have low volatility and high viscosity index. Vegetable oils also have a higher solubilising capacity for additives and contaminants than mineral oils. Long and polar fatty acid chain gives high strength lubricant films which reduce both friction and wear and interact strongly with metal. However vegetable oils have poor oxidation stability, primarily due to unsaturated double bonds. When the molecules undergoes oxidative degradation polar oxy compounds are formed which eventually results in insoluble deposits and increase in acidity and viscosity. Presence of esters also makes the oil more susceptible to hydrolytic breakdown and gives a poor corrosion protection. [6]

Reducing or eliminating unsaturation by genetic or chemical modifications can overcome these shortcomings. Structural modifications of vegetable oil are accompanied by economic implications and genetically modified lubricant base oils might in the future meet the same public resistance as have food products. Improvements can obviously also be made by adding additives. [9]

2.1.3 Synthetic base oils

Synthetic lubricants are those fluids which are chemically synthesised, unlike mineral oils that originate from crude oil. There are many different types of synthetic base fluids, but the most commonly used in lubricant formulation are polyalpha olefin (PAO) and different types of synthetic esters (SE). Desired characteristics of the synthetic base oil can be customized for each use of application and it is therefore often the cost that limits the use of these lubricants.

The price of a synthetic lubricant is often 2-3 times more than for a mineral oil based lubricant. [*4*]

Synthetic esters are an interesting alternative to traditional base fluids when switching to environmentally adapted fluids. Their properties can be altered to match different demands, they are nontoxic, and have good biodegradability. Vegetable oil, i.e. triglycerides, contains glycerol as the alcohol component. This makes them prone to hydrolysis and thermal degradation. If the glycerol is replaced by other polyols, e.g. trimtehylolprone (TMP), their performance is improved. [*10*]

2.2 Lubricant breakdown

Lubricant degradation lead to viscosity changes, corrosion and the formation of sludge and varnish. Viscosity changes and corrosion alter operating conditions, which can lead to machinery failure. Sludge and varnish causes deposits that can interfere with flow and machine mechanical movement; causing wear and corrosion. There are three main causes of lubricant degradation; thermal degradation, compressive heating, and oxidation (see Figure 1). Overall the oxidative ageing is the dominating process which influences the lubricant lifetime. [*11*]
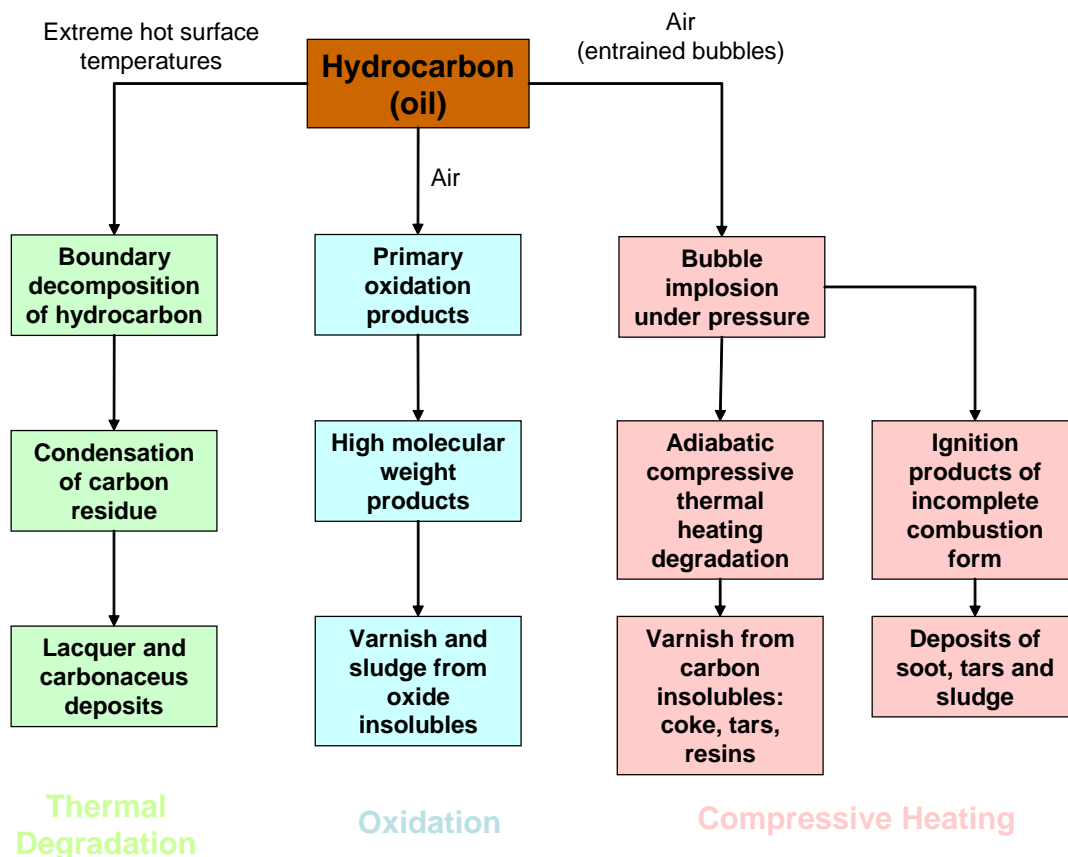
Figure 1. The paths of thermal degradation, oxidation, and compressive heating.
Figure based on reference [11].

2.2.1 Thermal and Compressive Base Oil Degradation

Thermal or compressive heating usually occurs when the base oil comes in contact with hot machine surfaces. It can also happen when there is a sudden and rapid increase in temperature associated with adiabatic compression of entrained air bubbles in bearings, pumps and other pressurized lubrication environments. The layer of oil that comes in contact with the hot surface or compressed air bubble can change chemically. The earliest indication of thermal failure is change in the oil's colour. This happens during oxidative failure as well, but faster when thermal degradation is the cause. The colour change is often due to the formation of chemical insoluble carbon and oxide by-products. [*11*, *12*]

2.2.2 Oxidation

The most common form of lubricant degradation is oxidation. Oxidation is the reaction of materials with oxygen. From a strict chemical perspective oxidation does not necessarily need to involve oxygen, but for the purpose of this study oxidation refer to the reaction between oxygen and a molecule which results in loss of an electron forming a free radical. Oxidation occurs gradually under mild conditions once the antioxidants have depleted. When the oxidation has started it will cause a chemical change that is severe and permanent to the oil by degradation of the base oil. A number of factors speed up the process; water, metals such as iron and copper, other contaminants and elevated aeration. However the most critical factor is temperature. Elevated temperatures accelerate the oxidation process and Arrhenius Rate rule states that for every 10°C increase the rate of oxidation doubles. [*11*, *13*]

2.2.3 Oxidation of base oils: mechanism of oxidation

The oxidation mechanism consists of four reaction steps; initiation, propagation, branching, and termination (see Figure 2).

Initiation	$RH \rightarrow R^{\bullet} + H^{\bullet}$
Propagation	$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$ $ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$
Branching	$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$ $RO^{\bullet} + RH + O_2 \rightarrow ROH + ROO^{\bullet}$ ${}^{\bullet}OH + RH + O_2 \rightarrow H_2O + ROO^{\bullet}$
Formation of aldehydes and ketones	$R_1R_2HCO^{\bullet} \rightarrow R_1CH{=}O + R^{\bullet}_2$ $R_1R_2R_3CO^{\bullet} \rightarrow R_1R_2C{=}O + R^{\bullet}_3$
Termination	$R^{\bullet} + R^{\bullet} \rightarrow R\text{-}R$ $ROO^{\bullet} + R^{\bullet} \rightarrow ROOH$ $ROO^{\bullet} + ROO^{\bullet} \rightarrow ROOH + O_2$
Peroxide decomposition	$ROOH \rightarrow$ various lower molecular weight compounds
Polymerisation	$ROOH \rightarrow$ Various higher molecular weight compounds

Figure 2. Oil oxidation mechanism

The initiation step occurs because of energy transfer to a hydrocarbon molecule in the form of heat, mechanical shear stress or UV-light among others. This process can also be catalyzed by metal ions (see paragraph 2.2.4). The reaction is usually very slow at room temperature but the rate often proceeds at temperatures above 100°C. How easy radicals are formed is determined by the C-H bond strength and how stable the resulting radical is. Hydrogens in alpha position to carbon-carbon double bound, tertiary hydrogens or aromatic rings are most disposed.

In the chain propagation step an alkyl radical reacts irreversibly with oxygen dissolved in the lubricant and form an alkyl peroxy radical. The second reaction in the propagation forms a hydroperoxide and another alkyl radical by removing hydrogen from a hydrocarbon molecule.

Thereafter there is chain branching where hydroperoxides are cleaved into alkoxy and hydroxy radicals. The activation energy of the reaction is large and therefore only significant at temperatures above 150°C. The radicals then react with hydrocarbons to water, alcohols, and more alkoxy radicals. Secondary and tertiary alcoxy radicals will form aldehydes and ketones.

The aldehydes and ketones condense through acid catalyzed aldol reactions. These condensates can thereafter lead to polymeric degradation products that become sludge and varnish deposits.

Termination can occur by combination of radicals. Two alkyl radicals can combine to form a hydrocarbon molecule, an alkyl radical can combine with an alkyl peroxy radical to form a peroxide or two alkyl peroxy radicals can form peroxide and oxygen. [13]

2.2.4 Metal catalysis of lubricant degradation

When metal such as iron and copper are present the initiation reaction can occur at much lower temperature. Metal ions can also catalyze the chain branching step. [14] Both of these reactions are shown in Figure 3.

Initiation	$RH + M^{(n+1)+} \rightarrow H^+ + R^{\bullet} + M^{n+}$
	$M^{n+} + O_2 \rightarrow M^{(n+1)+} + O_2^{\bullet -}$
Branching	$ROOH + M^{(n+1)+} \rightarrow ROO^{\bullet} + M^{n+} + H^+$
	$ROOH + M^{n+} \rightarrow RO^{\bullet} + HO^- + M^{(n+1)+}$

Figure 3. Metal catalysis of the initiation and chain branching reaction.
Where $M^{(n+1)+}$ typically is Fe^{3+} or Cu^{2+}.

2.2.5 Acidity and viscosity during lubricant degradation

The result of low-temperature oxidation is the formation of peroxides, alcohols, water, aldehydes, and ketones. Carboxylic acids are formed during oxidation of aldehydes and ketones. The mechanism for this reaction varies based on the type of lubricant derived. This means that the lubricant become more acidic during degradation. [13]

The reactions above should result in a decrease in viscosity because the hydrocarbon chain is decomposed to smaller molecules. However most lubricants used in field or subjected to oxidation tests generally undergo an increase in viscosity during the oxidation process. This can be explained by the condensation that starts as the levels of aldehydes and ketones become considerable. These aldol condensation reactions lead to the formation of oligomers and low molecular weight polymers and thus also to an increase in viscosity. The reduction in lubricant molecular weight caused by chain separation that form aldehydes, ketones and carboxylic acids is thereby counteracted by the increase in viscosity due to the aldol condensation. In the early stages of oxidation it may therefore be possible to register a viscosity drop but as the oxidation process progress the effects of the condensation overpower this, meaning that the overall result is an increase in lubricant viscosity. [*13*, *14*]

2.2.6 Sludge and Varnish formation

The by-products from oxidation mentioned above have a delimited solubility in the unoxidized part of the lubricant. They often contain high concentration of aromatic groups and will be chemically quite different from the rest of the lubricant which contains paraffinic and naphthenic oil molecules. Chemical changes in the oligomers will eventually be an insoluble in the unoxidized portion of the oil and separates from the lubricant in the formation of sludge and deposits. Sludge precursors form via acid or base catalyzed aldol condensation from aldehydes and ketones. Further reactions of these give high-molecular-weight products. These products give a viscosity increase and when they combine with each other sludge and varnish is formed. Sludge is usually characterized as insolubles in the bulk oil and deposits formed on metal surfaces are called lacquer or varnish. [*13*, *14*]

2.2.7 Nitration, Sulphation, and Soot

When organic compounds are exposed to high temperatures and pressure in the presence of nitrogen and oxygen, not only oxidation by-products are formed, but also nitration products. These are often nitrogen oxides, such as NO, NO_2 and N_2O_4, which are acidic and a major cause to build up of varnish and lacquer. Sulphur compounds can be found in crude oil and may also be used in additives. During oxidation SO_2 and SO_3 are formed which increase the production of sludge and varnish and catalyze further oil degradation. They can also react with water and produce sulphuric acid.

Soot is produced as a by-product from fuel combustion in engines. This is especially evident when too rich fuel-air mixtures are burned. An increase in soot content is therefore an indication of combustion problems or too long drain periods. Soot changes viscosity and clog filters and oil galleries. [*15*]

2.2.8 Hydrolysis of ester type base oil

Hydrolysis is the chemical reaction of the base oil molecule with water. Ester type base oils are susceptible to hydrolysis. Hydrolysis results in breakage of their chemical ester linkage which gives a permanent chemical change to the base oil molecule and also gives acidic by-products. This makes the oil more corrosive and catalyze further base oil breakdown. [*11*]

2.3 Additives

An additive is a chemical substance added to a lubricant base oil to give a new quality or enhance an already existing property in the base stock. The original attributes of the base oil and the sector of application for the final lubricant strongly influence quality and quantity of additives. Many different additives are usually added and it is therefore important that these do not interact with each other in an antagonistic manner. Sometimes additives work synergistically to enhance the effect of one another, which is desirable. [*16*] For the purpose of this thesis antioxidants are most important, other common additives are summarised in Table 1.

Table 1. Summary of common additives.
Table based on reference [16].

Additive type	Purpose	Functions
Antifoam	Prevents lubricant from forming persistent foam.	Alter the surface tension of the oil and facilitate the separation of air bubbles, which retard foam formation.
Antioxidant	Lessen oxidative breakdown	Control free radicals and terminate radical reactions.
Antiwear and extreme pressure agent	To reduce wear and friction	React chemically with metal to form a film with lower shear strength than the metal, preventing metal-metal contact
Corrosion and rust inhibitor	Prevent corrosion of metal parts in contact with the lubricant	Make a protective film by adsorption of polar constituent on metal surfaces or neutralize acids.
Detergent	Keep surfaces free of deposits	Chemical reaction with sludge and varnish precursors to neutralize them and keep them soluble.
Dispersant	Keep insoluble contaminants dispersed in the lubricant	Contaminants are prevented from clustering and kept in the suspension by the dispersant molecules by polar attraction which bond the contaminants to the dispersants
Metal deactivator	Reduce catalytic effect of metals on oxidation rate	Form inactive film on metal surfaces by joining with metallic ions (e.g. iron and copper).
Pour point depressant	Enable lubricant to flow at low temperature	Modify wax crystal formed by reducing ability to interlock.
Viscosity modifier	Reduce the rate of viscosity change with temperature	Polymers expanding with increasing temperature to counteract oil thinning.

2.3.1 Antioxidants

To stabilize the lubricant antioxidants are used to prevent from oxidation. Most antioxidants function by reacting with free radicals or decomposing peroxides. The mechanism of antioxidant function is dependent on the type of antioxidant as well as chemical composition of the lubricant. There are three main kinds of antioxidants; hindered and/or aromatic amines, hindered phenols, and dithiophospate derivates. [*14*]
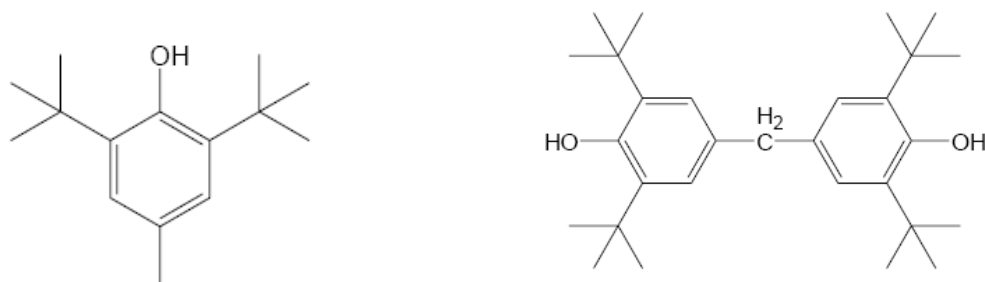
Figure 4. Structure of BHT and MBDTBP [17].

Aromatic amines and hindered phenols are called "radical scavengers". They are designed to control free radicals by donating a hydrogen atom so that a more stable molecule is formed. The antioxidant then becomes a free radical but a much more stable one. Some free radical antioxidants can also react with other radicals in the base stock which creates two relatively stable materials. Classical examples of hindered phenolics is 3,5-di-t-butyl-4-hydroxytoluene called BHT and 4,4´-methylenebis(2,6-di-tert-butylphenol) MBDTBP showed in Figure 4. [*17*]

MBDTBP is an effective antioxidant and will serve as a good example of a radical scavenger. Under oxidative conditions the MBDTBP molecule "scavenges" an alkyl peroxy radical which forms an alkyl hydroperoxide terminating the propagation step in the oxidation process. The MBDTBP molecule is transformed to a phenoxy radical which is much more stable than the radical it destroys. Before forming a galvinoxyl radical (G$^•$) the MBDTBP molecule is capable of scavenging three alkyl hydroperoxide molecules (see Figure 5). When oxygen is present the galvinoxyl will react further resulting in the cleavage of the MBDTBP molecule to a benzoquinone and a hydroxybenzaldehyde molecule. The benzaldehyde is an effective antioxidant as well and will destroy even more peroxy radicals. [*13*]
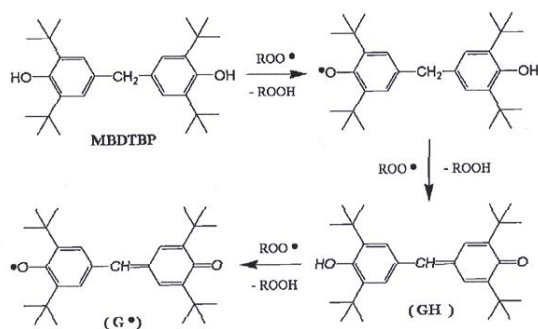
Figure 5. How MBDTBP react to scavenge three alkyl peroxy radicals (ROO$^•$) [13].

Important in the dithiophospate derivate group of antioxidants is zinc dialkyldithiophospate (ZDDP). It is a peroxide decomposer which means that it converts hydroperoxides into non-radicals and thereby prevents the chain propagation step. ZDDP can react in other ways but this is not as well known. Decomposition products can also react as an antioxidant. ZDDP is also an important anti-wear additive. [*18*]

If both phenols and amines are used in the right combination it is possible to produce an antioxidant system that regenerates. The amine reacts with the free radical from the oil

oxidation and is then regenerated by the phenolic (see Figure 6). The phenol radical is stable and does not react further to degrade the lubricant. [*17*]
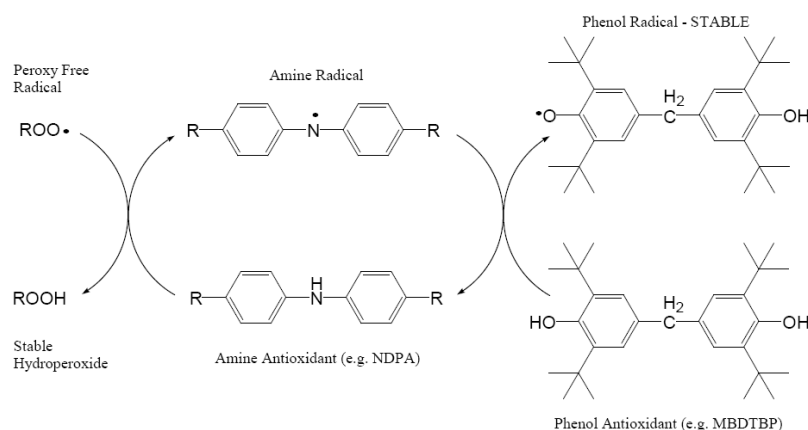
*Figure 6. How amine and phenol antioxidants interact synergistically to control free radicals [**17**].*

Antioxidants are sacrifical and first when the antioxidant level is low the base oil start to degrade and physical changes begin to occure. Studies reveal that this happens when 70-80 percent of the antioxidants have depleted. [*1, 19*]

2.4   Engine oils

Engine oils have to fulfil a wide range of different functions in engines. They have to guarantee the functional reliability of all friction points in the operating engine. Apart from these tribological tasks, engine oil have multiple additional functions such as sealing the cylinder and transporting sludge, soot, and wear particles to the oil filter. Water formed during the combustion process should be emulsified and at the same time protect against corrosion. Engine oil must reduce friction and wear at low temperature start-ups, as well as work well at high temperature and pressure in bearings and around piston rings. This means that the oil should still flow, be pumpable, and additives should not precipitate at low temperatures down to -40°C. At the upper end of the temperature scale, up to 250°C, the oil must offer good resistance to thermal and mechanical aging. Finally the stability of the lubricant film should not be diminished by fuel contamination. [*20, 21*]

In general engine oil consists of a base stock and various additives. The base stock is often based on either crude oil or synthetic derived oil. Engine oil contains large amounts additives compared to many other classes of lubricants. Often as much as 30 different additives are used whose percentage can range from 5 to 30% in total. [*20*]

There are different specifications for engine oil which describes their performances at different conditions. The most important property of a lubricant is viscosity which is temperature dependant. The viscosity of monograde oil is matched to work at a specific temperature and has to be changed between summer and winter. Multigrade oils, which are much common today, combine summer and winter oils. A common classification is the Society of Automotive Engineers (SAE) J300 classification scheme where a multigrade oil is described as SAE 15W-40. 15W is the winter classification referring to the dynamic viscosity measured at low temperature. 40 is the summer classification and refer to the kinematic

viscosity at high temperatures. General kinematic and dynamic viscosity is presented for different SAE classifications in Table 2. [*21*]

Table 2. SAE viscosity grades [21].

Viscosity grades	Kinematic viscosity at 40°C (mm²/s)	Kinematic viscosity at 100°C (mm²/s)	Estimated dynamic viscosity at -15°C (mPa·s)
SAE- 20W-50	144.8	17.8	5870
SAE- 15W-40	114.3	14.9	2940
SAE- 10W-30	72.3	10.8	1900
SAE -5W-30	57.4	9.9	1090
SAE 0W-20	44.4	8.3	690
SAE-30	91.3	10.8	3950

2.5 Hydraulic oils

Hydraulics describes the transfer of energy and signals through fluids. Hydraulic fluids are used in nearly all industries such as agriculture, construction, woodworking, and steel with the main purpose to transmit power. After engine oils, hydraulic fluids are the second most important group of lubricants. The most important elements of a hydraulic system are pumps, motors, cylinders, valves, and circuit components which mean that the hydraulic fluid must be resistant to both high pressure and relative high temperatures up to 90°C. The operating temperature for a hydraulic system is generally 40-50°C and for systems working at high pressures 60-70°C. [*20*, *22*] In contrast to engine oil the amount of additives in hydraulic oil is often small and in general only 1-2% [*8*].

Hydraulic oils are classified according to ISO (International Standard Organization) viscosity grades (VG). According to this system a hydraulic oil is named by ISO followed by a number equal to the oil viscosity measured in centistokes at 40°C, ISO VG 46 etc. [*20*]

2.6 Methods for oxidation

Methods described below were all candidates for oxidation in the core study in the beginning of the project. However, many more oxidation methods exist in the literature. Methods described are processes which both involve oxidizing the oil and evaluate the oxidation stability of the oil. The oxidizing part is the most important for the purpose of this report; different methods for analysing will be described in section 2.7. An important concept in many of the methods is oxidation induction time (OIT), which is defined as the onset of oxidation when the lubricant is subjected to an oxidizing gas at an elevated test temperature [*13*].

2.6.1 Rotating Pressure Vessel Oxidation Test, ASTM D 2272

Rotating Pressure Vessel Oxidation Test (RPVOT) is a test method that evaluates the oxidation stability of new and in-service oils. A quantity of the lubricant is placed in a pressurized vessel (bomb) together with water and a copper catalyst coil. The vessel is pressurized with oxygen to 620 kPa and placed in a heating bath set at 150°C. The bomb is rotated axially at 100 rpm placed at an angle of 30°. The pressure increases when the temperature of the vessel and its contents increases. The point at which it stabilizes represents

the start of the test and denoted as T_0. As a result of stress-induced additive depletion the oil's ability to resist oxidation decreases and the base oil starts to react with the oxygen. Oxygen is then being incorporated into the oil molecules and the pressure inside the vessel begins decreasing. The test is complete after the pressure drops more than 175 kPa which is defined as T_1. The time required from T_0 to T_1 in minutes is the oils RPVOT value. To modify the process the catalyst and water can be excluded. [23, 24]

2.6.2 Turbine Oil Stability Test (TOST), ASTM D 943

This is a method that evaluates the oxidation stability of steam-turbine oil, but can also be used to test other oils such as hydraulic oil. The oil's oxidation stability is tested in the presence of oxygen and a copper-iron catalyst. In ordinary TOST water is added as a second catalyst, in contrast to dry TOST where there is no water present. 300 mL oil is placed in a sampling tube with a copper-iron catalyst, with 3 L/h oxygen bubbling trough it and heated to 95°C. During the process samples are taken and acid number (AN) measured. Acid number is described in 2.7.1. The test continues until AN is 2.0 mg KOH /g and the time required for this is called the "oxidation lifetime". [25]

2.6.3 Jet Fuel Thermal Oxidation Test, ASTM D 3241 and Hot Liquid Process Simulator

Jet Fuel Thermal Oxidation Test (JFTOT) is used to evaluate the tendency of gas turbine fuels to deposit decomposition in the fuel system. In standard JFTOT fuel is pumped at a fixed volumetric flow rate through an aluminium rod heated to a maximum 350°C after which it enters a precision steel filter where degradation products can be trapped. Typically the test need 450 mL sample during a 2.5 h test. The essential data are the amount of deposits that has been etched during the test on the hot aluminium rod and the rate of plugging in the steel filter. Changes have been made to the JFTOT apparatus to make it more flexible and more adaptable for different types of petroleum based liquids. This more adaptive system is called Hot Liquid Process Simulator (HPLS). [26]

2.6.4 Hydrolytic Stability Test of Lubricants (Rolls Royce method)

This method evaluates the hydrolytic stability of lubricants under accelerated conditions such as water contamination and elevated temperature. 250 mL lubricant is mixed with 25 mL distilled water in a conical flask. A water trap filled with water is placed over the flask before placed in a 90°C oven. Every 24 hour the conical flask is shaken, a sample is taken and AN measured. After 120 hours samples are taken and measured every 48 hour. When AN is equal or higher than 5 mg KOH/g the test is finished. The time to reach this and the increase in AN after 120 hours is an assessment of the lubricants hydrolytic stability under accelerated conditions. [27]

2.6.5 Pressurized vessels, ASTM D 525

Pressurized vessels are originally used to determine the stability of gasoline, under accelerated oxidation conditions. A sample is oxidized in pressurized vessel with oxygen pressure at 690 to 705 kPa and heated to a temperature between 98 and 102°C. When the lubricant starts to oxidize the pressure will drop as oxygen molecules are incorporated into the oil. The pressure

13

is recorded continuously until breakpoint is reached. Breakpoint is defined as the point in the pressure-time curve where the pressure has dropped 14 kPa within 15 minutes and succeeded by a drop of no less than 14 kPa in 15 minutes. The time required to reach breakpoint is the oxidation induction time (OIT). [28]

2.6.6 Rancimat, EN 14112

The Rancimat method was developed to establish the oxidation stability of fatty acid methyl esters (FAME), but can be used for other applications as well. A small sample, 3 gram, is held at a 110°C temperature while purified air is passed through. The air together with vapours released during the oxidation process is conducted to a flask containing distilled water and an electrode. The electrode measures conductivity and is connected to a computer which measure and records continuously during the test. When volatile polar organic compounds such as aldehydes, ketones, peroxides, and carboxylic acids are absorbed in the water the conductivity is increased. Plotting conductivity against time gives an oxidation curve and the inflection point of this curve gives the induction time. [29]

Table 3. Method comparison

	RPVOT/RBOT	TOST	HLPS	Rolls-Royce	Pressurized vessels	Rancimat
Temperature	150°C	95°C	Max 350°C	90°C	100°C	110°C
Catalyst	Copper coil	Water/metal	-	Water	-	-
Water	Yes	Yes/No	No	Yes	No	No
Gas	90 psi oxygen	Oxygen 3 L/h	Nitrogen	Air (no flow)	Pressurized with oxygen	Purified air
Possible modifications	Catalyst and water can be excluded	Temperature Catalyst and water can be excluded	Temperature	Temperature Test duration	Temperature Water can be used as a catalyst	Temperature
Oil sample size	50 g.	300 mL	350 mL	250 mL	100 mL	3 g.
Test duration	Depending on OIT	~1500 h (hydraulic oils) ~2000 h (Turbine oils)	2.5 h	> 120 h	Depending on OIT	Depending on OIT

2.7 Methods for evaluation

Methods described below are candidates to assess the oxidation process in the core study. In the literature, a lot more candidates exist but are excluded due to limited space.

2.7.1 Acid number, ASTM D 974 and ASTM D 664

As mentioned above when lubricating oil oxidize (age) acidic by-products are formed. Acid number (AN), sometimes called total acid number (TAN), is expressed as the volume in milligrams of potassium hydroxide required to neutralize acids present in a sample of one

gram lubricant. There are two standard methods for measuring AN; colorimetric (ASTM D 974) or potentiometric (ASTM D 664) titration. Antiwear, EP, and corrosion inhibitor additives can create high initial AN-values. Generally starting AN value should decrease faintly with additive depletion and then increase with the build up of degradation compounds. Test results should always be compared to the result from new oil to determine the change that has occurred. High AN values generally means that the lubricant useful life is over and that the oil should be replaced. AN values above 4.0 are considered to be corrosive, but if starting points are high the judgement could be different. An increase that is slow over a long period of time is considered to be normal. Rapid changes are in most cases caused by oxidation from local heating, prolonged air entrainment or additive depletion. [30, 31]

2.7.2 Base number, ASTM D 4739

Additives are added to the lubricant that provides an alkaline reserve to neutralize acids produced during oil degradation. When this reserve is depleted the oil can become corrosive. The base number (BN) is a relative amount of basic constituents present and should be decreasing as the lubricant is ageing. The test method is similar to AN measurements but instead of using potassium hydroxide hydrochloric (ASTM D 4739) or peroclorid acid (ASTM D2896) is used to neutralize the alkaline oil. The result is reported in the same units (mg KOH/g sample) as for acid number but this represents the amount of KOH needed to neutralize the reagent acid used to neutralize the oil. Often two values are reported; base number and base number end point (EP) Base number is when the potential reach a specific buffer potential for example the potential corresponding to pH 3. Base number EP is chosen as the inflection point of the potential curve. To be valid the inflection point has to be in a specific inflection window. If two inflections are noted the last one is reported. [*31*, *32*] The selection of end points is illustrated in Figure 7.

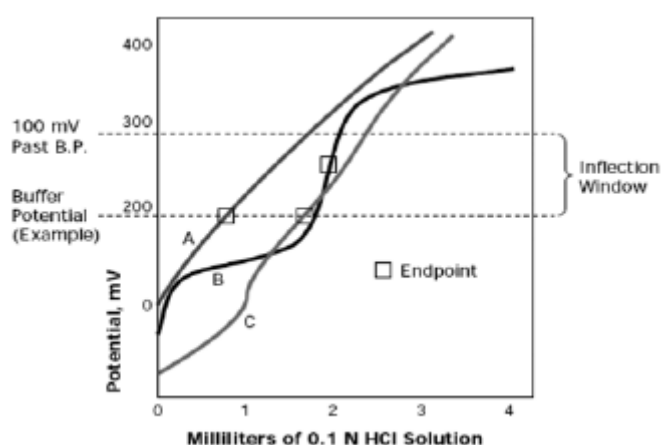*Figure 7. Titration curves to illustrate selection of end points [*32*].*
(A) Titration curve has no inflections. Take end points at the buffer potential.
(B)Titration curve has well-defined inflection within prescribed window. Take well-defined inflection as the end point.
(C) Titration curve has inflection prior to buffer potential but not in prescribed window. Take end point at the buffer potential.

2.7.3 Kinematic Viscosity, ASTM D 445

Lubricants need to have a specific viscosity to give correct operation on the equipment where they are used. Viscosity change when the oil oxidizes whereby this is an important parameter to measure when the oil condition is evaluated. A fixed volume of oil flows under gravity through a capillary and the time it takes for it to move a specified length is measured. The viscometer is calibrated and the temperature is constant and known. Two time interval must be measured for each oil sample and the average is used to calculate the kinematic viscosity by multiplication with a calibrated constant appertained to the capillary used. [33]

2.7.4 ASTM Color Scale, ASTM D 1500

This is a method that visually determines the colour of petroleum products such as lubricating oils, waxes, and diesel fuel oils. Determination of the colour of petroleum products is mainly used for manufacturing control purposes since colour is an important quality characteristic. If the colour range of a specific oil is known, a variation outside this may indicate contamination. Colour can also be used as an indication of the degree of refinement of the material. The sample is placed in a colorimeter with a standard light source and compared to coloured glass disks ranging in value from 0.5 to 8, where 8 is darkest. When an exact match is not found and the sample falls between two colours, the higher of the two colours is reported. [40]

2.7.5 Remaining useful life evaluation routine, RULER ASTM D 6971

This voltammetric test method evaluates the oxidative health of a lubricant by measuring the antioxidants in the fluid. A sample of 200-400 µL is placed in an electrolytic vial with an electrolyte test solution and a layer of sand. When the vial is shaken, hindered phenol, aromatic amine antioxidants, and other oil components soluble in the test solution are extracted into the test solution. Oil droplets are agglomerated by the sand (see Figure 8). Increasing levels of voltage is passed through the cell and an electrical current (potential) curve is produced. When the voltage is increased electro-active species such as phenolic and aminic compounds starts to oxidize at the electrode surface which produces an anodic rise in the current. As the potential is increased there is a decrease in active species concentration at the electrode surface and the exponential increase of the oxidation rate lead to a maximum in the current potential curve. [34, 35, 36]

Different antioxidants will react at different voltage which means that it is possible to distinguish between antioxidants. The greater the reaction is during the electric shock the larger amount of a particular antioxidant is present. A curve from fresh oil is used as a 100% reference sample, it is said to contain 100% antioxidants, and the test solvent electrolyte is used as the 0% standard. It is the area under each peak in the RULER curve which is compared to one another. If a peak area is half the area under same peak in the reference it is regarded to have 50% RUL for this particular antioxidant [1]. The RULER software also gives "RULER Area" which is the entire area under the curve including the total electro-chemical activity instead of focusing on a specific additive. This is also compared to the reference sample and given in percent [37].
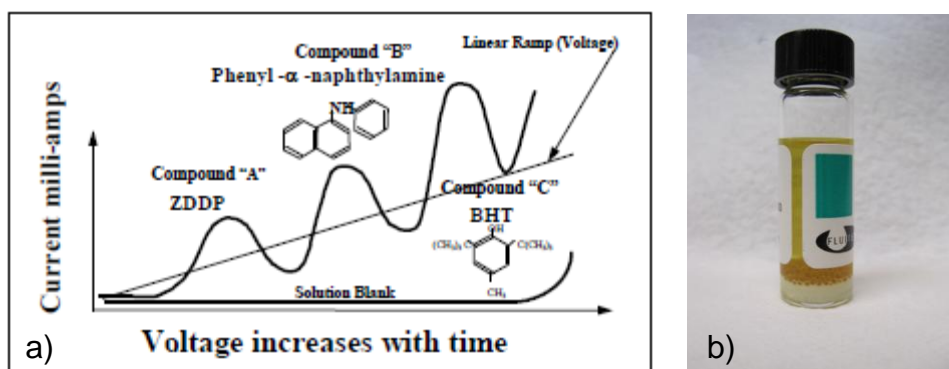
Figure 8. a) Example of three additives and their voltammeter response [36], b) RULER electrolyte vial.
In a) an oil containing three different kinds of antioxidants is exemplified. The voltammetric respond generates three distinct peaks during the RULER analysis, each corresponding to an individual antioxidant. Picture b) shows the electrolyte vial used in the RULER analysis. The sand with agglomerated oil droplets separate at the bottom, while antioxidants are extracted to the electrolyte solution on top where the voltammetric analysis is carried out.

2.7.6 Membrane patch colorimetry

Membrane patch colorimetry (MPC) is a method for analysing the insoluble contaminants in the oil with spectral analysis. The oil, preferable 50 mL, is mixed with an equal part heptane. Heptane, which is a non-polar solvent, dissolves into the base oil and decreases the solubility effect of the oil. When polar contaminants (e.g. oxidation products) are present in the oil, these will agglomerate and separate from the oil due to the decrease in solubility. The mixture is thereafter filtered through a 0.45 μm membrane filter with a vacuum pressure of 71 kPa and rinsed two times with heptane. The filter is dried at 80°C during 3 hours whereupon the spectral analyse is performed. An unused filter is used as background. The values given from filter with oxidize oil should be compared to one with unused/new oil. [*38*] The spectral analysis from the MPC test is translated into an orthogonal colouring system called CIE Lab. This system is based on three vectors; L* = Luminance, a* = red-value, and b* = yellow-value. When two colours, given in the CIE Lab colour space, is compared, it is possible to calculate CIE dE = difference in energy between the two colours. In the MPC-test, CIE dE is called MPC-index. Below are the significances of the parameters described:

MPC-Index: value between 1 and 100. The higher the value is the higher is the risk of deposition.

Luminescence (L*): Darkness of the filter; that is the decrease in white light reflected. A low luminescence means high darkness of the filter.

Red-value (a*): Is affected of corrosion and degradation of EP additive.

Yellow-value (b*): Degradation of antioxidants and components in the base oil.

With MPC a direct correlation is made from the colour and intensity of the insolubles to oil degradation. The method identifies soft contaminants, which are directly associated with oil degradation. Larger hard contaminants unrelated to oil degradation does not influence the test results much. The MPC-test is not yet published by ASTM. However, an ASTM draft exists which is up for approval. [*5*, *39*]

2.7.7 Gravimetric analysis of filter

The filter in the MPC method can be used to do a gravimetric analysis. The filter is weighted before the filtration process, dried and then weighted again after filtration. The difference in weight is adjusted to the weight difference of a control filter. The difference in weight compared to a filter with a reference (nonoxidized) oil is measure of the contaminants in the oil [39].

2.7.8 Fourier Transform Infrared Spectroscopy, ASTM E 2412

Fourier Transform Infrared Spectroscopy (FTIR) is used in oil analysis to monitor oil contamination and oil degradation. High concentration of degradation products, such as oxidation, nitration, and sulphation, and low concentrations of oxidation inhibitors are evidence to oil degradation. Infrared spectroscopy evaluates the oil's components at a molecular level. During the test infrared energy is passed through a fixed test cell with a fixed thickness of oil. The IR energy is absorbed at frequencies specific to the samples components. The IR energy signal is transmitted or absorbed and reflected which makes it attenuated. The signal is processed through a Fourier Transform function which creates a spectrum. The spectrum is used as a fingerprint of various components and compared with a new oil reference. When the bulk oil degrades due to oxidation a number of oxygenated by-products are formed that can be seen in the FTIR-spectra. One common by-product from oil oxidation is the carbon-oxygen double bond, a carbonyl group, with absorption of infrared light in the ~1710 cm^{-1} region. This peak at 1710 cm^{-1} is known as the oxidation peak and should increase as the oil oxidize. This oxidation peak is used to calculate the oxidation index (see Calculations). ZDDP could be monitored at ~980 cm^{-1} and as the oil degrades this peak should decrease due to additive depletion. [5, 15, 31, 41] Specific wave number for oxidation products and contaminants can be seen in Table 4 and Figure 9.
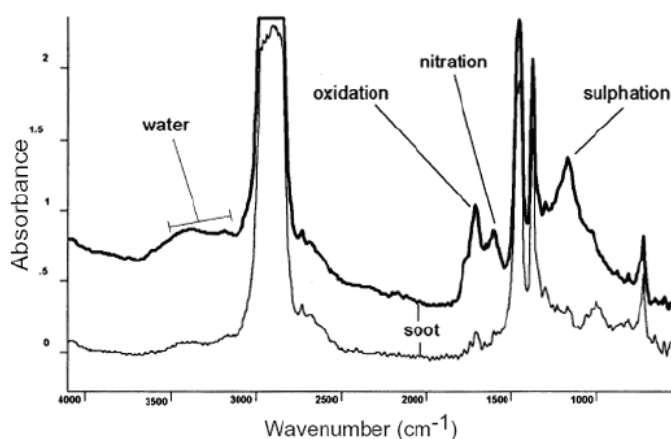

Figure 9. FTIR-spectra of new and used oil [5].
The upper thicker curve is used oil while the lower is new oil. The figure show were in the spectra changes could be expected and what causes these changes.

Table 4. FTIR wave numbers of some important molecule classes.

	Oxidation products: Organic Esters	Water contaminant in mineral oil	Soot contaminants	Oxidation products: Mineral Oil	Nitration	Sulphation	ZDDP-antiwear
Wavenumber (cm^{-1})	3595 - 3500 3330 - 3150	3500 -3150	2000	1800 - 1670	1800 - 1670	1180 - 1120	1025 - 960

2.8   Rig-testing

Lubricants work in complex system which means that a great number of parameters may influence the degradation process that is not present in the laboratory oxidation methods described above. Field-testing is when the tribosystem is operating in its real environment for example a test drive of a car or a truck. This type of testing gives the most reliable result but is both time consuming and costly. Operating conditions is also difficult to control and can vary between different test. Laboratory test on the other hand are easy to control and different operation conditions are easy to measure. This type of systems is reproducible and often relatively fast and inexpensive. Between field and laboratory tests there are different levels of bench and component tests for example free-standing engines in test facilities. These tests are called rig tests. The advantage with this type of testing is that is possible to control different parameters and that sampling is easier. [*42*]

3   Experimental details

3.1   Lubricant samples

The engine oils in the test slates are standard products from different manufacturers (see Table 5). Probably they are based on group II or III base oils and the additives they contain are unknown. Lubricant producers are highly secretive about this type of information.

Table 5. Engine oils used in the laboratory study

	Type	Application	Viscosity at 100°C according to manufacturer
Engine oil A.	Mineral oil 15W-40	Automotive gasoline and diesel engines.	14.0 mm^2/s
Engine oil B.	Mineral oil 15W-40	High power trucks and bus engines with turbo	14.4 mm^2/s
Engine oil C.	Mineral oil 15W-40	No information	No information
Engine oil D.	Mineral oil 15W-40	Heavy duty diesel engines and contractor, foresting, and farming vehicles.	14.4 mm^2/s

A mixture of Engine oil A and biodiesel was also tested to evaluate how biodiesel fuel contamination impacts the oxidation stability of the lubricant. Biodiesel are based on long-chain alkyl esters and are thereby more susceptible for oxidation than ordinary petroleum fuel. In addition biodiesel are less volatile than petroleum and will consequently not vaporize as fast as petroleum fuel. This means that biodiesel will remain in the lubricant longer. This together with the lower oxidation stability makes biodiesel contamination interesting to analyse.

Hydraulic oils 1 to 3 are environmental adapted lubricants. Due to the growing worldwide interest in environmental issues, biodegradable lubricants are growing on the industrial market. Contacts with the wood-processing accentuated that "biolubricants" are used in majority today but that they need more knowledge from the user to function right. Biolubricants are more prone to oxidation which makes them interesting to investigate and also give the advantage that they can be oxidized in the laboratory in fair amount of time. Hydraulic oil 4 which is standard mineral oil based hydraulic oil was chosen to compare with the other three biodegradable hydraulic oils (see Table 6).

Hydraulic systems often work in surroundings were there can be water contamination. To analyse how water influence the oxidation process of a hydraulic oil, a mixture of Hydraulic oil 2 and water was also tested.

Table 6. Hydraulic oils used in the laboratory study

	Type	Application	Viscosity at 100°C according to manufacturer
Hydraulic oil 1.	Based on synthetic esters.	Various hydraulic systems, with working temperature from -25°C to +95°C.	9.5 mm^2/s
Hydraulic oil 2.	Based on natural fatty oil (rapeseed oil).	Various hydraulic systems where there is a risk of environmental damage through leakage.	8-9 mm^2/s
Hydraulic oil 3.	Based on synthetic esters.	Various hydraulic systems.	9.1 mm^2/s
Hydraulic oil 4.	Mineral based hydraulic oil.	Standard hydraulic oil used in industry and for several different applications.	8.7 mm^2/s

3.2   Pre-study

The pre-study focus on finding the best methods to oxidize the two different types of lubricants.

3.2.1   Evaluation of oxidation methods for engine oil

As mentioned before engine oil has a lot of additives and is stable at very high temperatures. To check if it is possible to oxidize engine oil at temperatures achievable in the laboratory and under a reasonable time, different methods is evaluated.

The Rancimat (873 Biodiesel Rancimat, Metrohm), is used to give an indication on which temperature is needed to oxidize the oil. Instead of heating the samples at 110°C as in the standard two higher temperatures, 160°C and 200°C, are tested. Instead of 3 g per samples as in the standard, each sample is prepared with 6 g oil. The samples are stopped after different time intervals and analysed with AN and FTIR. All AN is measured potentiometric with an automatic titration device (702 SM Titrino, Metrohm) and diluter (776 Dosimat, Metrohm). FTIR- spectra was analysed (FTIR spectra GX, Perkin Elmer) using a sampling cell with a pathlength of 0.1118 mm. A test is also carried out where further modifications to the Rancimat standard is made to evaluate thermal reactions. The air flow and the conducting to the water trap are stopped. Before the test starts nitrogen is bubbled through the samples to reduce the amount of oxygen present. Two samples are held at 160°C and two samples at 200°C. One sample from each temperature is terminated after 24 hours and the other two after 48 h. The samples are analysed with FTIR.

The second method tested is pressurized vessels held at 140°C. The vessels are prepared with 100 mL engine oil and pressurized with oxygen to 7.2 kg/cm^2 (706 kPa). After 48 h one vessel is terminated and the other after 168 hours. During the test the pressure is recorded to give the induction time.

The third method evaluated is heating a conical with 200 mL oil on a hot plate keeping the oil at 140°C and with a condenser with cooling water refluxing to restore volatile compounds. After different time intervals AN is measured and FTIR-spectra analysed.

To analyse how biodiesel influence the oxidation properties of engine oil, a solution containing 5% biodiesel is mixed. Four samples are then processed in the rancimat, two at 160°C and two at 120°C. Two samples from each temperature are terminated after 44 and 138 h respectively and analysed with AN and FTIR.

3.2.2 Evaluation of oxidation methods for hydraulic oil

Hydraulic oil has fewer additives and should be easier to oxidize whereby not as many tests are needed to establish the best method for them.

Two vessels are pressurized like the ones in section 3.2.1 but held at 110°C for 72 and 120 hours. AN and viscosity is measured and FTIR-analyse performed on the oil from the two vessels.

A TOST is also tested but in contrast to the standard no metal or water catalyst is used and the heater block is held at 120°C. Samples were taken after 24, 48, 120, 144, 168, and 192 hours and AN and FTIR analysis is made to evaluate the samples at each time.

3.3 Core-study: Evaluation of MPC and RULER for engine oil and environmental friendly hydraulic oil

From the pre-study appropriate oxidation methods are decided (see section 4.1.3).

3.3.1 Engine oil

The engine oils are oxidized in pressurized vessels. One modification to the method described in the pre-study is made; the vessel is opened after 24, 72, 96, 120, and 144 hours, a 10 mL subsample is taken and the vessel is then re-pressurized to the initial pressure of 7.2 kg/cm^2. Each subsample is analysed with AN, FTIR, and RULER (RULER CE520, Fluitec). The vessel is terminated after 168 hours whereby the same analysis is made as to the subsamples and additionally kinematic viscosity (automatic viscometer Hertzhog), and ASTM color (Zeta Lovibond colour comparator, Seta Stanhope) tests are performed.

This was performed on all four engine oils described under Lubricant samples in section 3.1. A fifth vessel was also tested with a mixture of 95 mL Engine oil A and 5 mL biodiesel making a solution of 5% biodiesel.

3.3.2 Hydraulic oil

The hydraulic oils are oxidized using the modified TOST method described in the pre-study. Subsamples are taken after 24, 48, 72, and 96 hours. AN and RULER are analysed on each

sample. After 168 hours the test is terminated and additional to AN and RULER viscosity is measured and a MPC-analyse (F475, Fluitec) and gravimetric analyse performed.

A sample is also tested with hydraulic oil 2 and water added to the oil as a catalyst. 300 mL oil is mixed with 60 mL water making a mixture of 17% water. 350 mL is needed to perform TOST and 10 mL is saved as a reference.

The MPC-analyse is performed according to the ASTM draft (see more section 2.7.6). Filters used were Millipore HAWP-filters which are composed of mixed cellulose esters and with a pore size of 0.45 μm. The spectral analysis was made using Fluitec i-Lab Model F475.

3.3.3 SCANIA test rig

Eight engine oil subsamples from an engine test rig at SCANIA were also evaluated. These oil samples were collected from an engine driven cell motor after different time intervals. The engine is counteracted by an electric brake and runs after a specific operating cycle. The samples were analysed with RULER, AN, FTIR, base number, and base number EP. Lead concentrations were given from SCANIA.

3.4 Calculations

3.4.1 FTIR calculations

Oxidation index is calculated for all engine oil samples using the method described below. This is a method from SCANIA with the difference that the oxidation index is recalculated to be equal to the DIN 51 453 method [43].

$$\text{Oxidation index} = \text{Abs}(1710 \text{ cm}^{-1}) \ast 10/d$$

Where d is the path length of the cell in millimetres. $\text{Abs}(1710 \text{ cm}^{-1})$ is the corrected height from the calculated baseline with the height of the reference sample subtracted. The baseline is calculated using two points left of the peak at 1710 cm^{-1}. The first point is chosen by calculating the mean height in the interval 2180-2270 cm^{-1}. The point is then placed at the spot in this interval which corresponded to this height. The second point is chosen in the same way but in the interval 1885-1955 cm^{-1}. The method can be described as calculating a straight baseline which is vertically in the middle of the spectra curve between the two intervals. This is illustrated in Figure 10. [44]
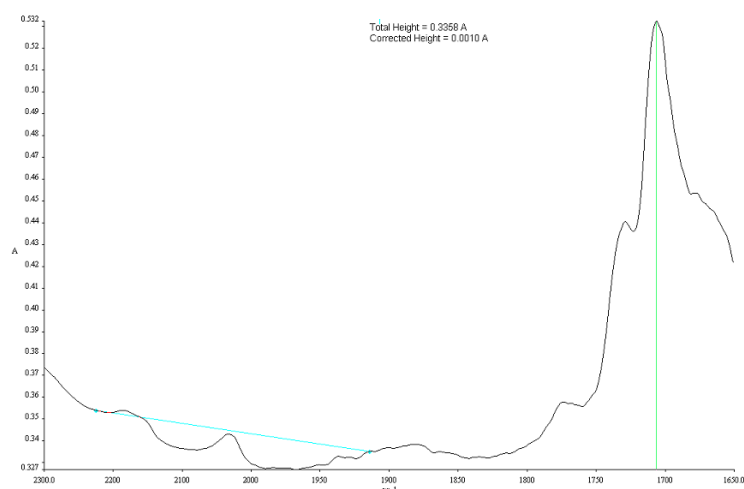
Figure 10. Oxidation index calculations.
A base line is decided, illustrated in blue in the figure. The oxidation peak is evaluated by its height, here illustrated in green.

ZDDP at ~980 cm^{-1} was also calculated using the FTIR software. The height was here calculated using a more common baseline drawn using two points placed on either side of the ZDDP peak. The height of the reference sample was set as 100% and the other oxidized samples were then calculated as the percentage from this.

3.4.2 Gravimetric calculation of filter weight

The weight of the filters are affected by air humidity and to counteract this effect the difference in the weight of the control filter need to be subtracted from the difference of the filter that has been filtered with oil.

$$m = (m_{f2}-m_{f1})-(m_{c2}-m_{c1})$$

m: weight of filter residues

m_{f1}: weight of filter before filtration

m_{f2} : weight of filter after filtration

m_{c1}: weight of control filter before filtration

m_{c2}: weight of control filter after filtration

3.4.3 RULER calculations

The RULER R-DMS software calculates the area under each peak and compares it to the chosen standard which gives a value in percentage of this particular additive peak. Area RULER is calculated in the same way, but here it is the total area under the RULER curve that is compared. The significant peaks for the standard curve, that is the measurements of new reference oil, is first located. After that the same peak is chosen in the curve for the oxidized sample. To compensate for additive peak shifting or interferences with oxidation products, additive valleys often needed to be relocated from the standard. Figure 11 shows a sample compared to reference where there is one significant additive peak.
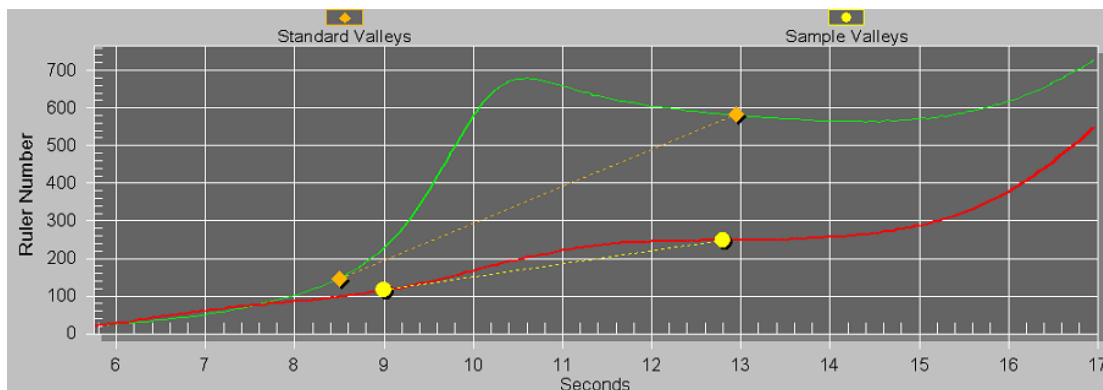

Figure 11. A typical RULER graph with one significant additive peak.
Reference sample is showed in green and oxidized sample in red. The figure show how the end point of the area measurements can be chosen.

Often the RULER curves show two or more additives and then these have to be evaluated one by one. In Figure 12 there is an obvious distinction between the two peaks. The additive content in the lubricant used in the tests is unknown whereby it is difficult to derive a peak found in the RULER curve with a particular additive. It is known that amine antioxidants give peaks earlier in the RULER curve than phenol antioxidants. However, even though a peak shows early in the RULER curve one cannot say with total certainty that it is an amine. In the result and discussion part different peaks are only compared to the correlating peak in the reference sample, no implications on what type of antioxidant this peak can present are made.
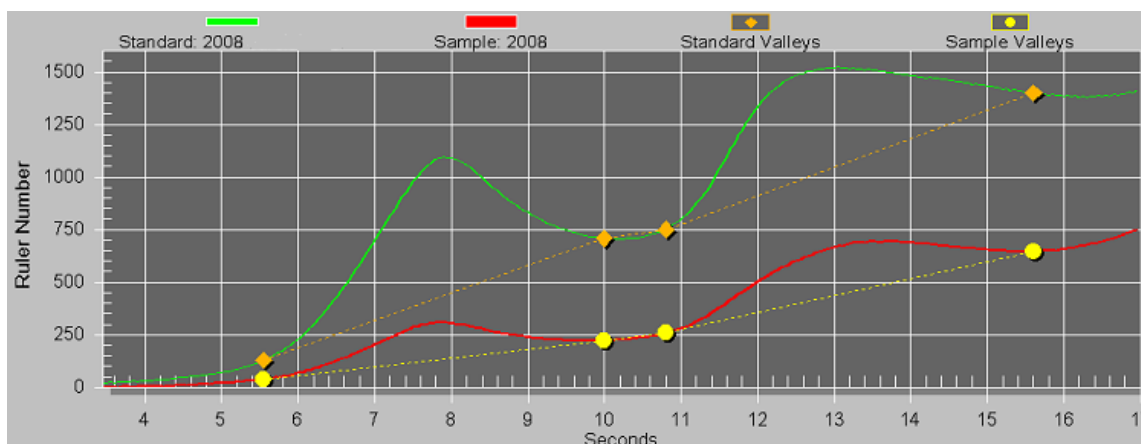

Figure 12. A typical RULER graph with two distinct additive peaks.
Reference sample is showed in green and oxidized sample in red. The figure show how the end point of the area measurements can be chosen.

4 Results and Discussion

4.1 Pre-study

In the pre-study Engine oil A and Hydraulic oil 1 were used to evaluate the appropriate oxidation method for engine and hydraulic oil respectively.

4.1.1 Evaluation of oxidation methods for engine oil

To establish an appropriate temperature to test in the others oxidation methods the rancimat was first used. AN and FTIR analysis on samples held at two different temperatures, 200°C and 160°C, showed that the lower temperature was enough to oxidize engine oil. During the oxidation in the rancimat the water in water trap became turbid and contained soggy white particles, meaning there was a depletion of additives and other volatile compounds.
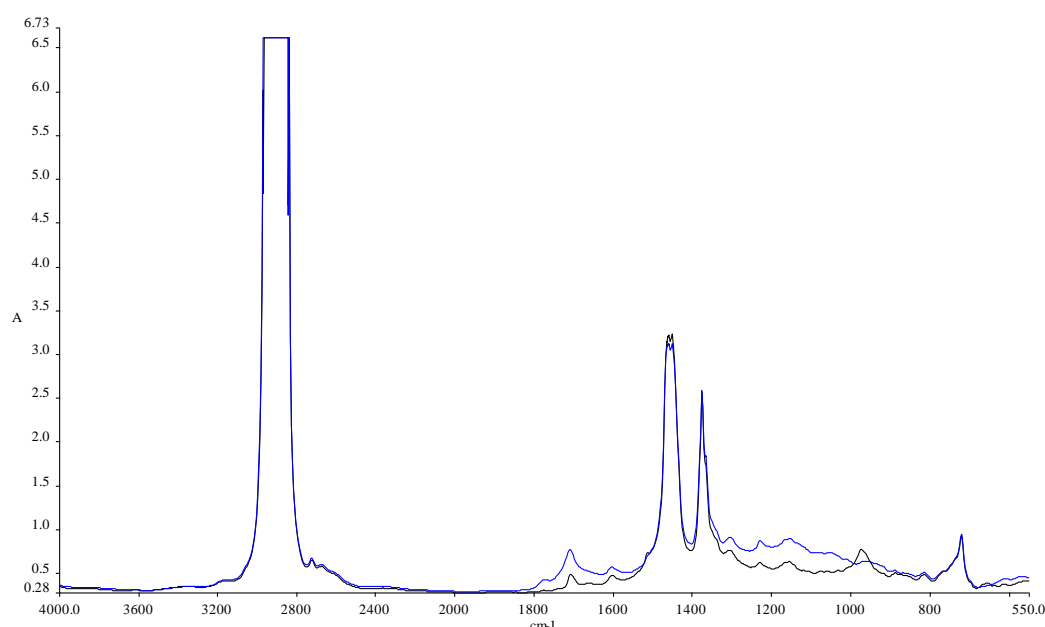

Figure 13. FTIR-spectra for sample oxidized in rancimat at 160•C.
Reference (black) and oxidized sample held at 160°C for 136 h. The increase at 1710 cm^{-1} and decrease at 980 cm-1 suggest that oxidation has occurred.

In the FTIR-spectra there is an increase for the oxidation peak at ~1710 cm^{-1} and for the nitration peak at ~1630 cm^{-1}. It is difficult to establish whether the sulphation peak at ~1150 cm^{-1} has increased as well or if it is the base line that has moved. The peak for ZDDP at ~980 cm^{-1} has decreased considerable meaning that the amount ZDDP additive has decreased during oxidation (see Figure 13). The oxidation and nitration peak together with the decrease of ZDDP strongly implies that oxidation has occurred.

The samples held at 200°C had a tar-like consistency already after 48 hours making it impossible to do any analyses and also showed an extended thermal reaction with a colour darkening after only 3 hours.

26

To investigate whether the observed oil degradation derive from oxidation instead of thermal degradation the same amount of oil were held at 160°C and 200°C in the rancimat without any in- or outflow from the sample tube. The samples were only exposed to heating to examining more about the thermal reaction occurring.
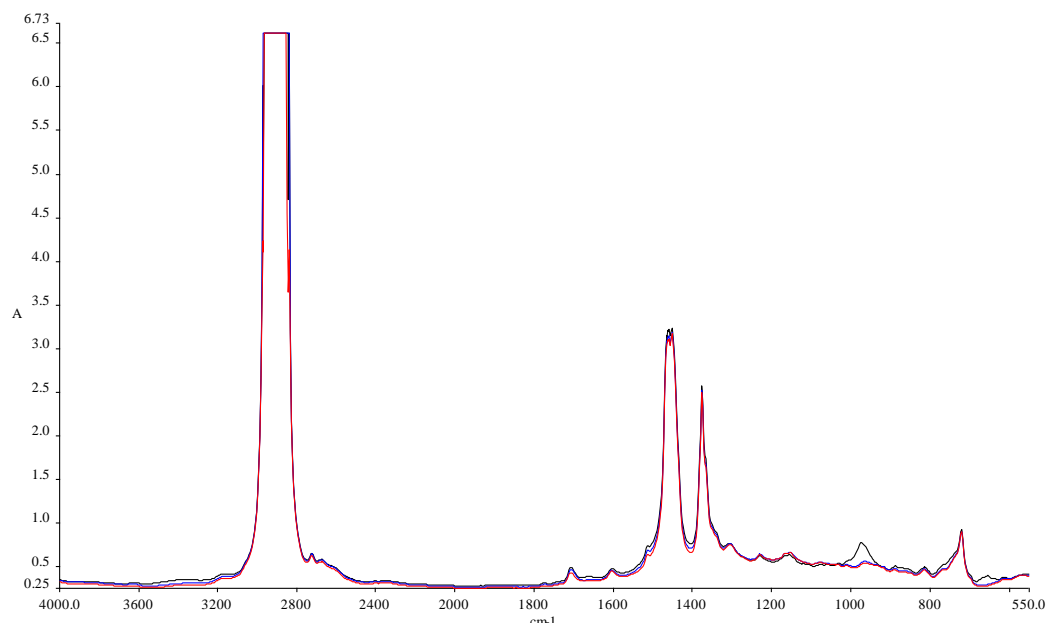

Figure 14. FTIR-spectra of engine oil subjected to thermal degradation in the rancimat.
Two samples were held at two different temperatures in the rancimat with no in- or outflow. Reference (black), thermal degradation 44 h 160°C (blue), and thermal degradation 44 h 200°C (red). There is no increase at oxidation and nitration peaks during thermal degradation meaning that those peaks can be used to estimate whether or not oxidation has occurred.

The FTIR-spectra shows that the reactions seem to be similar at the two different temperatures. There is no oxidation, nitration or sulphation peak increase, but a decrease in ZDDP (see Figure 14). There is no oxidation occurring, but the thermal reaction causes depletion of additives. This proves that oxidation is the cause of the increase at oxidation, nitration, and sulphation peaks in the previous case studied and that these peaks can be used to evaluate whether oxidation has occurred or not.

To analyse oxidation without vanish of volatile compounds, which was the case in the rancimat, two pressurized vessels or "bombs" were tested.
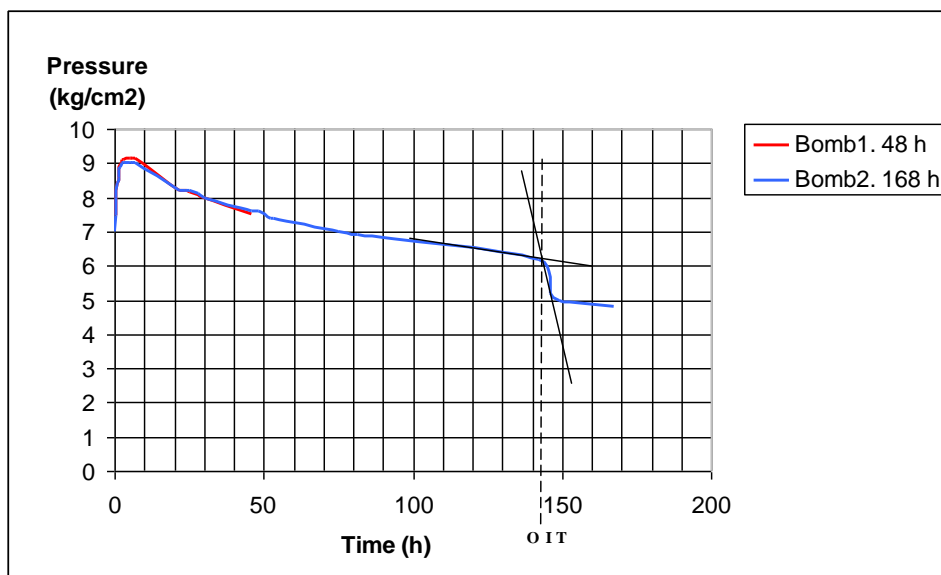
27

Figure 15. Pressure measured during oxidation of engine oil in oxygen pressurized vessel at 140°C.
Bomb 1 was stopped after 48h (red) and vessels stopped after 168 h (blue). The figure shows that the OIT is at 143 h.

The pressure was measured during the test duration. The first bomb that was stopped after 48 hours did not reach the oxidation induction time, but the second bomb stopped after 168 hours showed a distinct OIT at 143 h (see Figure 15). This shows that it is possible to oxidize engine oil in pressurized vessels during approximately a week. The oil was analysed with FTIR, AN, and viscosity. Results are shown in Table 7 and Figure 16.

Table 7. Acid number and viscosity measurements of engine oil oxidized at 140°C
Engine oil A was oxidized in two oxygen pressurized vessels. One bomb was stopped after 48 h and the other after 168 h.

	Ref. 0 h	Bomb1. 48 h	Bomb2. 168 h
Acid number (mg KOH/g)	2.62	1.6	2.92
Viscosity (mm^2/s)	13.94	13.95	14.04

After 48 h AN have decreased due to additive depletion and there is not any noticeable change in viscosity. After 168 hours both AN and viscosity is increasing indicating oxidation has started.
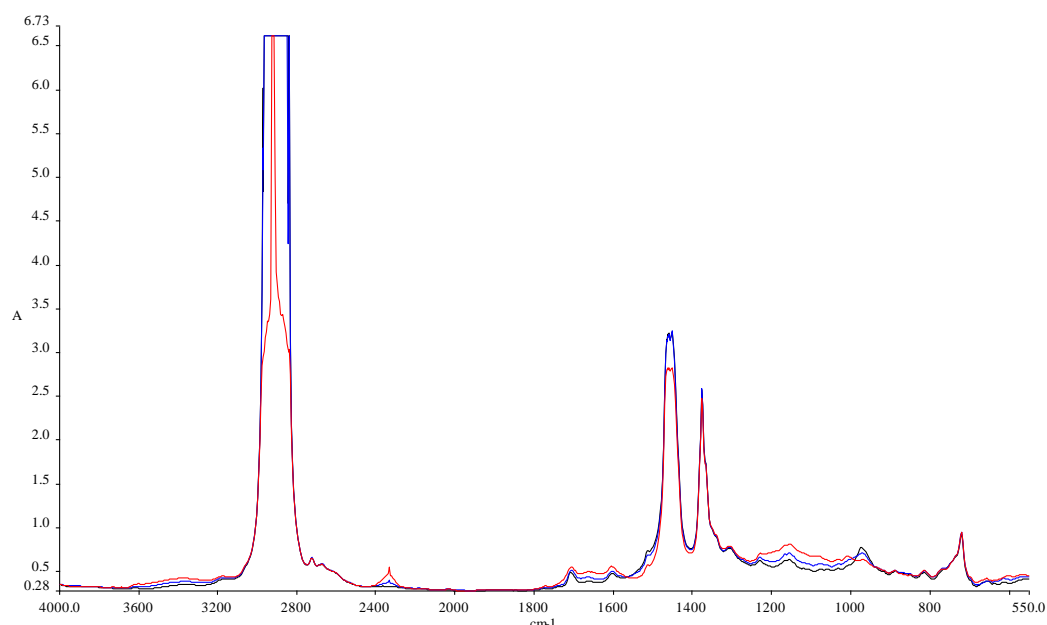
28

Figure 16. FTIR-spectra of engine oil oxidized in pressurized vessels at 140°C.
Reference oil (black), bomb 48 h (blue), and bomb 1 week (red). The figure shows increase at the oxidation peak at 1710 cm^{-1} and decrease at the ZDDP peak at 980 cm^{-1}. This indicates that pressurized vessels oxidize the engine oil.

The FTIR-spectra showed further evidence that the pressurized vessels worked well for oxidizing engine oil. Oxidation, nitration, and sulphation peaks are increased compared to unoxidized oil after 48 hours and after 168 hours they have increased more. After 168 hours it is also obvious that ZDDP has decreased (see Figure 16).

Oxidation of engine oil was also tested using a conical with a water cooled condenser, heating the oil to 140°C with a heating plate. During the oxidation it was difficult to keep a homogenous temperature with only the aid of magnetic stirring. The oil closest to the hot plate had different colour, thermal degradation, and oxidation did not occur uniformly in the oil.

4.1.2 Evaluation of oxidation methods for hydraulic oil

In the pre-study Hydraulic oil 1 was used.

Two vessels were pressurized like the ones used in the engine oil test but held at 110°C for 72 and 120 hours. The results are showed in Table 8 and Figure 17.

Table 8. Acid number and viscosity from pressurized vessels at 110°C with hydraulic oil.
Hydraulic oil A was oxidized in two oxygen pressurized vessels. One bomb was stopped after 48 h and the other after 120 h.

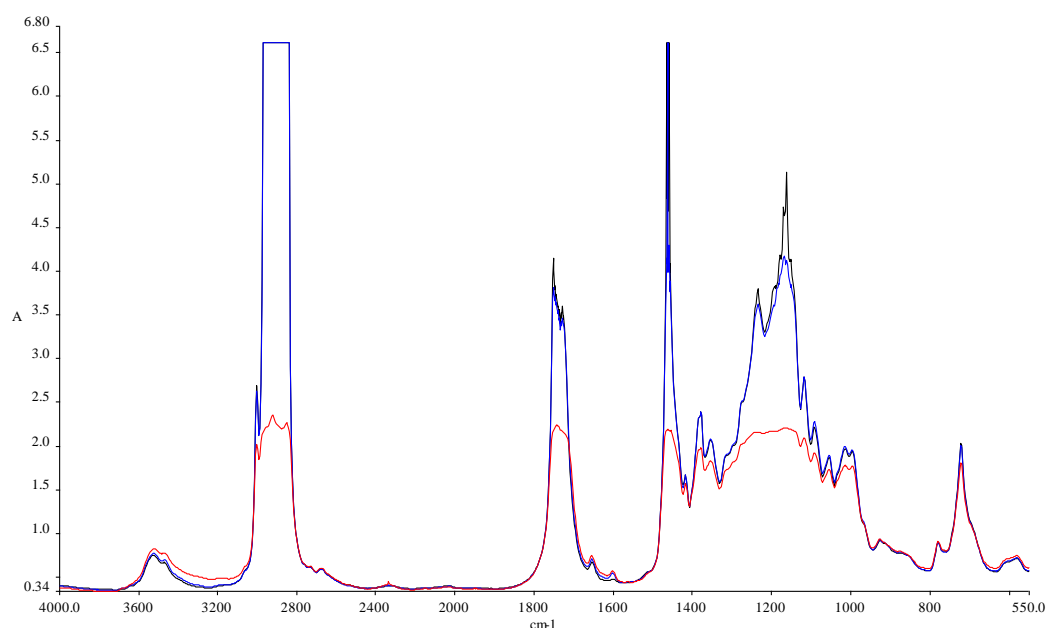|	Ref. 0 h	Bomb1. 48h	Bomb2. 120h
Acid number (mg KOH/g)	0.29	0.79	5.90
Viscosity (mm^2/s)	9.00	9.63	9.56

29

Figure 17. FTIR-spectra for hydraulic oil oxidized with pressurized vessel at 110°C.
Reference oil sample (black), bomb 48 h (blue,) and bomb 142 h (red). The spectra show some increase at the oxidation peak at 3540 cm^{-1}.

From this spectra it was noted that synthetic ester based lubricants are more difficult to evaluate using FTIR. Many peaks have decreased, but what each peak represent is not as obvious as it was for the engine oil. Oxidation of organic esters should show a peak around 3540 cm^{-1} where there is an increase for the sample held for 142 h (see Figure 17).

Table 9. Acid number for hydraulic oil oxidized with TOST at 120°C.
Hydraulic oil A was oxidized with TOST for 168 h, subsamples was taken after 24, 48, 72, and 96 h. The oxidation was stopped after 168 h.

	Ref. 0 h	**24 h**	**48 h**	**72 h**	**96 h**	**168 h**
Acid Number (mg KOH/g)	0.29	0.27	0.54	0.97	1.61	4.78

The AN in Table 9 shows good result from TOST. The AN have increased indicating that oxidation has occurred. Hydraulic oil oxidized with TOST shows a small decrease in AN when additive depletes, sample measurements after that show an increase meaning that oxidation occur.
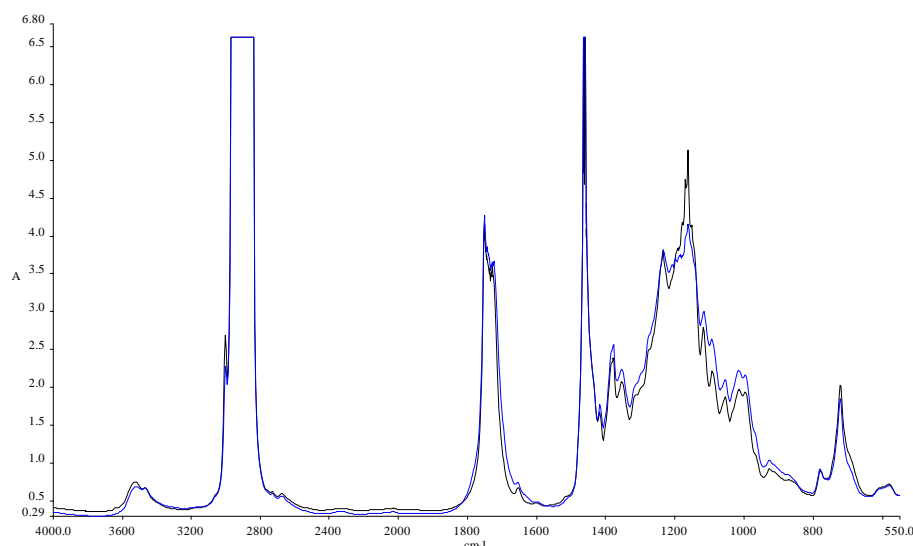
Figure 18. FTIR-spectra of hydraulic oil oxidized with TOST at 120°C.
Reference (black) and oil oxidized during 168 h in TOST (blue) .The figure shows no increase at 3540 cm $^{-1}$ for the oxidized oil even though AN measurements showed evidence of oxidation.

The other oxidation method tested was TOST at 120°C. The AN showed that oxidation occurred but the FTIR-analyse did not show as good correlation between the peak at 3540 cm $^{-1}$ and oxidation time as with the pressurized vessels shown in Figure 17 (see Figure 18). Shown in figure are a reference and oil oxidized with TOST for 168 h. When it comes to synthetic esters FTIR does not appear to be a reliable method to evaluate the process of oxidation. Very little could be found in literature about evaluating FTIR-spectra from oil based on esters. In this study FTIR was thereby not used to evaluate the hydraulic oils.

4.1.3 Oxidation methods

Deciding which methods should be used to oxidize the oil samples was made on the following basis:

- The methods should give an amount of oil that are enough to perform the analysis required to evaluate the oxidized oil.
- Each oxidation method should not take longer than one week to perform.

Methods from the literature study and conclusion from the pre-study was used to decide the best methods to oxidize engine and hydraulic oil.

In the pre-study the rancimat was used to find an approximate oxidation temperature for the different types of oil. Eight samples can be oxidized at the same time at two different temperatures, which makes it possible the collect samples and analyse them after different duration times. One drawback with the rancimat method is that the samples are very small and consequently it is not possible to oxidize oil and test it with analyses that require more than a few millilitres. To use the rancimat in the core study was never an option because only 6 gram could be oxidized in each sample and this is too small to do both AN and FTIR analyses and definitely not enough for a MPC-analyse which alone requires 50 mL. From the rancimat it was noted that volatile compounds are a big problem when trying to oxidize engine oil and to overcome this the oxidation process needed a closed system.

31

Pressurized vessels, ASTM D 525, showed that they could oxidize engine oil without the leaking of volatile compounds and additives. As mentioned in the Theory section engine oil in normal use is subjected to higher temperatures. To speed the oxidation process, higher temperatures than 100°C as in the standard is needed. An increase in temperature by 10°C doubles the rate of oxidation. The drawback with pressurized vessels is that it is not possible to take subsamples during the procedure. However there is a possibility to open a pressurized vessel, take a sample and then re-pressurize the vessel again. This probably would alter the pressure-time diagram where OIT is decided but not influence the oxidation process much.

The RPVOT test is reliable but time consuming. One other drawback is that it is not possible to collect samples during the procedure. The Rolls Royce method was not used because it is very little mentioned about this in other reports on the subject. For similar reasons the JFTOT/HLPS was discarded. When testing the hot plate and the conical with a condenser in the pre-study it was showed that this was not a reliable method. It was obvious that the oil layer close to the hot plate, despite the magnetic stirring, was subjected to thermal reaction. To give homogenous heating some type of heating cape or an oil bath should be needed. Because of this the method was discarded.

TOST showed good results for the hydraulic oils. As for the pressurized vessels higher temperature was needed. The TOST life for a hydraulic oil at 95°C as in standard is around 1500 h (see Table 3). The higher temperature quickens the oxidation process. TOST is a well known oxidation method. Only one sample at a time could be oxidized with this method whereby the engine oils never were tested with this method.

4.2 Core-study: Evaluation of MPC and RULER for engine oil and environmental friendly hydraulic oil

Four different engine oils and four different hydraulic oils were oxidized and thereafter evaluated by MPC and RULER. As mentioned in the Theory section of this report acid number should decrease in the beginning of oxidation when additives deplete and then increase with the build-up of degradation compounds such as carboxylic acids. Area RULER which is the total area under the RULER curve should decrease with the depletion of additives. RULER additive should also decrease, but in some cases there is a build-up of a new secondary additive when another depletes. Example of mechanism for this was mentioned in section 2.3.1. MBDTBP can give a secondary antioxidant when it is consumed and amine antioxidants can be regenerated by phenol antioxidants. In the diagrams in this chapter only the additives that depletes are shown, this to give a closer look at what is happening. In Appendix A and B diagrams which contain both the additive that depletes and the secondary one can be found.

In the pre-study MPC was tested on engine oil, but with no good result. The engine oil was impossible to filter. The filtered clogged due to some reaction or that the molecules in the engine oil were too big for the filter pores. For this reason MPC was not used to analyse the engine oils.

4.2.1 Engine oil

From the pre-study it was decided that the best method for oxidizing engine oil was pressurized vessels held at 140°C. The different engine oils used are described in 3.1.
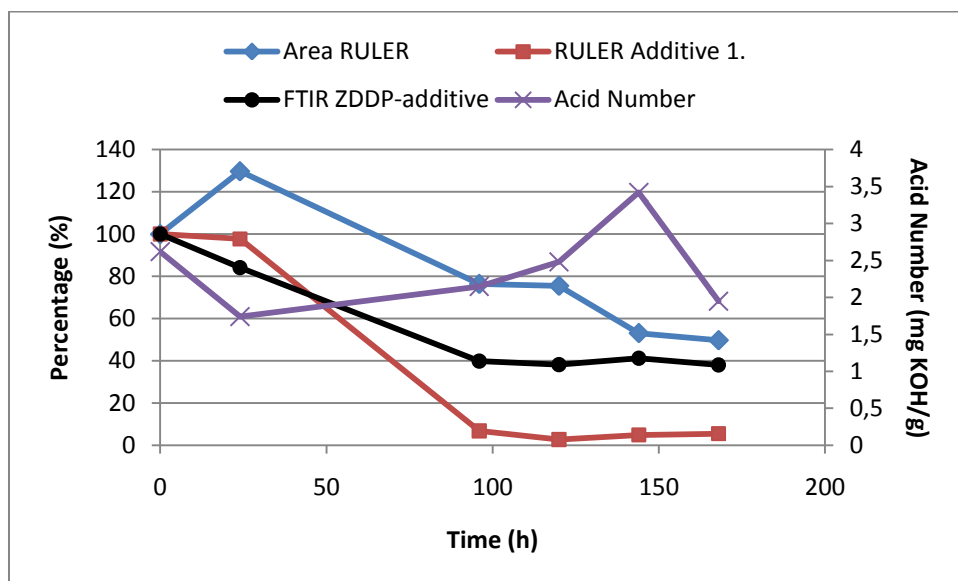

Figure 19. Influence of oxidation on engine oil A.
The engine oil was oxidized in an oxygen pressurized vessel placed in a heating block held at 140°C. At different time points, the pressurized vessel was opened and a subsample was withdrawn from the vessel on which Area RULER, RULER Additive 1, FTIR ZDDP-additive and Acid Number were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that acid number increase when the antioxidant depletes, acid number measurements at 168 h shows an unexpected decrease.
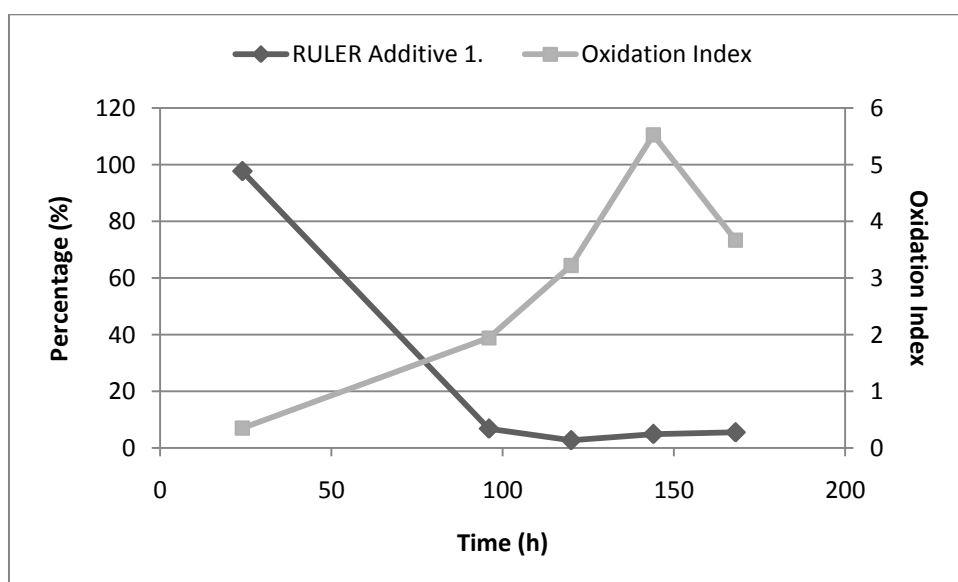

Figure 20. RULER Additive and Oxidation index for engine oil A
RULER Additive 1 (primary vertical axis) and Oxidation Index (secondary vertical axis) measurements from samples withdrawn from an oxygen pressurized vessel at 140°C. The figure shows that Oxidation Index increases when additives deplete. Oxidation Index has decreased at 168 h in the same way acid number has decreased at 168 h in Figure 19.

33

Figure 19 and Figure 20 shows the result from analyses of Engine Oil A. When Area RULER, RULER Additive, and FTIR ZDDP-additive decreases acid number and oxidation index increases. Acid number starts to increase when RULER Additive has reached a level of 25-20%.

Unexpected is AN at 168 h which has decreased compared to the sample taken at 144 h. This should probably be considered as mismeasurement if it was not that the oxidation index showed the same decrease at 168 h. Oxidation index measures, as mentioned in section 2.7.8, carbonyl groups (C=O) at 1710 cm^{-1} in the FTIR spectra .This indicate that carboxylic acids and other carbonyl group containing substances has been altered or depleted. A good explanation for this is hard to find. The RULER analyse showed a build-up of a new peak when the primary additive is consumed. This secondary component could as described in the antioxidant theory section also function as an antioxidant. This should only halter the oxidation process not detract acidic components and oxidation by-products.
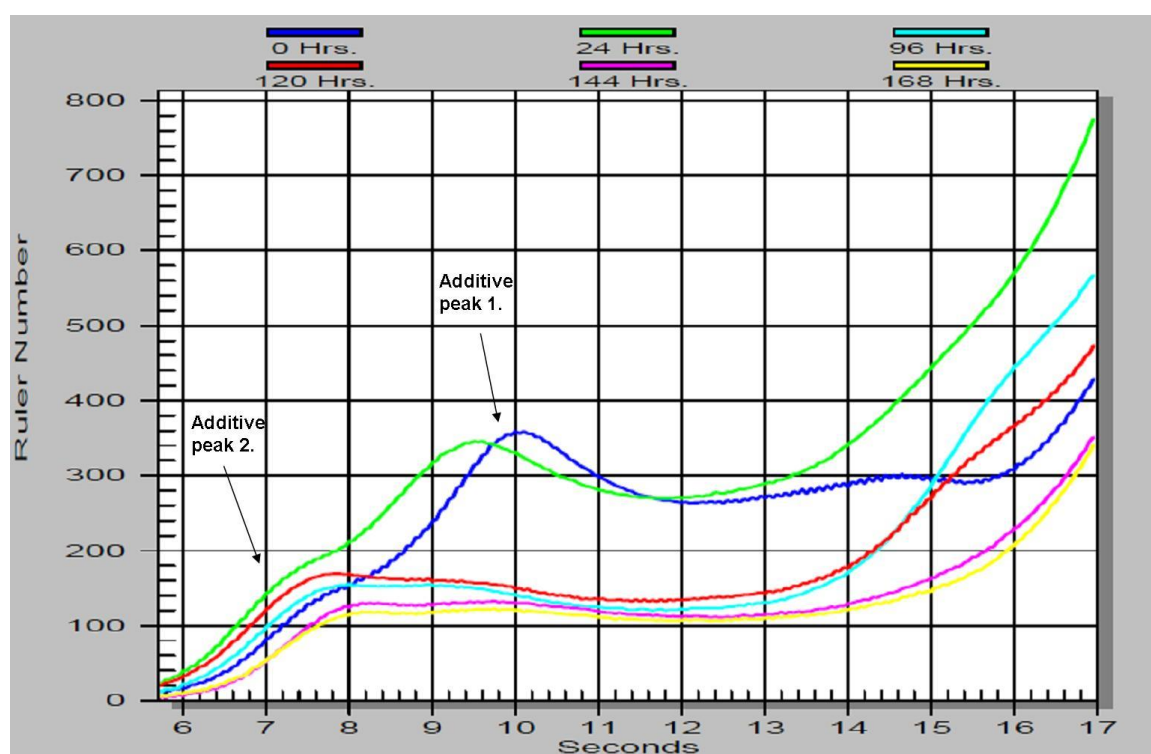

Figure 21. RULER curves of engine oil A samples.
The figure shows RULER measurements from samples withdrawn after different time intervals when engine oil A was oxidized in a pressurized vessel at 140°C. The figure shows one additive peak at 8.5-11.5 seconds which increases as the oxidation proceeds. Additive peak 2 at 6.5-8.5 seconds increases as the lubricant become more oxidized, meaning there is a secondary additive formed during oxidation.

The RULER curves from engine oil A measurements shows an example of when there is difficult deciding where different additives peak should be placed to calculate the peak area (see Figure 21). In this case two additive peaks were evaluated. Additive peak 1 decreases, meaning that this is an antioxidant that depletes during the oxidation process in the pressurized vessel. Additive peak 2 seems to increase meaning that this is probably a secondary antioxidant formed when the first additive depletes. Measurements from additive peak 2 are not showed in Figure 19 but can be found in *Figure A1* in Appendix A.
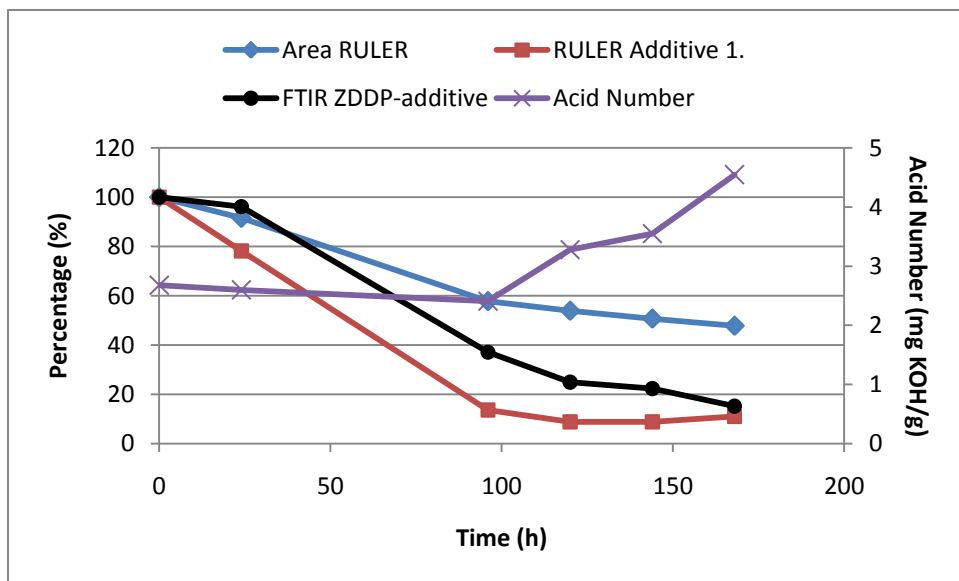
34

Figure 22. Influence of oxidation on engine oil B.
Engine oil B was oxidized in an oxygen pressurized vessel placed in a heating block held at 140°C. At different time points, the pressurized vessel was opened and a subsample was withdrawn from the vessel on which Area RULER, RULER Additive 1, FTIR ZDDP-additive, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that acid number increase when the additive depletes. AN starts to increase when RULER Additive 1 has decreased to 20%.

Measurements from engine oil B shows that Area RULER, RULER Additive 1, and FTIR ZDDP-additive decreases during test duration. When RULER Additive 1 has reach a level of 20% AN starts to increase (see Figure 22). This indicates that the oxidation with base oil degradation happens after the Additive has reached this level. RULER curves shows only one additive peak which decreases (see Figure 23).
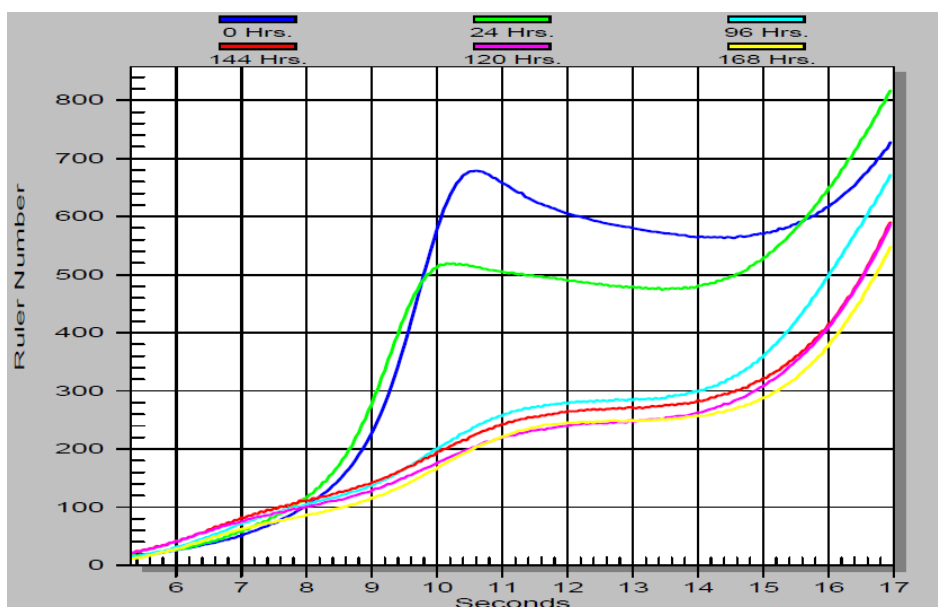

Figure 23. RULER curves of engine oil B samples.
The figure shows RULER measurements from samples withdrawn after different time intervals when engine oil B was oxidized in a pressurized vessel at 140° The figure shows one additive that decreases as oxidation proceeds, meaning that this additive depletes during the oxidation process.
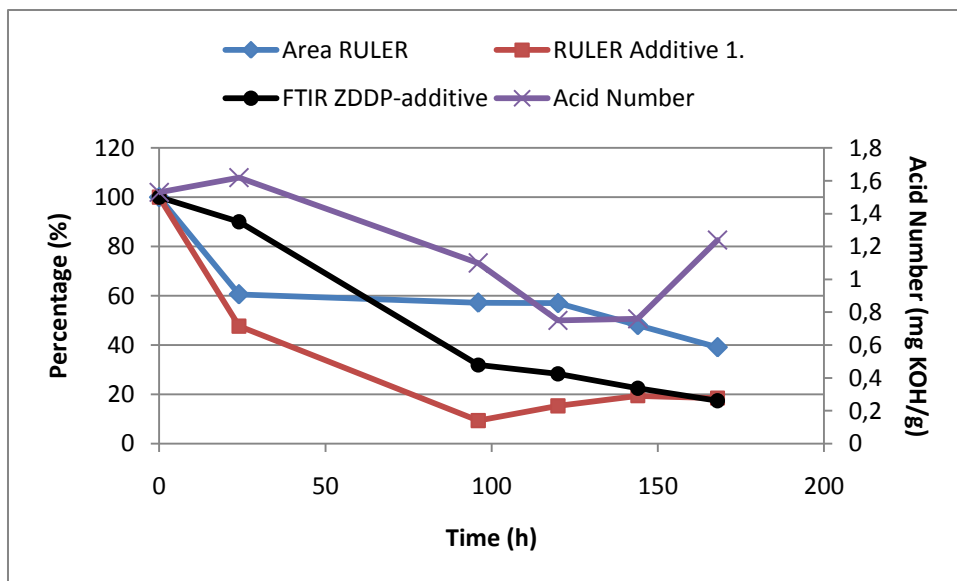
35

Figure 24. Influence of oxidation on engine oil C.
Engine oil C was oxidized in an oxygen pressurized vessel placed in a heating block held at 140°C. At different time points, the pressurized vessel was opened and a subsample was withdrawn from the vessel on which Area RULER, RULER Additive 1, FTIR ZDDP-additive, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that AN has started to increase and do not reach a high level where the oil is fully oxidized.

Measurement from engine oil C showed that the AN has started to increase, but AN has not reach a high level where there is certain oxidation occurring. RULER measurements of Additive 1 show that the additive has decreased to a low level at 96 h. The three following measurements show an increase in additive concentration indicating that there is a regeneration of RULER Additive 1 (see Figure 24). RULER measurements gave RULER curves similar to the ones showed in Figure 21 from engine oil A. The secondary additive that increases can be found in Figure A5 in Appendix A.

Engine oil D shows expected results. When the additives deplete the acid number increases. Acid number starts to increase when RULER Additive 1 has decreased to 25% (see Figure 25). The RULER curves only showed one additive peak indicating that there is no secondary antioxidant formed.
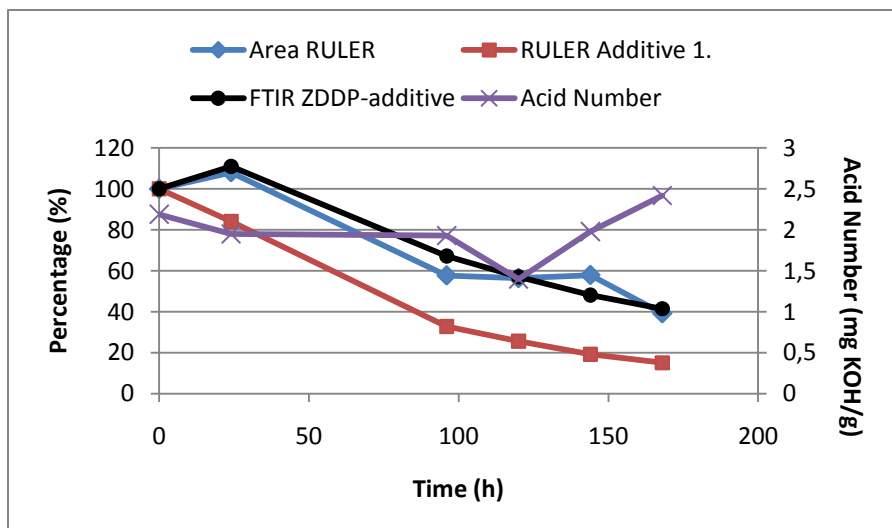
Figure 25. Influence of oxidation on engine oil D.
Engine oil D was oxidized in an oxygen pressurized vessel placed in a heating block held at 140°C. At different time points, the pressurized vessel was opened and a subsample was withdrawn from the vessel on which Area RULER, RULER Additive 1, FTIR ZDDP-additive, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that Area RULER, RULER Additive 1, and FTIR ZDDP-additive depletes as AN starts to increase. When RULER Additive falls decreases to a level of approximately 25% acid number starts to increase.

Engine oil A, B, C, and D showed overall expected results. The critical level when AN starts to increase seem to be when there is approximately 20-25% of the decreasing RULER additive left. As described in theory section 2.3.1 several literature references gives the value 20-30%, which consorts well with the value given from these tests.
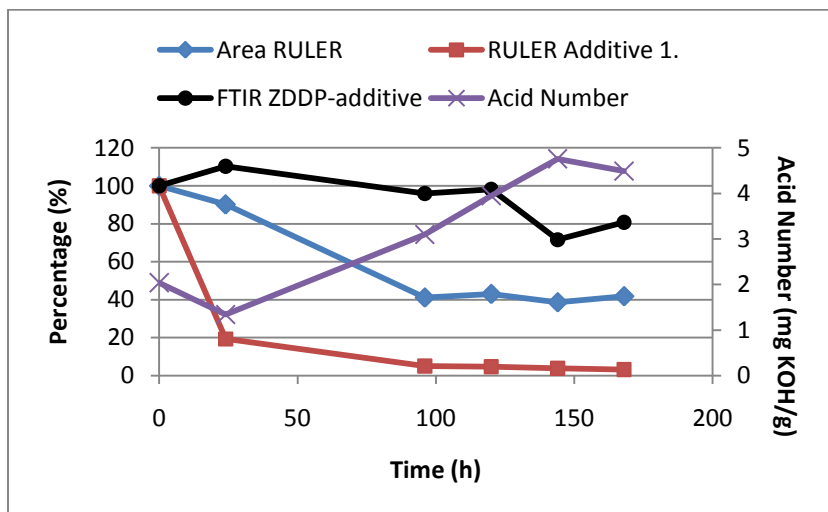

Figure 26. Influence of oxidation on engine oil A + 5% biodiesel.
A mixture of engine oil A and biodiesel was oxidized in an oxygen pressurized vessel held at 140°C. At different time points, the pressurized vessel was opened and a subsample was withdrawn from the vessel on which Area RULER, RULER Additive 1, FTIR ZDDP-additive, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that RULER Additive 1 has depleted to 20-25% before AN starts to increase. Area RULER did not show a decrease as it should. Area RULER measures the total area under the RULER curve and the biodiesel gave some extra peaks making Area RULER measurements unreliable.

The mixture of Engine Oil A and 5% biodiesel showed that biodiesel catalyze the oxidation process. RULER Additive shows that additives deplete fast and due to this AN starts to increase rapidly earlier in the oxidation process (see Figure 26).
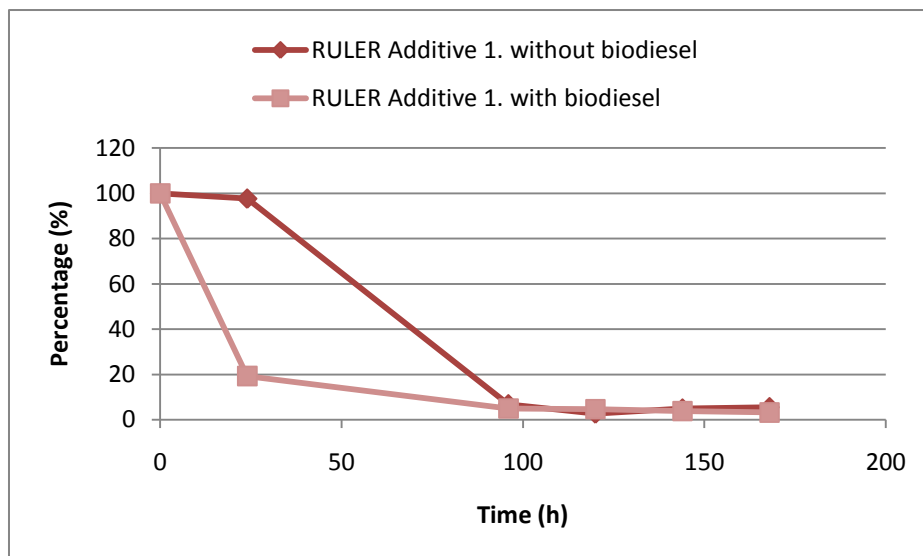

Figure 27. RULER Additive 1 without biodiesel compared to the depletion of RULER Additive 1 with 5% biodiesel.
The figure shows RULER Additive 1 measurements from engine oil A (see Figure 19) compared to RULER Additive 1 measurements from a mixture of engine oil A and biodiesel (see Figure 26). For RULER Additive 1 measurements from engine oil A it takes approximately 92 h to reach a level of 20% while this only takes 21hours for the mixture of engine oil A and biodiesel. The figure shows that biodiesel speed up the depletion of additives.

When comparing the depleted additives from Engine oil A without biodiesel to the blend with Engine oil A + 5% biodiesel it is apparent that the additive is consumed at a much faster rate when there is biodiesel involved. Looking at Figure 19 and Figure 26 it could be assumed that the acid number does not begin to increase considerable before the additive has reached a level where there is only 20-25% left. This takes approximately 90 h for engine oil without biodiesel and around 20 h for the engine oil with biodiesel. This means that 5% biodiesel shorten the time to reach the critical antioxidant level to only one fourth of what it is when there is no biodiesel involved. The depletion of RULER Additive 1 from Engine oil A with and without biodiesel is compared in Figure 27.

Table 10. Viscosity and ASTM color scale results from the engine oil tested.

	Ref. Engine oil A	Ox.168 h Engine oil A	Ref. Engine oil A + 5 % biodiesel	Ox.168 h Engine oil A + 5 % biodiesel	Ref. Engine oil B	Ox.168 h Engine oil B	Ref. Engine oil C	Ox.168 h Engine oil C	Ref. Engine oil D	Ox.168 h Engine oil D
Viscosity (mm²/s)	13.96	14.05	12.17	12.85	14.60	14.22	14.43	14.29	14.51	14.32
ASTM Color	2.5	7.5	3	>8	5	7.5	2.5	7	4.5	6.5

All four engine oils showed small deviations in viscosity after 168 h oxidation. The ASTM color scale showed however difference in colour after oxidation (see Table 10). Just by looking at the colour it is often possible in the laboratory to see if oxidation has occurred. This is more difficult in "real life "applications were the oil often is contaminated with soot, water, and other particles.

The colour change of the engines oil compared to each subsample is showed in Appendix A. Viscosity and ASTM color scale was only analysed for the reference sample at 0 h and after 168 h when the oxidation was stopped. The reason for this was that these analyses required 50 mL and each subsample taken during the oxidation process was only 10 mL. If the subsamples would have been bigger the volume change would have influenced the oxidation process more. The volume of the sample and how much of the oil volume is in contact with the oxidizing gas affect the oxidizing process. It should however be noted, that the volume from the beginning of the oxidation decreases by 40 mL when the four subsamples are collected during the oxidation process. This may influence the oxidation to some extent.

4.2.2 Hydraulic oil

From the pre-study TOST was chosen as the oxidation method to oxidize the four different hydraulic oils. When evaluating an MPC-analyse the two most important values are MPC-index and the b*-value because this two parameters tells which amount of degradation products there are and gives an indication on the risk for them to deposit.

Viscosity and ASTM color scale was only analysed for the reference sample at 0 h and after 168 h when the oxidation was stopped. Δm is the weight difference between the filter filtered with reference oil and the one filtered with oil oxidized for 168 h. The gravimetric analyses showed negative Δm for all hydraulic oils (see Table 11), meaning that there is a decrease in filter residues from oxidized oil compared to filter residues from new, reference oil. The filter residues from the gravimetric analyse is related to contaminants in the oil, indicating that the contaminants become less soluble or perhaps stick to the test tube used during TOST. This would make the decrease the contaminant concentration in the sample tested with MPC.

Table 11. MPC-analyse, viscosity, and ASTM color results from tested hydraulic oil.
Four different engine oils and a mixture of hydraulic oil 2 + water were oxidized with TOST. Δ m is the difference in weight between filter filtered with new oil and filter with oxidized oil.

|	Ref. Hyd. 1	Ox168 h Hyd. 1	Ref. Hyd. 2	Ox168 h Hyd. 2	Ref. Hyd. 2 + water	Ox168 h Hyd. 2 + water	Ref. Hyd. 3	Ox168 h Hyd. 3	Ref. Hyd. 4	Ox168 h Hyd. 4
MPC-index	2.58	49.41	20.92	22.43	-	-	2.50	6.65	16.67	3.78
L*value	99.28	67.10	95.00	94.42	-	-	98.12	97.92	92.86	99.30
a*-value	6.50	-0.41	-2.51	-1.43	-	-	-0.28	-0.69	-0.12	-0.48
b*-value	2.38	36.28	20.11	21.63	-	-	1.68	6.30	15.02	3.61
m (mg)	7.99	6.20	11.10	3.25	-	-	4.34	1.41	4.82	2.44
Δm (mg)		-1.79		-7.85	-	-		-2.93		-2.38
Viscosity (mm²/s)	9.08	20.18	8.35	25.73	8.28	7.75	8.60	9.29	14.51	14.32
ASTM Color	2	>8	1.5	6	7.5	8	0.5	5	5	7.5
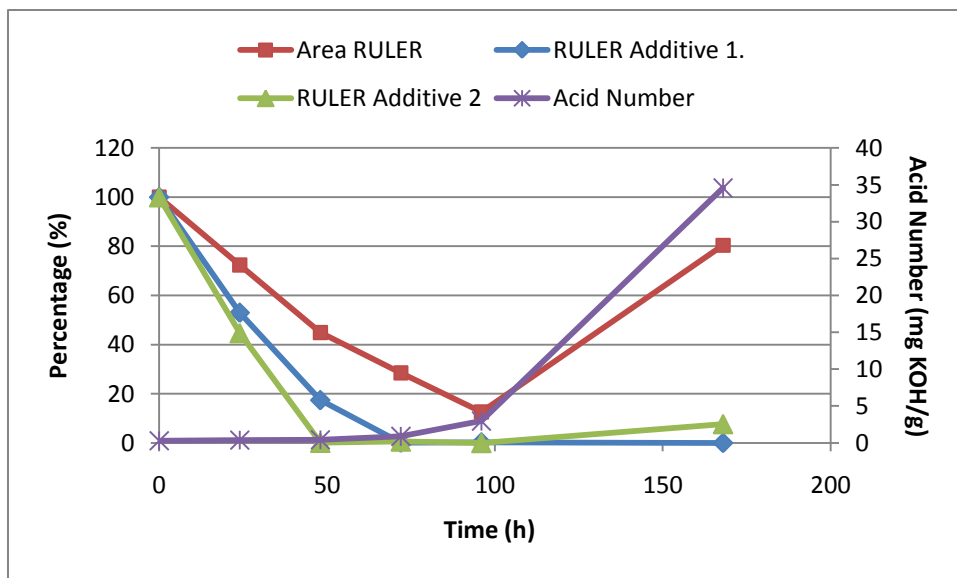
Figure 28. Influence of oxidation on hydraulic oil 1.
Hydraulic was oxidized in TOST at 120°C. Subsamples were taken at different time points. Area RULER,
RULER Additives, and AN were decided. In the figure these parameters are plotted against time. The primary
vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis.
The figure shows that Area RULER, RULER Additive 1, and RULER Additive 2 decreases before AN starts to
increase. AN starts to increase when the additives reach a low level of 2-5%.

Hydraulic oil 1 showed expected results. The RULER analysis showed two different peaks
whereby two different RULER Additives were evaluated. RULER Area and the two RULER
Additives decreases and when they reach a level of approximately 5%, acid number start to
increase rapidly (see Figure 28). The high increase in AN and viscosity for hydraulic oil 1
shows that the oxidation after one week with TOST is considerable. Area RULER have
increased at the last measuring at 168 h. This is due to the increasing in RULER Number
occurring in the RULER curve after 15 seconds which makes the total area, and consequently
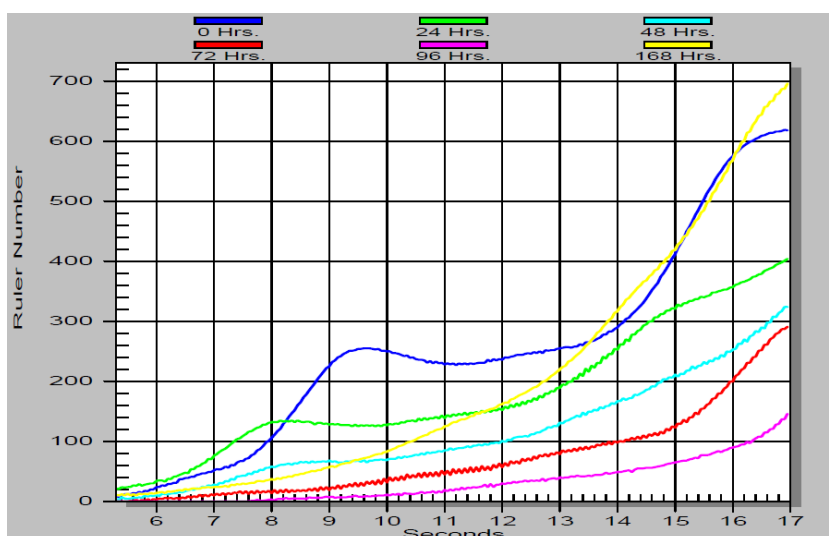Area RULER, higher for the sample oxidized for 168 h (see Figure 29).

Figure 29. RULER curves for hydraulic oil 1.
Hydraulic oil have been oxidized in TOST at 120°C. The figure shows that the curve for the sample collected
after 168 h (yellow) has an increase in RULER Number at the end of the scanning interval (after15 s). This
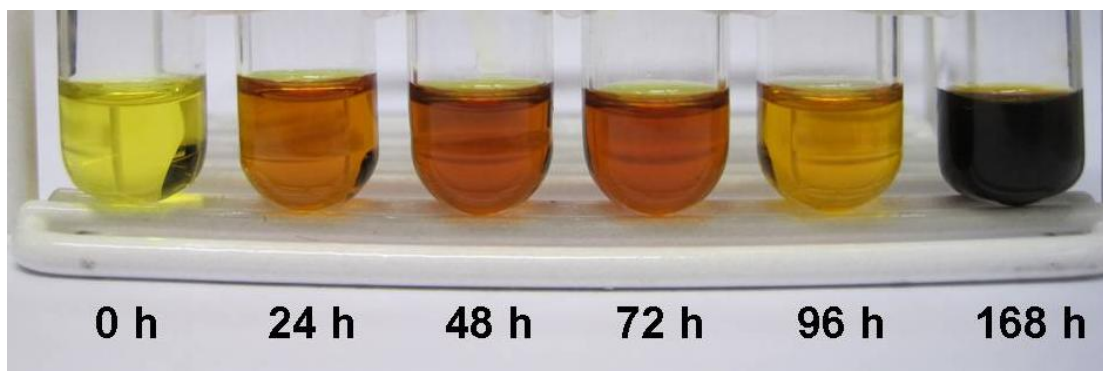*makes the Area RULER measurement higher for this sample.*

40

Figure 30. Colour change for hydraulic oil 1.
The colour change during the process of oxidation. There is an unexpected fade in colour after 96 h.

The colour change evaluated with ASTM color scale shows that the oil's colour has become much darker after 168 h. The sample oxidized for 96 h showed a decrease in colour (see Figure 30). This indicates that the colour changes when the antioxidants have depleted. Both additives have depleted sometime between 72-96 h (see Figure 28). The sample taken after 168 h shows darker colour indicating that the oil has started to degrade. Oil oxidized for 168 h in TOST also showed a high increase in MPC-index when compared to a reference (see Table 11). This means that there is a great amount of oxidation products in the oil and that these are not fully soluble in the oil. If this was a lubricant in real use there would be a high risk for deposits of degradation products in the system.
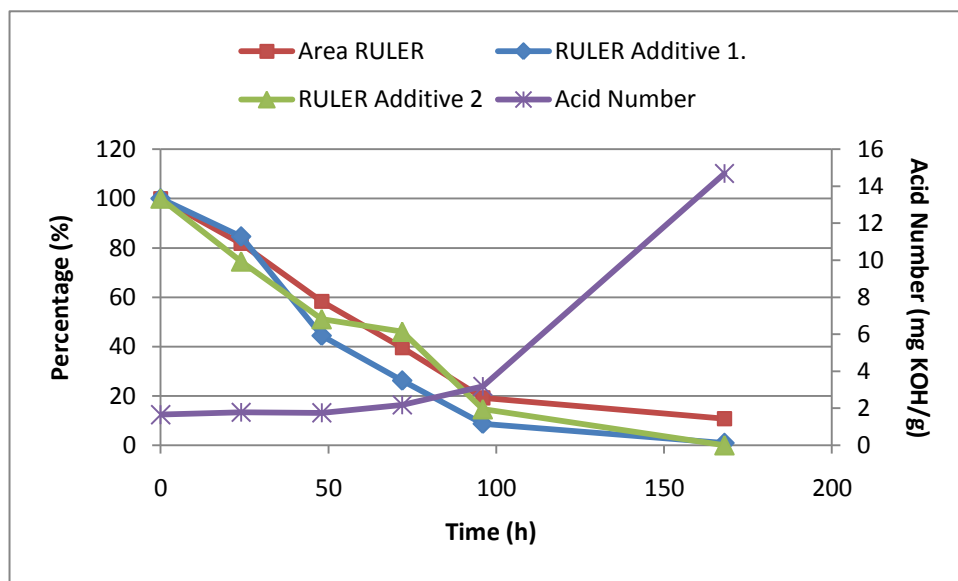

Figure 31. Influence of oxidation on hydraulic oil 2.
Hydraulic oil 2 was oxidized in TOST at 120°C .Subsamples were taken at different time points. Area RULER, RULER Additives, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that Area RULER, RULER Additive 1, and RULER Additive 2 decreases before AN starts to increase. When the additives has decreased to 20% AN starts to increase.

41

Hydraulic oil 2 oxidized with TOST for 168 hours showed that the increase in AN starts when the RULER Additives have decreased to 25-30% of the reference value. There is a high increase not only in AN but in viscosity as well (see Figure 31). Evaluating the colour change with the ASTM color scale was difficult due to the green colour of the oil that did not match the brown palette in the colorimeter. The oil did not show a major increase in MPC-index. This means that the oxidation degradation products are highly soluble in the oil phase and that the risk for deposits in the system is low. A low MPC-index and b*-value can also imply that the degradation products already has separated from the oil, in the system were the lubricant is used or in the container that been used to hold the oil before the analysis. The second should be prevented by shaking the container flask before starting the analysis and the risk for this is thereby low.
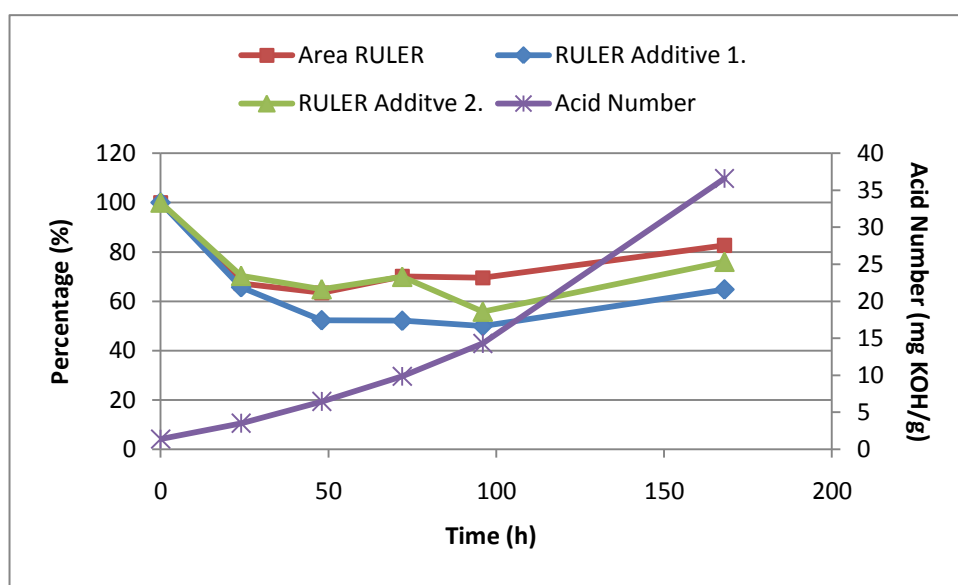

Figure 32. Influence of oxidation on hydraulic oil 2 + water.
A mixture of hydraulic oil 2 and water was oxidized in TOST at 120°C. Subsamples were taken at different time points. Area RULER, RULER Additives, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that Area RULER, RULER Additive 1, and RULER Additive 2 decreases before AN starts to increase. When the additives has decreased to 50% AN starts to increase. The early increase in AN before the additives have reach a low level indicates that hydrolysis is the cause rather than oxidation.

Hydraulic oil 2 oxidized with water added as a catalyst showed a higher increase in AN which indicate that water speed up the oxidation (see Figure 32). The RULER additive never decreased to the low level seen in the previous test where there was no water added. The mixture of the oil and water formed two layers where the water, having higher density than the oil, phased under the oil. Taking samples were thereby difficult and the part samples most likely contained different amount of water. This might affect the RULER analyses. The RULER curves were difficult to evaluate due to one extra peak that appeared in the last subsamples. Another cause of the high increase in AN before the additives have depleted could be hydrolysis. As mentioned in section 2.2.8, hydrolysis is a reaction that happens when

ester type base oil come in contact with water. This causes chemical breakage which could result in acid formation and consequently in an increase in acid number.

Hydraulic oil 2 oxidized in TOST with water as a catalyst was not possible to filter during the MPC-analysis. The filter used contains esters and these seem to react with the esters in the hydraulic oil making a gel which clogged the filter. Hydrolysis almost certainly also took place because the oil is ester based, it consists of rapeseed oil. Hydraulic oil 2 oxidized with no water did not react with the esters in the filter. This indicates that water made the ester in the base oil more prone to react with esters in the filter.
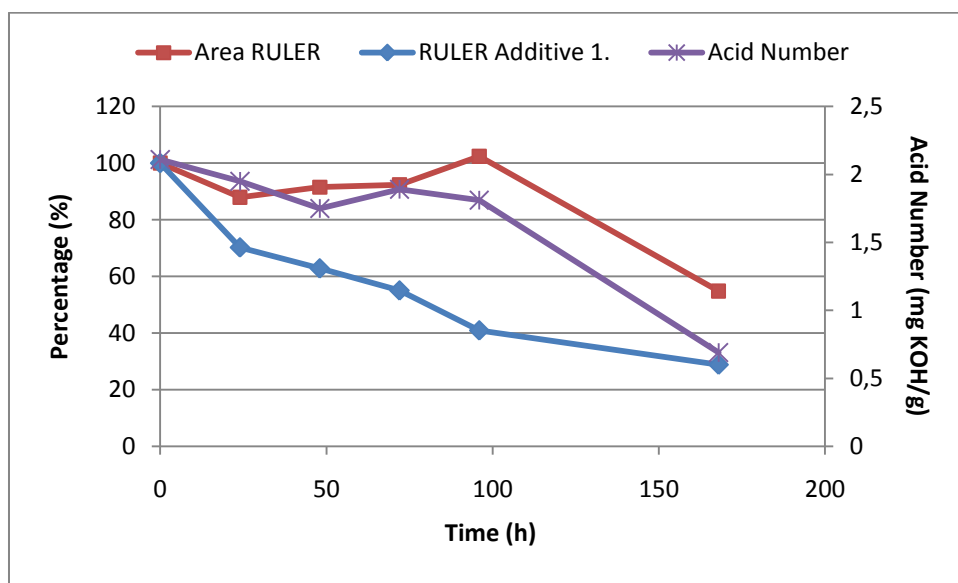

Figure 33. Influence of oxidation on hydraulic oil 3.
Hydraulic oil 3 was oxidized in TOST at 120°C .Subsamples were taken at different time points. Area RULER, RULER Additives, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The figure shows that Area RULER and RULER Additive 1 has started to decrease but have not reached a low level were oxidation should begin and additionally AN does not show an increase. To be fully oxidized engine oil 3 should needed longer time in TOST.

Hydraulic oil 3 was oxidized for one week as the other hydraulic oils. When examine the results it was clear that this was not enough and that extended time should be needed to oxidize the oil. The AN has only decreased and the expected increase in AN which is expected when the additive levels are low never begins (see Figure 33). The RULER curves also showed that the additive peak has not decreased considerable. There some initial decrease between the reference sample, 0 h, and the sample oxidized for 24 h. The following samples remain on the same level as the sample at 24 h until 168 h where the RULER curve has decreased and the curve have moved horizontally to the left (see Figure 34). This implies that something happens to additive after 168, but to further investigate this longer oxidation time should have been needed in TOST.
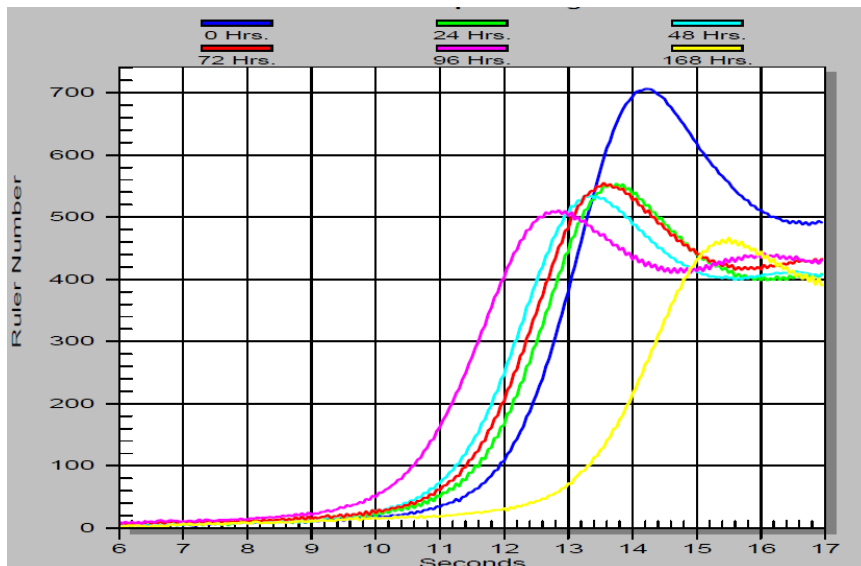
Figure 34. RULER curve for hydraulic oil 3.
Hydraulic oil 2 was oxidized in TOST at 120°C, subsamples where analysed with RULER. The figure shows that there is a decrease between the reference sample (0 h) and the sample taken after 24 h. The four following samples do not show any huge decrease from the one at 24 h. After 168 h there is a decrease and the curve have moved to the left. This implicates that the additive starts to deplete here. Extended oxidation time in TOST should have been needed to further follow this progress.

This indicates that hydraulic oil 3 has good resistance to oxidation and that longer time in TOST should be needed to completely oxidize the oil. The oil did however show some change in colour and a viscosity increase. Hydraulic oil 3 showed an increase in MPC-index and b*-value. Even though the real oxidation where the base oil starts to degrade has not begun the changes in the oil is observable with MPC (see Table 11).
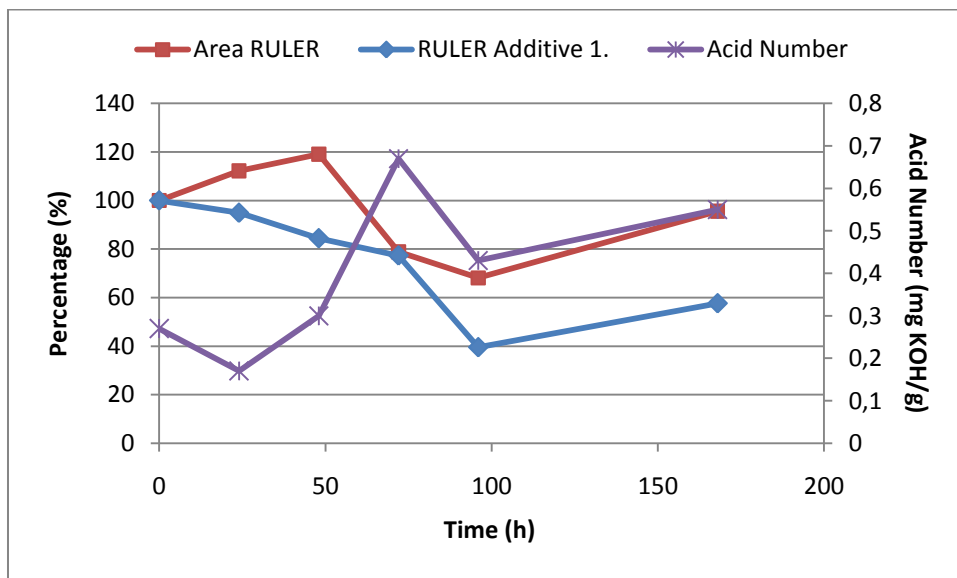

Figure 35. Influence of oxidation on hydraulic oil 4.
Hydraulic oil 2 was oxidized in TOST at 120°C .Subsamples were taken at different time points. Area RULER, RULER Additive, and AN were decided. In the figure these parameters are plotted against time. The primary vertical axis is in relative percentage of the initial value. Acid number is plotted on the secondary vertical axis. The RULER Additive has not reached a low level and consequently there is no high increase in AN. More time should be needed to fully oxidize engine oil 4.

44

Hydraulic oil 4 which is a mineral oil based lubricant was chosen to show the difference between environmental adapted hydraulic oil based on different types of esters and mineral oil based ones. Mineral based lubricants should have higher oxidation resistance then ester based lubricants. AN did not follow the usual pattern with a slight faint in the beginning and then a rapid increase when the additives are depleted. Instead the AN goes up and down during the measurements. The measurements are however in a close range and it is probably just the decrease before AN starts to increase for real. The RULER-analyse shows that the additive has not depleted enough for the oxidation to begin where the base oil degrades (see Figure 35). There is a small increase in viscosity but this is not by far as extended as for hydraulic oil 1 and 2 which were fully oxidized.

Hydraulic oil shows a greater viscosity increase when fully oxidized. From the MPC-analysis it was obvious that the type of oil, that is what base oil the lubricant is based on, had a great influence on the result.

4.2.3 SCANIA test rig

The samples taken from the motor rig at SCANIA had been oxidized to an extended level which was showed in all test performed. After 363 hours new oil is added to the system. This is apparent because RULER Area, RULER additive, and BN increases while AN and oxidation index decreases. The measurement data can be found in Appendix C.
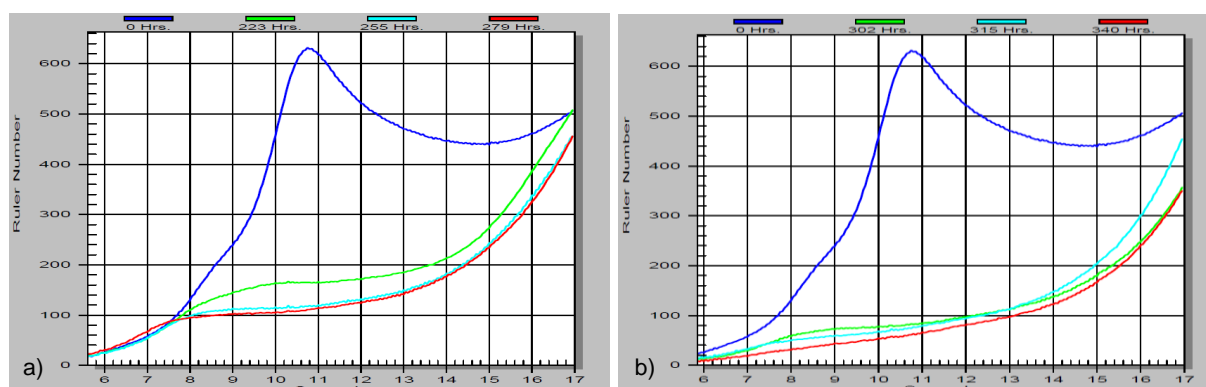

Figure 36. Multi-graphs of RULER curve of the samples from an engine test rig at SCANIA.
a) The RULER multi-graph to the left shows that 223, 255 , and 279 h starts at the same level as the 0 h reference sample. b) The graph to the right shows that 302, 315, and 340 h start at a lower level then the 0 h reference. The 3 samples in b) shows evidence of oxidation, while the samples in a) shows no sign of oxidation. This indicates that the level where the RULER curve starts can show whether or not oxidation has occurred.

The three first samples taken, after 223, 255, and 279 h, seem to start at the same level as the reference and follow it until about 7.5 s in the RULER graph. The following subsamples start at lower level and do not "follow" the reference sample in the same way (see Figure 36).
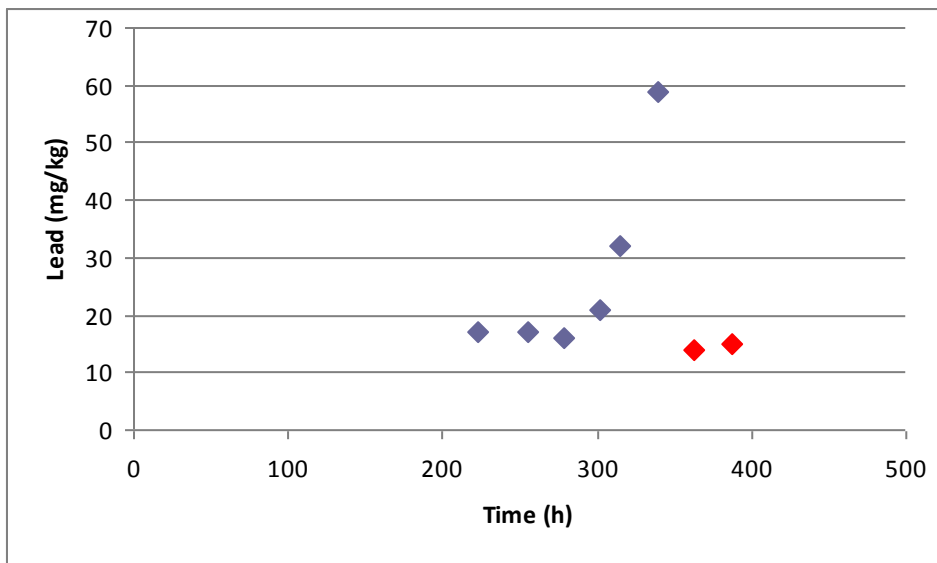
Figure 37. Lead concentration for samples from a test rig at SCANIA.
Samples taken after 223, 255, and 279 h do not show any evidence of acid attack but after 302 h something has happened and the bearings are affected by acids making lead leaking into the oil. The two points in red are after new oil was added.

Figure 37 shows that samples taken after 223, 255, and 279 h do not show any evidence of acid attack. The point at 302, 315, and 340 h shows an increase in lead. The increase in lead concentration indicates that acidic compounds are attacking the bearing making lead "slip out" to the oil. These three samples are the same starting at a lower level in the RULER multi-graph in Figure 37. The three points showing no sign of acid attack starts at the same level as the reference. For this particular oil the level at which the RULER curve start could act as a criteria to decide whether or not bearings are attacked by acids.
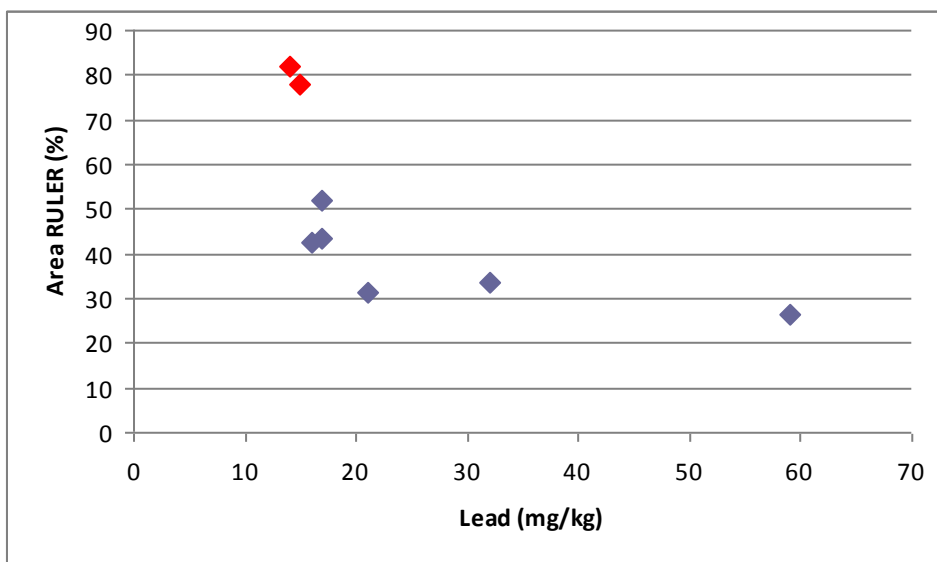

Figure 38. Area RULER measurements against lead concentration from samples withdrawn from an engine test rig at SCANIA.
The figure shows that the lead concentration starts to increase first when the Area RULER is below a level of approximately 35%. The two points in red are those after new oil was added.

In Figure 38 where Area RULER is plotted against Lead there is a knee at 35%. This indicates that the acid attack on metal surfaces does not start until RULER Area, that is additives, in the oil decrease to a certain level. First when the additives fall below this level the lead concentration begin to increase as a result of the acid attack which "unleashes" lead molecules to the oil. When Area RULER falls below 35% there is no longer any protection against oxidation.

Figure with plot containing:
$$y = 12.641x + 19.626$$
$$R^2 = 0.9805$$

Figure 39. Area RULER measurement plotted against base number for samples from an engine at SCANIA.
The figure shows a linear correlation between Area RULER and base number.

In Figure 39 Area RULER is plotted against base number. The figure shows linear correlation between the two with a R^2-value of 0.985.

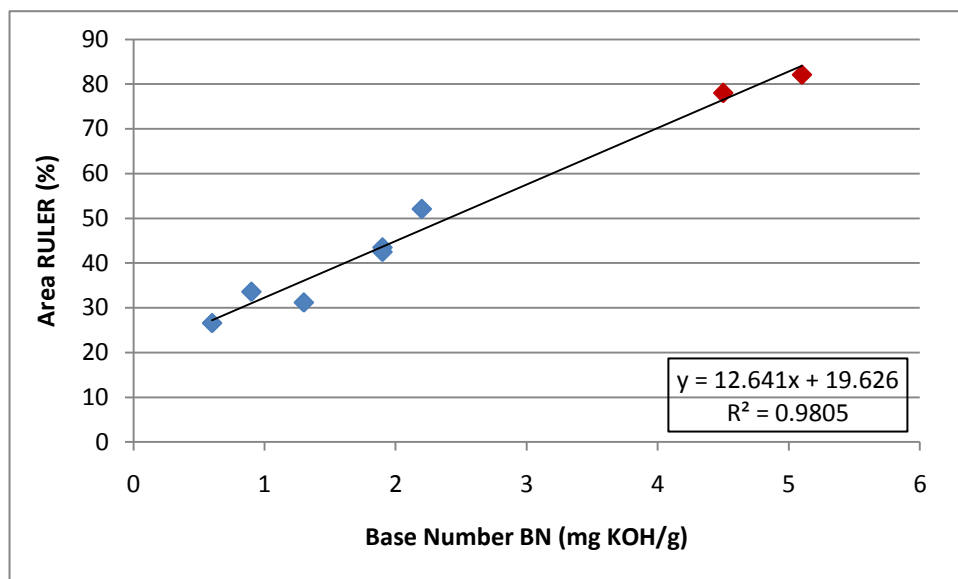Figure with plot containing:
$$y = 1.205x^2 - 4.6919x + 28.803$$
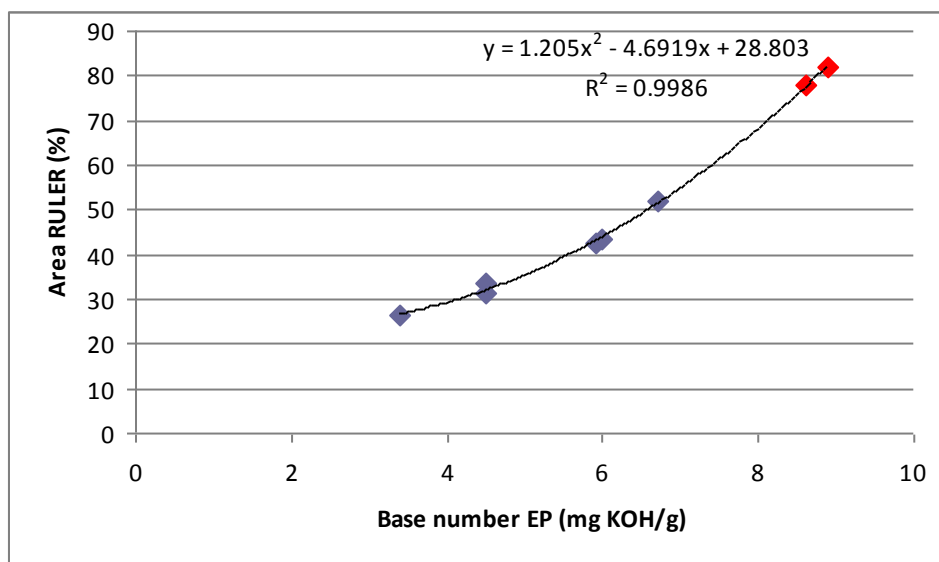$$R^2 = 0.9986$$

Figure 40. Area RULER measurement plotted against base number EP for samples from an engine at SCANIA.
The figure shows that the measurements follow a quadratic correlation.

When Area RULER is plotted against base number EP, see Figure 40, the values seem to follow a quadric curve instead. The two correlations in Figure 39 and Figure 40 seem to consort well with the type of oil tested; however it is not certain that these correlations will be the same for another type of oil. As mentioned before when antioxidants are consumed and Area RULER decreases acids are formed as products of oxidation. The base reserve is thereby consumed trying to neutralize this and consequently there is some relation between base number and Area RULER. To establish whether the found correlations are valid in a larger perspective more different types of oil need to be tested and more subsamples tested from each oil.

5 Conclusions

From the results in chapter 4, the following conclusions could be made concerning lubricant oxidation, RULER, and MPC:

- RULER tests showed that this method can predict when acid number starts to increase. Acid number is an indicator of lubricant degradation meaning that the RULER can predict the remaining useful life of a lubricant. During testing it was possible to follow the process of additive depletion of all tested engine and hydraulic fluids.

- Engine oil analysed with RULER showed that acid number starts to increase when RULER additive has reached a level of 20-25% of the initial value.

- The MPC-analyses showed that the type of lubricant affected the spectrophotometric result. Engine oils were not possible to filter and consequently not suitable for MPC-analysis. RULER worked well for all tested lubricants and should thereby be considered a more general method than MPC.

- Biodiesel quicken the oxidation process considerable when mixed with engine oil. Tests of mixture with 5% biodiesel showed that biodiesel made the antioxidants deplete four times faster compared to engine oil were no biodiesel was present.

- Water added as a catalyst in TOST made the acid number increase more rapidly, water also made the ester in the hydraulic oil more prone to react with esters in the filter used during the MPC-analyse. The reaction made it impossible to perform a MPC-analyse of oil oxidized with water.

- The RULER analyses of samples from a test rig at SCANIA showed that RULER worked just as well for analysing samples from a system closer to reality. These samples contained lead and soot etcetera which were not present in the samples oxidized in the laboratory.

- The samples from the test rig also showed a relationship between lead concentration and the level where the RULER curve starts. Samples which did not show any increase in lead concentration started at the same level as the reference sample in the RULER curve. Samples which showed an increase in lead concentration started at a lower level in the RULER curve. For this particular oil the level where the RULER curve start can be used as an indicator of the lead concentration in the oil and consequently also for oxidation.

- Additionally the rig test samples showed lead concentration starts to increase first when Area RULER has decreased to a level of approximately 35%.

- Area RULER showed a linear correlation to base number and a quadratic correlation to base number EP.

6 Recommendations and future work

RULER-analyses showed promising results and worked well for all lubricants tested in this study. However, investigating other types of lubricants such as turbine oil, gear, and transmission oil could be interesting. More testing of oil from real system and machinery in use, and comparing these results to those given from oil oxidized in the laboratory is another interesting aspect.

The mixture of engine oil and 5% biodiesel showed that the biodiesel quickened the oxidation process considerable. To establish if this is a general result, different types of engine oil could be tested. Additionally the affect of different concentration of biodiesel could be analysed to decide if there is a critical limit were the biodiesel starts to affect the oxidation of the oil.

The correlations found between Area RULER and base number were very interesting. To be able to decide whether or not this applies to other types of lubricants further testing should be needed. Further testing should also be needed to decide if the level of where the RULER curve starts has any connection to the lead concentration and thereby also to the degree of oxidation.

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Appendix A: Engine Oils

Engine Oil A

Table A1. Engine oil A measurements.

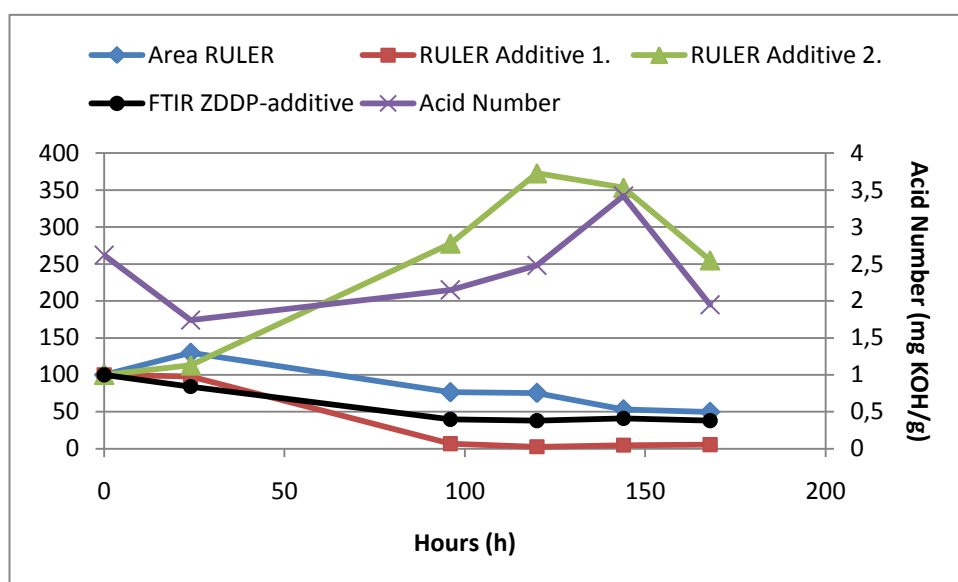| Time (h)	Area RULER (%)	RULER Additive 1 (%)	RULER Additive 2 (%)	Acid Number (mg KOH/g)	FTIR ZDDP-additive (%)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	100	2.62	100	13.96	2.5
24	129.8	97.7	112.8	1.74	84.14		
96	76.4	6.8	277.8	2.15	39.88		
120	75.5	2.7	372.9	2.48	38.17		
144	53.1	4.9	353.2	3.42	41.22		
168	49.7	5.5	255.1	1.95	38.08	14.05	7.5

Figure A1. Influence of oxidation on engine oil A with the secondary additive.
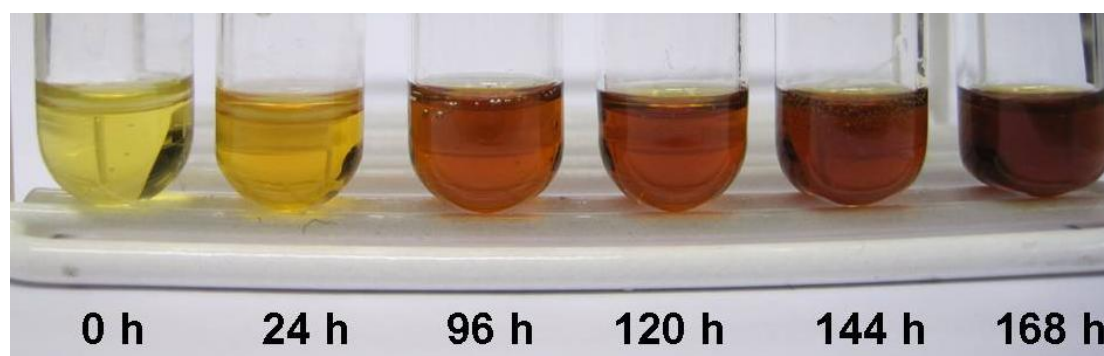

Figure A2. Engine oil A: colour of each subsample.

Engine Oil B

Table A2. Engine oil B measurements.

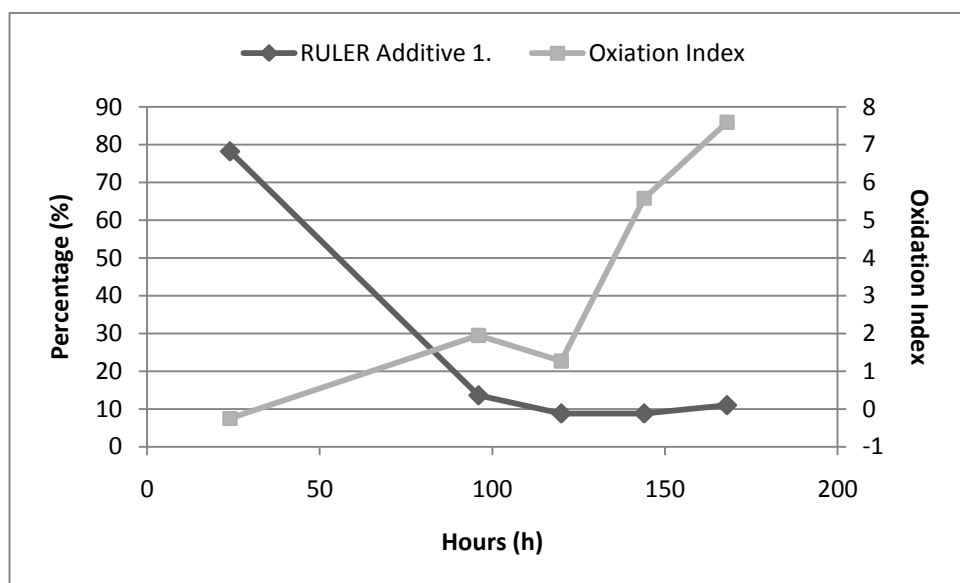| Time (h)	Area RULER (%)	RULER Additive 1 (%)	Acid Number (mg KOH/g)	FTIR ZDDP-additive (%)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	2.68	100	14.60	5
24	91.6	78.2	2.6	96.2		
96	57.8	13.6	2.41	37.1		
120	53.9	8.8	3.28	24.9		
144	50.7	8.8	3.55	22.3		
168	47.8	11	4.55	15.15	14.22	7.5

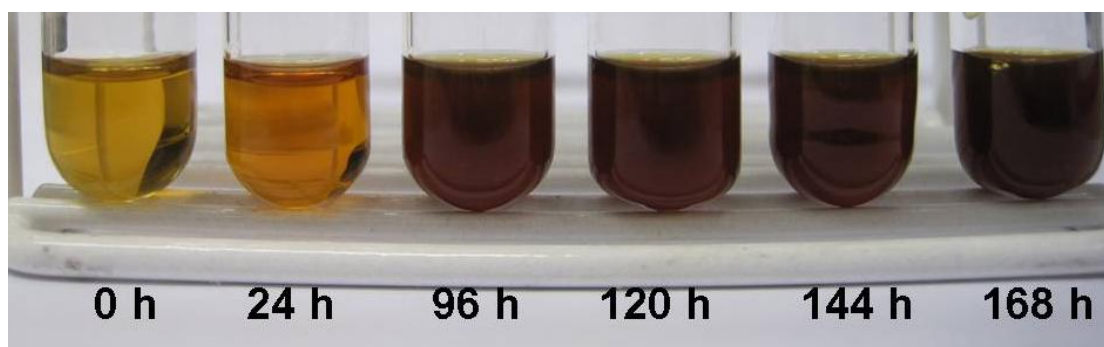*Figure A3. Oxidation index and RULER Additive 1 for engine oil B.*

Figure A4. Engine oil B: colour of each subsample.

Engine Oil C

Table A3. Engine oil C measurements.

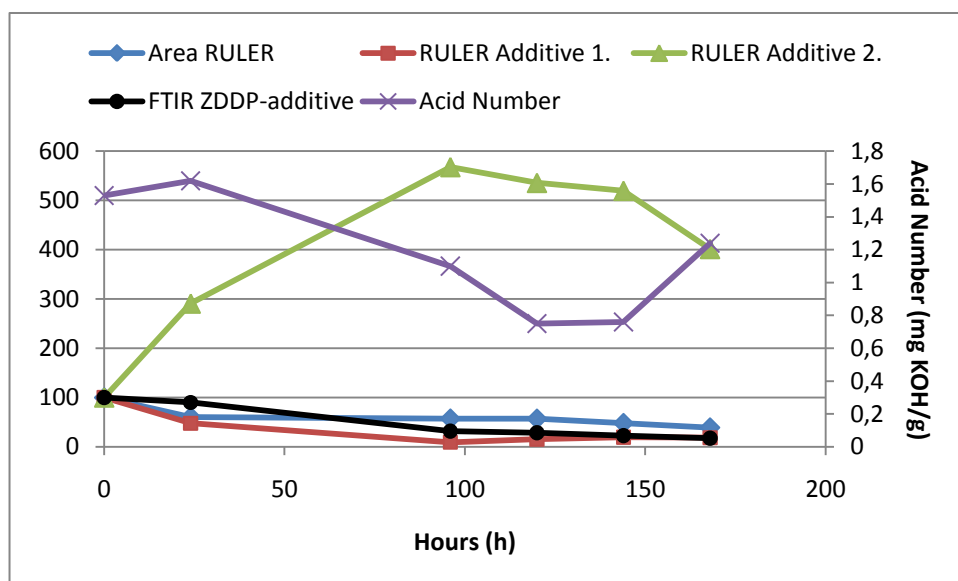| Time (h)	Area RULER (%)	RULER Additive 1 (%)	RULER Additive 2 (%)	Acid Number (mg KOH/g)	FTIR ZDDP-additive (%)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	100	1.53	100	14.43	2.5
24	60.6	47.7	290.7	1.62	90		
96	57.2	9.3	567.8	1.1	31.9		
120	57	15.3	535.7	0.75	28.3		
144	48.1	19.4	519.6	0.76	22.5		
168	39.1	18.5	401.5	1.24	17.4	14.29	7

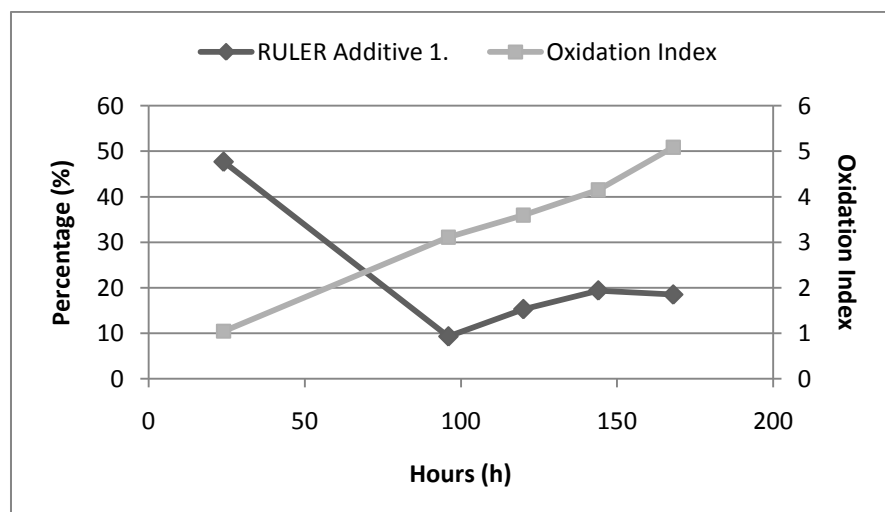*Figure A5. Influence of oxidation on engine oil C with the secondary additive.*

Figure A6. Oxidation index and RULER Additive 1 for engine oil C.
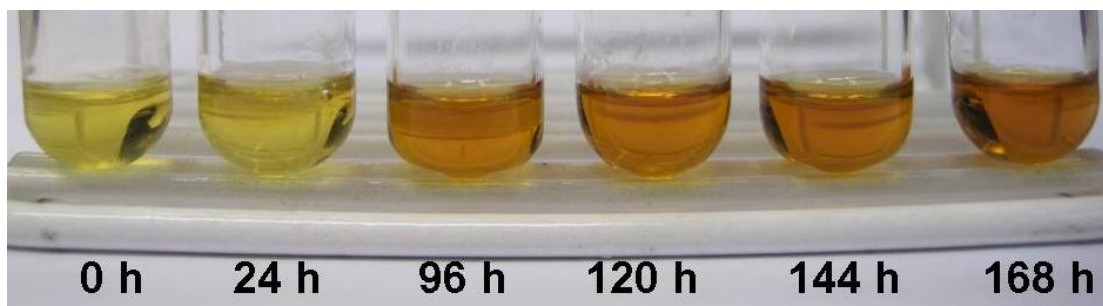
55

Figure A7. Engine oil C: colour of each subsample.

Engine Oil D

Table A4. Engine oil D measurements.

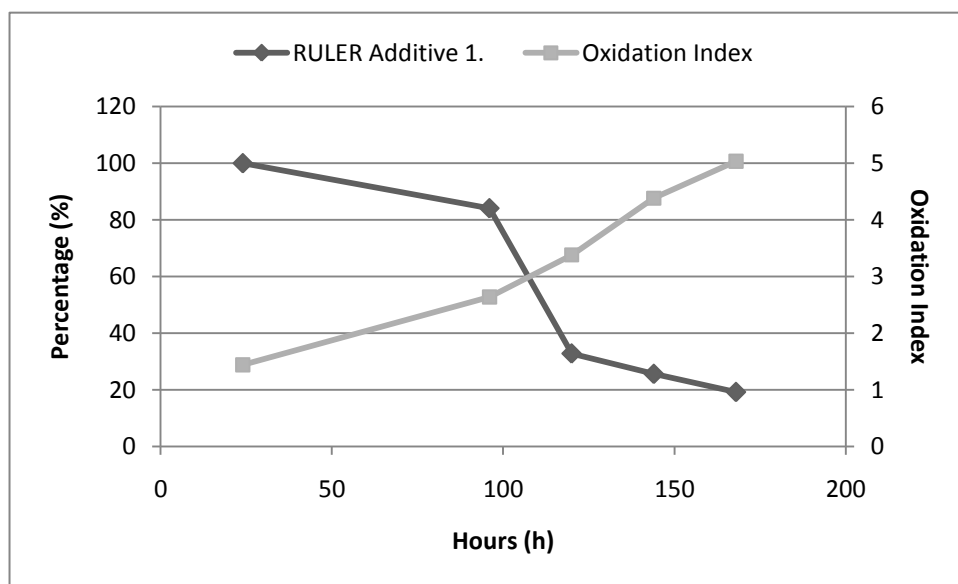| Time (h)	Area RULER (%)	RULER Additive 1 (%)	Acid Number (mg KOH/g)	FTIR ZDDP-additive (%)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	2.19	100	14.51	4.5
24	108.1	84.1	1.95	111		
96	57.7	32.8	1.93	67.2		
120	56.4	25.6	1.4	57.1		
144	57.9	19.2	1.98	48.1		
168	39.2	15.1	2.42	41.5	14.32	6.5

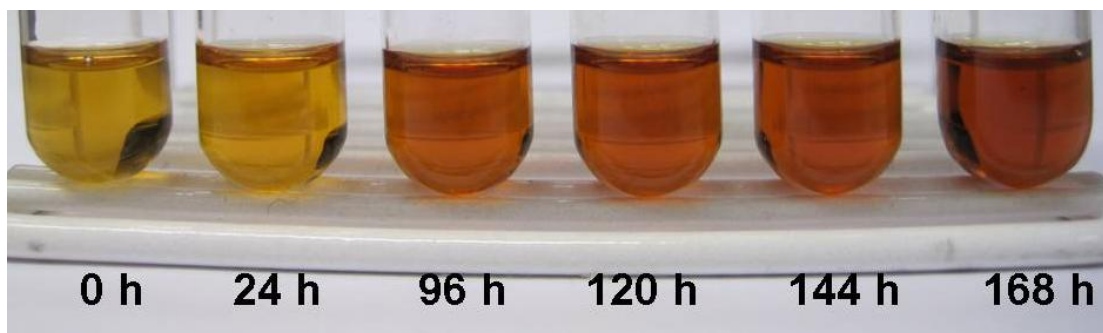*Figure A8. Oxidation index and RULER Additive 1 for engine oil D.*

Figure A9. Engine oil D: colour of each subsample.

Engine Oil A + 5% biodiesel

Table A5. Engine oil A + 5% biodiesel measurements.

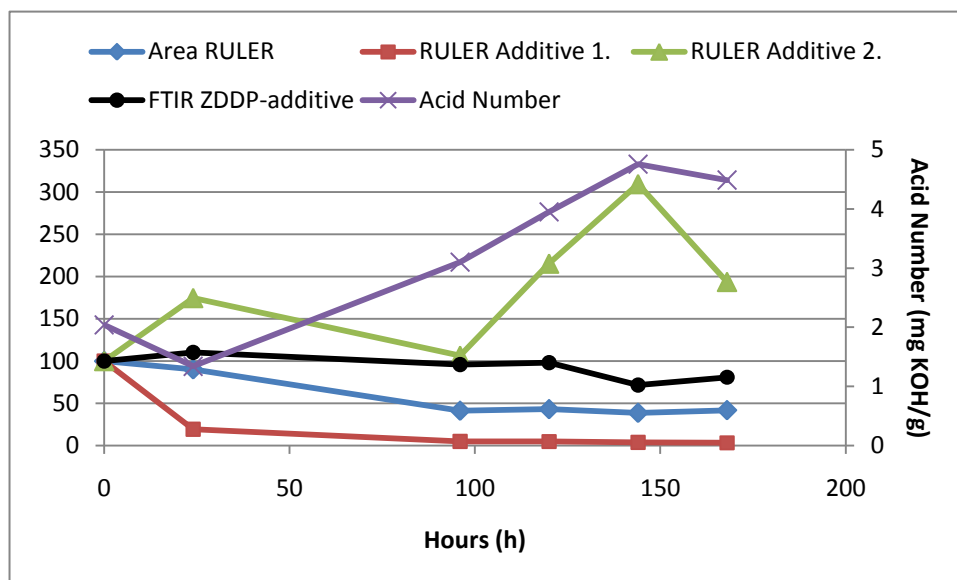| Time (h)	Area RULER (%)	RULER Additive 1 (%)	RULER Additive 2 (%)	Acid Number (mg KOH/g)	FTIR ZDDP-additive (%)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	100	2.04	100	12.17	3
24	90.2	19.3	174.7	1.34	110.25		
96	41.1	5	106.4	3.1	95.9		
120	43	4.7	215.5	3.95	98.1		
144	38.6	3.8	309.7	4.76	71.6		
168	41.8	3.2	193.8	4.49	80.82	12.85	>8

Figure A10. Influence of oxidation on engine oil A + 5% biodiesel with the secondary additive.
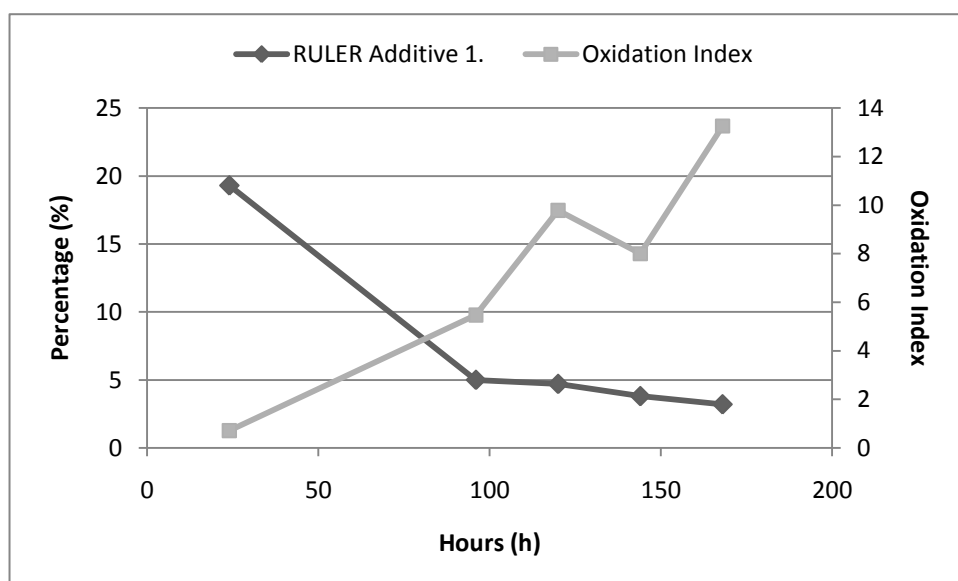
57

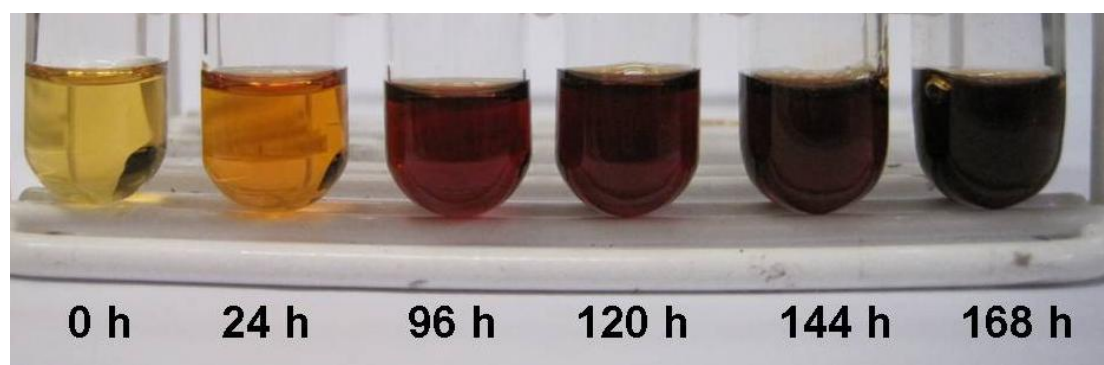*Figure A11. Oxidation index and RULER Additive 1 for engine oil A+ 5% biodiesel.*

Figure A12. Engine oil A+ 5% biodiesel: colour of each subsample.

Appendix B: Hydraulic oils

Hydraulic Oil 1

Table B1. Hydraulic oil 1 measurements.

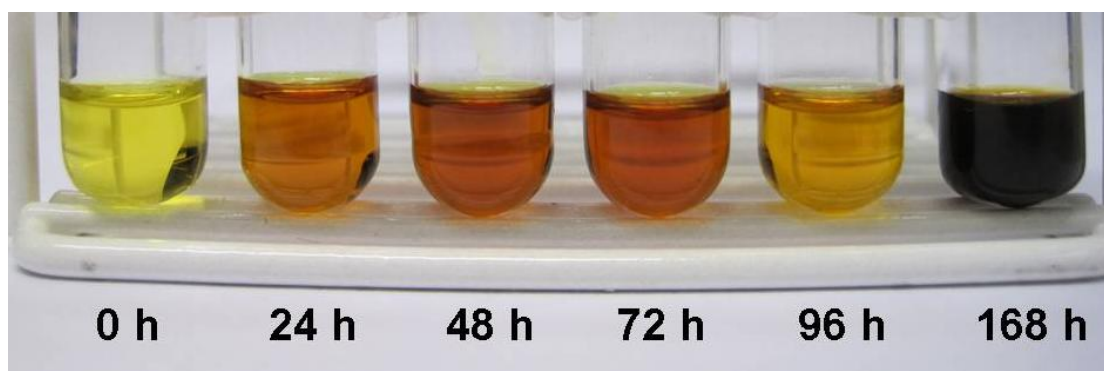| Time (h)	Area RULER	RULER Additive 1	RULER Additive 2	Acid Number (mg KOH/g)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	100	0.29	9.08	2
24	72.4	53	44.7	0.36		
96	44.9	17.4	0.1	0.43		
120	28.5	0.1	0.6	0.88		
144	12.6	0.2	0	2.96		
168	80.4	0	7.7	34.57	20.18	>8

Figure B1. The colour of each subsample from hydraulic oil 1.

Hydraulic Oil 2

Table B2. Hydraulic oil 2 measurements.

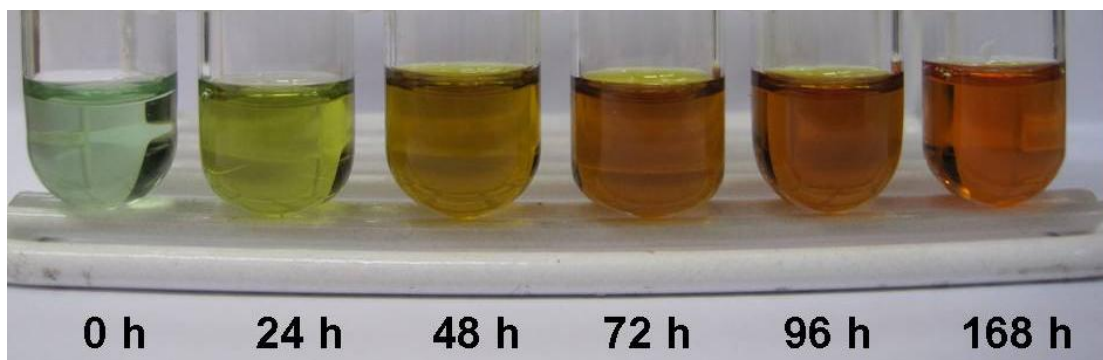| Time (h)	Area RULER	RULER Additive 1	RULER Additive 2	Acid Number (mg KOH/g)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	100	1.65	8.35	1.5
24	81.8	84.6	74.5	1.78		
96	58.3	44.4	51.1	1.75		
120	39.5	26.2	46	2.18		
144	19.2	8.7	14.6	3.18		
168	10.7	0.9	0	14.69	25.73	6

Figure B2. Hydraulic oil 1: the colour of each subsample.

Hydraulic Oil 2 + water

Table B3. Hydraulic oil 2 + water measurements.

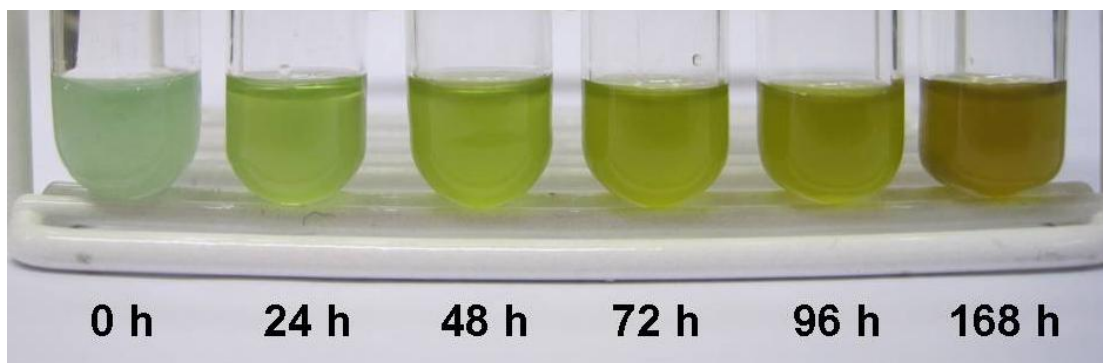| Time (h)	Area RULER	RULER Additive 1	RULER Additive 2	Acid Number (mg KOH/g)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	100	1.38	8.28	7.5
24	67.2	65.7	70.3	3.51		
96	63.4	52.3	64.9	6.45		
120	70.1	52.1	69.9	9.86		
144	69.5	50	55.8	14.29		
168	82.7	64.8	76	36.6	7.75	8

Figure B3. Hydraulic oil 2 + water: the colour of each subsample.

Hydraulic Oil 3

Table B4. Hydraulic oil 3 measurements.

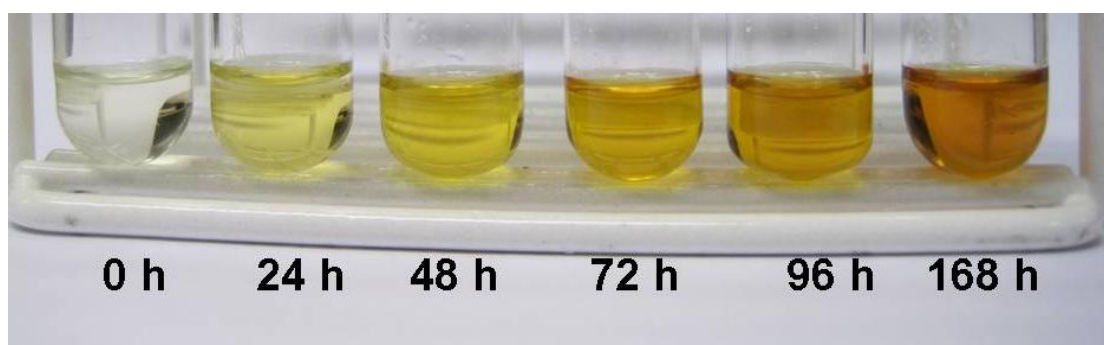| Time (h)	Area RULER	RULER Additive 1	Acid Number (mg KOH/g)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	2.11	8.6	0.5
24	87.9	70.2	1.95		
96	91.5	62.8	1.75		
120	92.3	55	1.89		
144	102.4	40.9	1.81		
168	54.8	28.8	0.69	9.29	5.5

Figure B4. Hydraulic oil 3: the colour of each subsample.

Hydraulic Oil 4

Table B5. Hydraulic oil 4 measurements.

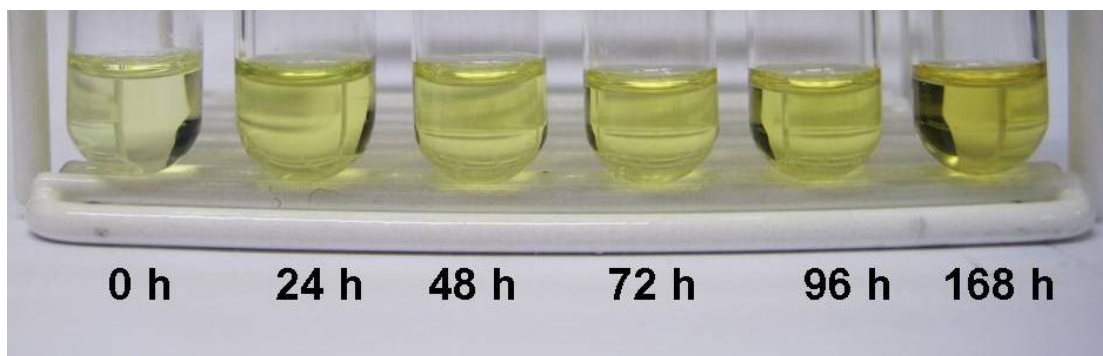| Time (h)	Area RULER	RULER Additive 1	Acid Number (mg KOH/g)	Viscosity @ 100°C (mm²/s)	ASTM color scale
0	100	100	0.27	14.51	5
24	112.2	94.9	0.17		
96	119.1	84.4	0.3		
120	78.8	77.3	0.67		
144	68.1	39.5	0.43		
168	95.6	57.6	0.55	14.32	7.5

Figure B5. Hydraulic oil 4: the colour of each subsample.

Appendix C: Samples from SCANIA

Table C 1. Test rig sample measurements.

Time total[1] (h)	Time oil[2] (h)	Area RULER	RULER Additive 1	Acid Number (mg KOH/g)	Base Number (mg KOH/g)	Base Number EP (mg KOH/g)	Pb (mg/kg)
223	178	52.1	1.8	3.7	2.2	6.7	17
255	210	43.5	0	1.7	1.9	6	17
279	234	42.5	0	5.6	1.9	5.9	16
302	257	31.2	0	6.9	1.3	4.5	21
315	270	33.6	0	9	0.9	4.5	32
340	295	26.6	0	4.8	0.6	3.4	59
363	18	82.1	42.2	2.2	5.1	8.9	14
387	42	78	31.2	3.8	4.5	8.6	15

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[1] Time total means the total time that the rig has been running.

[2] Time oil means the time the rig has been running since the last oil change.

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