Deposit formation on cylinder liner surfaces in medium-speed engines

by

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Preface

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Synopsis

The presence of deposits in the honing grooves in diesel engine cylinder liners can cause a severe increase in the consumption of lubricating oil. These deposits may appear amber in which case they may be referred to as 'liner lacquerer' or be nearly invisible in which case they are often referred to as 'transparent glaze' or 'bore glaze' in the marine sector. The formation of these deposits is believed to be influenced by engine design, engine load, fuel composition and lubricating oil composition. This relationship has, however, not been well understood and little material has been published on this subject. This thesis describes an investigation of this phenomenon. The problem has been approached by studying the composition of deposit samples, studying cases of deposit formation in the field and through experimental work.

As a result of this work, it is hypothesized that the root cause of the deposit formation is a mismatch between the rate of formation of oil insoluble material on or within the oil film and the oil film dispersing power and exchange rate. A large number of parameters will affect this balance which explains the sliding shift in appearance and composition of 'liner lacquer' and 'bore glaze' and the difficulty in identifying the cause of this problem.

A combined mass balance and chemical kinetics approach is used to bridge the gap between fundamental deposit theory and tangible engine related parameters. It is thus possible to rationalize the formation of deposits on cylinder liners. This understanding is sufficient to point out which factors should be considered in terms of the prevention of deposit formation and to present a viable hypothesis on the reason for the deposit formation in the engines that have been investigated in the course of this work as summarized in the following paragraph.

The presence of deposit indicates that the dispersing power and transport rate of the oil film is insufficient to deal with the deposit precursors being formed. This is believed related to extensive low load operation which is associated with both low liner temperatures and low nominal oil consumption in these engines. Low liner temperatures will encourage the formation of insoluble material due to condensation of sulphuric acid precursors, while low oil consumption is believed to indicate low oil film exchange which reduces the transport of matter and also contributes to oil film oxidation by prolonging the exposure to combustion gases.

Nomenclature

ACEA	Association des Constructeurs Europeéns de l`Automobile (Association of European Automotive Manufacturers)
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BDC	Bottom dead center. Lower reversal of piston movement.
Brightstock	Lubricant base made of de-asphalted vacuum residue
Bsfc	Brake specific fuel consumption
Bsoc	Brake specific (lubricating) oil consumption
C	Carbon
CEC	Coordinating European Council
Cetane Index	Prediction of fuel autoignitability based upon distillation and density data.
C_F	Concentration of involatile material in oil film
CIMAC	International Council on Combustion Engines
C_L	Concentration of involatile material in liquid losses
C_{OIL}	Concentration of involatile material in fresh oil
C_{DOWN}	Concentration of involatile material in oil removed by piston rings
COLGO	Coker Light Gas Oil.
CRC	Coordinating Research Council
C_V	Concentration of involatile material in volatile losses
DMA	Standard 'distillate' quality gas oil specified by ISO 8217
EDS	Energy dispersive spectroscopy
FBP	Final boiling point
FT-IR	Fourier Transform Infrared Spectroscopy
H	Hydrogen
IBP	Initial boiling point

ICP	Inductively coupled plasma (here: emission spectrometry)
Kinematic Viscosity	Measure of the resistance of a fluid to flow under gravity, unit [mm^2/s = cSt]
LCO	Light Cycle Oil
MCR	Maximum continuous rating.
MEP	Mean Effective Pressure
R	Generic hydrocarbon
Mw	Molecular weight [g / mol]
R_a	Average surface roughness
R_z	Average maximum peak to valley height
SA	Sulphated Ash. Weight of ash converted to sulphate
SAE	Society of Automotive Engineers (Also: viscosity grade)
SEM	Scanning Electron Microscopy
SN	Solvent neutral base oil fraction
Surfactant	Surface active molecule
TBN	Total Base Number. Alkaline reserve in oil measured by titration and expressed as KOH equivalent [mg KOH/g]
TBN index	Used oil TBN / Fresh oil TBN
TDC	Top dead center. Upper reversal of piston movement.
TEM	Transmission Electron Microscopy
V_{DOWN}	Volume of oil film removed by piston rings
V_F	Volume of oil film
V_L	Volume liquid losses
V_{UP}	Volume fresh oil supplied to oil film by piston rings
V_V	Volume of volatile losses
Dynamic Viscosity	A measure of the resistance of a liquid to flow, unit [Pa*s = 10^3 cP]
XRD	X-ray diffraction spectroscopy
XRF	X-ray fluorescence

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Chapter 1

Introduction

1.1 Background

The diesel engine has been the workhorse in the marine industry for more than 50 years and is continuously developed. Over the years this has resulted in smaller and lighter engines with higher working temperatures and pressures. The development of new refining processes, better catalysts and improved process control has caused a change in marine fuels composition towards more complex mixtures of increasingly converted hydrocarbon. I later years, international agreements to reduce maritime pollution such as the IMO-NO_x restrictions and legal limits on fuel sulphur content have made further impact on engine design and fuel composition. Forthcoming regulations on heavy fuel sulphur levels may affect the composition of all grades of marine distillate fuels

Diesel engine technology is a mix of accumulated experience and knowledge with more thorough theoretical foundation. Component design has benefited from the increasing use and capabilities of FEM, however processes like combustion, lubricant degradation and formation of pollutants are difficult to model and hence predictions and development rely largely on tests and experience. Developments challenge the established knowledge and it may be difficult to identify the causes of problems that were not anticipated. The formation of cylinder liner deposits is such a phenomenon.

Cylinder liner deposits cause high oil consumption which is a waste and also a source of excessive soot pollution. Additionally, liner deposits demand extra maintenance in form of internal cleaning or they may cause collateral damage.

A solution to the liner deposit problems will save oil, reduce maintenance and off-hire costs and save the environment from unnecessary particulates and soot emissions caused by the excessive combustion of lubricating oil.

1.2 Motivation

The motivation for the work is the need to better understand the mechanisms that cause the accumulation of cylinder liner deposits in order to find the best solutions to deal with this problem.

1.3 Approach

A possible approach in this situation is to examine what has changed since the problems started. This may be revealing, however it has shortcomings since

- the start of this problem is not well defined
- nearly everything changes when examined closely
- the number of factors to consider is large and documentation scarce
- it may not be possible to revoke the change if found

For this reason, a more fundamental understanding of problems is desired. The following activities were initiated in order to increase our understanding of these deposits:

1. Investigate the composition to understand what liner deposits are
2. Investigate reasons for their accumulation

The first activity is essentially a case of specialized chemical analysis, demanding in terms of obtaining and preparing samples as well as interpretation of results. The second necessitates the identification of conditions that fulfil the following postulates:

- Whenever the conditions are met, deposits are formed
- Deposits are never formed whenever the conditions are not met

Such criteria are only practical and useful if the fundamental process is being studied. When a diesel engine is studied, the parameters that are actually monitored and / or controlled may be distant to the fundamental process. For instance, the oxidative stress of the lubricating oil on the cylinder wall may differ between engines under what appears to be identical conditions judging by general diesel engine design and operating parameters. Moreover, a given change can cause the stress to increase in one engine, and decrease in another. It is thus not certain that general relations between engine parameters and deposit formation exist, and a correlation derived from experiments with one particular engine can not be generalized forthwith. While loosely defined risk factors possibly could be identified, this would not increase our fundamental understanding.

Many of the uncertainties associated with research on diesel engines can be avoided in studies using simpler laboratory setups where postulates regarding cause and effect may be applied. Knowledge obtained this way can provide insight, but the relevance and application to diesel engine problem solving may sometimes be questionable. Secondly, increasingly simple or fundamental experiments are increasingly likely to be described in literature, hence the choice of approach is not self-evident

In light of the previous considerations, the following approach was made to the problem of liner deposits:

1. Study relevant scientific literature
2. Get first hand experience through case studies
3. Investigate distribution and chemical composition of liner deposits
4. Attempt to replicate deposit formation in the laboratory

1.4 Framework for the thesis

The approach to the problem is described by four ordered points, however work in all areas has been simultaneous. The organization of this thesis reflects the structure of the approach but is not chronological. The thesis has seven chapters:

1. Introduction
2. Literature
3. Liner deposits
4. Field studies
5. Experimental work
6. Discussion
7. Conclusion

The Introduction includes the current section as well as a brief introduction to cylinder liner deposits.

The Literature chapter covers an extensive study of scientific literature needed to describe the cylinder liner environment, chemical reaction mechanisms, fuels lubricants, additives, as well as other deposit phenomena.

The Liner deposits chapter provides background information on analytical techniques, and interpretations of results from chemical analysis. Information on deposit distribution and solubility in selected solvents is also presented. Somewhat in spite of the chapter title, other deposits found in conjunction with liner deposits are also briefly investigated in this chapter.

The Case studies chapter reviews information obtained from field studies of liner deposits and also some reliable unpublished but written second-hand information.

The Experimental works chapter reviews test aiming to replicate liner deposits in an accelerated test.

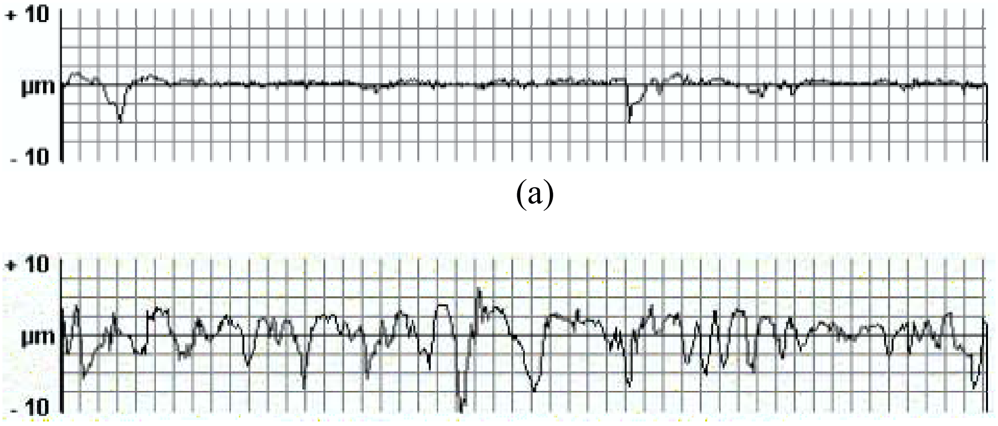
The Discussion and conclusion chapter ties the former work together and uses a combined mass balance and chemical kinetics approach to discuss the fundamental process. A hypothesis for the deposit formation is presented and suggestions to further the research on this important topic are made.

1.5 Introduction to cylinder liner deposits

Liner deposits are usually found in four-stroke medium-speed marine diesel engines fuelled by gas oil. Fundamental aspects and a definition of liner deposits is presented in the following while a more extensive and general review is provided in chapter 2.

1.5.1 The effect of liner deposits

Cylinder liners have a carefully machined surface with a plateau on which the piston rings run and grooves that help retain oil on the liner. The grooves are machined in two directions in a crosshatch pattern. Liner deposits accumulate in these grooves, thereby interfering with the proper lubrication of the piston cylinder assembly. As a consequence of this, more lubricating oil is mixed with the combustion gas and ejected via the exhaust. Surface traces showing a deposited surface prior to and after cleaning with acetic acid is shown in Figure 1.



(a)

(b)

Figure 1. *Surface trace of typical liner surface. (a) with deposit (b) same surface without deposit.*

The severity of the deposits varies from case to case. A few typical oil consumption histories are shown in Figure 2 which shows the oil consumption recorded in three vessels. The oil consumption is expressed as a percentage of fuel consumption to reduce the effect of engine operation. Inaccuracy in oil consumption measurements as well as differences in service history makes it difficult to define a clear-cut starting point of the deposit problems.

The non-linear increase in oil consumption which develops progressively over an extended time period is a typical symptom of liner deposits. High oil consumption may lead to formation of deposits in other locations due to incomplete combustion of the lubricating oil, particularly on the piston crown.

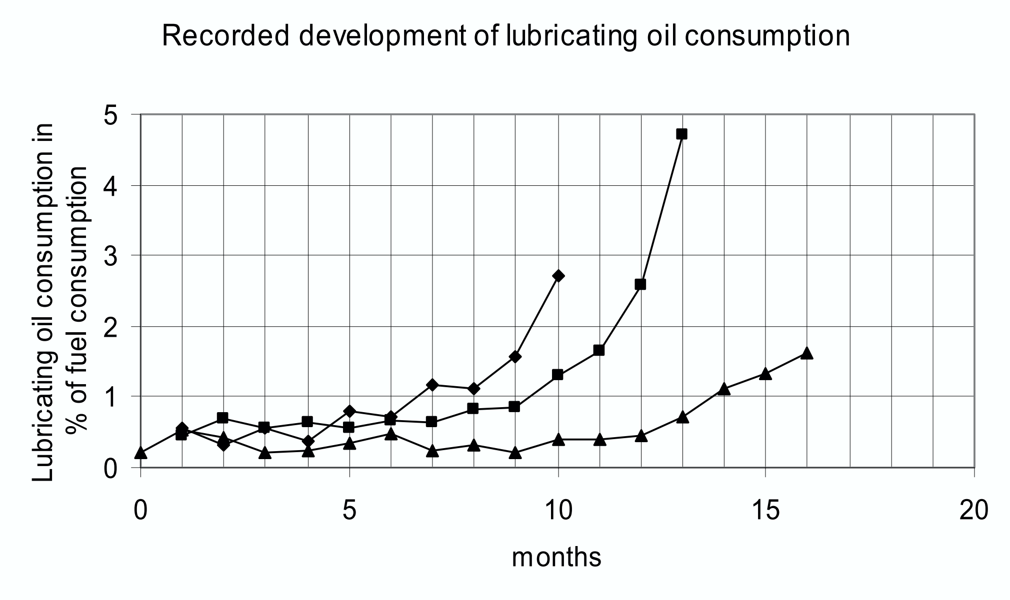


Figure 2 *Lubricating oil consumption in engines with liner deposits*

1.5.2 Oil consumption and deposits

The link between high oil consumption and liner deposits has already been presented. The arguments that support this well established view are as follows:

The oil consumption rate returns to normal levels when the surface is restored to the original condition by honing.

Liner deposits cause a measurable smoothing of the liner surface. The purpose of the honing grooves is to help retain lubricating oil on the liner, hence an increased amount of oil may be scraped in front of the piston ring when the oil groove volume is critically reduced.

Excessive smoothing due to abrasive wear normally referred to as 'bore polishing' is also known to cause high oil consumption. [1] [2]

Severe deposits are also found on pistons in some cases of high oil consumption. Arguably, piston deposits can affect oil consumption, however the high oil consumption level associated with liner deposits suggests that the mechanism described in [2], i.e. disturbed the pressure build-up over the top ring is not the dominating mechanism. Other known mechanisms like clogged oil scraper ring drain holes and stuck piston rings can be eliminated by visual inspection.

The link between deposits and oil consumption has also been forwarded in literature [3] and appears broadly accepted. Confidence in this relationship is strong enough to make it the core of the definition of liner deposits used in this work.

1.5.3 A definition of liner deposits

The following definition of the liner deposits is used in this research:

Liner deposits constitute any deposit formed upon cylinder liners that bring about a change in the surface topography to cause an increase in lubricating oil consumption.

1.5.4 Liner deposits at a glance

The appearance of liner deposits vary from case to case. A frequent categorization of liner deposits in the marine context is 'liner lacquer' meaning amber and brown deposits, while term 'bore glazing' is used to describe 'invisible' deposit. This classification of deposits has been adapted in this thesis. The reader is advised, however, that the terms lacquer and glaze are applied in other contexts to describe a variety of different deposits.

The deposit may discolour entire liners, but closer scrutiny has revealed an uneven deposit distribution in all cases investigated. Deposits usually appear darker when viewed at an angle, probably because more observed light is reflected from the grooves wherein most deposit is located. Some sample pictures are provided in Figure 3.

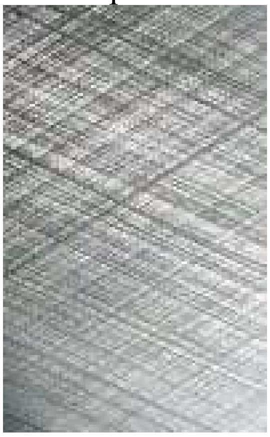
Amber lacquer Close up: 	Dark lacquer Close up: 	Glazed liner Close up: 
Same liner at an angle: 	Same liner at an angle: 	Same liner at an angle: 

Figure 3 *Different types cylinder liner deposits*

Chapter 2

Literature Review

Scientific information on liner deposits is scarce. Based on the review of the liner deposits phenomenon in the forthcoming chapter 2.1 it appeared rather obvious that the literature review should include information on fuels, lubricating oils, engine design and operational factors that determine the conditions on the cylinder liner in addition to general deposit formation theory.

As is usually the case when seeking answers to difficult scientific questions, the deeper answers frequently bring along new questions or restrictions on the validity of the answer. A balance must be found between level of detail and general applicability. Secondly, the width of this topic also limits the level of detail than can be studied. The literature review has been divided into six parts:

- Liner deposits
- Chemical kinetics and radical mechanisms
- Marine fuels and lubricants
- The cylinder liner environment
- Engine deposits
- Deposit formation

2.1 Review of information on liner deposits

In spite of a determined search, few publications dealing with liner deposits have been found. Patents and papers published by industry show that liner deposits has been the subject of some research outside of public domain. In the absence of scientific papers, other sources of information have been surveyed. These are:

- Reports from industry organizations CEC and CIMAC
- Industry papers and advertisements
- Patents
- Service reports
- Non-scientific journals
- Expert opinions and engine user experience

Although claims from these sources may be unsubstantiated scientifically speaking, and cannot be regarded as completely unbiased, it should not be ignored. Some ideas and formulations recur several times in this material. It is sometimes not clear whether the author relies on unique observations or information from previous work.

2.1.1 General interactions

There is general agreement amongst the sources that formation and accumulation of deposits appears dependent on the interaction between fuel composition, lubricant formulation, engine design and loading.

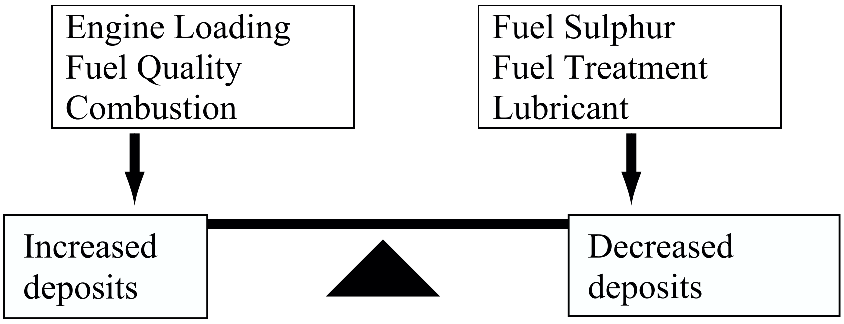


Figure 2-1 *Lacquer balance by Allen* [7]

This relationship was illustrated by Allen [7] as shown in Figure 2-1. Observations and claims in literature are reviewed below. The material generally refers to 'liner lacquer' which is amber or brown liner deposits.

2.1.1.1 History and background

The history of liner lacquer deposits is not well documented. Incidents of liner lacquering have been reported with at least two engine manufacturers since the mid seventies, but the CEC report [4] indicates a marked increase in the problem frequency in the eighties. A Dutch surveyor [5] reported that 'liner lacquering and bore polishing' in his experience was most severe from 1985-1992 at which time other problems became more dominant. A survey conducted by the CEC indicated that problems were specific to certain geographical areas, however deposit have been observed in Europe, Asia and America suggesting that if it is a local phenomenon, the deposit 'risk zones' are widely distributed. One engine manufacturer claims that the phenomenon in middle of the nineties is more or less a world-wide phenomenon, while liner lacquer is mentioned as a European problem in the 1998 Annual Review of the Bulletin of Japanese marine engineering society. [6] Transparent bore glaze deposits have been seen in tractors and trucks as well as marine engines.

2.1.1.2 Influence of engine type and design

The problem is most frequently encountered on four stroke medium-speed engines. The problems are seen in engines with different designs and by different manufactures. Some factors that have been mentioned as indicative of increased risk of liner deposits are: [4] [3]

- engines designed for high mean effective pressures (>20 bar)
- engines designed for low bsoc and bsfc
- higher fuel injection pressures
- reduction in cylinder liner temperatures
- modifications to liner roughness
- piston ring designs
- flat combustion chamber

Low liner temperatures was identified as problematic in a full scale experiment, where the fuel injector angle had been raised such that more burning fuel impinged on the liner leading to increased liner deposits. [8]

An engine manufacturer using flat combustion chambers has observed the opposite in the field, i.e. that high liner temperatures should be avoided.

One manufacturer claims that the use of flame ring can reduce liner lacquer. Liner deposits have also been observed on two stroke engines. A case study of wear associated with a deposit on a cylinder liner has been presented in [9].

2.1.1.3 Influence of fuel on liner deposits

Liner deposits typically form in engines burning low sulphur distillate fuel. A critical level has not been defined but problems have been reported with sulphur levels <0.5 % weight. Today, <0.2 % w/w fuel is required by law in the North Sea area hence all fuel used in this area can be considered 'low sulphur' with regards to the aforementioned observations. It is sometimes postulated that the effect of the fuel sulphur is to prevent deposit accumulation by a continuous deposit dissolving mechanism.

Liner lacquer deposits have also been observed in spark ignited medium speed engines fuelled by natural gas, and bore glaze in gasoline fuelled engines. It has, however, been suggested by Allen[3], as well as in patent applications [10] and advertisements [11] that formation of liner deposits is related to high boiling point and or aromatic fuel fractions. However, a report from 1993 [4] states that *it has yet to be clearly established whether the use of light cycle gas oil in the heating fuel pool had any influence on the liner lacquering problem. Nor have data on fuel aromatic contents become available to establish a link with fuel constitution*. The claims in the patents and advertisements are more recent than this report, but they are not substantiated by data.

The effect of fuel blending stocks was investigated in the full scale experiment in [8]. An observation in this work was that different fuels created different distributions of deposits between liner and piston and it was stated that *fuel clearly influences liner lacquer formation, though the differences between gasoils from different sources is small*.

One patent application [13] claims that synthetic liner deposit can be made using anthraquinone as a model for condensing fuel.

2.1.1.4 Influence of combustion

The combustion of the fuel is dependent upon the interaction of engine design, load, fuel composition and engine ambient conditions. The formation of deposits has been hypothesized to be related to condensation of products of incomplete combustion or increased thermal load from the combustion to the liner oil film. One company has expressed the view that *liner lacquers are a direct result of incomplete combustion of the high molecular weight components often present in marine gas oil*.[11]

2.1.1.5 Influence of lubricating oil

Some lubricants appear to perform better than others with regards to the prevention of liner deposits. Analysis by an engine manufacturer indicated a relationship between deposits and oil SA and TBN in the sense that higher TBN and SA indicated a higher deposit risk. The same trend was observed in engine tests performed by an oil company. [8], however lowering the additive treat rate will be at the risk of other problems. One company has proposed an 'advised range' for the TBN number depending on the fuel sulphur level to simultaneously prevent liner deposits and other problems [12]. Other lubricant manufacturers have not provided such explicit guidelines. One reason may be that TBN alone is not a generally consistent indicator of oil performance, as discussed in [11], hence this relationship may be valid only for certain lubricants.

The difference in performance between oils may also be related to differences in oxidative stability. This was mentioned in the CEC report [4] and also in several advertisements for high performance oils. However, several different anti-oxidant additive technologies including radical scavengers and hydroperoxide decomposers were evaluated in the engine tests reported in [8], but none of the tested anti-oxidants had any effect on the deposit formation in these accelerated tests.

A representative of an engine manufacturer whose engines due to the use of tapered piston heads typically use lower TBN / SA oils than other reported that they did not have amber or dark deposits, but had experienced glazed liners. Recently, an additive producer has claimed that liner lacquer can be reduced by use of complex detergents [15].

2.1.1.6 Influence of engine loading

The reported liner deposits were usually observed in engines operated with cyclic loading, the high load typically being 100% MCR or overload. Engine tests performed by an oil company indicated that continuous high load operation was more severe than cycling load. A reduction in oil consumption (and thus lacquer deposits) is reported in cases where general engine loading was reduced.

Several sources recommend that the engine is not heavily loaded at low speed because this will cause unfavorable combustion conditions. It is also recommended that inlet air temperatures should not be 'too low'

2.1.1.7 About the composition of the deposits

Liner deposits are reported to consist of inorganic material that is derived from lubricant additives. According to [8] the inorganic material may constitute 80% of the deposit by weight, most of which reportedly are salts of Zn and Ca. Reference [4] report that calcium in form of calcium carbonate has been detected at significant levels. Liner lacquer deposits are also reported explicitly not to contain soot.

The deposit also typically consists of organic material that is believed to be polymerized hydrocarbon. This material is typically referred to as a resin and suspected to act as a binder for the inorganic salts. Whether the hydrocarbon resin is primarily derived from the lubricant or the fuel has not been established. A calcium sulphonate glaze where resins were not detected has also been reported.

Liner deposits can be removed by alcoholic acetic acid. This has been interpreted as a support to the claim that inorganic salts are predominant components.

Deposits have not been observed to be uniformly distributed around nor down the liner. It has been claimed that the deposits initiate in the top of the liner on the antithrust side of the engine, and that it eventually covers the upper 1/3 of the liner.

It has also been reported that liner lacquer deposits frequently are accompanied with oil insoluble material and piston deposits.

2.1.1.8 Proposed mechanisms of formation

It has been suggested that liner lacquer deposits are formed when a resinous material that adheres strongly to the liner is formed on the cylinder wall. This material is believed to be the initiated by either or both mechanisms suggested below:

1. The lubricant oil film is degraded by prolonged exposure to combustion gases and increased thermal stress.
2. Reactive species formed from cracking and partial combustion of fuel condense or impinge on the cylinder liner.

The resinous material is formed by oxidising and polymerizing reactions within the oil film. Additive material is believed to be entangled or bound

by this resinous material and distributed on the liner by the piston rings. [4][8]
A mechanism to explain the formation of glaze in marine diesel engines has not been proposed.

2.1.2 Liner deposits outside the marine sector

Deposits on cylinder liners have been reported in many applications including tractor diesel engines, four stroke gasoline engines found in motorcycles, vintage cars, light propeller aircraft and lawnmowers. The distinction between lacquer and glaze appears to be used primarily for medium speed engines. In case of other engines the term 'glaze' or 'bore glaze' appears universally applied to liner deposits with appearances ranging from invisible to dark black and blueish deposits.
Bore glaze is frequently reported during break in following cylinder overhaul. Montgommery [16] found that a smoothing surface coating consisting of Fe3O4 and a carbon was formed during simulated running-in experiments. These constituents were also found in authentic glaze formed during run-in. A mechanic with extensive engine service and teaching experience provided the observations on the topic of glaze formation presented in Table 2-1. [17]

Personal correspondence with this author has established that glaze in these engines is typically black or blue in colour and is related to the use of multigrade oils. The use of a high performance monograde reportedly eliminated this problem. It was also established that the engines frequently were running on less than full oil levels.

2.1.3 Comment to review

The difficulties in determining a cause of liner deposits and the apparent lack of consistency in the material reviewed above can be related to two core issues: As discussed in the introduction, the parameters we observe do not consistently describe what the conditions are upon the cylinder liner where the deposits are formed. Secondly, the deposit may appear similar even if they are not be the same or caused by the same mechanism.

TABLE 2-1 ABOUT BORE GLAZE IN SMALL ENGINES [17]

- *Glaze describes oil burned and baked onto a surface.*
- *Glaze is insulative, very hard, polishes to a high shine, wears piston rings, and can be removed only with an abrasive material or a cylinder hone.*
- *A glazed bore is invariably the result of surplus lubricating oil being left behind by the piston rings because they have not been "pushed hard enough" against the cylinder bore surface to remove most of the oil.*
- *The piston rings of any engine under a too light load will not be pressed as firmly against the cylinder bore surface as in an engine under a heavier loading.*
- *Piston rings scrape harder against the cylinder bore surface during the combustion and exhaust strokes as the gas pressure increases between the piston rings and piston ring grooves.*
- *When excess oil is left behind it is burned onto the bore surface and forms a very hard glazed smooth finish.*
- *Light or under load running will always result in a glazed bore.*
- *The time taken to glaze a bore will vary according to the lubricating oil used, the load applied, the length of time run under light load, and local air temperature.*
- *Any engine with a glazed cylinder bore will always use lots of oil and will cause complete engine failure if not quickly and correctly repaired.*
- *A glazed bore will usually be restored to standard by re-honing and fitting new rings.*
- *A glazed bore is not an engine fault it is an operator or application problem.*
- *Sometimes the only solution to overcome light loading is to include a dummy load such as an electric bar heater on a generator.*
- *Most petrol engines prefer 60% to 80% loading if running for long periods of time.*
- *Diesel engines are "happier" with 75% to 90% loading if running for long periods of time.*
- *Engines (using correct grade and quantity of frequently changed oil) that run at variable speeds and changing loads very rarely get a glazed bore.*

2.2 Chemical kinetics and Radical mechanisms

This chapter reviews fundamental theory on chemical kinetics and mechanisms of hydrocarbon (fuel and lubricant) transformation. The reader will find relatively few references to scientific papers in this part as this material is generally well established and presented in specialist text books.

2.2.1 Basic chemical kinetics

Chemical reactions are believed to occur as molecules collide with sufficient energy at an angle that is suitable for the reaction. This theory is expressed in the Arrhenius equation where the chemical reaction rate k is expressed as:

$$k = Ae^{-E^*/RT}$$

The factor A expresses the frequency of collisions with correct geometry while the exponential term deals with the collision energy. E* is known as the activation energy while R is the universal gas constant and T is absolute temperature.

Higher temperatures will increase molecular movement and the energy in the collisions; hence a higher fraction of the collisions will lead to reaction. Increased concentration of reactants will lead to an increased number or collisions between the reacting species, also speeding up the reaction rate. In addition to concentration and temperature, catalysts, inhibitors and the surface area of the reactants will influence the speed of reactions.

Chemical reactions often involve multiple steps and temporary transition states, however the slowest step will determine the overall reaction rate such that the Arrhenius equation is suitable to describe complex reactions. The Arrhenius equation has been applied to engine deposits [18], and is also used by several authors in a modified form including a pressure term to describe ignition delay in diesel engines. [19]

2.2.2 Hydrocarbon oxidation theory

Combustion of fuel and oxidation of liquid lubricant is principally governed by similar fundamental reaction mechanisms, however differences in temperature, pressure and availability of oxygen greatly affect the rate and completeness of the oxidation as well as the reaction pathways.

2.2.2.1 The radical chain mechanism

The oxidation of lubricant hydrocarbons can be described as a four step radical chain mechanism. This is well accepted theory that may be found in textbooks as [20] and [21]. The oxidation process is initiated by the formation of free radicals. The free radicals take part in a circular reaction pattern in which hydrocarbons are oxidized. The reaction slows down as the concentration of hydrocarbon is reduced, and free radicals reacts with each other to yield uncreative species. The reaction is thus halted. In short, the free radical mechanism can be described as follows:

- creation of free radicals
- radical chain reactions
- chain branching
- chain termination

Creation of free radicals

Free radicals can be formed in a lubricant in a metal catalyzed reaction between dissolved oxygen and hydrocarbons or in un-catalyzed reactions between unstable heterocyclic or aromatic impurities, from cracking, or from bond scissure due to electromagnetic radiation.

Radical chain reaction

The free radicals a reacts swiftly with oxygen to form a peroxy radical. The radical chain reaction continues when the peroxy radical takes a hydrogen atom from another hydrocarbon to create a new hydrocarbon radical. The rate of this reaction is lower than the reaction involving oxygen. Thus, the concentration of peroxy radicals is high compared to other radicals, and the rate of this reaction will normally determine the overall rate of oxidation.

Chain branching

Various types of hydroperoxides are generated during the early phase of the oxidation. These hydroperoxides may cleave homolytically to form an alkoxy and a hydroxy radical. This mechanism is very slow at low temperatures, but the reaction becomes important at temperatures above ~ 120° centigrade, or under the influence of a metal catalysts. Chain branching results in a net increase in active radicals and can cause 'explosive' ignition as well as rapid oxidation of lubricants at higher temperatures.

At high concentrations, hydroperoxides may react with each other through a bimolecular mechanism yielding diffrent radicals and water. Radicals formed in chain branching reactions abstract hydrogen from other hydrocarbons to form further radicals, oxidised hydrocarbons or water in the case of hydroxy radicals.

Chain termination

The radical chains are terminated when reactions where radicals react with each other to form unreactive products become dominant. This occurs when the concentration of unconsummated hydrocarbon decreases. In lubricating oils, the oxidation halts before the hydrocarbon is completely consumed.

Base oil effects on reaction path

The reaction pathway will depend upon the composition of the base oil. The presence of certain aromatic hydrocarbons with weak C-H bonds can increase the initial radical formation; however when the radical is transferred to an aromatic ring during chain propagation, the rate of oxidation is reduced due to an increased stability of the radical. This mechanism is analogous to radical scavenger (or radical inhibitor) antioxidants as described below. [22]

2.2.2.2 Implications of the radical chain mechanism

The reaction steps described above illustrate the basic theory of hydrocarbon oxidization. At low temperatures, the radical chain reaction rate determines the overall rate of the oxidation. At higher temperatures (above ~ 120ºC), or in the presence of catalyst, chain branching is the rate determining reaction mechanism.

Rapid oxidation will only occur after a sufficient amount of radicals have been formed. The delay during which the driving radicals are formed is termed the induction period.

The induction period is a significant contributor to the ignition delay that is observed in diesel engines. The temperature and pressure dependency of the elementary reactions in the radical chain is believed to be governed by fundamental principles implied in the Arrhenius equation, and it has been shown that for simple hydrocarbon mixtures the ignition delay depends exponentially on the reciprocal of the temperature [20]. This relationship is also utilized in the characterization of ignition delay [19]. The radical chain mechanism is also fundamental to the function of anti-oxidant lubricant additives which works by decomposing hydroperoxide radicals or chemical 'absorption' of radicals.

2.2.2.3 Prevention of oxidation in lubricants

Oxidation of lubricants can be limited by

1. limiting the lubricant temperature and oxygen exposure
2. limiting lubricant exposure to oxidation accelerating catalytic contaminants such as salt water, metal particles and, ferrous rust
3. the use of antioxidant lubricant additives

Antioxidant additives work by interfering with the radical chain reaction.

Radical scavengers antioxidants
Radical scavenger molecules are more reactive towards the radicals than the hydrocarbon. The final product of a radical scavenger-radical reaction is chemically stable; hence the chain propagation reaction is inhibited. Examples of radical scavengers are:

- Sterically hindered phenols
- Aromatic amines

Hydroperoxide decomposer antioxidants
Hydroperoxide decomposers prevent the chain branching mechanism by reacting with and eliminating the hydroperoxides. Examples of hydroperoxide decomposing additives are:

- Organosulphurous compounds
- Zink dialkyl dithiophosphates and carbamates
- Organophoshorous compounds

Combining additives working by the same or different mechanism may sometimes give synergistic effects far outperforming the effect of single additives. The synergism of anti-oxidants is due to the fact that oxidation occurs along a multitude of chemical pathways, and the ability of additives to inhibit each pathway varies [23]. However, any combination of anti-oxidant additives can only slow the oxidation; they cannot prevent the oil from eventually oxidising

2.2.2.4 Results and products of oxidation

Results of incomplete combustion of fuel
Complete oxidation cannot be accomplished in diesel engine combustion primarily due to imperfection in the fuel air mixture formation. Incomplete combustion leads to the formation of particulates. At high temperature, these particulates consist mainly of carbon, but as the temperature drops, heavy organic molecules condensate upon these particulates. These particulates can aggregate to form soot. Briefly summarized, incomplete combustion yields:

- Formation of soot
- Formation of oxygenated hydrocarbons like aldehydes and ketones
- Condensation of reactive hydrocarbon
- Emission of particulates and HC

Fuel sulphur is related to particulate emissions such that the combustion of fuels with lower sulphur contents will generally yield less particulate matter in the exhaust.

Result of lubricant oxidation
Oxidation of the lubricant can lead to the formation of ketones and alcohol. These molecules may be oxidized to acids or be decomposed causing the emission of volatile species including water and CO2. In summary lubricant oxidation will cause:

- formation of acids
- increase of viscosity due to polymerization and polycondensation
- formation of insoluble products like sludge and varnish
- emission of volatile hydrocarbons and hydrocarbon fragments

2.2.3 Thermal cracking

Thermal cracking of fuel which subsequently condense on the liner has been suggested as an initiating mechanism for formation of resins, a part of liner lacquer deposits. Thermal cracking or pyrolysis is the decomposition of hydrocarbons at high temperature.

The activation energy for hydrocarbon cracking is high; hence cracking is typically a high temperature phenomenon. It has been shown that the activation energy for cracking of paraffins it is approximately equal to the energy of disassociation for the bond that is broken. [24]

The cracking mechanism becomes increasingly complex with increasing hydrocarbon molecular weight. Cracking results in the formation of radicals, and radical chain reactions will follow. The chain is terminated by inter radical reactions yielding non radical products.

Thermal cracking of heavier molecules results in a high number of possible reactions and even more of secondary reactions. The energy of disassociation of a C-C bond is much lower than that of a C-H bond. The initial rupture of a molecule is nearly always at a C-C bond. Larger molecules have a higher number of bonds per carbon atom compared to smaller molecules. This explains in part why larger molecules crack more readily than smaller molecules. Large hydrocarbon radicals may split unimolecularly into an olefin and a smaller hydrocarbon radical, thus thermally cracked fuel contains much olefin.

Cracking of Aromatics

Aromatics are stable compared to other hydrocarbons, although alkyl groups attached to the benzene ring is more vulnerable than the ring itself. Pyrolysis reactions may cause the aromatics to condense into polycyclic structures. These structures have a high molecular weight. Polycyclic aromatic hydrocarbons are active in forming insolubles like tar and coke.

2.2.4 Influence of nitrous oxides

Nitrogen oxide is formed during combustion and is present in the exhaust and blowby gas. In the surplus of oxygen in the diesel engine, significant amounts of the oxide will be converted to nitrogen dioxide and nitrogen dioxide radicals. The dioxide radicals are very reactive and act as oxidation initiators [25]. In this scheme, the nitrous oxide creates unstable hydrocarbon radicals by abstracting hydrogen while nitrogen is not bonded to the hydrocarbon. Other mechanisms, however, may lead to formation of nitrogen acids in lubricants, a phenomenon which is referred to as nitration.

2.2.5 Oxidative Polymerization

Unsaturated hydrocarbons can join together in straight or branched chains under favorable conditions. This process is known as polymerization. If a small molecule (such as water) is released as the molecules are joined, the process is called polycondensation. Polymerization and polycondensation are radical chain reactions and will increase in the presence of free radicals. Polymerization reactions will thus accompany and interact with the oxidation reactions. Oxidative polymerization of fuels and lubricant can yield vary large molecules, often in excess of 10 000 atomic weight units.

The properties of the polymer are dependent on the structure of the polymer macro molecule. Molecules with more cross bindings form networks that are stronger and more resistant to solvents and high temperatures.

Oxidative polymerization reactions lead to the formation of insoluble deposits. This topic is further described in a later chapter of the literature study.

2.3 Marine Distillate Fuels and Lubricants

Marine fuels and base stocks for marine lubricants are both derived from crude petroleum. The composition of the crude will depend upon local factors such as the nature of the organic sediments, temperature, pressure presence and types of catalysts as well as naturally occurring separation and migration; hence crude oils are widely different. Important characteristics are the content of heteroatom (oxygen, sulphur and nitrogen), the content of metallophyrins (principally vanadium, nickel or iron) as well as the boiling range. [26] This subchapter reviews aspects of production, analysis and performance enhancing additives of marine fuels and lubricants.

2.3.1 Marine Distillate Fuels Manufacture

The crude oil is fractionated at the refinery by distillation at atmospheric and subsequently reduced pressure to yield 'straight run' distillates following removal of water, salts and other contaminants.

Refineries are designed to maximize the yield of selected products from crude oils within a given specification. The layout of the refinery and choice of conversion and treatment processes will reflect the priorities, be it production of fuels, olefinic gases for petrochemicals, lubricant base stocks, or something else. Most conversion processes yield distillate gas oils as a by product. The properties of such gas oils are different from their straight run equivalent due to differences in molecular structure. Chemical conversion processes that yield gas oil fractions are reviewed below.

Catalytic cracking

Catalytic cracking is principally used to convert heavier cuts into fractions suitable for gasoline blending. The cracking causes C-C bond cleavages in the hydrocarbon feed. Because of a hydrogen deficit, olefins and coke is formed. Alkyl side chains are removed from heavy aromatic and napthenic molecules, resulting in fractions that may be heavier and higher boiling than the feed. Sulphur in the hydrocarbon feed is deposited on the catalyst (which is continuously regenerated) hence the catalytically cracked products are low sulphur.

Cycle oils

The fractionator bottoms from the catalytic cracker are usually recycled into the feed of the cracker. Recycled fuel molecules circulate at the expense of the overall productivity of the cracker. Although it is theoretically possible to recycle to obtain 100% conversion, a fraction of the cycle oil is usually drawn off continuously to optimize production rate and yield. This output is known as cycle oil.

Coking

Coking is a process used to extract low boiling hydrocarbons from heavy residue by thermal decomposition. The process is usually realized as delayed coking i.e. by heating the residue while it is flowing at a speed sufficiently high to ensure that coke is not formed before the residue has flowed into coke drums where it can be removed with relative ease. About 30% of the feed end as coke, a large fraction of the product is in the gas oil range. The coker products contain significantly more aromatic and olefinic species than straight run fractions.

Hydrocracking

Hydrocracking is catalytic cracking in a hydrogen rich atmosphere. The presence of hydrogen contributes to saturation of the products.

Hydrotreating

Hydrotreating is a catalytic process at high temperature in a hydrogen rich atmosphere that is useful to reduce the sulfur level of the feed to produce low sulfur gas oils. The hydrotreatment will also remove some nitrogen and trace metals as well as saturate some olefins and aromatics. Saturation will improve the cetane number and reduce the density of the gas oils.

2.3.2 Fuel specification and characterization

The marine distillate diesel fuel is blended from available gas oil range fractions in accordance to international specifications as well as local and 'in house' specifications. Small amounts of performance additives may be used, primarily to improve lubricity or inhibit wax formation.

International specifications of marine distillate fuels are available from ISO and CIMAC. ISO specifies four grades of distillate fuels. The ISO and CIMAC specifications for distillate fuels have evolved to become more or less identical. The remaining differences regards sediments, carbon residue, ash levels and the fact is that CIMAC explicitly prohibits the inclusion of residuals in some fuel grades (DMX and DMA).

In order to prevent properties that are relevant only in segments to gain worldwide influence and to avoid unduly high cost of testing, the number of criteria is kept to a minimum. The International fuel specifications may be regarded as a least common denominator of fuel quality and as a basis for fuel trade; however they cannot cover all aspects of performance. Fuel performance areas that are not specified relate to aspects such as

- combustion characteristics apart from ignition properties
- fuel lubricity
- stability (oxidative, emulsive etc.)
- how corrosive the fuel is and general compatibility issues
- filter plugging
- trace contaminants

These properties are handled by fuel manufacturers on individual 'customer care' basis and local fuel specifications. Also, niche products that do not fit this international specification may be sold locally.

The composition of a fuel is broadly characterized by its content of paraffin, olefin, napthene and aromatic species. Different standardized test principles may be used to identify some or all of these hydrocarbon types. These include ultraviolet and infrared spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy, different chromatographic techniques and thermal diffusion. Each method has its application, merits and flaws, and results may differ. Content of sulphur is usually determined by x-ray fluorescence.

The boiling range gives important information of fuel properties. The high end of the boiling range of marine distillate fuels cannot be determined by normal distillation because the least volatile fractions decompose below their boiling point. Instead, a theoretical boiling range, a 'simulated distillation' is obtained by chromatography.

The combustion characteristics of the fuel are of special interest with regards to the formation of engine deposits. In engine terms, combustion characteristic usually refers to the rate of heat release in the cylinder calculated from the pressure curve. The complete combustion properties of distillate fuels can be measured in laboratory equipment such as constant volume bombs, rapid compression machines or test engines. No such tests have been adopted as international standard, although some instruments like the fuel ignition analyser, FIA [27] are commercialized.

Fuel ignition properties are well predicted on basis of distillation and density data. Theoretically, more combustion characteristics like combustion speed may be determined from the hydrocarbon composition of the fuel. The relevancy of combustion speed is illustrated in [45]. Today, however, such correlations are not determined for the lack of standard combustion parameters and tests.

2.3.3 Marine Lubricants Base Oil Manufacture

The manufacture of lubricant base stocks starts with the fractionation of the atmospheric residue in a vacuum distillation unit that operates at a lower pressure and with higher reflux than fuel manufacturing units.

Napthenes, aromatics, wax, sulfur, nitrogen and other impurities must be removed before the base oil can be used. Solvent neutral oils are base oils derived from vacuum distilled paraffinic crude oils that are de-waxed, refined and stabilized. Marine diesel engine oil base oils are often based upon solvent neutral (SN) oils, but may include hydrorefined fractions or brightstock. Brightstocks are de-asphalted vacuum residual oil that has been refined and de-waxed.

Lubricant base oil must have suitable physical properties, the most important being viscosity, viscosity index, pour point, flash point and volatility. The oxidative stability of the lubricant base is also of primary importance. The oxidative stability of base oils decreases with increasing content of multi-ring aromatics and naptheno-aromatics or by trace contaminants including high polarity basic nitrogen species. [28] The oxidative stability may increase with increasing amounts sulphur in the base oil because they can decompose hydroperoxides into chemically inactive products, however final deposit levels tend to increase with sulphur content as discussed later.

As opposed to the marine fuels, the marine lubricant uses large amounts of additives. The quality of the base oil does not only depend upon the physical properties and stability of the base oil itself, but also on its response to additive treatment. The selection of base stocks and additives for marine diesel engines is a demanding process that relies largely on predictions from empirical results leading to screening tests and finally full scale trials and acceptance tests in commercial vessels.

2.3.4 Marine Lubricant Additives

Only the oil formulators know the exact composition of lubricants, however the basic types and characteristics of marine lubricant additives is known. Common marine lubricant additives are listed in Table 2-2 which is derived from [31] and [21].

Since cylinder liner deposits are known (from later investigation) to be oil insoluble and contain significant amounts of Ca, S and Zn in addition to C and O, it seems reasonable to take a closer look at the additive groups that contain these elements and also at the dispersant whose mission is to solubilize otherwise insoluble material.

2.3.4.1 Detergent additives

The simplest form of detergent, the neutral detergent, consists of a polar headgroup attached to a hydrocarbon chain that makes the detergent oil soluble. The polar headgroup contains sulfur, oxygen and a single calcium atom which may be replaced by Mg, Na or Ba.

Detergents are also available as alkaline or overbased detergents. The overbased detergents contain relatively more basic species and are more effective in neutralizing acids. Overbased detergents like calcium sulphonates and phenates have the structure of a reverse micelle which is schematically illustrated in Figure 2-2. The reverse micelle has a spherical core of amorphous material typically calcium carbonate and some hydroxide. Surfactant molecules similar to neutral detergent surround this core and suspends the core in the lubricant.

TABLE 2-2 TYPICAL MARINE TRUNK PISTON ENGINE LUBRICATING OIL ADDITIVES

Additive class	**Duty**	**Typical chemical components**
Detergents	Prevent deposits, neutralize acids, rust protection	Alkaline ('overbased') sulphonate, phenate, salicylate of calcium, magnesium sodium or barium.
Dispersants	Suspend sludge, water and combustion by-products	polyisobutylene- succinimides, ester succinimides
Anti-oxidants	Prevent oxidation of the oil	aromatic amines, hindered phenols, zinc dithiocarbamates, zinc dithiophosphates
Anti wear and Extreme pressure EP	reduce wear through formation of surface films	zinc dithiophosphates, sulphurised fatty esters, disulphides, sulphurised alkenes, zinc dithiocarbamates
Anti Foam	Reduce surface tension to prevent foaming	Silicone polyacrylate
Corrosion inhibitors	Prevent rust	Neutral sulphonates, phosphonates N-dispersants
Demulsifiers	Assist water shedding	Etoxylated Alcohols
Corrosion fix	Protect yellow metals (Cu)	N dispersants, S components

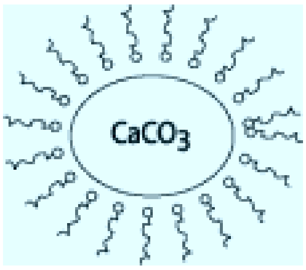


Figure 2-2 *Schematic illustration of reverse micelle*

Typical core diameters are in the range of 4 to 14 nm while the total diameter of the core and surfactant layer is 8-18 nm. [32] [33]. The actual micelle size is related to the type of surfactant and production process. Generally, the average micelle size increases if is produced at a high specific alkalinity [34] [35]. The micelles have been shown to remain stable also outside their original environment, and although they may deform slightly under pressure, they will not coalescence. [36].

Overbased additives are synthesized from neutral detergents and the production process may result in the detergent additive being a mix of overbased and neutral detergents [29]. The detergents offer protection against deposits by neutralizing acids which contributes to deposit formation. Detergents may also possibly attach to deposit precursors thereby sterically hindering deposit growth in the same manner as dispersant additives.

Complex detergents are alkaline detergents where surfactants of different chemistries are combined i.e sulphonate and phenate in one macromolecule. Traditionally, detergent chemistries are mixed by mixing macromolecules with different surfactant chemistries.

Important properties of overbased additives are given in Table 2-3. These data are from [21] [38]. Overbased calcium sulphonates also have anti-wear properties and may form a granular anti-wear film during mild wear. The grain size is slightly larger than the size of the micelles of the original overbased additive less the organic shell which is believed lost in the film forming process [37]. Lubricant additives interact strongly and, the tabulated properties can be affected by the presence of other additives.

TABLE 2-3 PROPERTIES OF OVERBASED LUBRICANT ADDITIVES

Property	**Phenates**	**Sulphonates**	**Salicylates**
Approx, commercial TBN range (ASTM D2896)	0-300	0-500	0-300
Sulphur %	0.5-4	0-4	0
Sulphonic acid	No	Yes	No
Carboxyclic acid	No	No	Yes
Hydrolytic stability	good	moderate	good
Oxidation stability	very good	poor	very good
Thermal stability	excellent	excellent	excellent
Detergency	good	good	excellent
Rust inhibition	low	good	low
Antioxidant effect	very good	none	very good

Neutralization of sulphuric acid by a calcium based detergent will cause the formation of calcium sulphate. Neutralization of acids that are products of hydrocarbon oxidation result in formation of calcium hydroxide. Both calcium sulphate and calcium hydroxide are oil insoluble. These species are both found within cylinder liner deposits as well as piston deposits.

2.3.4.2 Multifunctional zinc containing additives

Zinc is introduced into the lubricant principally through the use of multifunctional lubricant additives called zinc-dithiophosphate (ZDTP or ZnDTP) and zinc-dialkyl-dithiocarbamate. These additives both have anti-oxidant and anti wear properties.

Zinc-dialkyl-dithiocarbamate is believed to prevent oxidation by acting as a radical scavenger and by the formation of sulfur acids when the additive is oxidized by hydroperoxide. The sulfur acid may serve as a catalyst for ionic decomposition of hydroperoxides.

The ZDTP is available in a number of variations. The properties of three main groups distinguished by the nature of its hydrocarbon chains are shown in Table 2-4. This table illustrates the fact that the most reactive additives, which are the least thermally stable, offer the best protection.

TABLE 2-4 STRUCTURE-ACTIVITY DEPENDENCE OF ZDTP [21]

Structure	**Oxidative inhibition**	**Wear protection**	**Thermal stability**	**Hydrolytic stability**
Primary ZDTP	satisfactory	satisfactory	good	satisfactory
Secondary ZDTP (ZDDP)	good	good	moderate	good
Aryl ZDTP	moderate	bad	very good	bad

It is interesting to note that reference [23] mentions that thermal decomposition of ZDDP in diesel tends to produce 'lacquer' in the ring zone, an effect that is also indicated in [39].

2.3.4.3 Dispersant additives

The purpose of the dispersant additive is to solubilize material which would otherwise precipitate or agglomerate and subsequently settle out.

The dispersant consists of a polar head group attached to a long chain hydrocarbon that makes it hydrocarbon soluble. The dispersant is thus similar in structure to the neutral detergent additive, however the hydrocarbon chain is considerably longer and the head group is made polar using oxygen or nitrogen functionalities rather than metal.

Effects of oxidative and thermal decomposition of different dispersant additives have been investigated by Bartha et al. [40] Some data from their investigation are provided in Table 2-5. Three selected dispersants are shown. These are PIBMSI and PIBBSI dispersants which contain poly-butenyl-succinimides and PIBAE which is an ester amide type dispersant. The initial decomposition temperature has been determined in an oxidative environment using a differential scanning calorimeter. The panel coker merit was determined from a mix of 1.7 m/m% dispersant into a base oil fortified with detergent and anti-oxidant and polymethacrylate, which is commonly used as a pour point depressant. The merit rating is given on a scale from 1 to 10 where 10 is best. The loss of washing efficiency is an expression of loss in dispersant efficiency during the panel coker test. Table 2-5 shows that different dispersants with similar performance level may have widely different alkalinity and start to decompose at different temperatures.
The loss in washing performance after a panel coker test is not directly related to the temperature of initial decomposition. The authors suggested that the decomposition products of the PIBAE had dispersive power which enabled it to retain the washing power after the panel coker test.

TABLE 2-5 DISPERSANT PROPERTIES [40]

Property	**Ashless dispersant type**		
	PIBMSI	PIBBSI	PIBAE
Nitrogen [m/m%]	3.07	1.19	0.65
TBN mg [KOH/g]	78.3	19.0	11.2
TBN / N	25.5	16.0	17.2
Initial decomposition temperature [°C]	188	244	209
Panel coker merit	7.5	7.5	7.5
Loss of washing efficency after panel coker test [%]	23	6	-2

2.3.5 Characterization of marine lubricants

Automotive lubricants are tested according to procedures determined by institutions like the API and ACEA. In case of marine medium speed engines, the normal procedure is that engine and lubricant manufacturers cooperatively test candidate oils in the field leading to an approval if the test is successful. Engine operators then select oil from a list of accepted lubricating oils.

Precise characterization of lubricants is complex and entire books are devoted to this subject. The purpose here is to discuss some fundamental concepts that are relevant to forthcoming case studies. These are viscosity, alkalinity, ash and volatility.

Viscosity

The viscosity is the resistance of the lubricant to motion or flow. It is essential to hydrodynamic lubrication but also oil spreadability. The 'true' measure of viscosity is the dynamic or absolute viscosity which is usually measured in using rotary viscometers, unit [Pa*s = 10^3 cP]. The kinematic viscosity is the viscosity divided by the density of the fluid, unit [cSt]. The kinematic viscosity is measured as flow through capillary tubes immersed in constant temperature baths. This allows measurements with high simplicity and great accuracy. For this reason, the kinematic viscosity is used in preference to dynamic viscosity wherever this can be justified. Oil viscosity is reduced at high temperature and shear rate compared to that at normal conditions. This effect is particularly severe in multigrade oils because of their low base oil viscosity and the reduced effect of the VI improver additive at high shear. Dynamic viscosity is thus most relevant for multigrade oils subjected to high temperature and high shear stress such as gears and bearings. Since marine oils are mostly monogrades, the requirement is that the kinematic viscosity in cSt. measured at 100°C resides within a designated range.

Alkalinity

The alkalinity of the oil is expressed by the total base number (TBN) which gives the amount of potassium hydroxide base which has equal neutralizing power as the oil sample. The unit of TBN is mg KOH/g. The TBN test is performed by diluting the sample and titrating with acid. The TBN rating is dependent upon the strength of the neutralizing acid and the polarity of the solvent medium used in the test. Different standard tests are available. ASTM D-2896 and ASTM D-4739 are both effective in measuring readily available base such as detergent additive, however they differ in their ability to detect weaker base like ashless dispersants or amine antioxidants [14],[25]. ASTM D-2896 is the more sensitive method in terms of detecting weak base and is recommended by CIMAC and commonly used in the marine industry.

Total base number is a useful indicator; however it does not give information about the speed of neutralization, or neutralization strength [29],[14]. The reproducibility between laboratories of the TBN has been determined to be 7% for standard titration.

Ash

The amount of ash left from the combustion of a lubricating oil is measured as sulphated ash. This procedure involves heating an oil sample to a temperature where it will ignite. The sample is burned at this elevated temperature until no smoke is emitted. The residue is cooled and treated with sulphuric acid before it is heated to 775°C. This temperature is retained until the sample reaches constant weight. This weight is the % sulphated ash. The sulphur treatment improves the repeatability of the method because sulphates are heavier than oxides [25].

Volatility

Theoretically, volatility of inhomogeneous substances like lubricant base stocks are best characterized by boiling point curves. In case of where high boiling point exceeds the temperature of thermal decomposition, the boiling point curves can be simulated by gas chromatography. This approach requires expensive equipment and differentiation of the high boiling point constituents can be problematic.

For many applications, the volatility determined as a weight loss sustained at prescribed conditions of temperature and gas flow over the sample such as the ASTM D5800 (NOACK) test is well suited to characterize volatility. Performance additives are known to reduce the volatility of the finished lubricant hence the net volatility depends on both base oil and additives. [30]

Used Oil Analysis

Viscosity and alkalinity are also often used to characterize used oils, which are also characterized by oxidation products and other contaminants like soot or water. Since lubricant additives are consumed, the performance of the lubricant will deteriorate if the loss of additives is not compensated for and contaminants removed. The oil sump is regularly refilled to replenish consumed oil and oil is drawn of to be filtered and centrifuged. The balance between oil consumption and additive consumption will determine the long term equilibrium additive level and hence oil performance. In engines with high oil consumption, this top up oil will be sufficient to maintain oil performance. In engines with low oil consumption, the equilibrium oil performance level will be significantly less than that of the new oil [31]. In cases where volatile losses are high, the additive content in the oil may exceed that of the new oil. [41][42]

2.4 The Cylinder Liner Environment

This subchapter reviews factors that affect the conditions on the cylinder liner.

2.4.1 Cylinder design

Marine medium speed diesel engines are with few exceptions four valve engines with a centrally located fuel injection nozzle. Some engines have relatively flat combustion chambers where the fuel is injected nearly horizontally towards the cylinder liner wall or deeper piston bowls where fuel in injected at a lower angle into this bowl. Most modern marine medium speed engines are equipped with 'flame rings' which are metal inserts in the top of the liner. They are designed to scrape deposits off from the piston crown land and thereby prevent such deposits to cause liner wear known as bore polishing. In this case, the lubricated part of the cylinder liner may not be exposed to the combustion gas until the primary combustion has been completed. A cylinder liner with flame ring is illustrated in Figure 2-3.

The cylinder liner is normally lubricated by crankcase mist. This is oil that has been cooled, filtered and pumped at a controlled rate from the system oil tank into bearings in the crank mechanism and cooling cavities in the piston. The oil is dispersed to a mist as it exits the rapidly moving piston and bearings at elevated pressure. Some of this mist will impinge on the cylinder liner which is exposed when the piston is in an elevated position. Some medium speed engines, particularly the larger, may have oil feed directly to the cylinder liner through bores in the piston or liner.

Piston rings form the seal between the cylinder liner and the piston. The lower piston ring, the oil control ring, is designed to collect and distribute oil on the cylinder liner. Some piston lubricated engines have oil flowing into the oil control ring grove, while other engines are fitted with drain holes to allow excess oil within or below the oil control ring to escape. Some terms and design details for piston and piston ring are shown in Figure 2-4.

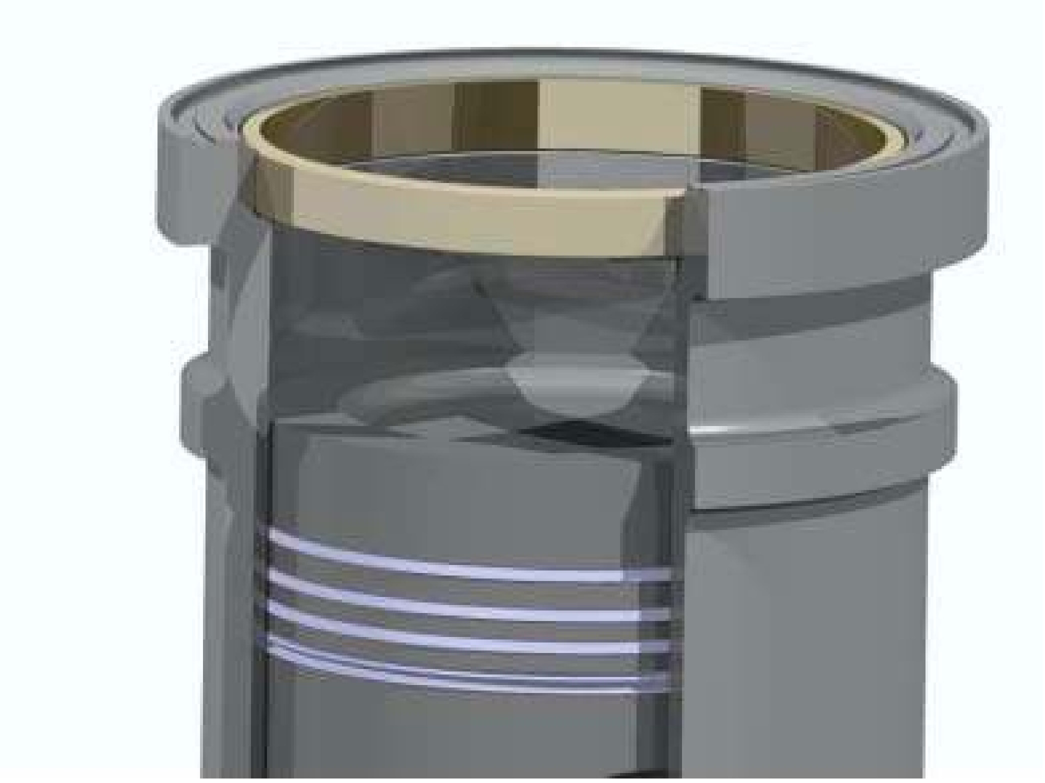


Figure 2-3 *Cylinder liner with flame ring and piston*

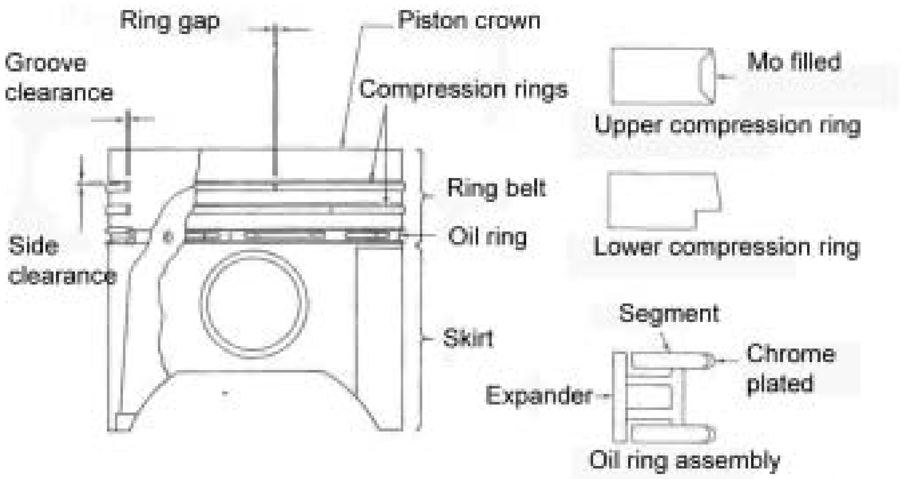


Figure 2-4 *Piston and piston ring terms* [55]

The distribution of the oil on the cylinder liner is maintained by the oil control ring which carries oil up and scrapes oil down, leaving a thin oil film which lubricates the upper piston rings. The piston rings will further distribute the oil film. The movement of the piston ring is determined by inertia and pressure forces which are dependent upon speed and load. It is currently difficult to predict the oil flow and exposure time on the liner surface, and also the thermal and oxidative loads as discussed in the following.

2.4.2 Combustion and heat transfer

The combustion and the combustion gas greatly affect the conditions on the cylinder liner. The most intense combustion occurs when the piston is close to TDC and the cylinder liner is only marginally exposed.

2.4.2.1 Diesel combustion

The diesel combustion is commonly divided into four phases.

Ignition delay

There is a delay from the start of the fuel injection until the fuel autoignites which is related to the buildup of a critical level of reactive radicals which is known as the ignition delay. Fuel hydrocarbon is partly oxidized during the ignition delay. These species can act as precursors of polymeric hydrocarbon deposits as described by Burgess. [43].

Premixed combustion

When sufficient radicals have been formed, the fuel that has been injected during the ignition delay is rapidly burned. This is known as the premixed combustion phase. Most partly oxidized fuel is believed to be consumed during this rapid combustion phase.

Diffusion burning

When the premixed fuel is consumed, the rate of combustion is limited by the mixing of fuel and air. This phase is known as diffusion combustion.

Late combustion

As the piston descend, the temperature and pressure drops and combustion proceeds more slowly. At some time, diffusion is no longer rate determining and the combustion enters the final phase known as late combustion. The transition between diffusion combustion and late combustion can be vague since diesel fuels are inhomogeneous and some fuel species may enter this phase at temperatures and pressures where others still burn quite rapidly.

2.4.2.2 Flame and gas temperatures

Diesel flame temperatures are high, a peak temperature of 2700 K have been measured on basis of flame luminescence. Heat loss to the engine metal and excess air causes the 'average' temperature in the gas to be significantly lower. Decreasing fuel/air ratio at reduced load reduces the average gas temperature. The average gas temperature is also reduced as the piston expands.

2.4.2.3 Heat transfer modes

Heat is transferred from the combustion via three basic mechanisms

- Conduction
- Convection
- Radiation

The thermal conductivity of the cylinder gas is low which will lead to the formation of a thin boundary layer with rapidly decreasing temperature close to the oil film surface as illustrated in Figure 2-5.

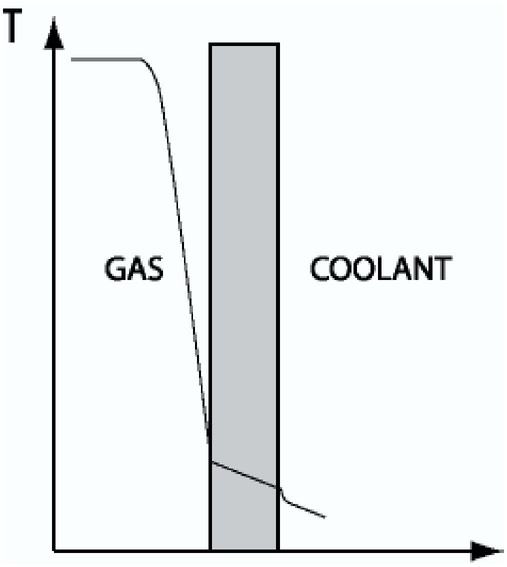


Figure 2-5 *Schematic temperature profile near wall surface.*

The boundary layer will limit conductive and convective heat transfer unless disrupted by mechanisms like severe turbulence, pressure waves or combustion spray impingement as discussed later.

2.4.3 Cylinder liner temperatures

Published diesel engine temperature data are usually focused on the high temperature zones which are the cylinder head, piston crown and upper cylinder liner.

Some published liner top temperature data are provided in Table 2-6. The distance from the liner surface to the thermocouple used to record these data has a large effect on the measurement.

TABLE 2-6 REPORTED CYLINDER LINER TEMPERATURES

Test engine	**Fuel type**	**Speed (rpm)**	**Load (bmep, MPa)**	**Thermocouple depth (mm)**	**Max. Liner Temp. (€)**	**Ref.**
Matsui Iron Works MU323DGSC	Residual Residual	420	1.55	0.5	240-290 287	44 45
Ruston 6 APC	Residual	750 750 750	1.72 0.86 0.43	2-3 2-3 2-3	171-180 141-151 120-128	46
Ruston 6 APC	Distillate	750 750 750	1.72 0.86 0.43	2-3 2-3 2-3	168 139 126	46

A difference in temperature between distillate and residual fuels is also noticeable, the distillate fuel causing a lower liner temperature than the residual fuel. The tabulated temperature is the maximum which is measured near the top of the liner. The temperature is lower in lower parts. This table also show that the liner temperature increases with increasing load.

2.4.3.1 Influence of fuel composition and combustion characteristics on cylinder liner temperature

A relationship between liner temperature and distillate fuel oil composition has not been found in the literature; however a large body of work on the combustion characteristics of residual fuels is presented in [46]. These data which include one gas oil sample suggests that fuel composition can significantly affect the temperature measured by thermocouples immediately below the surface of the cylinder liner, and hence most certainly also the temperature of the oil film.

This work is done in a 6 cylinder long-stroke medium speed engine rated at 17 bar BMEP. Seven residual test fuels, one reference fuel and one gas oil were tested. Cylinder liner temperatures were recorded amongst other data. The liner temperature was measured with thermocouples positioned 2-3 mm below the liner surface. It was planned in this work to include a test fuel consisting of pure light cycle oil (LCO), however large cycle to cycle pressure variations, high exhaust valve temperature and knocking combustion caused this test to be abandoned.

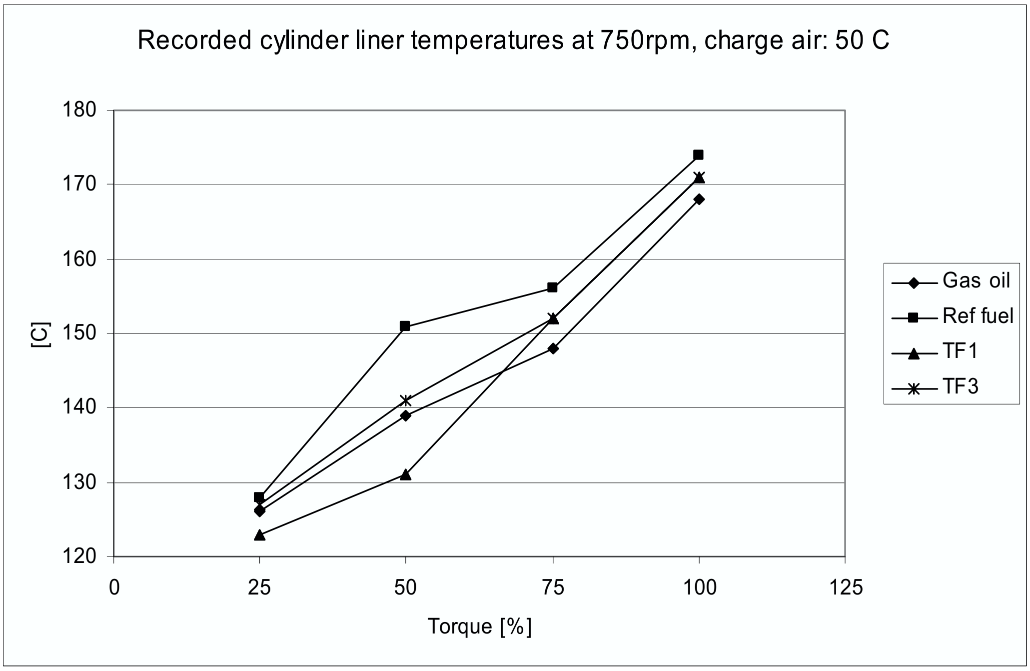


Figure 2-6 *Load and fuel dependent maximum cylinder liner temperature Drawn from measurement data obtained in* [46]

Data from [46] established that the liner temperature measurement could vary as much as 20°C amongst the residual fuels that were tested, however at maximum load and hence maximum liner temperature, the differences measured were only 8°C. Data for full speed of 750 rpm and scavenge air temperature of 50℃ are provided in Figure 2-6. Only some of the fuels tested in [46] are shown to ease reading.

The largest deviations in surface temperatures were detected at 50% load. The premixed combustion is largest at this load condition in this engine for the majority of the fuels. Large premixed combustion causes a high rate of pressure rise which is assumed to cause a breakdown of the boundary layer between cylinder air and metal surfaces. Hence the effect of fuel on liner temperature as shown above could equally well be described as the effect of combustion characteristics on liner temperature.

2.4.3.2 Effect of charge air temperature on liner temperature

The charge air temperature was increased from 50 to 70 or 75 degrees in some part load experiments in [46]. The temperature measured within the cylinder liner generally increased, however there were exceptions indicating that the combustion effects in some instances dominates the charge temperature effect. The suggested cause is reduced charge air temperature causing increased premixed combustion which contributes to increased heat transfer. It is thus not possible to generalize the effect of charge air cooling on the cylinder liner.

2.4.3.3 Influence of flame proximity on liner temperature

The temperature on the cylinder liner is higher in line with the fuel spray. Experiments using heavy fuel in a medium speed engine revealed a difference of 97℃ between a thermocouple mounted in the top of a cylinder liner in line with the fuel spray and another mounted at the same height but in-between spray axes [45]. The difference in temperature was attributed to flame proximity. This paper also presented a strong correlation between the combustion duration measured in a fuel ignition apparatus and the cylinder liner temperature in the engine tests and concluded that fuel evaluation should put emphasis not only on ignitability but also combustion speed.

The implicit understanding of these results is that the slower burning fuel burns closer to the cylinder liner. It is interesting to note that lower charge air pressure will increase the speed and penetration of the fuel spray. Models based upon experimental data presented in [47] indicate an increase in speed and penetration in excess of 30% when the charge density is reduced according to a reduction in charge pressure from 3 to 1 bar and fuel injection pressure is constant. This effect is also documented by engine tests using constant pressure common rail injection [48]. This study also observed the expected increase in ignition delay with reduced charge air pressure. Hence low load and corresponding low charge air pressure will contribute to an increase in fuel spray speed. The fuel injection pressure, however, is not independent of load in most marine engines.

At constant speed conditions, the fuel pressure increases at a rate which is load independent, however at low load, the injection is aborted before maximum pressure is obtained. The spray in the first part of the injection is thus expected to be significantly longer in the low charge density case; however the effect on maximum spray length is unknown.

At reduced speed, both pressure increase rate and maximum obtainable pressure are reduced. These interacting and counteracting factors as well as the influence of the ignition delay make prediction of the flame position within the combustion chamber difficult. Additionally, reduced scavenging efficiency will cause a decrease in oxygen concentration in the charge which will cause the flame speed to be reduced. [49]

Experiments using a rapid compression machine suggest that the heat transfer rate increases with the velocity of the flame which contacts the wall surface [50].

The heat transfer from the gas to the cylinder wall has been observed to increase with increasing cylinder wall temperature [51] which is contrary to what might be expected from classic heat transfer theory. This phenomenon has not been completely explained, however it has been suggested that the increased heat transfer is related to the thinner boundary layer formed when the wall temperature increases.

2.4.3.4 Local variations in liner temperature

The local liner temperature is affected by the charge motion within the cylinder. Proximity to the charge air intake will have a cooling effect while the liner surface close to the exhaust outlet may face a higher thermal load. This effect is clearly measurable with thermocouples mounded within the cylinder liner.

2.4.4 Calculated liner and oil film temperature

The temperatures in Table 2-6 are temperatures of the cylinder liner metal. The temperature in the oil film itself is difficult to establish as it is alternately exposed to the cold charge air and the hot combustion gas. The temperature of the cylinder liner will be more stable than the oil film due to the 'thermal inertia' of the liner metal.

Mathematical models can predict the instantaneous temperature level on the liner surface which cannot be measured. One such model was presented by Guohua, Wang and Heywood at the 19th CIMAC conference. [52]. This finite elements model (FEM) takes into account the unstable heat transfer due to radiative and convective heat transfer. The cylinder liner surface temperature data for a heavy duty truck type diesel engine calculated by this method is shown in Figure 2-7.

The predicted temperature in the top increases during the combustion, but the increase is relatively low. The temperature in the mid stroke (level 3 in Figure 2-7) fluctuates less while temperature fluctuations are largest in the lower part of the liner (that is exposed to combustion gas like level 5) although the absolute temperature is significantly lower.

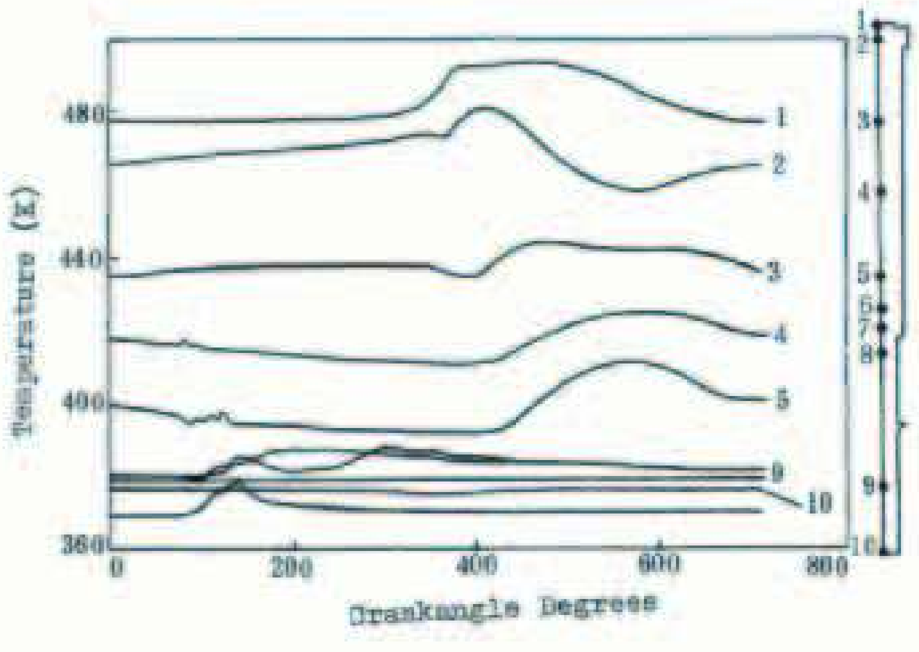


Figure 2-7 *Calculated cylinder liner temperature profiles in heavy duty on road diesel engine at full load* [52].

Since temperature measurements in the cylinder liner surface are stabilized by the 'thermal inertia' of the liner, temperature measurements in the top region are more representative of the 'true' thermal load than measurements obtained in the lower region where the relative thermal fluctuations are large.

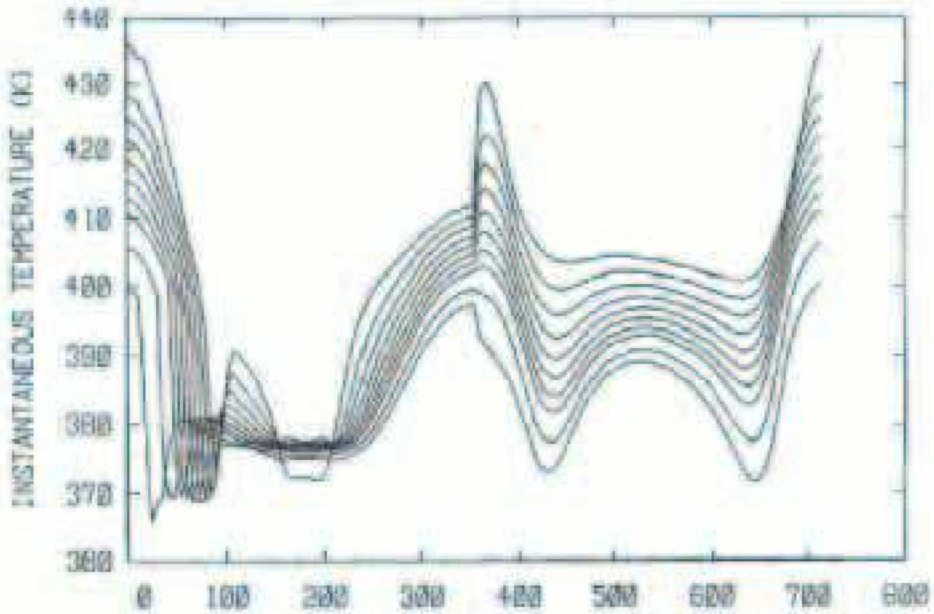


Figure 2-8 *Calculated temperature of oil film between piston and liner.* [52]

Figure 2-8 shows the temperature in the oil film residing between the piston and as calculated by the authors of [52]. The temperature of the oil film between the piston and the wall increases in this model when the piston rises. Interestingly, this model predicts that the maximum temperature is reached during the charge exchange and not during the combustion.

The estimated oil film temperature in this position is lower than the cylinder liner. The temperature in the oil film that is not separated from the combustion gas by the piston was not calculated, but is expected to be close to the liner temperature in Figure 2-7 due to the insulating effect of the boundary layer.

2.4.5 Volatile losses and chemical degradation

The oil film of the cylinder liner will loose material due to evaporation of light base stock components and also due to thermal decomposition of the lubricant. Evaporative losses can cause the viscosity and also the concentration of additive elements to increase on the cylinder liner as reported by [61]. Volatile losses cause the concentration of additive material in the oil sump to increase as well as reported in [41], [42] and seen in our case studies of liner deposit. This is in contrast to the expected behavior of modern low oil consumption engines where additive depletion in the sump has been a concern [31]

The composition of the oil film is also dependent upon exposure to water, partly oxidized fuel, sulphuric material, soot and other contaminants. The sensitivity of the oil film to such species is depending upon the base oil type, additives and the residence time of the oil film on the cylinder liner.
Analysis of oil sampled from the cylinder liner of a 190 mm bore medium speed two stroke Bolnes 3DNL engine in reference [61] revealed that the concentration of calcium in the liner oil film was larger than that of the new oil and that it increased when the gas oil fuel was changed to a hotter burning heavy fuel. The liner oil samples also contained calcium sulphate and iron sulphate which are main constituents in liner deposits.

2.4.5.1 Ring groove sampling

The piston ring groove is an area where deposit formation is common and the oil condition in the groove is subject of significant research. Ring groove deposits are often associated with high piston temperatures and high blow-by. The relationship between the liner oil film and ring groove oil condition is largely unchartered and is not likely to lend itself to simple generalisations.
Analysis of oil sampled from ring grooves indicate that ring groove oil is depleted in additive concentration and has significant carbonyl content [62]. Other researchers have observed a loss in groove oil dispersing power and also increase in content of calcium and phosphorus [58]. A recent development is the in situ characterization of the lubrication oil on the liner using FT-IR. This technology enables stroke by stroke variation in lubricant condition to be observed, and also indicates that the liner oil film deviates from ring groove samples by a stronger presence of what could be nitration products. [63]
Experiments with ring groove sampling by Fox [62] show that the oil flow to the top ring groove was approximately 1/5 of the oil in the second ring groove in a modern heavy duty commercial diesel engine. A magnesium tracer element added to the oil sump was detected in the lower ring groove after 6 minutes; it took 26 minutes for this tracer to migrate to at upper ring groove and 72 minutes to reach the upper land. This is indicative of a very slow migration speed of the tracer element in the ring pack.

2.4.6 Oil film exposure time

The overall degradation of the cylinder liner oil film is dependent upon the exposure time as well as the environmental factors. The oil exchange process involves dilution, mixing as well as volatile and mechanical losses in a non homogeneous mixture, hence residence time is a question of what part of the lubricant is considered.

The 'average' time the oil spends on the liner is difficult to assess and measure. Direct measurements of oil film residence time have not been found in the literature. Instead, oil film thickness and oil consumption are discussed as they may be indirectly related to exposure time.

2.4.7 Oil film thickness

Investigation of the oil film thickness is primarily done by measuring the amount of lubricant passing a window using laser induced fluorescence (LIF) or the distance between the piston ring and the liner using capacitance sensors. Such studies indicate that there is a thin film of oil on both the piston and the cylinder liner and that there may be a foam or mist behind the piston rings. Neither measurement type is ideal to estimate the volume of oil on the liner since the capacitance measurement gives the thickness under the piston ring while LIF only have measurements in one location.

The thickness of the oil film between the piston ring and the liner is dependent primarily upon viscosity, sliding speed, geometry and contact load. Classic hydrodynamic lubrication theory predicts that oil film thickness is greater at higher speed, however Takeguchi et al. [64] found that this effect is most important at lower speeds, presumably due to a reduction of viscosity caused by increased oil film temperature at high speed. The thickness often varies between thrust and antitrust which is believed to be an effect of secondary piston motion. Field measurements have determined that ship motion affected the oil film thickness in a slow speed 2 stroke engine. [65]. Typically, oil film thickness is measured to be in the range of 1-10 micron. The oil film below the top ring is generally considerably thinner than below the oil control ring.

An oil transport analysis based upon oil film thickness measurements has indicated that local oil transport is in the region of 35-500 times larger than oil consumption. [66] This analysis is based upon laser induced fluorescence (LIF) measurements through a single window on the liner where film thickness measurement indicated that upstrokes typically had higher oil film thickness. These results are not wholly in agreement with results measured in other engines using LIF [67] or a capacitance [64]. The aforementioned results should hence be considered with care.

Cylinder liner sampling experiments showed that the amount of oil that could be sampled from the Bolnes 3DNL test engine was severely dependent upon sampling height. About 0 - 0.1 gram of oil could be sampled in one hour using a probe situated near the top of the liner (between the first and second ring at TDC) while a probe situated in a lower location (below the lower ring at TDC) sampled 3.7 - 4.5 gram per hour. The sampling valve was open when the piston rings passed as explained in [61]. This suggests that little oil is present in the top region of this liner. These results are also in agreement with theoretical film thickness models and measurements which predict a thicker film in the lower region.

2.4.8 Oil consumption mechanisms

The oil consumption in diesel engines is the combined loss from a number of complex mechanisms. In terms of design of piston, rings and bores, it is possible to name at least 40 features which affect oil consumption [53]. In general, however, the oil consumption may be broken down into four basic mechanisms. [54]

- Evaporation from the liner
- Throw-off of oil accumulated in front of the piston ring
- Oil mist carried in the reverse blow by
- Piston scraping oil off the cylinder liner

For instance, bore polishing will cause oil to accumulate in front of the piston ring to increase throw off. Bore distortion will affect an increase in local oil film thickness which also causes the expected oil throw of to increase. Ring instability caused by piston deposits [2] or critical load and speed conditions opens an upwards escape path for oil mist. Piston secondary motion which will affect the piston ring liner contact geometry can also influence oil consumption [56]. Increased oil consumption due to unfavourable thermal gradients in the cylinder liner of a marine medium speed engine is reported. [57]

The importance of each mechanism will vary from case to case. Volatile losses are primarily dependent upon oil composition, temperature and pressure. Throw-off is caused by inertial effects and may hence be speed dependent. Field tests suggest that oil viscosity affect oil consumption and that an optimal viscosity exists that minimizes oil consumption. In a well functioning modern engine, the amount of oil on the liner is low and the main mechanisms should be volatile losses and mist entrained in the reverse blowby [58]. In this case, the oil consumption can be virtually independent of speed as realized in [56] but will increase with load which will cause an increase in temperature and inter-ring gas pressures and flows.

A detailed mathematical model for the evaporative losses of a diesel engine is presented in [59]. This model predicts that the majority of the oil evaporates during intake and compression strokes while a smaller fraction evaporates during the expansion and exhaust strokes. Similar theoretical results are reported by other researchers [60].

The volatile losses predicted in [59] constitute 10-17% of the oil consumption expected for this heavy duty on-road diesel engine. The calculated volatile losses varied little with engine speed. As previously discussed, total engine oil consumption is speed dependent in some engines [41] [56].

Piston ring movement

The piston ring is loosely fitted into the ring groove. Inertial forces and differential pressures will cause the piston ring to move relative to the piston. This behavior is dependent upon its design in terms of ring face profile, groove clearances, ring gap clearance, ring stiffness and ring tension. The ring may twist and bend, and the contact between the piston ring and the piston may vary around the circumference of the piston.

The radial movement of the ring is determined by the radial pressure balance and the internal tensioning and flexibility of the ring. When the combustion pressure is altered, the pressure working behind the ring is also altered which may cause the oil film thickness below the ring to change.

The desired piston ring motion to minimise oil consumption in a two compression ring pack is such that the top ring to remain on the lower groove flank during compression and combustion [56]. In this case, the top ring sealing is relatively good and the pressure below the top ring is relatively low. This pressure is also the pressure above the second ring. When it is low, the second ring may lift near TDC due to inertial forces, and allow gas above it to escape down. This ring motion pattern hence encourages blowby. If, however, the pressure below the first ring is high, the second ring remains seated and blow-by is reduced. On the other hand, this pressure also encourages the top ring to lift which results in 'reverse' blowby and high oil consumption. The gas flow pattern is more complex and less predictable when the number of compression rings increases.

Two oil consumption maps for a 7.8 l truck diesel engine is shown in Figure 2-9. The optimization includes the use of a ring pack that achieves desired ring motion, but also improved skirt guidance, oil drainage and honing. The older baseline design generally has higher oil consumption, but there is also a difference in pattern. While the specific oil consumption typically decreases with increasing load in the baseline case, the specific oil consumption increases with increasing load in the optimised system. Thus the oil consumption is very low at low load in the optimised system. This figure is believed to be illustrative of the trend in oil consumption development. In case of medium-speed engines, the oil consumption levels have been reduced significantly; design values today are typically around 0.3 g/kWh compared to 1 g/kWh which was commonplace 10 years ago.

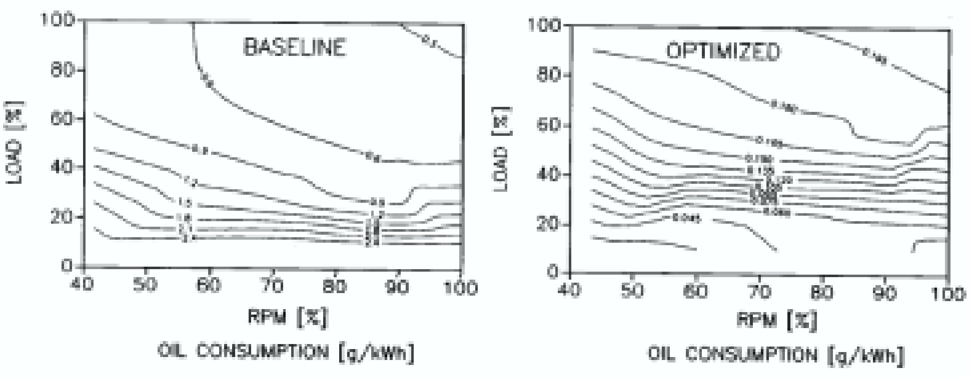


Figure 2-9 *Oil consumption maps of original and optimized piston ring system for truck diesel engine.*[56]

2.5 Engine Deposits

A variety of deposits may form in engines. The purpose of this subchapter is to discuss engine deposits in general and two types of deposit that have attracted special interest in the research of liner lacquer. These are the engine 'varnish' and 'lacquer' type deposits which are similar to liner lacquer in appearance, and carbonaceous piston deposits which contain some of the same substances as liner deposits.

2.5.1 Characterization of Engine Deposits

Engine deposits are traditionally classified on the basis of location such as piston deposits, valve deposits; their effect such as oil ring clogging, port plugging or their appearance such as varnish, lacquer, black paint, rather than their chemical nature. Common terminology may also be slightly misleading. Terms like 'piston carbon', 'top land carbon' and 'carbon deposits' have been used to describe black deposit containing significant amounts of non-carbon material.

CRC defines 'varnish' as deposits appearing as a film on interior engine parts that is insoluble in pentane and cannot be removed by wiping with a soft cloth. This definition covers both liner lacquer and lacquers formed from oxidized and polymerized hydrocarbons. Gruise [68] proposed that the term 'lacquer' should be reserved to deposits that were insoluble in acetone, while soluble deposits should be classified as varnish. This distinction was, however, not generally accepted. A reference book [69] distinguishes lacquer from varnish by labeling such deposits lacquers when found in diesel engines but 'varnish' when found in gasoline fuelled engines.

Chemical analysis may give a clue to the deposit source. However deposits of identical composition can be caused by different mechanisms [68] and deposits originating in the same root cause may have differences in composition due to differences in oil additive chemistry or more subtle causes. Deposits may be non-homogeneous, and the deposit criticality depends upon its location. It is therefore important to gather information about both deposit chemistry and location in order to be able to properly evaluate the deposit.

Deposit assessment

Accurate assessment of deposits is crucial to deposit research. Engine deposits can be evaluated according to deposit rating systems that are adapted to the deposit type and test. Deposits can also be quantified by weight or area. Varnish deposits are typically assessed by CRC standard procedure, which is a rating by expert judgment or video computer system. The deposit is given a merit rating based on area covered by the deposit and the intensity of the deposit on a scale from 0-10, 10 being clean. Sometimes, a demerit rating is used instead, where 10 is a dirty and 0 clean (used because evaluators find it more natural to rate the deposit than the cleanliness.) Varnish is often soluble in which case the deposit can be dissolved, dried and weighed. The deposit weight has been observed to show a poor correlation to varnish rating as indicated by

Spilners et al. [70]. Deposit weight alone may be a bad criteria as deposit that cause problems in one area may be harmless elsewhere. Some deposit types may also be difficult or impossible to dissolve. It is sometimes difficult to correlate deposit ratings to engine performance. For instance, McGeehan [2] reports that piston top deposit is difficult to rate and correlates poorly with bore polishing and oil consumption even though such correlation was expected.

2.5.2 Liner deposits in low speed two stroke diesel

Deposit formation on cylinder liners in a large two-stroke engine was investigated by Sayles [9]. These deposits were described as both varnish and lacquer (without implying any distinction). These deposits usually appeared in regions where the cylinder liner surface was severely worn due to some unknown mechanism, typically in the mid-stroke region of the cylinder liner. Increased liner temperature reduced the wear rate considerably although the wear pattern was not changed. Used oil analysis did not detect corrosive wear metals; however the levels of particles associated with adhesive and abrasive wear were significant, as were non-metallic crystalline particles. The composition of the liner deposits was not investigated.

The cylinder liner was very smooth in terms of short wavelength roughness in areas with deposit; however it did exhibit waviness which could allow thick deposits to form in some regions. The author of [9] suggested that the cause of the liner deposits could be formation of lacquer which caused scuffing by forming an insulating layer that prevented dissipation of frictional heat.

The vertical distribution of wear observed in this case study is similar to the distribution profile of liner deposits in medium speed engines presented in chapter 9. Hence the regions of high wear reported in this low speed two-stroke engine correspond roughly to the areas where deposits were found in the engines with liner deposits. The effect of liner deposits in medium speed engines is to smooth the surface and cause high oil consumption, presumably as less oil is allowed to escape beneath the piston ring as it passes. One would expect a similar effect in the two stroke engine, however this engine is lubricated by a constant oil supply so these deposits may instead cause local oil starvation which could account for the scuffing reported in [9]

2.5.3 Varnish deposits

Varnish is light brown to reddish or near black deposit in either gasoline or diesel fuelled engines. The CRC engine rating system defines varnish as a resinous deposit which cannot be removed by wiping with a soft cloth. Similar in appearance to liner lacquer, varnish can be formed upon almost any surface in the engine not subject to vigorous wiping. [68]

Varnish deposits once caused controversy whether a high or low cylinder wall temperature was most beneficial to avoid deposit formation. It was later established that multiple mechanisms were at work; gasoline engine varnish could be induced both by hot spots and by condensation of unburned fuel when a cold engine was running. Varnish can sometimes form on piston skirts, in which case it is referred to as piston lacquer or piston varnish.

2.5.3.1 Formation of varnish

The formation of varnish is attributed to a polymerization of hydrocarbons in the lubricant initiated by oxidation or incomplete combustion of fuel and or lubricant. It is catalyzed by nitrous oxides. The catalytic influence of metals is important, presumably as oxidation promoters. The reactions leading to the formation of varnish involve or occur in the oil sump. The deposition of varnish seems to be dependent on the oxidation product solvency of the oil, as varnish precursors can be precipitated. Synthetic oils yield less varnish than mineral oil based lubricants, even under conditions when varnish precursors are fuel derived. This is party explained by the fact that lubricants with stable synthetic base oils, like polyalphaolefins, are less stable as media for free radical type oxidations and condensations. Engine tests reported in [18] indicated a good agreement with piston lacquer ratings and the levels of insoluble oxidized resins in the lubricating oil. A comparison of 'liner lacquer' and 'varnish' is presented in
table 2-7.

2.5.4 Carbonaceous Piston Deposits

Hard, carbonaceous deposits are typically found on piston crowns, piston lands or ring grooves. Other piston deposits include piston varnish or lacquer deposits typically seen on lower lands and piston undercrown deposits which are deposits found inside oil-cooled pistons.

Hard piston top land deposits can cause abrasive wear on the cylinder liner leading to increased oil consumption. It has also been observed that soft top land deposits can cause an increase in oil consumption in engines

TABLE 2-7 A COMPARISON OF LINER LACQUER AND VARNISH

Characteristic	**Liner Lacquer**	**Varnish**
Appearance	Thin smooth and hard deposits. Light amber to dark reddish.	Thin smooth and hard deposits. Light amber to dark reddish or black.
Location	Cylinder liners in marine medium speed engines.	Piston lands and skirts, rings, valve stems, inside piston crown and more.
Constituents	Oxidized hydrocarbon 'Resin', inorganic salts, wear particles,	Primarily oxidized hydrocarbon.
Effect	Fills honing grooves and causes increased oil consumption.	Interferes with heat flow, can release hard particles or flakes, may contribute to ring sticking and clogging of oil control rings.
Solubility	Soluble in acetic acid, sometimes water. Generally insoluble in petroleum solvents and acetone	Often soluble in acetone
Mechanism of formation	?	Caused by formation of oil-insoluble oxidation products May be carried in the bulk lubricant until it is deposited.
Hydrocarbon source	?	Fuel, Lubricant, Or both.
Mechanism of control	?	Controlled by alkaline detergent and dispersant lubricant additives.
Source of percursors	?	Partly oxidized fuel in blow-by or products of lubricant oxidation
Site of reactions	?	Oil sump is involved
Known catalysts	?	Nitrogen oxides, Metal particles

with large top land clearance, a problem which is believed to be caused by inadequate pressure buildup above the piston rings [2]. If hard deposits are formed within ring grooves they will disrupt the proper action of the piston rings, and may also cause an increase in lubricating oil consumption. Apart from the oil consumption issue, piston deposits can be detrimental to the lifetime of engine parts due to increased wear and heat loads caused by disruption of heat transfer.

Lubricating oil formulation is known to be an important factor in the formation and prevention of piston deposits. Piston deposit is a performance criterion in lubricating oil acceptance tests, and has been subject to much research.

Three major factors influencing the formation of piston deposits in high speed diesel engines running on distillate fuels has been identified in [18]:

- high piston temperatures
- sulphur in the fuel
- soot formed during the combustion process

Note that fuel sulphur level and combustion soot are not independent.

2.5.4.1 Composition of carbonaceous Piston Deposits

Piston crown and top land deposits in highly rated diesel engines are usually black and grow thicker than typical varnish films. Researchers have reported that deposits consist of soot and resin binder [43] or ash, organic soot and resins [2], where ash is the remains, predominately inorganic salts, remaining after TGA analysis, i.e. heating in an oxygen atmosphere while increasing temperature until the sample weight stabilizes. A temperature exceeding 900 C was used in [12], a temperature where even carbonates are oxidized. Using full scale truck engine test McGeehan [2] found salts of Zn and Ca in the piston deposits. In a cut back piston top engine, the parts of the calcium salt was identified to have the form of $CaSO_4 \cdot 1/2\ H_2O$ (plaster). Covich [71] and co-workers found that lubricating oil chemistry had a major influence on deposit composition, while combustion soot appeared to be a minor constituent in single cylinder test engine deposits. Reference [71] also reported that rectangular crystalline particulates rich in calcium and sulphur appeared to work as a binder for hard crown land piston deposit formed in a test engine. The authors suspected that this was $CaSO_4$.

These authors observed that at high magnification, the oxidized organic phase was seen to obscure the features which are characteristic of soot, wear particles and inorganic crystals in SEM micrographs. This observation was taken to support the idea that organic deposit material may work as a binding matrix. This interesting paper also revealed data showing that increased sulphated ash content in the lubricating oil result in an increase in the content of ash in the piston deposits, but that the amount of deposit expressed as % crown land carbon is not related to lubricant SA in this engine test. This is contrary to the opinion expressed in [72], and also experience reported in [73] illustrating again that what is true for one or more engines, lubricants and test conditions need not be generally applicable.

Using infrared spectroscopy, Shurvell et al. [74] detected residues of dispersant additive as well as calcium sulphate, calcium phosphate and carboxylate salts in piston deposit samples.

Smith et al. [75] studied the composition of engine deposits formed at special piston inserts in an engine test using advanced surface analysis techniques including TEM and EPS. Their results suggest that the organic content of the 'matrix' increases with the distance from the metal surface which is covered by a thin layer of metal oxides and phosphates originating from lubricant additive. They also observed that regions richer in calcium, zinc and phosphates are found within this matrix and calcium sulphate crystals near the metal surface. It was hypothesized that these sulphates were grouped following an annealing process. [75] Further research has been devoted to the development of model deposits as discussed in the following.

2.6 Deposit formation

Since cylinder liner deposits are formed under the lubricant film, the emphasis in this subchapter is on deposit formation from or within lubricants. However, deposition from mists and gas is also reviewed, as is deposit removal.

2.6.1 Research methods

Research on combustion deposits can be carried out in test rigs, miniature engines, single cylinder engines or full size 'production' engines in lab or in the field. As discussed in the introduction to this thesis, engine tests are demanding because of the complexity of the system under study, i.e. the number of processes that cannot be directly controlled, and because it is generally difficult measure the deposit. Engine tests usually therefore have only a fair degree of repeatability. For the same reasons, it is difficult to create lab tests that correlate well with engine tests. Close correlations with field data are even more difficult since usually unknown variations in fuel and oil quality, engine production tolerances, engine wear, loading and ambient conditions come into effect.

Engine test are usually used primarily to evaluate oils, fuels, additives and correlation to lab setups, while the more fundamental research is carried out in the latter.

2.6.2 Oxidative deposit formation

Several tests to investigate deposit formation from lubricants were reviewed by Hsu in 1981. [76]. These test result are typically a visual deposit characterization by colour or demerit ratings, or by weight. In the opinion of Hsu, the problem of controlling oil film thickness, test surface cleanliness and oil residence time on the surface were critical to the success of deposit tests.

Since different mechanisms may lead to deposit formation, a selection of complementary test procedures are used to evaluate different aspects of deposit forming and inhibiting properties of lubricants. For instance, a screening protocol for heavy duty diesel engine piston deposits prevention reported in [77] consists of:

- visual rating of deposits in a heated glass tube where oil flows with air,
- the weight of deposits formed from a heated stationary oil sample under air flow and
- a measurement of the oxidation induction time measured by high pressure differential scanning calorimetry HPDSC.

Oxidation reactions cause the formation of insoluble molecules which settle out as deposits. Exactly which molecules are soluble will depend upon the solvent properties of the base oil including the presence of additives. The net deposit formation is thus influenced both by oxidation and solubility. The base oil hydrocarbon structural composition also influences deposit formation. For instance, naphtenic base oils typically form varnish more readily than paraffinic oils, but less acidic material.

Paraffinic oils are more resistant to oxidiation than napthenics, and do not precipitate sludge until the oxidation is well advanced.
Oil insoluble deposits formed from different base oils in thin film oxidizing conditions reported by [22] contained about 20% oxygen by mass and around 7% hydrogen. The remainder is carbon apart from small amounts of impurities such as sulphur. These insolubles contain a higher level aromatics and sulphur than the fresh oil. These tests showed that sulphuric base oil species initially act as oxidation inhibitors but cause an increase in the formation of insoluble products following extended oxidation. The composition of insoluble deposits formed in a thin film oxygen uptake test (TFOUT) in [22] and a varnish film from an engine as reported by [68] is shown in table 2-8. Engine varnish of this type is thus well simulated by thin film oxidation.
Oil insoluble material group together as small spherical particles which may eventually settle out [22], [79]. The ability of the insoluble material to wet the surface is reported to influence the rate of deposits formation, hence accumulation of these deposits is dependent of surface material.
The weight of tetrahydrofuran (THF) insoluble deposit formed when a thin film of oil is exposed to a slow oxygen stream, is determined in the Penn State micro-oxidation test. This test principle has been used to create 'lubricant stability maps' showing the effect of temperature and oil composition on final deposits from base oils [79] and also formulated lubricants [80].

TABLE 2-8 COMPOSITION OF OIL INSOLUBLE OXIDATION PRODUCTS

Type	**C [% m/m]**	**O [% m/m]**	**H [% m/m]**	**Difference [%m/m]**	**Ref**
Varnish	74.6	17.8	6.9	0.7	68
ME oil insoluble	72.1	18.8	7	2.1	22
NS oil insoluble	70.8	21.5	7.4	0.3	22

These maps show that the level of deposits decrease with temperature due to an increase in volatile losses. The level of deposits reaches a minimum at roughly 350∓€. The level of deposits typically increases above this temperature due to thermal cracking effects. More volatile base stocks yield comparatively less deposits than heavier base stocks, hence this and other research have shown that deposit formation from hydrocarbon material at elevated temperature is a mechanism where evaporation and formation of volatile species compete with polymerization reactions.

2.6.3 Precursors of deposits

Partially oxidized hydrocarbon act as precursors for insoluble deposits. A study of such oxidation processes using n-hexadecane revealed that products of partial combustion separated in an organic and an aqueous phase upon condensation [43]. Additionally, a lacquer deposit formed on the glass wall of the test rig prior to the cold trap which was used to collect the partial combustion products.

The aqueous phase would form an insoluble 'red oil' upon heating while insoluble material was not formed in the organic phase even after prolonged heating. The IR spectrum of the red oil was similar to that of a lacquer which deposited on the test rig, but the average molecular weight was lower. The red oil would harden to a lacquer upon heating in air. The authors concluded that the lacquer deposited in the rig and red oil arose from the same precursors and only differ in degree of polymerization. Further experiments revealed that neutralization of the aqueous phase prevented the formation of red oil when the aqueous phase was heated. This illustrates how varnish formation can be controlled by alkaline detergent additives. Red oil formation could also be prevented if carbonyl and peroxides were removed.

Since the deposit precursors are oil insoluble they may be expected to separate from the oil, possibly forming a dispersed phase. The authors of [43] verified experimentally that fuel hydrocarbon is partially oxidized during the ignition delay, but not during diffusion burning.

Oxidation of a liquid lubricant oil film may also be considered a partial oxidation and will lead to the formation of an aqueous and hydrocarbon phase as described above [43] [22]

2.6.4 Deposits from lubricants with performance additives

Using the micro-oxidation test at different temperatures, it was seen that the hydroperoxide decomposing ZDTP anti-oxidant was only effective in reducing deposit formation up to 250€ in this type of test, above which there was no difference in deposit level.

Using a thin film oxygen uptake test (TFOUT) it was observed that radical scavenging antioxidant additives had little effect on the final amount of insolubles formed. [22]

Micro-oxidation tests with fully formulated lubricants indicated that the additive package was effective with respect to final deposits at temperatures below 250°C The level of deposit from a formulated lubricant was higher than from a base oil alone at test temperatures of 250°C and higher, the difference in deposit was considerable at 325 and 350 degrees. This difference was attributed to residues formed by the less volatile VI improver and the non volatile ash component. [80].

Unlike the base oils investigated in [79] the final deposit level of a formulated lubricant would first increase with temperature, reach a maximum and subsequently decrease. A similar trend was observed for top groove fill in an engine test.

The formation of lacquer from a thin film on an aluminum piston was studied by the authors of [39] In this test, the oil film was continuously replenished from a cool reservoir, a notable difference compared to the above mentioned microoxidation test. In this case, it was observed that the less viscous and presumably more volatile oils generally yielded more lacquer than did heavier oils. A considerable difference was observed at high temperatures between oils of equal viscosity. It was also observed that a small amount of ZnDTP would decrease the rate of lacquer formation while an amount larger than 1% wt. would increase the lacquer formation rate. Increasing amounts of calcium sulphonates resulted in decreasing formation rate of lacquer deposits.

Comparing the results from the micro oxidation test and the thin film aluminium piston lacquer deposit formation is not simple as one test focuses on the final deposit level, while the other focuses on the deposit formation rate. Investigation of the deposit formation rate in the micro-oxidation apparatus has determined that the formation rate and final deposits level are independent [81]. There is also a significant difference in the deposit formation on aluminium and iron surfaces [82]

2.6.5 Model Piston Deposits

Piston deposits typically contain a significant fraction of inorganic material such as calcium sulphate. In order to investigate piston deposit formation Papke and co-workers designed a test rig where a thin oil film was lifted from a cold oil reservoir onto a heated metal plate by a reciprocating mechanism[78] [82]. The metal surfaces on either side had surface temperatures of 250°C and 320 °C respectively. This test rig was used to form model deposits which were subsequently analyzed using different techniques including EPS, FT-IR and SEM. The similarity between this test rig and the second deposit rig used in this research makes these results particularly interesting.

Following each test, the metal plate with deposits was immersed into an ultrasonic heptane bath which removed less adherent material. Similar to the oxidation products discussed above the simulated piston deposits were in the form of sub-micron spherical particles, only in this case these spheres contained inorganic material as well. The authors found that when an overbased calcium sulphonate detergent was added, calcium carboxylate was found in the deposit. When the base oil contained sulphur, calcium sulphonate salts were also found in the deposit, hence base oil sulphur contributes to the formation of calcium sulponhate. Both sulphonate and carboxylate salts are oil insoluble and end up in the simulated piston deposit. These constituents are also found in authentic piston and liner deposits. The spheres of oil insoluble material were found to adhere more strongly to iron than to aluminium surfaces. Further investigation revealed that this was caused by a difference in the wetting of these surfaces by the insoluble material.

2.6.6 Model liner glaze

The formation of a smoothing glaze on a gray cast iron cylinder liner surface was replicated in experiments by Montgomery [16]. In this experiment a cast iron test block was 'run in' using a carburized steel piece as reciprocating 'piston ring' and an uninhibited lubricant.

The cast iron surface was smoothed by the formation of a glaze, and the coefficient of friction decreased during this experiment. This coating was visually identical to the graphite in the iron structure. Analysis suggested that it consisted of carbon and iron oxide in the form Fe3O4. The carbon was believed to be graphite but some inclusion of oil could not be eliminated. Analysis of glaze removed from engines in field also contained significant carbon (believed to be mainly graphite) and Fe3O4, but also contained about 30-40% other elements believed to be contaminants such as sand, dust etc. This deposit is thus different in composition from the glaze studied in this thesis, and also differs in the fact that it is not primarily situated in surface grooves.

2.6.7 Deposition from gas phase

Material carried within a gas may deposit by way of condensation and thermophoresis. Thermophoresis causes large molecules to migrate against thermal gradients because the average energy of the collisions is higher on the hot side. This mechanism can cause the concentration of elements like soot to increase in cold boundary layers near walls. High turbulence and gas velocity tend to counteract this mechanism.

High molecular hydrocarbon which condenses may bind other particulates like soot which does not adhere by itself. The surface temperature will have strong influence on deposit characteristics. For instance, deposits due to fuel impingement on a probe in the prechamber of a diesel engine were pitch like at probe temperature of 150℃. Thick, solid deposits were formed in the range from about 200 - 550℃ while only a fine non-adhering dust was seen at temperatures above 550℃ [83]. Time also influences the composition. Gas chromatographic investigation has revealed that the average number of C atoms in the deposit molecules decrease with time, presumably as the large binder molecules are increasingly blended with the smaller molecules they bind. [84]. Experiments where a lubricant mist was oxidized then deposited on aluminium test surfaces, showed that the deposit formed spheroids at lower temperature and oxygen concentration, resulting in a dull black surface. At higher temperatures, the deposit wetted the surface resulting in a featureless smooth but shiny surface. [85] These observations agree well with what has been observed within oils [78]

2.6.8 Deposit removal mechanisms

The true problem with engine deposits is not so much their formation as their accumulation. Deposit accumulation is naturally dependent upon both formation and removal mechanisms. A literature review in [84] revealed 6 mechanisms of removal of engine deposits:

1. Evaporation
2. Oxidation
3. Desorption
4. Abrasion
5. Break off due to differences in thermal expansion
6. Wash off by liquid flow

Evaporation, oxidation and desorption will normally increase with temperature although increased temperature can also cause reactions which may harden the deposit.

Abrasion is mechanical deposit removal by scraping or blowing while break off refers to deposit decomposition or possibly delamination due to shearing stress caused by change in temperature and difference in thermal expansion between deposit and substrate.

Chapter 3

Characterization of Cylinder Liner Deposits

A number of complementary techniques have been used to identify main constituents and characterize liner deposit samples. Techniques used in this work are reviewed and results of their application to liner deposit samples and other relevant samples are presented.

3.1 Techniques for analysis and characterization of deposits

The analytical techniques used are all based upon advanced 'off the shelf' tools that are adapted as needed to suit our requirements. While these instruments generally are easy to operate, care and insight is required to prepare samples and interpret the data. The techniques used are:

1. Fourier transform infrared spectroscopy (FT-IR)
2. Scanning electron microscopy (SEM)
3. Transmission electron microscopy (TEM)
4. Energy dispersive spectrometry (EDS)
5. X-ray diffraction spectrometry (XRD)
6. Digital photography
7. Surface profilometry

Sample preparation, analysis and interpretation has been done by the author in all cases except XRD analysis which was preformed by Elin Nielsen and analyzed using Diffrac Plus software. The author also received extensive assistance from John Walmsley in TEM sample preparation and analysis.

3.1.1 Fourier Transform Infrared spectroscopy

Transmission of infrared light is characteristic of the transmitting material In IR spectroscopy, a transmission spectrum is generated from electromagnetic radiation with continuously varying wavelengths in the range 2.5 to 50 μm.

The electromagnetic radiation induces intra-molecular vibration in polar molecules within the sample and may also induce dipoles onto molecules that are normally non-polar. If the frequency of the radiation approaches the resonance frequency of a vibration mode in a molecule, an energy loss is observed as a characteristic absorption. Theoretically, each molecule has a characteristic spectrum that can be used for identification purposes. An IR spectrum may therefore be used to 'fingerprint' matter. Samples with identical adsorption spectra are likely to be identical. However, many substances, particularly ionic substances or symmetric molecules may absorb little or no infrared radiation and thus be 'invisible' to IR analysis. The intensity of absorption is related to the quantity of absorber, hence under ideal conditions and assuming that only one species absorbs at a certain (set of) wave number(s), the IR absorption can be used for quantitative analysis of this species.

Absorption peaks in the IR spectrum of a pure substance is normally caused by a particular mode of vibration in one particular functional group. The location and intensity of the absorption may shift depending upon the structure of the host molecule. For instance, stretching-vibration in the C-H band causes absorbance around 3000 cm^{-1}. Alkanes generally have C-H stretch absorption immediately below 3000 cm^{-1}, while aromatics and alkenes typically have C-H stretch absorption just above 3000 cm^{-1}.

When complex mixtures such as liner deposits are investigated, the transmission spectrum will also be complex and finer features may be obscured by more dominant absorptions. If the deposit can be fractionated by dissolution, more detailed information may be obtained as demonstrated by Shurvel et al. [74].

A comprehensive list of functional group absorbencies with relevance to the analysis of formulated lubricating oils is provided in [25]. Characteristic absorbance peaks with more general relevance are found in [86], [87] and [88]. The use of such tables requires some apriori information about what one might expect to find in the deposit to eliminate unreasonable candidate species. Comparison with other types of engine deposits is useful in this context as is information about oil additives.

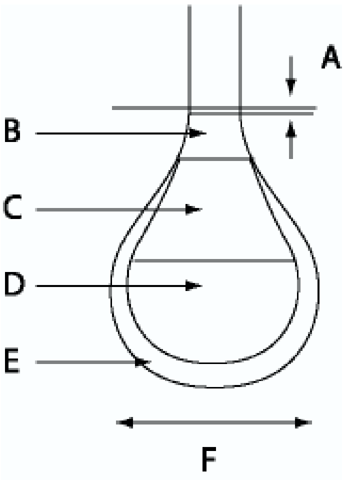
The spectra used in this work are obtained using single beam Fourier transform IR instruments equipped with a single bounce diamond reflection cell. Each spectrum is derived from multiple interferograms. The spectra are corrected by subtracting a background spectrum to correct for absorption in the atmosphere surrounding the sample.

3.1.2 Scanning electron microscopy (SEM)

The scanning electron microscope is a powerful and versatile tool. It is based upon analyzing electron emissions from the specimen as it is irradiated by a finely focused electron beam. The electron microscope has a resolution and depth of field that are far superior to optical microscopes. Electron beam interactions with specimens cause many effects from which information can be gathered. A short review based upon [89] [90] is given below.

Elastic and inelastic scattering of electrons occur as a result of the electron beam irradiation. Elastic scattering causes a change in the direction of the electron, but the electron does not loose energy. Multiple elastic collisions cause some of the electrons to leave the surface as back scattered electrons.

Inelastic interactions between the electrons and the specimen causes energy to be transferred, resulting in the emission of secondary electrons, Auger electrons, characteristic X-rays, continuum x-rays, cathodoluminiscence and more. Secondary electrons are electrons with low energy, below 50 eV. They can only escape if they originate close to the surface, and the intensity of the signal depends upon the angle between the electron beam and the surface, therefore secondary electrons are suited to create high resolution topographical images. Because of the energy-definition, backscattered electrons with low energy are counted as secondary electrons, and backscattered electrons can cause emission of secondary electrons as it exits the surface. Figure 3-1 illustrates the interaction between an electron beam and a sample. The electrons penetrate deep into the surface and are scattered. The electron and x-ray emissions due to the electron beam irradiation thus originate from a bulb shaped volume below the sample surface and the x-ray resolution is lower than that of the beam or secondary electros.



A: Auger electrons
B: Secondary electrons
C: Backscattered electrons
D: Characteristic X-rays
E: Continuum x-rays
F: X-ray resolution

Figure 3-1 *Electron beam interaction with sample surface*

The volume of the specimen that is affected by the electron irradiation is affected by the composition of the specimen and the energy of the electron beam. The intensity of backscattered electrons is dependent upon the angle between the beam and the surface, thus the topography of the specimen can be observed from backscattered electrons also. The amount of backscattering is also dependent upon sample density or atomic number, thus the backscattered image also provides an atomic number contrast.

The electron irradiation will cause a charge build-up if the specimen is not sufficiently conducting. This will degrade the image as the static charge will affect the path of emitted electrons, and in severe cases the electron beam can be deflected. Local charging will result in 'voltage contrast' in the picture. A negatively charged area (relative to the detector) will encourage the emission of secondary electrons and appear brighter, while a positively charged area will suppress secondary electron emission and appear darkened.

The resolution of the electron microscope is limited by the area that is irradiated by the electron beam, called the spot size. However, when the spot size is reduced, the signal to noise ratio is reduced. A larger spot size may be desirable at low magnification when the high resolution potential is not utilized. Depth of field can be optimized by using a small aperture and increased working distance. The electron microscope is frequently equipped with other analytical instruments like the EDS that analyses x-rays emitted as the electron beam hits the specimen.

3.1.3 Transmission electron microscopy (TEM)

The transmission electron microscope directs a beam of electrons through the sample that is to be investigated. The principle is analogous to slide projector which transmits light through the slide onto the viewing screen, forming an enlarged image of the slide. The sample must be ultra thin, in the order of 50 nm, in order to be electron-transparent.

The TEM provides information about the internal composition of the sample; this is particularly true when cross section samples are used. Combination of dark field and bright field electron microscopy with electron diffraction techniques permits direct visualization of crystallite sites. For this reason, the TEM is particularly useful in localizing crystalline particles deep within a deposit matrix. It is also possible to identify diffracting particles within the sample by studying their electron diffraction pattern. This approach is analogous in many respects to X-ray diffraction analysis which is described below.

3.1.4 Energy dispersive spectrometry (EDS)

One of the interactions that occur as a specimen is irradiated by an electron beam is temporary inner shell ionization of a specimen atom by the ejection of an electron from an inner shell by a high energy (beam) electron. The ionized atom immediately responds by dropping an electron from an outer shell to fill the inner vacancy. The inner shell is a lower energy state, and the energy difference is rejected as an x-ray photon. The energy of this photon is equal to the difference in energy between the electron shells. Because the energy difference between the electron shells is a characteristic of atoms, the emitted x-ray energy (or wavelength) is a characteristic of the type of atom irradiated. Therefore, the x-ray emissions can be used to characterize the composition of a specimen. Elemental analysis using the energy-dispersive x-ray detector (EDS) can be combined with both SEM and TEM.

3.1.4.1 Qualitative elemental analysis by EDS

The shell structure of the atoms is of primary importance to EDS analysis. Hydrogen and Helium have only one electron shell and cannot be detected by EDS. Elements with atomic number 3-10 have only one characteristic emission which makes them harder to identify by EDS, particularly those elements that have very low characteristic energy and is at risk of being absorbed in the detector window. Atoms with atomic number greater than 10 have multiple characteristic emissions. For instance, Sodium (11) has two inner shells and three characteristic emission energies; if the inner shell (K) is ionized, the vacancy can be filled from either of the two outer shells; if the middle shell (L) is ionized the vacancy will be filled from the outmost shell.

An incoming electron must have critical ionization energy in order to expel an electron from a particular electron shell in an atom. This energy is higher than the characteristic energy of the electron shell. The electron beam must therefore have sufficient energy in order to detect the element. However, a high energy beam penetrates deeper into the specimen, and the average pathway from x-ray generation to the detector increases. More of the low-energy x-rays will be absorbed and corresponding light elements may remain undetected. Qualitative analysis should therefore be done at different beam energy levels.

The detection limit of the EDS is dependent upon measurement condition and presence of masking elements. Overlapping peaks may be resolved by quantitative spectral deconvulsion.

3.1.4.2 Quantitative elemental analysis by EDS

The generation of characteristic x-rays under an electron beam is proportional to the concentration of the element; therefore the x-ray signal can be used to assess the quantitative distribution of the elements. Unfortunately, the x-ray signal that reaches the detector is not identical to this theoretical signal. X-rays may be absorbed within the sample before it reaches the detector. The absorption causes a reduction in the signal, and may also generate new x-rays of lower energy by excitation of other atoms. This latter effect is referred to as x-ray fluorescence. Surface roughness and tilt may also alter the signal. Additionally, a calculation of composition based upon x-ray signal assumes a homogeneous substance. Since these factors cannot be controlled in our samples, quantitative analysis is not possible by EDS.

3.2.4.3 Elemental Maps

EDS can be used to produce compositional images. The location of elements upon a surface is visualized.

3.1.5 X-ray Diffraction Spectrometry (XRD)

X-ray diffraction spectrometry is a technique where the sample is irradiated by X-rays with known wavelength. The irradiation of copper by a high energy electron beam is a commonly used source of x-rays for this purpose. Interestingly, this is an 'inverse' application of the principle used in EDS analysis where the element (copper) is identified by the x-ray energy or wavelength.

Most of the x-ray beam passes through the sample, however a fraction of the radiation is absorbed. The absorbed electrons are immediately re-emitted. This process is known as electron scattering. Constructive and destructive interference will occur in the emitted x-rays if the atoms are organized in planes (i.e. the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays. A relationship between wavelength (λ), atomic spacing (d) and angle of observation (θ) is expressed by the Bragg Equation.

$$n\lambda=2d\sin(\theta)$$

A strong interference maximum in the x-ray signal is seen at angles where the conditions in the Bragg equation are met resulting in a characteristic pattern in the emitted x-rays. The pattern depends both on what atoms make up the crystal lattice and how these atoms are arranged.

Crystals can have many sets of planes passed through their atoms. Each set of planes has a specific interplanar distance and will give rise to a characteristic angle of diffracted X-rays. A set of 'd-spaces' obtained from a single compound represent the set of planes that can be passed through the atoms and can be used for comparison with sets of d-spaces obtained from standard compounds.[91] These spectra can become complex when many different crystalline elements are present in the sample. An advanced software system with an extensive database is used to identify possible candidates. Combination with other analysis is used in our analysis to narrow the list of candidate elements.

3.1.6 Digital Photography

Digital Photography is used extensively in this work to capture and report the visual condition of cylinder liners.

The curved metal surface is prone to setting up reflections that make the interpretation and comparison of images very difficult. When liners are photographed, the image is severely dependent upon the lighting and reflections. The image will often be radically different if it is photographed with rather than without the use of flash and other lighting.

A special technique was developed to obtain repeatable conditions for photographing cylinder liners. This is based upon the placement of a tubed hood onto the lens protruding from a standard high performance digital camera. The hood is equipped with a small light bulb to provide sufficient light for the camera auto focus to function properly, and a larger orifice to permit light from the standard built-in camera flash to light up the picture zone. The lens hood is shown in Figure 3-2.

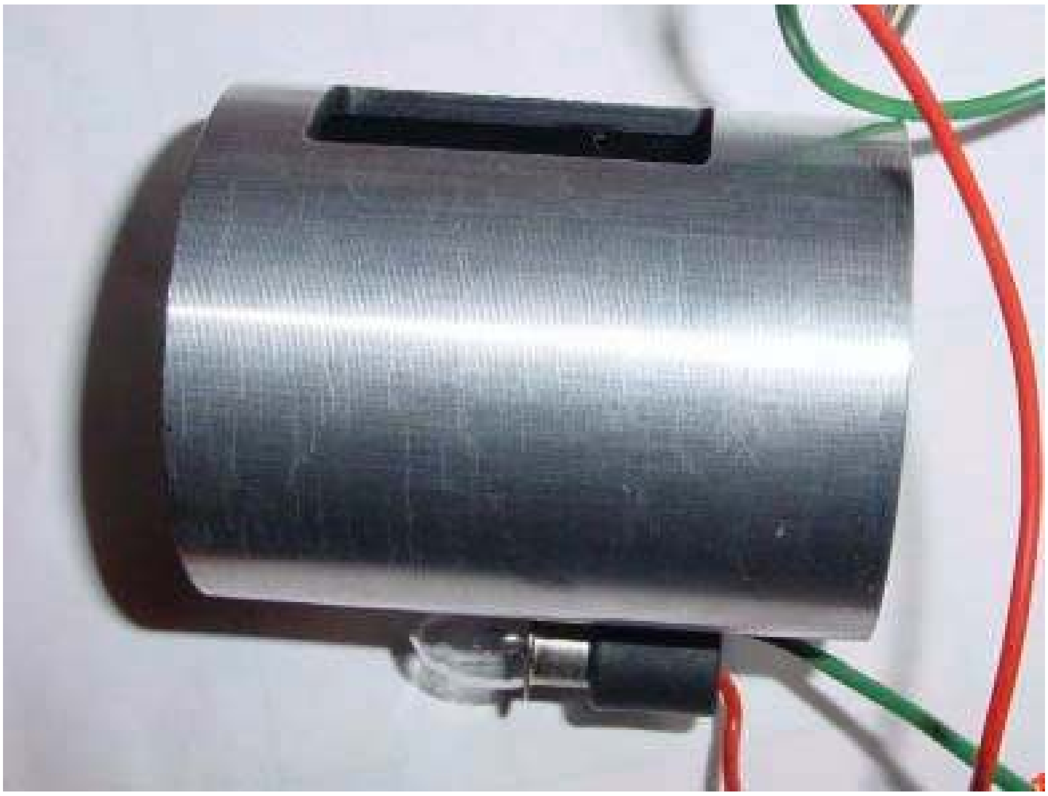


Figure 3-2 *Lens hood used to obtain repeatable light conditions for photographing cylinder liners*

Pictures are taken with the hood placed in direct contact with the liner surface. A white paper mask is used to locate whereupon the liner the picture is to be taken and also to assist brightness adjustment within the camera as seen in Figure 3-3. A special procedure is used for setting camera variables such as white balance, flash level, zoom, resolution and more.

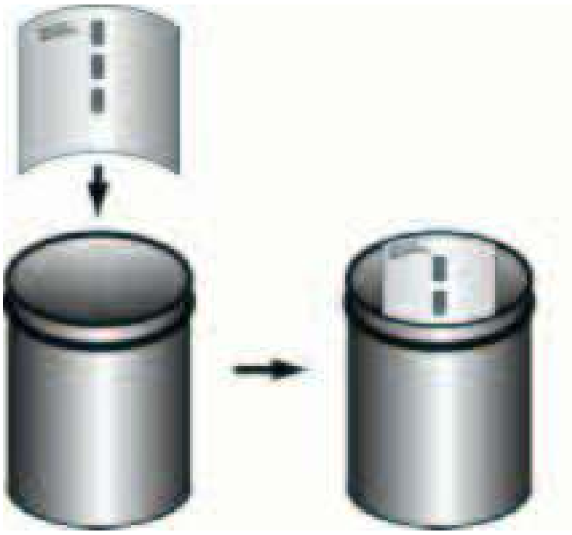


Figure 3-3 *Paper mask for photographing liners*.

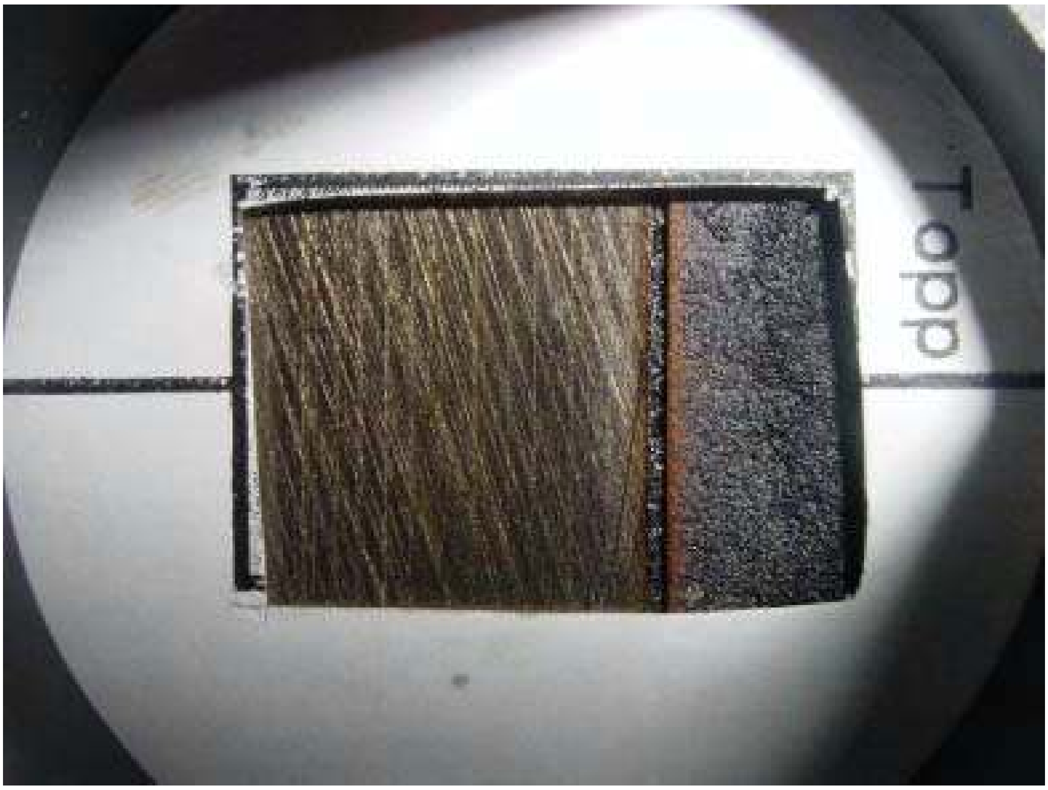


Figure 3-4 *Crude image of liner deposit*.

Images created this way are vastly more repeatable than images photographed at an arbitrary angle and in uncontrolled lighting, however images photographed in this way may appear cleaner than when the liner is photographed at an angle, probably because most deposit is located in the grooves which will reflect a comparatively larger fraction of the light when the liner is viewed at an angle.

A crude photographed using this technique obtained from a case study is provided in Figure 3-4. The crude images are subjected to a manual post treatment routine in which they are rotated and the uninformative paper is cut away.

3.1.7 Surface roughness measurements

All surfaces show some irregularities when subjected to close scrutiny. Such irregularities can be visualized in a surface trace. A surface trace can be interpreted as a magnified cross-section of the surface. In order to save space and give a better overview, the surface trace is compacted longditudally. This is illustrated in Figure 3-5 which has been reworked from [92]

The surface profile is obtained by drawing a sharp lightly loaded stylus at a constant speed over the surface that is to be examined. The movement of the needle is recorded as the surface trace.

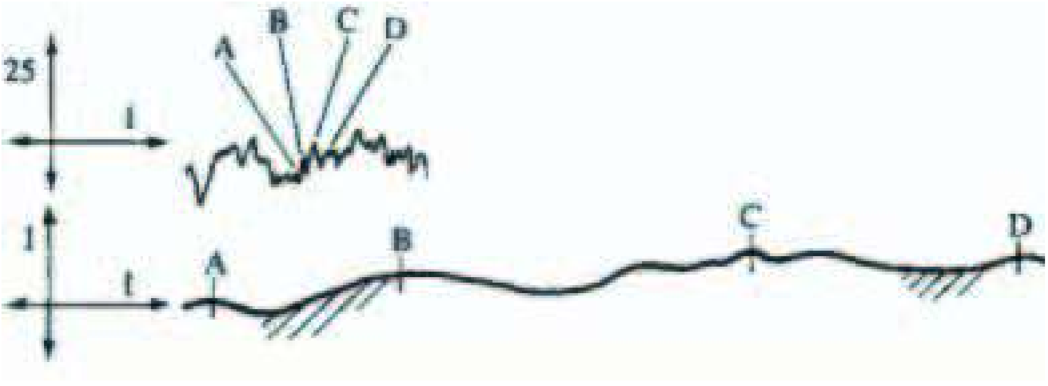


Figure 3-5 *equally and differentially magnified surface* [92]

The portable profilometer used in this work measures the profile height relative to a skid that is drawn after the stylus. This makes the setup of the instrument relatively simple. The principle is illustrated in Figure 3-6

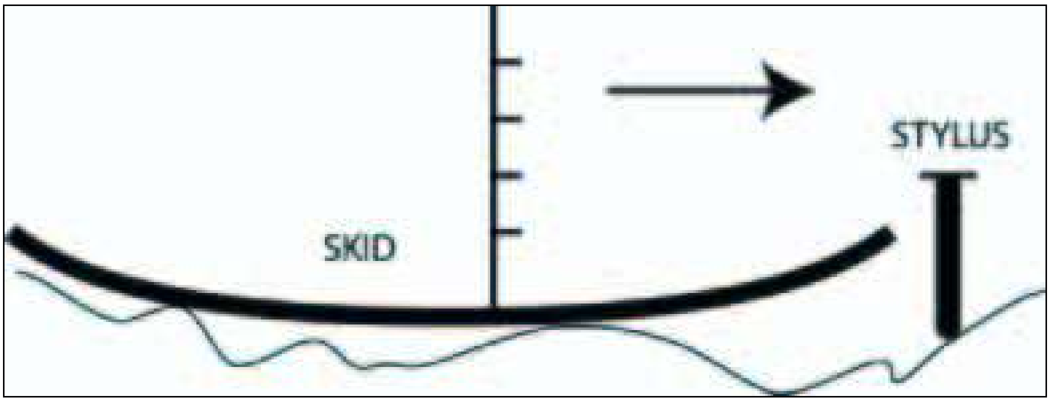


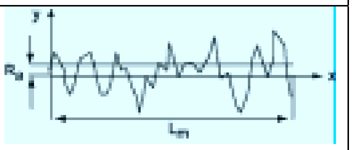
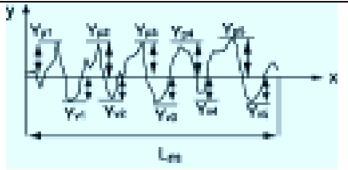
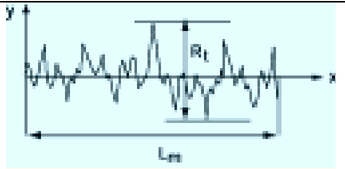
Figure 3-6 *Skid and stylus principle (not to scale)*

Figure 3-6, which is not drawn to scale, illustrates two important aspects of this principle of measurement. The first aspect is the relationship between the diameter of the stylus tip and the ability of the stylus to penetrate narrow cracks and grooves. The diameter of the stylus tip will effectively limit the ability of the instrument to detect short wavelength patterns (narrow cracks) in the surface. The second effect that can be appreciated in Figure 3-6 is the relationship between the size of the skid and the ability of a relative measurement between the skid and stylus to detect low frequency variations (waviness) in the surface. The maximum and minimum wavelengths that will be recorded also depend on the instrument sampling frequency in relation to the stylus traversing speed and the high pass filter used in the signal converter. The high pass filter characteristics are expressed by the cut off length, the wavelength at which transmission is 75%.

A number of parameters may be used to describe a surface numerically. Some widely used parameters are given in table 3-1. These parameters have been developed because it is convenient to quantify the condition of a surface. However, interpretation must be done with care as they cannot distinguish widely different surface profiles that coincidently may have the same characteristic value. The parameters in table 3-1 can be calculated by the Hommel T-500 profilometer used in this work.

The surface characteristics are statistical parameters calculated on basis of a surface trace. All surfaces are subject to random variations, the extent to which a single trace is representative of the surface condition in a given area is subject to variation. This may be assessed by repeated measurements. The length of the trace may influence Rz and Rt, as the likelihood of encountering high peaks and deep valleys increase with increasing trace length.

TABLE 3-1 COMMON SURFACE PARAMETERS

Parameter	Definition [ISO]	Illustration
Ra	Arithmetic mean of the deviation of the filtered roughness profile from the center line within the measuring length lm.	
Rz	Average maximum peak to valley height. The average of maximum and minimum observations within the filtered roughness profile .	
Rt	Maximum peak to valley height within the measuring length.	

The surface parameters listed in table 3-1 does not reveal if the surface is characterized by particularly high peaks or deep valleys: The suitability of surface parameters is dependent upon what the surface that is to be described looks like. Special means of characterization have been developed for special surfaces such as a cylinder running surface.

For instance, DIN 4776 specifies a family of parameters that together are designed to characterize a honed surface. [93] More recently, a new set of parameters that estimate the standard deviation of the surface resulting from a two step manufacturing process have been developed. [94]. These ideas have now been adopted in international standards [95]. Unfortunately, these advanced surface characteristics cannot be obtained using the surface profilometry equipment available in this project. A discussion of the selection of available surface parameter for detecting liner deposits on a honed cylinder surface is provided in appendix A1

3.2 Distribution of liner deposits

The distribution of liner deposits varies from case to case, however there are some recurring patterns.

3.2.1 Visible patterns in liner deposits

Cylinder liner deposits vary in color from nearly invisible to dark brown. Recall from the introduction that a frequent categorization of the deposits is 'liner lacquer' meaning amber and brown deposits, while the term 'bore glazing' is used in this context to describe 'invisible' liner deposit. The deposit may discolor entire liners, but closer scrutiny has revealed visible unevenness an irregularities in the distribution in all cases investigated as discussed below.

Horizontal lines - Piston ring imprints

The deposit may have horizontal lines. The distance between the lines, the width of the line as well as its general appearance indicates that they are imprints of the piston rings. This suggests that deposit can be carried on piston rings. This idea is substantiated by observations in one engine of hard, thick and brittle yellow deposits on parts of the piston ring face that was not in contact with the liner. Horizontal deposit lines are shown in Figure 3-7


(a) (b)

Figure 3-7 *Deposit stripes - piston ring imprints*

Fluid movement

Liner lacquer deposits frequently show traces of fluid movement. The fluid appears to originate either from the sooted area above upper ring reversal or from points on the liner itself.

(a) (b)

Figure 3-8 *Traces of fluid movement*

The traces of fluid movement appear to have formed in a standing engine. They appear to originate either from the area above top ring travel or what appears to be a leak from the oil control ring. These stains are suggestive of presence of a severely degraded but liquid lubricant.

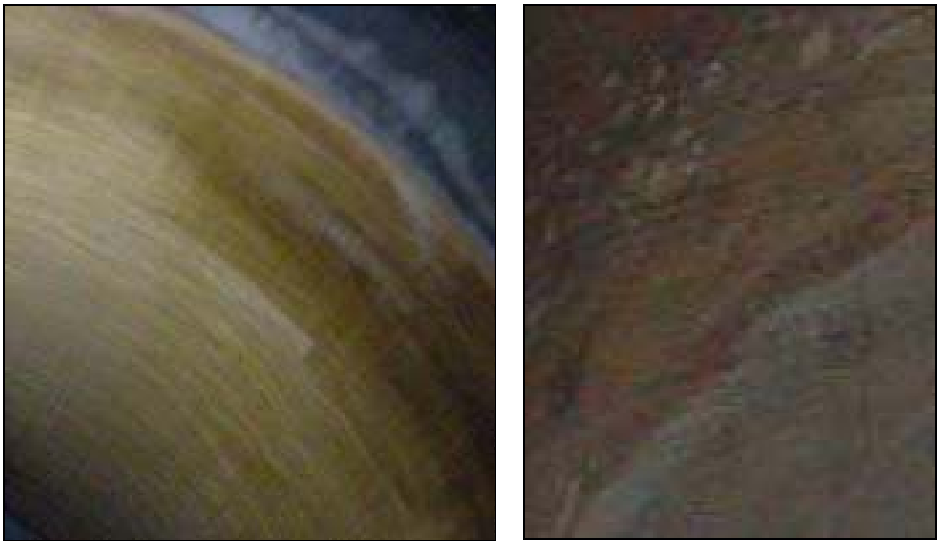
Deposit steps or regions

In some cases, the deposit seems concentrated in regions with sharp boundaries as seen in Figure 3-9. The visible lacquer is often concentrated in the top.

Surface measurements have shown that the surface roughness need not be significantly altered when the sharp visible boundaries seen in Figure 3-9 are crossed. Investigation using optical end electron microscopy showed that difference in perceived overall colour is primarily related to the amount of deposit on the liner plateau. Figure 3-9 a) have strong vertical stripes which terminate abruptly. This could possibly be related to non conformity of piston rings to the liner.

In case of horizontal stripes, the step distance seen in Figure 3-9 a) and other pictures (not shown) conform with piston ring distance which strongly suggests these areas are related to the piston rings.

Deposits that are receding due to oil change or use of fuel additives has been observed to show blisters. Liners may also have small spots or stains on the liner, as shown in Figure 3-10.



(a) (b)

Figure 3-9 *Visible deposit concentrations and deposit 'steps'*

(a) (b) (c)

Figure 3-10 *Deposit stains*

3.2.1.1 Picture Ratings

Photographs taken during field studies of liner deposits have been rated using three alternative deposit grades: Dark, Amber or Clean. The cylinder liners were rated two or three heights: upper ring pack reversal, 45% downstroke and, if taken, 85 % downstroke. The ratings are taken at four points around the circumference. The pattern in the glaze deposits from repeated inspections of 6 cylinders (216 pictures) is shown in table 3-2 while the ratings from repeated inspections of 9 cylinders (192 pictures) with lacquer deposits are shown in table 3-3. Lacquer and glaze deposits are both cleaner in the lower region than in the top. Dark deposits are seen predominantly in the top in both cases.

TABLE 3-2 AVERAGE COLOUR DISTRIBUTION - GLAZE

	Amber	Dark	Clean
High	43%	27%	29%
Midstroke	6%	4%	90%
Low	4%	6%	90%

TABLE 3-3 AVERAGE COLOUR DISTRIBUTION - LACQUER

	Amber	Dark	Clean
High	26%	48%	26%
Midstroke	62%	4%	34%
Low	63%	0%	38%

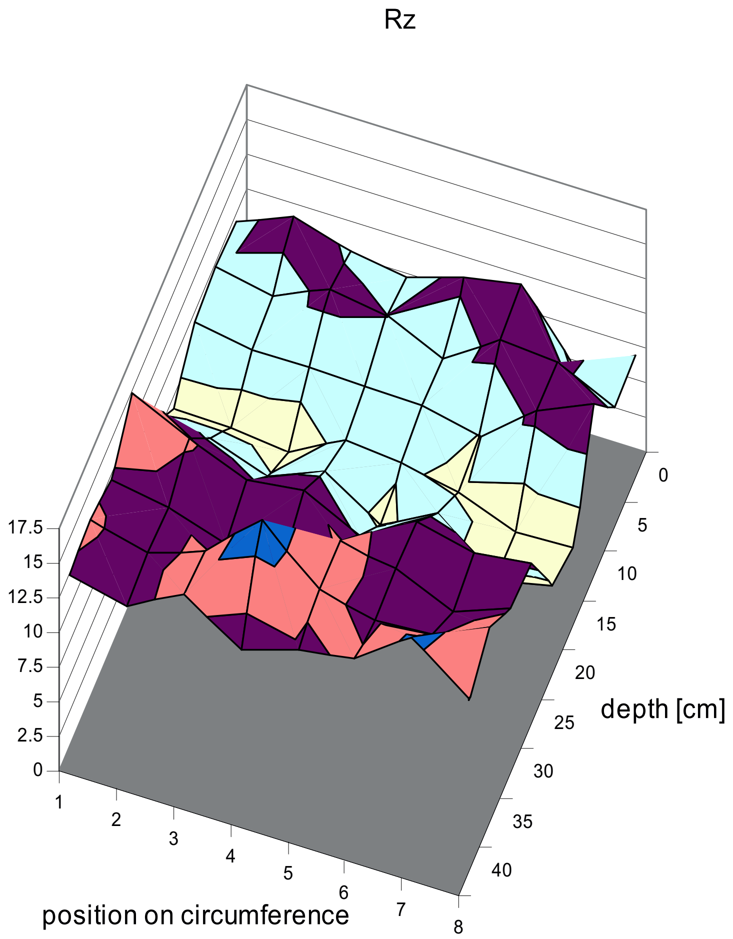


Figure 3-11 *Example of roughness distribution. The low region around 15-20 cm is interpreted as a belt of liner deposits*

3.2.2 Macroscale deposit distribution

The distribution of the deposits on the cylinder liner can be indicated by a map of the surface roughness, low roughness indicating deposits. More information regarding this type of measurement is given in appendix A1. Detailed deposit maps were constructed from liner samples brought to the lab using measurements taken with 5 cm intervals along the height and either 4.9 or 9.8 cm intervals around the circumference. Each data point in these maps is the averages of five measurements.

The distribution of roughness of a 'glazed' liner is shown as an example in Figure 3-11. There is a tendency in this figure of high roughness values in the low region corresponding to low roughness in the top region at the same circumferential position. This effect is not strong and not seen in other liners, and the use of average roughness values around the circumference to describe this deposit seems reasonable.

Figure 3-12 shows the deviation in roughness from a reference level (45 cm below flame ring) averaged around the circumference of four cylinder liners, and the total average which is the thicker line. This figure indicates that the deposit is thicker in the mid-stroke region of the cylinder liner. The lubricating oil film is expected to be thickest in this part of the liner since the piston speed is high, which is beneficial for hydrodynamic film formation. To verify that the reduced roughness in the mid stroke region is due to deposits rather than wear or other factors, the change in surface roughness due to cleaning of one cylinder is shown in Figure 3-13.

3.2.2.2 Circumferential variations in distribution

The vertical deposit distribution pattern shown in Figure 3-12 is recognized in other field measurements from this engine, however the relative uniformity around the circumference seen in Figure 3-11 is not always seen in all engines this same design.

Figure 3-14 shows the pattern observed in liner lacquer based upon field measurements. The roughness measurements in this figure are given in Rz [microns] at different distances [cm] below the top of the liner in different directions with 90 degree increments.

This liner deviates from the previously observed symmetry in roughness around the circumference, however the roughness measurements indicate that there is little deposit in the lowest region 27.5 cm below the top, but significant deposits in the midstroke region 14.5 cm below the top regardless of direction.

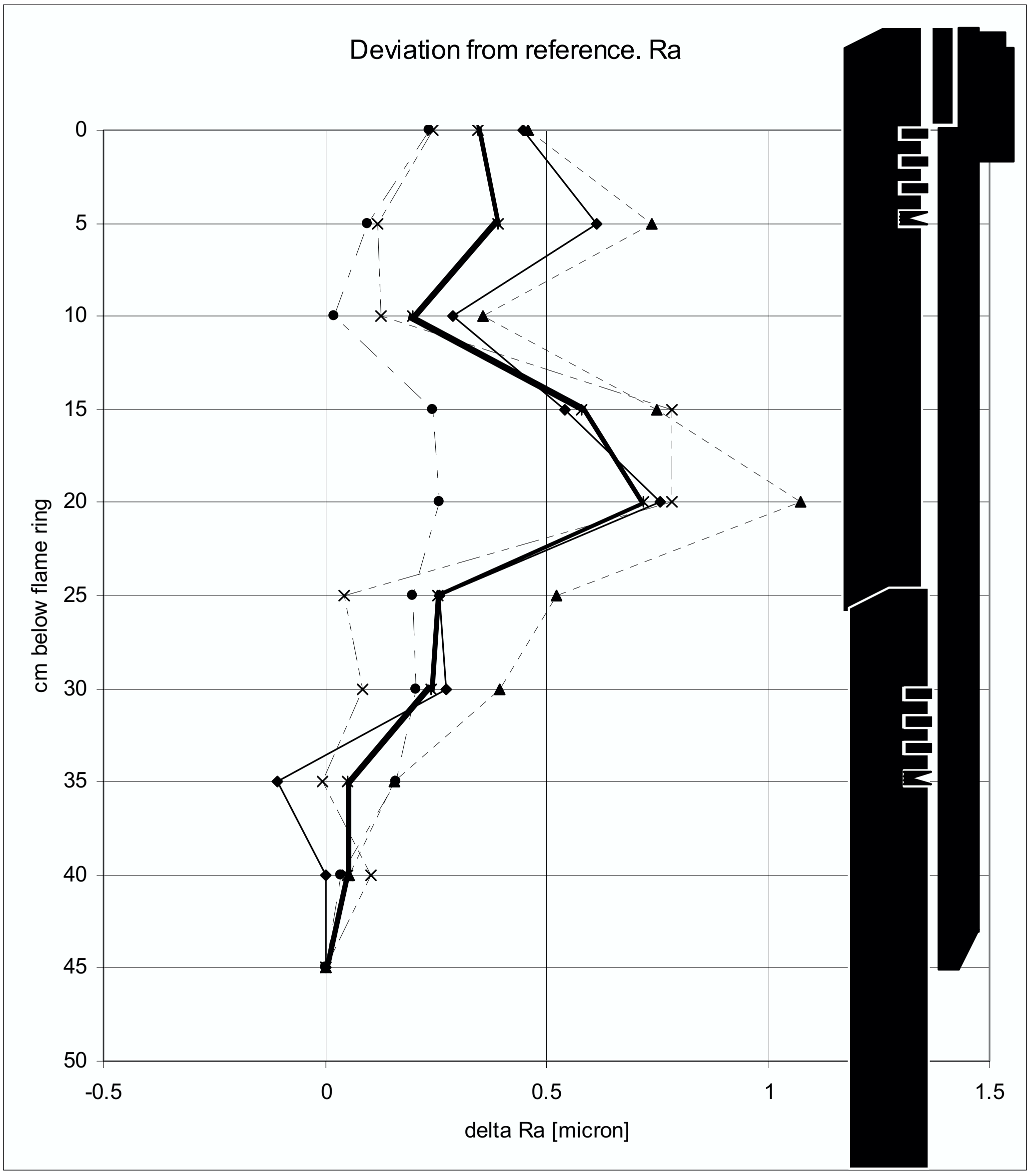


Figure 3-12 *Average distribution of deposits in relation to piston movement*

This pattern was seen in two engines with opposite directions of rotation, hence effects related to thrust or antithrust sides are not believed responsible for the lack of deposit symmetry. Detailed test bed temperature measurements provided by the engine manufacturer revealed that the liner temperature as measured by thermocouples 2 mm below the surface in the higher regions of the liner also varied around the circumference. Measurements at hours 6 and 9 were generally lower than direction (hour)3 which was lower than direction 12. Hence the deposit appears concentrated on the 'cold' side of the cylinder.

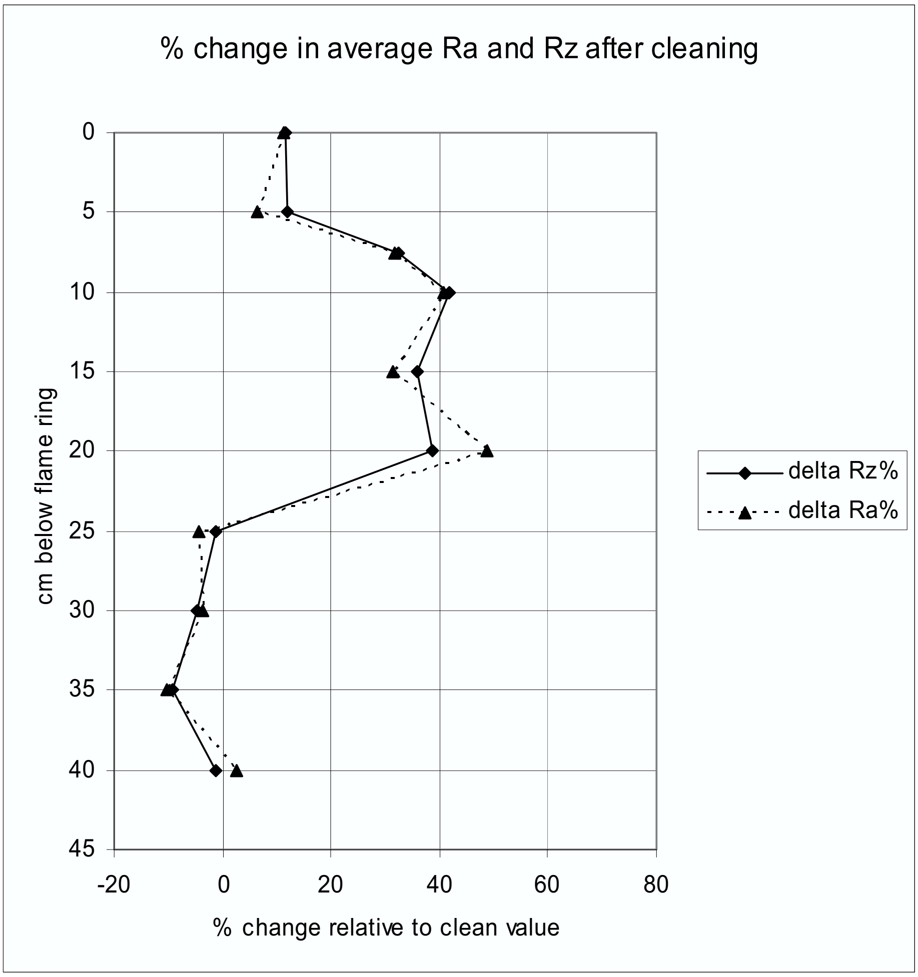


Figure 3-13 *Change in average surface roughness parameters after cleaning liner with acetic acid.*

A third case study of deposits in this type of engine revealed sticky deposits. The average distribution of five cylinders is indicated in Figure 3-15 .

The typical shape of the horizontal distribution pattern is retained in all these case studies, however there is some individual variation from cylinder to cylinder. The glaze deposit in our case studies seems more uniformly distributed than does the liner lacquer, however it is unknown if this is related to deposit type, deposit age or other effects.

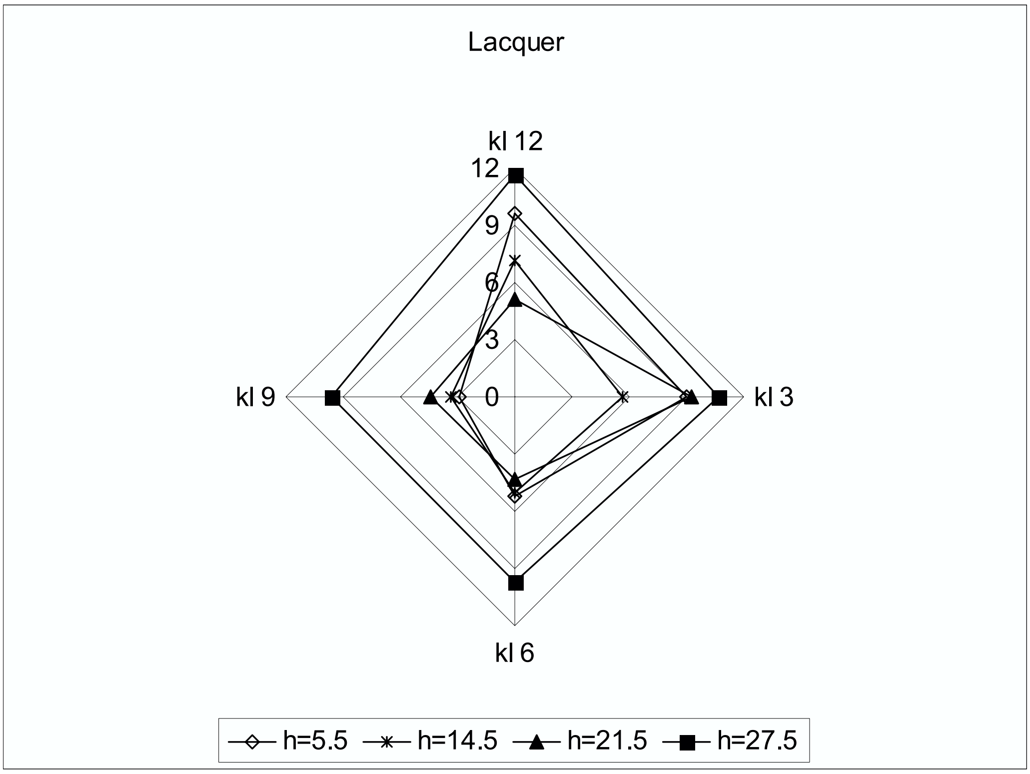


Figure 3-14 *Illustration of liner lacquer deposit pattern in engine A*

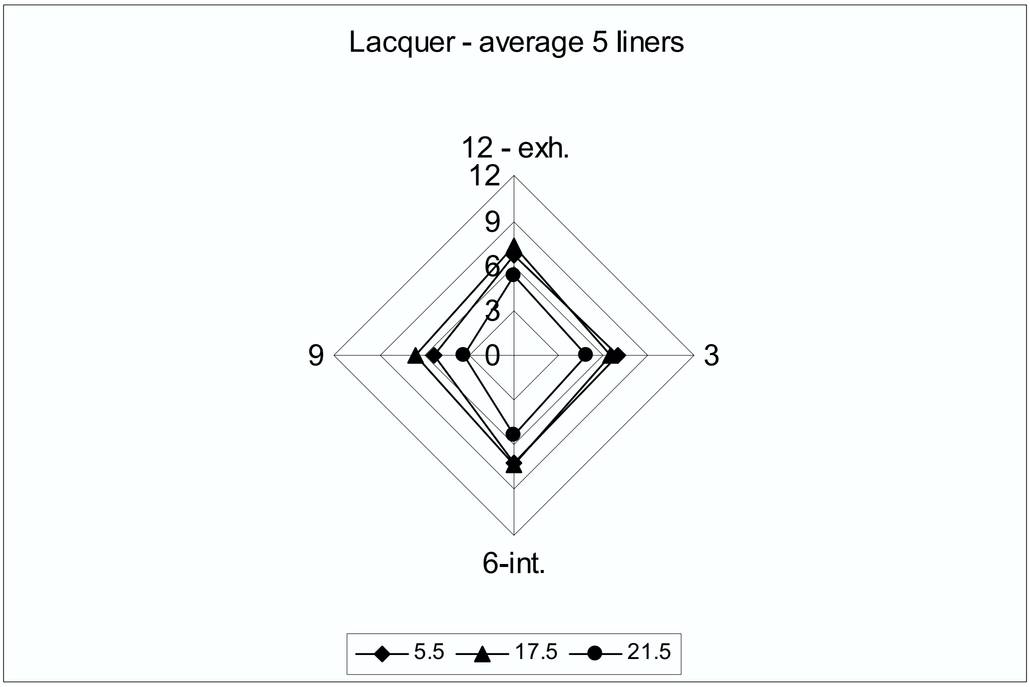


Figure 3-15 *Average distribution of five cylinder liners in engine A.*

3.2.3 Microscale Deposit Distribution

The micro scale distribution of liner deposits has been investigated using optical and electron beam based microscopic techniques. Deposits on samples cut from one 'glazed' and one 'lacquered' liner have been studied. Samples were taken at different heights and circumferential locations on these liners. Sample locations were selected to ensure reasonable distribution on the liner but also to cover spots that appeared interesting either visibly or by surface measurement. Approximately 15 samples from each liner were investigated. This investigation clearly confirms that the deposit primarily resides in honing grooves and pits in the surface. The deposit may also form a film upon parts of the surface plateau in which case this region will be perceived as darker than areas where the deposit is confined to the grooves.

The detailed micro scale distribution of liner deposits varies from sample to sample and also within small samples. This effect, the limited number of samples, and the fact that the samples are taken from but two cylinder liners makes generalizations based upon these pictures difficult. However the selection of pictures that is presented in the following convey important impressions from this investigation:

Figure 3-16, Figure 3-17, Figure 3-18, and Figure 3-19 show liner lacquer images from the high and low deposit region of the side with most deposit, i.e. corresponding to hour 9 in Figure 3-14. The term 'top deposit region' meaning top third top ring stroke while the 'center deposit region' corresponds to the center third of the top ring stroke. The reader is advised to pay attention to the magnification which varies slightly amongst these images.

These images show that the deposit can be found on either or both sides of the cylinder liner grooves. When the deposit is seen on both sides, the distance may vary to the point where the deposit may fill the entire groove. Possibly, these images reflect the development of lacquer deposit such that the deposit grows from groove edges towards complete filling.

Figure 3-16 *Liner lacquer on one groove side (center liner region)*

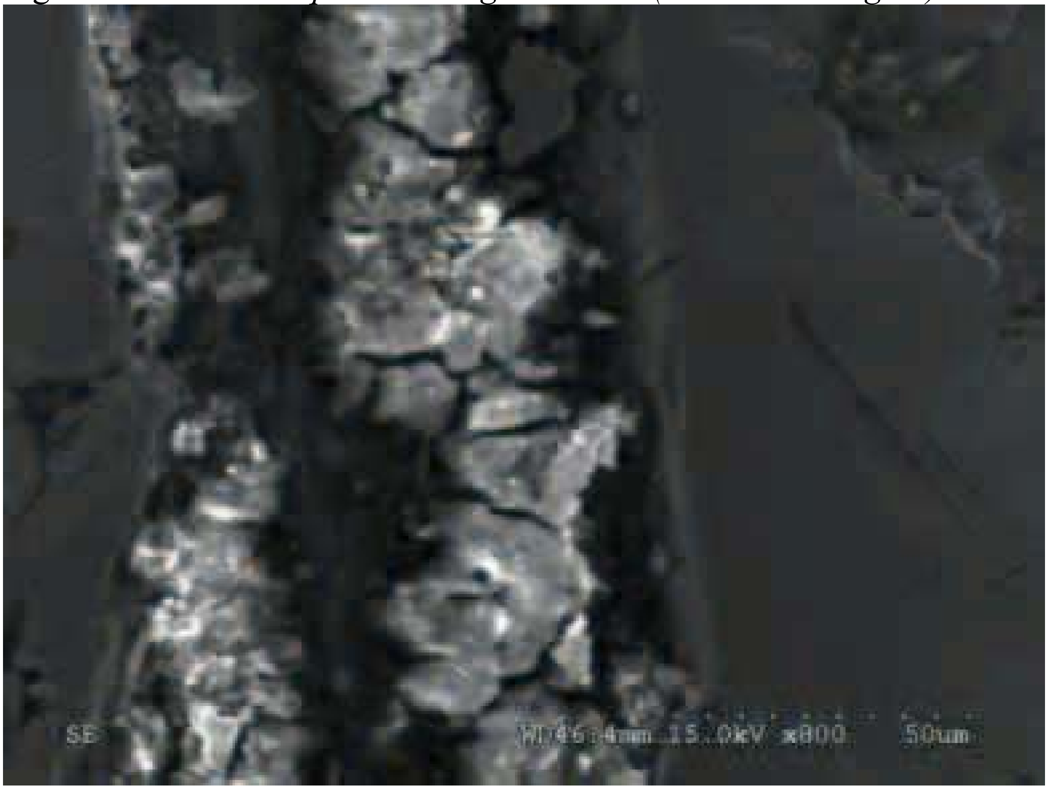


Figure 3-17 *Lacquer on both sides of the groove. (top region)*

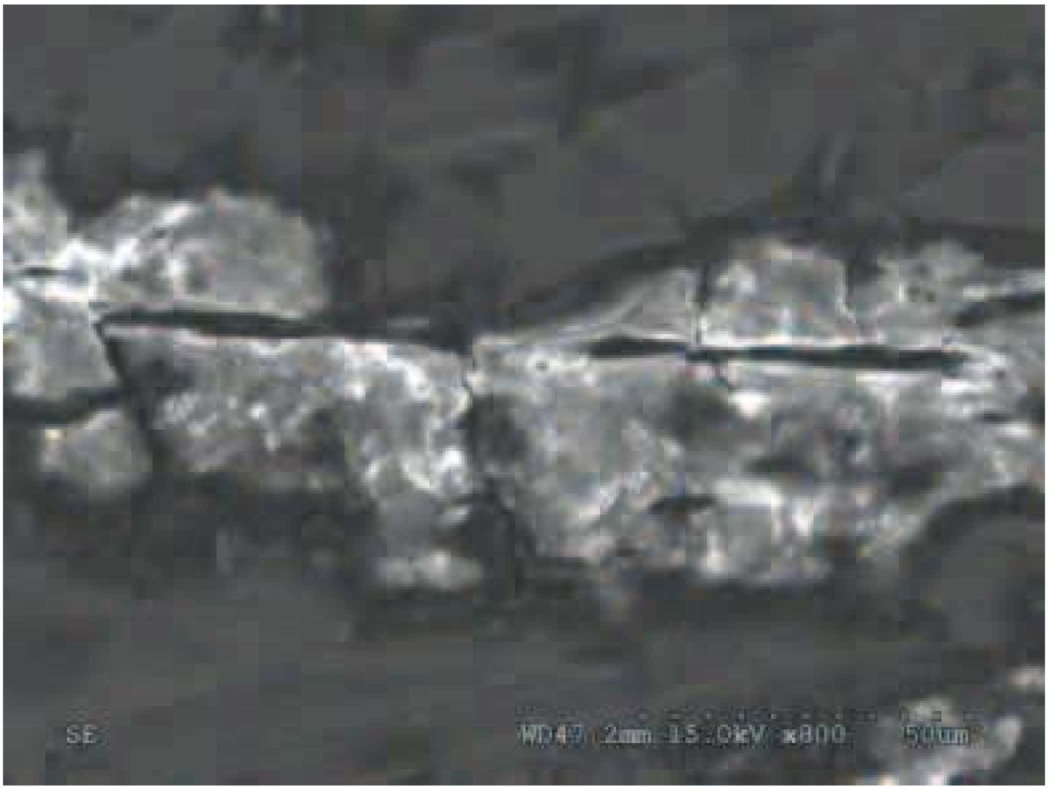


Figure 3-18 *Lacquer with crack parallel with groove (center region)*

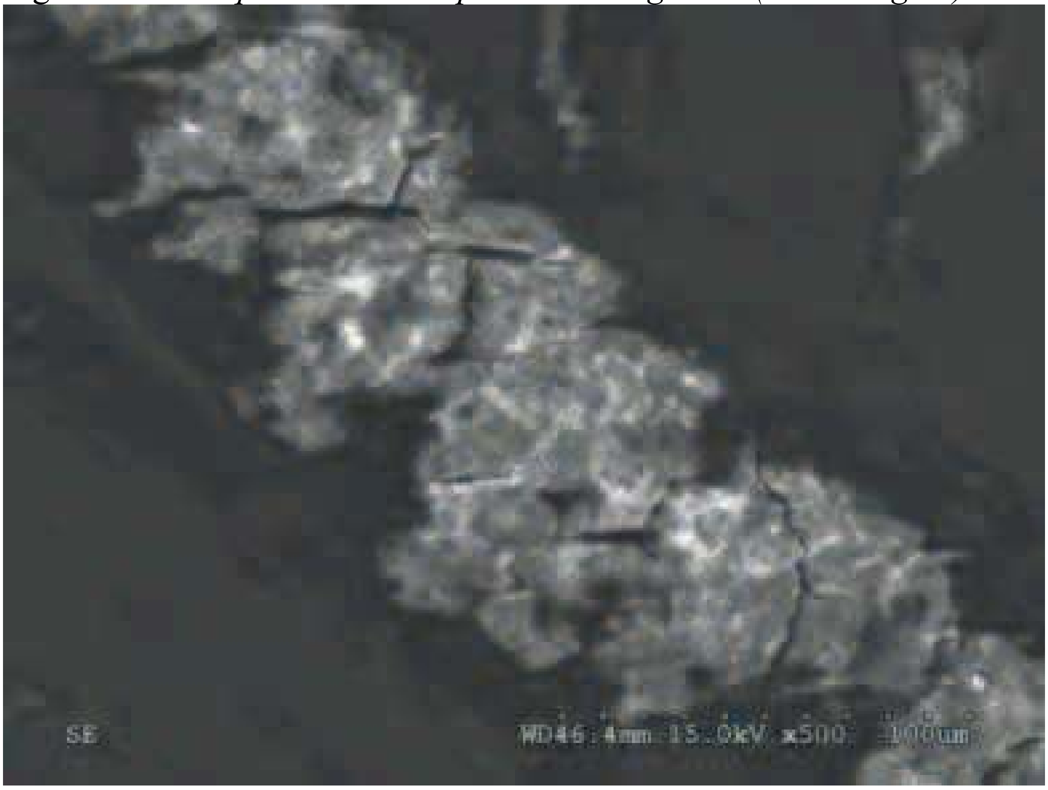


Figure 3-19 *Dense lacquer with dispersed cracks (top region)*

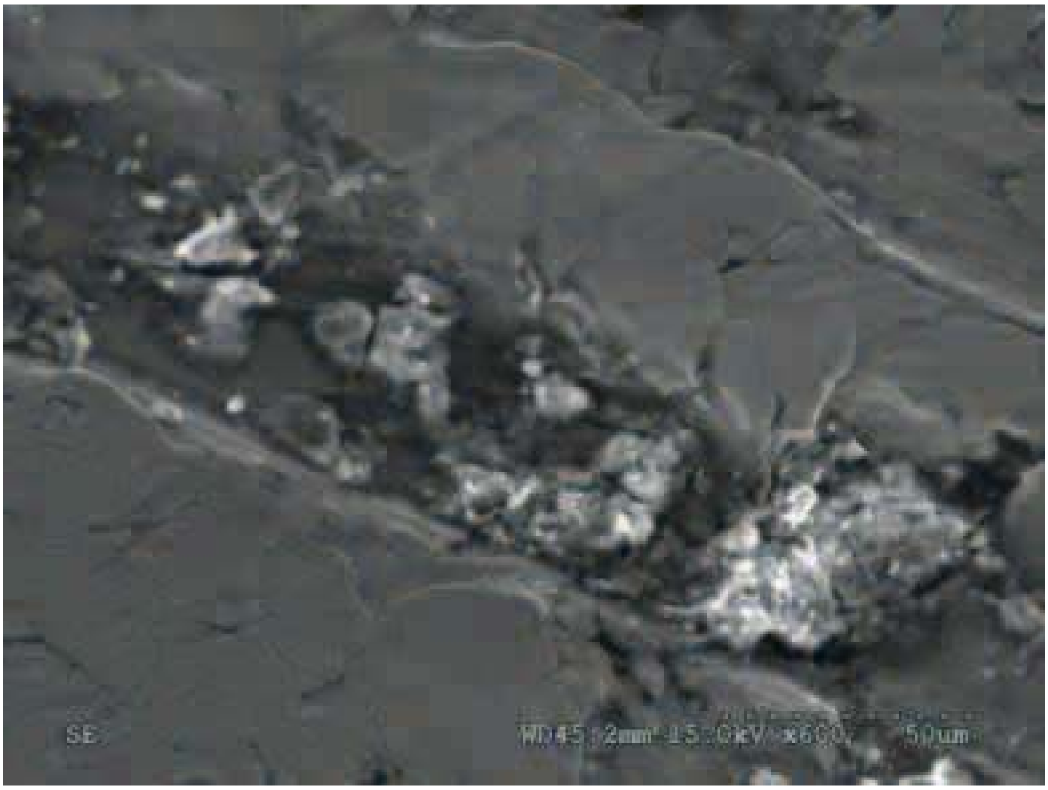


Figure 3-20 *'Randomly' distributed glaze (top deposit region)*

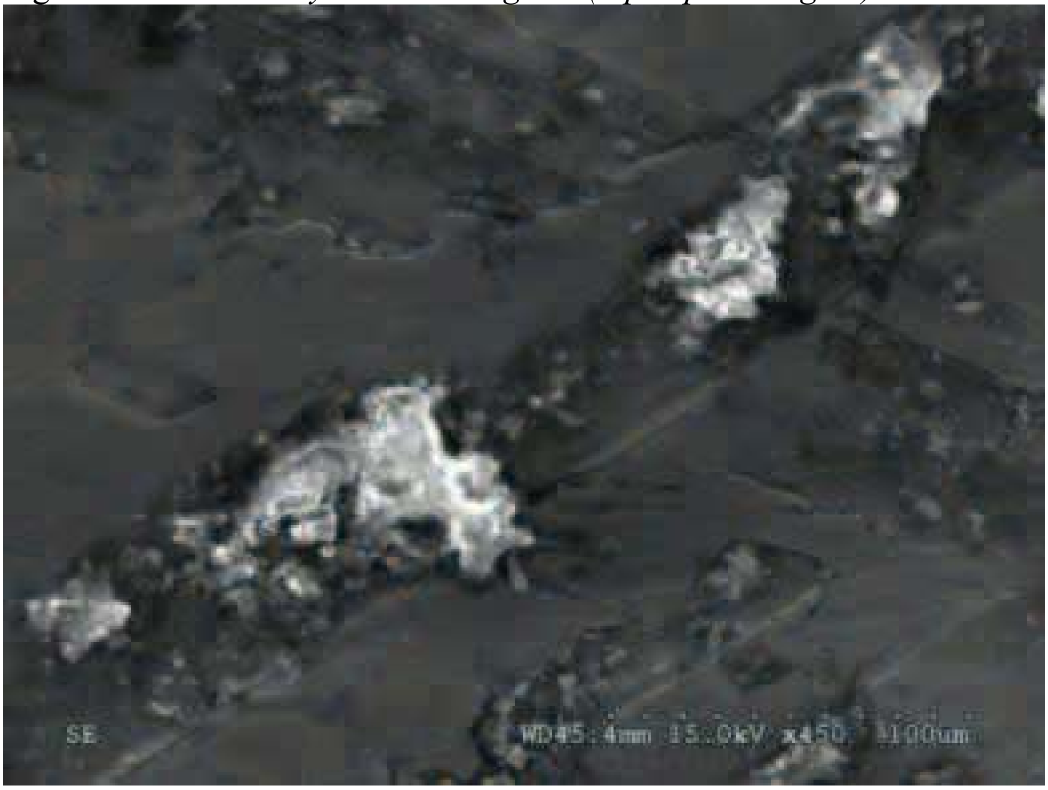


Figure 3-21 *'Randomly' distributed glaze (top deposit region)*

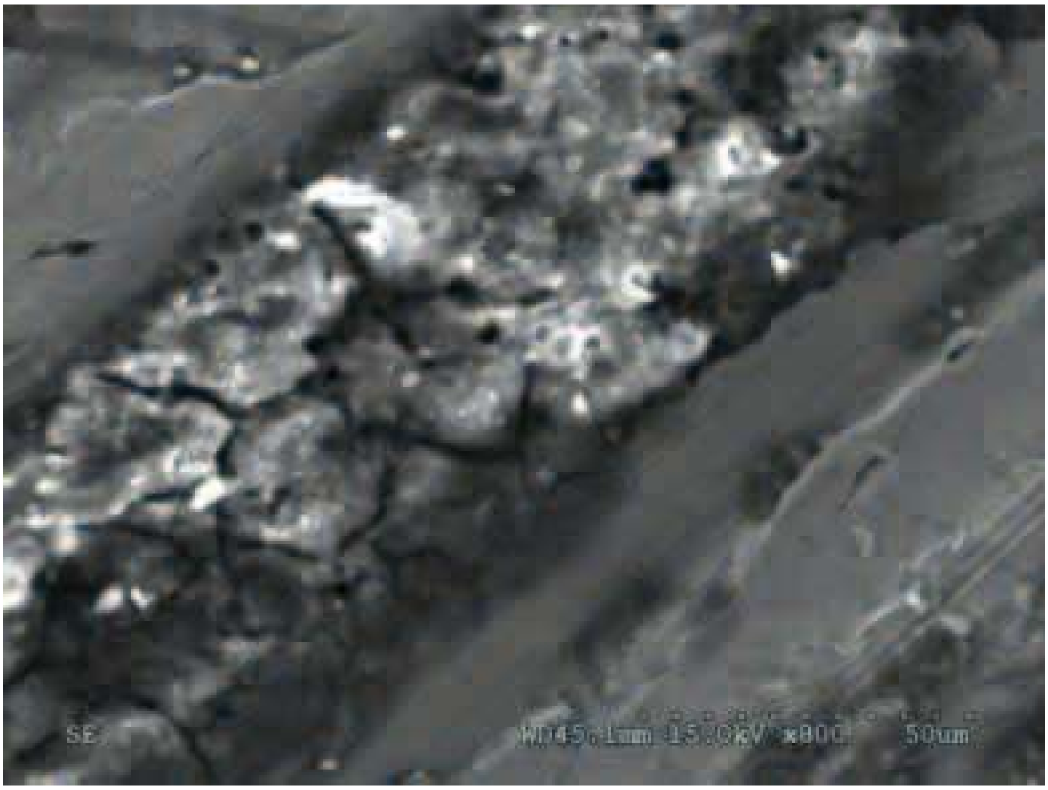


Figure 3-22 *Groove completely filled with glaze (center deposit region)*

The position of deposits in the grove edge may be the result of piston ring scraping influence on deposit distribution. Indeed, thick deposits very similar in composition to lacquer was seen on the piston ring in this engine.

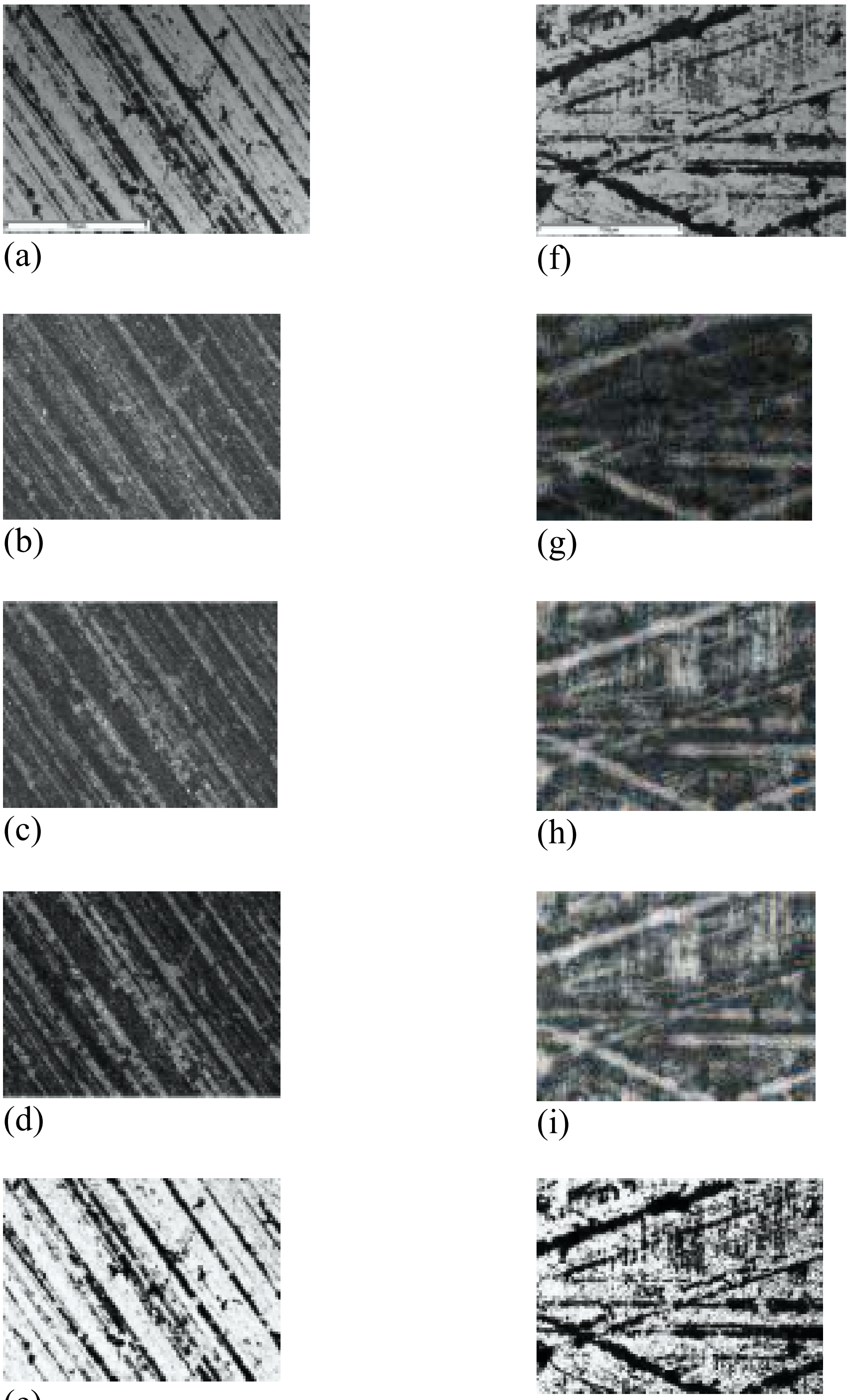
In the case of liner glaze, the deposit is visibly thicker in the centre deposit region and most grooves are completely filled. Grooves may also be filled in the top region, but partial filling by randomly positioned fragments appears more common. These grooves appear to have lost large pieces of deposits. One possible explanation of this phenomenon is that the deposit is fragmented and partially delaminated when the cylinder liner contracts due to reduced temperature when the engine is stopped. Images from the higher deposit region are provided in Figure 3-20 and Figure 3-21, while the deposit in the lower region is illustrated by Figure 3-22.

The distribution of lacquer seems different from that of glaze both at macro and micro level. A mechanism that could account for this difference is the presence of a 'sticky resin' This resin could interact with piston ring movement to cause deposit formed in the groove center to be dislodged and either redeposited on the plateau or groove edges or carried to other parts of the liner

3.2.4 Patterns in elemental distribution

The combination of a scanning electron beam, an EDS detector and digital signal treatment enables maps of elemental distribution to be created. The resolution of these maps is dependent upon the time spent obtaining it, is this case this is in the range of hours. The appearance of these maps is also dependent upon the energy of the electron beam which influences the penetration depth and the ability to detect elements as described in the chapter about 'analytical techniques'.

The distribution of the most abundant elements in lacquer and glaze is shown in Figure 3-23. The brightness and contrast of these artificial images has been adjusted for clarity. This figure shows that carbon, calcium and sulphur are preferentially found in the honing grooves, and that they partake in a deposit that blocks emissions of x-rays characteristic of iron. A thin film containing calcium and sulphur covers the plateau region of the surface of the lacquer. This feature is typical of lacquer, however plateau coverage has also been observed with the bore glaze deposit. The lack of cross-hatching in the glaze sample is a random local surface error which is not considered significant.


(a) (f)

(b) (g)

(c) (h)

(d) (i)

(e) (j)

Figure 3-23 *25 kEv backscatter scanning electron images of (a) bore glaze and (f) liner lacquer; maps corresponding to emissions from bore glaze characteristic of: (b) C, (c) Ca, (d) S, (e)Fe. Characteristic emissions from lacquer: (g) C, (h) Ca, (i) S, (j) Fe.*

3.3 Composition of cylinder liner deposits

The composition of cylinder liner deposits has been investigated using previously reviewed analytical techniques. Results from deposit sample analysis using infrared transmission spectroscopy (IR), x-ray diffraction spectroscopy (XRD), energy dispersive x-ray spectroscopy (EDS) and transmission electron microscopy (TEM) are presented in the following.

3.3.1 Sample removal

Some analytical techniques require that samples are removed from the cylinder liner prior to analysis. For this purpose, samples of bore glaze and liner lacquer were removed from the cylinder liner using a surgical blade. SEM investigation of the cylinder liner after the scraping with the surgical blade clearly showed that most deposit was removed in this process. Investigations of the material that was removed revealed that it contained flakes of iron, some of which had heavy deposits. Only very small samples can be removed in this manner, which restricts the possibilities for analysis.

3.3.2 Deposit Analysis by IR Spectroscopy

Cylinder liner deposits were sampled at different regions of the cylinder liner using a surgical blade as described above and analyzed using an FT-IR single bounce reflection apparatus. Samples have been obtained both 'in field' and from cylinder liners that have been 'dissected' in the laboratory. IR spectra of such deposit samples are shown in Figure 3-24. These spectra are broadly similar in the 4000-650 cm^{-1} wave number region, but subtle differences indicated that neither the glaze nor lacquer samples are entirely homogeneous over a given cylinder liner and also that they vary from liner to liner. The spectra in Figure 3-24 are ordered to illustrate what appears to be a gliding transition from transparent glaze (A) to dry (C) and progressively more sticky lacquers (E).

The absorptions between 2400 and 2300 cm^{-1} in Figure 3-24 and in some of the following figures are caused by CO_2 contamination and is not an integral part of the deposit. Water can be embedded in hydrated material. Presence of water will cause absorption due to O-H stretching vibration. This absorption starts at 3600 cm^{-1} and may extend as a broad absorption down to about 3000 cm^{-1} depending upon the level of hydrogen bonding.

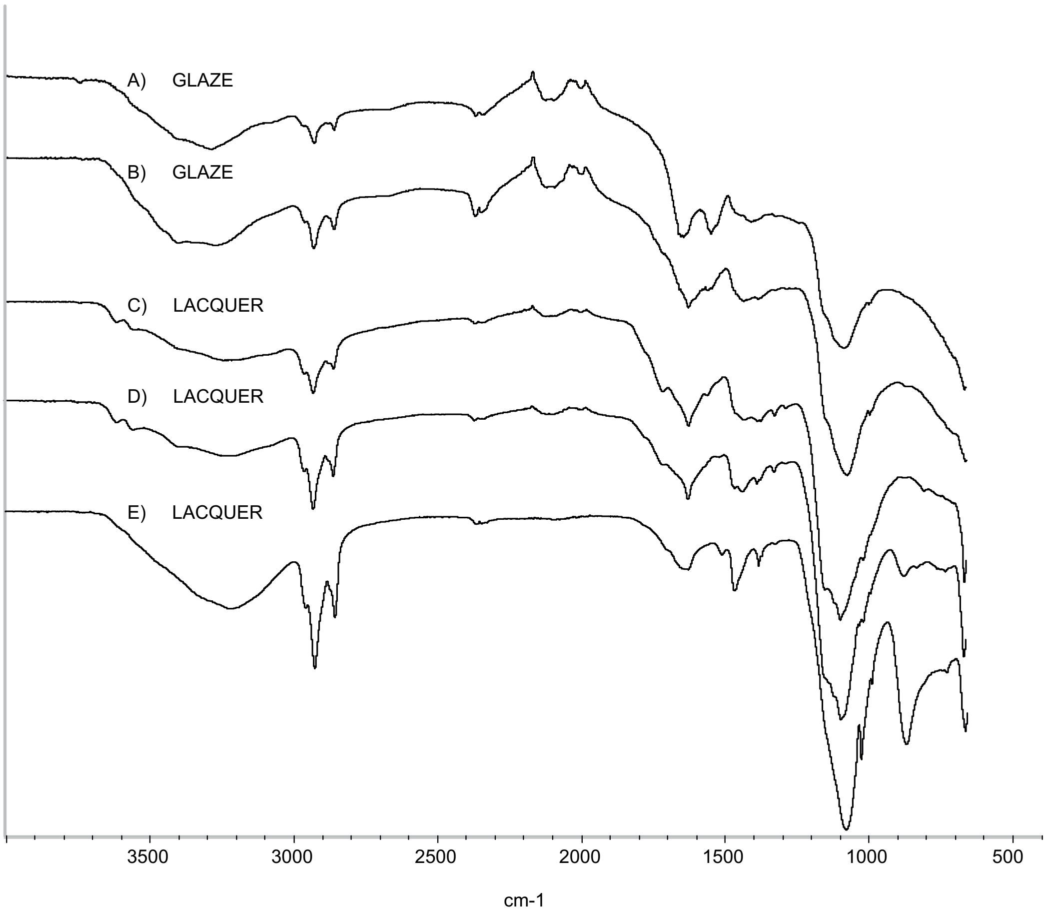


Figure 3-24 *IR transmission spectra of untreated cylinder liner deposits.*

The absorption spectrum in the 2250 to 1900 cm^{-1} region as well as the linearly decreasing absorption on the right hand side of this region is typical of soot. IR spectra of soot samples are provided in Figure 3-25 for comparison. The activated coal shown in this figure is a high purity 'synthetic' carbon for laboratory use while the soot sample has been removed from the fuel injection nozzle of a marine medium speed engine.

Different hydrated states of calcium sulphate were identified in both types liner deposits by XRD analysis as discussed later. The IR spectrum of a precipitate formed by mixing a small amount of sulphuric acid into an approximately 50 TBN mix of base oil and calcium sulphonate detergent is shown in Figure 3-26 along with an analytical grade calcium sulphate reference.

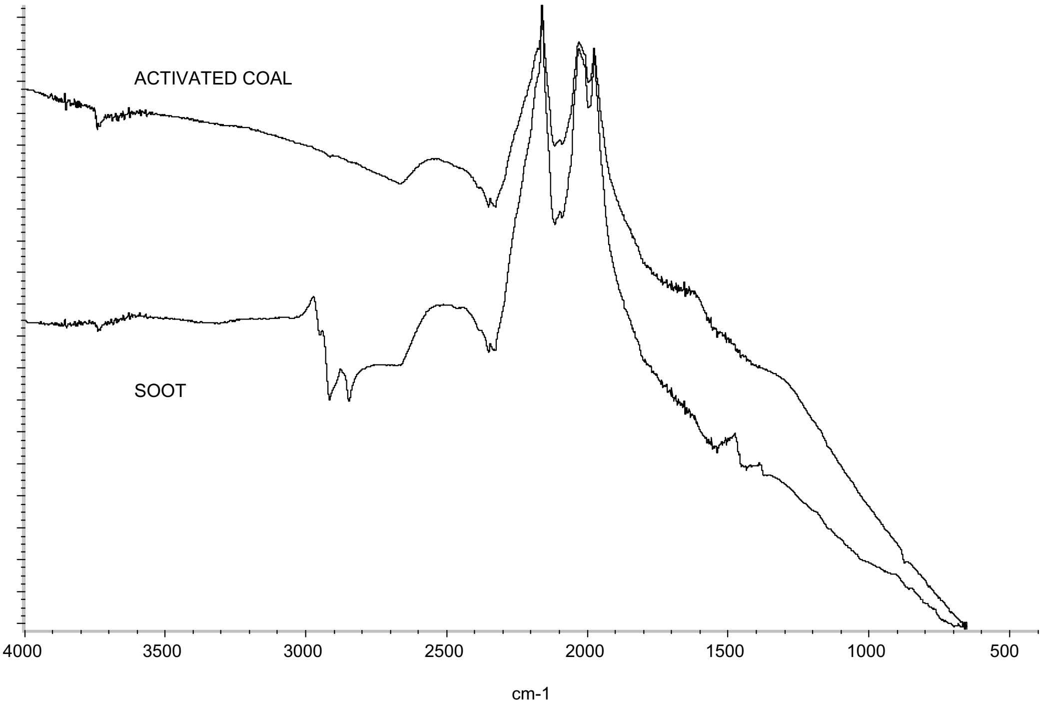


Figure 3-25 *IR transmission spectra of soot and activated coal.*

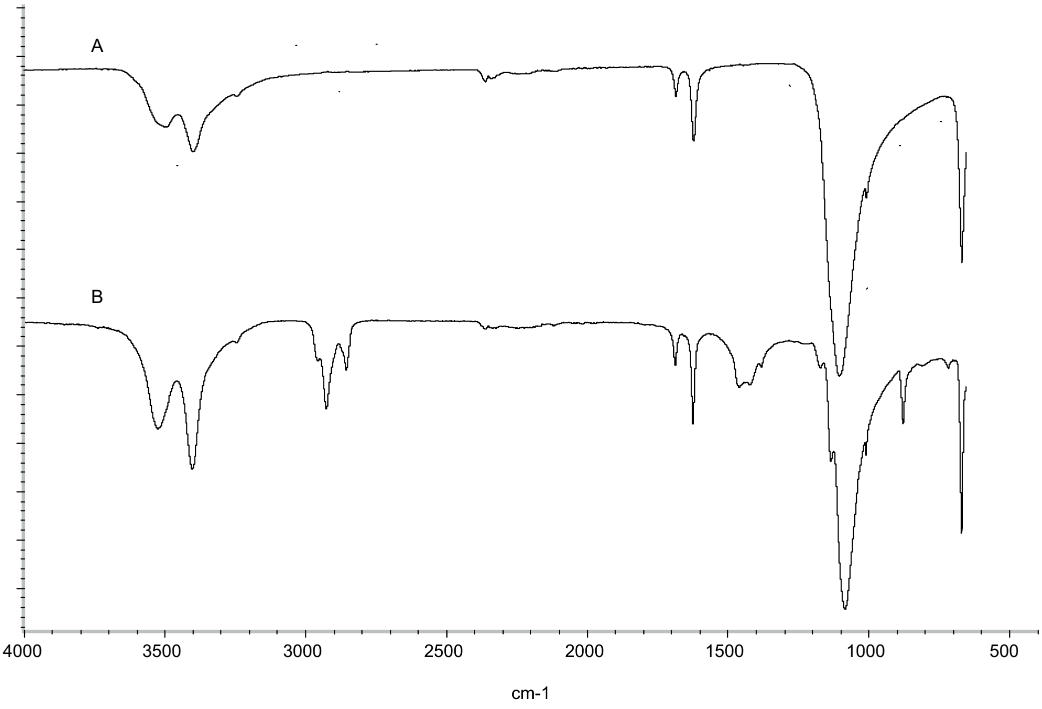


Figure 3-26 *IR spectra of a) Analytical CaSO4*2H2O, b) Precipitate from calcium sulphonate detergent and sulphuric acid*

The main difference between these spectra is the presence of aliphatic hydrocarbons absorbing at 2850 and 2900 cm^{-1} and calcium carbonate identified by a broad absorption around 1450 cm^{-1} combined with a pointed absorption at 860 cm^{-1}. The precipitate and the calcium sulphate share many features with the liner deposit although peaks are sharper due to the increased homogeneity. For instance, the calcium sulphate absorbs at approximately 1620 cm^{-1} which corresponds directly to absorptions in lacquer samples 'C' and 'D' as well as glaze sample 'B' in Figure 3-24. The calcium sulphate also absorbs strongly at 1100 cm^{-1}, a feature that can also be recognized in these samples. Iron sulphate, detected in glaze, also absorbs at this wave number.
The presence of aliphatic constituents is seen as broad peaks around 2920 and 2850 cm^{-1} in all deposit samples in Figure 3-24. The aliphatics increase in content from lacquer C to lacquer E which is also the order of perceived stickiness of the deposit.

Samples of both lacquer and glaze were immersed in hexane and centrifuged to determine whether the aliphatics were incorporated into the deposit or simply a coating of residual base oil. The IR spectrum following this treatment is shown in Figure 3-27 for lacquer and Figure 3-29 in case of glaze. A faint but possibly significant absorption is seen at 1720 cm^{-1} in the lacquer prior to and after the hexane treatment. This is suspected to be caused by C=O stretching, possibly from sticky, resinous hydrocarbon. To explore this further, the sample was treated by acetone which is a polar solvent that will dissolve most low molecular weight oxidation products. The acetone treatment resulted in the removal of the 1720 cm^{-1} absorption seen in Figure 3-28. Acetone will not remove deposits form the liner surface, hence any material that was removed was probably part of a coating.

The originally faint soot signal in the lacquer was also diminished; however the soot survived acetone treatment in case of the glaze. The progressive increase in CO_2 contamination seen in Figure 3-27 and Figure 3-29 is caused by a decrease in signal noise ratio due to diminishing sample size as a result of losses in treatment.

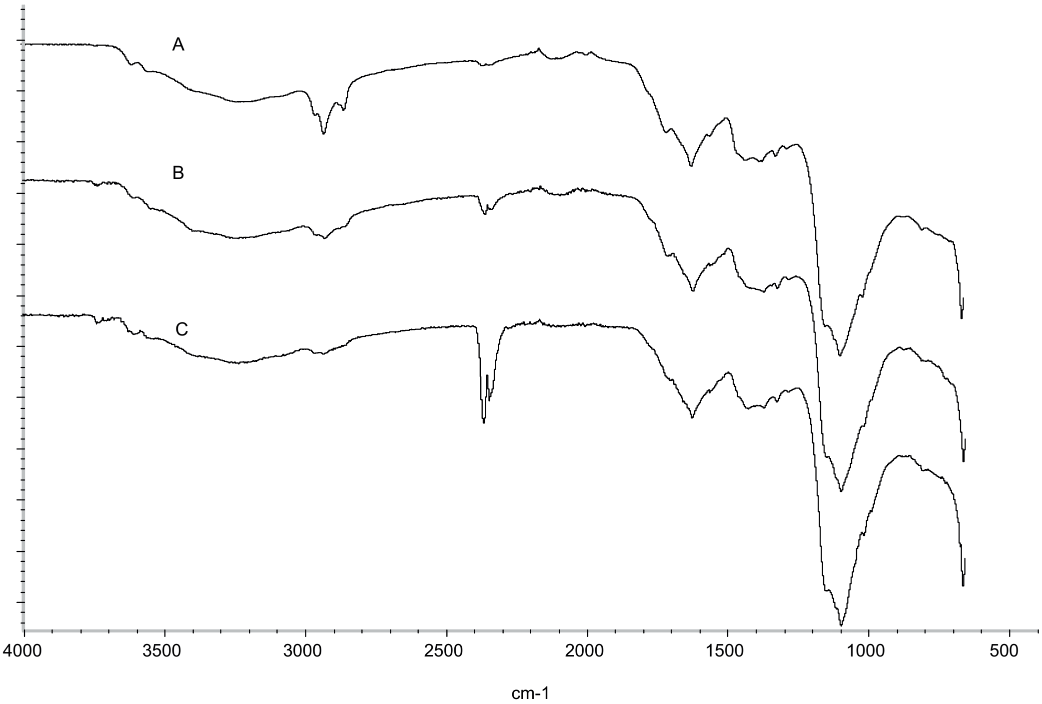


Figure 3-27 *IR spectra of a liner lacquer sample a) untreated, b) hexane treated, c) acetone treated*

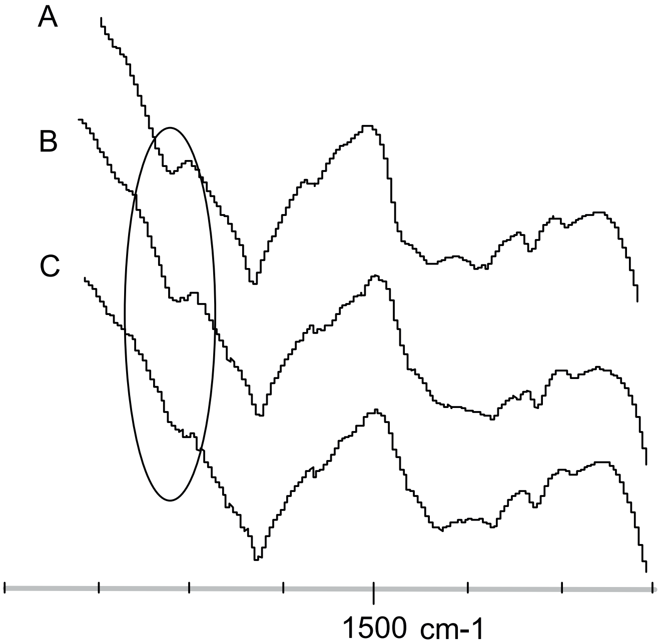


Figure 3-28 *Enlarged spectrum detail showing a reduction of the absorbance at 1720 cm^{-1} (circeled) when the original lacquer spectrum a) is treated with b) hexane and c) acetone*

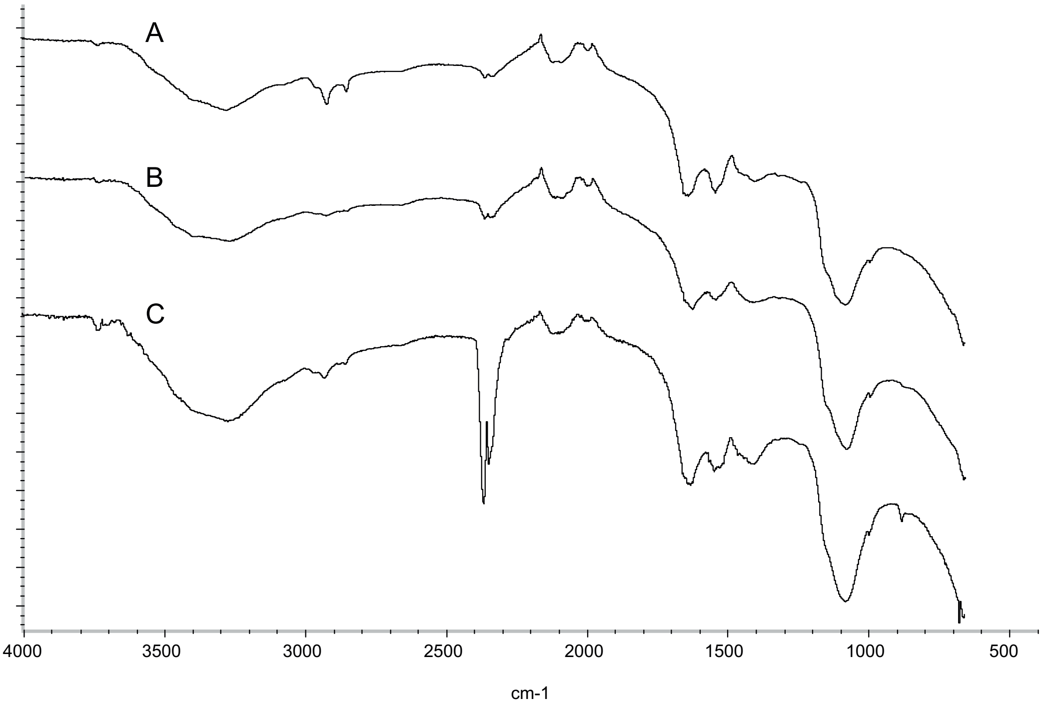


Figure 3-29 *IR spectra of bore glaze a) untreated, b) hexane treated, c) acetone treated*

The liner deposit has many features in common with IR spectra of piston deposits. The glaze has an absorption between 1500 and 1600 cm^{-1}. Similar absorptions in piston deposits have previously been assigned to carboxyl salts [18], [71]. The existence of such salts is in agreement with the XRD analysis which suggested the presence of undefined crystalline material in the glaze. A broad absorption is seen around 1400 cm^{-1} in both deposit samples. A similar absorption is assigned to CH2 and CH3 deformation and carboxylate in piston deposit analyses by Shurvel [74] and Smith [75]. Additionally Covith et. al. [71] assigned piston deposit peaks at 1400 to 'nitrates'.

3.3.3 X-ray diffraction analysis

Samples of liner lacquer and bore glaze removed from the liner using a surgical blade were subjected to x-ray diffraction analysis. An untreated diffraction pattern from a liner lacquer sample is provided in Figure 3-30 and a pattern without the background signal is provided in Figure 3-31.

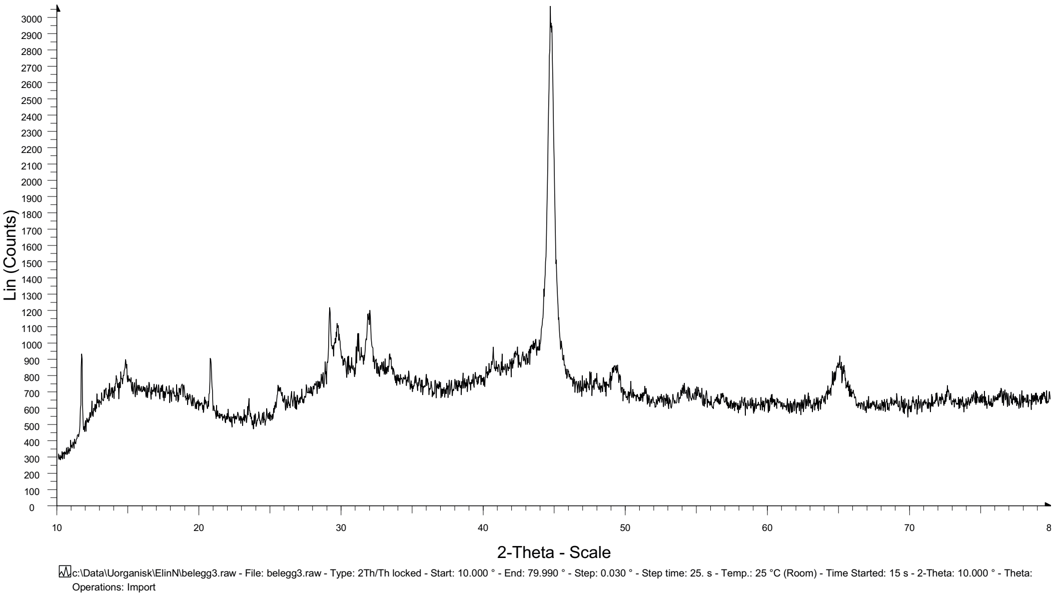


Figure 3-30 *Crude XRD spectrum of liner lacquer sample.*

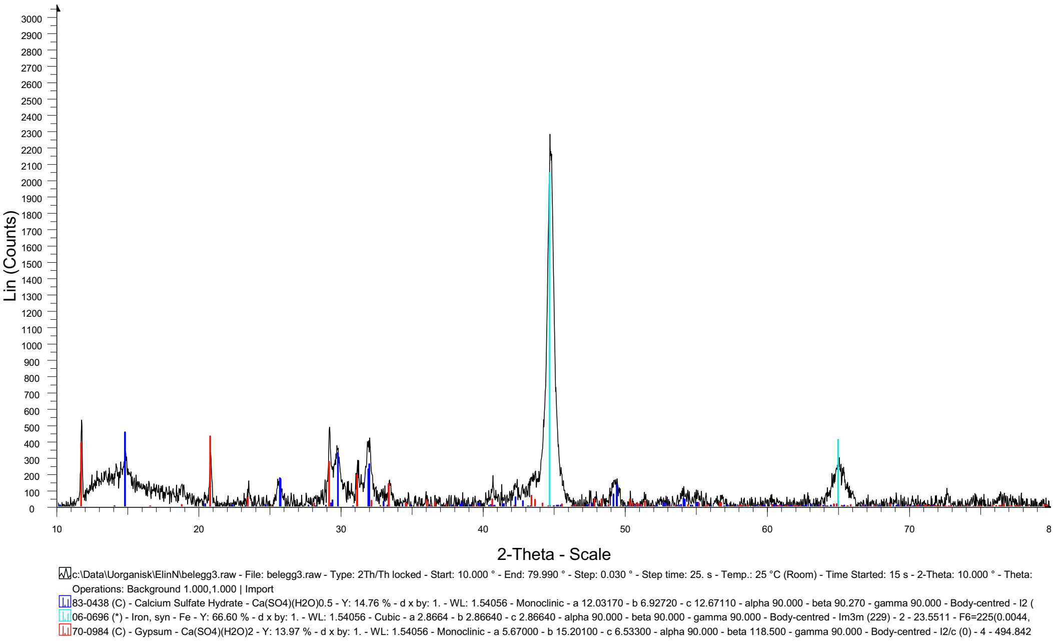


Figure 3-31 *XRD spectrum of a liner lacquer sample less background signal and with peak assignment.*

The analysis of the lacquer revealed the presence of iron as well as calcium sulphate hydrated to $CaSO4 \cdot 0.5H2O$ and $CaSO4 \cdot 2H2O$. SEM /

EDS analysis showed that the deposit sample contained large iron particles. The deposit adhered to these particles so that an attempt to purify the sample using a magnet resulted in a loss of sample to an extent which inhibited analysis. It was initially assumed that this iron could be related to the deposit removal procedure. However the TEM analysis showed that iron particles appeared to be incorporated in the deposit.

A raw XRD spectrum of a bore glaze sample is provided in Figure 3-32 while a spectrum without background and with peak assignment is shown in Figure 3-33.

The spectrum analysis gives a good match for iron sulphate in the form $FeSO4 \cdot 4H2O$, anhydrous $CaSO4$ and $CaSO4 \cdot 0.5H2O$. A number of peaks in the right hand spectrum could not be identified in this analysis. IR analysis has suggested the presence of carboxylate salts which might explain these unidentified peaks. The iron sulphate may be related to the soot which was detected in the glaze by IR since soot generally contains sulphuric acid [31].

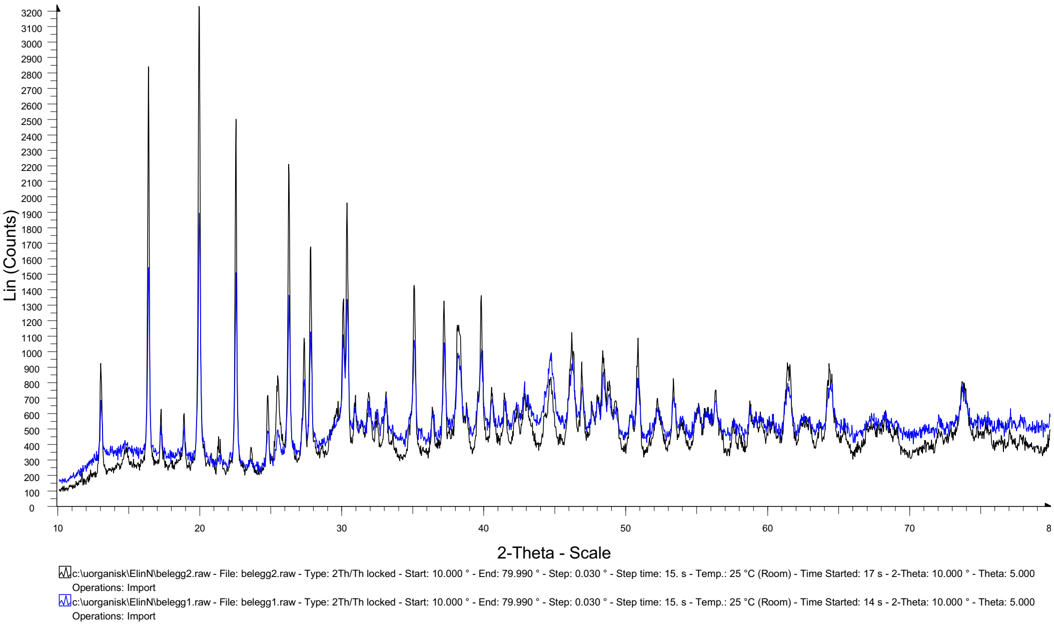


Figure 3-32 *Crude XRD spectra from two consecutive analysis of a bore glaze sample.*

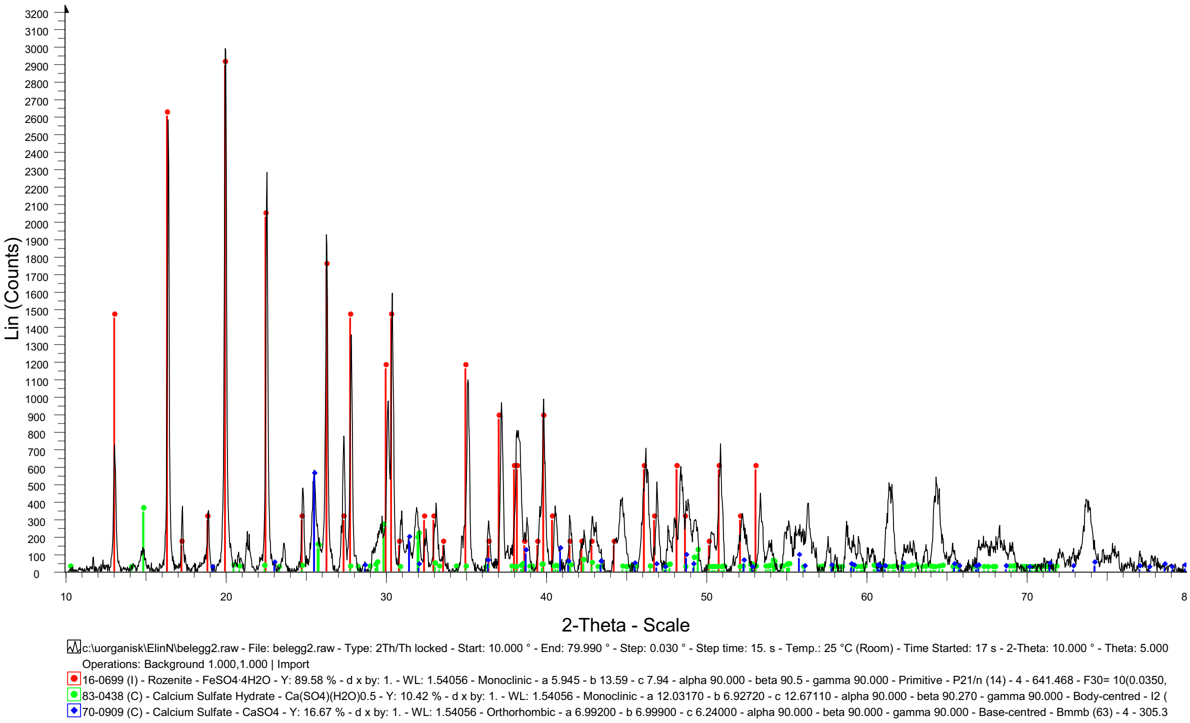


Figure 3-33 *Background treated XRD spectrum of bore glaze with peak assignment suggestions*

3.3.4 EDS analysis

EDS analysis has already been used to provide the elemental maps in the 'deposit distribution' section. However, EDS analysis can naturally also be applied to samples that have been removed from the liner surface.

EDS spectra can be obtained from the entire field of view or from selected regions in both SEM and TEM. To obtain a best possible spectrum, the area should be selected so that the material within the scan area can be assumed to be fairly homogeneous.

An x-ray energy spectrum of a liner lacquer sample with peak assignment suggestions from the INCA software is shown in Figure 3-34. This spectrum shows several features of EDS spectroscopy as well as the deposit. Several peaks are assigned to the same element because each element has a characteristic x-ray emission energy for each possible electron shell to shell transition. Carbon and oxygen which have two shells only have one characteristic peak. This figure also shows that the differences in characteristic energy are small in the low energy region which makes peak assignment in mixtures of light elements such as liner deposits challenging. The software uses combined peak information and spectral deconvulsion routines for spectral peak assignment.

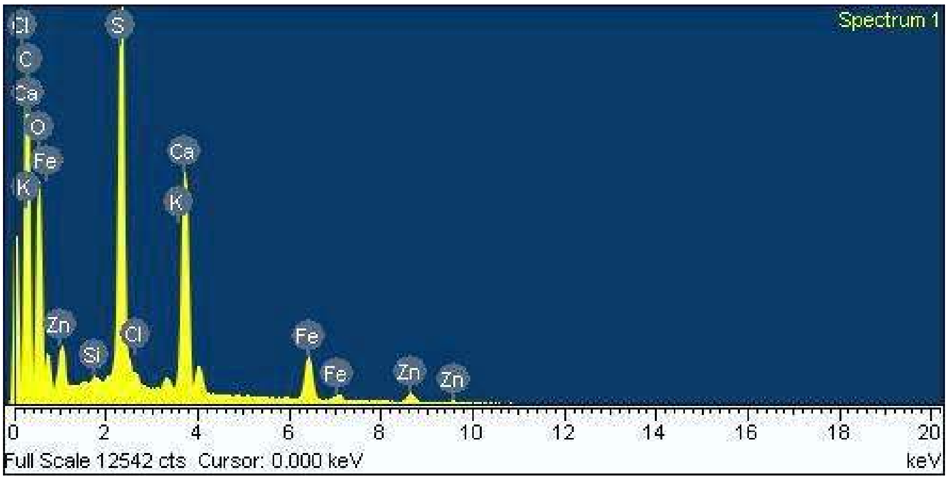


Figure 3-34 *EDS surface spectrum of liner lacquer sample.*

The potassium and chloride peaks in this spectrum are only trace elements. The peak at 0.25 keV is seen to be caused primarily by carbon while the peak around 0.5 keV is mainly caused by oxygen, hence this spectrum primarily show C, O, Zn, S, Ca and Fe. The height of the peaks is proportional to the number of characteristic x-rays that has been detected. However this cannot be directly converted to molar fraction as discussed in the section on analytical techniques.

The EDS spectral analysis reveals more detail than the previously shown EDS element maps. A list of elements frequently observed in lacquer and glaze as well as their probable origin is provided in Table 3-4.

TABLE 3-4 ELEMENTS FREQUENTLY INDICATED BY EDS SURFACE ANALYSIS

Element	**Possible origin**
C, Ca, Zn, P, S, Mg, Mo	Lubricating oil or additive
Fe, Cr, Mn, Ni, Al, Cu	Wear elements
O, Si, N, Na, Cl,	Charge Air containing sea water
K	Unknown (id error?)

No distinction between lacquer and glaze is made since systematic variations in elemental presence were not detected. Assistance in scientifically guessing the probable origin of deposit constituents can be found in tables of wear metals and lubricant additive elements such as provided in [25] and [96].

Some elements like copper and molybdenum may originate as lubricant additive, wear elements or both. Potassium, however, is neither a typical wear element nor lubricant additive, and could be detected as a result of erroneous peak identification. A seen in Figure 3-34, the potassium peak closely overlaps that of calcium. The EDS spectra obtained from SEM and TEM are largely similar.

Figure 3-35 *Iron flake with deposit*

The combined EDS investigation clearly shows that the deposit contains a small amount of wear elements. It also contains sodium and chloride which may originate in sea water carried within the charge air. The EDS analysis is also employed to aid image interpretation. EDS was used to determine that the electron micrograph of a deposit sample in Figure 3-35 shows an iron flake with deposit attached. This explained why it proved difficult to separate metal from liner deposits in the samples that had been removed from the liner by surgical blade.

3.3.5 Transmission Electron Microscopy (TEM)

The liner deposit TEM samples were prepared by gluing a strip of liner metal with deposits onto another metal piece with the same curvature using epoxy resin and curing it at elevated temperature to maximize its strength. The sample was then filed to a cylindrical rod 3mm in diameter and sliced using a diamond blade saw into approximately 0.5 mm thick disks. This is a critical step as shearing forces strain the thin glue line causing frequent sample break-up in this stage. The surviving samples were temporarily glued onto a holder and polished using fine grinding paper then thinned in the centre region only using diamond paste and a dimple grinder machine. The final step in the sample preparation is thinning, using a low angle ion gun. This process is ended when the centre of the specimen transmits light at which point the fringes of this hole were electron transparent, probably a few hundred nanometres in thickness.

The preparation of sample for TEM is demanding, and only a single glaze and a single lacquer deposit sample were successfully prepared and examined at 300 kVe in a Phillips SC30 analytical TEM. Both samples originated in the lower part of the liner.

Glaze sample

A cross section view of the glaze deposit is seen in Figure 3-36. The glaze in this picture is found in what appeared to be a minor groove or a recession in a plateau area. The thickness of the deposit in this area is about 0.1 micrometer.

A close-up of this deposit is shown in Figure 3-37 and Figure 3-38. Both figures clearly reveal the presence of crystals with sizes up to approximately 50 nm which is an order of magnitude larger than the inorganic cores of the micellar detergent additive.

The diffraction pattern from an area centered on one of the larger deposit crystals is shown in Figure 3-41. Part of this diffraction signal is caused by secondary fluorescence and scattering of electrons from nearby iron however other Debye-Scherrer rings are characteristic of the deposit.

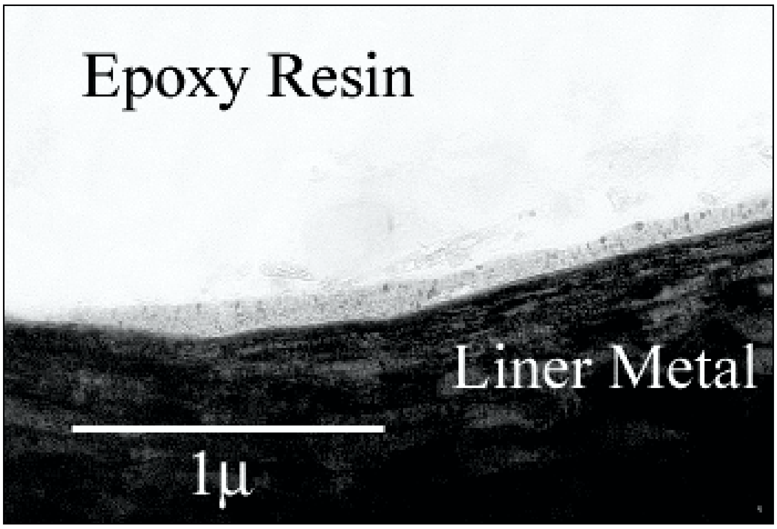


Figure 3-36 Cross section view of glaze film

The distance between these rings was estimated using a diffraction image from a non graphite section of the cylinder liner as reference. Rings with spacing approximately 5.96, 3.41, 2.98 and 2.75 Å were identified, which give a reasonable match for slightly hydrated calcium sulphate.

Lacquer Sample

The liner lacquer deposit sample turned out to be comparatively thicker than the glaze sample and looked more homogeneous as seen in Figure 3-39. The liner lacquer appears partly delaminated from the liner surface which could be a result of the sample preparation. The sample also contains a large iron fragment seen in the center of the picture which has deposits on all sides and appears to be a wear particle. Lacquer has been determined by x-ray diffraction to contain crystalline material however no evidence of crystals was apparent in the lacquer deposit sample. Possibly, the sample is to thick or the crystals are to small to be resolved in this TEM image. Less likely but also possible, this sample is compositionally different from the XRD sample which is much larger and hence more representative. A second image of the liner lacquer deposit is shown in Figure 3-40. In this area, the deposit exhibits some structural features which look like fracture lines, possibly a result of shearing forces due to thermal cycling. The deposits also appear to contain some closed loop features which resemble grain boundaries.

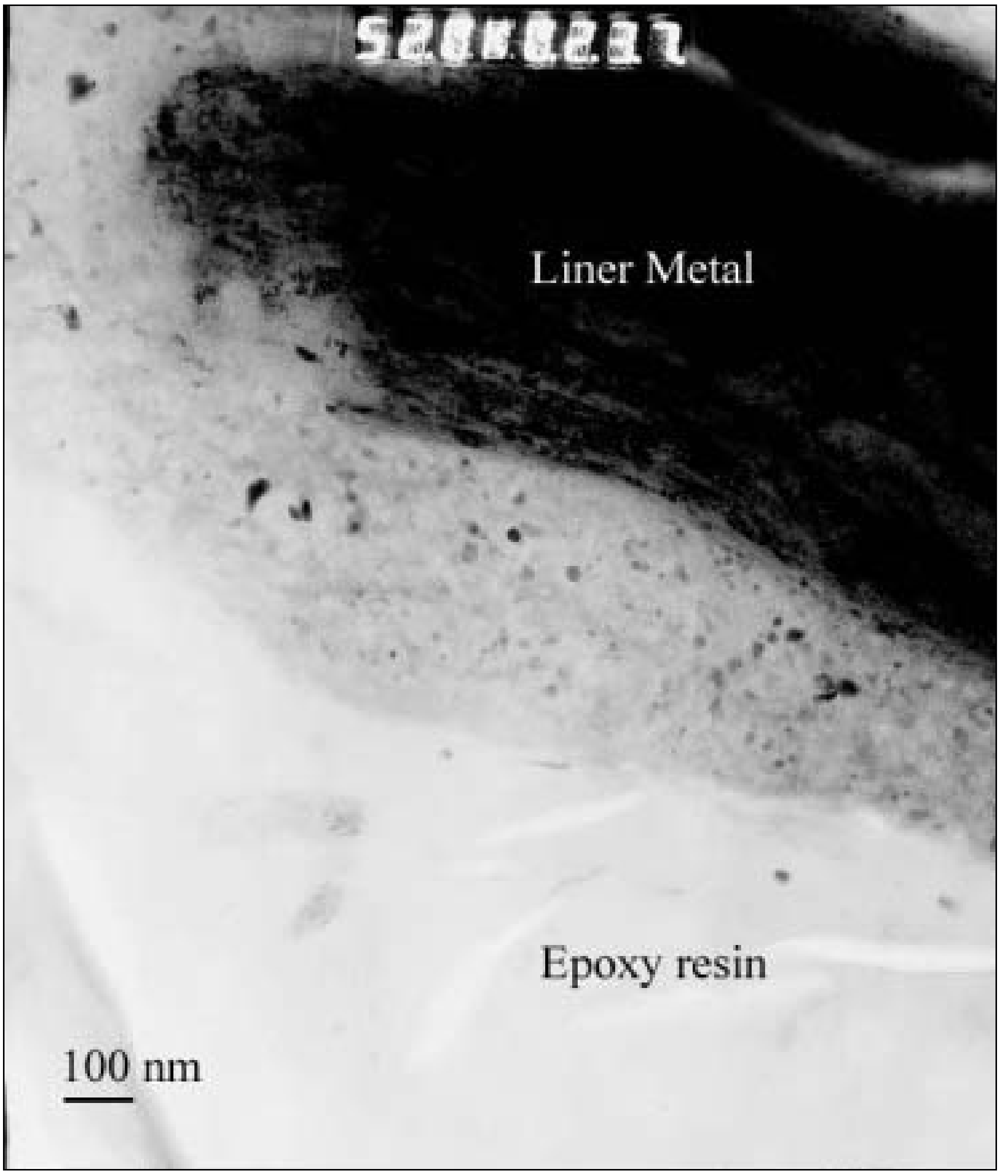


Figure 3-37 *Brigthfield close-up of glaze deposit. Dark spots in the deposit are caused by diffracting crystals.*

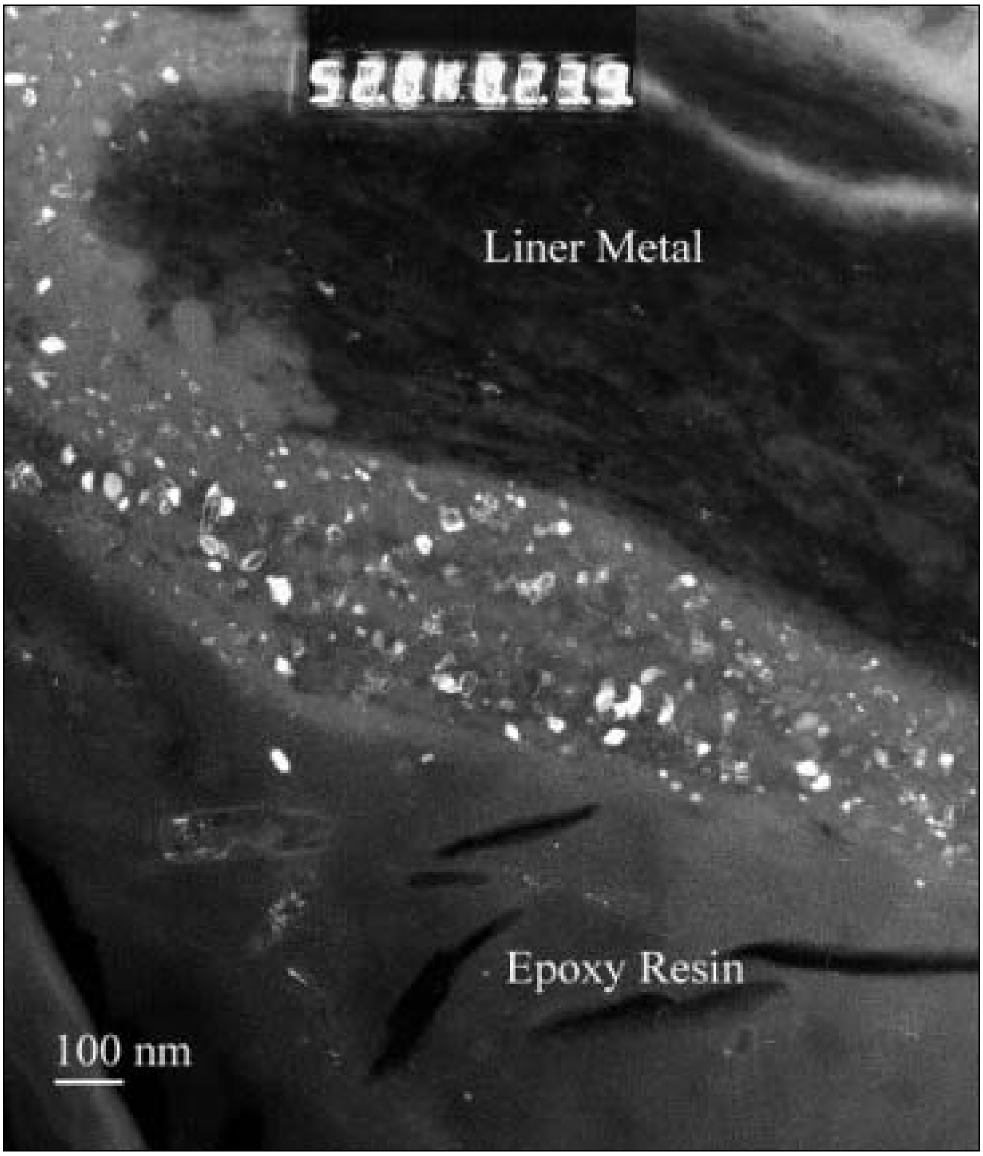


Figure 3-38 *Darkfield closeup of glaze deposit. White spots are caused by diffracting crystals.*

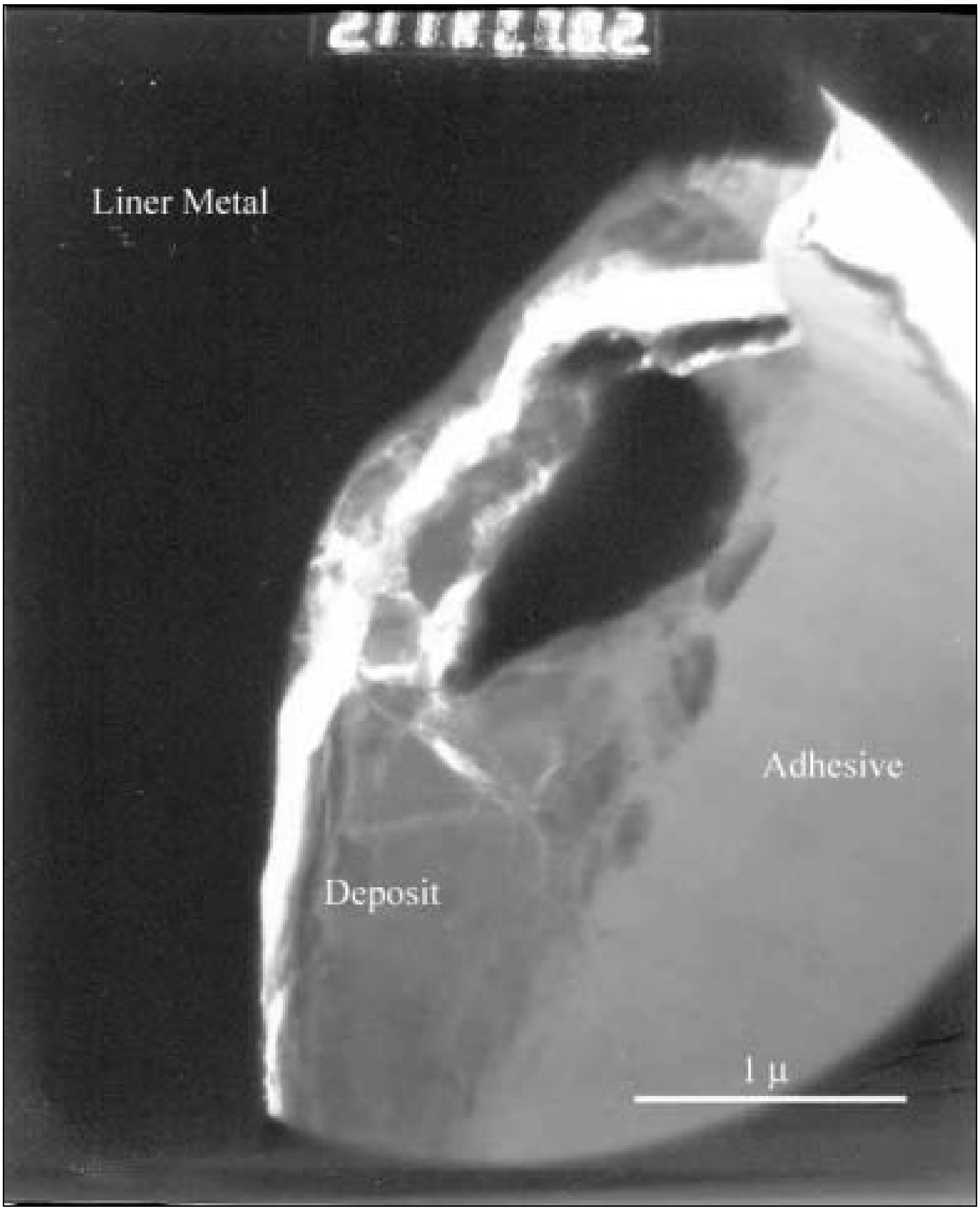


Figure 3-39 *TEM of lacquer deposit. The black spot in the center was confirmed to be iron by EDS.*

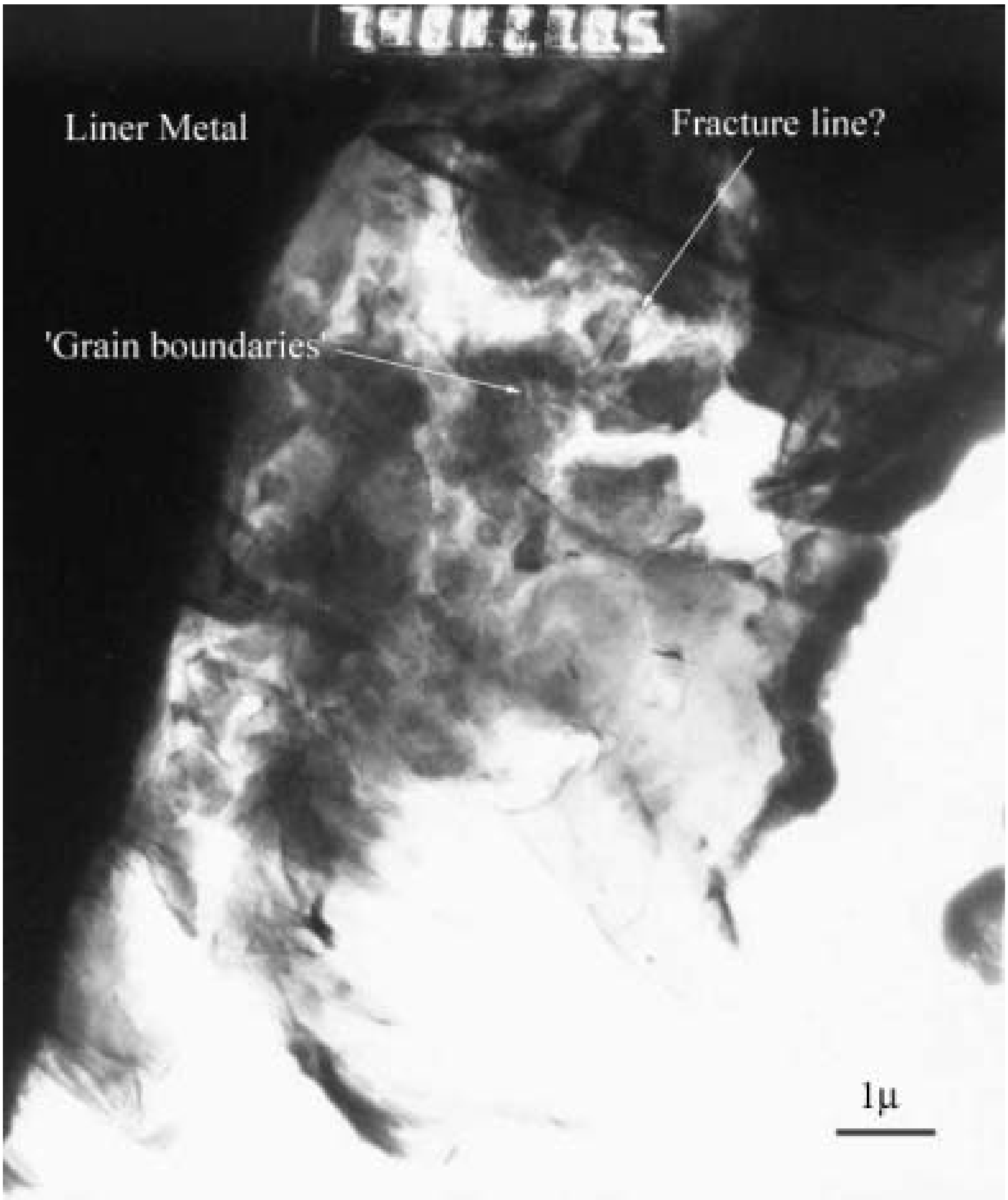


Figure 3-40 *TEM of lacquer deposit. Straight lines, possibly fracture lines, are seen within this deposit.*

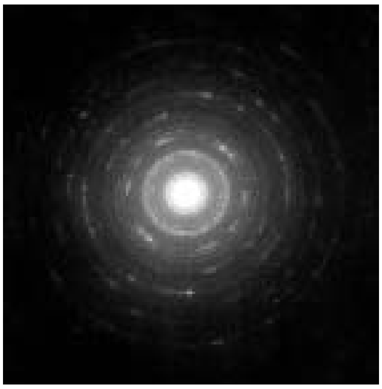


Figure 3-41 *Electron diffraction pattern from glaze deposit crystal.*

3.4 Composition of deposits found near deposited liners

The formation of liner lacquers and bore glaze is not an isolated event. Liner deposits are usually accompanied with deposit formation in other parts of the engine. Most notable is the formation of deposits on the piston crown, piston top land and flame rings. These deposits are often considered a by product of liner deposits since high oil consumption will cause more oil to be burned resulting in the formation of more ash. This is, however, only one of many factors that may be contributing to such deposits.

An investigation of surrounding deposits was undertaken as it could give valuable insight. These related 'neighboring' deposits have mostly been analyzed by FT-IR alone which is a rapid and informative technique that requires only a very small sample. The reader will realize that the composition of the samples cannot be unambiguously determined from IR spectra alone. Reasonable assumptions can be made however, when the spectra are interpreted using results from detailed published analysis on comparable samples as well as our own previous multi-technique analysis.

3.4.1 Piston ring face deposits

The piston ring face is usually clean, even when liner deposits are formed. However, a thick, non-continuous and otherwise unevenly distributed deposit was found on the ring face of the second and third ring in one engine from which liner lacquer deposit samples were obtained.

Like liner deposits, the ring face deposit was amber and soluble in acetic acid.

The piston ring deposit was located on the lower unworn part of the ring face which probably did not contact the cylinder liner. Ring face deposits are rare and could be the related to an abnormal cylinder liner honing pattern seen on this particular liner. The IR absorption spectrum of a sample of this deposit as well as a sample removed from the corresponding cylinder liner are shown in Figure 3-42.

The piston ring face deposit sample has a relatively dominant absorption from 3600 to 3000 cm^{-1} typical of O-H stretching. This may be attributed to hydrated species. The 1450 cm^{-1} to 1700 cm^{-1} region is broader in the ring face than in the cylinder liner deposit, possibly due to carboxyl salts. The liner deposit appears to contain a tiny amount of soot. The absorptions just below 1100 cm^{-1} of both deposits are probably due to calcium sulphate. Neither deposit sample appears to contain significant amount of calcium carbonate, hence significant unreacted detergent additive is not incorporated into either of these deposits.

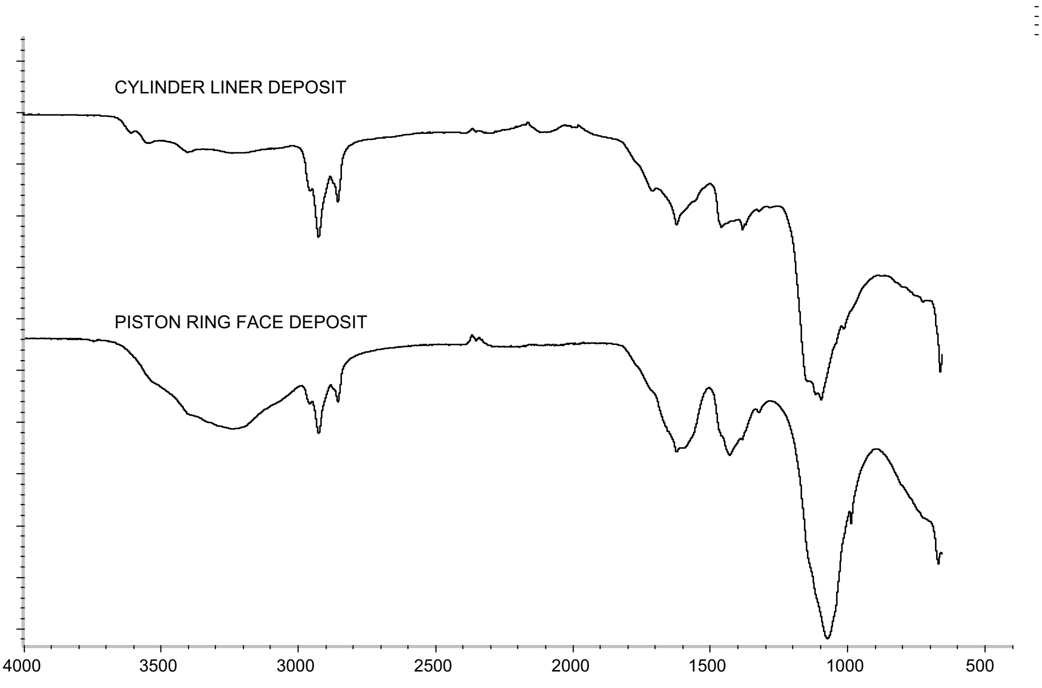


Figure 3-42 *Comparison of cylinder liner deposit and deposit sample removed from piston ring face.*

The ring face deposit was washed with pentane and acetone and subsequently analyzed by FT-IR in an attempt to characterize it further. As seen in Figure 3-43 the solvent washing had little effect on the IR transmission spectrum of the piston ring face deposit apart from the elimination of aliphatic material by pentane. This substantiates the impression that the aliphatic material is a coating.

Considering the similarity between liner deposits and ring face deposits in terms of solubility, appearance and IR spectrum, the formation of ring face deposits could very well be an integral part of the liner deposit formation or distribution. While thick ring face deposits are infrequent, the horizontal piston ring imprints shown in pictures in chapter 9 are more common and could represent the same basic mechanism.

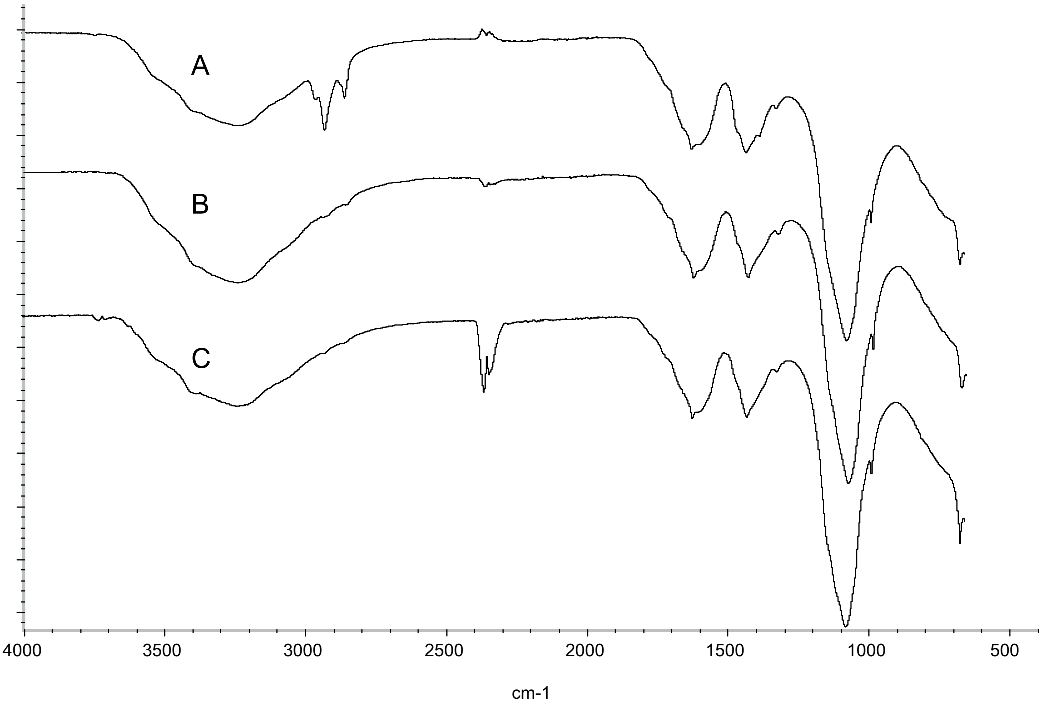


Figure 3-43 *Piston ring face deposit: a) untreated, b) pentane treated, c) acetone treated*

3.4.2 Piston deposits

Samples of piston deposits were obtained from an engine different from the one in which piston ring face deposits were formed. The ring groove, top land and piston crown deposits were all black and insoluble in acetic acid. The piston skirt deposit is amber but darker than the liner deposit. The darker shade could be a result of the soot content. A significant difference, however, is the fact that the piston skirt deposit is insoluble in acetic acid. Transmission spectra from deposits obtained at different parts of the piston are seen in Figure 3-44.

The piston crown deposit resembles anhydrous calcium sulphate, the presence of which was verified by XRD. ICP analysis of a piston crown deposit from an earlier case study detected about 30% Ca, 4.5% Zn and 1.5 Mg. (sulphur and oxygen are not determined in this ICP test). Piston crown deposits can thus be expected to contain sulphates of Zn and Mg as well.

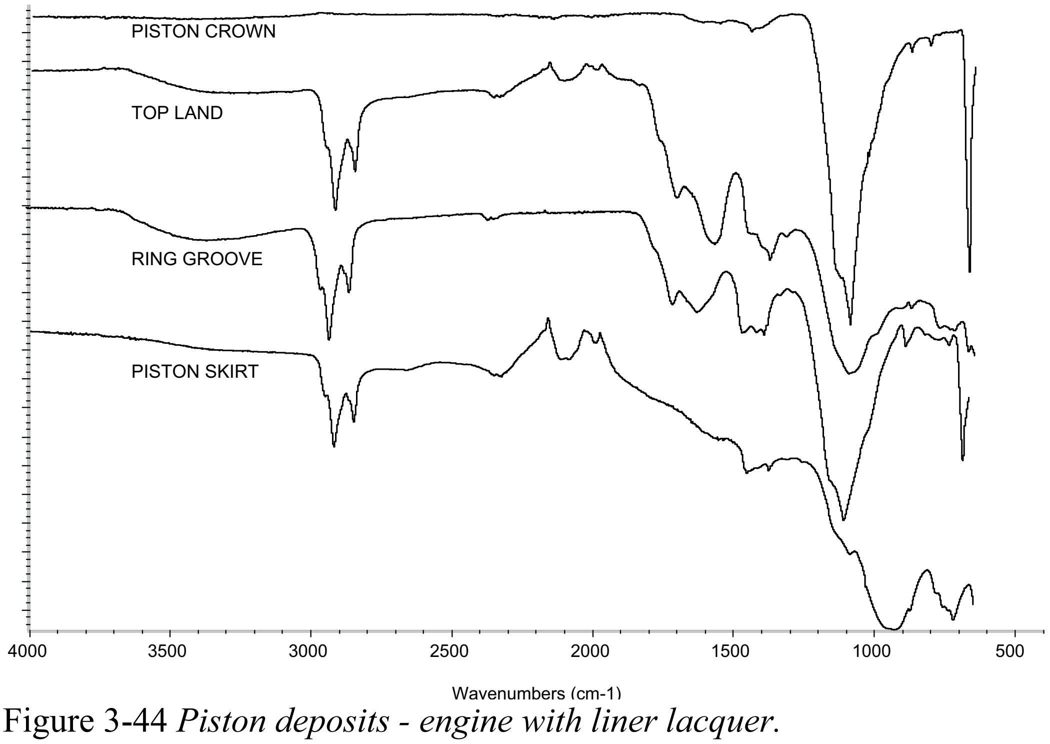


Figure 3-44 *Piston deposits - engine with liner lacquer.*

This ratio between Ca, Zn and Mg determined by ICP was comparable to that of the lubricating oil use in the particular case study and suggested that these elements accumulated unselectively in the piston crown deposit.

The top land appears to contain calcium sulphate in addition to aliphatic material, soot, oxygenated hydrocarbon and carboxylate salts. The ring groove deposit sample appears similar to the top land deposit apart from the absence of soot and a higher relative content of sulphate.

The piston skirt deposit apparently contains aliphatic material and soot but does not appear to contain much calcium sulphate. The strong absorption around 950 cm^{-1} is unfamiliar. Correlation charts [25], [87], suggest that this could be olefin C=C stretching, phosphorus or silicone compounds, however this is uncertain. Piston skirt deposits are generally harmless and have not attracted attention in the literature. Apart from this exception, the main features of these piston deposits can be recognized from previously published piston deposit spectra.

3.4.3 Flame ring deposits

A relatively thick deposit often forms on the flame ring in conjunction with cylinder liner deposits. The thickness of these deposits can be appreciated in Figure 3-45.

Figure 3-45 *Severe flame ring deposits.*

A sample of such deposits was obtained from en engine with liner lacquer deposits. The engine from which these deposits originate, had particularly sticky lacquer deposits which were rich in calcium carbonate, aliphatic material and oxygenated hydrocarbon resins but devoid of soot. The resin and calcium carbonate in the liner deposit would easily wash away in pentane. The untreated IR spectrum of this liner deposit is shown in Figure 3-46 along with the IR spectrum of a sample removed from the flame ring in the same engine.

The deposit removed from the flame ring share main features with the liner deposit. Both include aliphatic material, calcium sulphate and probably also calcium carbonate. There are salient differences as well. The liner deposit has a broad absorption at 3600-3000 cm^{-1}, which is typical of O-H stretching most probably due to hydration of the sulphates. Another noticeable difference is absorption centered around 1650 cm^{-1} in the liner deposit which is typical of carboxyl salts. The flame ring deposit appears to contain a relatively larger amount of calcium carbonate as identified by the strong peak at 1500-1400 cm^{-1} combined with the sharp peak at 870 cm^{-1}.

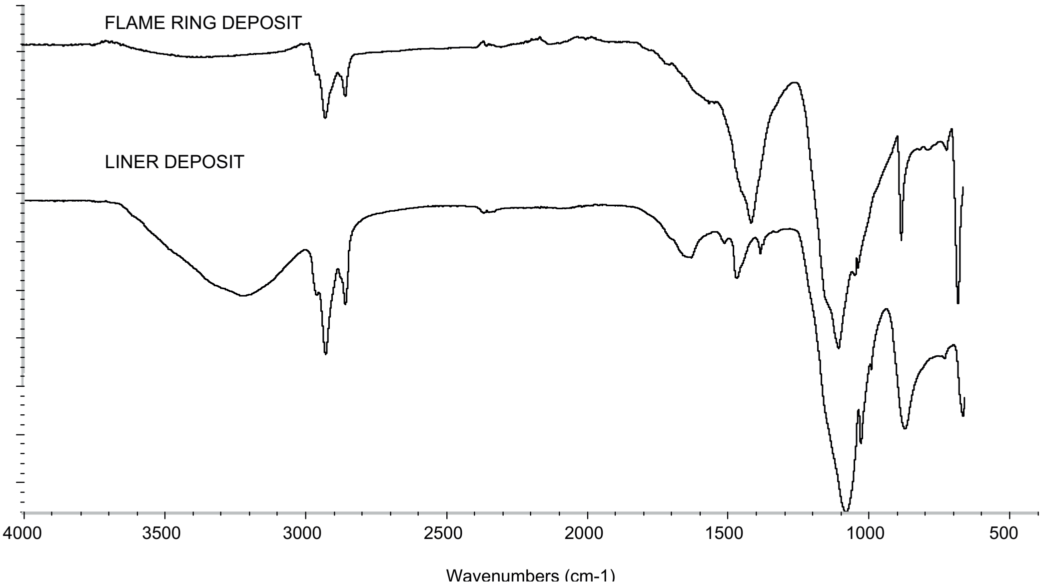


Figure 3-46 *Liner and flame ring deposit sample from* the same engine as the above piston deposits.

The composition of the flame ring deposit is similar to the piston crown deposit with the noticeable difference of aliphatic content and calcium carbonate. The calcium carbonate is likely to be a residue from oil detergent additive material. The rough and chunky rather than smooth appearance of this deposit suggest that it has not been in regular contact with the piston top land. Additionally, neither the piston top land nor piston crown appear to contain calcium carbonate. It is thus suggested that the calcium carbonate has migrated on the cylinder wall upward from the top ring reversal point. This could possibly be caused by top ring lubricant 'scrape up'; an effect which is believed progressively aggravated by liner smoothing.

3.5 Summary of results

The investigation of the deposit distribution has shown:

- That lacquer deposits tend to discolour the full ring-liner contact area, starting in the top, while glaze discoloring is seen primarily in the top area.
- Visible patterns suggestive of liquid deposits and piston ring distribution effects
- That the thickest deposits accumulate in the mid stroke region
- There appears to be a tendency in some engines towards lacquer deposit formation on one side of the cylinder liner (incidentally, this is known to be the colder side of the cylinder liner.)
- That lacquer deposits are more often seen on groove edges and plateau than does glaze.
- Glaze deposits appears to loose fragments in the higher part of the liner.

The investigation using IR, XRD, EDS, TEM and FT-IR has enabled the following characterization of liner deposits.

Liner deposits consist primarily of C, O, S, Zn and Ca. The calcium is primarily seen as calcium sulphate but also organic calcium salts. Additionally, carbon may be found in the form of soot and resin in addition to organic salt.

The bore glaze in this study was characterized by iron sulphate and a higher soot and carboxylate salt content compared to the liner lacquer samples, while the lacquers contain more aliphatics, 'resins' and calcium carbonate. The glaze contained visible crystals with sizes up to 0.5 micrometer, while crystals were not discernable in the lacquer sample - it is not clear wether this is due to sample thickness or crystal size. Overall, the transition between these types of deposits appears to be gliding

Both liner lacquer and bore glaze samples contain traces of other additive elements, wear metals, sea water and dust. These analyses revealed that liner deposits did not contain significant embedded calcium carbonate although calcium carbonate was expected in light of statements in [4] and [12].

The liner deposit constitutes oil insoluble species all of which are naturally occurring during normal engine operation. Liner deposits have compositional features in common with piston deposits as reported in the literature.

Investigation of the solubility properties of liner deposits presented in Appendix 7 revealed that liner deposits were generally soluble in acetic acid, and that the acid tended to delaminate deposit particles.

Chapter 4

Case Studies

This section presents data collected in 5 field studies and also includes some information from 3 cases where the author did not inspect the engine, but extensive and reliable written information was obtained.

These ships are all in service and inspections have to be made at times where they would not interfere with commerical needs. For this reason, the intervals between inspections are irregular, and there is a need to immediately rectify the problem. It has thus never been possible to monitor the development of the deposits without making changes it was hoped could reduce the problem.

4.1 Review of Case Studies

The field studies involved surface measurements, solubility tests and photographic documentation and also the collection service information such as operating characteristics, previous operation problems, oil consumption history as well as engine operating data.

Service histories are usually documented in reports from repair yards; however documentation is more frequently lost or incomplete than might be expected. Particularly, information gets lost when a ship changes owner and crew. Available information also has a natural bias towards what need to be fixed or replaced rather than why. For this reason, the investigation into service history typically revealed that there may have been problems; however this information lacked the detail to be useful[1] It is, however, clear that high oil consumption is a recurring phenomenon. In some cases the problem has been temporarily solved only to return after some years of trouble free operation. In other cases, oil consumption levels have been stable, yet unusually high for extended periods.

All the ships that have been inspected routinely record engine data at full load to monitor the performance of the engine. These data include temperatures and pressure of charge air, jacket water, exhaust gas temperature and more and have been studied in detail.

Oil consumption is recorded by the quantity of top-up oil needed to refill the normal oil level. The average time between oil top up is variable, hence the number of oil refillings per month is variable. This effect as well as inaccuracy in oil level readings is responsible for the jagged appearance of typical oil consumption curves at low oil consumption levels. The importance of these errors diminishes at high oil consumption levels.

The oil consumption of an engine is dependent upon load, which may vary. The engine loading is not recorded. However this effect can be partly corrected by relating the oil consumption to the fuel consumption which increases with load.

In the case of used oil analysis, the time between the last oil refill at the time of sampling is often variable; hence the fresh oil dilution effect on samples is variable. This effect and possibly also poor sampling may cause a sudden change in apparent oil quality.

4.1.1 List of case studies

Five ships have been inspected, some of them several times as shown in Table 4-1. Cases A - C are reviewed in detail in subsequent chapters.

In addition to the information obtained from inspections in Table 4-1, some well documented case studies have been reviewed based upon information obtained from users with deposit problems or from service reports obtained from engine manufactures.

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[1] There is a notable difference between shipping companies in their information handling, particularly in their use of computers. In one case, oil and fuel consumption was recorded in a book in-between other data, while a state of the art computer was stationed in the mess for entertainment purposes only. Improvement in this area could not only assist the ship engineer to notice high oil consumption before the accountants, but also improve the overall quality of maintenance and facilitate data sharing.

TABLE 4-1 SUMMARY OF FIELD INSPECTIONS

Case	Service type	No. insp
A	Passenger / Ferry	5
B	Line fishing	5
C	Offshore supply	3
D	Offshore supply	1
E	Offshore supply	1

TABLE 4-2 ADDITIONAL CASE STUDIES

Case	Service Type
F	Offshore supply
G	Power generation
H	Offshore supply

Liner lacquer formation has been described as a complex interaction involving engine load, engine design, fuel properties and lubricant properties. This review addresses these factors as they appear in our case studies. Further factors such as for instance the use of fuel additives are discussed case by case.

4.1.2 Engine load characteristics

All case engines operate at low load during a significant part of the time. Offshore supply vessels spend a significant fraction of time waiting on weather or opportunity to service offshore installations while the ferry idles in port. The most extreme case is the line fishing vessel which spends about 65% of the time pulling a line at 2 knots, the resulting engine load is only 17% - 30% MCR depending upon the use of shaft generator. Overload has not been reported in any of these engines, and, the operating profile is such that systematic load above MCR does not occur. Seven of eight of these engines operate at constant speed: The thrust is varied by changing the propeller pitch while the governor maintains engine speed. The remaining engine operates by propeller law, but still carries a shaft generator by way of a hydraulic variable speed transmission system.

An indication of a load effect on deposit formation rate was observed in a twin engine offshore supply vessel. The engines in this ship are identical and both are equipped with a shaft generator. They receive the same level of maintenance, use the same type lubricating oil and share the same fuel. Even so, the oil consumption increased more rapidly in one engine as shown in Figure 4-1. The corresponding high and low oil consumption levels observed in month 4 suggest an error in registration; however, this could not be documented. The oil consumption is given as a percentage of the fuel oil consumption. In terms of total consumption, the port engine averaged 60 liters pr 24 hours while the starboard used about 40 liters pr 24 hours. Hence both specific and total oil consumption level is higher in the port engine.

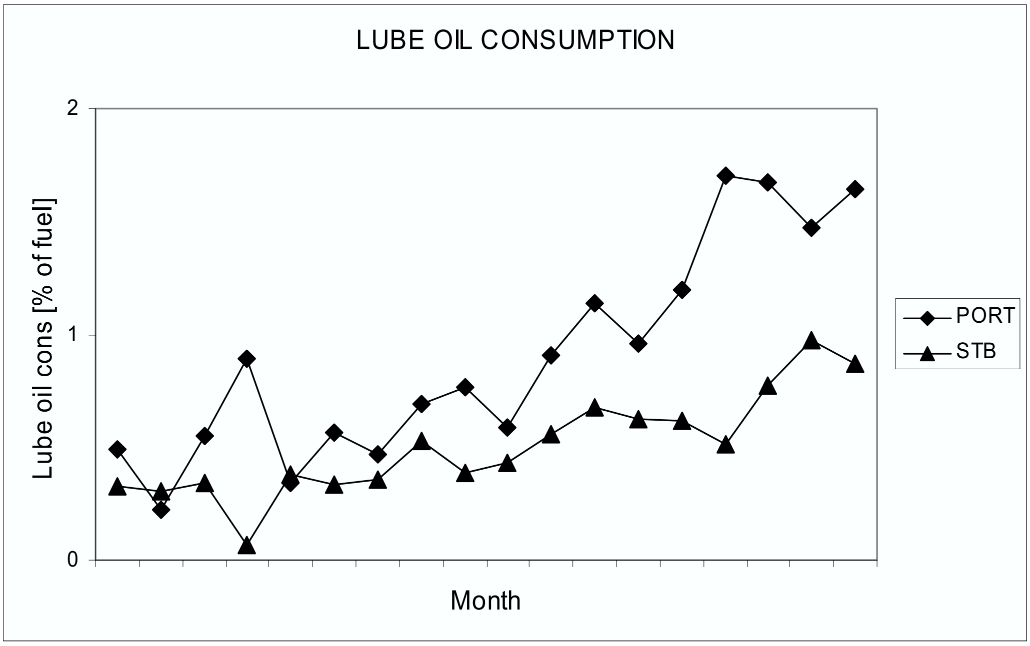


Figure 4-1 *Oil consumption development in twin engine ship (Case E)*

Investigations revealed that for practical reasons, the starboard engine always pulled the shaft generator at standby. The use of the shaft generator in standby condition results in an increase in charge air temperature from 41-43°C to 58-60°C and also an increase in charge pressure. This is expected to significantly improve combustion. The systematic difference in loading could be documented by the average fuel consumption. During the last 18 months, the average fuel consumption of starboard engine is 161 kg/h while port only consumed 138 kg/h. Both engines are run simultaneously and have accumulated the same number of running hours.

In eight of eight cases of liner deposits, low load is a significant part of the operating profile while overload is rare or nonexistent. This is not in agreement with observations reported by [7], [8] which have focused on overload or cyclic loads. Our selection of cases, however, cannot be considered truly random as they constitute the group of ships with liner deposits that have some indirect connection to NTNU and ship owners that were interested in participation in this project. Possibly, low load accelerates a deposit forming mechanism; however our only firm conclusion is that liner deposit clearly can accumulate in engines with typical low load profile.

4.1.3 Engine design factors

Engine design has been reported to influence deposit formation. Since some engine types are preferentially selected for some types of applications, the exposure to potentially severe operating conditions may differ between engine types.

Liner deposits have been encountered in different designs. Like virtually all medium speed engines they are of four valve design with a centrally mounted multihole fuel injection nozzle and jerk type fuel pumps. Apart from that, they represent a variety of designs in terms of characteristic combustion chamber features as listed below:

- with or without flame ring
- flat or deep piston bowl design
- correspondingly different injection nozzles.
- gas flow parallel or perpendicular to the crankshaft
- variations in piston ring design

The engines with deposit problems that have been investigated have stroke / bore ratios of 1.2 or higher and rated MEP of 17-22 bar. A connection between obvious design features and liner deposits cannot be made. Less obvious but highly relevant features are the compression ratio, fuel injection timing, duration and pressure and also valve timing.

For what it is worth, a comparison of an engine with liner deposits to an engine mounted in a similar ship used in the same trade in the same area revealed that the older ship which reportedly did not have deposit problems had a significantly different fuel injection timing. The ship which did not have problems started fuel injection 9 degrees earlier which allows more time for injection hence the fuel injection pressure is lower, and also allows the fuel more time at pressures favorable for combustion.

In a different case, Case E, high oil consumption was first observed following an engine overhaul in which the combustion was retarded 2 crank angle degrees to reduce NO_x formation.

These observations are in agreement with CEC report [4] which identified higher injection pressures and revised injection timings as having a potentially negative influence on liner deposits. This report also identified reduction in liner temperature as potentially having negative influence.

Our case studies do not give a clear indication on this matter. In case F, a faulty thermostat caused an overcooling of both charge air and the cylinder liner which coincided with lacquer deposit formation, while in case A, high charge air and liner temperature due to weeds in a heat exchanger coincided with deposit formation. In the majority of the cases, the prescribed liner temperature was maintained. It thus seems that a generalization regarding liner temperature is not justified on basis of our case studies.

The cylinder liner surface condition has also been claimed to potentially influence deposit formation [4]. Two liners of different surface technology were tested in one case study as discussed later.

The condition of the fuel injection nozzle has been investigated, however apart from soft deposits on the nozzle tips the fuel injection nozzles generally did not appear degraded. In a few cases, their functioning was tested in an injection bench in which case they performed well.

A majority of the vessels have been troubled with excessive soot formation. In part, this soot could originate as a result of poor fuel combustion, however partly burned oil is likely to be important as the oil consumption increases.

4.1.4 Fuel Properties

A number of fuel samples sufficient for trend analysis was collected in two of the case studies. The extent of these fuel analyses is shown in Table 4-3.

TABLE 4-3 'STANDARD' FUEL ANALYSIS

Property	**Method**	**Unit**
Density	ASTM D-4052	kg/l
Sulphur (XRF)	ASTM D-4292	mass%
Kin.visc. @ 40℃	ASTM D-445	cSt
Centane Index	ASTM D-47737	-
Total Aromatics	IP-391/95	% mass
Mono Aromatics	IP-391/95	% mass
Diaromatics	IP-391/95	% mass
Tri + aromatics	IP-391/95	% mass
Distillation	D-86	-
Simulated Distillation	D-2887	-

Additionally, fuel analysis certificates were obtained in a third case study. These certificates do not include aromatics content or simulated distillation.

An oil consumption index is used to evaluate the influence of fuel properties on oil consumption and to enable comparison between cases. This index is the oil consumption at a given time divided by the average annual oil consumption.

Since increased oil consumption to some extent is the result of accumulation deposits, there may be a delay between the inception of deposit formation and the increase in oil consumption. It is thus possible that a change in fuel composition should be expected some time prior to the increase in oil consumption. Once deposits are formed, improved fuel may not cause their removal so that oil consumption is not reduced. On top of this, it is not possible to accurately predict the combustion characteristics of a fuel by its chemical analysis; hence what is arguably the most important fuel characteristic is not directly represented in this type of analysis. For these reason, strong correlations should not be expected even if fuel composition does play a role. The relationship between cetane index and relative oil consumption at the time of fuel sampling is shown in Figure 4-2. This overall impression is that a decreasing cetane index is detrimental; however in case B the oil consumption seems independent of cetane index.

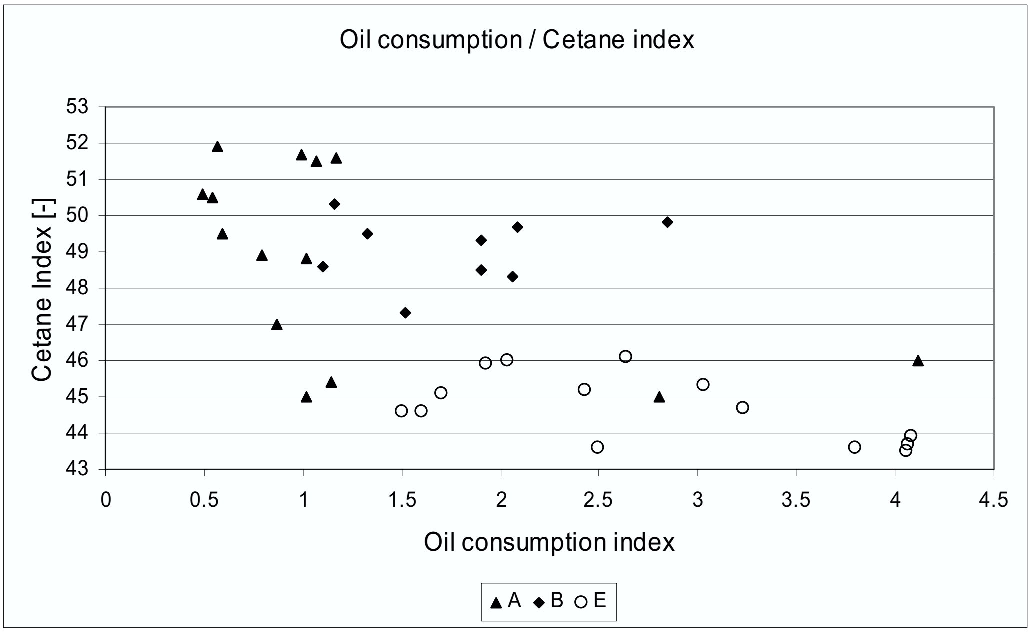


Figure 4-2 *Relative oil consumption and cetane index*

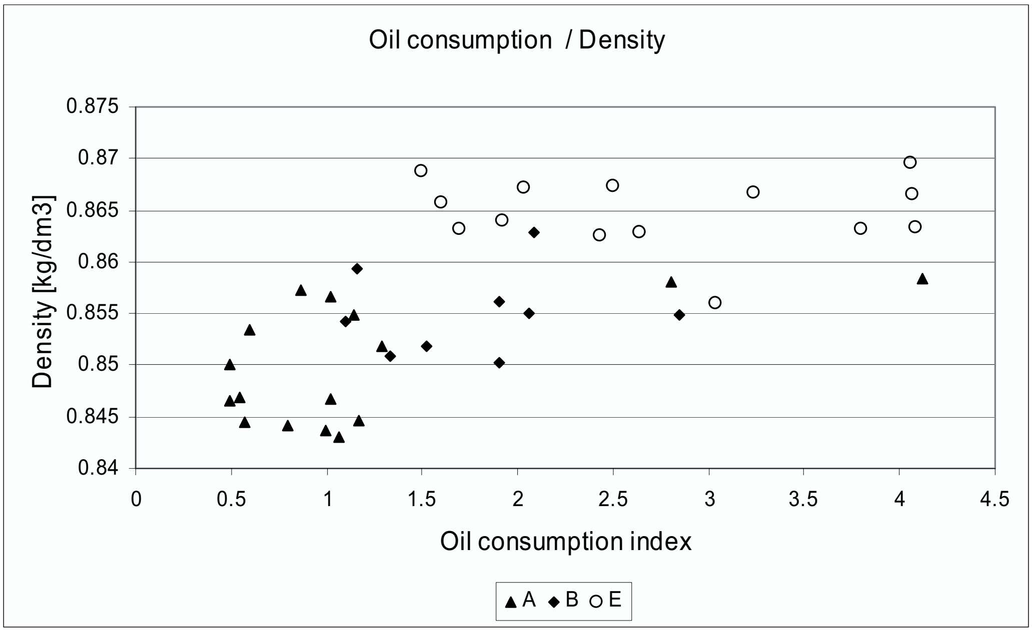


Figure 4-3 *Relative oil consumption and density*

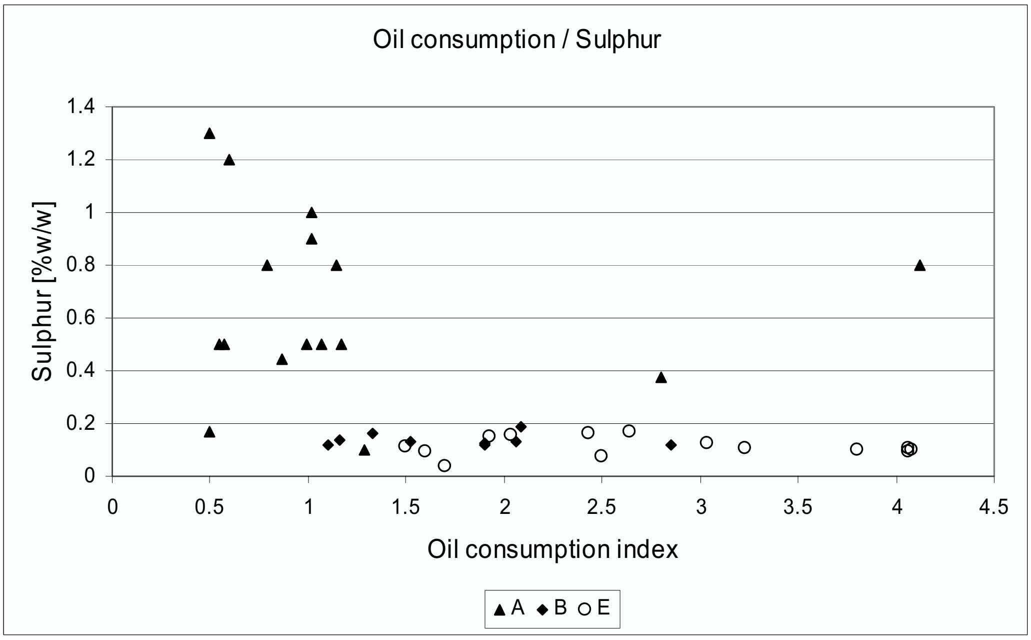


Figure 4-4 *Relative oil consumption and fuel sulphur*

The relationship between density and oil consumption is shown in Figure 4-3. Increasing density could be associated with high oil consumption in case A and B; however, density does not appear to affect oil consumption in case E

The effect of fuel sulphur is presented in Figure 4-4. Oil consumption may be considered independent of fuel sulphur in cases B and E.

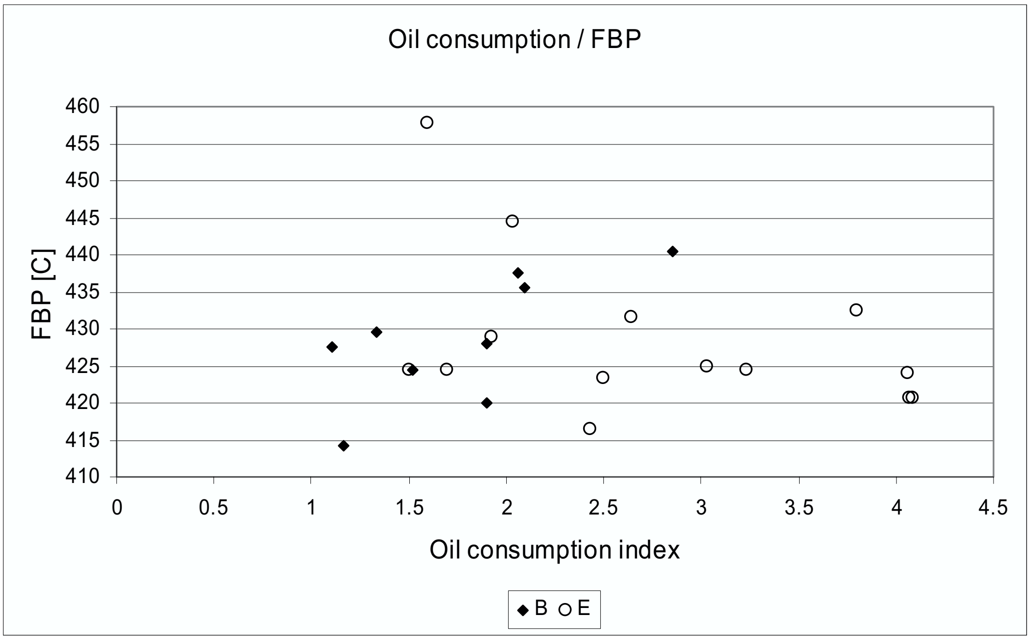


Figure 4-5 *Relative oil consumption and FBP (ASTM D-2886)*

The final boiling point as determined by simulated distillation is shown in Figure 4-5. From this figure, it may seem that increasing FBP contributes to increase oil consumption in case B while the opposite is indicated in case E.

Scientifically speaking, any number of trends and datasets cannot prove a mechanism, however even small datasets can disprove hypotheses. The fuel analysis data that has been obtained do not provide a consistent relationship between oil analysis data and oil consumption. Thus a direct relationship between these fuel analysis variables and high oil consumption clearly does not exist. This, however, does not mean that fuel cannot influence deposits formation, merely that other factors are also involved and that the importance of mechanisms vary case by case.

4.1.5 Basic Lubricating oil properties

Liner deposit problems are not limited to certain oil brands or formulations. The case oils range in viscosity grades from SAE 30 to 40 and alkalinity levels from 10.4-15. These oils include standard formulations and special lubricants with low ash levels or increased dispercancy levels. Only L1 and L6 are regular oils, the others are top range products selected specifically to counteract liner lacquer. These oils originate from several different oil development communities. Specific information of the composition of these lubricants is proprietary information; however, typical values of basic data on these oils are presented in table 4-4.

TABLE 4-4 CASE OIL PROPERTIES

OIL CODE	SAE	TBN	SA
L1	30	14.5	1.95
L2	30	15.0	2.1
L3	30	11.2	1.35
L4	40	15.0	1.65
L5	40	15.0	2.1
L6	40	12.0	1.65
L7	40	15.0	2.2
L8	30	10.6	1.3
L9	40	15.0	-
L10	40	10.6	1.3

Lubricant L4 differs from the other oils by a relatively low ash content in relation to its alkalinity. This could be related to the type of detergent and also to the type and amount of dispersant additive.

4.1.6 Used oil analysis

A review of used oil analysis data revealed that the alkalinity of most lubricants increased when the oil consumption increased. The relationship between relative oil consumption level and relative base number of these lubricants is shown in Figure 4-6. To allow comparison, the alkalinity is referenced to the alkalinity of fresh oil, and the oil consumption level referenced to 'normal' oil consumption level for the engine in this application. Oil L3 and L6 had to be excluded due to insufficient data. It was determined, however, that the alkalinity of oil L3 increased 30% at unknown oil consumption while oil analysis data for L6 are unavailable. The nominal alkalinity used to create the TBN index is the typical analysis value as stated by the supplier.

Increase in alkalinity or additive concentration has been observed by several authors [41][42] and is believed to be an effect of high volatile losses. This idea is substantiated by the fact that the more viscous and presumably less volatile SAE 40 oil increases in alkalinity in response to increased oil consumption at a lower rate than the SAE 30 oil as seen when comparing Figure 4-7 and Figure 4-8.

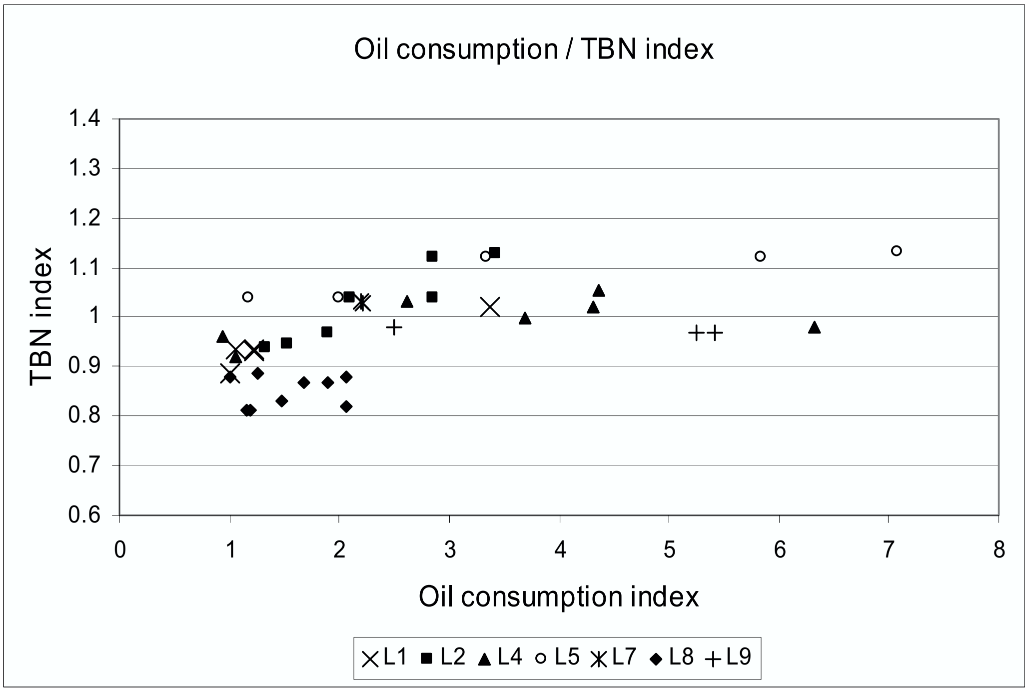


Figure 4-6 *Relative oil consumption and relative change in base number*

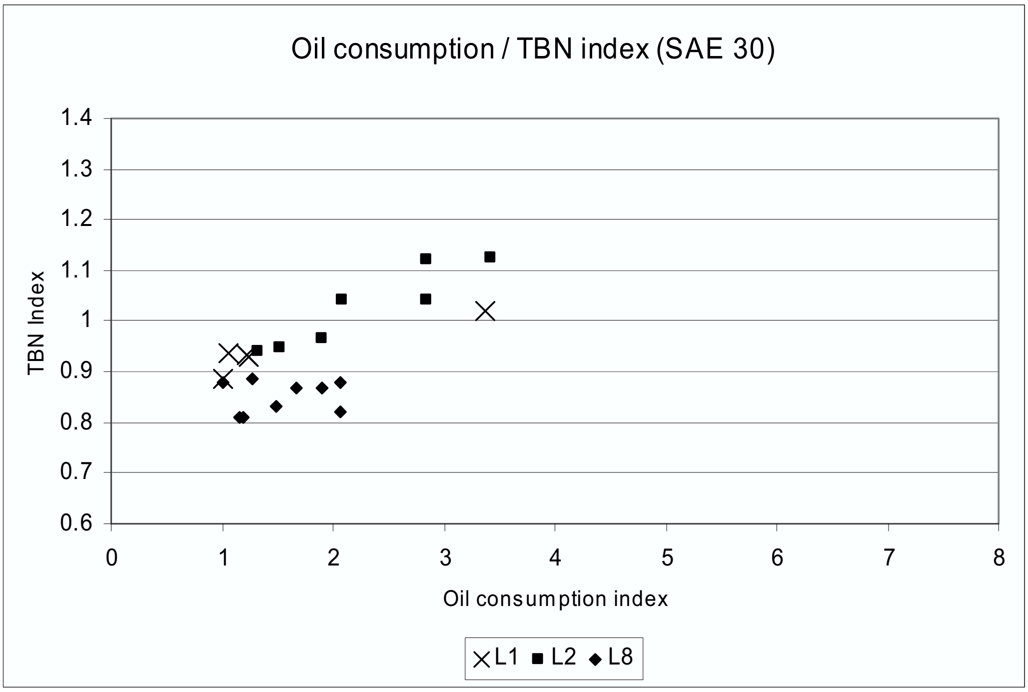


Figure 4-7 *Oil consumption index and TBN index SAE 30 oils only*

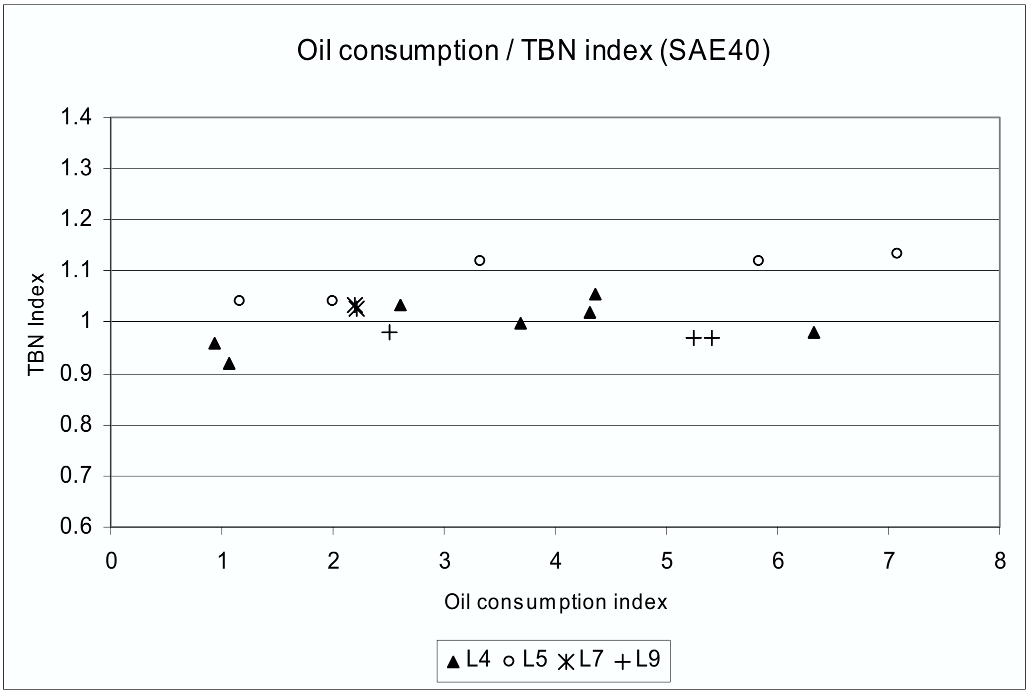


Figure 4-8 *Oil consumption index and TBN index SAE 40 oils only*

This effect is, however, confounded by engine design factors since different engine types typically operate on different viscosity grades. For the same reason, one should not conclude that oil consumption levels are higher when SAE 40 oils are used compared to 30 oils. This would be erroneous since the final oil consumption index is related to how high the ship owner allows the oil consumption to be before overhaul, a decision which is strongly affected by commercial factors.

In most case studies, the oldest data is found in the lower left corner where oil consumption is low and the alkalinity of the oil is lower than that of fresh oil while the later data are found in the upper right where oil consumption is higher and alkalinity exceeds that of the fresh oil charge, but there are some exceptions:
L4 shows typical behaviour, but as the oil consumption increased to extreme levels, the TBN level dropped again at maximum oil consumption. Lubricant L8 was applied to an engine with deposits. The deposits were gradually removed and oil consumption decreased as did relative alkalinity.
The alkalinity of L9 seems independent of oil consumption level. This is not believed to be effects of poor sampling since other analysis data from this oil vary significantly.

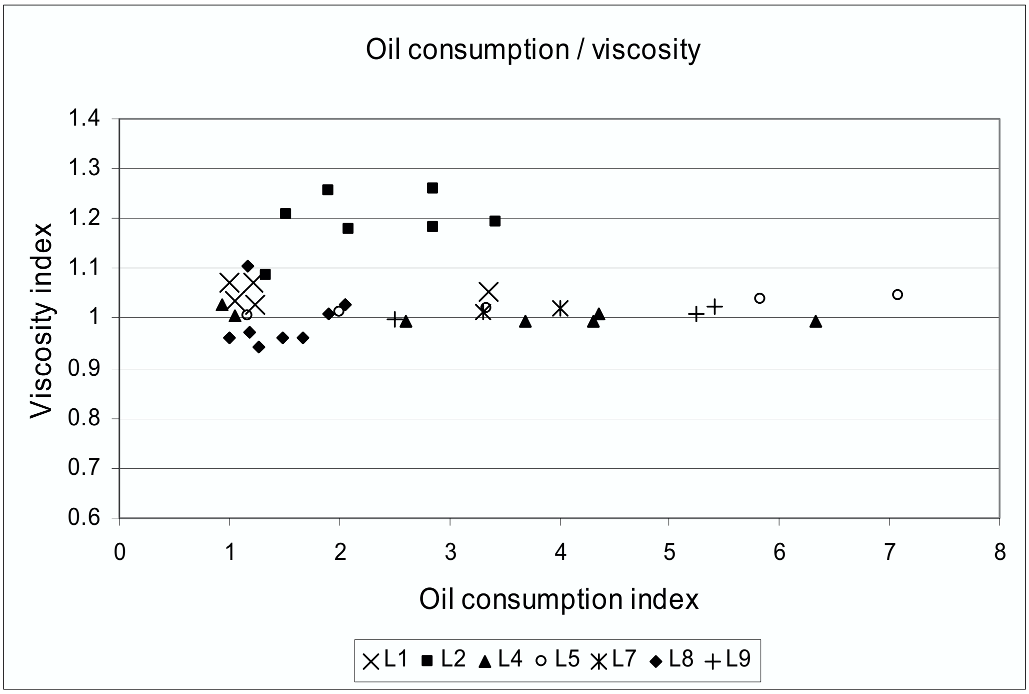


Figure 4-9 *Relative oil consumption and relative viscosity increase.*

The relative increase in viscosity is plotted with the relative increase in oil consumption in Figure 4-9. The nominal viscosity level is determined from the typical new oil analysis value given by the manufacturer. This analysis indicated that the viscosity of oils L2 and L5 increased when the oil consumption increased. These lubricants are 'sister formulations' of different SAE grade and are marketed as particularly high dispersancy oils.

4.1.7 Comparative tests

Three 'back to back' comparisons of engine oils were made in twin engine installations by switching the oil formulation in one of two engines. In one case only the top-up oil was changed while in the two other, the sump was drained. The advantage of the former approach is primarily that it is simple and does not generate waste oil. While it is true that the volume of oil spent in less than two weeks with high oil consumption may easily exceed that of the oil sump, this will allow possible contaminants to carry over from to the new oil.

These back to back tests could not discriminate between oils. One possibility is that there is little difference between the oils, another being that existing deposits will not be removed by the lubricating oil once formed. Lubricating oils are primarily designed to prevent deposit formation and to suspend the insoluble that forms, not to remove adhering material. The type of test described does not solely evaluate the oils on is 'design' ability thus important performance differences need not be detected in these tests.

In one case, however, the switch of oil formulation apparently did give positive results. This test, however was a sequential test is a single engine installation. In this case, a low volatility low ash oil L8 was used in place of a high ash oil L2. This is discussed in a following case study report.

Our lessons from these tests are that while such comparisons are potentially valuable; they must be rigorously performed. The tests should be initiated at overhaul on fresh oil sumps and extended until clear distinction can be made or until next engine overhaul required by deposits.

Experience with lubricants from different development communities indicate that none of these lubricating oils are able to offer complete safeguard against deposits. It is, however, possible that different lubricants form deposits at a different rate in given engine and application. Ship owners wishing to investigate this are advised not to make their judgment on a pass/fail deposit / no deposit level but try to estimate 'time to high oil consumption', where high oil consumption is a predefined level suitable to the current engine.

4.2 Liner lacquer in domestic ferry

This case study involved a twin engine ship with lacquer deposits in both engines. The study lasted from September 2000 until March 2002; about 18 months accumulating approximately 7600 operating hours in each engine. The liner lacquer was combated using an anti-lacquer fuel additive which is a mix of two active ingredients, a combustion catalyst and a detergent. The use of the fuel additive was stopped after 12 months, but the monitoring of the engine continued 6 months thereafter at which time the engine was overhauled.

The oil consumption was reduced when the fuel additive was used, but this effect is confounded with a simultaneous reduction of charge air and liner coolant temperature. The area above the upper ring reversal point on the liner was significantly cleaner when the fuel additive was used. The occurence of deposits resembeling a solidified liquid flow was lower when the fuel additive was used.

4.2.1 Background

The lubricating oil consumption had increased to about 5 times the 1999 average at the start of this case study. All 24 cylinders were inspected by boroscope and showed amber deposits. Two cylinder heads were removed and the liners were washed with acetic acid. The deposits were easily removed by acetic acid but not by lubricating oil, diesel or petroleum spirit. It was therefore concluded that liner lacquer was present, and the likely cause of the high oil consumption. Discoloration was seen on all parts of the liner that are visible when the piston is at lower dead centre.

The history of the oil consumption in percentage of fuel consumption during this case study is shown in Figure 4-10.

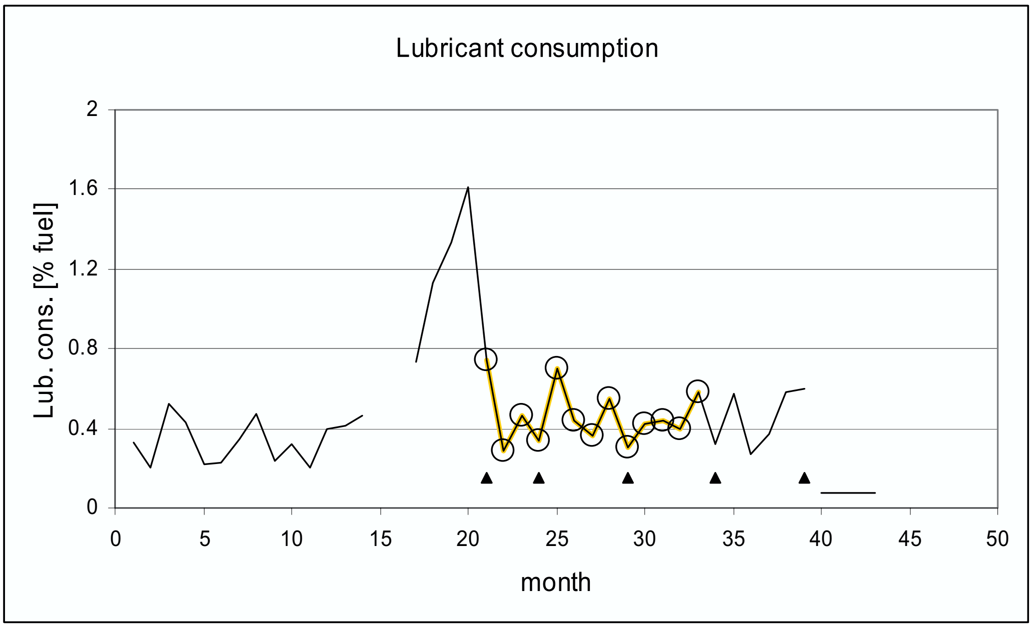


Figure 4-10 *Oil consumption history. The ship was out of service in month 15 and 16 due to grounding. Use of fuel additive is marked by circles. Triangles indicate cylinder inspections. The step reduction in oil consumption at month 40 is the result of complete engine overhaul.*

Concerns regarding cost and environmental effects related to the high oil consumption as well as the risk of consequential damage prompted immediate action to reduce the amount of lacquer. A fuel additive that is designed to combat liner lacquer was selected for testing. The additive combines additive components with cleaning and combustion enhancing properties. This additive is further described in reference [97]. The additive was mixed with the fuel during bunkering at a treatment rate of 670 ppm using a fluid powered additive injector system. The oil consumption decreased sharply after the additive was used; however this effect is confounded with the cleaning of the seawater cooler.

The lubricating oil consumption is estimated at the end of each month by calculating the amount of oil added to maintain correct oil level in the sump. The oil consumption is then divided by the fuel consumption to get an estimate of the relative oil consumption that is suitable for comparison. January 1999 is month 1, February 1999 is month 2 and so forth in the timeline used in this case study. Liner lacquer is most pronounced in month 19 and 20 which confers to July and August 2000.

Fuel additive treatment was discontinued after approximately one year. The oil consumption remained at the same level for a period of six months; however the oil consumption level was still about 30% higher than the average of the previous year. The cause of high oil consumption is believed to be a combination of bore polish and also remaining liner deposits. The cylinder liners were rehoned in April 2002 and the oil formulation was substituted for a newer oil formulation that performed well in case study 2. The oil consumption dropped to a low level following this change.

The engine has been inspected 5 times during this case study as shown in Figure 4-10 and listed in Table 4-5.

TABLE 4-5 ENGINE INSPECTIONS

Insp.	**Date**	**Description**	**Month**
1	04 Sept. 2000	Lacquered engine before treatment.	21
2	12 Dec. 2000	After three months additive treatment	24
3	04 May 2001	After eight months additive treatment	29
4	05 Oct 2001	After additivation was stopped	34
5	21 Mar 2002	After 6 months without fuel additive	39

An engine inspection involves opening one cylinder in each engine. The deposit is tested for solubility and photographed. Surface roughness measurements were made from inspection 3 and onwards, as was a technique for close up photography of the liner in four directions and two heights.

4.2.2 System description

The engines in this vessel are identical apart from the port engine being connected with a shaft generator. Both engines are coupled to a variable pitch propeller. The engines were built in 1991, have a V12 configuration and are rated at 17 bar MEP at 825 rpm. The engines have a flat combustion chamber and are not equipped with a ‘flame ring'. The nominal full load pressure of the impulse charged turbocharger is 1.6 bar, the charge air temperature is adjusted to 40℃ at normal operation. The cylinder liners are cooled by water that enters the engine block at a nominal temperature of 70℃. The stroke / bore ratio of this engine is 1.30.

The engines have a dry oil sump and a common oil reservoir. Only the combined oil consumption of both engines can be recorded. The oil reservoir is fitted with two external lubricating oil cleaning units working in parallel including a lubricating oil separator. The oil separators are of the clarifier type and discharge contaminants every 30th minute. The nominal throughput of the unit is 600 l/h, the oil separation temperature is 80℃ degrees.

4.2.3 Operating profile

The engine operating cycle is subject to seasonal variations. The ship runs short legs, the typical duration is 4 hours, some shorter voyages are also made. The engine is loaded about 80% during normal transit, but the load may increase to about 90% due to special circumstances such as alternate routes or heavy summer traffic. The engines are typically kept idling when the ship calls to port. On average, the ship stops its engines once every 24 hours during summer, twice during winter.

4.2.4 Engine history

The engines have been troubled with high oil consumption related to liner lacquer twice before, in 1993 and 1997. The engine has also seen some problems with carbonaceous deposits and fuel injection cam wear. (These problems were not related to each other) Annual lubricating oil analysis has not revealed any problems. The engines have operated on the same lubricating oil formulation since 1993 or longer. The entire load of lubricating oil was last changed in 1996. The oil formulation was changed in April 2002.

4.2.5 Survey of operating parameters

Engine operating parameters were investigated using manual engine room reports which include some weather and ship load data. The parameters available for analysis are tabulated in Table 4-6.

TABLE 4-6 ENGINE DATA AVAILABLE IN LOG.

Brigde	**Sea water cooler**	**Individual Cylinder**
Ship Speed	Inlet pressure	ind. firing pressure
Cargo Load	Inlet temperature	ind. comp. press.
Ambient conditions	Outlet temperature	exhaust temp.
Engine	**Charge air cooler**	**Lube oil**
Engine speed	Inlet pressure	Pressure before filter
Fuel rack position	Inlet temperature	Temp. after pump
T C speeds	Outlet temperature	Pressure after filter
Exhaust Temperatures		
Fuel press. aft. filter		

The operating data were analysed for correlation with engine oil consumption. An apparent relationship between oil consumption and both charge air and liner coolant water temperature was revealed. This is shown in Figure 4-11 and Figure 4-12. The temperature data are recorded individually for each engine, however the average is shown in this figure. The increased temperature that coincided with the lacquer formation was caused by weeds in the seawater cooler which accounts for the simultaneous increase in charge air and cylinder liner coolant temperature. The cooler was cleaned immediately; that is some time between month 20 and 21 in the figures. An increase in exhaust gas temperature associated with the high charge air temperature was also indicated

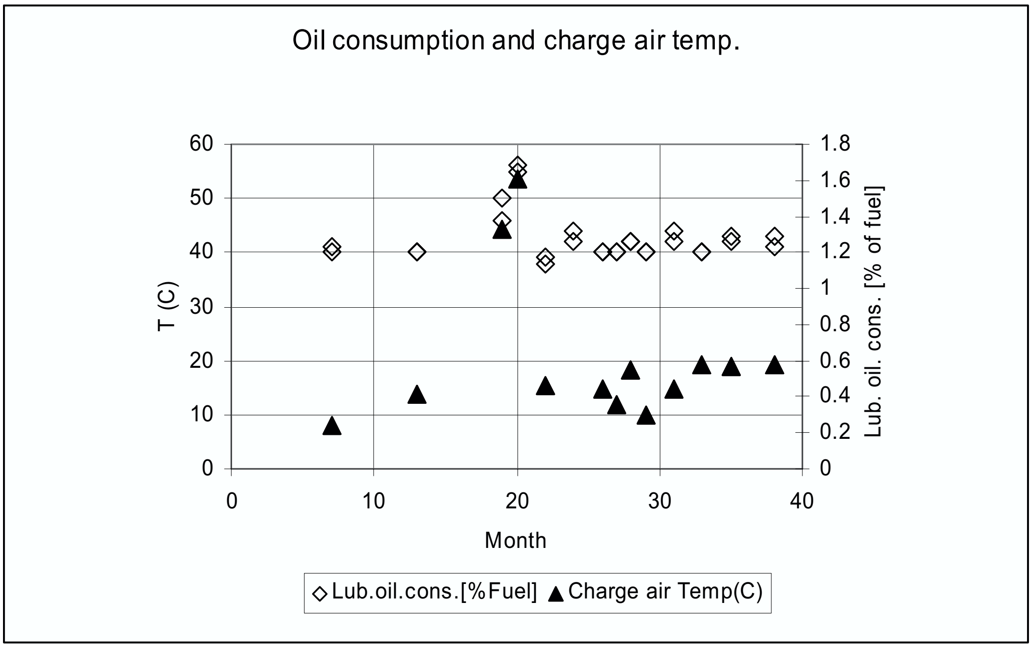


Figure 4-11 *Charge air temparture and oil consumption history. Severe lacquer levels in month 19 and 20. (Fuel additive used from month 21)*

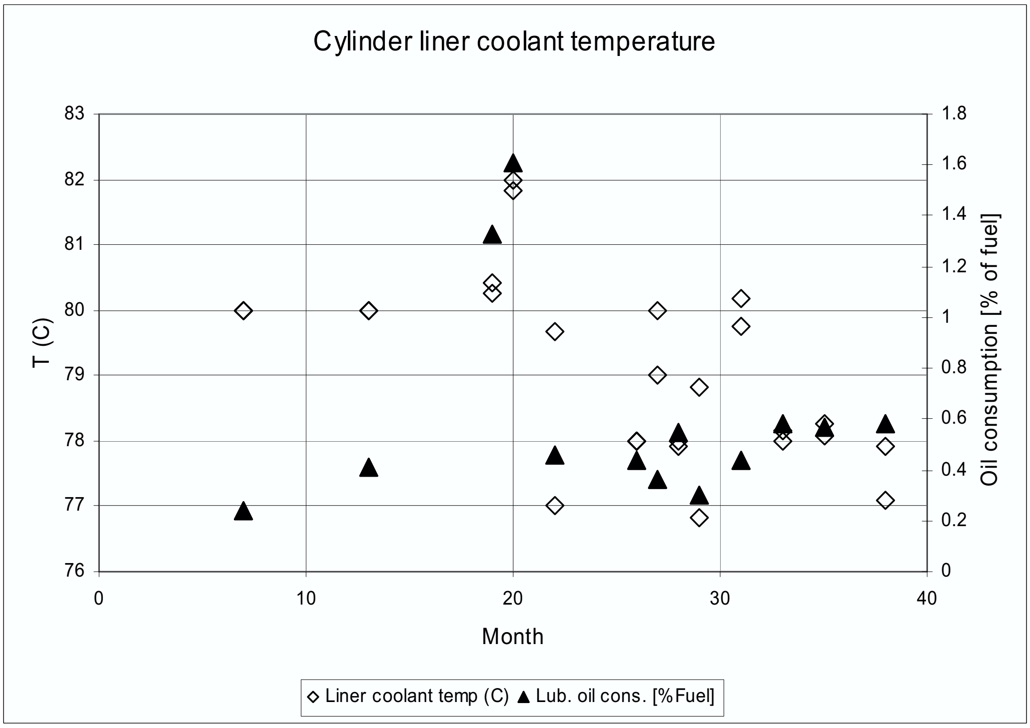


Figure 4-12 *Liner coolant temperature and oil consumption history. Severe lacquer levels in month 19 and 20. (Fuel additive used from month 21)*

4.2.6 Fuel analysis

Fuel analysis data were obtained from fuel certificates provided by the fuel supplier. While simulated distillation and content of aromatics is not included in standard analysis, a great advantage was that historic fuel data could be obtained.

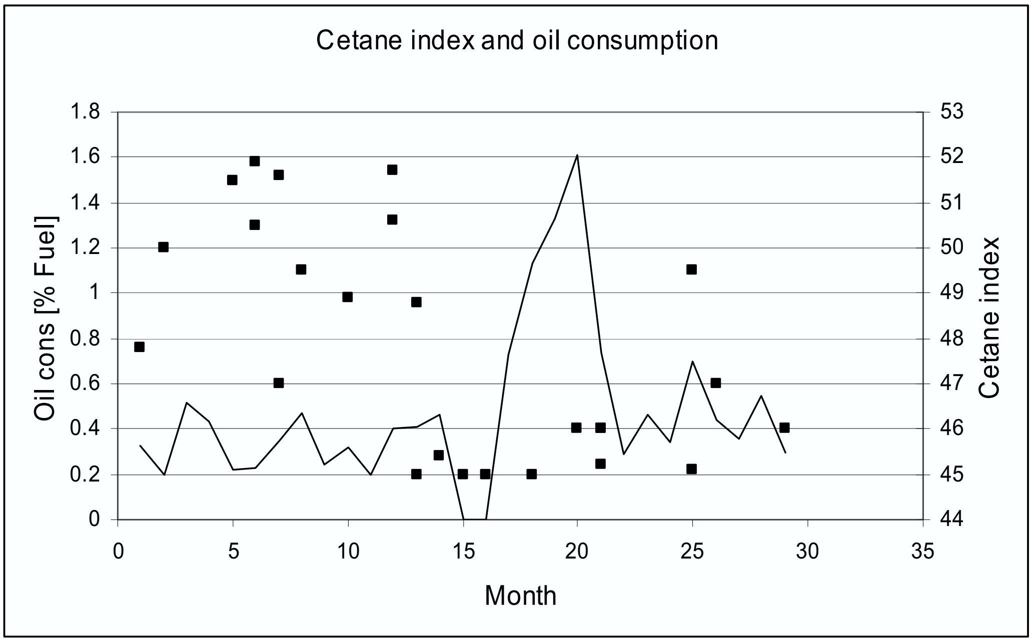


Figure 4-13 *Historic fuel analysis data- cetane index*

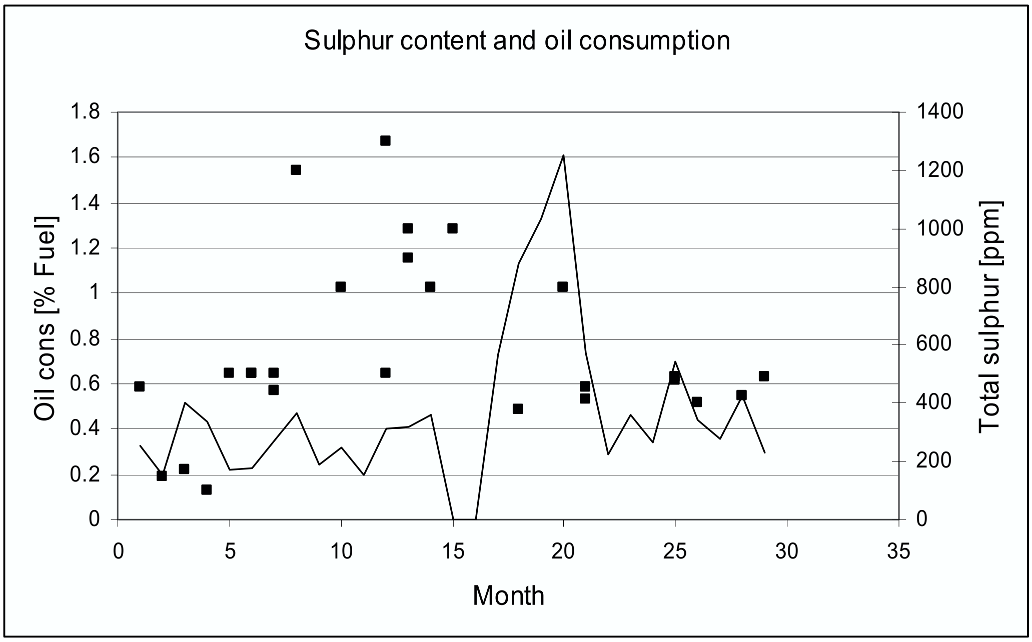


Figure 4-14 *Historic fuel analysis data- fuel sulphur content*

This analysis revealed that a step change in cetane index had occured in this region prior to the formation of liner deposits shown in Figure 4-13, however the cetane index is still 10 points higher than the international spec. level for the best quailty gas oil intended for regular use (DMA). Low sulphur content is commonly associated with lacquer. However in this case fuel sulphur content is elevated prior to and during deposits formation (Figure 4-14).

4.2.7 Used oil Analysis

The TBN level increased above its nominal 'fresh oil' level of 15 at the time of the high oil consumption, and was restored to normal levels when the fuel addive was used. This is shown in Figure 4-15. The sump base number peaked a few months before the oil consumption increase. The relative reduction in alkalinity when the oil consumption increased rapidly could be a result of increased dilution that counteracts volatile losses.

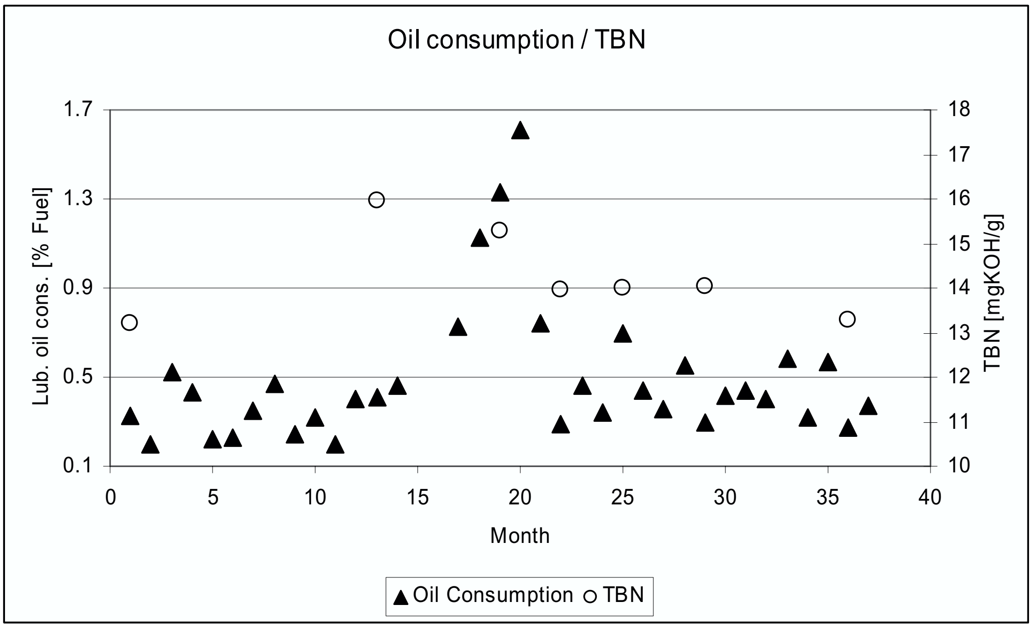


Figure 4-*15 Used oil TBN and oil consumption*

The alkalinity and calicum content of oil samples are shown in Figure 4-16. This figure shows that the content of calcium peaks in the oil sample taken at maximum oil consumption, but diminishes with time as oil consumption is restored. TBN is unaffected, thus the oil is progressivly purified from neutral calcium containing material like dispersed calcium sulphate and calcium carboxylate.

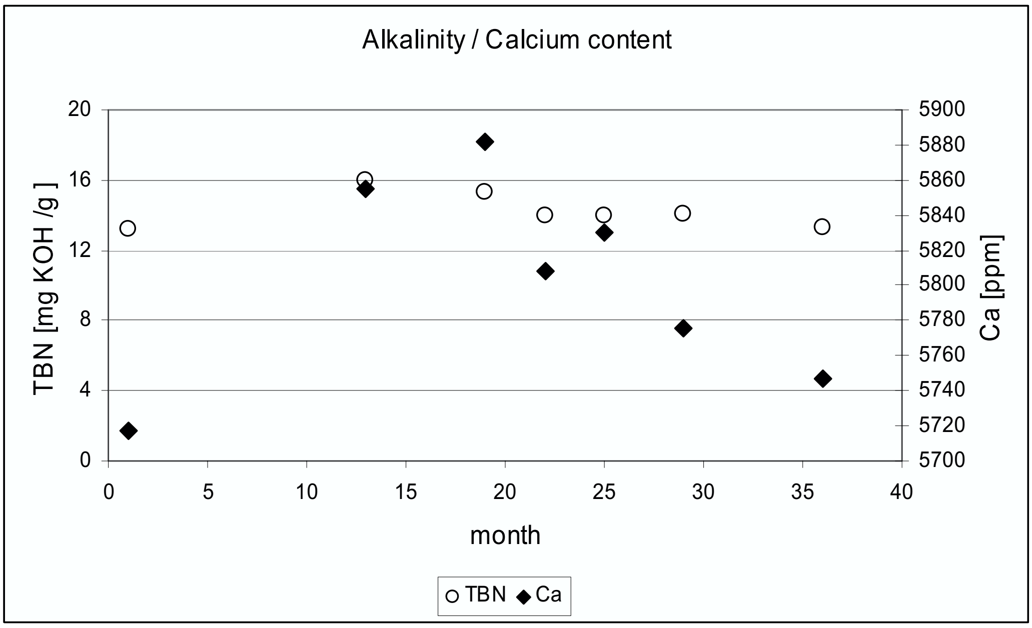


Figure 4-16 *TBN and calcium content*

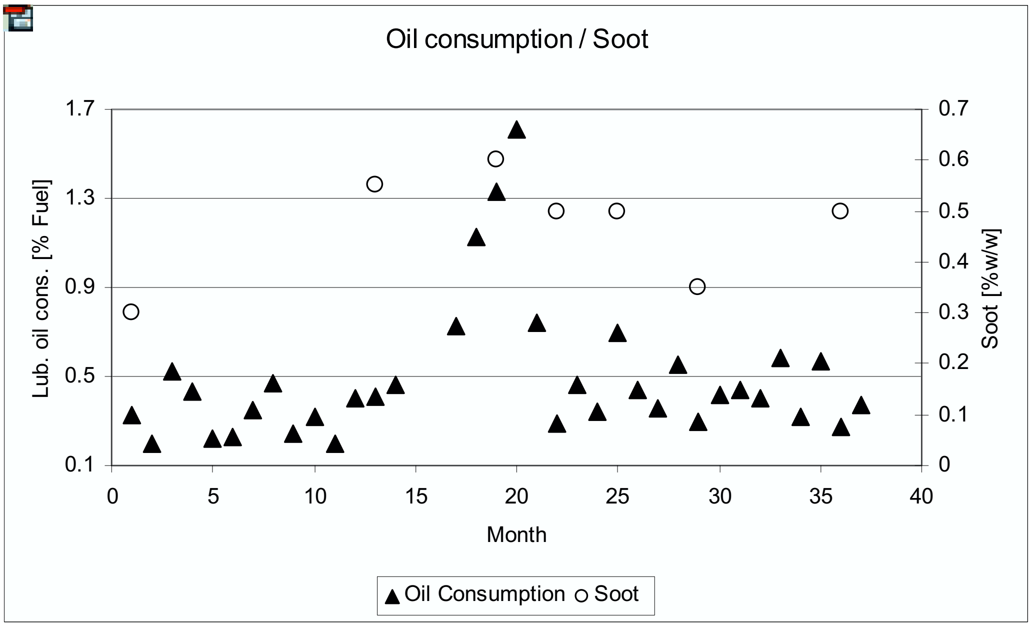


Figure 4-17 *Used oil soot and oil consumption*

The bulk lubricant thus shows an increase in excess of 100 ppm in the amount of what can be described as 'spent calcium' during deposit formation. This increase correlates reasonably well and is also physically related to fuel sulphur levels. Assuming that the alkalinity of the top up oil did not significantly exceed the nominal level of 15, the increase in alkalinity in month 13 must be a result of high volatile losses in relation to oil consumption occuring prior to the observed cooling failure and also prior to the change in fuel oil composition.

The soot contentration increased slightly with high oil consumption as seen in Figure 4-17. Figure 4-18 shows the viscosity of oil samples. The viscosity of 105 cSt at month 1 is approximately fresh oil level. The viscosity increases towards the high oil consumption, however the viscosity fluctuates significantly from sample to sample. There is no clear-cut explanation of this but viscosity is very sensitive to dilution so that the level of fresh oil in the sump (or sample) may contribute to such changes without significantly affetcing other analysis values.

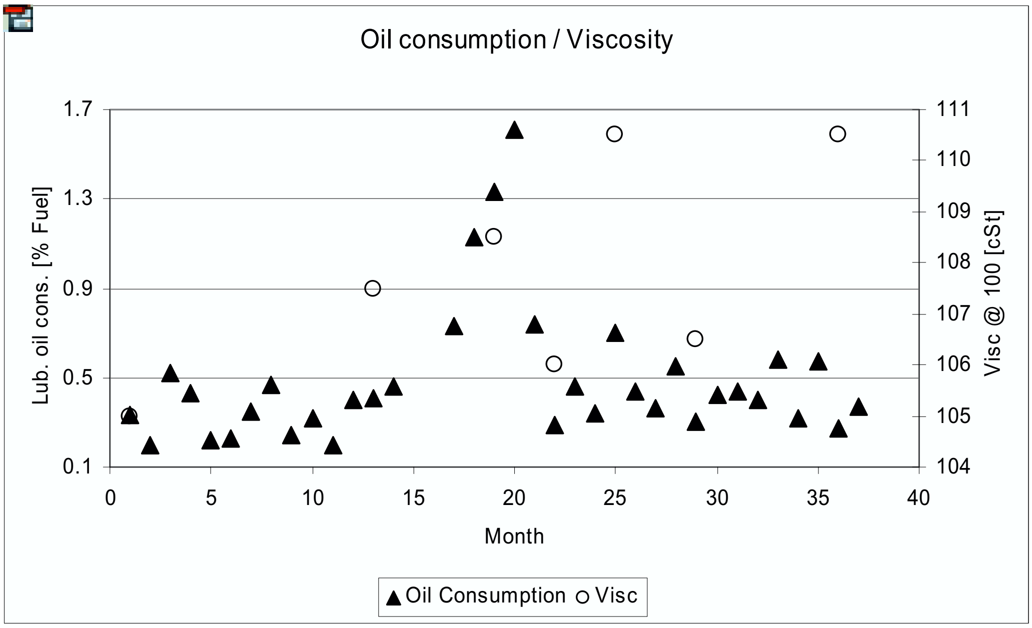


Figure 4-18 *Used oil viscosity and oil consumption*

4.2.8 Observations

Oil consumption was high and amber lacquer was seen on all visible parts of the liner at the first inspection. The intensity of the colour varied as seen in Figure 4-19. More details are presented in Figure 4-20.

Figure 4-19 *Liner at the first inspection - prior to fuel additive treatment*

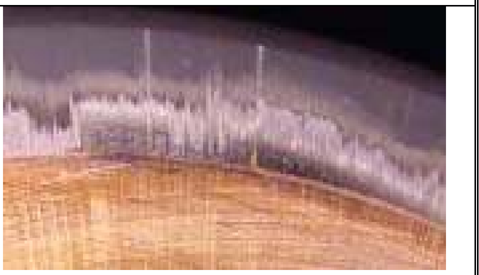
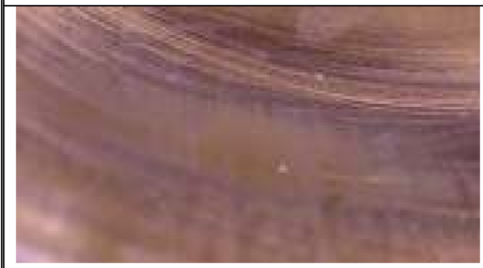
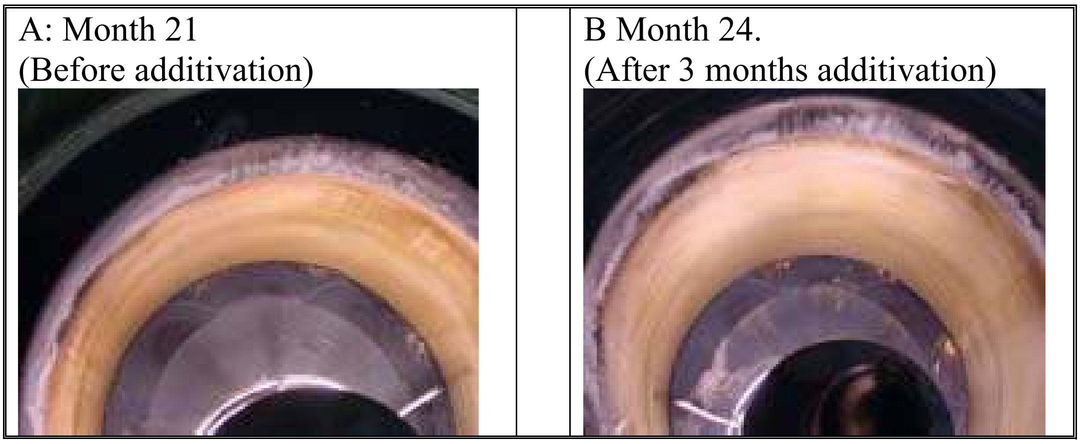
A Black soot	B Soft, grey soot
	
C Various shades of soot	D hard 'soot particles'
	
E: Polish and running lacquer.	F: Running lacquer
	

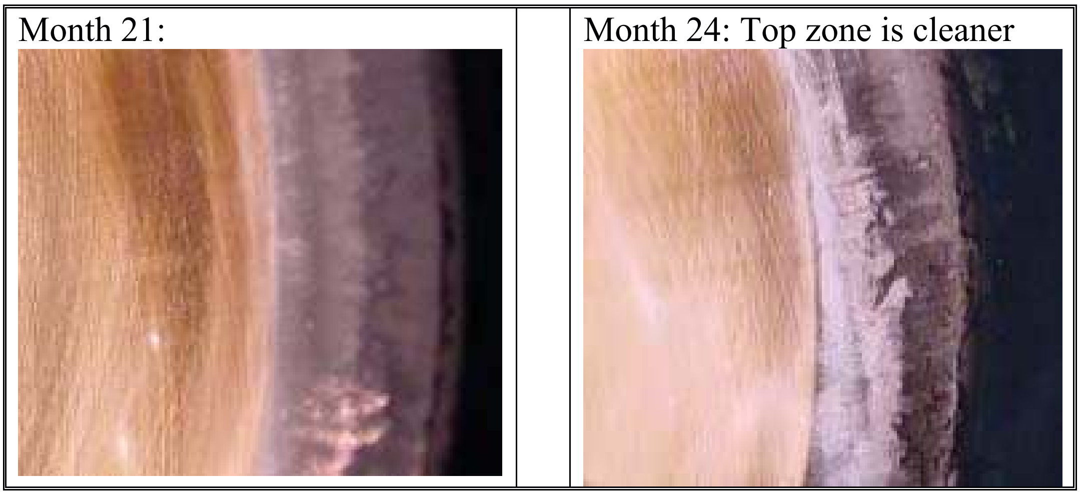
Figure 4-20 *Liner details - at the first inspection*



A: Month 21
(Before additivation)

B Month 24.
(After 3 months additivation)

Figure 4-21 *Picture of cylinder liner before and after additive treatment.*



Month 21:

Month 24: Top zone is cleaner

Figure 4-22 *Picture details from the top of the liner*

'Before' [month 21]

'After' [Month 29]

Figure 4-23 *Cylinder B5 before and after 8 months fuel additive treatment. Lacquerish deposits replace the soot above upper ring reversal.*

The close up pictures of the cylinder liner in Figure 4-20 show hard black soot as well as softer grey soot above the upper ring reversal point on the cylinder liner. There is also some wear in this zone. This wear is associated with piston top land deposits.

In some regions, the deposit looks as if it has been flowing down along the liner and solidified (Confer picture E and F in Figure 4-20). This deposit is similar to lacquer with respect to colour and solubility.

The ship was in regular service approximately three months before the cylinders were inspected a second time on December 12. The pictures in Figure 4-21 show the liner of cylinder A5 on port engine before and after approximately three months of additive treatment. The visual indications of liner lacquering were still notable although the oil consumption level had dropped to a quarter of the maximum level.

Details from the top of the liner are presented in Figure 4-22. The liner appears to be cleaner above the upper ring reversal and the darkened lacquer spot seems reduced in size. Some traces of what appeared to have been liquid deposits were found in this inspection also, but to a lesser extent than at the first inspection.

A third inspection was made in month 29 when the engine was dismantled due to classification. The engine oil consumption level had stabilised at around 0,43 % of the fuel consumption at this time. The area above the upper ring reversal was clean of soot. However lacquerish deposits were still present. No 'running' deposits were identified. A comparison of the condition of the top area is shown in Figure 4-23.

The fuel additive was used four further months. The ship bunkered every week, typically topping fuel tanks that could be up until 50% filled. When the addition of additive was stopped, some additive material was still mixed into the fuel remaining in the tanks. The effective additive treatment was therefore rapidly decreased as the additive was diluted and spent. On October 5th 2001, the ship had been running nearly a month without adding fresh fuel additive. It was estimated that the fuel additive concentration had been reduced to less than 6,25% of the previous treatment rate[2].

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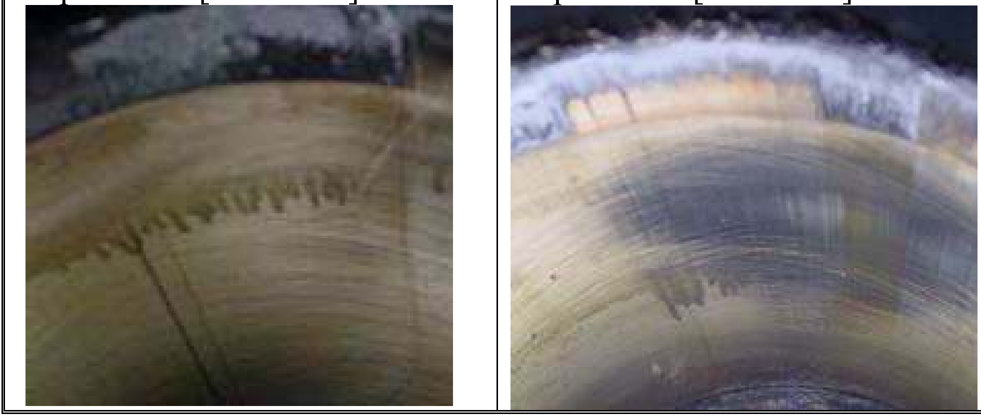
[2] Assuming complete mixing and 50% fuel remaining in all tanks; assumptions likely to over-estimate the fuel additive content.

Pictures in Figure 4-24 show that the deposits above ring reversal are returning, and also growth of lacquered spots. The average oil consumption of current and preceding month was 0.45% of the fuel consumption.

B5 during fuel additising [Month 29]

B5 shortly after fuel additising has been discontinued [Month 34]

Figure 4-24 *Return of deposits with discontinued use of fuel additives.*



Inspection 5 [Month 39]

Inspection 5 [Month 39]

Figure 4-25 *Return of solidified 'running' deposits observed after 6 months without fuel additive treatment.*

A fifth and final inspection was made after the ship had operated 6 months without use of the fuel additive.

Deposits that appear to have been fluid at one time were observed at the fifth inspection as is shown in Figure 4-25. An interesting detail in the rightmost picture in Figure 4-25 is that the deposit seems to flow out of the black deposit above the upper ring reversal. Differences in piston induced wear around the liner circumference does not appear as a good explanation of these deposits because of the irregular drop-like shape of the lower end of the amber deposit.

TABLE 4-7 CLOSE UP PICTURES OF TOP REGION

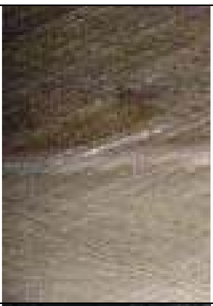
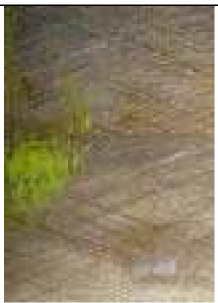
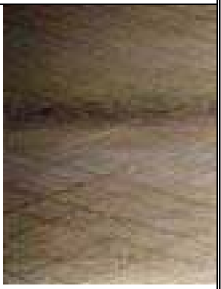
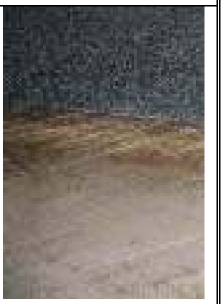
Month	Thrust side	Anti-thrust	Exhaust side	Air side
29 Additive				
39 No Additive				

TABLE 4-8. CLOSE UP PICTURES 10 CM BELOW TOP

Month	Thrust side	Anti-thrust	Exhaust side	Air side
29 Additive				
39 No Additive				

During this case study, a technique to take close-up photos of the cylinder liner was developed. Eight locations on the cylinder were identified according to the scheme discussed in the 'analytical techniques' section.
Close-up pictures illustrate the difference in cleanliness above upper ring reversal as shown in Table 4-7. These pictures also indicate a possible difference in deposit structure around the circumference of the liner. Apparently the deposit is grainier when it is not located on the thrust or the antithrust side of the piston.

A sample set taken 10 cm below the picture series in Table 4-7 is shown in Table 4-8. These images appear unaffected by additive treatment, however, the thrust side looks markedly cleaner which is probably a result of polishing wear.

The condition on the liner after 6 months without fuel additive treatment resembled what was observed prior to additive treatment (during liner deposit formation) with respect to formation of deposits above upper ring reversal and visible running deposits. The oil consumption, however, had not significantly increased and the amount of 'neutral calcium' was reduced.

4.2.9 Surface Roughness Measurements

Surface measurement data obtained from this engine did not give a consistent picture or clear trend with regards to circumferential variation; however the data were reasonably consistent when averaged around the circumference at each measurement height as shown in Figure 4-26.

Surface roughness was higher in the top than further down which is consistent with observations in other engines. The roughness measurements were initiated at a late phase in this case study, hence measurements prior to the use of the fuel additive are not available. Recall that inspection 3 was during the use of fuel additives, inspection 4 one month after the end of fuel additive treatment and inspection 5 after about 6 months without fuel additive treatment.
The average surface roughness is generally reduced in time which is believed to be a result of polishing wear which was evident in some regions and also possibly some accumulation of deposits.
Cleaning the low region with acetic acid at the end of this inspection yielded a significant increase in roughness, thus the surface roughness is

not completly resored in the lower part of the liner by the use of the fuel additive. This may also be the case in the upper part of the liner although the 'clean' surface roughness may be lower in the top; thus such a difference - if existing - is smaller in the top than furter down.

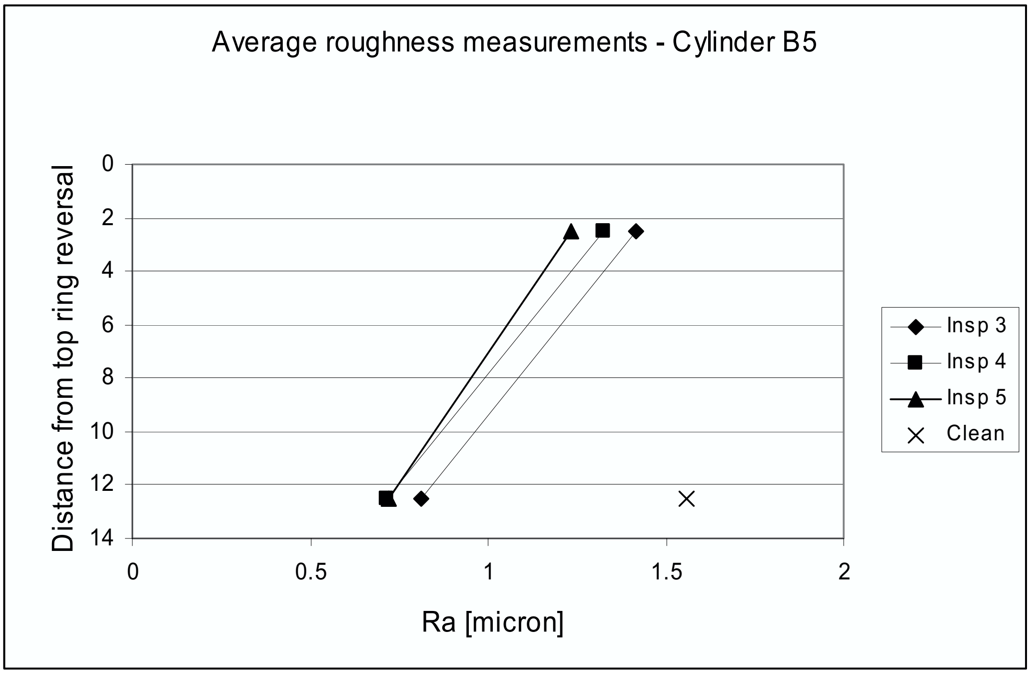


Figure 4-26 *Roughness measurements averaged around the circumference*

4.2.10 Discussion of observations

The alkalinity and amount of 'spent' calcium in the oil increased prior to the increase in oil consumption. This is believed to be a result of volatile losses that are high in relation to general oil consumption. The weed growth in the sea water cooler caused increased temperatures in the engine, which is the most likely explanation of increased volatile losses, however deviations in coolant temperatures were not detected at a until later stage than alkalinity increase.

Nevertheless, the increased temperatures on the cylinder liner combined with increased concentration in the oil of deposits constituents like 'spent' calcium and involatile material could increase the rate of deposit formation.

Pictures taken during this case study suggest that the area above top ring TDC may act as a reservoir where fuel and lubricant material may reside and oxidise before flowing down onto into the cylinder liner. If so, carbonaceous deposits in this area may increase the time the fuel or oil spends in this area, thus increasing the degree of oxidation of the material that reaches the cylinder liner.

Pictures show that the fuel additive efficently cleans the area above the upper ring reversal. This cleaning effect could extend some way down, but surface measurements show that significant liner deposits remained on the lower part of the liner during fuel additive treatment. Since oil consumption levels were stable, these low deposits may be considered 'low severity deposits' in this engine.

This case study clearly demonstrated the complexity of liner deposits formation. While the additive treatment did seem effective in removing deposit, deposits formation did not cause high oil consumption in a six month period following the end of additive treatment. Possibly, deposit formation is very slow or nonexistent in the absence of a triggering event such as of excessive weed growth.

4.3 Liner lacquer in a line fishing vessel

This case study reviews deposit formation on the cylinder liners in a fishing vessel powered by a single propulsion engine with rated brake power of 808 kW. The ship operates on a severe low load profile; typically less than 50% load nearly 80% of the time and 30% load or below nearly 65% of the time. The engines have seen recurring problems with liner lacquer, oil sooting and excessive soot in the exhaust.

During this study, the oil formulation was changed and the oil consumption was stabilised and gradually reduced. The first inspection was made in February 2001. The final was made one year later, in February 2002.

4.3.1 Background

This vessel has seen recurring problems with high oil consumption and soot at various times since it was commissioned. In February 2000, the engine was serviced. The top ring was found to be broken on all except one piston. New liners with flame rings were installed and a new piston ring configuration. The maintenance engineers made a point in their report that the intake and exhaust valves were in borderline condition but they were not overhauled at this time.

The engine was serviced again after approximately 3700 engine hours, in September 2000. The charge air cooler was cleaned and the turbocharger was overhauled. Only little lacquer deposits were reported at this time.

The engine was, however, emitting much soot and soot levels in the engine oil was high. This was temporarily rectified by the overhaul. The oil consumption was low during the first voyage following this overhaul, but then increased 4.5 times on the next voyage.

Inspection of the engine by boroscope following this voyage revealed that the oil on the liners was nearly black and the liners were dark brown, apparently covered by dark liner lacquer. The deposit could not be inspected directly as the cylinder head was not removed at this time. Oil analysis revealed that the oil contained an alarming amount of soot.

It was decided to change the lubricating oil formulation in an attempt to deal with the lacquer. Following this change, the lubricating oil consumption was stabilised and gradually reduced over a period of about one year. The average lubricating oil consumption for each voyage is shown in litre pro 24 hours in Figure 4-27. The highest oil consumption level in this figure corresponds to about 1% of the fuel which is high but considerably less than other case studies. Engine overhauls are indicated by black diamonds in this figure. The two first overhauls include cylinder rehoning and the oil consumption following these overhauls is low.

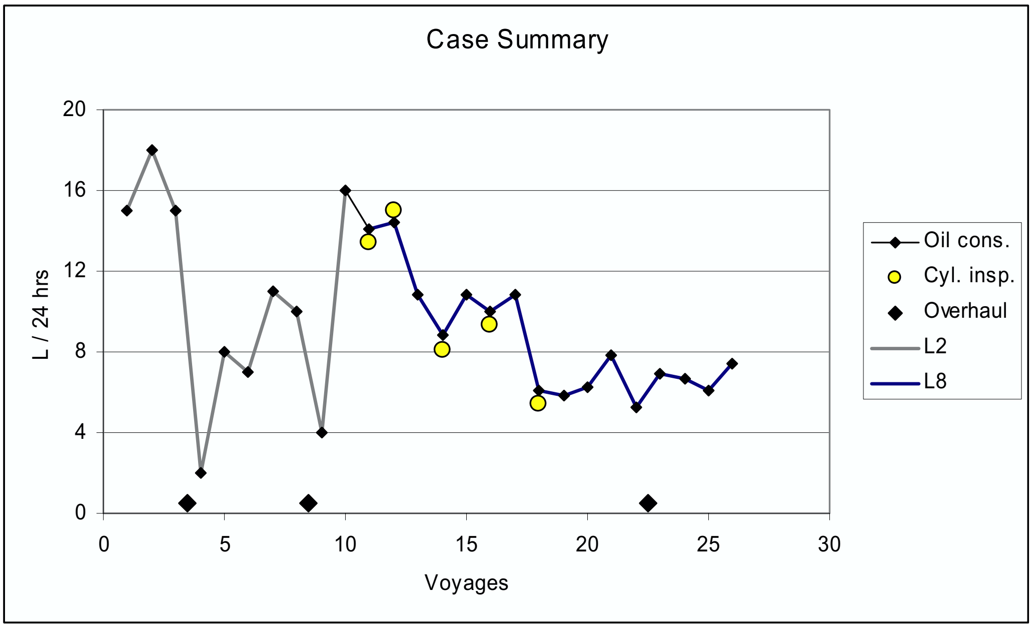


Figure 4-27 *Lubricating oil consumption and key events*

The timeline used in this case study is based upon voyages made by the vessel. The vessel makes 7 voyages a year; the length of these voyages is typically 45-50 days.

TABLE 4-9 ENGINE INSPECTIONS

Insp.	Date	Description
1	20.02.2001	After 1 voyage using oil L8
2	11.04.2001	After 2 voyages using oil L8
3	31.07.2001	After 4 voyages using oil L8
4	04.11.2001	After 6 voyages using oil L8
5	20.02.2002	After 8 voyages using oil L8

The engine has been inspected five times during this case study as shown in Table 4-9. At the fifth inspection, the engine was dismantled for routine inspection by the classification society. The valve guides were found to be worn beyond specification and changed.

4.3.2 System description

The engine has a flat combustion chamber with 'flame rings' inserted at the top of the liner. The engine is coupled to a variable pitch propeller and a generator. The generator is equipped with a hydraulic transmission permitting variations in engine speed while maintaining generator speed. The engine does not have a lubricating oil separator, but lubricating oil is filtered before it enters the engine.

4.3.3 Operating profile.

A voyage starts by transit to the fishing banks. The fish is caught by line with bait and hook. When the line is deployed the ship must move at approximately 7 knots to avoid line entanglement. When the lines are out, the speed is reduced to 1.8 knots. The ship makes occasional runs at full speed between line deployments to find optimal positions to catch the fish. The ship uses slightly more propulsion power on the return leg due to the load of the fish and also more electric cooling power. The typical 'fish hunting' loading is about 75% of MCR and line pulling load is only about 30%. Occasionally, the line is pulled when the shaft generator is not used. In this case, the load is about 17%. MCR. Pulling the line is the dominating activity occupying approximately 65% of the time, deployment of the line is second with about 14%. The ship is typically at sea 350 days a year accumulating 8400 engine hours.

Briefly summarised, the ship operates on continuos low load, less than 50% load nearly 80% of the time and only 30% load 65% of the time at sea. The very low loading of this ship emphasises that if engine load is a factor in these deposit problems, it is 'low load' rather than overload that should be addressed in this case.

4.3.4 Engine history

The engine has reportedly had occasional problems related to liner lacquer since the ship was new, however details about this are lost due to changes in crew and ownership. Broken piston rings detected during engine overhaul in February 2000 was a signal of a serious combustion zone lubrication problem characterized as a 'soot problem' by service engineers in their reports. A rapid increase in lubricating oil consumption was seen in December 2000, the cause of which is believed to be liner lacquer.

4.3.5 Survey of engine log data

Key engine operating parameters are recorded periodically at full load at sea as part of a condition monitoring programme. These data include:

- weather, ship speed and ship load which affect engine loading.
- fuel rack position and engine revolutions
- charge air temperature and pressure
- temperature and pressure of cooling water circuits
- temperature and pressure of the lubricating oil circuit
- pressure before and after lube oil filter.
- fuel oil pressure
- exhaust gas temperatures for individual cylinders and combined

An analysis of these data did not reveal any difference between the time during which the oil consumption was increasing and its decrease that can be considered significant. Data recorded at reduced load conditions revealed that the charge air pressure during line pulling is typically near zero and the exhaust temperature is around 140 °C when the hydraulic shaft generator is not operating. This condition is practically idle run and is demanding in terms of ignition quality of the fuel. Variations in exhaust gas temperature from cylinder to cylinder could exceed 50 °C suggesting unequal load distribution amongst the cylinders. When the shaft generator is engaged, the exhaust temperature is about 260 °C and cylinder by cylinder variations are about 5 degrees.

4.3.6 Used oil analysis

Oil analysis data revealed soot contamination to be a historically persistent problem. The soot level could increase dramatically from one trip to another. Several factors affect this, however, the oil filter was occasionally bypassed due to clogging without immediate replacement. These events will seriously affect soot content.

An apparent relationship between oil consumption and TBN measured at the end of a voyage is shown in Figure 4-28. The lowest oil consumption index was obtained immediately after engine overhaul. At low oil consumption the oil overall TBN index is < 1, which is normal. At high oil consumption, the TBN exceeds 1 which is suggestive of significant volatile losses in relation to oil and additive consumption

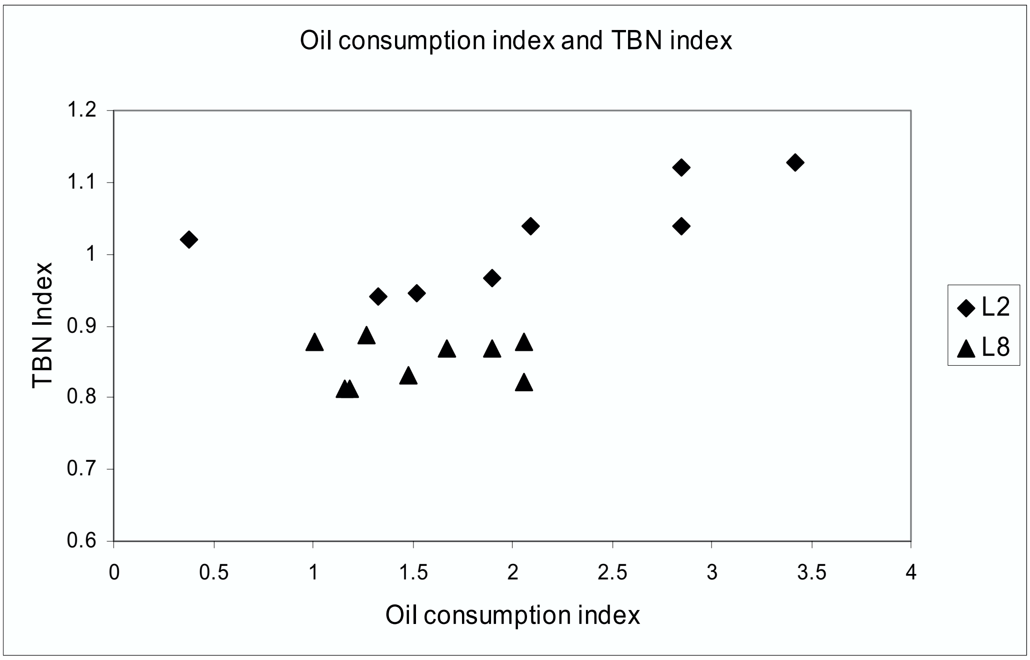


Figure 4-28 *Oil consumption index and end of voyage TBN index*

The voyage with the lowest oil consumption level has a relatively high TBN index which is probably a carryover effect from preceding months with high oil consumption since the bulk lubricant was not changed. The historic trend of TBN index and oil consumption is shown in Figure 4-29.

The concentration of additive material such as magnesium also increased with oil consumption while the level of silicone and copper did not follow this trend. The level of iron, Figure 4-30, also increases with oil consumption in case of L2 which may be explained by high volatile losses or possibly by increased wear.

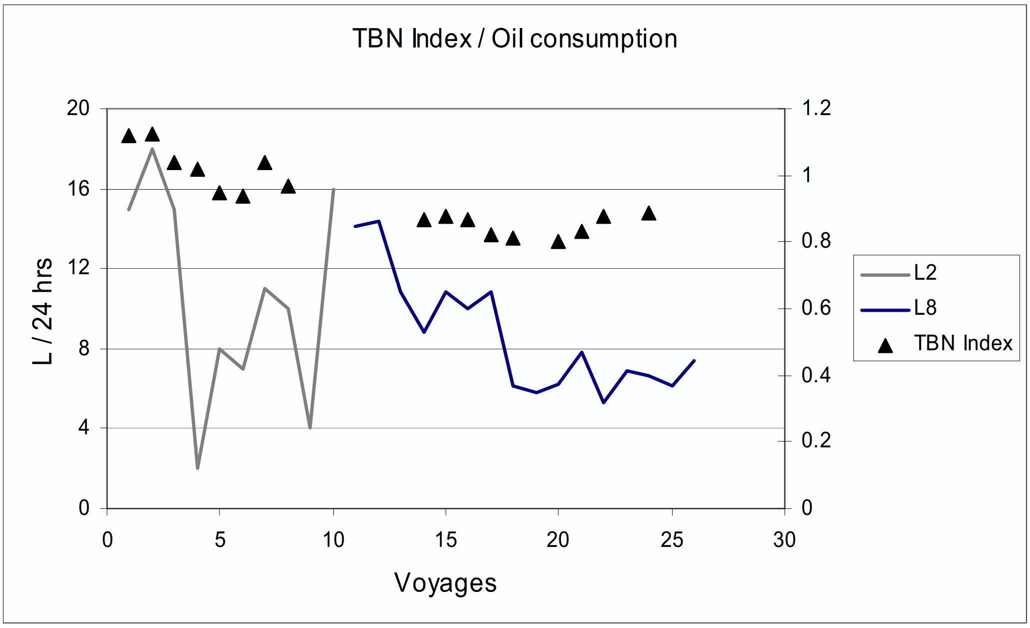


Figure 4-29 *Lubricating oil consumption and end of voyage TBN index.*

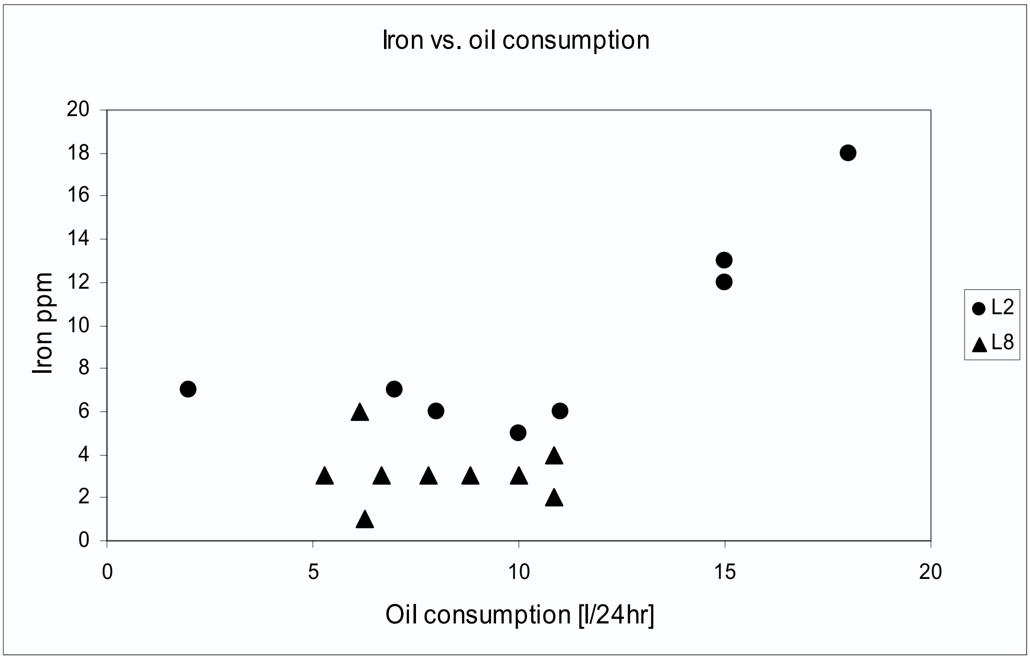


Figure 4-30 *Level of iron in used oil versus oil consumption*

The viscosity is typically high at times with high oil consumption as indicated in Figure 4-31. The highest viscosity observed with L8 is related to excessive soot content as seen by comparing Figure 4-31 and Figure 4-32.

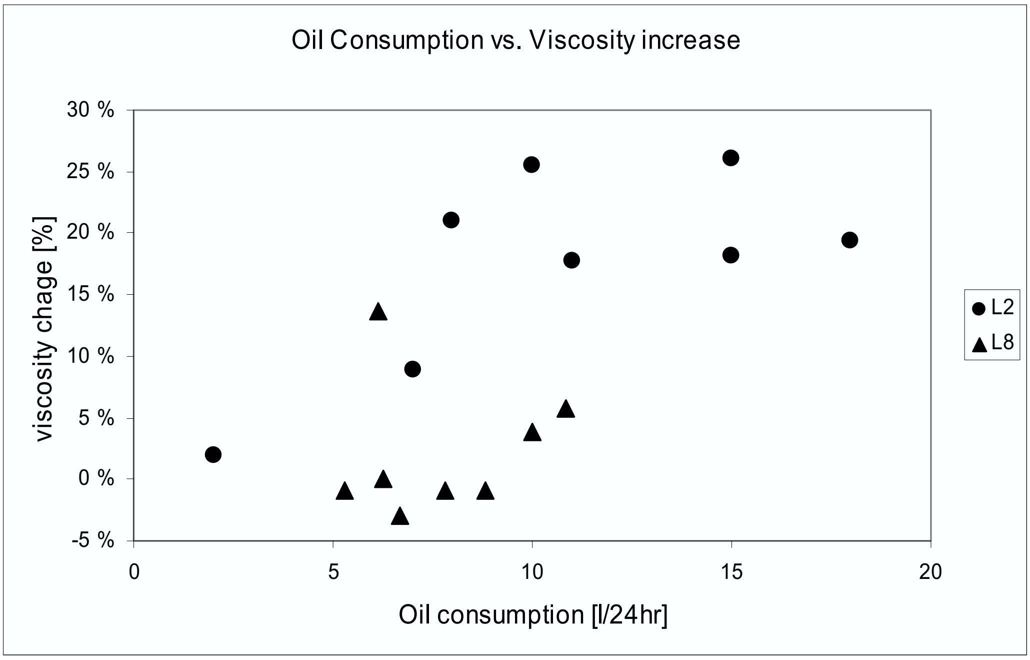


Figure 4-31 *Lube oil consumption and viscosity increase*

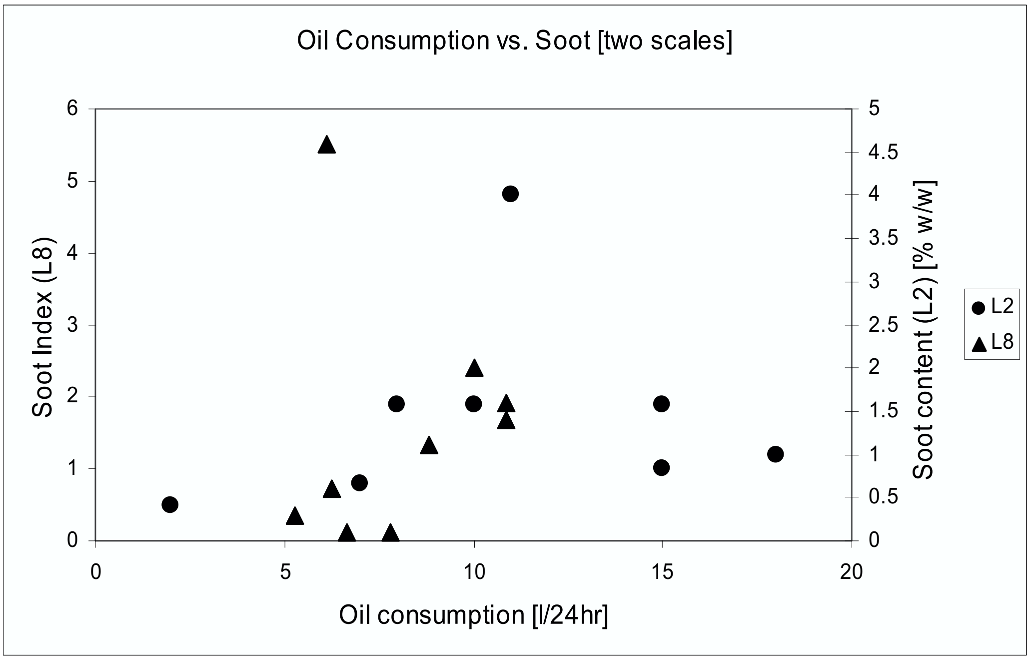


Figure 4-32 *Lube oil consumption and soot content.*

4.3.7 Fuel analysis data

Fuel samples were retrieved and analysed as part of this case study. The fuel analysis includes the fuel properties listed in Table 4-3 in the previous review of case studies.

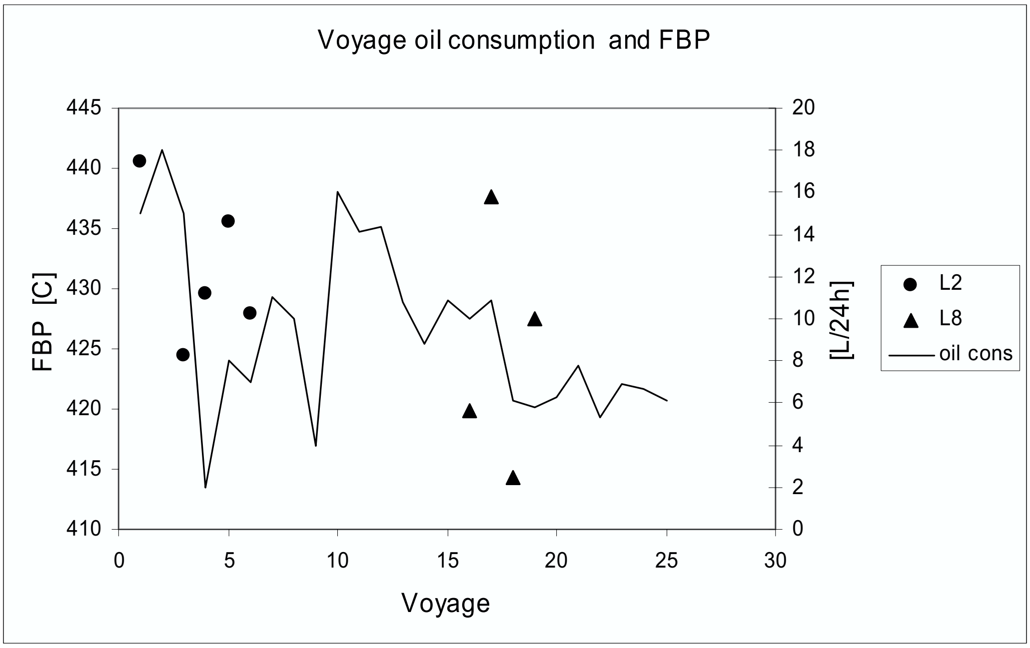


Figure 4-33 *Final boiling points [ASTM D-2887] and oil consumption by voyage*

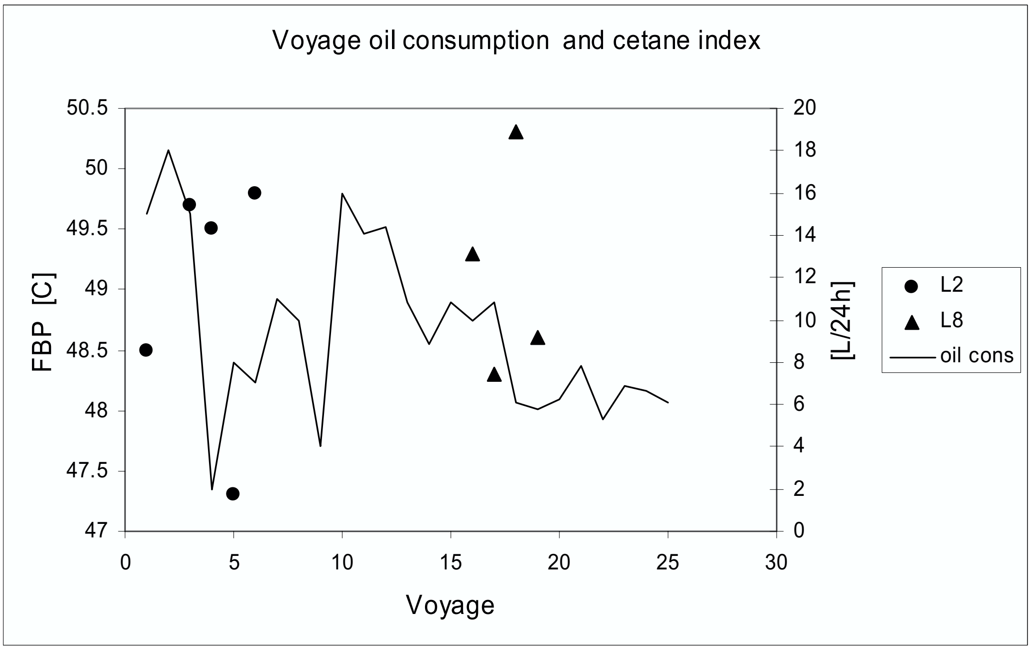


Figure 4-34 *Cetane index and oil consumption by voyage*

Figure 4-33 and Figure 4-34 show the final boiling point determined by simulated distillation and cetane index of the fuel samples in relation to oil consumption.

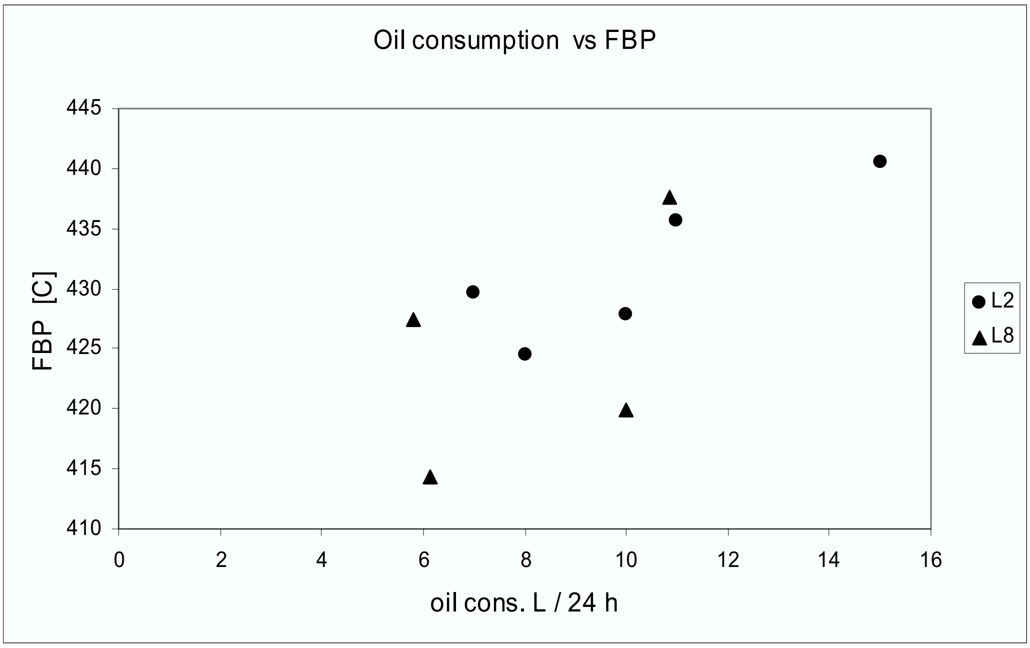


Figure 4-35 *Oil consumption, oil type and fuel FBP (ASTM D-2887)*

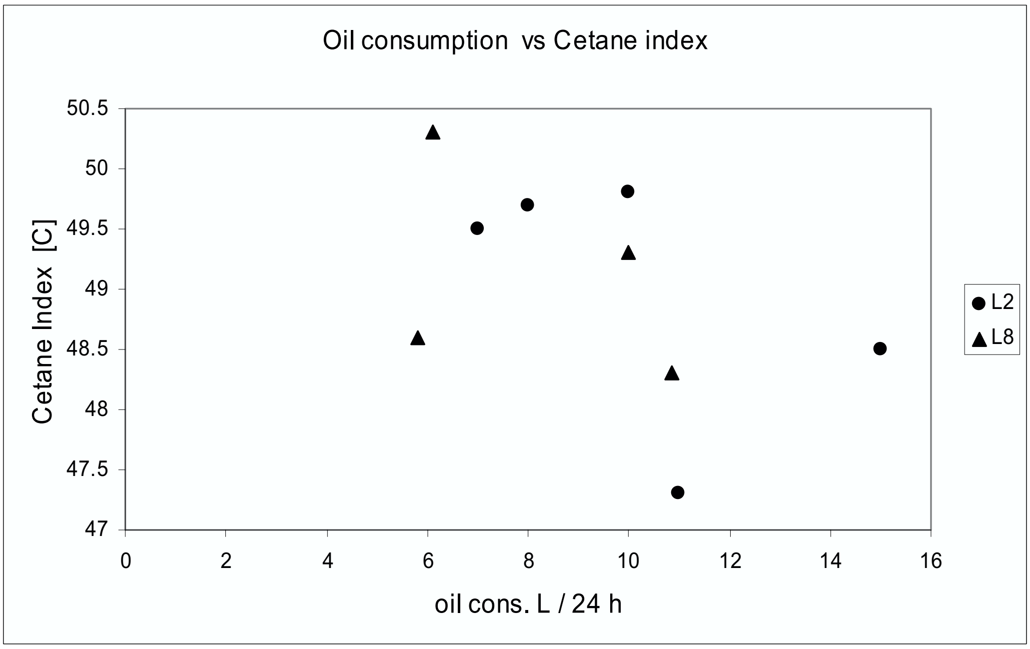


Figure 4-36 *Oil consumption and fuel cetane index*

The oil consumption and final boiling point of the fuel used in the particular voyage is shown in Figure 4-35. The fuel analysis is not extensive, however the trend is in agreement with Allen [3] in saying that high final boiling point could be considered a 'risk factor' in terms of deposits (and thus oil consumption.) Neither density nor sulphur content depicts any trend in this data. The cetane index was observed to change during a previous case study. In this case, the cetane index correlated at best weakly with oil consumption, as shown in Figure 4-36.

4.3.8 Development observed in the engine

The first inspection was made after the engine had made one voyage using L8. All liners were investigated by boroscope. The deposit level appeared similar in all the liners. Cylinder number 5 was opened for examination at each inspection.

The deposits found on the liner after the first voyage using the new oil are shown in Figure 4-37. An amber deposit is situated around the top of the liner while the lower region appears clean or grey. Circular gray spots were seen in the deposit.

Figure 4-37 *Picture of the liner at inspection one*

Close up shots were taken at two heights in four clockwise directions at each inspection. The pictures are shown in Figure 4-38 while the picture rating is shown in Table 4-10.

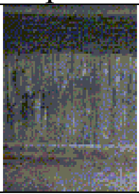
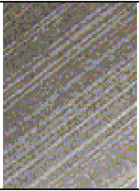
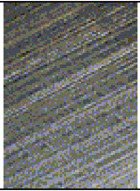
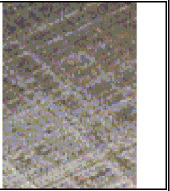
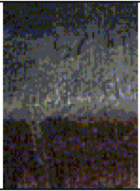
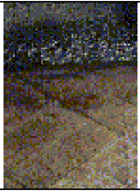
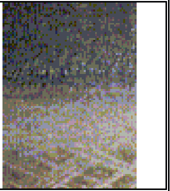
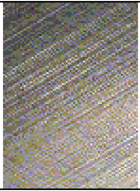
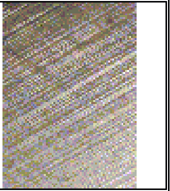
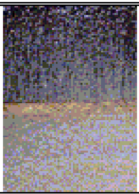
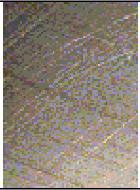
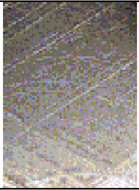
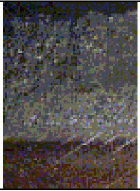
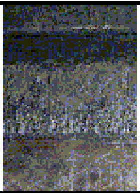
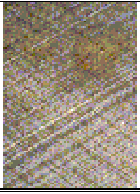
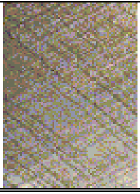
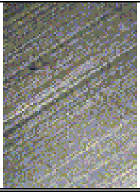
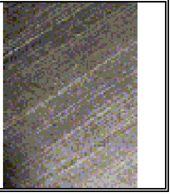
	Insp. 1	Insp. 2	Insp. 3	Insp. 4	Insp. 5
Exhaust High					
Exhaust Low					
Intake High	N/A				
Intake Low			N/A		
Thrust High					
Thrust Low					
Antithrust High					
Antithrust Low					

Figure 4-38 *Close up pictures of cylinder liner*

TABLE 4-10 PICTURE RATINGS

Exhaust	Insp.1	Insp.2	Insp.3	Insp.4	Insp.5
Flame ring				B	
High	D	D			
Low	D	D			

Intake	Insp.1	Insp.2	Insp.3	Insp.4	Insp.5
Flame ring	N/A		B	B	
High	N/A	D		D	
Low	D		N/A	D	

Thrust	Insp.1	Insp.2	Insp.3	Insp.4	Insp.5
Flame ring	B	B	B	B	B
High					D
Low					D

Anti Thrust	Insp.1	Insp.2	Insp.3	Insp.4	Insp.5
Flame ring					
High		D			D
Low	A				

Count	Insp.1	Insp.2	Insp.3	Insp.4	Insp.5
Flame ring	1	1	2	3	1
High	1	3	0	1	1
Low	2	1	0	1	2
Total	3	5	2	5	4

The photos of the cylinder liner indicate that the liner grew progressively cleaner. Pictures were rated by classifying the flame ring region bordering the top ring reversal as black (B) or grey (-). The area immediately below the flame (high) and the picture taken in the lower region (low) is rated as darkened (D) or amber (A) or clean (-).The best rating is seen at inspection 3 which followed a trip with lower oil consumption than in preceding voyages

At inspection 5, the soot above the flame ring has receded. However, oil analysis revealed a serious soot accumulation during this voyage as expressed by a soot index increase from 1.6 to 4.6 which was explained by bypassing of the oil filter towards the end of the voyage. The engine was dismantled at this time by routine order of the classification society and the oil charge changed due to soot contamination.

4.3.9 About the effect of the lubricating oil

It is impossible to truly determine to what extent the change in oil formulation is responsible for the reduced oil consumption in this case study.

Apart from routine cleaning of the oil and water cooler, which did not affect engine coolant temperatures, the change of lubricant was the only controlled change prior to the gradual decrease in oil consumption. Fuel analysis did, however, reveal subtle variations in fuel quality

Some differences between the oil formulations is shown in

Table 4-11. There may be other significant differences in performance and chemistry.

TABLE 4-11 KEY OIL DATA

Parameter		L2	L8
TBN	[mg KOH/ mg]	15	10.6
Ash	[% weight]	2.1	1.3
Volatility [Noack]	[%]	5.6	5.0
Viscosity @ 100≠€	[mm2/s]	5.6	5.5

The difference in volatility may contribute to the oil consumption being lower using L8. L2 has a higher additive treat rate, which was indicated as detrimental in terms of liner deposits formation in the experiments of [8]. Hypothetically, the lower overall volatility and additive treat rate of oil L8 could result in a lower concentration of involatile and potentially reactive material on the liner, which could alleviate deposit formation.

4.3.10 Surface Roughness Measurements.

Trip by trip variation in surface roughness was not significant, but measurements revealed significant variation in roughness around the circumference. The average roughness was lower in the top region than below which is in fact the opposite of what has been observed in other cases where significant deposits have been detected in the lower liner region.

Cleaning the liner with acetic acid made a significant visual impact. Attempts to measure deposits by measuring surface roughness prior to and after cleaning with acetic acid were unsuccessful in detecting significant changes. It is unclear if this was due to an inability of the acetic acid to remove deposits, of if there simply were no deposits to remove in these particular locations.

4.3.11 Discussion

This case study is valuable as an example of liner lacquer in an engine with very low average and maximum engine loading. The deposits investigated in this case cannot reasonably be attributed to engine overload.

The fuel and lubricating oil analysis is naturally inconclusive; however claims that high fuel FBP is detrimental and low TBN / SA / volatility is beneficial with regards to oil consumption are in agreement with observations in this case study.

The increase in alkalinity during high oil consumption suggests that the volatile losses are high compared to other oil losses.

4.4 Bore glaze formation in an offshore supply vessel

This case study discusses observations of bore glaze deposits in a twin engine offshore supply vessel. In this study, a fuel additive was used to counteract the lacquering and experiments were made with the honing of the cylinder liners. It was observed that deposits continued to accumulate in spite of fuel additive treatment although the fuel additive seemed to have a cleaning effect on the upper part of the cylinder liner.
Cylinder liners that were retrieved from this engine provided the material for investigation chemical composition and distribution of 'bore glaze' deposits discussed in the liner deposit section of this thesis.

4.4.1 Background

The case ship is reported to have had problems with lacquer since its delivery, but detailed information of this is not available. The case study was initiated in April 2002. At this time, the oil consumption level on one engine was 4.7% of the fuel consumption which is almost 10 times normal consumption. The condition in the other engine was better, the oil consumption level was only 5 times the normal, however this engine had been overhauled only 10 months earlier. The development of the oil consumption and key events in this case study are shown in Figure 4-39.

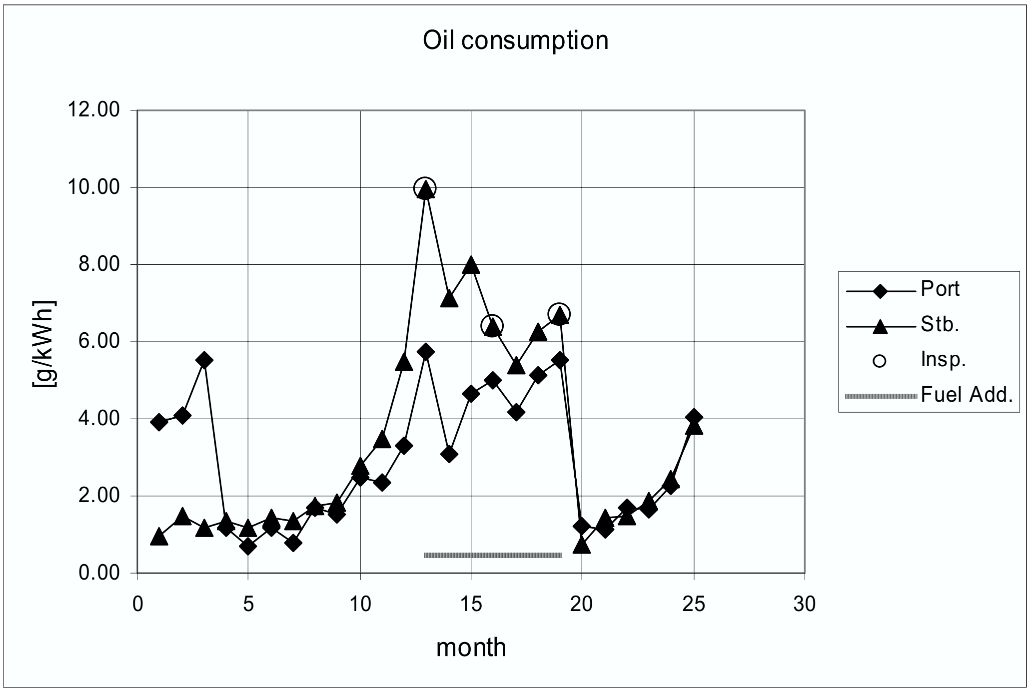


Figure 4-39 *Oil consumption development and summary of events.*

The first inspection of this ship was made at month 13 in the timeline in Figure 4-39. A fuel additive treatment was started at this time and two liners in each engine were replaced. The fuel additive was the combination of combustion catalyst and detergent functionalities as described in [97]. The inspections made in this case study are summarized in Table 4-9.

At inspection three, the oil consumption level had increased in consecutive months. A docking opportunity arose and it was decided to discontinue the fuel additive treatment and all cylinders apart from the reference cylinders were overhauled. The oil consumption following the overhaul was initially low, but increased; hence this situation has not been resolved.

TABLE 4-12 ENGINE INSPECTIONS

Insp.	Date	Description
1	07.04.2002	Start of fuel additive treatment, installation of test liners
2	12.07.2002	After ~1500 hours using fuel additive and test liners
3	04.10.2002	After ~3000 hours using fuel additive and test liners

4.4.2 System description

This oilfield supply vessel is about 67 meters long and has displacement of approximately 5000 ton. Main propulsion is provided by two 9 cylinder engines delivering 2005 kW brake power at 825 rpm. The engine has a piston bowl type combustion chamber. 'Flame rings' are inserted at the top of the liner. The engines are coupled to a variable pitch propellers and shaft generators. The stroke / bore ratio of this engine is 1.2

4.4.3 Operating profile.

The vessel operates in a repeating pattern, each voyage lasting about one third of a week. A voyage starts by transit to the oilfields which may last about 12 hours depending upon the platform served. In transit, the ship is running at service speed which corresponds to engine loading of 80-90% MCR. The ship typically spends the greater fraction of the time at sea in standby waiting on demand and suitable weather to service the oil rigs. In waiting condition, the engine load is very low. However, the use of a shaft generator ensures that the load on one engine is higher than the other. The port and starboard shaft generator are used alternately so that the long term average load is equally distributed amongst the engines. The dynamic positioning system and other equipment used when the oil rig is serviced, ensure a higher load on both engines in this mode of operation.

4.4.4 Engine operating parameters

Engineers routinely record engine operating data every month to assess the engine condition. These data include:

- cylinder maximum pressure, exhaust temperature and fuel rack position
- turbocharger pressure and charge air temperature
- cylinder cooling water pressure, inlet and outlet temperature
- lubricant temperature and pressure and fuel inlet pressure
- draft, trim and weather data

A review of these data did not reveal any change that could be associated with the increase in oil consumption

4.4.5 Used Oil Analysis

Chemical analysis of the bore glaze deposit from this engine revealed that it contained soot. The exhaust soot emission from this engine is excessive, probably due to the high oil consumption. The soot levels in the used oil is, however, low and does not appear affected by the high oil consumption. Oil viscosity and dispersing power varied between samples, but was within normal levels.

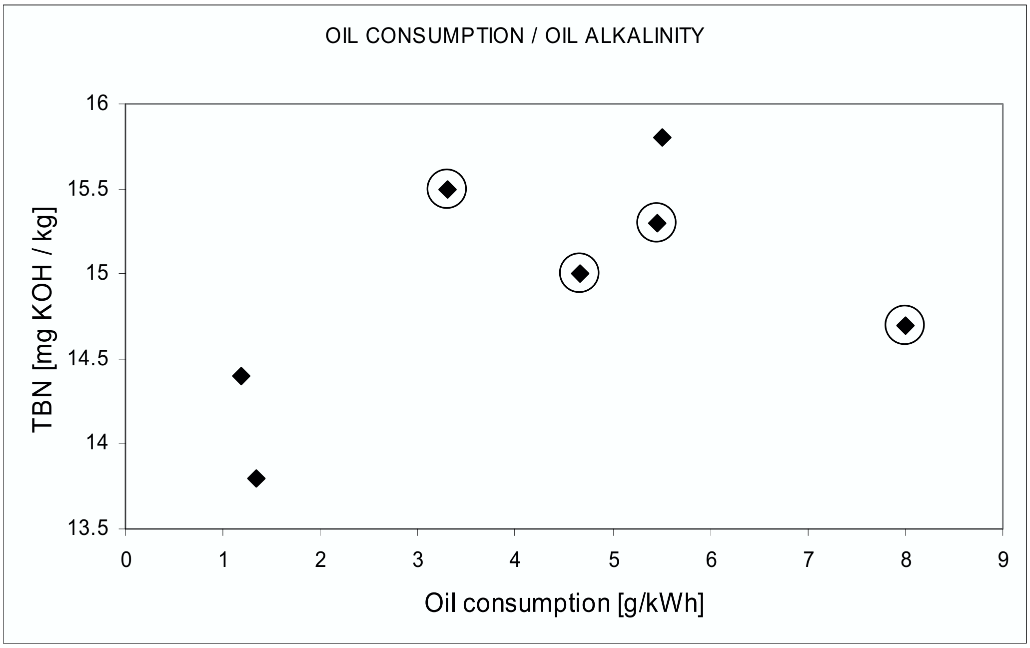


Figure 4-40 *Specific lubrication oil consumption and used oil TBN. Circled data points imply that fuel additive is used.*

Used oil analysis did, however, reveal the typical tendency towards high alkalinity with high oil consumption as seen in Figure 4-40. In some instances, oil alkalinity exceeded the new oil level of 15; however, oil alkalinity was not maximized when oil consumption is maximized. The alkalinity at maximum oil consumption is slightly below the nominal level of 15; hence additive depletion is a stronger effect than volatility at this time. The lubricant used, L4, has a relatively high TBN / SA ratio which indicates that in contains significant alkaline material that is not in the form of overbased detergent and which may be more readily volatilized or otherwise depleted compared to other lubricants that are more prone to TBN increase.

4.4.6 Cylinder liner appearance

The cylinder liner looked almost clean at all inspections which is characteristic of bore glaze. A photomontage to illustrate a typical glazed liner is shown in Figure 41.

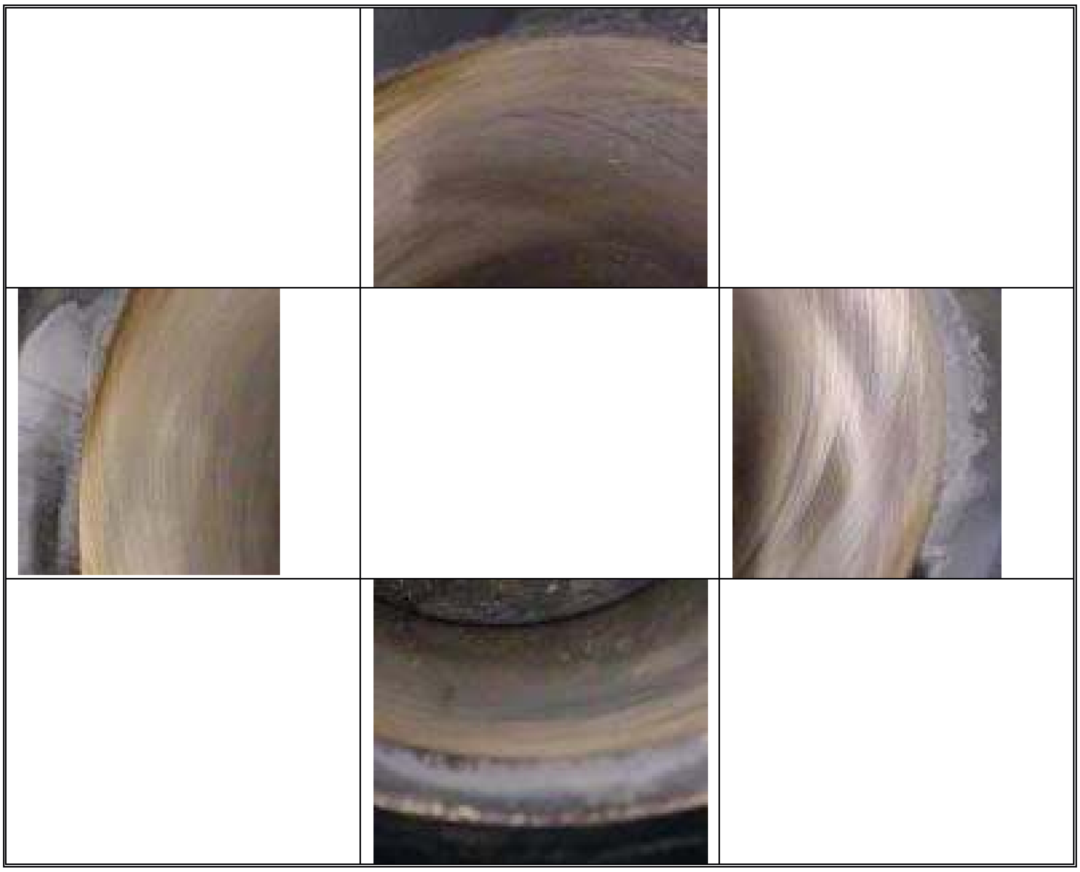
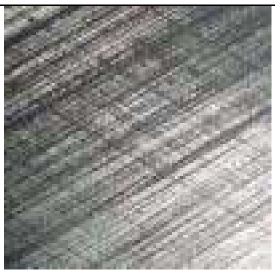
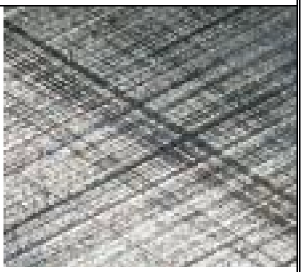
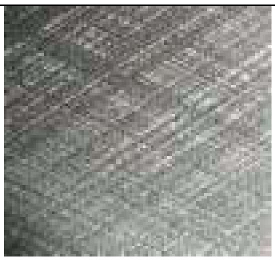
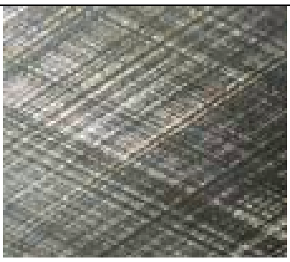


Figure 41 *Photomontage illustrating the 'clean look' of the cylinder liner but also the amber traces in the upper liner region.*

A set of sample close-up photographs are provided in table 4-13. Picture ratings based upon such close-ups reveal that 29% of the 72 pictures taken in the top region appear clean, while 90% look clean in the center and low picture region. The majority of the non-clean pictures in the top region were classified as amber. In a previous case study, the fuel additive was seen to have a large impact on the area above upper ring reversal. Such difference was not obvious in photos from this case study. Surface measurements, however, gave valuable insights on fuel additive effects as discussed below.

TABLE 4-13. SAMPLE CLOSE UP PHOTOGRAPHS. STB 6, DIR. 3

	Insp. 1	**Insp. 2**	**Insp.2**
High			
Mid			
Low			

4.4.7 Effect of using a fuel additive

As already mentioned, a combined combustion catalyst and detergent fuel additive was mixed into the fuel at the start of month 14 of this test. At the same time, two of nine cylinder liners on each engine were replaced with new test liners. Since the oil consumption is related to liner deposits, the introduction of clean liners is expected to cause a reduction in oil consumption.
The development of the oil consumption is shown in Figure 4-39. The oil consumption dropped immediately following the start of fuel additive treatment and change on liners in month 14, however the oil consumption level appears to converge towards a level between 2.5 to 3 % of the fuel consumption towards the end of the fuel additive test although the long term effect of this additive is unclear.

A prediction of the effect of introducing clean liners into the engine can be estimated assuming that:

- the oil consumption is not increasing but remains stable at 2.7% and 4.7% of the fuel oil consumption, and that
- the 4 new liners each have an individual oil consumption contribution of 0.5% of the fuel which is the normal level in Figure 4-39.

The prediction is made by weighted average being:

(2.7%*7/9 + 0,5%*2/9)= 2.2% for port engine and
(4.7%*7/9 + 0,5%*2/9)= 3.8% for starboard engine.

The oil consumption drops below these predictions, hence the fuel additive is probably having an effect on oil consumption. Since the trend with rapidly increasing oil consumption rate in both engines is reversed, the effect can be considered larger than the difference between predicted and observed oil consumption level.

The condition in two reference cylinders was monitored by surface measurements and photography during this investigation. Detailed investigation of several cylinder liners reviewed in the 'deposit distribution' chapter revealed that the roughness did not much depend upon the circumference in this engine. Hence the surface roughness data can be averaged around the circumference of the liner as shown in Figure 4-42.

The average surface roughness increases with time in the top two measurement locations while the surface roughness decreases in the lowest measurement location. This is interpreted as a reduction in the deposit level in the top two locations and an increase in deposit in the lower region. Physically, the detergent additive appears to clean the top of the cylinder liner but not further down. The cleaning in the high region appears rapid while the growth in the low region appears slower.

It is not clear why the additive is most efficient in the top region; however proximity to the point of fuel injection is one possible factor. The decreasing ring back pressure and increasing oil film thickness as the piston descends could reduce the efficiency of mechanical removal of deposits. It is also possible that deposit material removed from the top region is accumulating in the lower region.

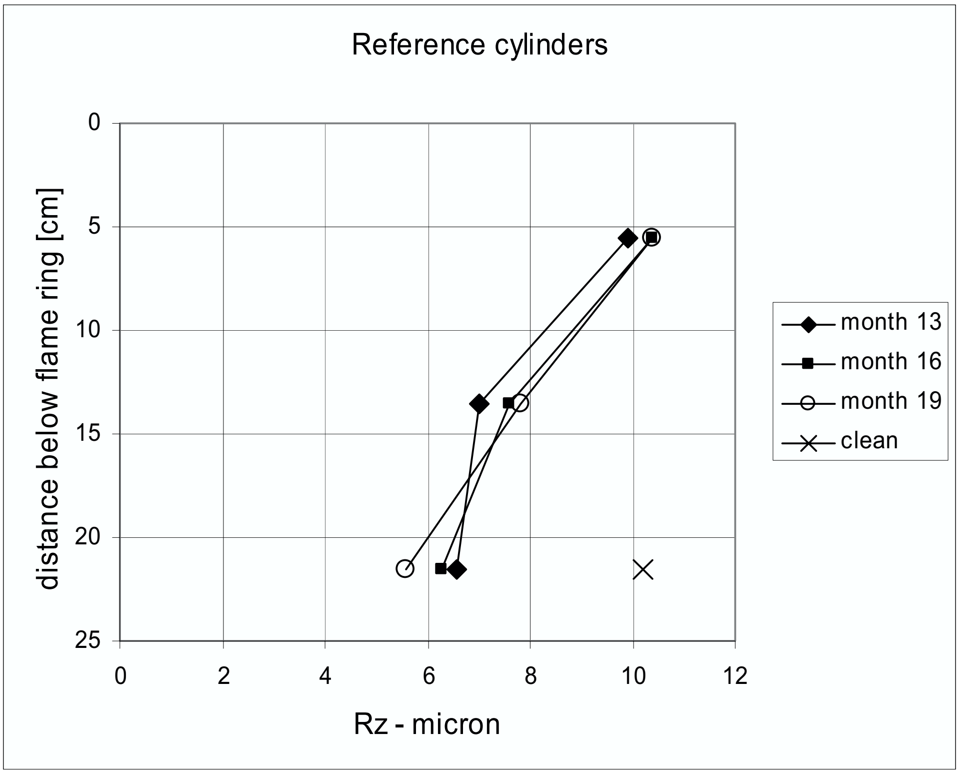


Figure 4-42 *Development of surface roughness with fuel additive treatment.*

Four cylinder liners were replaced as part of this case study. These cylinder liners were manufactured with two different surface finishes. Surface finish A is an advanced plateau finish, while surface B is a single stage honing. One cylinder liner of each surface type was inserted into each engine.

The change in roughness as time progressed is shown in Figure 4-43 and Figure 4-44. These figures clearly show that the surface roughness is reduced in the lower region as time passes.

The attempt to recover the surface roughness by cleaning is only partially effective in case of surface pattern A. It seems likely that the failure to recover initial surface roughness of surface A is a result of ineffective cleaning. If this is true, the reduction in roughness compared to the initial value is caused by deposits. Otherwise, if these measurements were interpreted as a true, permanent change in surface properties, severe wear must have been present, which seems less likely since the presence of deposits in this region is well documented on other liners from this engine while we have previously not witnessed severe wear in this region.

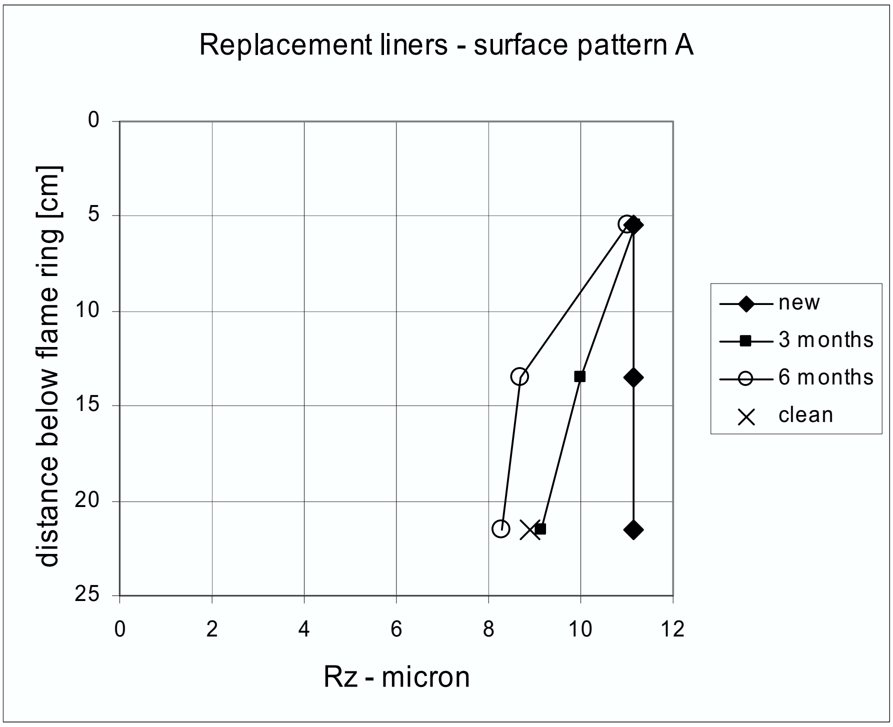


Figure 4-43 *Development of surface roughness on replacement liners type A*

In case of surface pattern B, a uniform reduction in surface roughness was recorded after three months which is considered to be running in wear. After six months, the roughness is lower in the lower part of the liner, and cleaning restores the surface to the level observed three months earlier. This is indicative that the change during the latter three months of this test is caused by deposits. The curve is roughly linear at this time which is similar to what is observed in the first three months using the plateau honed surface A. It thus seems that the development using surface patterns A and B is similar in these engines after a delay caused by running-in.

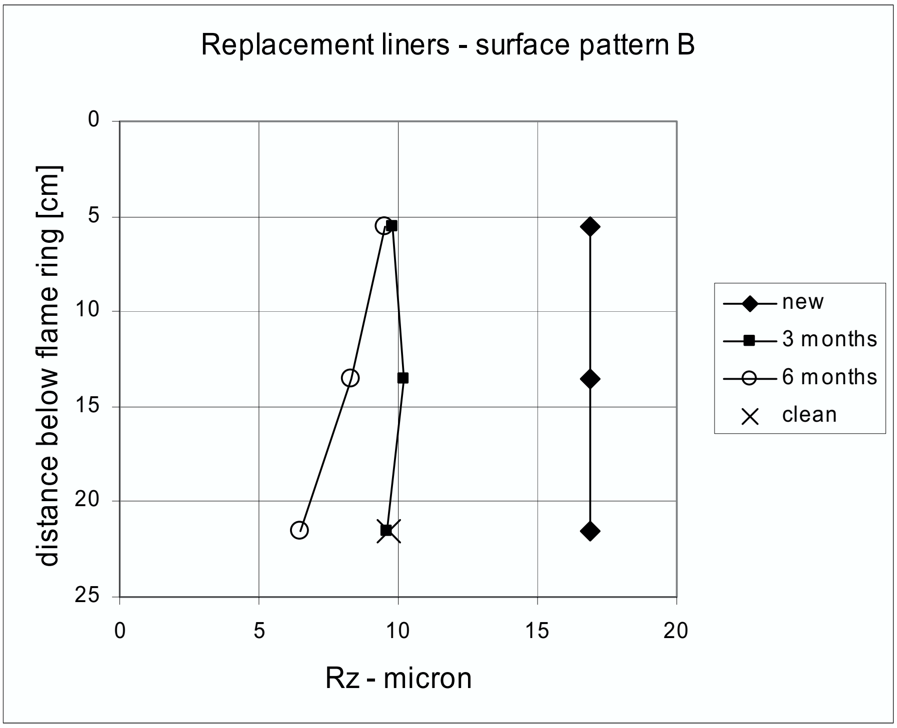


Figure 4-44 *Development of surface roughness on replacement liners type B*

The reduction on R_z during the three month intervals is an expression of deposit growth rate although the change in R_z does not necessarily relate to deposit volume. In the case of surface A, it is initially fastest in the lowest part of the cylinder liner. However, the growth in the centre point catches up as time passes. Due to the influence of the fuel additive, it is not possible to generalize this observation; however the shape of the 6 month deposit curve with surface A is remarkably similar to the shape of the reference cylinders at the start of this experiment. It is thus quite possible that the glaze accumulation starts in the low region of the liner.

4.4.8 Discussion

The bore glaze distribution in an engine with fuel treatment did not appear significantly different in plateau honed cylinder liners compared to a rougher finish, although deposit formation seemed to be delayed by the running-in process.

The effect of the fuel additive treatment in this pair of engines seems to be the removal of deposit from the top region of the cylinder liner but not suppression of deposits formation.

Chapter 5

Experimental work

The experiments presented in this thesis are mainly attempts to replicate deposit formation according to different hypotheses under controlled laboratory conditions. Principally, a better approach would be to design experiments that could disprove these hypotheses; however no such experiments were envisioned. Instead, these experiments attempt to assess the potential that different mechanisms (or hypotheses) have for forming relevant deposits.

As seen in Table 5-1, four unsuccessful approaches were made to synthetic deposits formation before a deposit with relevance was formed. Some of these investigations were made at a time where authentic samples of liner deposits had not been obtained and analysed and our impression of liner deposits was based on information from literature. It is not difficult to understand why some of these attempts were unsuccessful when seen in the light of later experience and information on deposit composition. However, this is but the thorny path to wisdom as described by Danish scientist, genius and poet Piet Hein:

The road to wisdom? - Well, it's plain and simple to express:
Err and err and err again - but less and less and less.

At least, our changing idea of what deposits are show that we have learned something - albeit not necessarily from the experiments reviewed in this chapter.

5.1 Review of experimental work

A short review of experimental investigations is given in Table 5-1. The fifth approach resulted in the formation of relevant deposits. To keep this thesis as short and to point as possible, only a short review of the first four approaches is given here, more details are located in the appendix.

TABLE 5-1 EXPERIMENTAL WORK

No.	Equipment	Idea / Hypothesis	Outcome
1	High Pressure oxidation apparatus	Create resinous hydrocarbon matrix binding inorganic lubricant additives.	Hydrocarbon content of deposits invariably too high.
2	Chemistry laboratory	Investigate highly concentrated colloidal detergent additive	Differs in solubility and strength
3	Chemistry laboratory	Repeat experiment published in patent application to synthesize liner lacquer	'Deposit' in this test is oxidized metal, unsuitable as a model deposit.
4	KR3 Test engine	Copy alleged 'case' deposit formation by using special fuel and contaminated lubricant	No deposits formed within 100 hours.
5	Inclined plane deposit rig	Oil flow over a hot thin film oxidation test area to selectively accumulate material	Deposits with similar appearance, solubility and surface smoothing were formed

5.1.1 High pressure oxidation tests

These experiments involved exposing a thin stationary oil film on a metal surface to elevated air pressure and temperature. Experiments resulted in the transformation of the bulk lubricant into an amber varnish consisting primarily of oxidized hydrocarbon. The fraction of inorganic material in this deposit had to be low because it is initially low and can only increase in this test as a result of volatile losses. The weight loss during tests was low and the elevated pressure in this test counteracts volatile losses and may act to increase formation of organic deposit material. The high content of oxidized hydrocarbon was also evident from IR spectroscopic investigation of deposits. The original intent of this test was to expose the oil film to combustion as described by Zepter [98], however this approach was not explored as the introduction of more hydrocarbon into the test volume was not believed to increase the ratio of inorganic material. While thin film oxidation alone might have relevance to liner deposits formation, the formation of such deposits is well documented in the literature, and a different approach was favoured. More detail on these experiments and results is given in appendix A2.

5.1.2 Highly concentrated colloidal additives

Liner deposits have been reported to contain significant calcium carbonate. This material originates in detergent lubricant additive. Micellar additive material can be extracted using the approach described in [99] which involves diluting the original solvent to reduce solubility and subsequently centrifuging the sample. It was observed that concentrated 'overbased' detergent share similarities with liner lacquer, however it does not alone possess the strength nor the resistance to selected solvents that is associated with liner lacquer. In order to gain these properties, it must somehow be bonded, strengthened or transformed. More details are given in appendix A3

5.1.3 Repeat experiment to create model deposit

The formation of a synthetic liner lacquer is described in a patent application [13]. The deposit in question is formed by dissolving anthraquinone in warm (65°C) acetic acid to form a saturated solution which is pipetted onto a warm (60°C) steel dish where the acetic acid is evaporated to leave a brown-orange lacquer [13]. This synthetic deposit obviously does not contain residues from lubricating oil additives; however it is intended to model a 'deposit binder'. The metal surface attained the brown-orange color as expected in the repeat test, however a control test using pure acetic acid and no anthraquinone attained the same color. The 'deposit' seen in this test is believed to be oxidation of the metal which is accelerated by the acetic acid. This approach to synthesize liner deposits was not investigated further. More detail is provided in appendix A4.

5.1.4 KR3 engine test

Liner deposits generally accumulate very slowly; it is thus time consuming and also expensive to research their formation in engines. Liner deposits have been formed in accelerated engine tests [8] where the engine design has been modified. This approach was not copied partly because it would be unclear if the test replicated the mechanisms that dominate 'in field' since this test concluded that continuous high was critical while low load dominates in our case studies.

Since the conditions under which deposits are formed are not really known, the logical approach would be to design a test matrix where principal test parameters were varied. This, however, had to be prioritized against limited resources and viewed in the light that these results might only be applicable to this engine design. To some extent, this type of information can also be obtained from case studies.

Reliable oral reports mentioned that liner deposits did at one time form very rapidly in an engine similar to this test engine. In this case, the lubricant had been contaminated with fuel and the fuel was of exceptional poor quality. Unfortunately, details were not well documented and this case is hence not discussed in the case studies section which is based entirely on first hand experience or extensive written documentation. It did, however, provide the inspiration for a test that combined the necessary potential for rapid deposit formation and realism.

No details on fuel composition, extent of lubricant dilution or engine loading was available nor was it certain that the fuel composition or lubricant dilution was the prime cause of deposits. Again, a test matrix of fuels and dilutions was considered, however extended test duration was prioritized. The test might thus be considered more like a shot in the dark than a careful scientific approach; however the reasoning was that if this approach had merit to justify further tests at least some trace of deposits would form within 100 test hours with cyclic variable load.

It turned out that it no deposit was formed and further exploration of this approach was not prioritized. New honed liners were used in this test. A later case study revealed that deposits did not accumulate during running in, hence the use of new liners may have negatively affected the outcome of this test. Details of the test are given in appendix A5.

5.2 Inclined liner surface rig

The experience with the high-pressure rig, field observations as well as the literature study resulted in the interest in a test apparatus to study the formation of deposits as a result of a possible selective accumulation within honing grooves. The following criteria were set for this new test

- oil flow through a test area to allow selective accumulation
- authentic surface finish of test specimens
- piston ring movement to distribute the oil film
- groove filling by deposits is used as a principal test parameter.

An apparatus that fulfilled these requirements was developed as described below.

5.2.1 Test principle

The test rig and principles of operation is shown in Figure 5-1. The inclination of the plate is exaggerated in the figure; in reality the plane is inclined about 10 degrees. The figure shows two modes of operation. To the left, oil circulates from a heated sump, to the right, fresh oil is supplied.

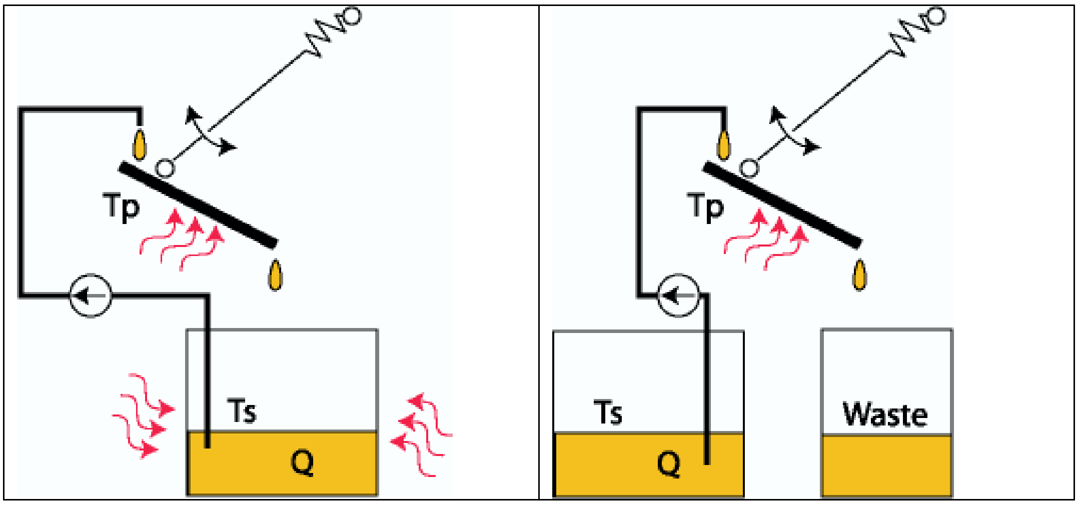


Figure 5-1 Inclined Plane Coker principle. Test with oil sump shown left

The temperature of the test plate is controlled by a thermocouple inserted into the hot surface immediately below the test plate. The thermocouple is connected to a PID regulator that governs the power supply to electric heat elements by an on/off switch. The purpose of the piston ring mechanism is to distribute the oil and to assist flow. The contact pressure, which is adjusted by spring force, is kept low in order to avoid wear of the test plate. A modified test rig was made at a later stage. The piston ring was mounted on a wagon in the modified rig which enabled constant contact geometry between the test plate and the piston ring, significantly altering the oil flow.

5.2.2 Test Rig Details

Oil supply is provided by silicone tubing and a VWR 'mini pump' peristaltic pump. The flow is regulated by a combination of pump speed controlled by the voltage supplied to the DC motor and the effective diameter of the tube on the pump head. Power is supplied to the pump motor by an EA 0316 laboratory power source which proved more reliable than the built in potentiometer. A Fluke 87 digital multimeter is used to monitor the voltage in the circuit as it is easier to read than the analogue voltage display of the EA 0316.

TABLE 5-2 CONTROLLABLE TEST PARAMETERS

Oil sump temperature (if applicable)	T_s	[€]
sump volume (if applicable)	V_s	[ml]
Plate heater set temperature	T_{set}	[€]
test plate core temperature	T_P	[€]
ring pressure	F	[N]
oil flow	Q	[ml/h]
test duration	t	[h]

The oil supply is calibrated for each test. In long tests, the flow is measured before and after the test to monitor drift. Flow is calibrated by volume or, in later tests, by weight which proved more convenient and accurate. A summary of the controllable parameters in this test is shown in Table 5-2. Some pictures of the test rigs is shown in Appendix 8

2.5.2.1 Test plates and measurements

The use of cylinder liners with authentic surface finish permits direct measurements of deposit formation within the honing grooves. The surface measurements used to characterize the deposit have a certain inherent randomness due to the random nature of the micro surface and microscale variations in the placement of the instrument. This problem is limited by making a number of measurements which are averaged to obtain an estimate of the 'inherent' surface roughness in this area. However, the average surface parameter varies from area to area on new cylinder liners. This does not mean that the relevant surface details necessarily are much different, since R_a and R_z are not ideal descriptors of plateau honed surfaces as discussed in [94]. For this reason a certain variation in surface roughness as measured by R_a and R_z had to be accepted in between experiments even when the test plates are cut from the same freshly honed cylinder liner. The accuracy of surface measurements and the surface measurement procedure is discussed and explained in detail in appendix A6.

5.2.3 Test procedure

The following basic test procedure was adopted. Some modifications were made according to need.

- Ensure that the rig and piston ring mechanism is clean
- Measure test plate surface
- Fill oil reservoir and calibrate pump
- Insert test plate and mount piston ring in BDC position
- Set temperature regulators and ensure that the thermocouples are in place
- Preheat plate to 100 C
- Start oil pump
- Engage piston ring when the oil reaches the piston ring.
- Change plate set point to test level
- Record time

- Test duration

- Switch off plate heating
- Stop oil and piston ring
- Immediately remove piston ring and test plate
- Wipe plate dry with soft cloth
- Let cool
- Measure test plate

- Repeat *or* clean with acetic acid and,

- Measure test plate surface

The result of the test is reported as change in surface roughness relative to initial and cleaned surface.

5.2.4 Tests with oil circulation

Initially, tests were made with oil circulation and test lubricant L1. The objective in these tests was to investigate if long term circulation at elevated temperature would cause accumulation of deposits in the grooves. These tests were made at test plate core temperatures that were at the same level as what has been measured on cylinder liners; 130-220 °C. The oil sump was 50 ml in these tests. Ring pressure was kept constant. To prevent oil from spilling over the sides of the test plate, the upper limit of the oil flow rate is about 0.5 ml/min.

Tests resulted in rapid formation of an amber oxide on the liner; however this deposit did not accumulate in the grooves. Dark semi-solid material tended to accumulate outside the ring zone. Significant oil thickening was observed towards the end of extended (100 hours+) tests at high temperatures ($T_P > 200$).

One of the hypotheses of deposit formation is that calcium carbonate from overbased detergent additive was entrained or bound by resinous material. Tests on approximately 10 and 100 TBN mixtures of calcium sulphonate detergent into SN150 or SN600 base oils did not result in groove deposits and there was less deposits outside of the ring area, particularly in case of the high TBN oils. In hindsight, these results may not be entirely surprising as the detergent likely inhibited the formation of insoluble material.

Subsequent tests were made where a 'model resin' in the form of a high viscosity residual oil from earlier long term tests was mixed thoroughly with fresh oil. The volume of the oil sump was decreased at the same time to increase test severity. This approach did result in formation of deposits in the grooves. Test details are summarized in Table 5-3.

TABLE 5-3 SELECTED TESTS WITH OIL CIRCULATION

ID	**OIL**	**V_s [ml]**	**T_P [°C]**	**Q [ml/min]**	**t [h]**	**Groove deposit**
N1	L1	50	150	0.24	200	No
N2	L1	50	200	0.24	262	No
N3	Mix	25	150	0.26	41	Yes
N6	Mix	25	200	0.21	110	Yes

The mix used in tests N3 and N6 is a mixture of 10% of oil from test N2 into L1. This test produced a significant reduction of surface roughness in 40 hours as seen in Figure 5-2.

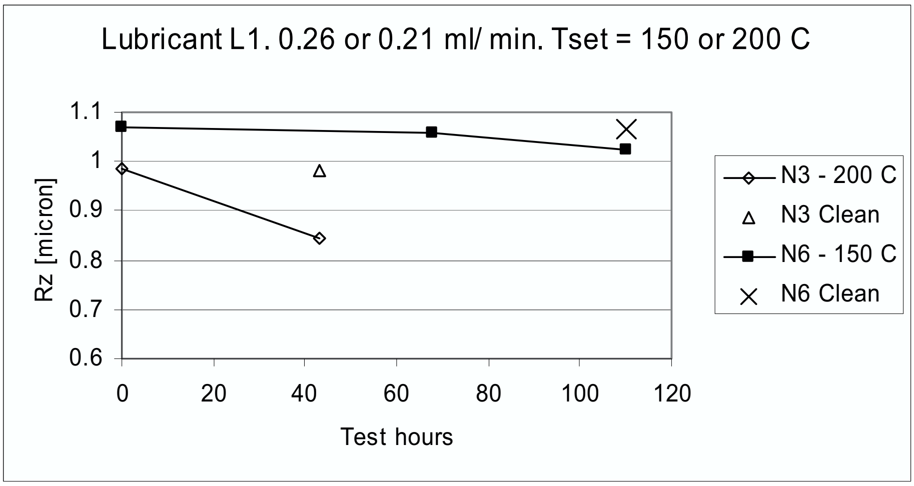


Figure 5-2 *Test conditions and results of test with contaminated oil.*

Although acetic acid restored the bright surface of the metal, the deposit in the grooves was not soluble in acetic acid. Acetone, however restored the surface to original level or roughness but had no impact on surface color.

Investigation of this deposit in the SEM revealed a comparatively smooth deposit surface without the typical elemental distribution patterns seen in field deposit samples with the exception of carbon as seen in Figure 5-3.

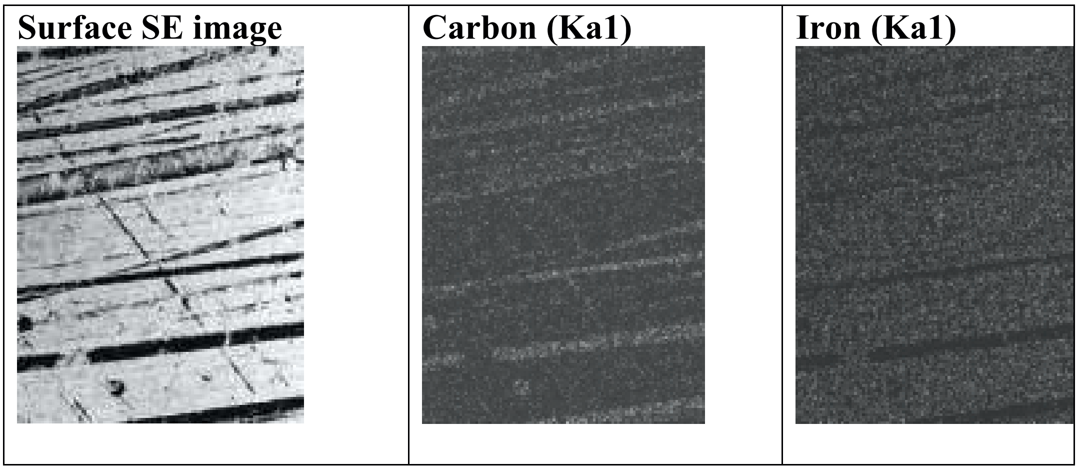


Figure 5-3 *SE image and element maps of model liner deposit. Only carbon and Iron displayed a discernable pattern.*

The EDS did detect some Ca, S and Si, however the major peaks belonged to C, O and Fe. A pattern could not bee seen in the concentration of oxygen, probably because both the iron surface and the hydrocarbon deposit contained oxygen.

The deposit formed in this test thus seems dominated by oxygenated hydrocarbon that is insoluble in the lubricant. The deposit rate was higher at higher temperature which could be a result of increased separation rate due to reduced viscosity.
In spite of significant degradation of the oil sump and formation of deposits outside the ring zone, the test with oil circulation did not lead to deposits that seemed relevant. This path was thus abandoned in favor of tests at higher temperatures and lower flow rates which would increase the thermo-oxidative load on the oil film and emphasize the process on the surface over overall lubricant degradation.

5.2.5 Tests without oil circulation

The test severity increases both with increasing temperature and decreasing oil flow rate when the oil is not circulating. The maximum temperature in our equipment is limited to about 300 °C in the core of the heating block which corresponds to a core temperature of the test plate of about 270 °C. The minimum flow rate is about 0.015 ml /min

Tests at the maximum severity condition did result in the formation of deposits within the grooves in addition to deposits outside of the grooves. Two different test plate surfaces were used. A few tests were made at lower temperatures; however they did not result in deposit formation.
The time history of the average roughness Ra of such an experiment is given in Figure 5-4 and Figure 5-5.

The Ra values presented are the average of 30 measurements and the change in surface roughness over the test is significant at 99% confidence or more. The effect of cleaning with acetic acid is also illustrated in the figures.

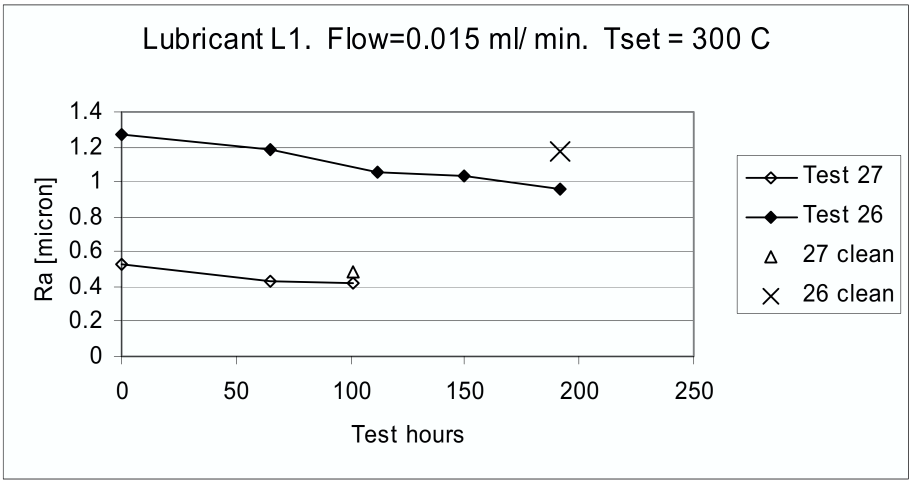


Figure 5-4 *Development of Ra with time and after cleaning. Different types of test plate.*

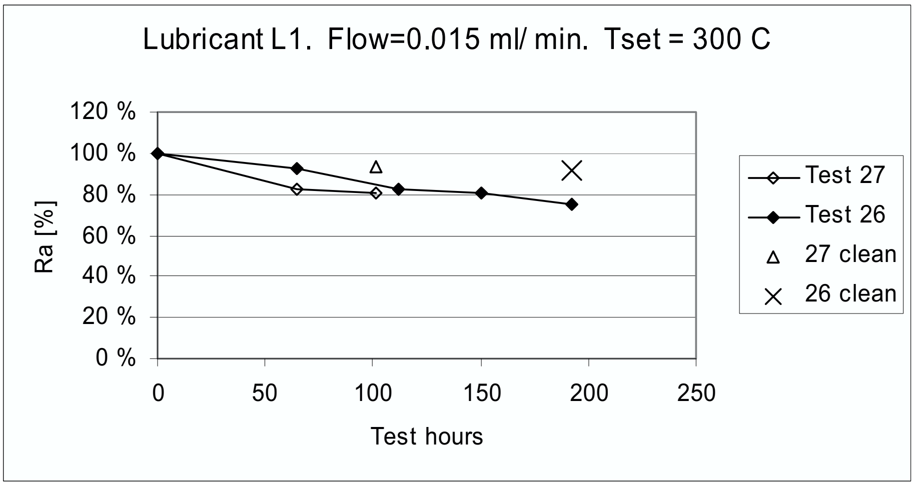


Figure 5-5 *Development of Ra as percentage of initial roughness*

Figure 5-6 *Closeup on test disk (vertical line is BDC). Right: after cleaning with acetic acid.*

The deposit looks like dark lacquer. A picture of a test plate with deposit is shown in Figure 5-6.

The visible effect of acetic acid is apparent, however the amber deposit in the area behind the ring travel does not dissolve in acetic acid nor acetone. The surface roughness is not completely recovered when the test plate is washed with acetic acid.

5.5.2.1 The composition of amber acid soluble deposit

The composition of the acid soluble deposit was investigated by FT-IR and SEM/ EDS. The IR spectrum of a sample of this deposit and a liner lacquer deposit removed from an engine is shown in Figure 5-7.

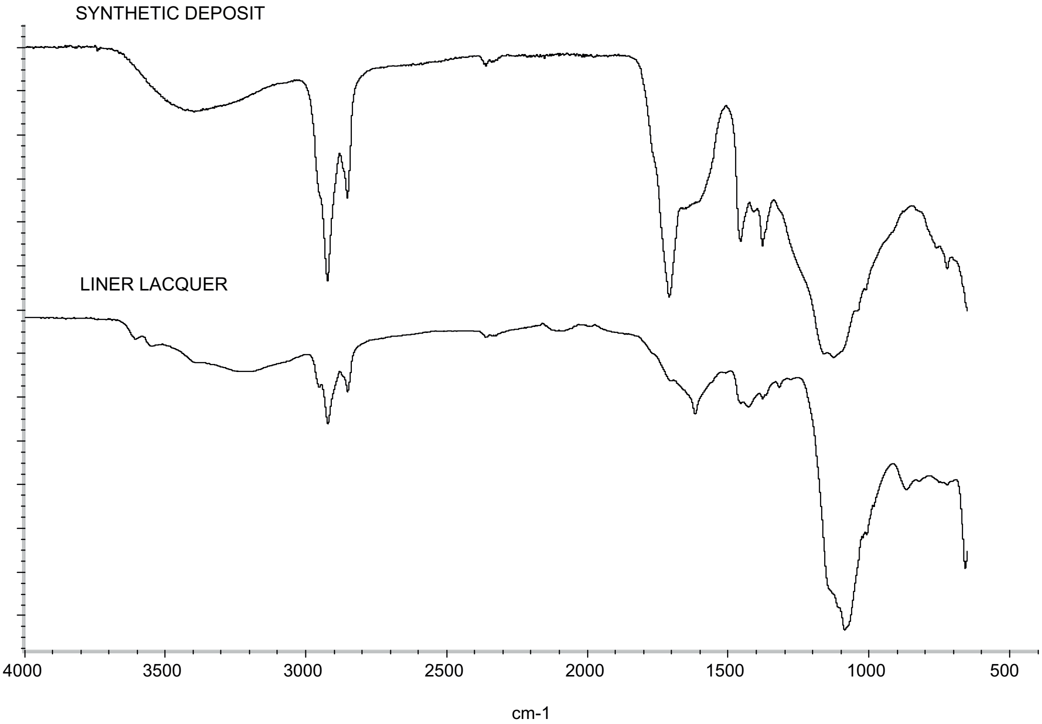


Figure 5-7 *Comparison of synthetic (top) and authentic liner lacquer.*

The deposits analysed in Figure 5-7 are similar in appearance. Both are resistant to acetone and both will be removed by acetic acid; however their composition shows salient differences. Most apparent is the absorption at 1710 cm^{-1} in the synthetic deposit that is attributable to oxidation products. The relative content of alkanes appears larger in the synthetic deposit. A major absorption seen around 1100 cm^{-1} in both deposits, however the shape and 'center of gravity' of this absorption in the synthetic deposit is more typical of sulphonate than sulphate.

The synthetic deposit absorbs at 1456 cm^{-1}. This is indicative of calcium carbonate only when combined with absorption around 870 cm^{-1} which cannot be discerned here, hence this deposit does not appear to contain calcium carbonate. Using table 1.17 in [25] as a guide, the absorption at 1456 cm^{-1}could be $=CH_2$ while its neighbour at 1377 cm^{-1} may be related to $-C(CH_3)_3$.

A SEM image of the deposit surface is shown in Figure 5-8. Regions with thick deposits appear bright due to local sample charging effects. This effect tends to blur and further lower the quality of images of higher magnification.

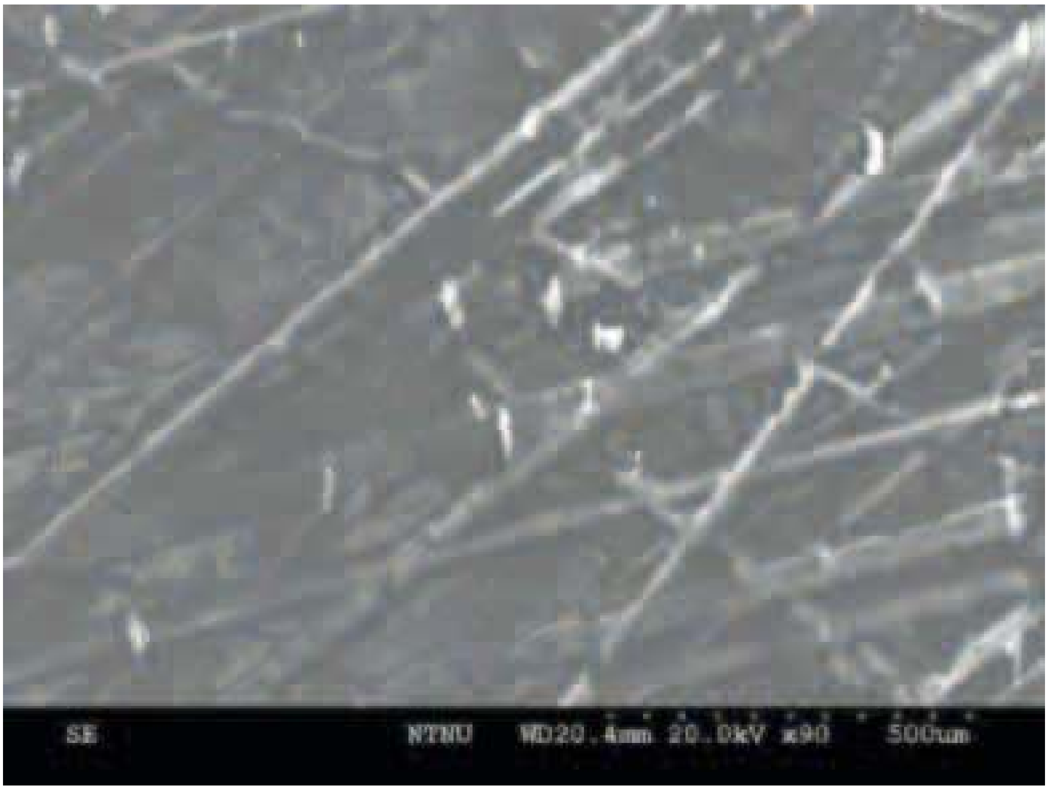


Figure 5-8 *Low magnification SEM image of synthetic deposit*

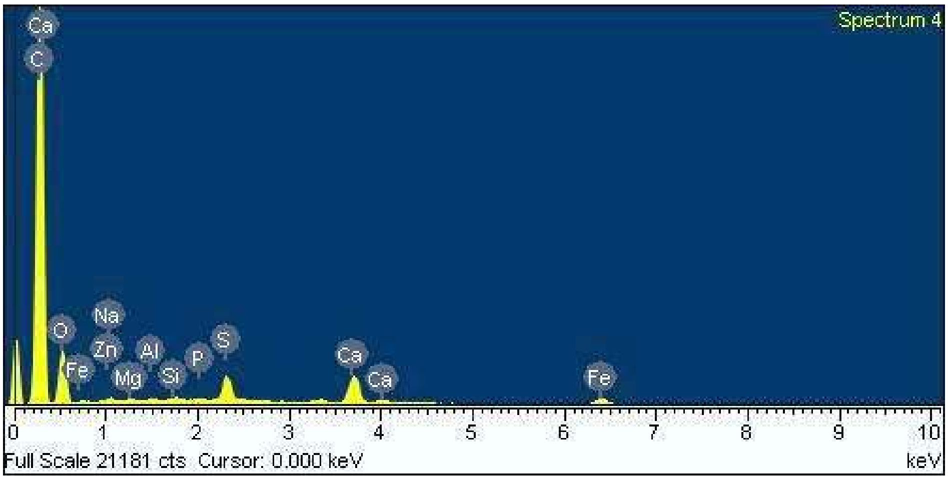


Figure 5-9 *EDS spectrum from test plate groove region*

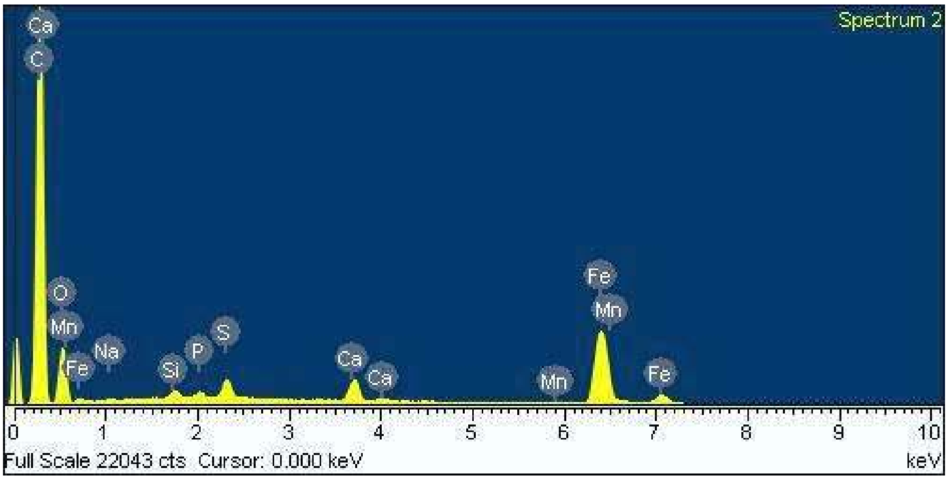


Figure 5-10 *EDS spectrum from test plate plateau region*

An EDS spectrum obtained form a groove region is shown in Figure 5-9 while Figure 5-10 shows an EDS spectrum from a typical plateau region. Both spectra show significant presence of calcium and sulphur which is believed to be calcium sulphonate when seen in light of the IR spectrum.

The EDS spectra differ in the number of iron counts. Elemental maps did not reveal differences in emissions except in the case of iron, possibly because of deposits on the plateau area or due to insufficient time allowed for the generation of these maps.

5.5.2.2 Modified test rig design

Although interesting deposits were formed in the original rig, general repeatability of the test was low and the oil flow and ring movement in the rig was not as intended.
The spring loaded piston ring had a tilting movement which made it effective in scraping oil upwards. This resulted in a small pool of oil collecting in front of the piston ring. Oil that escaped below the ring formed deposits which possibly acted as a barrier for further liquid escape below the test plate. The oil pool above the top ring was not intended, and is not representative of what is expected in a diesel engine.
The pool was eliminated by improved control over the ring motion and oil flow. This was realized by replacing the original piston ring mechanism by a piston ring mounted in a linearly oscillating wagon. This modified test rig successfully improved the oil flow and eliminated the accumulation of oil above the top ring; however liner deposits resulting in surface modification were not formed even after 200 hours at maximum test severity. (Maximum permissible temperature and minimum oil flow).

A significant effect of the removal of the oil pool is the reduction of the average residence time of the oil on the cylinder liner. This is believed to be the most salient difference between the two test rigs, and is believed to be the cause of the elimination of the deposits. These results thus illustrate the influence of mass transport on deposit accumulation.

It was originally intended to run tests using oils of different sulphur content and volatility in combination with known additives in an effort to study the effect of oil volatility and base oil sulphur on deposit formation. This is considered relevant since Pabke et. al. [75] experienced an influence of base oil sulphur content on the content of sulphonate in a model piston deposit. Even if these plans were abandoned since the 'improved rig' did not yield deposits, the work with this and the original rig has provided insight.

5.2.6 Conclusions from inclined surface rig tests

Deposits similar to liner lacquer in appearance and solubility may form as a result of high temperature and extended exposure time of lubricants. These deposits may be interpreted as the result of the formation of oil insoluble material due to high temperature, and possibly also detergent surface activity. Since there is no impingement of contaminants like sulphur oxides and soot in these tests, the synthetic deposits must differ significantly in composition compared to the 'glaze' deposits we have found in the case studies. The synthetic deposit can, however, be considered to partly represent amber lacquer deposits, although products of oil film contamination are also seen in authentic lacquer samples.

Chapter 6
Discussion

Liner deposits have been shown to contain material that is generally oil insoluble but normally found only in low concentrations within the lubricant on a cylinder liner. Lab tests indicated that deposits similar in appearance and solubility are preferentially formed when oil residence time is high, an observation which is in agreement with literature. The case studies identified details that appeared influential in the individual cases, but no overall trend could be found. The following discussion aims to put these pieces together to form an understanding of what happens in the engine when liner deposits are accumulated on the cylinder liner.

6.1 Fundamentals of deposit accumulation

The accumulation of deposits must be related to the following factors:

- Rate of formation of deposits
- Rate of removal of deposits

The formation of deposits must be the result of a series of interactions between reactive molecules. The rate of chemical reactions is governed by the:

- concentration of reactants
- temperature
- presence of catalysts or inhibitors

- surface area of the reactants

The concentration of reactants must be dependent upon the replacement of the oil film containing deposit precursors with oil from the crankcase mist unless this mechanism is compromised by contamination of the entire oil sump. Foreign material such as soot and calcium sulphate must be transported away. The lubricant transport on the cylinder liner is thus influential on reaction rate by influencing the concentration of reactive species. Additionally, volatile losses will tend to concentrate the material on the cylinder liner.

The ability of the lubricant to remove insoluble material is dependent upon sufficient dispersing power. The dispersing power also affects the surface area available for reaction since reactive material can be separated by dispersant and other surface active molecules.

The rate of removal is dependent upon chemical and mechanical mechanisms which dislodge deposits; however in order not to be redeposited they must still be transported away from the cylinder liner.

6.1.1 Concentration of reactants

A simple mass balance model was created to better understand the interactions between lubricant volatility, liner wall volume and oil refresh rate on the concentration of insoluble and non-volatile material on the liner oil film.

A simple mass balance

Consider a film of lubricating oil on a cylinder wall. The volume of the oil film is V_F, the volume of volatile losses is V_V and a volume V_{UP} of fresh oil is supplied to the liner by the oil control ring at each stroke. The concentration of involatile material in the fresh oil is C_{OIL} and the concentration of involatile material in the volatile losses is naturally 0. An amount M of insoluble 'foreign' material is formed at each stroke. By assuming that this is a stepwise process and that the oil supplied to the liner mixes perfectly, the equilibrium concentration of the insolubles on the cylinder wall can be modeled as a function of evaporation and oil supply rate. The principal parameters in this model are shown in Table 6-1 and Figure 6-1. The sequence of events is described in Table 6-2.

The procedure can be iterated by setting the starting conditions to the resulting conditions of the previous calculation; $V_F = V_5$ and $C_F = C_5$, in which case this mass balance is converted to the series in equation 1.

$$C_{n+1} = C_n * \frac{V_F + V_V}{V_F + V_{UP}} + C_{OIL} * \frac{V_{UP}(V_F + V_V)}{V_F(V_F + V_{UP})} + \frac{M}{V_F} \qquad (1)$$

TABLE 6-1. PARAMETERS IN MASS BALANCE

V_V	Volume of volatile losses
C_V	Concentration of involatile material in volatile losses (=0)
V_F	Volume of oil film
C_F	Concentration of involatile material in oil film
V_L	Volume liquid losses
C_L	Concentration of involatile material in liquid losses (=CF)
V_{UP}	Volume fresh oil supplied to oil film by piston rings
C_{OIL}	Concentration of involatile material in fresh oil
V_{DOWN}	Volume of oil film removed by piston rings
C_{DOWN}	Concentration of involatile material in oil film removed by piston rings (=CF)

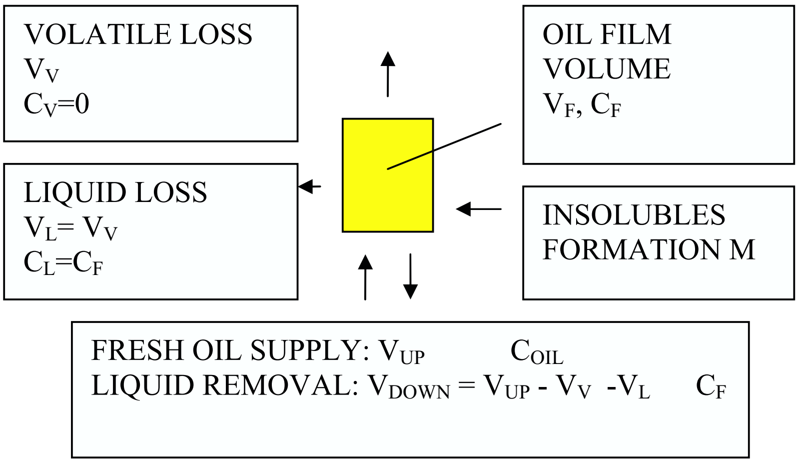


Figure 6-1 *Oil film mass balance*

TABLE 6-2 SEQUECE OF EVENTS - OIL FILM MASS BALANCE

No.	Piston	Event	Oil film condion
1	BDC	Start	V_F C_F
2	TDC	Mix with fresh oil	$V_2=V_F+V_{UP}$ $C_2=(C_FV_F+C_{OIL}V_{UP})/V_2$
3	BDC	Liquid removal	$V_3=V_2 - (V_{UP}-V_V-V_L)$ $C_3 = C_2$
4	BCD	Evaporation	$V_4 = V_3 - V_V$ $C_4 = C_3*V_3/V_4$
5	BDC	Ins. Formation	$V_5 = V_4$ $C_5 = (C_4V_4+M)/V_4$

The concentration will rapidly approach infinity if the film volume V_F should approach zero. The concentration will also be high if the volume of volatile losses approaches the volume of oil that is added at upstroke, V_{UP}.

The amount of liquid losses on the oil film does not affect the result in this simplified model. In reality, these liquid losses could nevertheless be important because:

- liquid losses could affect V_F or V_{UP}
- liquid losses must be replaced with top-up oil, hence liquid losses have a long term purifying effect on the sump oil condition.

The effect of volatility and volume of upstroke on the concentration of involatile material is visualized in Figure 6-2.

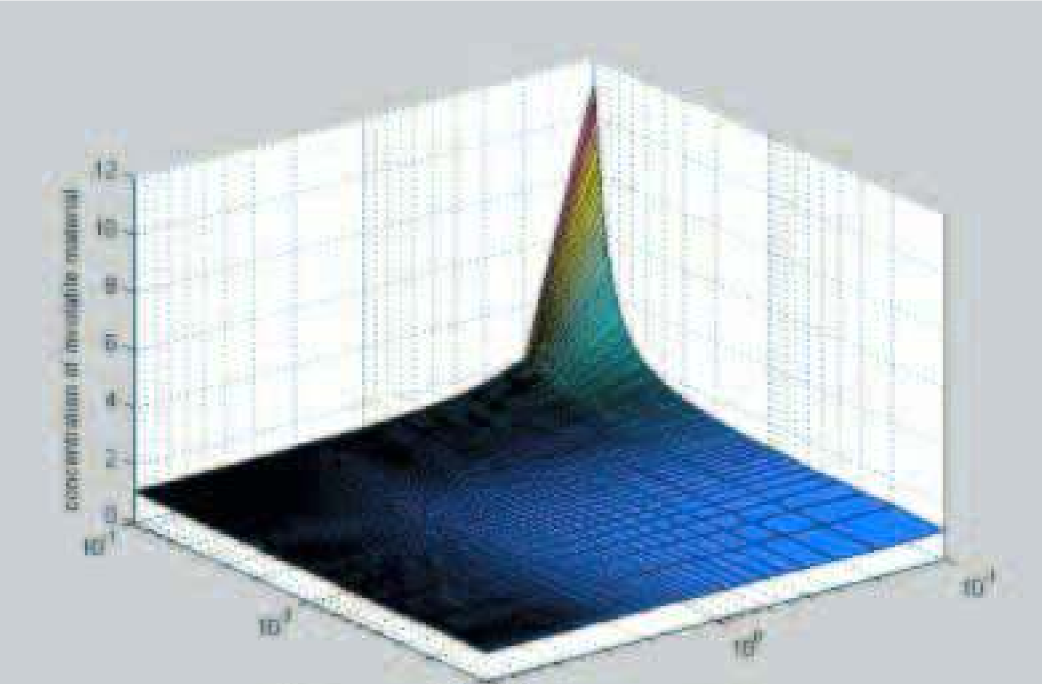


Figure 6-2 *Concentration of involatile material on the liner as function of volatile losses V_V and added volume V_{UP}.*

The concentration is given in arbitrary units and the calculated also assumes unit oil film volume and zero formation foreign material. This figure clearly illustrates that the concentration is generally stable but increases rapidly when the volatile losses approach the oil refreshment rate.

The concentration of lubricant additive material is of primary importance to oil film performance. Additive concentration can be modelled as in the figure above. However additives are consumed which can be expressed by a negative 'M' value. The concentration of additive material as a function of volatility and oil up is plotted in Figure 6-3. The additive consumption rate is fixed.

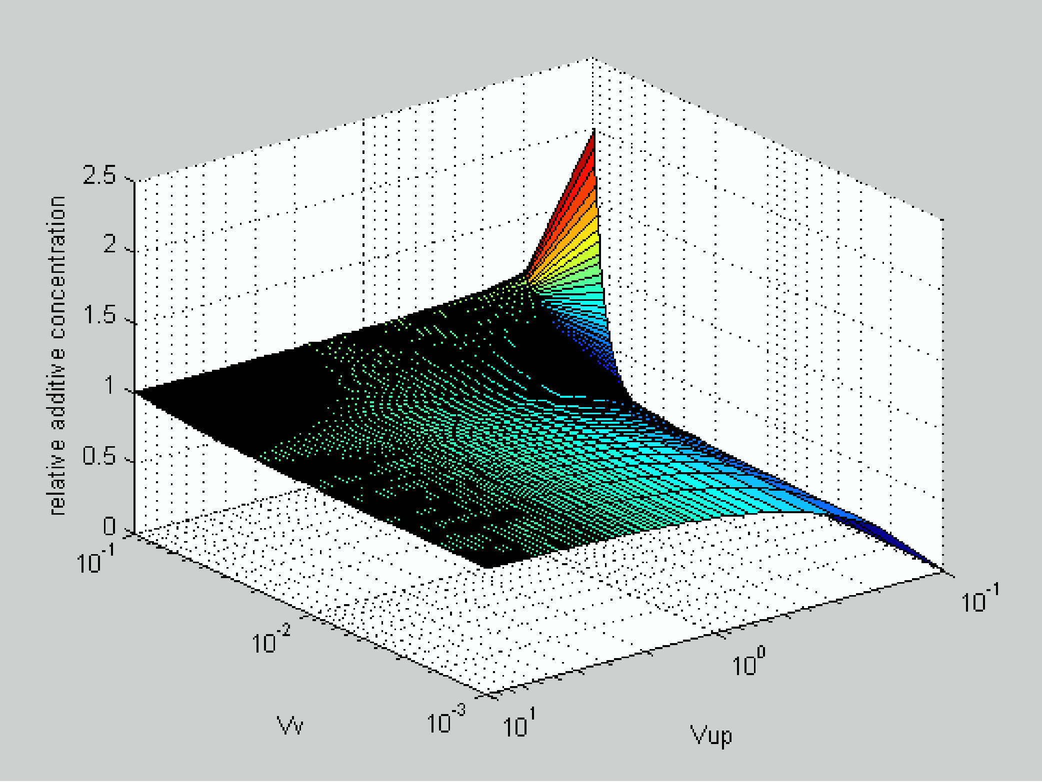


Figure 6-3 *Schematic dependence of oil additive concentration on volatile losses and oil refreshment rate.*

A ratio of $M/C_{OIL} = -0.09$ was used to create the surface illustrating additive depletion in Figure 6-3. Variations in the M/C_{OIL} ratio can distort the shape somewhat; however the overall properties remain: a reduced rate of refreshment will cause additive material to be depleted except when the volatile losses approach oil refreshment rate.

The depletion of additive material will cause the formation of insoluble material. The rate of formation of this material is considered independent of oil supply in this simple model, although it need not be if the oil is depleted. In addition, material such as soot can impinge on the liner, a process which is clearly independent of fresh oil supply.

The concentration of insoluble and 'foreign' material is plotted in Figure 6-4. Although the material theoretically is insoluble, it is considered in this model to mix perfectly with the oil film due to oil film movement and dispersant additive. The figure is drawn assuming that there is no insoluble material in the fresh oil, C_{OIL} = O while the rate constant M is arbitrarily assigned the value 1.

Comparing Figure 6-2 and Figure 6-4 shows that the concentration of material that originates on the cylinder liner is more sensitive to the oil film exchange rate than is the material which originates within the lubricant. There is also a strong effect of volatility at low rate of oil refreshment. Is should be noted that Figure 6-4 has a logarithmic z axis.

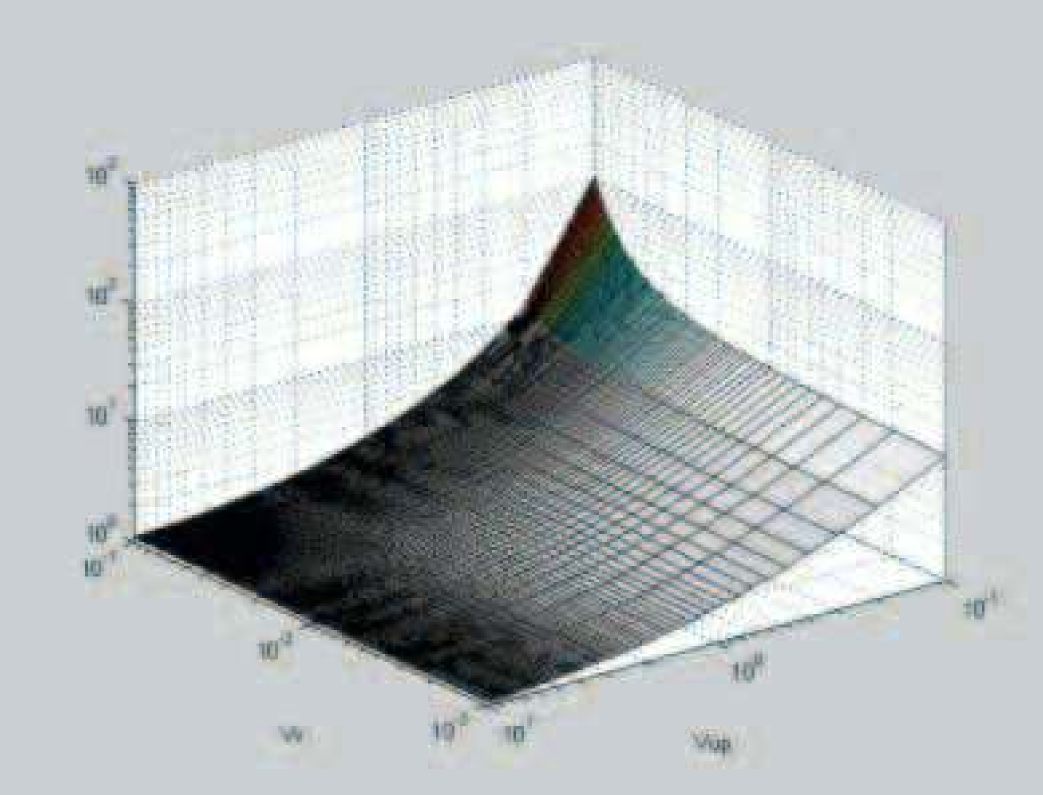


Figure 6-4 *Accumulation of foreign material on the cylinder liner.*

The fundamental difference between the mechanisms of accumulation seen in these figures is that reduced oil refreshment also reduces the amount of involatile material supplied to the liner while the formation rate of foreign material is considered independent of oil supply. In order to keep the concentration of potentially harmful species on the cylinder wall low it is necessary to:

- keep a sufficiently thick oil film in relation to the rate of formation of insoluble material (low M/V_F)
- have a refreshment rate that is large in relation to the volume in the film (high V_{UP}/V_F)
- have a refreshment rate large in relation to volatility (high V_{UP}/V_V)

The first design criterion to avoid liner deposits should thus be to ensure that the relative amount of oil supplied to all parts of the liner is sufficient at all times. Failure to satisfy this requirement may lead to an elevated concentration of the foreign matter formed on the liner while the concentration of oil additives is not correspondingly increased but more likely depleted. Increased volatile losses will increase the concentration of additive material which is beneficial; however volatile losses also increase the concentration of foreign material. The effect of volatile losses is thus not generally predicable but will depend upon the rate of insolubles formation relative to the rate of additive treatment. In practice, increased volatile losses may also affect other parameters like oil film thickness further complicating this discussion.

The above mass balance was created considering the entire cylinder surface; however its principle is also applicable to smaller volumes. If, for instance, the film thickness should increase in one area, due for instance to bore distortion, this would lead to a local increase in concentration of 'foreign' material and a relative reduction in oil film renewal and hence additive concentration.

6.1.2 Temperature

Temperature affects the rate of chemical reactions. The analysis of liner deposits suggest that reactions leading to the:

- formation of organic acids and insoluble organic salts
- formation of sticky insoluble organic 'resin' seen in liner deposits

are of particular interest. High temperature will increase volatile losses and the rate of decomposition of the oil film and its additives. Other principal deposits constituents are soot and calcium sulphate salts. The formation rate of these elements is limited by the supply of reactants which is believed inversely related to liner temperature as thermophoresis is influential on soot impingement, and sulphate salt originate in sulphuric acid from condensation of water and sulphur oxide.

The review of the cylinder liner environment in chapter 2.4 revealed several factors influencing thermal load on the liner. Engine load is obvious but the heat transfer from the hot combustion gas to the liner surface is also of critical importance. The heat transfer rate can be affected by a number of factors including:

- combustion speed which may affect the proximity of the burning fuel spray;
- charge density which affects ignition delay, fuel spray development and combustion speed,
- the extent of premixed combustion which can cause pressure waves that increase heat transfer

6.1.3 Catalysts, inhibitors and surface area

The presence or action of catalysts for deposit formation is unknown; however significant oxidation inhibitors are present within the oil. Alkaline detergents inhibit the formation of oil insoluble products of hydrocarbon oxidation. These inhibitors are consumed, the rate of which process is temperature dependant. Sufficient oil film renewal is required to maintain the concentration of inhibitors.

Dispersant additives prevent insoluble material from aggregation by surrounding them and thus limiting the surface area available for reaction. Sufficient refreshment is needed to maintain the dispersing power of the oil. High temperatures may cause decomposition of this additive and also increase the formation of oxidation products which may attract dispersants. Insufficient dispersant level could reduce the ability of the oil film to carry the insoluble material away from the cylinder liner.

6.2 Recommendations

Engine design, lubricant formulation, fuel composition and engine loading were identified as factors that may influence deposit formation prior to the start of this work. Allen [3] described this relationship using a balance as shown in figure 2-4. More fundamentally, however, as outlined in the previous discussion, liner deposit problems are believed to originate when the balance between the oil film load and renewal is upset as illustrated in Figure 6-5.

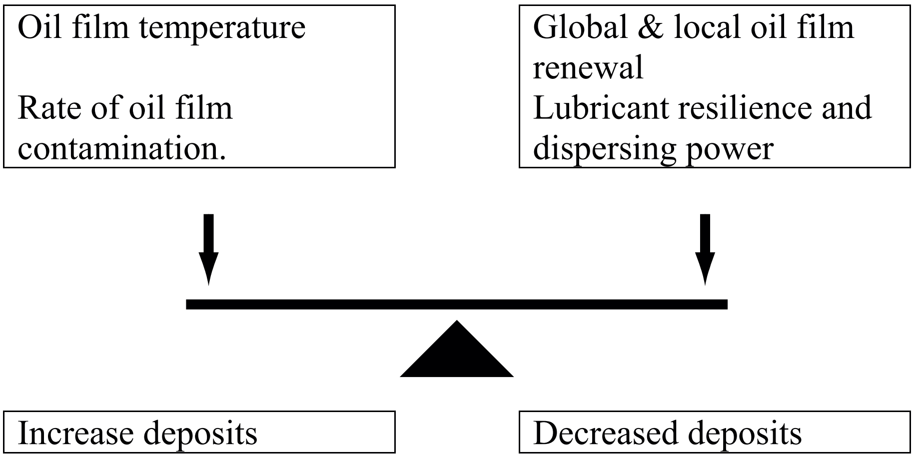


Figure 6-5 *Fundamental deposit balance*

This figure conveys an important principle, that some factors are balanced by others. However, extremities cannot be practically compensated. Excessive temperatures can cause adherent deposits to form in the oil film in-between stokes, and insufficient oil film exchange will eventually cause the amount of insolubles to overcome the dispersing abilities of any oil film. To better understand the deposit formation rate, the basic principles of Figure 6-5. must be linked to tangible features of engine design, operation, fuel composition et. cetera. This gap can be bridged by the construction of a tree diagram as shown in Figure 6-6 from which the following general recommendations can be made.

Engine design
Engine design should focus on ensuring that the oil film in all regions on the liner is regularly and rapidly replaced under all load conditions, and that the temperature on the oil film is limited.

Lubricant formulation
A lubricant to prevent liner deposits should have high dispersing power derived from thermally resistant dispersant additives and be resistant towards forming insoluble deposits. Low volatility is believed desirable, but this cannot be argued from the point of the mass balance alone.

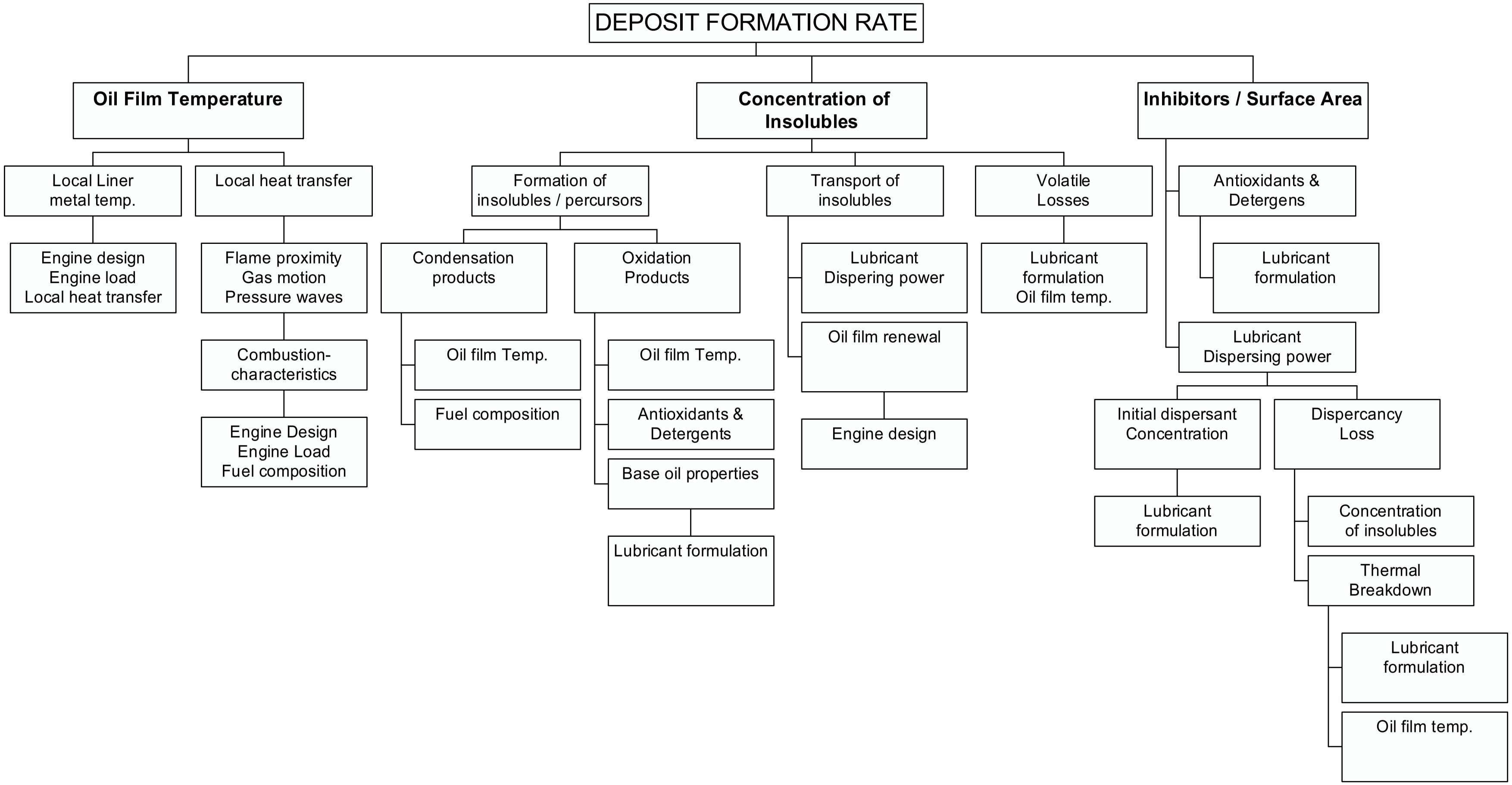


Figure 6-6 *Deposit formation rate - This figure is intended to be illustrative but not exhaustive*

Engine operation and ship design
Engine operators should avoid low load to the extent possible, and also avoid engine overload. This is also a ship design issue.

Fuel blending
More research is needed to better understand the combustion properties of complex fuel mixtures. Ideally, a reliable test for fuel combustion characteristics should be used to identify possible correlations between standard fuel analysis data and characteristic combustion parameters such as combustion speed. In the long run, this will be helpful to optimize engine design, improve fuel quality and fuel selection, thus avoiding problems and restricting possible undue speculation.

6.3 Interpretation of deposit composition

It is nearly impossible to accurately predict the condition on the cylinder liner by studying the engine from the outside. However, the composition of the deposit can give insights on this matter.

The investigation of glaze revealed a significant content of soot and also large crystals of calcium sulphate. Relatively large amounts of iron sulphate were also seen which was interpreted as a result of acid attack on the liner surface. The sulphur content of the fuel used in this engine was generally below 0.2% by weight while the TBN of the oil was 15, which is considered high in relation to the fuel sulphur. The composition of the deposit is thus indicative of a rate of soot and acid formation on the liner which is high relative to the oil film renewal rate. This may lead to a relatively high concentration of insoluble species and relatively low concentration of dispersing additives which eventually cause some of the insoluble material to be deposited on the cylinder liner.

The amber lacquers contained less or no soot. Their IR transmission spectrum and general appearance also suggest that this deposit contained relatively more 'resin' than did the glaze. A higher temperature could increase the oxidative load on the oil film, and could also reduce the amount of sulphuric acid and soot on the cylinder liner. Hence the temperature could cause the shift in composition. Lubricant composition could also be a factor.

Other reports of liner lacquer have focused on high load, and also on high content of calcium carbonate in deposits. These deposits are reported to originally form in the top of the liner. Since engine load is high, the oil consumption rate is high relative to the formation of soot and calcium sulphate. The temperature, however, is high, which will increase the rate of oil film oxidation but also reduce the viscosity of the oil film to a point where mild wear could occur. Micellar detergent additives can prevent such wear; however, this results in the formation of an anti-wear film consisting primarily of calcium carbonate which - unlike many other antiwear films - does not adhere to the surface. Thus high temperature can induce wear to cause the formation of insoluble calcium carbonate particles in the oil film, which could end up within liner deposits.

6.4 Suggested cause of formation

Case studies revealed that low load is seen to be a dominant part of the operating profile in engines with deposits. Oil consumption per hour may be very low at low load. The net increase in oil sump alkalinity observed in some case studies indicates that the liquid oil consumption is low in relation to volatile losses. Low liquid oil consumption could negatively affect the effective oil exchange rate on the cylinder liner. Secondly, the generally colder liner surface at low load will result in a thicker film which could also reduce the relative oil exchange rate (as shown in the mass balance, the residence time of the oil on the liner is dependent on the relative exchange rate.)
The rate of accumulation of insoluble deposit material such as soot and calcium sulphate is likely increased at low load due to poor combustion and low liner temperatures. This will contribute to increased concentration of 'reactants'. Hence low load combines low oil film exchange with high rate of impingement.

However, if the oil film renewal increases with increased oil consumption, then one might expect deposit formation to be reduced when oil consumption increases. Why need this not be the case?

Oil consumption in a well functioning engine should be dominated by volatile losses and oil mist in reverse blow by. Liner deposits will cause more lubricating oil to be swept up towards the top of the cylinder liner; hence the mechanism of oil consumption is believed different. The up-scraping of oil due to liner deposits may cause a tiny reservoir to collect above upper ring reversal or on the flame ring. Material from this reservoir may interact with the liner oil film, particularly when the engine is standing; causing the phenomenon described as 'running' deposits in the introduction of this thesis. Additionally, this oil pool causes the net amount of oil on the liner to increase, leading to an increase in the average residence time of the oil on the liner. This will also aggravate deposit formation.

This hypothesis also helps explain the observation why liner deposits are rarely seen in high speed engines since high speed will increase the rate of oil film renewal in relation to time for condensation. On the other hand, slow speed engines compensate by having direct oil supply to the liner so that the oil film exchange rate is maintained at a controlled rate under all load conditions.

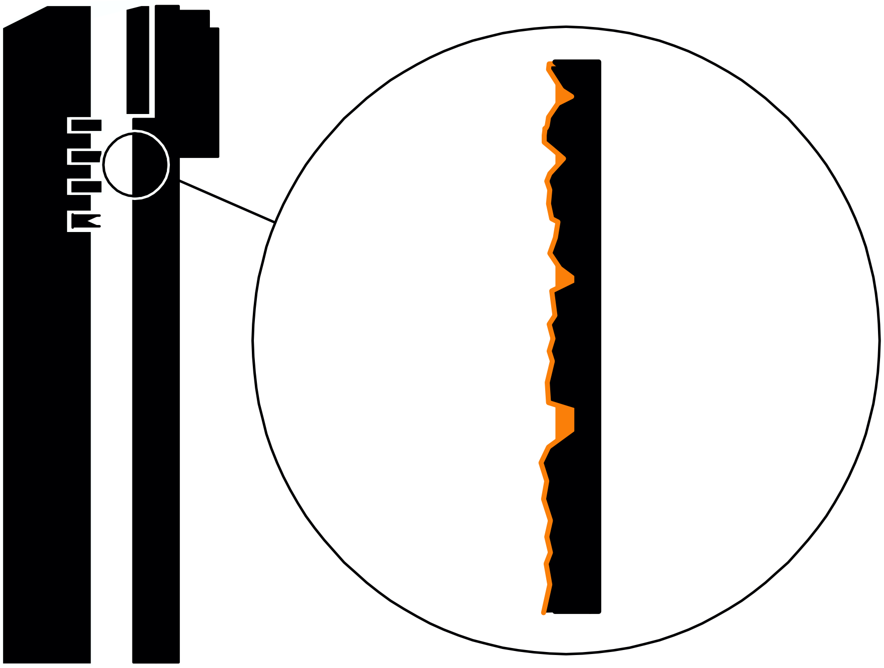


Figure 6-7 *Schematic of location with conditions particularly suitable for deposit formation. The plateau is considered extra vulnerable.*

The mass balance revealed that the combination of high temperature, high volatility and low oil refreshment rate is the critical condition in terms of reaction rate. This is applicable to the liner as a whole but the oil film on the micro plateaus on the surface top region of the cylinder liner is especially vulnerable in this respect - particularly the area which is above the oil control ring at TDC. This area is illustrated in Figure 6-7.

Insoluble aggregates could form in this area, even from initially dispersed material like calcium sulphate and soot. The elevated position of the plateau makes the insoluble material vulnerable to mechanical removal by piston rings if it should deposit, however it will be well protected within the grooves in the hydrodynamically lubricated area of the cylinder liner which might allow deposit to accumulate here.

Chapter 7
Conclusion

The formation of deposits on cylinder liners in marine medium speed engines has been investigated. These deposits were predominantly found in the mid-stroke region of the cylinder liners in engines operating extensively on low load. The deposits contained variable amounts of oil insoluble species including significant amounts of hydrated calcium sulphate and also a smaller amount of wear metals.
In addition, nearly invisible deposits termed 'Bore glaze' in this research also contained iron sulphate, carboxylate salts and soot, which indicated that the alkaline detergent has been entirely consumed, while amber deposits termed 'liner lacquer' in this work contained more oxidized hydrocarbon. The transition between lacquer and glaze appeared gliding.

The root cause of liner deposits is postulated to be a mismatch between the oxidative and contaminating load on the liner oil film and its dispersing power and exchange rate.

A combined mass balance and chemical kinetics approach is used to bridge the gap between fundamental deposit theory and tangible factors. It is thus possible to rationalize the formation of deposits on cylinder liners and how factors related to engine design, operation, fuel composition and lubricant formulation affect deposit formation. This understanding is sufficient to point out which factors should be considered in terms of the prevention of deposit formation and to present a viable hypothesis on the reason for the deposit formation in the engines that have been investigated in the course of this work.

The presence of deposit indicates that the dispersing power and transport rate of the oil film are insufficient to deal with the deposit precursors being formed. This is believed related to extensive low load operation, which is associated with both low liner temperatures and low nominal oil consumption levels in these engines. Low liner temperatures will encourage the formation of calcium sulphate by condensation of sulphuric acid precursors while low oil consumption is believed to indicate low oil film transport. Slow oil film exchange will also contribute to oil film oxidation by prolonging the exposure to combustion gases.

Other reports indicate that deposits may also form at high engine load and may differ in composition to what is seen in this research. This is reasonable on basis on the fundamental balance presented in chapter 6.2, and the deposits seen in our case studies may be considered 'low load' or 'cold' liner deposits.

7.1 Suggestions for further work

This investigation has revealed that little is known in the literature about oil film transport on the cylinder liners. More information in this area is much desired.

A compositional analysis of deposits formed in engines at high load would be interesting in order to investigate a possible difference in composition. Furthermore, a more detailed characterisation of all types of liner deposit is also desired, and more information on deposit distribution patterns, particularly in the cases where the deposit is not evenly distributed around the circumference.

Engine builders with deposits formed at low load which are similar in distribution and composition to those seen in this thesis may attempt to improve the oil film exchange rate, particularly, perhaps, at low load. Direct oil feed to the liner or revised piston ring designs are possible approaches to this end.

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Appendix A1

Characterization of diesel engine cylinder liner deposits by surface measurements

Paper published in "Tribotest", March 2004(10), 207.

Appendix A2

The high pressure rig

The research of liner lacquer at NTNU started as a student project with the design of a test rig to investigate liner lacquer by Zepter in 1995 [98]. This design was never built, but a test rig using the principles outlined by Zepter was made in 1998 by converting an apparatus originally designed for analysis of fuel ignition properties [100]. This rig has been christened 'high pressure rig'. Valde continued the technical development of the rig in 1999 as described in [101]. Further technical refinements and test development work was then performed by Rune Haugland and his co-workers at Statoil before the test rig was passed on to this PhD program.

1 Test rig objective and principle

The original design of the test rig is based upon a hypothesis regarding lacquer formation in which four important mechanisms were envisioned:

1. Thermal cracking within fuel droplets
2. Formation of resins in the lubricant initiated by incursion of cracked fuel
3. Condensation of combustion products.
4. Lacquer hardening by piston ring movement and evaporation of oil.

According to this hypothesis, thermally cracked fuel and condensed fuel hydrocarbons are believed to initiate the formation of resins within the oil film which subsequently bind the material that fills the honing grooves.

2 Description of the high pressure rig

An illustration of the high pressure rig is shown in Figure 1. The high pressure rig consists of a pressure chamber into which a test plate is inserted. Heat can be applied through electric heat coils in the side of the pressure chamber. The test disk rests on a stand which is cooled underneath by water. The disk surface may be continuously scraped by a rotating device. The test setup also includes a fuel injection apparatus. After the test, the disk is removed for analysis. In test development, this analysis is generally limited to appearance and the ability of acetone and acetic acid to remove the deposit; however some samples were investigated by FT-IR.

The test plate is a circular disc made of cast iron. The test plate rests on a cooled support and will therefore be cooler then the surrounding walls and is subject to condensation. The rotating scraper device provides movement of the oil film and a polishing and scraping effect on the deposit. The scraping device also ensures that liquid samples are maintained in a thin film by countering surface film effects that in some experiments would cause the oil sample to form drops and dry spots on the test disc.

A fuel injector is mounted on the top of the pressure vessel. A cross section of the test rig is shown in Figure 1.

The temperature of the chamber is regulated by a control circuit with input from the thermocouple inserted into the gas from the top of the vessel. This unit controls the power to the heating coils that surrounds the chamber.Pressure is created and maintained by a connection to a high pressure bottle and a control valve. This system automatically compensates for leakage from the system; however leakages must be controlled in order to control the air supply during tests.

The temperature of the test disc is measured by a thermocouple inserted from below. This is input to a second control circuit that is connected to a valve that regulates the flow of cooling water through the chamber below the test disc. A computer monitors and records the pressure temperature history of tests. This makes it possible to ascertain that the regulators have maintained stable conditions throughout the test.

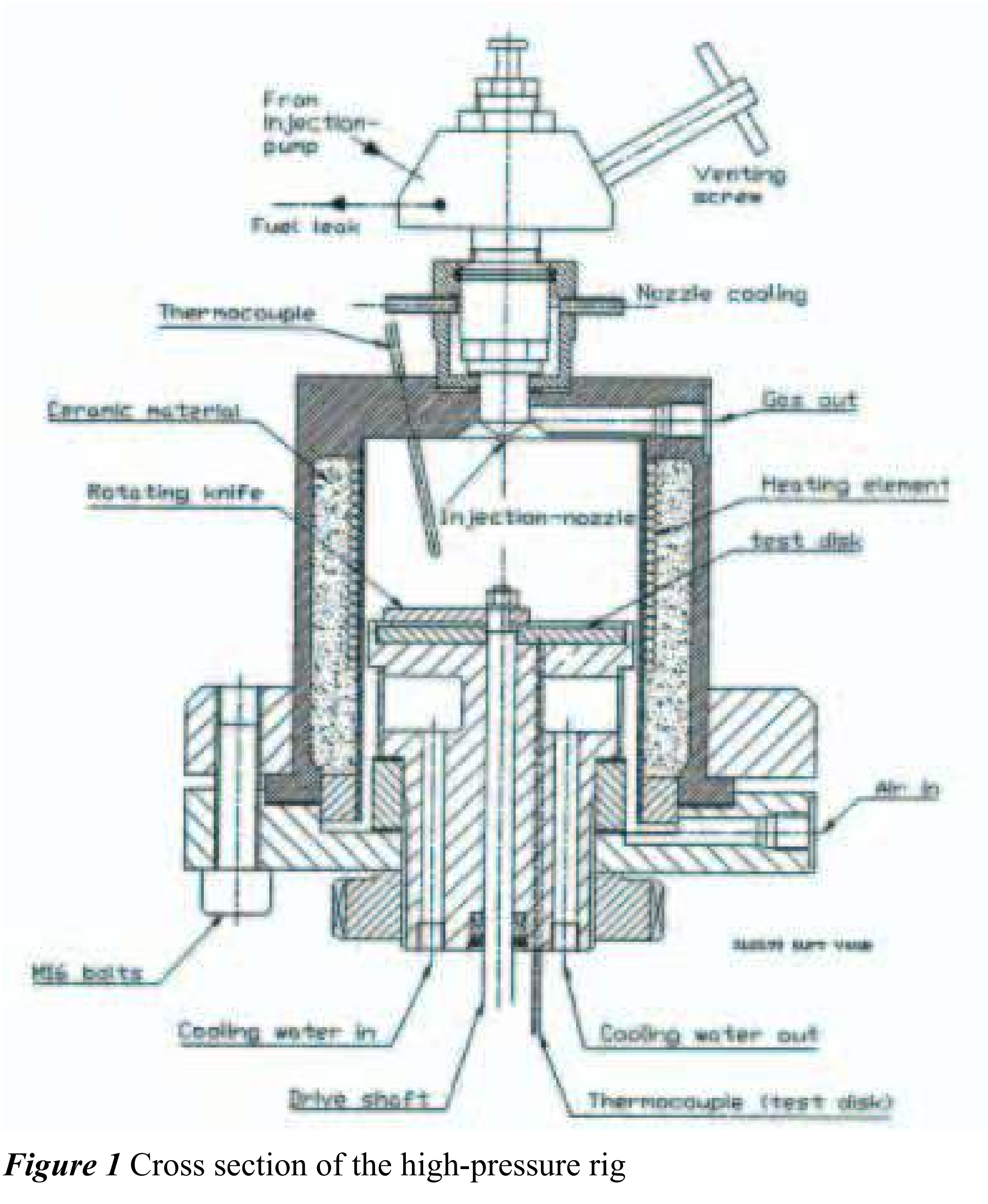


Figure 1 Cross section of the high-pressure rig

2.1 Instrumentation of the test rig

The test rig has two thermocouples and a pressure sensor. An analogous manometer is also fitted. An oscilloscope is used to detect lift of the injection needle when the injector is used.

TABLE 1 INSTRUMENTATION

Instrument	**Position**	**Parameter**
Pressure sensor (type:)	The sensor is positioned in the exhaust line, before exhaust valve.	P
Thermocouple gas	Pressure chamber, positioned as centrally as possible without being driectly subjected to injection spray	T_g
Thermocouple disc	This thermocouple is situated 0.5 mm below the surface onto which the test plate rests.	T_p

The positioning of the manometer on the exhaust line sensor is beneficial because the surrounding temperature is low. The dynamic response and location of the sensor makes it impossible to detect a pressure rise due to combustion.

2.2 Test processes and governing parameters

A process to create lacquer was proposed in [98], however the blending fraction, i.e. how much is required of each process or product must be determined through experimental development.

Controlling the four complex processes (cracking, resin formation, condensation and hardening) in one apparatus is very ambitious. There are some interactions in this apparatus that requires careful consideration and places some restrictions on test flexibility. Table 2 lists critical processes from the formation hypothesis and the expected relation of these processes to controllable rig parameters.

This short review of parameters expected to govern rig processes serves to point the finger at an important fact: A high oxygen concentration which is desirable with respect to some processes may have a negative effect on other possibly critical processes. Because compressed air is used, the availability of oxygen increases with increasing pressure. These processes cannot be investigated independently. Furthermore, the instruments on the rig do not give any data suitable to judge the degree of each process. This is a particular concern with regards to combustion and possible fuel cracking which are severely dependent upon the fuel injection quality. In fact, this test rig suffers from the shortcomings as engine test discussed in the introduction to this thesis - the lack of control of and information on the fundamental processes that are to be investigated.

TABLE 2 PARAMETERS EXPECTED TO GOVERN PROCESSES

Process	**Increase**
Thermal cracking within fuel droplets	-P; $+T_g$; $-O_2$ +droplet size
Combustion	+P; $+T_g$; $+O_2$ -droplet size
Condensation of partial combustion products	- T_p +P
Initial resin formation	+P; $+T_p$; $+O_2$
Evaporation from oil film	- P, $+T_p$ (t)
Oxidation of deposit	+P; $+T_p$ $+O_2$, t
Polymerisation of deposit	+P; $+T_p$ $-O_2$, t

2.3 A simplified test

The idea with the simplified test is to remove some of the processes from the original setup to better understand what happens in the rig and enable the design of useful experiments. The lubricant is required to form lacquer because lacquer contains residue from lubricant additives. The influence of cracked fuel and combustion products however is uncertain and theoretically, the desired 'resins' could be created from oxidized lubricant base stock as well as partly oxidized or cracked fuel. The extent of cracking and combustion at each injection is difficult to measure and assess in this rig. It was therefore decided to run a test setup without fuel injection. The governing parameters of this test are shown in Table 3.

TABLE 3 GOVERNING PARAMETERS - SIMPLIFIED TEST

Process	**Increase**
Evaporation from oil film	- P, $+T_{p,}$ t
Oxidation of deposit	+P; $+T_p$ $+O_2$,t
Polymerisation of deposit	+P; $+T_p$ $-O_2$,t

This test may be described as a high pressure thin film oxidation. Unlike liner lacquering, oil film oxidation has been subject of many publications. [22][76][81] The simplified high pressure rig test is different from these tests in that it operates under high pressure.

3 Tests in the high pressure rig

Literature on oil oxidation concludes that temperature and oxygen diffusion through oil samples are critical to test results. The purity and composition as well as other inherent sample properties like oxygen solubility are also important; however these factors may be considered part of the oil quality which is to be assessed in this test. The temperature is controlled in the test. Oxygen diffusion is dependent upon the film thickness which is indirectly controlled by the distribution of a controlled amount of oil on a fixed area.

3.1 Test procedure

The disks are cleaned by polishing the test disk with a rotating electric steel brush until it is completely brilliant. The disk surface is subsequently washed with acetone and blowed it dry with compressed air. The scraper is cleaned in a similar manner but using a manual brush.

A sample is oil is measured using a syringe and distributed on the test disk. The test rig is preheated until it has reached a stable condition with respect to gas temperature and disk support temperature. The sample and scraper is inserted and the clock started. This procedure will cause a brief drop in both gas and disk support temperature, but these are both rapidly recovered. The rig is then closed with seven M16 bolts. Pressure is applied and the scraper engaged five minutes after the sample is inserted.

Pressure is relieved when the test duration expires. The bolts are then removed but the rig is kept closed until five minutes after test time, when the rig is opened and the test plate removed. A test of 30 minutes will thus subject the sample to a total of 30 + 5 minutes heating and 30-5 minutes of pressure. This is done to ensure adequate time to tighten and unfasten the bolts that keep the rig together.

3.2 Initial tests

Test conditions were selected on basis of experience from pervious workers and are given in Table 4. Four oils were selected. A standard base oil was selected as a reference. In addition, severely hydro treated napthenic base oil was tested. Two commercial lubricants of different anti-lacquer performance were also tested. Basic data is shown in Table 5

TABLE 4 TEST CONDITIONS

General test conditions	
Gas pressure	40 bar
Gas temp.	380 °C
Disk temp	120 °C
Disk surface temp	180 °C
Scraper speed	23 rpm
Oil sample quantity	300 l
Test duration	30, 60 and 90 minutes

Initial test results are summarized in Table 6. The term ‘soluble’ and ‘insoluble’ implies that the deposit mixes with the solvent. Washable indicates that the thickened oil or deposit is easily removed, but not necessarily mixed or dissolved in the washing media. The lubricant itself is soluble in neither acetone nor acetic acid. It is observed that oxidation of the lubricant base oil at these conditions will result in acetone soluble varnish. However the formulated oils darken faster than the paraffinic base oil and yield deposits that are insoluble in acetone. The varnishing process as observed in these test can be described as follows:

- oil becomes sticky
- the oil darkens towards orange and reddish
- a hard smooth and glossy varnish is formed.
- the varnish dries, becomes brittle and is eventually scraped away

TABLE 5 TEST OILS

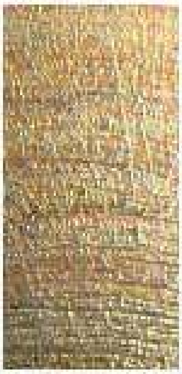
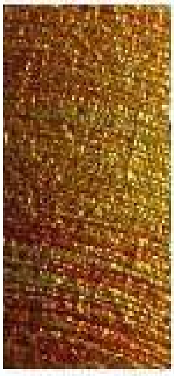
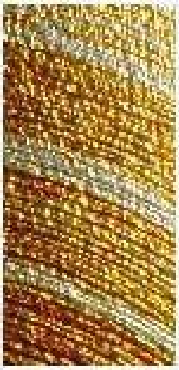
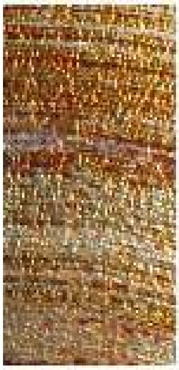
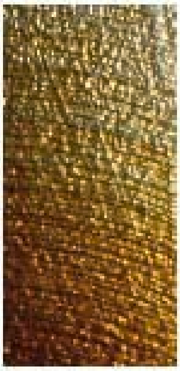
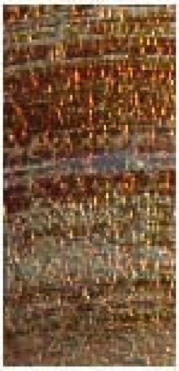
	'Base'	**'T-400'**	**'A'**	**'E'**
Description	Standard paraffinic base oil	Severely hydrotreated napthenic base oil	Commerical marine lubricant	Commerical marine lubricant
Performance with respect to liner lacquer	-	-	Below average	Above average
Viscosity @100 cSt	11,5	18,5	11,5	11,6
TBN	-	-	14,5	15
Sulphated Ash	-	-	1.95%	2,1%
Density		0,924		0,893

TABLE 6 TEST RESULTS

Oil Type	**Time [min]**	**ref. no.**	**Visual**	**Acetone**	**Acetic Acid**
‘Base’	30	201	light	soluble	washable
	60	206	medium	soluble	insoluble
	90	213	medium	soluble	insoluble
‘A’	30	233	medium	soluble	washable
	60	204	dark	insoluble	insoluble
	90	216	dark	insoluble	insoluble
‘E’	30	221	medium	soluble	insoluble
	60	208	dark	insoluble	insoluble
	90	222	dark	insoluble	insoluble
‘T-400’	30	219	medium	soluble	insoluble
	60	205	medium	soluble	insoluble
	90	220	dark	soluble	insoluble

Pictures of test disks are shown in Table 7.

TABLE 7 PICTURES OF TEST DISK

	30 min	60 min	90 min
'Base'			
'T-400'			
'A'			
'E'			

These pictures are manually cropped from pictures of the entire test disk, but are otherwise not manipulated. The pictures are taken with the camera mounted on a bracket within a closed cabinet with special lighting. The pictures should therefore be comparable.

The deposit formed from formulated lubricants tended to be scraped away to a larger extent than the un-additized base oils. In fact, the additized oils appeared more prone to form insoluble and dark deposits than were the pure base oils.

The infrared transmission spectrum of a formulated test lubricant and a typical solid acetone soluble deposit is shown in Figure 2 and Figure 3 respectively. These spectra clearly show that the aliphatic base oil constituents around 2900 cm^{-1} in the test oil are consumed. The double absorption at 1460 and 1380 in the new oil is also associated with aliphatic base oil material. The relative intensity of these absorptions are inverted and shifted towards lower wave numbers.

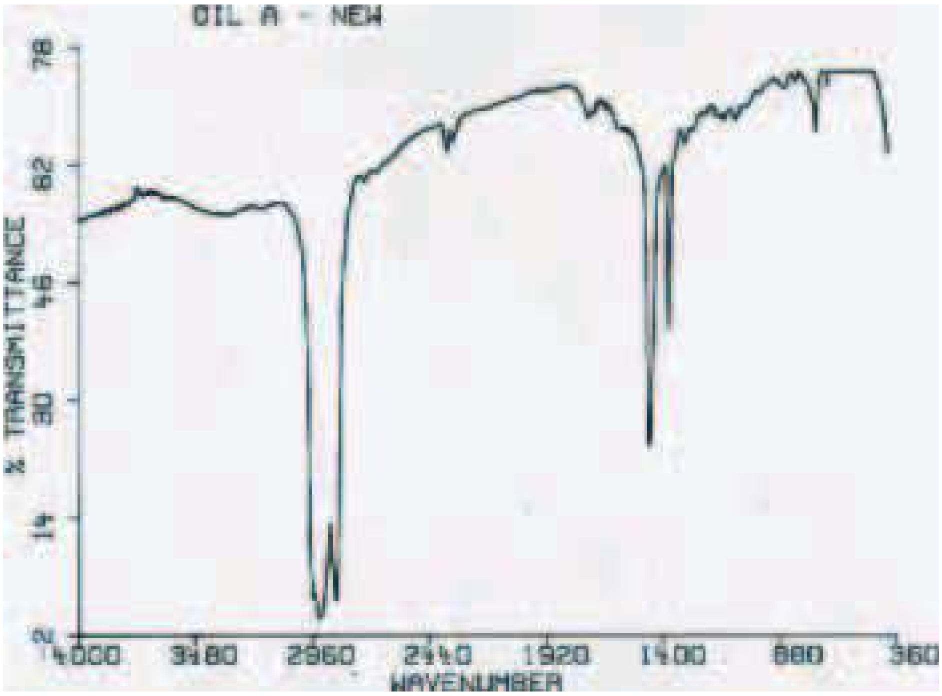


Figure 2 *IR spectrum of test lubricant*

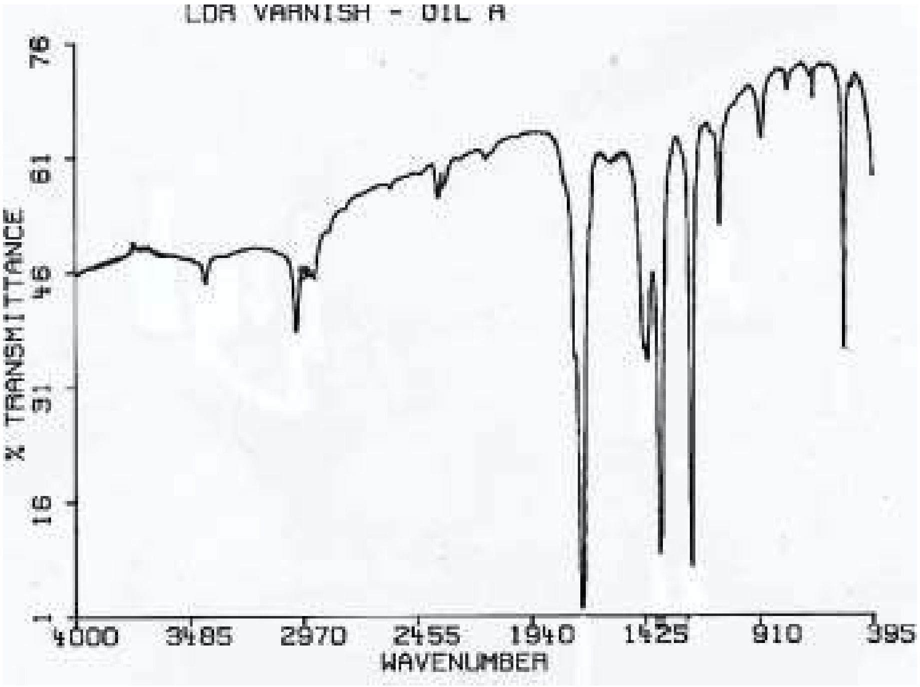


Figure 3 *IR spectrum of acetone soluble deposit.*

The strong peak in the varnish at 1715 cm^{-1} is caused by C=O absorption form oxygenated species. These IR spectra thus confirm the impression that base oil oxidation is a primary process in the deposit formation in these tests.

3.3 Discussion of initial test results

The principal escape route for organic material in this test is evaporation of volatile components. Polycondensation may also contribute to volatile losses. By weighing the test disk before and after a test without using the scraper, a weight loss of about 55% is recorded after 60 minutes using oil A. All in all, it is highly probable that the content of inorganic material in this deposit is much lower than what is reported for liner lacquer as is also indicated in Figure 3.

In the engine, the evaporation will be assisted by hot flames and exhaust gas passing the surface at very high velocity at low pressure. Also, the piston ring arrangement will bring fresh oil to the liner and remove old oil. The concentration of the inorganic material may be the result of accumulation by precipitation in addition to the 'distillation residue' effect reproduced in this rig. Facing this fact, the following conclusions were drawn.

- Earlier reports of lacquer formed during test runs with this rig by [100] are believed to be a misinterpretation of oxidation of the test disk metal surface, the same effect as discussed in appendix A4
- The inclusion of any amount of cracked, partly oxidized or unmodified fuel components are not expected to result i a significant increase in the content of inorganic material in the deposit
- In order to create a deposit similar to liner lacquer, the test must be modified to enable a higher content of inorganic material in the deposit. Ideally, this should be achieved by incorporating the two previously mentioned mechanisms from the diesel engine that is not replicated the rig, namely oil circulation to allow liquid hydrocarbon escape and flow of hot gas over the surface to assist evaporation..

This would require significant modifications to the test rig. In stead, new tests with a different approach were conducted as described in the following.

4 Tests on modified lubricants

The ratio of inorganic material in the deposit and particularly calcium could be increased if the tests were run using special test mixtures. Several such paths were followed:

- Increased amounts of complete additive package
- Increased levels of overbased detergents
- Addition of precipitated overbased additives
- Addition of analytical calcium carbonate

Increasing the additive package concentration resulted in sticky semi-liquid 'deposit' immiscible with both acetone and acetic acid.

Increasing the level of overbased detergent in a formulated lubricant resulted in deposits that did not adhere to the test disk, but was scraped away by the rotating device.

The concentration of additive material can be increased even beyond the pure additive package using material may be precipitated from the detergent by means of diluting with a mix of acetone and pentane. The results from these tests was a white, brittle powder like deposit.

Adding less than 10% by weight of calcium carbonate to formulated lubricant yielded a paler deposit than was the case from pure lubricant, however this was not sufficient to change its solubility properties. In tests with higher concentrations of calcium carbonate, where the surface was smooth but not dry right after the tests, the CaCO3 will group together in small particles resembling dust or grains of sand in the oil. If duration was increased, the deposit would be scraped away by the rotating device.

5 Summary

The high pressure rig is suitable to create varnishes from oil samples, however these varnishes have a high content of oxidized hydrocarbon and is thus significantly different from the liner deposits to be investigated. The work with this rig has emphasised the importance of oil circulation to deposit formation and passed doubt on the idea that resins as above are prone to bind calcium carbonate to form a hard deposit.

Appendix A3

Extraction of overbased detergent additives

1 Background

Calcium carbonate is incorporated into the lubricant by surfactant molecules. A fundamental question is wether the calcium carbonate reportedly found in lacquer is contained in the original additive structure. In lack of actual deposit samples, the properties of a model deposit consisting of highly concentrated detergent additive micelles was investigated.

2 Extraction of overbased sulphonates

A sample overbased calcium sulphonete with a TBN value of 396 corresponding to a calcium carbonate content around 38,2% was obtained. The detergent micelles are dispersed in an oil, most of which must be removed to bring the fraction of inorganic matter towards 80%, the typical figure for content of inorganic material given in [8]

A procedure adapted from [19] was used. A sample of 3.2 g was diluted by 25 ml n-pentane. 30 ml acetone is added making the solution turbid. The sample is then centrifuged 30 minutes in a Hettich EBA III centrifuge at 5000 rpm and subsequently decanted. This yielded 1,4 g of a sticky, amber resin-like substance labelled extract 'A'. In a second experiment, the extraction with pentane and acetone is repeated, using only 5ml n-pentane and 10 ml acetone for the second exctraction. The sample is centrifuged 30 minutes at leaving 1,1 g, designated extract 'B'. After the second decanting the sample was dried in vacuum. The result is transparent amber solid. Examples of such extracts is shown in Figure 1

Figure 1 Extracted calcium sulphonate

IR spectroscopic analysis revealed the same functional groups before and after the extractions. The samples can readily be re-dissolved in pentane without residue. It is therefor assumed that the sample is concentrated overbased calcium sulphonate additive, the difference being the amount of dillutant oil. The content of calcium in sample 'A' was determined by ICP to be 27% corresponding to a theoretical content of than 67.5% $CaCO_3$, although some calcium may be in the from of hydroxide. A comparison of the substances is given in Table 1.

Sample 'B' crumbles to white powder if grinded. It will not melt, but darkens around 380 C. The material lacks strength resistance to solvents both initailly and after heating. A binding material could correct this. This observation is not unexpected, as the existence of such a binder is fundamental to some hypotheses of laquer formation.

TABLE 1 COMPARISON OF POSSIBLE SYNTHETIC LACQUERS.

Property	**'A'** **once extracted**	**'B'** **twice extracted**	**liner** **lacquer**
colour	amber	amber	amber
hexane	soluble	soluble	insoluble
acetone	insoluble	insoluble	insoluble
30% acetic acid	insoluble	sparingly soluble	soluble
texture	sticky	hard but brittle	hard

These hypotheses envision a binding material created by oxidation and polymerisation of hydrocarbon material. Such material can be obtained from the high-pressure rig. It was thereby possible to investigate the properties of a mix of resins from the high-pressure rig and overbased additive extract.

3 Mix of 'test rig varnish' and extracted additive material

An oxidized hydrocarbon varnish was manufactured in the high-pressure rig from a 30 min standard simple test described in Appendix A2. This deposit is solid, but can easily be dissolved in acetone. This material was mixed with extracted micelles to determine the properties of such a mixture. The mixing was realised by the following procedure.

1. The extracted micelles were dissolved in pentane.
2. Dissolved micelles were mixed with varnish dissolved in acetone
3. Acetone and pentane was evaporated at low pressure in a rotating evaporator

Different blending rations were tested. The mixture was initially tacky, possibly because it still contained some acetone and pentane, but hardened with time. The deposit generally adhered to glass, but stronger to it self making it easily peelable and scrapable. It showed simmilar behaviour when deposited on metal. The mix of varnish and micelles would become soluble in acetone as well as pentane, thereby making the deposit less akin to liner lacquer.

Extracted micelles were also mixed with oil prior to a test in the high-pressure rig. In this case, a dry deposit was formed which was scraped away by the scraper device in the rig.

4 Summary

Concentrated overbased detergent share simmilarities with liner lacquer, however they alone do not possess the strength nor the resistance to selected solvents that is associated with liner lacquer. In order to gain these properties, they must somehow be bonded, strengthened or transformed.

Appendix A4

Repeat of a published experiment to synthezise liner lacquer

1 Background

A procedure to sythesize 'liner lacquer' in the laboratory is published in the international patent application WO99/35217 [13]. The synthetic liner lacquer is formed by the following procedure:

Anthraquinone is dissolved in warm (65€) acetic acid to form a saturated solution. This is pipetted onto a warm (60€) steel dish where the acetic acid is evaporated to leave a brown-orange lacquer. [13]

It is evident that this synthetic deposit cannot not contain residues from lubricating oil additives. Such residues constitute the majority of liner depsoits, however the company behind this patent has stated that liner lacquer is:

the direct result of incomplete combustion of the high molecular weight components often present in marine gas oil [11].

Hence this deposit could model the hydrocarbon resin part of the deposit which is often considered the root cause as it is believed to bind the inorganic material.

2 Repeat experiment

The repeat of this experiment revealed several interesting observations.

Anthraquinone is very sparingly soluble in acetic acid. Different concentrations of acetic acid and water were used as well as pure acetic acid.

When pipetted onto a steel dish, crystals of anthraquinone were formed. These crystals were visible to the bare eye, and very simmilar to unreacted pure anthraquinone.

The surface of the test disk attained the brown-orange colour as foreseen, however a control test using pure acetic acid (no anthraquinone) attained the same colour, and was visibly identical to the the first plate apart from the absence of anthraquinone crystals.

It is thus postulated from these observations that:

- Anthraquinone does not react in this test with either acetic acid, water of the metal surface.
- The 'deposit' seen in this test is oxidation of the metal which is accelerated by the acetic acid.

A brief EDS investigation of the test surface detected principally iron and oxygen which substatiated this view. The amber deposit was not suitable for investigation by IR as it was very difficult to remove. Although the crystals found on the surface could be scraped away, they were not investigated as they did not resemble liner deposit.

This approach to synthesize liner deposits was not investigated futher.

Appendix A5

Engine Test

The engine test was performed on a KR3 engine test bed. The background for this engine test was an attempt to replicate deposit case as explained in section 4 'experimental work'. Main particulars of the test engine are given in Table 1. The measures to provoke deposit formation are listed below:

Poor fuel

A mix of 50% LCO (light cycle oil) and 50% COLGO (coker light gas oil) was used for fuel except to start and stop which was done on regular diesel fuel. The cetane index of the test fuel was low, 36.2, density high 0.8779 as was aromatic content while the sulphur level was low. Fuel data is provided in Table 2.

Poor lubricant

A standard lubricant was diluted by 5% fuel which would decrease the oxidation stability of the lubricant. 5% represented the maximum dilution possible without bringing the calculated lubricant viscosity below the engine design minimum.

Variable load cycle

The engine load was cycled 1 hour idle / 1 hour 'full load' (16 bar BMEP) generator speed a total of 76 test hours. Since no deposits were formed a second test was cycle consisting of 2 hours at 100 bar BMEP at 500 rpm (near the TC surge line) and 30 min at 18 bar full speed was run for a total of 25 hours.

TABLE 1 ROLLS ROYCE KR3 ENGINE DATA

Data	**Unit**	**Value**
Stroke	[mm]	300
Bore	[mm]	250
No. cylinders	[-]	3
Mean Effective pressure, max	[bar]	22
Speed, max	[rpm]	900

TABLE 2 TEST FUEL ANALYSIS

Analysis	**Method**	**Unit**	**Value**
Density at/15 °C	D-4052	kg/l	0.8785
Sulphur (XRF)	D-4294	mass-%	0.037
Cetane Index	D-4737		36.4
Total aromatics	IP391/95	mass-%	52.6
Mono aromatics	IP391/95	mass-%	39.5
Di aromatics	IP391/95	mass-%	11.3
Tri aromatics	IP391/95	mass-%	1.8
Kin visc. @ 40 C	D-445	mm^2/s (cSt)	2.479
Con.carbon 10%	D-4530	mass-%	<0.1
Distillation	D-86		
IBP		°C	156.6
5 %		°C	189.1
10 %		°C	200.2
20 %		°C	219.6
30 %		°C	235.9
40 %		°C	248.2
50 %		°C	256.6
60 %		°C	273.6
70 %		°C	291.2
80 %		°C	312.2
90 %		°C	335.7
95 %		°C	350.3
FBP		°C	358.6

Appendix A6

Surface Measurement Procedures

This appendix may seem large considering the somewhat crude-looking surface measurement results presented in the thesis. However since surface measurements are crucial in determining the presence of deposits, these considerations are very important, particularly to the inclined surface rig.

1 Equipment data and suitability

Technical data for the profilometer used in this work is given in Table 1. In practical terms, these data define the measuring conditions and imply that the instrument will not reliably detect wavelengths exceeding 0.8 mm or the full depth of cracks narrower than 5   m.

Instrument resolution is depending upon the variation in height along the sample and instrument setting. If the centerline deviation is less than 20   m in both directions a 10 nm resolution can be obtained, otherwise the resolution is 20 nm.

TABLE 1 INSTRUMENT DATA

Feature	**Description**
Instrument	Hommelwerke T-500
Stylus diameter	5 m
Skid longditudal diameter	30 mm
Cut of lenght (selected)	800 m
Effective traverse length (selected)	4.0 mm
Resolution (depending on surface)	10 (20) nm
Surface Parameters	Ra, Rz, Rmax

A leading engine builder specifies the width of the deep grooves to range from 25-70 m with a maximum depth up to 16 m. The honing process makes the simultaneous occurrence of maximum depth and minimum groove width unlikely. However, maximum depth and minimum groove width may be used to define a borderline case to represent the most pointed cracks. This borderline groove and circle representing the stylus point is drawn to scale in Figure 1.

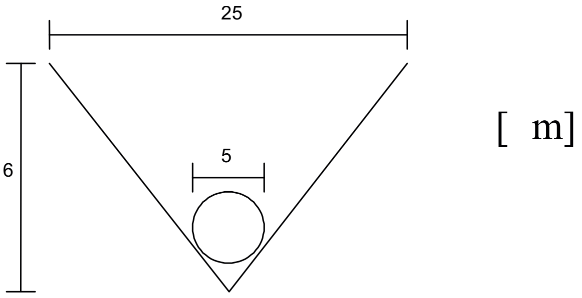


Figure 1 *Schematic of borderline crack and stylus point.*

The stylus will detect almost 90% of the depth of this extreme groove. The 5 m tip stylus is thus capable of detecting the deep groves of a liner manufactured to the above-mentioned specification with reasonable precision. The widest grooves according to this specification are 70 m, which is less that 10% of the maximum detectable wavelength. The instrument may therefore safely be used to measure the honing grooves of the surface.

2 Measurement errors

The sources of error can be categorized as:

1. intrinsic instrument error
2. instrument drift and decay
3. contaminant error
4. random effects

Intrinsic instrument error

The intrinsic instrument error was investigated by making 25 measurements on a uniform test surface. The instrument was not moved between measurements. Results are presented in Table 2.

TABLE 2 TEST MEASUREMENTS

	Average	**Max**	**Min**	**Range**	**Emp.st.dev**
Ra	2.9096	2.9200	2.9000	0.0200	0.0035
Rz	9.1552	9.1700	9.1400	0.0300	0.0087

The intrinsic instrument variation is relatively low; the variation in the empirical standard deviation is smaller than its resolution. There may also be a constant error term as the test plate certificate claims a higher Ra (= 2.975). No other parameters are certified. The certificate value is measured using an instrument with a finer stylus tip and a different filter, as well as a different measurement procedure, all of which may account for part of the discrepancy. Fortunately, a static error is of less concern as the purpose of our measurement is to monitor change and constant error terms will cancel out when change is considered.

Instrument drift and decay

The instrument is pre calibrated, however the instrument performance may deteriorate over time. This applies both to the electronics and the mechanical stylus drive, but also to wear of the stylus itself. Drift and decay is monitored by routine testing using a pre calibrated test specimen. Excluding a case where a stylus was damaged and replaced, significant instrument drift has not been observed.

Contaminant error

The nature of surface profilometry makes it vulnerable towards contamination. Small debris can alter the profile and characteristic values. Liners and test plates usually have a thin residual oil film. Residues of solvents and cloth may also be present if cleaning has been attempted.

The effect of a liquid film will naturally depend upon its thickness and viscosity. Figure 2 shows the effect of several substances on roughness measurements.

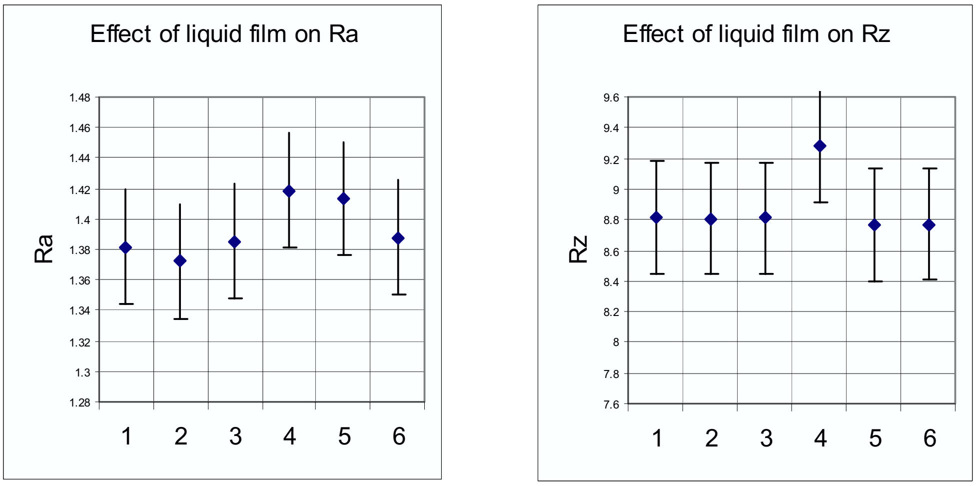


Figure 2 *Average of 15 observations with 95% confidence interval for another average of 15 observations.*

1. Clean liner
2. Liner with water
3. Liner with 30% acetic acid, (70 % water)
4. Thick oil film
5. Liner with thin oil film (wiped clean)
6. Liner after thorough wiping

The Ra value observed with the thick oil film (4) is barely outside the 95% confidence interval based on the clean liner. The corresponding Rz value is clearly outside. When the liner is wiped clean (5), the Rz returns to normal while the Ra value is still high, although within the 95%

confidence interval of the clean surface. Thorough wiping (6) practically restores the surface

The oil film caused an *increase* in Ra of 3% and Rz of 5%. The increase in observed roughness may be contrary to expectation as it is natural to assume that the oil will dampen the movement of the stylus. This effect, however, is small in comparison to the lifting effect the oil film is likely to have in the skid. These results show that unless the oil film can be properly removed, Ra and Rz will be overestimated. Ra is also more sensitive to liquids because Ra is dependent upon the baseline, while Rz is baseline independent.

Random effects
Unknown factors that were not present when the instrument intrinsic error was assessed may also contribute to measurement errors.

2.1 Analysis based upon average measurements

The average is an estimate of an inherent surface property. This can be expressed as follows:

$$r_x = r + r_{lx}$$

where

r_x	Roughness at location x
r	Inherent surface roughness
r_{lx}	Local surface roughness effect

and $\lim_{n \to \infty} \sum_n r_{lx} = 0$ for measurements within a defined area.

However, measuring r_x introduces errors.

$$r_{xm} = r + r_{lx} + e_m$$

r_{xm}	Measured roughness at location x
e_m	Measurement error

The precision of the average as an estimator of r

$$\hat{r} = \frac{1}{n} \sum_n r_{xm}$$

relies on the implicit assumptions that $\lim_{n \to \infty} \sum_{n} r_{lx} = 0$ and $\lim_{n \to \infty} \sum_{n} e_{m} = 0$.

By definition, the first assumption holds true if the area restriction is not violated. The second assumption is true only in special cases. However, the law of large numbers requires the error to approach some value e_0 when $n \to \infty$

thus $\hat{r}$ is really an estimate of $r+e_0$

Types of errors are summarized in Table 3.

TABLE 3 MEASUREMENT ERRORS

ID	Source	Type	Comment
1	intrinsic instrument error	Static	Small
2	drift	Static	Measurable, controlled
3	contaminant error	?	Must be avoided
4	random effects	Random	Averages to zero

Within this work, the purpose of roughness measurement is to monitor change or to compare results with other measurements made with the same equipment. A small static contribution to e_0 is thus not a problem.

3 Measurement Procedures

All surfaces have random variations such that two measurements with a perfect instrument will be different unless the instrument is perfectly relocated or they appear the same by chance. Relocation sufficiently accurate to measure the exact same trace before and after some process is not possible with the equipment used in this project.

Using the results from repeated measurements is the only viable option. Local effects must be considered when averaging is used. A key issue is to assess the effect of local variations and their frequency (or area).

The measurement procedure must specify the area in which measurements are to be made, the number of measurements required to obtain a reasonable estimate and how to avoid contaminant errors.

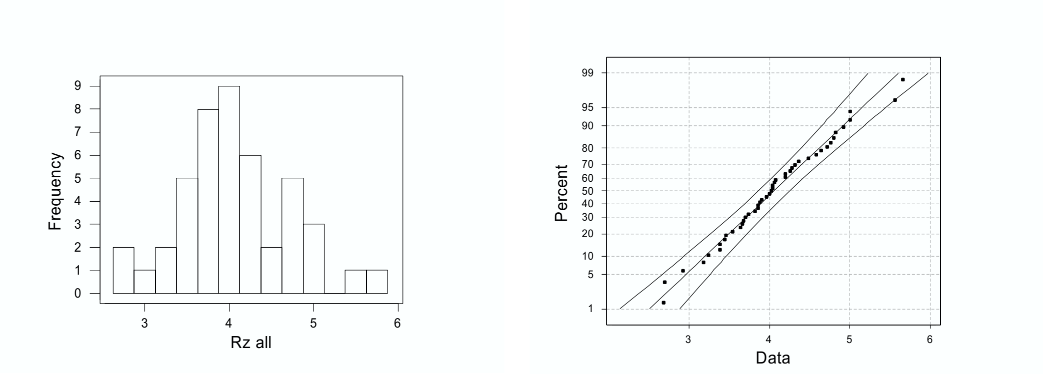
Furthermore, a decision must be made upon which surface parameters are most suitable. Because different surface characteristics emphasize different surface features, their response to possible local variations may differ. In this context, the parameter that is most resistant to (or ignorant of) local variations may be preferable because it will be more reproducible. However, it must be sensitive to deposit buildup.

Measurement statistic

The surface characteristics of a honed cylinder liner are not entirely well approximated by the normal distribution, as shown in Figure 3.

Rz - Histogram

Rz - probability plot



Ra - Histogram

Ra - probability plot

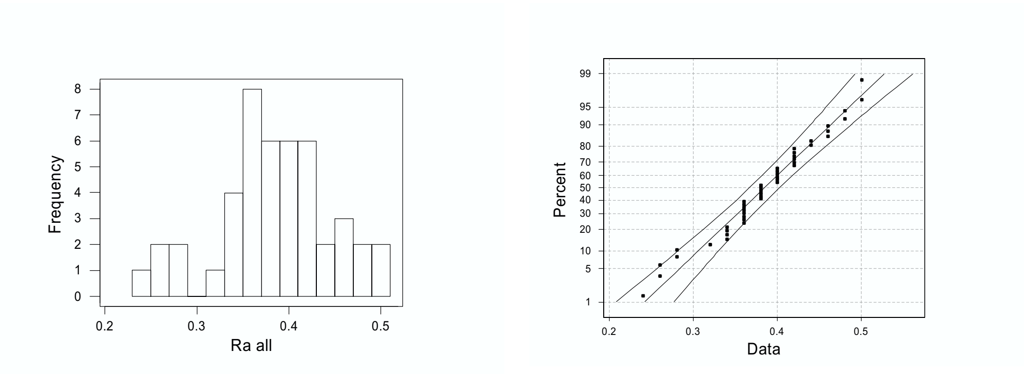


Figure 3 *Distribution of Ra and Rz sampled in one location on an arbitrary plateau honed liner sample.*

It appears that some values are much less likely to occur than would be expected from a normal distribution. This effect is probably induced by 'stepwise' increases in roughness when additional honing groves are encountered by the stylus.

Extreme values may have undue influence on the average, particularly when few measurements are made. The possibility that other statistics like the median or the average after filtering high and low values may give a more consistent description of the surface should be investigated using a substantial data set.

The behavior of different statistics on Ra and Rz was evaluated using three measurement series of thirty measurements on three different test disks, bringing the number of individual measurements to 270. 5 statistics were compared:

- the average value
- the median value
- the mean after removing the upper and lower 20 % (filter)
- the mean after removing the upper 10 % and lower 30% (bias +)
- the mean after removing the upper 30% and lower 10% (bias -)

Since the plate has not been altered, the statistic that displays lesser change between series is the better. The biased estimators were less stable as were the median in case of Ra. The median could be affected by the resolution of these measurements (0.02) which is relatively large compared to Ra. The filtered and unfiltered averages both seemed well suited, but the relative change in Ra was smaller than Rz.

The selection of Ra or Rz is not only a question of stability, but also the sensitivity of the parameter to deposits as discussed in appendix A1.

Number of measurements required

The number of measurements and uniformity of the surface influences the minimum change in roughness that 'always' will be detected with high statistical significance. In the event that two estimated roughness values are to be compared, a hypothesis test must be constructed. Because the variances are unknown, the t-distribution must be used. The probability of accepting the null hypothesis as a function of number of measurements and the true difference is shown in the operating characteristic curve. The operating characteristic curve of a two tailed test at 95% confidence is shown in Figure 4.

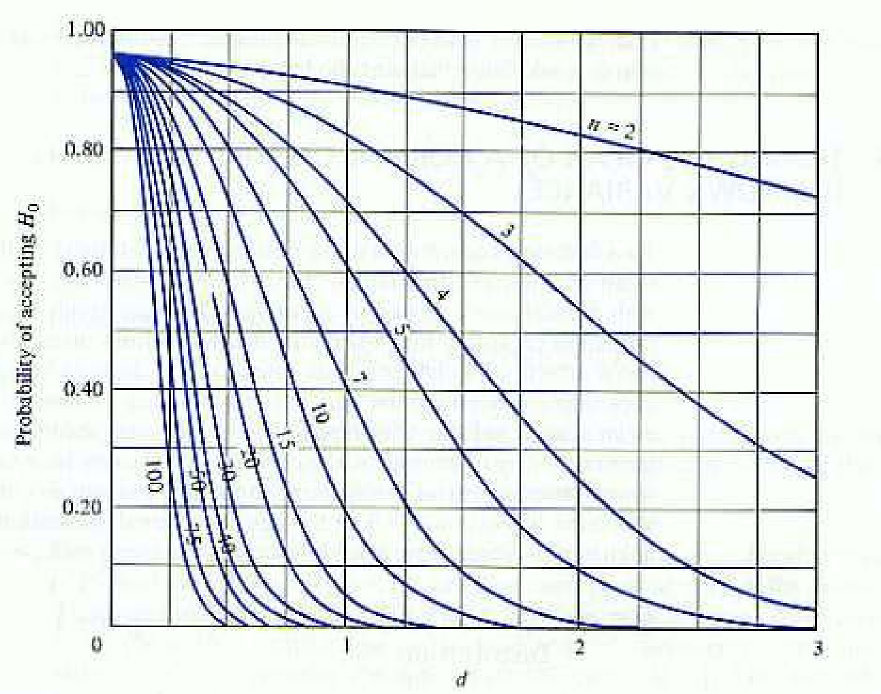


Figure 4 *OC curve for t test at 5% significance level. From [102]*

The y axis shown the probability of accepting the null hypothesis while the x axis is the standardized difference in true means, d

$$d \text{ ㅂㅌ} \frac{\left| {}_0 \text{ ㅈ} \right|}{O}$$

The figure shows that at n=100 measurements, d must be about 0.5 for a near zero probability of accepting H_0. In other words, the detection limit at 100 measurements is 0.5O Using 5 measurements, the detection limit would be 3O If the confidence level of the test was increased, the detection limit would increase as well.

The variance can estimated as the empirical standard deviation S, but the precision of this estimate is low.

The ㄹㅂㅅlevel confidence interval for the estimate of the variance is given by:

$$\frac{(n-1)s^2}{\chi^2_{\alpha/2}} \le \sigma^2 \le \frac{(n-1)s^2}{\chi^2_{(1-\alpha)/2}}$$

The confidence intervals for the variance at α=0.10 is shown in Table 4.

TABLE 4 CONFIDENCE INTERVALS FOR VARIANCE AT α=0.10

n_p	$\frac{(n-1)s^2}{\chi^2_{\alpha/2}}$	$\le \sigma^2 \le$	$\frac{(n-1)s^2}{\chi^2_{(1-\alpha)/2}}$
10	0.37 s^2	$< \sigma^2 <$	1.88 s^2
30	0.61 s^2	$< \sigma^2 <$	1.47 s^2
60	0.72 s^2	$< \sigma^2 <$	1.32 s^2
180	0.83	$< \sigma^2 <$	1.18

The confidence interval is large even at n=60. A precise estimate of the variance for each plate is impractical. However, in selecting n=15 the pooled sample variance is calculated from n_p=2n=30 observations and $p(\sigma^2 < 1.5\ s^2) > 0.95$. Thus

$\sigma^2_{max} = 1.5\ s^2$ <=> $\sigma_{max} = 1.22\ s$

is a conservative estimate of the variance. A conservative detection limit δ_{min} at 5% significance level for different sample sizes is estimated in Table 5.

TABLE 5 MINIMUM DETECTION LIMIT ESTIMATE

n	σ^2_{max}	σ_{max}	d	δ_{min}
5	1.88 s^2	1.37 s	3.00	4.1 s
15	1.47 s^2	1.21 s	1.38	1.7 s
30	1.32 s^2	1.15 s	0.95	1.1 s
90	1.18 s^2	1.09 s	0.5	0.54 s

This relationship has been investigated for three types of surfaces using averaged surface data. The surfaces that were investigated were

1. Standard honing procedure, unused surface
2. Very fine plateau honed surface
3. Run in cylinder liner (scrap)

Data collected from three such samples with conservative detection limit is given in Table 6. For ease of comparison, a relative detection limit is estimated as:

$$\text{ㅅㅈ}_{\min,r}\ \text{ㅂㅌㅅㅈ}_{\min}/\bar{R}_i$$

TABLE 6 TEST PLATE SAMPLE DATA AND RELATIVE DETECTION LIMIT ESTIMATES

Plate		n=5			n=15			n=30		
		$\bar{R}$	s	$\text{ㅅㅈ}_{\min,r}$	$\bar{R}$	s	$\text{ㅅㅈ}_{\min,r}$	$\bar{R}$	s	$\text{ㅅㅈ}_{\min,r}$
1	R_z	7.44	1.29	0.81	7.18	0.81	0.19	7.64	1.05	0.15
	R_a	1.04	0.11	0.50	1.02	0.11	0.18	1.11	0.17	0.17
2	R_z	7.11	0.45	0.30	7.37	0.53	0.12	7.32	0.51	0.08
	R_a	1.20	0.07	0.27	1.21	0.05	0.07	1.22	0.09	0.08
3	R_z	7.71	0.17	0.10	7.13	1.03	0.25	7.24	0.92	0.14
	R_a	0.86	0.15	0.82	0.83	0.13	0.27	0.84	0.13	0.17

It is important to realize that due to the randomness in the determination of s^2, the estimates of $\text{ㅅㅈ}_{\min,r}$ are themselves random variables and must be interpreted accordingly.

A difference in surface uniformity between the test plates is apparent. In this instance, the minimum detection level on the plateau honed test plate is almost halved compared to the other plates.

If the number of measurements is increased from 30 to 90, then $\text{ㅅㅈ}_{\min}$ is reduced from 1.1s to 0.54s, effectively halving the detection level if the estimated coefficient of variation is unchanged.

It is thus reasonable to assume that a 10% detection level is obtained with 30 measurements if a plateau honed disk is used, or else 90, although more experiments would be necessary to substantiate this. Further elaboration of this point is not justified, but the actual detection limit can be determined in the analysis of each test.

4 Test plate measurements procedure

In the field, the magnitude of change in surface parameters due to deposits has been observed to exceed 40%[1], however it is desirable to detect lower deposit levels in the lab rig.

While perfect relocation of the profilometer is not feasible, it is still possible to relocate the instrument within a small area by use of a guide. The test plate and guide is illustrated in Figure 5. The guide is placed over the plate and longitudinally positioned by aligning the rear edge of the guide with that of the plate. The profilometer is aligned with the test plate and placed upon it with its 'nose' centered on one of the tick marks on the guide. The tick marks are distributed 5 mm from the center position.

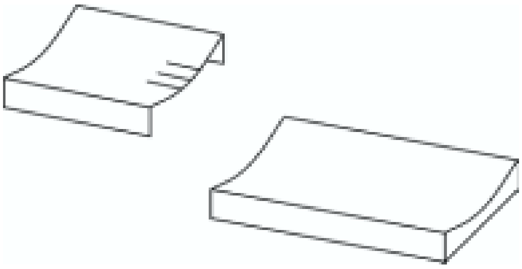


Figure 5 Test plate and guide

A procedure was developed to make measurements that represent the area immediately behind the tick marks on the guide.

1. A guide indicating three possible transverse positions of the 'nose' of the profilometer is placed upon the test plate.
2. The instrument is placed at the center position and a measurement is taken

---

[1] Measured before and after cleaning with acetic acid.

3. The instrument is then moved to position left and a measurement is taken
4. The third measurement is made at position right.
5. The fourth is made with the nose centered between the left and the center mark.
6. The fifth is made with the nose centered between the right and the center mark.
7. Subsequent measurements are made in repeating order

Deposits may vary along the length of the test plate. It is therefore necessary to systematically measure the deposit at different longditudal positions. The test plate is illustrated in Figure 6. The colored area is the area that is swiped by the piston ring. A, B and C indicate the longditudal positions that are used, 45, 30 and 16 mm measured from the right edge of the plate. In the transverse direction, measurements are centered on the centerline.

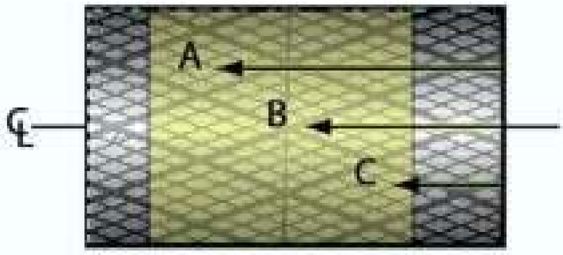


***Figure 6** Illustration of instrument placement on the test plate*

The area that is covered by these traces are shown in Figure 7

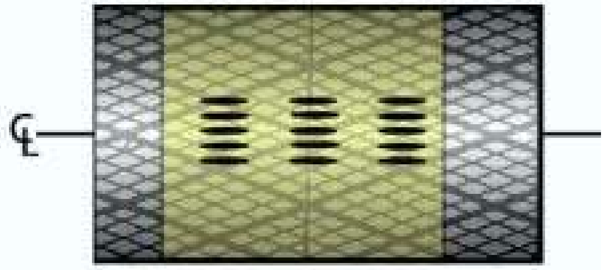


***Figure** 7 Illustration of area covered by measurements on the test plate*

5 Field measurements procedure

Field measurements differ from those in the lab in many respects

1. The instrument must be held in position by hand
2. The area to be investigated (cylinder surface) is much larger than the test plate
3. Time pressure to finish and limited opportunities for control measurements
4. The test surface and environment is frequently more dirty than lab conditions
5. It is more difficult to assess wear effects, making interpretation more challenging.

Point one and four introduces an extra error; point four could perhaps be mitigated by cleaning of the cylinder liner. Cleaning, however, may disturb the deposit, and is therefore limited to wiping with a soft cloth.

Since only a limited number of surface traces can be made, the selection of measurement locations must be done with care in order to make them as informative as possible. One possible strategy is to randomize the location of all the measurements and consider the average. This would cancel out any unknown effects; however it would deprive us of information about local variations. Anticipated in-engine effects that should be considered are:

1. piston induced wear, thrust and anti-thrust side as well as 'inert' sides
2. gas flow and temperatures - inlet and exhaust sides
3. distance from combustion, liner temperature

The following locations were selected: Piston thrust side and positions rotated 90, 180 and 270 degrees from this position were selected as were three measurement heights, 20, 45 and 70 % down into the liner. Initially, only two measurement heights were used. These positions are identified on the liner by means of a guide with 2x3 cm windows as shown in Figure 8.

A total of twelve locations must be measured per cylinder. Time usually limits the number of measurements in each location to five.

Measurements are made at random locations within the guide windows. Experience indicates that the average of five measurements may not yet have converged. Comparing individual locations is therefore not likely to be meaningful, however when height or position is grouped, the number of observations is 15 or 20, which increases the power of our comparisons. Because multiple cylinders are measured at each engine inspection and engines are inspected several times throughout a case study, the complete data set is clearly capable of monitoring major trends.

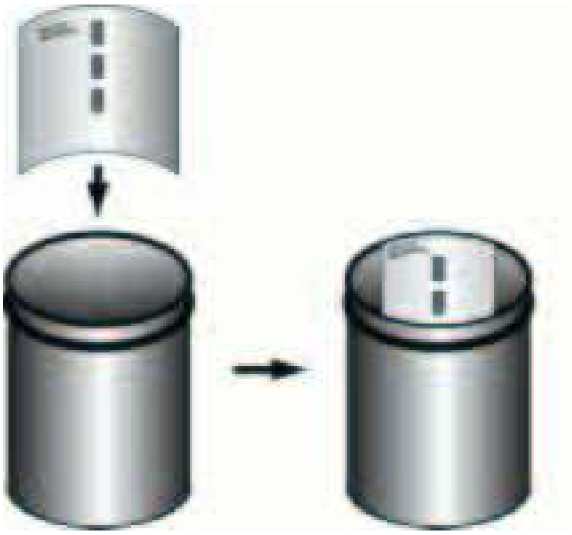


Figure 8 *Guide to identify positions on the liner.*

The procedure for field measurement is as follows

1. Thoroughly wipe the surface with a soft dry rag
2. Position the guide
3. Make 5 measurements in random locations within each guide window

Appendix 7

Deposit solubility tests

1 Solubility tests in the SEM laboratory

The effect of solvents on 'glaze' and 'lacquer' cylinder liner deposit samples was investigated using the SEM. The following solvents were tested:

1. Water
2. Acetone
3. Chloroform
4. Benzene
5. Methanol
6. 30% acetic acid in water

These tests were performed by studying a randomly selected sample with deposits before and after treatment with the solvent in question. The treatment consisted of four series:

1. Placing a drop of solvent on the deposit sample, letting it work 30 seconds before it was carefully dried off using a cotton stick
2. Vigorously washing with cotton sticks and solvent.
3. Storing the deposit sample immersed in solvent
4. Ultrasonic cleaning in solvents

Figure 1 Liner lacquer deposit prior to acetic acid sprinkling

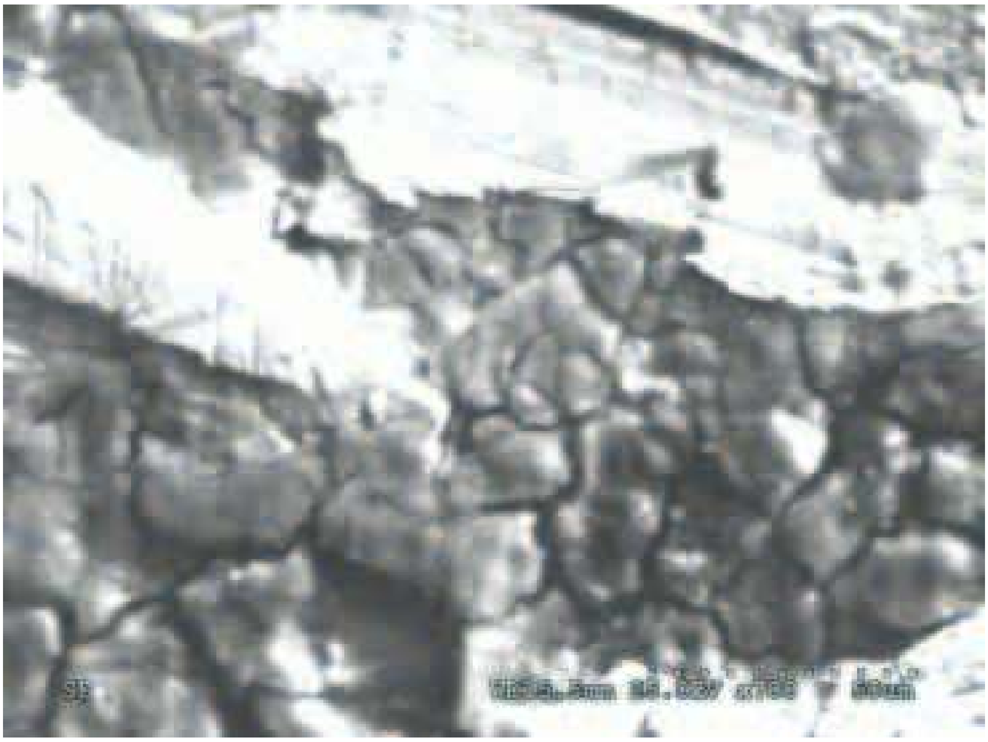


Figure 2 Liner lacquer deposit after brief sprinkling of acetic acid

These test revealed that acetic acid was the only of the selected solvents capable of removing these deposits. The SEM study also showed that small pockets with deposit frequently remained in inaccessible locations after cleaning with acetic acid.

The initial effect of acetic acid on the deposit is shown in *Figure 1* and *Figure 2* which show the same area before and after treatment. A void is seen in the lower left corner of *Figure 2* which is not seen in *Figure 1*. It thus appears that the acetic acid removes deposit by delamination rather than chemical dissolution. Possibly, the acid penetrates these cracks and dissolves a boundary layer between the deposit and the liner surface.

2 Solubility tests in the field

The composition of cylinder liner deposits is variable; hence the solubility of the deposit is also variable. In some cases deposits have been soluble in water in spite of water having no effect on the deposits investigated in the lab. Since deposit material may be removed by delamination as indicated in *Figure 1* and *Figure 2*, the number of cracks in the deposit could be important to its ease of removal.

Tests with hexane and acetone have removed material to stain the cloth used to clean the surface, but failed to restore the surface roughness. 30% acetic acid in water is usually an effective solvent for deposit; however in certain cases the use of this results in the formation of a grey film which will not be removed by acetic acid or any of the aforementioned solvents.

Appendix 8

Inclined liner surface rig photos

1 Original rig

Fig.1 Original rig

2 'Improved' rig

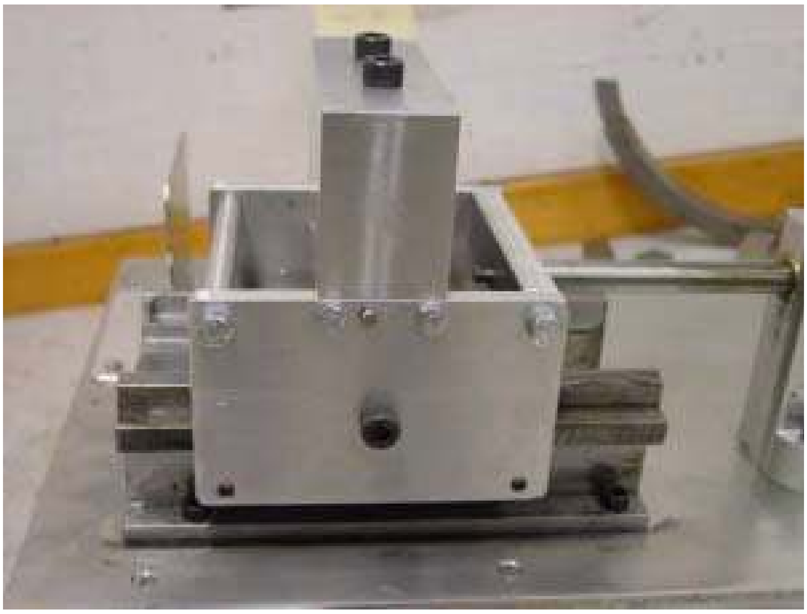


Fig 3. Rigid wagon carrying piston ring assembly

Fig 4. Wagon carriage seen from front (Heating block not mounted)

3 Miscellaneous

Fig. 5 Peristaltic pump

Fig. 6 Test plate

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