THE DEVELOPMENT OF HIGH QUALITY LUBRICATING OIL FOR TRUCK'S ENGINE

[IMPACT OF SOOT CONTAMINATION ON METAL WEAR AND OIL PROPERTIES USING FOUR-BALL TRIBOLOGY TEST]

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ABSTRACT

Internal combustion engine produces soot as a result of incomplete fuel combustion. Ideally, complete combustion in cylinder would only produce carbon dioxide and water, but no engine is completely efficient. In automotive engine oil, soot has a detrimental effect on engine life. It is the cause of increasing more wear of the engine parts which lubricating oil flow through.

This thesis is a study of the characteristics of soot in the internal combustion engine affecting on the abilities of lubricating oil and leading to result in engine components wear. The behavior was studied by means of a Four-Ball tribology test with friction and wear measured and also investigate wear roughness in micro-scale by high resolution optical microscope and 3D rendering optical technique. Soot particle contamination was simulated using carbon black. Effects of oils with different additive on size distribution was studied by laser diffraction technique. Morphology and nanostructure of particles were studied by transmission electron microscope. Moreover, physical and chemical properties of used oil were investigated and determined soot contamination.

The results showed that soot contaminated in engine used oil is about 1% by weight and it affected on changing oil's properties. Modern oil additives can control the agglomeration of soot very well by keep soot size in small diameter. Based on tribology test, soot contamination in oil made more wear on tested steel ball and reduced friction during test comparing to the test with fresh oil.

In conclusion, the appropriate particle size, which is near to oil film thickness between metal surface contacts, is the dominant cause of making wear. By the way, the too large particle size compared to oil film thickness will escape out and too small particle size will not effect on wear. Furthermore, high level of proper particle size contaminated in oil will increase probability of rubbing process then make contact surface smoother or make lower in roughness.

Keywords: Internal combustion engine, Soot, Engine life, Lubricating oil, Engine component wear, Four-ball tribology, Roughness, Laser diffraction technique, Oil additive, Oil film thickness.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

Page

CHAPTER 1

INTRODUCTION

On the introduction chapter, it consists of the significance of this thesis which present about the problems of soot to automotive engine then followed by the objectives of this study and the limitation of the study.

1.1 Statement and Significance of Problems

Automotive engine oil constitutes about 55–60% of the total world lubricants and fluids. These lubricants have also attracted maximum attention of engine manufacturers, standardization organizations, and organized users, resulting in defining the automotive oil quality very clearly. However, this extensive activity brought in complexities in the development and evaluation of automotive passenger car oils. Environmental issue also led to extensive improvements in engine design and oil quality. In passenger cars, both gasoline and diesel engines are used.

In a motor engine, the critical parts that wear out are the piston and ring assembly, liners, valve train, valves and bearings. The minimum lives of these parts determine the life of an engine. In a normal engine, the natural wear is far less than the wear due to contaminants in the oil, such as metal debris, dust from environment in which the engine is working, and the most important contaminant is the soot.

Soot particle has a detrimental effect on the life of internal combustion engine. It has been disputed for a long time about soot behavior and continues to be high interesting to car manufacturers. Internal combustion engine produces soot as a result of incomplete fuel combustion. Ideally, complete combustion in cylinder would only produce carbon dioxide and water, but no engine is completely efficient.

Nowadays, wear mechanism induced by the presence of soot is not fully cleared yet. More fundamental knowledge is needed. Thus, the properties of soot and their influence on wear and also friction were in the focus of my thesis. To success, how soot behave to engine metal surface, tribology test has been conducted to this thesis.

1.2 Goals and Objectives

These are several objectives of this thesis which were set to be met with the knowledge about the soot behavior and the mechanism on engine wear as following.

1) To investigate diesel engine lubricating oil properties after use in both physical and chemical properties.
2) To investigate the amount of soot contamination in diesel engine used oil.
3) To study morphology of soot from diesel engine exhaust system and commercial carbon black.
4) To study the effect of modern oil additives on soot particle distribution in liquid and oil.
5) To study the effect of soot contamination in oil on metal wear
6) To study the effect of soot contamination in oil on friction

1.3 Scope of the Study

This study is try to investigate used oil from only in diesel engine. It is not included the data from gasoline engine. The tested used oil is kept from different type of passenger car and truck. No attempt to control the type of car. This is to investigation the information from wide range of the uses.

About soot particle, it is sampled from exhaust pipe of diesel dyno engine. Normally, on dyno, engine can be controlled to vary load and engine speed. However, this study is not try to study the effect of load and speed on soot properties. Soot is kept form tail pipe of various load and speed randomly.

Commercial formulated oils are used in this study for testing the ability of dispersing soot and the properties relating to wear and friction. They are all same SAE viscosity grade which are the grade that generally used. This is not try to compare with the special viscosity grade or racing grade.

The Bottom Line

The information above induced the author doing this thesis. Next chapter will be explained the theory and the study of other researchers which lets us known the results of experiments that have done. Then, the author has already the clearly designed the methodology for doing case studies on chapter 4, and followed by the results of each cases and also conclusion on chapter 5 and 6, respectively.

CHAPTER 2

LITERATURE REVIEW

In crankcase engines, lubricating oil is filled in the sump and is splashed or pumped onto the various parts of the engine during its operation. The oil has to carry out several functions in addition to reducing the friction between moving surfaces. It has to provide a seal to the cylinder, cool the engine, transport soot, sludge, and wear particles to the oil filter. Soot, sludge, and other deposits are formed during the combustion process of the fuel. The oil is also subjected to a wide range of temperature, -40°C in arctic region to above 300°C under the piston crown. The blow-by gases, soot, and sludge particles produced by incomplete combustion go into the oil. Therefore, most of the engine lubricant problems are related to these issues, that is, entry of fuel combustion products in crankcase and decomposition/oxidation of lubricant itself at high temperatures in the presence of various metals and materials present in the system.

The main causes of engine malfunction due to fuels and lubricant quality are as follows, expressed by Guatum [1]:

1) Deposit and sludge formation at different parts of engine
2) Contamination such as dust and dirt, wear particles, coolants, and water
3) Fuel and lubricant oxidation products
4) Oil thickening due to thermo-oxidation and soot loading
5) High oil consumption due to oil evaporation and high wear
6) Ring sticking due to deposits in piston grooves

The goal of this thesis is to study the characteristics of soot in the internal combustion engine that affecting on abilities of lubricating oil and lead to result in engine components wear. To understand how soot behaves to lubricating oil and engine component, a number of literatures were reviewed as the following topics.

2.1 Soot Generation

Soot is a microscopic carbonaceous particle that is a product of incomplete combustion of hydrocarbon. It consists of carbon, ash, and unsaturated hydrocarbon (unburned hydrocarbon). The unsaturated hydrocarbon are essentially acetylene and polycyclic aromatic hydrocarbons. These components have particularly high levels of acidity and volatility. Measurements have shown that it typically contains 90 percent Carbon, 4 percent Oxygen, and

3 percent Hydrogen with the remainders consisting of Nitrogen, Sulphur, and traces of metal. These have been investigated by Clague *et al.* [2].

From a number of literatures, it has been found the fact that the properties of soot particle very much depend upon thermodynamic of combustion in the engine. The structural complexity of soot varies depending on type of engine and its operating conditions. The primary soot particles are typically spherical in shape. While most are only around 0.04 microns in size, they often clump together to form larger particle. Because of soot's colloidal properties, the particles agglomerate up to size of approximately 500 nm, with a mean soot agglomerate size of 200 nm.

In 2002, Lee *et al.* [3] studied in a topic as "Morphological Investigation of the Microstructure, Dimensions, and Fractal Geometry of Diesel Particulates". They had investigated morphology of diesel particulates and analyzed size distribution of primary particles. There was soot from diesel engine at three different operations, low load, medium load, and high load condition. They found that mean size of soot from low load condition (engine operate at 675 rpm and no load) is 34.4 nm. Mean size of soot from medium load condition (operate at 1400 rpm with 15% load) is 32.3 nm. Last condition (1400 rpm with load 50%), mean size is 28.5 nm. This has been noticed that soot size become smaller when engine operates at high pressure which represented by the case of high load condition.

Soejima *et al.* [4] investigated size of soot in 4 lubricating oil samples, SAE 10W-30 used oil, SAE 20 oil with 5% soot, SAE 20 oil with dispersant additive and 5% soot, and SAE 20 with dispersant and ZnDTP additive and 5% soot. Finally they analyzed the distribution of soot size and found that sizes are 54 nm, 2.935 μm, 433 nm, and 323 nm respectively. This may be noticed that oil additive may affect to soot distribution when contaminating in oil.

In 2004, Park *et al.* [5] studied in a topic as "Structural Properties of Diesel Exhaust Particle Measured by Transmission Electron Microscopy (TEM): Relationships to Particle Mass and Mobility". They had set the diesel engine operation at 1400 rpm with 50% load, then measured particulate size emitted from exhaust pipe. They suggested to say that average diesel soot size is 32 nm.

In 2005, Zhu *et al.* [6] studied in a topic as "Effects of Engine Operating Conditions on Morphology, Microstructure, and Fractal Geometry of Light-duty Diesel Engine Particulates". They were interested to compare particulates changing due to different engine operating conditions. They found that soot diameter size is 29 nm as engine operating at 780 rpm and non-load, and 20 nm at 2500 rpm with 100% load.

In 2013, Bhowmick *et al.* [7] studied in a topic as "Influence of Physical Structure and Chemistry of Diesel Soot Suspended in Hexadecane on

Lubrication of Steel-on-steel Contact". They had compared the soot collected from 3 different sources, fire flame, engine oil, and engine exhaust. They concluded the flame soot is smaller than engine. Mean diameter of flame agglomerate and diesel soot agglomerate are 350 nm and 450 nm, respectively.

Rocca *et al.* [8] studied in a topic as "The Nanostructure of Soot-in-oil Particles and Agglomerates from an Automotive Diesel Engine". They had shown the distribution curve of primary particle size collected from heavy duty diesel engine, and found that the primary particle diameters are 10-35 nm and mean value is 20 nm.

In 2014, Wang *et al.* [9] studied in a topic as "Effect of Lubricant Oil Additive on Size Distribution, Morphology, and Nanostructure of Diesel Particulate Matter". They had provided the statistical results and size distributions of primary particles. For pure diesel, the mean primary particle diameters are 22 and 25 nm at 1200 and 2400 rpm, respectively. While for blended fuel, the values are 24 and 21 nm at 1200 and 2400 rpm, respectively.

Because of the way that fuel is injected and ignited, soot formation occurs more commonly in diesel than in gasoline engine. Unlike gasoline engine, where the fuel-air mixture is ignited with a spark, fuel and air entering the diesel cylinder ignite spontaneously from the high pressure in combustion chamber. The fuel and air mixture in diesel engine typically do not mix as thoroughly as they do in gasoline engine. This creates fuel-dense pockets that produce soot when ignited. Diesel engines are operated at higher air-to-fuel ratios, which tend to produce greater levels of engine soot. While the majority of soot easily escapes through the exhaust, some gets past the piston rings and ends up in lubricating oil.

The majority of modern diesel engines operate using direct fuel injection and swirl within the combustion chamber to assist fuel-air mixing. Combustion initiates close to the injection point and occur very rapidly as a diffusion flame. At this point, the air and fuel mix well, but the mixture is very fuel rich, causing very high levels of soot to be produced. After diffusion burning, the combustion process progresses through the rest of the combustion chamber, which slowly burns the majority of the remaining fuel. This slow burning produces more particulates and unburned hydrocarbons at the end of combustion process.

Throughout the combustion process, soot particles are produced and destroyed. They are created by the process explained above and destroyed by oxidation. Oxidation is a mechanism that occurs when soot come into contact with various oxidizing species. When this happens, the hydrocarbons that are trapped inside the soot are burned out and the particle size reduces. During the diffusion burning stage of the combustion process, the soot particles produced in the initial phase of the combustion process come into contact with a much higher volume of air compared with fuel, and a large proportion of the soot particles are oxidized.

Further oxidation is required to reduce the amount of soot finally exhausted. When the exhaust valve opens, the combustion products are emitted to the exhaust system, which contains more oxidizing species. Oxidizing catalytic converters are used to reduce further the amount of soot emitted from the tailpipe. The majority of the soot formed is oxidized prior to exhaust. This is possibly why most soot particles are absorbed by the lubricant and relatively little is exhausted, concluded by Kennedy [10].

The concentration of the soot particles produced increases with an increasing air-to-fuel ratio. When the air-to-fuel ratio nears stoichiometric (14.5 for diesel fuel), the rate of soot production increases dramatically. This is because near the stoichiometric ratio there is not enough time and oxygen in the cycle to burn all the fuel completely. There will also be a low proportion of oxidizing species to oxidize the soot. Generally, at values of 20% fuel lean of stoichiometric and higher, which are now being used, excessive amounts of soot are produced from the combustion process. Excess air is required to increase diesel cycle efficiency and to reduce hydrocarbon emissions.

Investigations have shown that soot contained in the engine lubricant and soot emitted from the tailpipe are quite different, investigated by Clague *et al.* [2]. This may be partly due to the oxidation processes that the combustion products go through. As mentioned above, soot contained in lubricants has a very high carbon content and a low oxygen content. Soot particles are generally assumed to be extremely hard individually and much softer when agglomerated.

2.2 Soot Simulants

To investigate soot wear, there are essentially three options to choose from regarding the test particles. These are as follows:

- Used engine oil
- Extracted engine soot mixed with fresh engine oil
- Carbon black mixed with fresh engine oil.

Used engine oil is the most realistic option, but adds complications as the oil will contain other contaminants and wear debris, all of which will affect wear results. An extra complication of testing with used oils is that they are naturally degraded, but this is extremely dependent on use. Test oils would each need to be produced in an identical manner in an attempt to degrade the lubricant consistently by the same amount each time, as used engine oils will be mixed together to produce the required soot content for testing purposes. However, even this will not allow full control over the final amount of soot produced, which will vary from batch to batch. Laboratory techniques exist for ageing engine oils outside of an engine (without producing soot), studied by Mascolo *et al.* [11]. This is quite an unpredictable process, however, and would add further complications to the process. The process of producing used engine oils is expensive and time consuming.

The second method of extracting engine soot alone from a used lubricant allows for the assessment of the effect of soot alone on wear without any other contaminants or lubricant degradation issues. Using this method, the extracted soot is simply mixed in with the desired test lubricant. This method is more time consuming and expensive than the first method and reasonably practical for experimental purposes.

The final method of using carbon black has for many years been the standard method for assessing the wear level due to soot contamination. This method is quick and inexpensive. The major drawbacks of this method are that carbon black, although very similar to engine soot, is not engine soot, and produces results that industry has argued may be relative to tests with soot from used engine oil, but not directly comparable.

Carbon black particles do have the capability of mimicking the behavior of soot from engine oils, investigated by Clague *et al* [2]. Findings showed that, when looking at primary soot particles (30–50 nm) using electron microscopy techniques, there is very little difference between engine soot and carbon black. There was a great deal of similarity in particle size and structure, confirming that the two are essentially the same on a nanometer scale. When investigating agglomerated soot and carbon black particles (up to 500 nm), carbon black was again found to be similar to engine soot, although a slight difference was discovered. The carbon black particles disperse in a similar fashion, but create a larger agglomerate diameter than extracted engine soot, greater by approximately 50 nm. Chemical analysis of soot and carbon black particles showed that carbon black particles display higher carbon contents and lower ash and volatile contents. Oxygen and hydrogen were shown to concentrate on the surface of the carbon black, creating a relatively polar surface, meaning it will tend to have a greater tendency to interact with other polar species, for example, other carbon black particles. Prior to extraction from its lubricant, the engine soot displays a higher polar surface than carbon black, but, once the soot has been extracted from the lubricant, it becomes less polar than carbon black. This explains why carbon black particles created a larger-diameter agglomerate than extracted engine soot.

In 2013, Hu *et al.* [12] investigate and measured the size of commercial Carbon Black then compared to the engine soot. They found that The Carbon Black average particulate diameter was 40 nm and the engine soot was 45 nm.

In 2014, Uy *et al.* [13] had compared characteristic of gasoline soot and diesel soot by studied on morphology and chemistry. Soot from gasoline turbocharged direct injection engines (GTDI) and diesel engine from exhaust and extracted from oil, were characterized by XRF, XPS, Raman spectroscopy, and HRTEM. They concluded that soot in all case are different in morphology and chemical composition and can lead to change in the polarity and hardness of the soot particles and also measured carbon black particle size. Its size is only 24nm.

2.3 Tribology Tests

Torbacke *et al.* [14] wrote an introduction to tribological test methods that there are many reasons for carrying out tribology test or tribotest. One reason is to study wear and friction mechanism appearing in specific tribological application. Other reasons are ranking of materials and lubricants for existing equipment or selection of materials and lubricants for new application. Tribotesting may also be performed for general characterization of wear and friction.

Tribotests can be classified into tests that simulate the function of real components or tribological systems and tests that simulate the critical tribological load. The former class includes field tests, bench tests and component tests. The latter class comprises different model tests. All testing aims at increasing the tribological understanding at the fundamental or system level in order to enable development of design, construction and function of tribological systems. The complexity of testing may differ as well as the time and cost for testing, seeing on Figure 2-1.

With testing involving contaminants, it is essential that a good representation of the contact motion, loading, and geometry is achieved if bench testing is to be used. Entrainment of the contaminants will be directly affected by these and is key to determining which wear process may occur. This means that the best approach would probably be to use actual components.

Engine tests are always problematical. It is difficult to control many of the test parameters and to provide good wear measurements. However, standard engine test cycles designed to promote soot production have been defined, as will be outlined in a later section, that allow soot wear studies to be carried out.

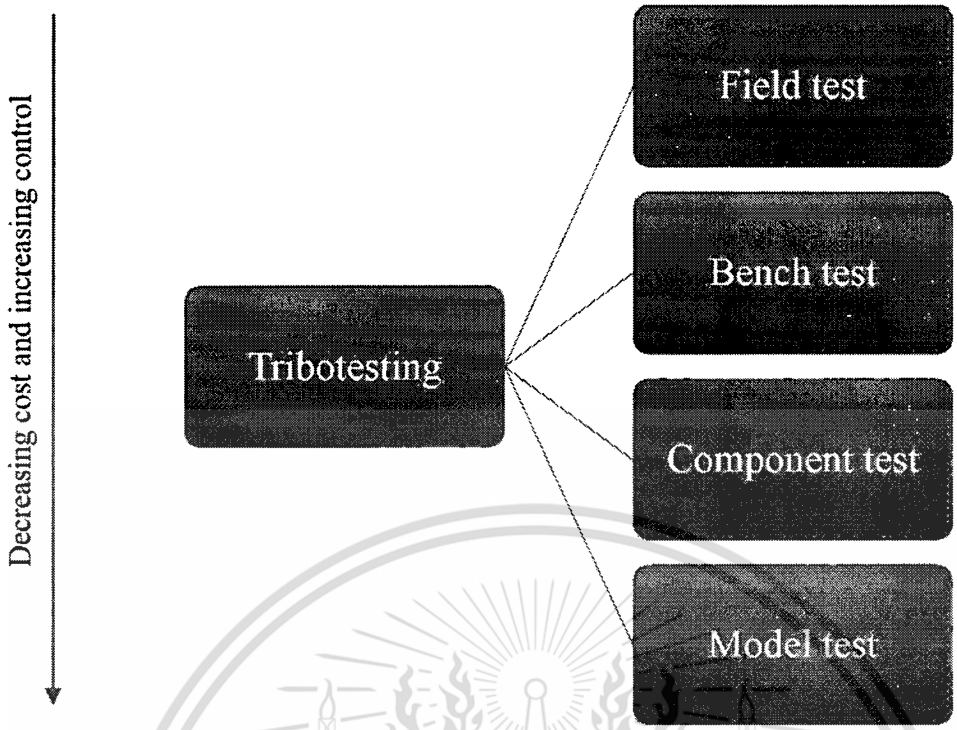


Figure 2-1. Different types of tribology test [14]

The model test selected should provide the closest possible resemblance to the application in mind. The first step is to evaluate the contact geometry that is the form or shape of the contacting bodies and whether the contact is formed. The contact geometry directly affects the local conditions in the contact and is considered to be the primary variable for selecting model test and for scaling up and scaling down of tests. Finally, the test duration must be set long enough for the test to be correctly evaluated.

The combustion engine is lubricated with one lubricant operating in the boundary to the full-film regime. Two parts of a combustion engine have been selected to show the use of model testing, seeing on Figure 2-2. The piston–cylinder liner and the cam–follower represent two different types of lubricated contacts in an engine. Due to the combustion in the engine, the piston–cylinder is exposed to very high temperatures. The cam–follower is exposed to very lower temperatures.

The piston–cylinder liner shows a start–stop phenomenon at the turning points of the piston, that is reciprocating motion. The lubrication regime changes from boundary to mixed lubrication for each stroke. Therefore, the reciprocating tribotest is chosen. The environment can be controlled and monitored by adding a hood to the tribotest. This will make it possible to run tests at temperatures relevant for the application.

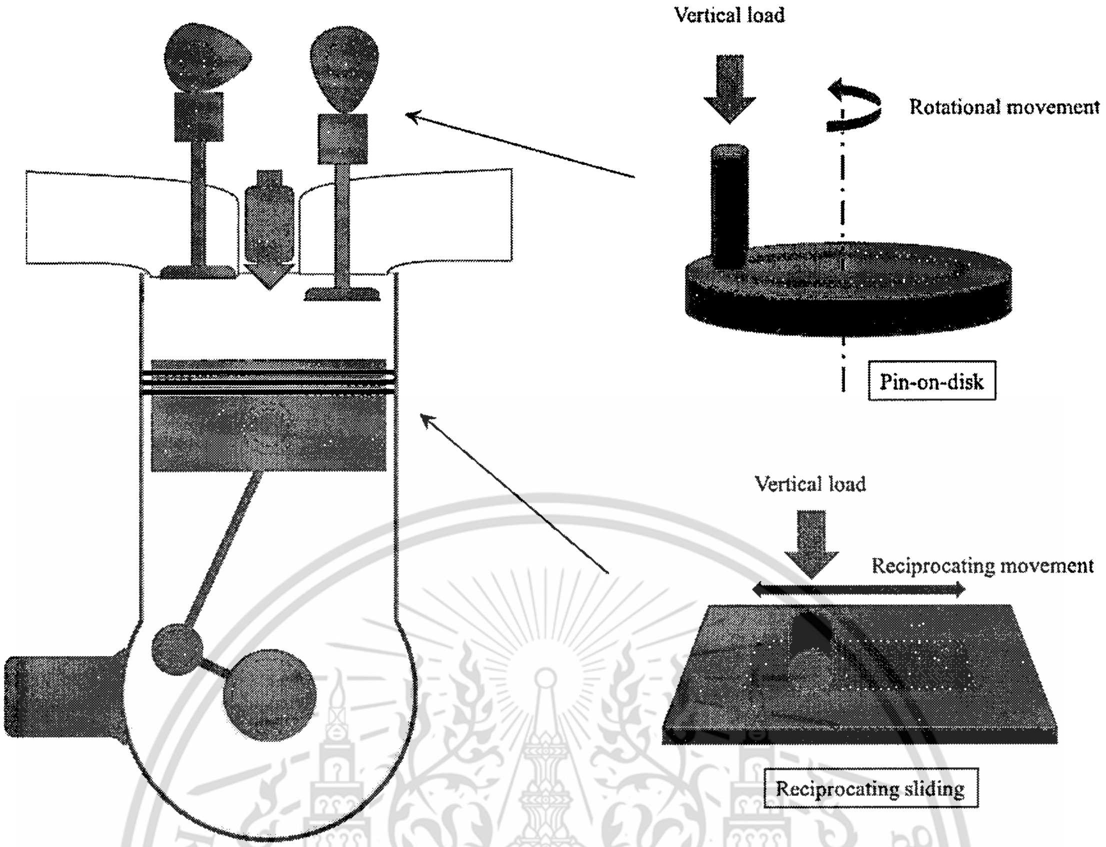


Figure 2-2. Tribology selection for typical combustion engine [14]

The cam–follower is a sliding contact with different velocities in both mixed and boundary lubrication. This contact is usually difficult to lubricate due to uneven wear rates of the cam. Therefore, it is very interesting and important to find materials and lubricants that keep the friction and the wear rates at a minimum. This can be simulated in a pin-on-disc, where a flat surface contact is in contact under unidirectional relative motion. Both materials and lubricants may easily be evaluated under different conditions.

In early work on soot wear, the most popular test method was the four-ball approach in which various soot-contaminated lubricant formulations were tested in a standard four-ball wear tester. High frequency reciprocating rigs was tested by Green *et al.* [15], pin-on-disc was tested by Ramkumar *et al.* [16], and ball-on-flat rolling sliding apparatus was tested by Yamaguchi *et al.* [17], have also been used in more recent times.

These methods have their limitations. It was necessary to test the levels of wear using test equipment that was designed to replicate the engine components in question, rather than generic wear testers. Tests have been carried out since then using test conditions related to actual components, suggested by Green *et al.* [15], as well as some with actual components. Engine tests have also been used to study soot-related wear, usually through industry standard engine tests.

The measurement of wear data to assess the effects of soot contamination is generally carried out through imaging of the wear scar produced after each test. This involves the use of optical microscopy or, for a more detailed analysis of the wear surface, scanning electron microscopy (SEM).

In 1999, Guatum *et al.* [18] determined the mechanism of wear qualitatively. They had performed the experiments on Ball-on-flat which set on a milling machine. Stainless steel balls, 0.25 inch indiameter, were worn against a gray cast iron surface in the presence of soot-oil formulations at 35 lbs. load for 30 minutes.

Diatto *et al.* [19] studied in atopic as "Investigation on Soot Dispersant Properties and Wear Effects in the Boundary Lubrication Regime". Their aim of work is to investigate wear phenomena induced by soot contamination in lubricated contacts, as it occurs typically in diesel engines. The wear tests were run under pure sliding condition using the high temperature Pin-on-disk tribometer. The working conditions operated at lubricant temperature of 135 °C, a typical value of full-warmed engines, high enough to ensure ZnDTP reaction. Minimum load and maximum speed are 1 N and 0.1 m/s, respectively. Finally, the running time is 60 minutes.

In 2002, Soejima *et al.* [4] had tested the tribology test to clarify the friction and wear mechanism of the contact between cam and follower in the valve train incorporated in an EGR system. Cam-follower bench test was conducted for this tribology testing. A follower specimen slip in contact with a cam specimen rotated by an outer electric motor. The contact load between cam and follower was set at 930 N maximum value with an adjusting device of valve spring assembly. The rotating speed of camshaft was constant at 400 rpm as a high wear rate situation. The longest test duration was 250 hr.

In 2005, Truhan *et al.* [20] had evaluated the friction and wear behavior of piston ring and cylinder liner materials for heavy-duty diesel engine applications. A high-frequency reciprocating bench test was employed. All tests were conducted with a 10 mm stroke at 10 Hz.

McQueen *et al.* [21] studied in a topic as "Friction and Wear of Tribofilms formed by Zinc Dialkyl Dithiophosphate Antiwear Additive in Low Viscosity Engine Oils". There were 2 laboratory tests. A high frequency reciprocating rig was conducted for testing new and used oil at low and elevated temperatures. Another one is a sliding valve train bench test for measuring the friction and wear performances of fresh engine oils added with some additives.

In 2007, Wu *et al.* [22] studied in a topic as "Experimental Analysis of Tribological Properties of Lubricating Oil with Nanoparticle Additives". The aim of this test is to study the friction-reduction and anti-wear abilities. A reciprocating sliding friction tribotester was employed. The friction coefficient and contact resistance between the rubbing specimens ware measured. The resistance can be used to study the film-forming process of nonconductive chemical film of lubricating oil additives. During test, the mean sliding speed of moving specimen are 30mm/s and 120 mm/s under load 100 N and 100 N. Temperature is ranging from 40 °C to 160 °C. The test is lasting for 120 min.

Dienwiebel and Pohlmann [23] studied in a topic as "Nanoscale Evolution of Sliding Metal Surfaces during Running-in". They used a Pin-on-disk tribometer. In the experiment setup, the oil was heated to a temperature of 80 °C. The experiments were carried out at a constant nominal pressure of 75 MPa and sliding speed of 2.5 m/s. Wear was measured on-line using the radionuclide technique.

Aldajah *et al.* [24] investigated the effect of exhaust gas recirculation (EGR) contamination of diesel engine oil on wear. Friction and wear tests were conducted with a Four-ball tribometer. All of the tests were conducted for 1 h at a constant load of 73 N, rotating speed of 1200 rpm, and ambient room temperature. Even though the temperature increased while test, no attempt was made to control the temperature.

In 2010, Antusch et al. [25] studied the tribological behavior of soot by means of a Pin-on-disk tribometer. They have set the experiments with a custom-built pin which made from real camshaft. Wear was measured continuously by the radionuclide wear measurement technique. The contact pressure in all experiments was 13 MPa, the sliding velocity 0.3 m/s, the oil temperature was kept constant at 120 °C, and the duration of all experiments was 40 hours.

In 2013, Abdullah *et al.* [26] studied in a topic as "Reducing Wear and Friction by Means of Lubricants Mixtures". The aim is to test the abilities of mixed Lubricants. Thus, a Four-ball tribometer was set to perform the test. There are 2 different forces applied in test, 147 N and 392 N. The temperature of mixed lubricant is set at 75 °C and the upper steel ball is rotated at 1200 rpm for duration of 60 min.

Hu *et al.* [12] studied the influence of soot contamination on the tribological behavior of engine lubricants. The candidate lubricants were a formulated engine lubricant and a base oil. Soot particle contamination was simulated using a Four-ball tribometer.

In 2014, Uy *et al.* [13] had set a reciprocating Ball-on-flat to investigate characteristic of gasoline soot and diesel soot. The steel ball was reciprocated on a polished steel flat with a load of 100 N, stroke of 2.5 mm, and a temperature of 150 °C for approximately 2 hours.

2.4 Effect of Soot on Oil Properties

Excessive soot level in oil could overwhelm the dispersant additives in engine oil. As the dispersants become depleted, soot particles clump together, attach themselves to engine surfaces and lead to reduce lubrication due to impeded oil flow through the engine as well as through the oil filter.

In 2005, Truhan *et al.* [20] investigated oil viscosity which are changed due to soot content. The result of viscosity is illustrated at 40 and 100 °C. They found that both viscosity has been increased among the soot concentration is increasing.

In 2007, George *et al.* [27] studied in a topic as "Effect of Diesel Soot on Lubricant Oil Viscosity". They found that the soot contaminating in lubricant changes the chemical properties resulting in lubricant creasing to perform its function. This causes an increase in viscosity of the engine oil causing pump ability problem. The performance of anti-wear lubricant additive can also be negatively impacted and lead to increase wear and premature engine failure. High oil soot level can also lead to be a higher lubricant viscosity which impedes oil flow and increase engine wear.

In 2012, Esangbedo *et al.* [28] studied the characteristics of diesel engine soot that lead to excessive oil thickening. They concluded that severe oil thickening during a heavy duty diesel engine test is linked to soot agglomeration in engine oil. The ineffectiveness of dispersant to retard particle growth is attributed to poor soot functionalization.

In 2013, Hu *et al.* [12] added Carbon Black into the base oil and formulated lubricant at mass percentages of 0, 2, 4, 6, and 8 % (wt.). This was distributed using an ultrasonic bath for 30 min to reduce experimental deviation. The kinetic viscosities of oil samples were measured using a viscosity meter at 40 °C and 100 °C. They found that the viscosity has slightly increased when raising the containing of Carbon Black.

2.5 Effect of Soot on Friction

It has been shown that soot which is produced within the engine, only 29% reaches to the atmosphere through the exhaust pipe, studied by Daido *et al.*

[29]. The remainder is deposited on the cylinder walls and piston heads. Soot which is retained in the engine, mainly in lubricant, 3% is attributable to blow-by gases. The remainder results from piston rings scraping away soot deposits in the cylinder, which then end up in the sump. Then it is transported around the engine where it can be entrained into component contacts.

In 2013, Hu *et al.* [12] had tested Four-ball tribometer. During test, the friction was measuring. They added Carbon Black into lubricating oil samples and compared with other formulated oil. They found that the friction coefficient has trended increasing among the samples which have more content of carbon black. However, it has been noticed that the friction coefficient was small drop at low percent concentration of carbon black.

2.6 Effect of Soot on Metal Wear

Individual soot particle poses little risk to engine parts, but clumps of soot can cause damage. Dispersant additives in recent engine oil keep the individual soot particle from forming damaging clumps.

Until now, many conflicting, incomplete ideas and explanations about the properties and effects of soot particulates on the wear mechanism have been published. Some authors showed that soot is not abrasive but adsorb anti-wear additive, thus diminishing anti-wear properties. However, Ryason *et al.* [30] concluded that soot particles are abrasive because they were found to generate grooves and breakouts in metal surfaces. Ratoi *et al.* [31] showed that dispersed carbon black rapidly abraded additive reaction films. Guatam *et al.* [18] found more wear with soot contamination in oil than without. Aldajah *et al.* [24] and Yamaguchi *et al.* [17] found that the presence of soot particles reduces the thickness of anti-wear films and act as an abrasive element. Truhan *et al.* [20] concluded his study that the chemical activities of soot particles and their reactions with additive prevent the formation of liquid boundary layers on metal surface so the surface becomes easier for scratching.

In 1999, Gautam *et al.* [18] studied the influence of soot on wear using reciprocating Ball-on-flat tribology test. There were 8 samples for testing and prepared by mixing two different base stocks. After testing, they analyzed the variation in the average wear for all the oil samples with and without soot contamination. The detrimental effect of soot is quite clear evident as the average wear from 6 of 8 with soot contamination is higher than wear without soot contamination. However, the rest of oil samples, wear results give the opposite results.

In 2002, Soejima *et al.* [4] had conducted the Cam-follower bench test with many conditions. They found that used oil has more wear than fresh oil, and also same trend as adding Carbon Black. The oil adding Carbon Black give the result in more damaged than fresh oil. In case of adding dispersant, they found the particle size is kept small but note that this case made more wear rate too.

In 2005, Truhan *et al.* [20] had tested a reciprocating Ring-and-flat bench test to demonstrated mechanism in cylinder liner. They found that wear rate of piston wall has trended to increase when soot content is raising but there is not affecting to the case of piston ring. They concluded the soot and particulate contents have a major effect on wear of the cast iron flat and less of an effect on the ring. Note that they also suggested the viscosity was related to the soot content rather than the oxidation levels.

In 2007, Aldajah *et al.* [24] had conducted a Four-ball tribology test. There 4 samples lubricating oils were tested which are different in soot containing. They found that there appears to be no clear relationship between the soot content and steel ball wear volume. The fresh oil gives the result as near to zero wear volume, an oil adding soot of 6.9% made wear volume of 10 mm^3, the oils adding 9% and 12% soot made 4 mm^3 and 6 mm^3, respectively.

In 2013, Hu *et al.* [12] had operated a Four-ball tribometer. They contaminated Carbon Black into a formulated oil SAE 15W-40 from 2% to 8% (wt.). After test, they found that the average wear scar diameters of steel ball have increased among soot content increasing. However, the test result also showed the opposite trend. The pure base lubricating oil and adding additive, they made average wear scar diameter smaller over the soot content increasing.

The Bottom Line

Based on all of the studied literatures, it could be concluded that wear mechanism induced by the presence of soot is not successfully understood yet. More fundamental knowledge is required. Thus, the properties of soot and their influence on wear and also friction were in the focus of my thesis. To understand the behavior of soot reaction on engine metal surface, the tribology test is conducted to this thesis.

CHAPTER 3

RELATED THEORY

When we talk about lubrication, we usually imply liquid lubrication that is by the use of lubricating oil, which is normally a blend of oil and additives that perform various functions. Lubrication efficiency of an oil depends not only upon its properties, such as composition, consistency, flow properties, and surface activity, but also on the needs of the tribology system.

Rizvi [32] wrote a book that Lubrication environments, often called lubrication regimes, are primarily defined by considering these needs. The factors that are considered include gross geometry of the contacting surfaces, their texture and roughness, the nature of the contact (rolling versus sliding), the contacting load, ambient pressure and temperature, the environmental conditions, material composition, and the properties of the surface layers. Lubrication effectiveness is measured by the film thickness, the ability to handle pressure (load-carrying capacity), and the coefficient of friction.

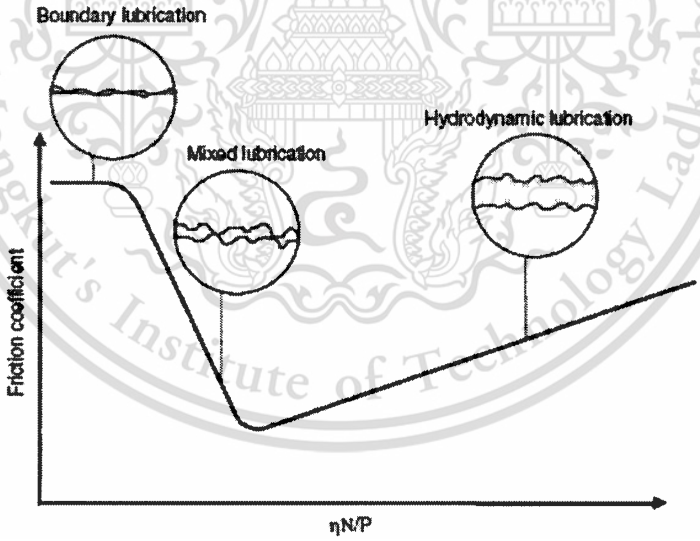


Figure 3-1. Schematic of a Stribeck curve related to lubrication regimes [33]

Richard Stribeck is credited with conducting the first systematic experiments revealing a clear view of the characteristic curve of coefficient of friction versus speed. In recognition of his contribution, this type of curve is universally referred to as the Stribeck curve. Figure 3-1 presents a schematic of such a curve as an overall view of friction variation in the entire range of lubrication as a function of the bearing parameter called the Hersey number, $\eta N/P$ (where η is the dynamic viscosity of the lubricant, N the rotational speed, and P the bearing load in terms of average pressure). Three lubrication regimes can be clearly presented in the Stribeck curve: namely, the full-film, the mixed, and the boundary lubrication regimes [33].

On this chapter, there are 4 theory topics explained for helping understand the designing of experiments and also for describing the results of the test which related to the theories as following.

1) Lubrication regime
2) Wear mechanism
3) Engine oil additives
4) Film thickness estimation between two sphere contacts

3.1 Lubrication Regime

The primary functions of a lubricant are to minimize friction between the surfaces in contact, prevent wear, and remove frictional heat. Tribology parameters that usually define a lubrication environment are friction, lubricant viscosity, and the equipment speed and load. The relationship of the coefficient of friction (μ) and the oil film thickness to lubricant viscosity (Z), equipment speed (N), and equipment load, or pressure (P), are graphically presented by the Stribeck curve [32] in Figure 3-2.

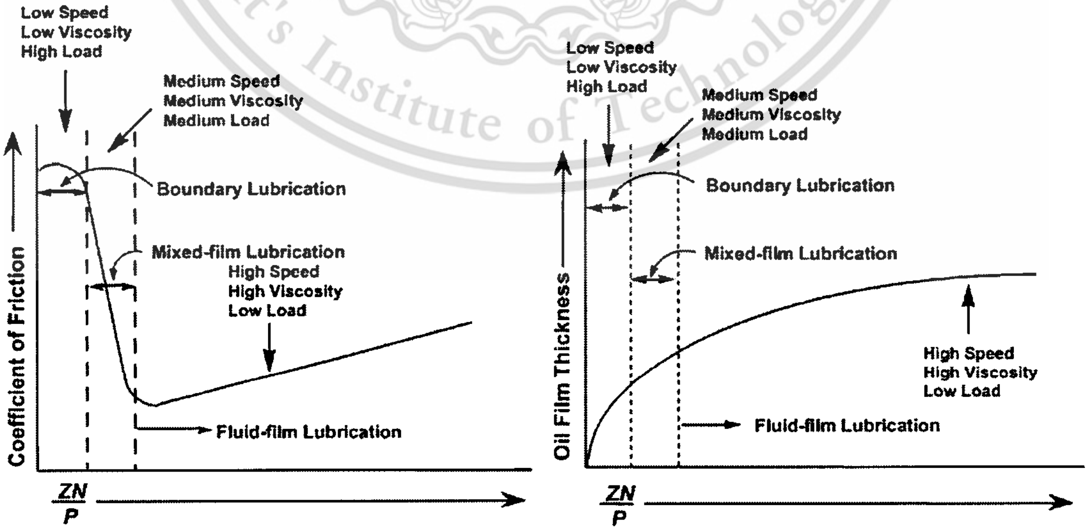


Figure 3-2. Type of lubrication [32]

The ratio of ZN/P is related directly to the oil film thickness but inversely to the coefficient of friction (μ). This implies that high lubricant viscosity (Z), high equipment speed (N), and low equipment load (P) will allow the formation of a thick lubricant film, and hence the equipment will encounter little or no friction. Conversely, low lubricant viscosity, low equipment speed, and high equipment load will create a situation where the film thickness will be inappropriate and the equipment will encounter high friction, as indicated in the figure.

Incidentally, the observed initial drop in the coefficient of friction while moving from fluid-film to mixed-film lubrication reflects a decrease in viscous drag due to a decrease in lubricant viscosity. Depending upon the lubricating environment, lubrication regimes can be divided into fluid-film, boundary, mixed-film, and hydrostatic types. The first three of these states of lubrication are depicted in Figure 3-2 [32].

3.1.1 Fluid-film lubrication (Hydrodynamic lubrication)

Fluid-film lubrication, also known as hydrodynamic lubrication, is the most desirable type. This type of lubrication depends upon the viscosity of the lubricant and is effective only when the load in the contact zone is low. Under these circumstances, the sliding or the rolling surfaces are separated by a lubricant film several times the thickness of the surface roughness (asperities). The film thickness in this lubrication regime is estimated to be 2–100 μm. Lubrication of the thrust bearings, journal bearings, and most of the internal combustion engine parts experience fluid-film lubrication.

Another type of hydrodynamic lubrication, referred to as elasto-hydrodynamic lubrication, or EHD [32], commonly occurs in roller element bearings (ball and roller Types), cams, and gears. In this type of lubrication, the lubricant is exposed to high contact pressures and undergoes a large viscosity increase. This results in an extremely rigid lubricant film (0.01–5.0 μm thick), which causes elastic deformation of the surfaces in the lubricating zone.

3.1.2 Boundary lubrication

Boundary lubrication represents the opposite extreme of the lubrication environment spectrum. Under this kind of lubrication, high loads and very slow speeds produce extreme pressures that can lead to the lack of effective lubrication. The film thickness in this regime is in the order of 0.0 - 2.0 μm only, and hence maximum metal-to-metal contact occurs. If not controlled, the resulting dry metallic friction will cause catastrophic wear, and ultimately will lead to total seizure. Reactive chemicals called anti-wear and extreme pressure agents provide protection in this kind of lubrication environment.

Examples of equipment that rely exclusively on boundary lubrication include reciprocating parts of an engine and compressor pistons, slow-moving equipment such as turbine wicket gates, and gears. It is important to note that the anti-wear agents are effective only up to a maximum temperature of about 250°C (480°F), above which they essentially become ineffective. Typically, heavy loading causes the oil temperature to increase beyond the effective range of the anti-wear agents. This is because the degree of contact between the surface asperities further increases due to flattening and the consequence being greater friction, hence higher temperatures. When the load exceeds the equipment's recommended limit, the asperities, instead of sliding, experience shearing and removing the lubricant and the oxide layer.

3.1.3 Mixed-film lubrication (Mixed lubrication)

Mixed-film lubrication falls between the two extremes mentioned above and contains characteristics of both the fluid-film and the boundary lubrication. There are regions of no metal-to-metal contact and of extensive metal-to-metal contact.

3.1.4 Defining lubrication regimes

A general description of the friction behavior in a lubricated contact can be seen in Figure 3-3, where the dependence of the coefficient of friction (μ) versus the film parameter (Λ) is shown [14].

The film parameter (Λ) is calculated as

$$\Lambda = \frac{h}{\sqrt{R_{qA}^2 + R_{qB}^2}} \tag{3.1}$$

Where (h) is the lubricant film thickness and (R_{qA}) and (R_{qB}) represent the surface roughness of the two surfaces A and B in contact. The contact is classified as boundary, mixed or full film (Fluid-film) lubricated depending on the degree of mechanical contact between the solid surfaces. The curve in Figure 3-3 originates from the Stribeck curve.

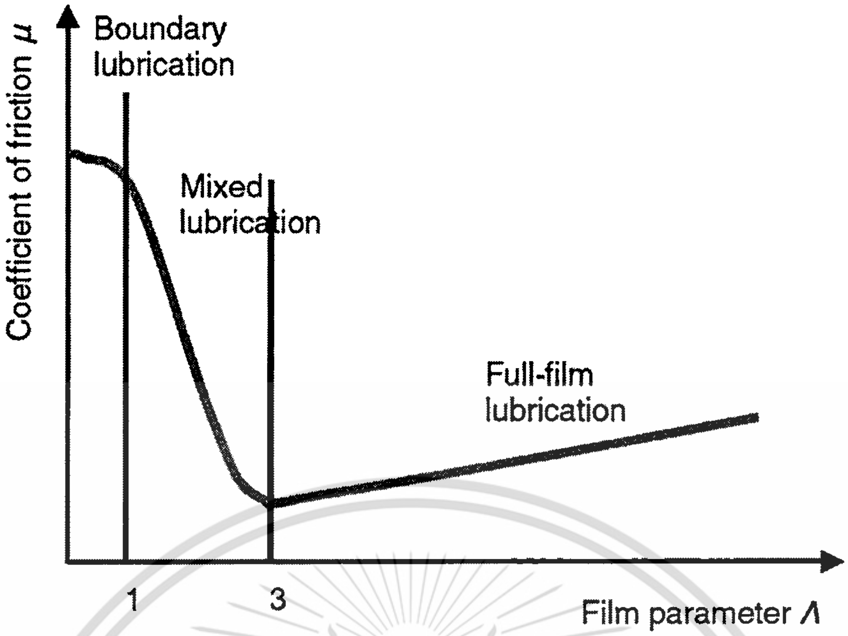


Figure 3-3. Coefficient of friction versus film parameter in lubrication sliding contacts [14]

Boundary lubrication implies heavy contacting between the asperities with a Λ-value below 1. The load is carried by the solid surfaces in contact. The lubricant is mainly acting as a carrier of additives. The presence of additives is necessary to ensure the performance and build-up of a boundary film. This regime is characterized by high load and low speed. A slowly rotating shaft and a bushing mainly work in the boundary lubrication regime even if they are lubricated.

In mixed film lubrication the surfaces are less separated than in the full film regime. The surfaces are close enough for asperity contact to occur occasionally. The mixed film lubrication regime is a combination of full film lubrication and boundary lubrication with Λ-values between 1 and 3. Thus, the load is carried partly by a pressure in the fluid film and partly by the asperities in contact. The lubricant will support the contact with necessary additives to reduce wear.

In full film lubrication (Fluid-film lubrication) the solid bodies are lubricated by a thick enough lubricant film to ensure full separation of the surfaces. In this regime the coefficient of friction is very low. A Λ-value higher than 3 indicates full film lubrication. Hydrodynamic bearings are examples of machine components carefully designed to operate in the full film regime.

Elastohydrodynamic (EHD) lubrication is part of the full film regime. In this regime the load is high enough to cause elastic deformation of the surfaces.

Elastohydrodynamic lubrication can be found in nonconformal contacts, such as a ball on a flat surface when the motion is rolling or rolling and sliding. Performance in the EHD conditions is mainly governed by the viscosity and the viscosity–pressure dependence.

The lubricant film thickness (h) is determined by the lubricant properties, the operating conditions, the contact geometry and the solid surface's material properties. In practice, typical lubricant film thicknesses are about 1–100 μm.

Although boundary lubrication is encountered in certain parts of the engine, such as valve train, cylinder bores, and piston rings, most of the lubrication in an engine is hydrodynamic in nature [32], see Figure 3-4. Boundary lubrication is more common in rear axles, gears, and bearings. The surfaces in these parts are designed to mesh closely so as to efficiently transfer power generated by the power source to parts that work. Figure 3-5 shows the lubrication regimes encountered in various automotive applications.

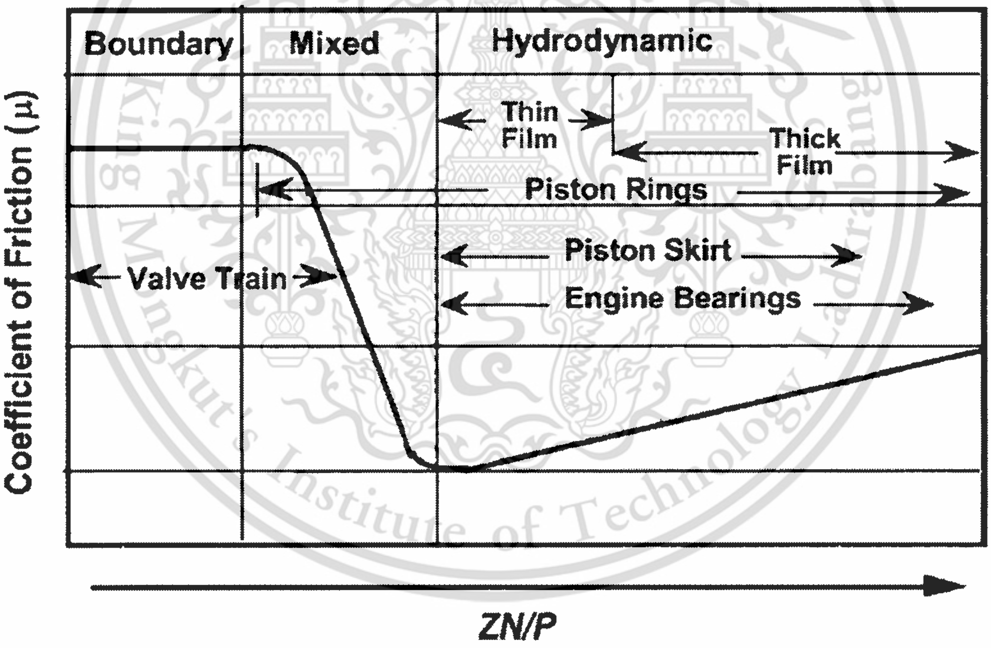


Figure 3-4. Strikbeck diagram showing the type of lubrication encountered by various engine parts [32]

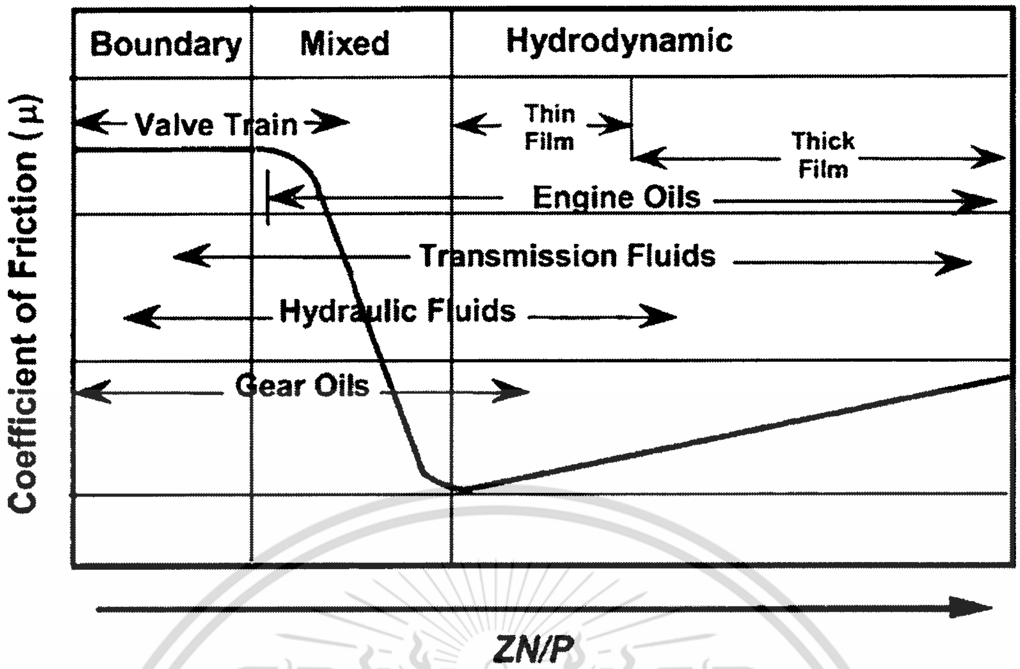


Figure 3-5. Stribeck diagram showing the types of lubrication encountered in various automotive applications [32]

3.2 Wear Mechanism

Lakshminarayanan *et al.* [34] explained about wear in engine. Modern design procedures are detailed and well established against gross failures like fatigue, breaking and loosening. Therefore, only the micron sized failures at the surfaces that result in wear affect the life of an engine. Apart from the basic design aspects that are grounds for ‘normal’ wear or aging, extreme loads, environments like a dusty atmosphere plus quality of maintenance, fuels and oils bring an earlier end to the life of an engine. If the engine that has lasted its wear life is studied, only less than 0.01% of the total mass of the engine has been wasted away. In other words, more than 99.9% of the mass has survived when the parts are replaced at the end of their wear life.

If the normal and abnormal wear is understood early based on the application or design of an engine, it is possible to incorporate features and protections in the design so that the engine is able to complete its expected life with sufficient margin.

Wear is the progressive loss of substance resulting from mechanical interaction between two contacting surfaces and occurs because of the local mechanical failure of highly stressed interfacial zones. The failure mode will often be influenced by environmental factors. These surfaces are under load in relative motion, either sliding or rolling. Mechanisms of wear associated with failure signatures in engine bearings can be broadly divided as adhesive wear, abrasive wear, fatigue wear and wear by chemical reaction (Figure 3-6).

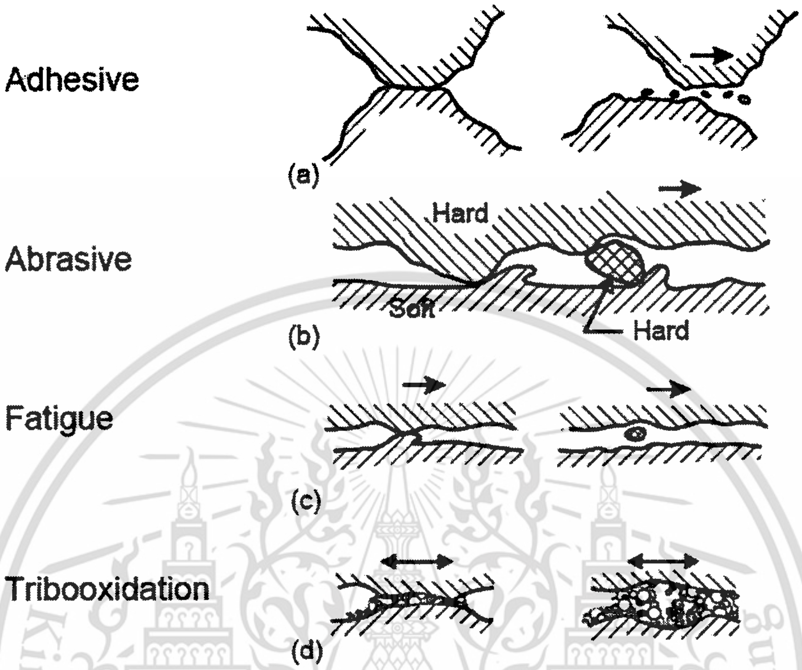


Figure 3-6. Wear mechanism models [34]

3.2.1 Adhesive wear

This form of wear occurs when two smooth bodies slide over each other or one surface adheres to the other. The strong adhesive forces arise out of intimate interaction at molecular level. In this process, the wear particles are pulled off from the softer surface and become welded to the harder surface. For example, cylinder bores will wear at the top ring reversal zone due to the adhesive action of piston rings under gaseous load.

3.2.2 Abrasive wear

Abrasive wear occurs when a rough surface slides against hard particles, causing a series of scratches on the smoother surface, and the material from the softer surface is displaced in the form of wear particles. For example, a diesel engine running on heavy furnace oil undergoes wear of the piston grooves due to abrasive action of hard carbon particles produced by combustion.

3.2.3 Fretting wear (fatigue wear)

Fretting wear arises when contacting surfaces undergo oscillatory tangential displacement of small amplitude. It is a type of wear because of the cycling motion that produces a displacement (under high contact pressure) that is so small that it may be difficult to anticipate a large volume of wear debris. The wear of the inlet valve seat due to micro-scale displacement under highly load conditions illustrates fretting mode of wear in diesel engines.

3.2.4 Corrosive wear (Tribooxidation)

Virtually all materials except noble metals like gold or platinum corrode in the normal environment. The most common form of corrosion is oxidation. Most metals react with oxygen in air or water to form oxides. Abusive conditions, for example low or high temperatures, increase the rate of chemical reactions and the corrosive wear increases abruptly, leading to mechanical destruction of the surface layer due to sliding or rolling contact of two mating bodies. Typically, the greyish lapped appearance of liner surfaces under cold running condition is an example of corrosive wear.

3.3 Engine Oil additive

Additive [14] are chemical compounds added to lubricant oils to impact specific properties to finished oils. They are mainly added to the base fluid to enhance the viscosity index and the pour point, the friction and wear properties under boundary and mixed lubrication, and the lubricant life.

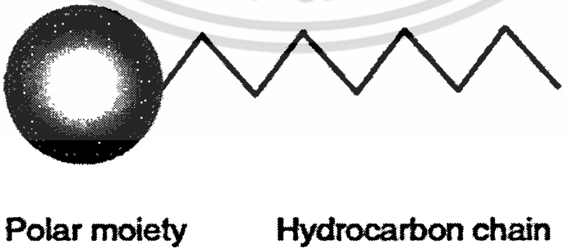


Figure 3-7. A generalized structure of an additive molecule with a polar moiety and hydrocarbon [14]

Additives can be classified regarding different aspects. Important and helpful for the understanding of additives is the following differentiation that takes into consideration which part of the tribology system is influenced by the additives. According to this considerations additives can be classified into types that

1) Surface Active Adsorbing Additive
    - Corrosion Inhibitors
    - Friction Modifiers
    - Antiwear Additives
    - Extreme Pressure Additives
2) Bulk Active Additive
    - Dispersants
    - Detergents
    - Antioxidation

3.3.1 Surface Active Adsorbing Additive

Surface active additives acting at the solid–liquid surface are added to the lubricant in order to protect the solid from corrosion and wear and to reduce friction. They are sometimes referred to as film-forming additives.

The action of surface adsorption involves several steps, such as removal of water and gas, transfer of the additive from the bulk lubricant to the surface and adsorption on the metal surface. Sometimes the adsorbed layer reacts with the surface.

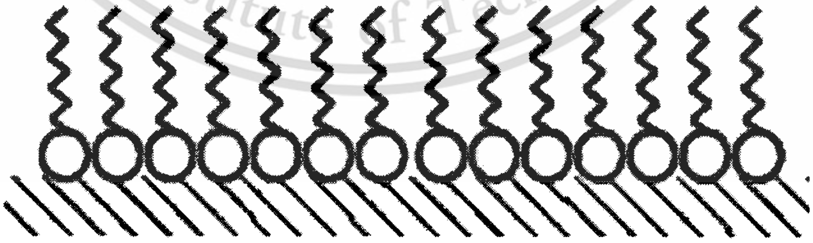


Figure 3-8. Active additive layer on metal surface [14]

Corrosion inhibitors are used in nearly every lubricant to protect the metal surface from the attack of oxygen, moisture and aggressive products. The base oil itself forms a kind of protective layer on the metal surface. But in general this will not be sufficient especially when highly refined oils without natural inhibitors are used. Then highly efficient anticorrosion additives are necessary.

Friction modifiers (FMs) are added to the lubricant to modify the friction in the mixed lubrication regime of the tribology contact. Adding 1% is enough to give a significant change in friction. They are active in the mixed lubricating regime at moderate temperatures and loads, but will desorb at high temperatures and high loads. Friction modifiers work at temperatures where AW and EP additives are not yet reactive by forming thin monomolecular layer.

Antiwear (AW) additives are mainly designed to reduce wear when the running system is exposed to moderate stress whereas EP additives are much more reactive and are used when the stress of the system is very high in order to prevent the welding of the moving parts that otherwise would lead to severe damage. Typically, EP additives increase wear effects due to their high reactivity or multilayers of physically adsorbed polar oil-soluble products.

Extreme pressure (EP) additives modify the metal surface in order to avoid scuffing and control wear in the boundary lubrication regime. They form protective, low shear strength surface films that reduce friction and wear. However, too high concentrations may cause excessive corrosion and wear. EPs are needed in slow moving, heavily loaded gears (i.e. gear oils) and metalworking fluids.

3.3.2 Bulk Active Additives

Dispersants prolong the life of the lubricant by dispersing sludge, suspending soot, reducing deposit formation and keeping parts clean. Dispersants are bulk active and perform by dissolving polar contaminants (or dirt) in the lubricant by physical action. Dispersants prevent the contaminants from adhering to each other (i.e. forming aggregates) by adsorbing to their surfaces. The hydrocarbon chains point outwards when adsorbed (i.e. forming a micelle structure) (see Figure 3-9). Thus, dispersants are identical to surface active molecules that is they have a polar part and a hydrocarbon chain, even though they act in the bulk.

Detergents react with contaminants or combustion residues in order to keep engines clean, thus having a similar function to dispersants in the lubricant. Detergents occur in two different types: neutral and over based. Normally, the TBN number of a used lubricant indicates the amount of the remaining detergent concentration.

Antioxidants are added to the lubricant in order to slow down the rate of oxidation. Exposure of hydrocarbons to oxygen and heat will accelerate the oxidation process. The lubricant oils consist of hydrocarbon with (C20 – C70) carbon atom. At higher temperature these hydrocarbons are oxidize to form fatty acid, fatty alcohol, fatty aldehydes and ketones. All these compounds form the solid asphaltic materials. For this reason, the addition of antioxidants is necessary to all lubricant oils to prevent the formation of such compounds.

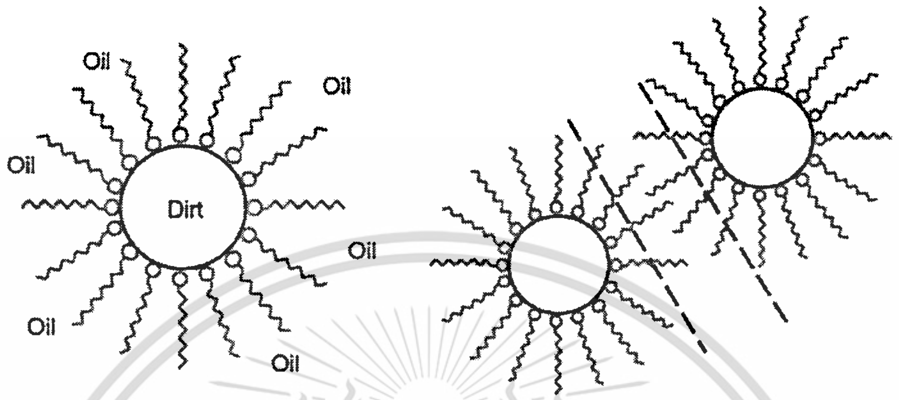


Figure 3-9. Active additive in oil bulk [14]

3.4 Film Thickness Estimation between Two Sphere Contacts

Stachowiak *et al.* [35] introduced history and explanation to estimate oil film. In the 1940s a substantial amount of work was devoted to resolving elastohydrodynamics and the first realistic model which provided an approximate solution for elastohydrodynamic film thickness was proposed by Ertel and Grubin. The work was published by Grubin in 1949.

In this topic, the fundamental mechanisms of film generation in elastohydrodynamic contacts, together with the methods for calculating the minimum film thickness between spherical balls.

The shape of the contact area depends on the shape (curvature) of the contacting bodies. For example, point contacts occur between two balls, line contacts occur between two parallel cylinders and elliptical contacts, which are most frequently found in many practical engineering applications, occur when two cylinders are crossed, or a moving ball is in contact with the inner ring of a bearing, or two gear teeth are in contact. The curvature of the bodies can be convex, flat or concave. It is defined by convention that convex surfaces possess a ‘positive curvature’ and concave surfaces have a ‘negative curvature’. The following general rule can be applied to distinguish between these surfaces: if the center of curvature lies within the solid then the curvature is positive, if it lies outside the solid then the curvature is negative. This distinction is critical in defining the parameter characterizing the contact geometry which is known as the reduced radius of curvature.

The configuration of two elastic bodies with convex surfaces in contact was originally considered by Hertz in 1881 and is shown in Figure 3-10.

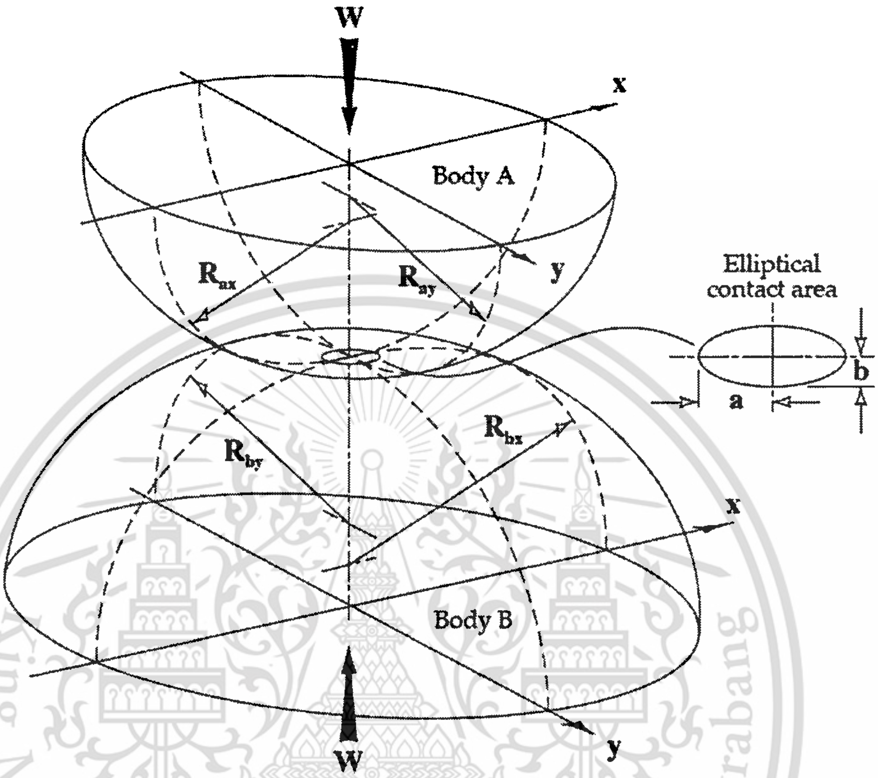


Figure 3-10. Geometry of two elastic bodies with convex surfaces [35]

The reduced radius of curvature for this case is defined as:

$$\frac{1}{R'} = \frac{1}{R_x} + \frac{1}{R_y} = \frac{1}{R_{ax}} + \frac{1}{R_{bx}} + \frac{1}{R_{ay}} + \frac{1}{R_{by}} \tag{3.2}$$

Where:

$$\frac{1}{R_x} = \frac{1}{R_{ax}} + \frac{1}{R_{bx}}$$

$$\frac{1}{R_y} = \frac{1}{R_{ay}} + \frac{1}{R_{by}}$$

R_x is the reduced radius of curvature in the x direction [m].
R_y is the reduced radius of curvature in the y direction [m].
R_{ax} is the reduced of curvature of body A in the x direction [m].
R_{ay} is the reduced of curvature of body A in the y direction [m].

R_{bx} is the reduced of curvature of body B in the x direction [m].
R_{by} is the reduced of curvature of body B in the y direction [m].

The contact area between two spheres is enveloped by a circle. The formulae for the main contact parameters of two spheres in contact, shown in Figure 3-11, are summarized in Table 3-1.

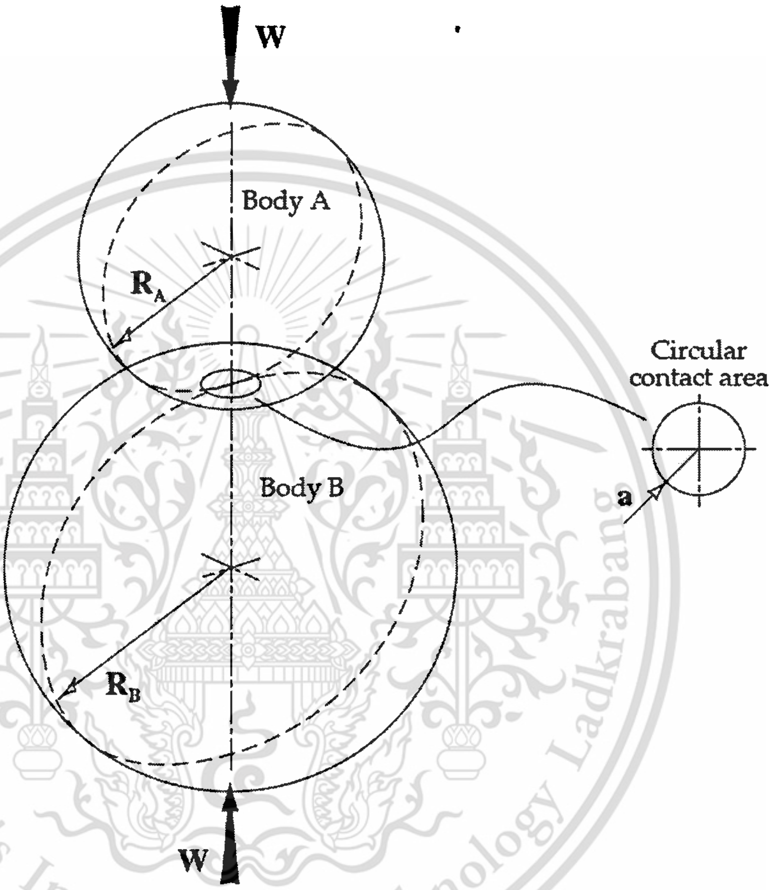
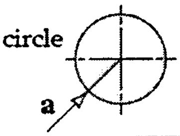


Figure 3-11. Geometry of the contact between two spheres [35]

Table 3-1. Formulae for contact parameters between two spheres [35]

Contact area	Maximum contact pressure	Average contact pressure	Maximum deflection	Maximum shear stress
$a = \left(\frac{3WR'}{E'}\right)^{1/3}$ circle  a	$P_{max} = \frac{3W}{2\pi a^2}$ Hemispherical pressure distribution	$P_{ave} = \frac{W}{\pi a^2}$	$\delta = 1.0397\left(\frac{W^2}{E'^2R'}\right)^{1/3}$	$\tau_{max} = \frac{1}{3}P_{max}$ At a depth of $z = 0.638a$

Where:

a	is the radius of contact area [m].
W	is the normal load [N].
P	is the contact pressure (Hertzian stress) [Pa].
δ	is the total deflection at the center of the contact [m].
τ	is the shear stress [Pa].
z	is the depth under the surface where the maximum shear stress acts [m].
E'	is the reduced Young's modulus [Pa].
R'	is the reduced radius of curvature [m].

The reduced Young's modulus is defined as:

$$\frac{1}{E'} = \frac{1}{2}\left[\frac{1-{\vartheta_A}^2}{E_A} + \frac{1-{\vartheta_B}^2}{E_B}\right] \tag{3.3}$$

Where:

ϑ_A and ϑ_B	are the Poisson's rations of the contacting bodies A and B.
E_A and E_B	are the Young's moduli of the contacting bodies A and B.

For example, reduced Young's modulus for contact between steel spheres of $\vartheta_{steel} = 0.3$ and $E_{steel} = 2.1 \times 10^{11}\ Pa$ is $E' = 2.308 \times 10^{11}\ Pa$.

It can be noted that for the spheres:

$$R_{ax} = R_{ay} = R_A \ and\ R_{bx} = R_{by} = R_B$$

Where:

R_A and R_B	are the radii of the spheres A and B, respectively.

Substituting into equation (3.2) gives:

$$\frac{1}{R'} = \frac{1}{R_x} + \frac{1}{R_y} = \frac{1}{R_A} + \frac{1}{R_B} + \frac{1}{R_A} + \frac{1}{R_B} = 2\left(\frac{1}{R_A} + \frac{1}{R_B}\right) \tag{3.4}$$

Where:

$$\frac{1}{R_x} = \frac{1}{R_y} = \frac{1}{R_A} + \frac{1}{R_B}$$

The exact analysis of elastohydrodynamic lubrication by Hamrock and Dowson provided the most important information about EHD. The results of this analysis are the formulae for the calculation of the minimum film thickness in elastohydrodynamic contacts. The formulae derived by Hamrock and Dowson apply to any contact, such as point, linear or elliptical, and are now routinely used in EHL film thickness calculations. They can be used with confidence for many material combinations including steel on steel even up to maximum pressures of 3–4 GPa. The numerically derived formulae for the central and minimum film thicknesses, as shown in Figure 3-12, are in the following form:

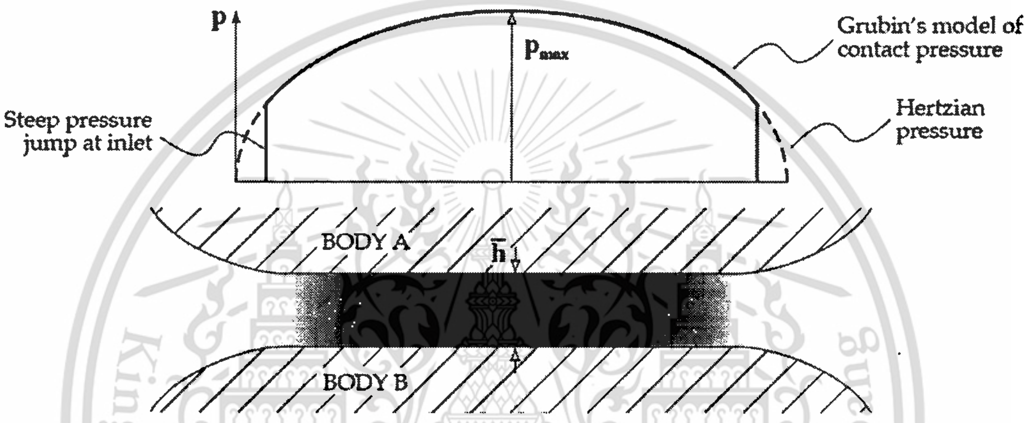


Figure 3-12. Approximation to film thickness within an EHD contact [35]

$$\frac{h_c}{R'} = 2.69\left(\frac{U\eta_0}{E'R'}\right)^{0.67}(\alpha E')^{0.53}\left(\frac{W}{E'R'^2}\right)^{-0.067}(1-0.61e^{-0.73k}) \qquad (3.5)$$

$$\frac{h_0}{R'} = 3.63\left(\frac{U\eta_0}{E'R'}\right)^{0.68}(\alpha E')^{0.49}\left(\frac{W}{E'R'^2}\right)^{-0.073}(1-e^{-0.68k}) \qquad (3.6)$$

Where:

h_c is the central film thickness [m].
h_0 is the minimum film thickness [m].
U is the entraining surface velocity [m/s], $U = (U_A + U_B)/2$.
η_0 is the viscosity at atmospheric pressure of the lubricant [Pa.s].
E' is the reduced Young's modulus [Pa].
R' is the reduced radius of curvature in the direction of rolling [m].

α is the pressure-viscosity coefficient [m^2/N].
W is the contact load [N].
k is the ellipticity parameter defined as: $k = a/b$ where 'a' is the semiaxis of the contact ellipse in the transverse direction [m] and 'b' is the semiaxis in the direction of motion [m].

As mentioned already, the approximate value of the ellipticity parameter can be calculated with sufficient accuracy from:

$$k = 1.0339\left(\frac{R_y}{R_x}\right)^{0.636} \tag{3.7}$$

Where:

R_x and R_y are the reduced radii of curvature in the x and y directions.

It can be seen that for line contacts k = ∞ and for point contact k = 1. It has been shown that the above EHL film thickness equations are applicable for 'k' values between 0.1 and ∞ [35].

The non-dimensional groups in equations (3.5) and (3.6) are frequently referred to in the literature as:

- The non-dimensional film parameter $\boldsymbol{H} = \frac{h}{R'}$
- The non-dimensional speed parameter $\boldsymbol{U} = \left(\frac{U\eta_0}{E'R'}\right)$
- The non-dimensional materials parameter $\boldsymbol{G} = (\alpha E')$
- The non-dimensional load parameter $\boldsymbol{W} = \left(\frac{W}{E'R'^2}\right)$
- The non-dimensional ellipticity parameter $k = \frac{a}{b}$

CHAPTER 4

RESEARCH METHODOLOGY

This thesis is a trying to understand what behavior occurred in lubricating oil in engine, especially on diesel engine. To achieve that goal, the experimental case study was designed and tested in to 4 experiments. Each step of the study has been explained as following.

1) The study of physical and chemical properties of diesel engine used oil
2) The study of diesel engine soot and commercial carbon black morphology
3) The study of soot particle distribution in liquid
4) The study of effect of soot contamination in oil on metal wear and friction by means of four-ball tribology test

4.1 The Study of Physical and Chemical Properties of Diesel Engine Used Oil

This is the investigation of physical and chemical properties of diesel engine used oil. The test was designed to record statistical data about oil degradation in diesel engine. There are typical properties that widely used to determine used oil (related to ASTM standard).

1) Oil condition investigation
    - Viscosity @ 40°C (ASTM D-445)
    - Viscosity @ 100°C (ASTM D-445)
    - Oxidation (ASTM E-2412M)
    - Nitration (ASTM E-2412M)
    - Total base number (ASTM D-4739)
2) Oil contamination
    - Soot contamination (ASTM E-2412M)
    - Water contamination (ASTM E-2412M)
    - Fuel contamination (ASTM E-2412M)
    - Metal particle contamination (ASTM D-6595)

This study is trying to inspect the amount of soot contamination in used oil and expecting to see the relationship between soot contamination level and oil condition changing. The assumption is that soot particle is consisting of carbon, unburned hydrocarbon, and other combustion products such as sulfur, oxygen, nitrogen. Then when soot particle contaminates into lubricating oil, it may react with oil by chemical reaction and then oil's properties change (oxidation, nitration, TBN). It may also react with oil by physical reaction and then viscosity change. Furthermore, from all publication literature review, they suggested that soot particle contamination is the main factor which induces more wear in automobile engine.

The target of this is to conduct used oil samples from various type of car to study a wide range of results which occur in real operating in diesel engine, so there is not the attempt to specific or control type of car in this test.

Used oil samples are kept from diesel engine crank case through oil level deep-strip hole. The volunteer cars are from different mile age and all cars are at end of oil change interval.

Lubricating oil sampling equipment consist of vacuum pump, plastic tube, and plastic bottle. They are shown in Figure 4-1 where this assembly of these equipment is shown in Figure 4-2. Figure 4-3 is shown keeping oil sample from engine through oil level deep-strip hole.

Figure 4-1. Lubricating oil sampling equipment (upper) vacuum pump (lower left) plastic tube (lower right) plastic bottle

Finally, there are all 17 volunteer car in this case study. Most of them are passenger car which the engine size is in range of 2,000cc to 3,500 cc. Only 2 samples are kept from heavy duty diesel truck. The test is not conducted at all standard test which mentioned above. The test is involved in inspecting oil viscosity (related to standard ASTM D-445, [36]), oxidation (ASTM E-2412M,

[37]), nitration (ASTM E-2412M, [37]), total base number (TBN, ASTM D-4739, [38]), soot contamination (ASTM E-2412M, [37]), and metal particle contamination (ASTM D-6595, [39]).

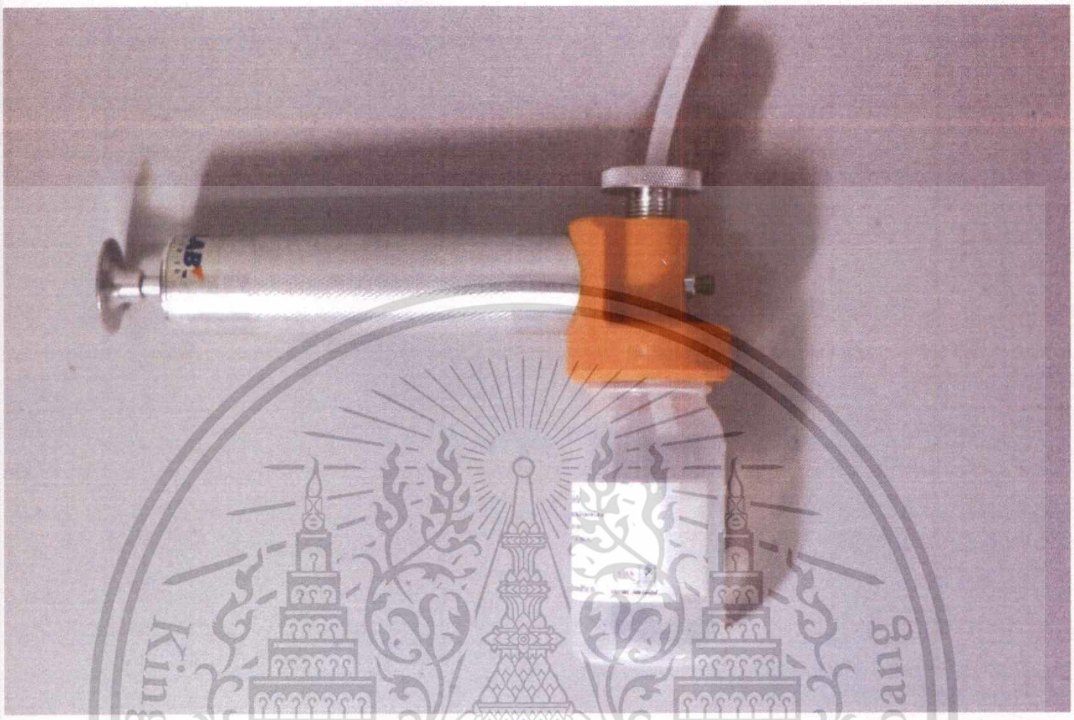


Figure 4-2. Assembly of lubricating oil sampling equipment

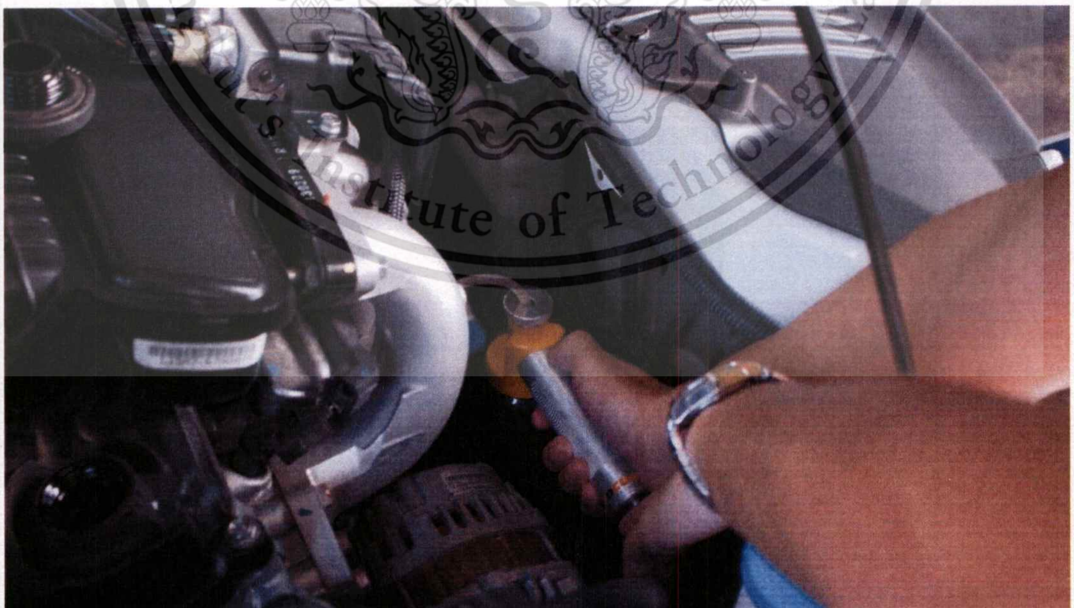


Figure 4-3. Keeping the lubricating oil from engine of tested car

4.2 The Study of Diesel Engine Soot and Commercial Carbon Black Morphology

Nowadays, there are synthetic carbon blacks which are very different in size and structure, they are commercially available. In this study, a commercial carbon black was used as representative of practical soot particulate. Furthermore, size distribution, morphology and nanostructure of carbon black and diesel engine soot particles were studied. Transmission Electron Microscope (TEM) was employed to investigate morphology and nanostructure parameters of primary particles and also agglomerate particles. The TEM machine which conducted in this thesis is shown in Figure 4-4. The main target is to define the mean size of these commercial carbon black and diesel engine soot particulates.

A transmission electron microscope (TEM) is an analytical tool allowing visualization and analysis of specimens in the realms of microspace to nanospace. High resolution can be used to analyze the quality, shape, size and density of quantum wells, wires and dots. The transmission electron microscope is a very powerful tool for material science. A high energy beam of electrons is shone through a very thin sample, and the interactions between the electrons and the atoms can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries.

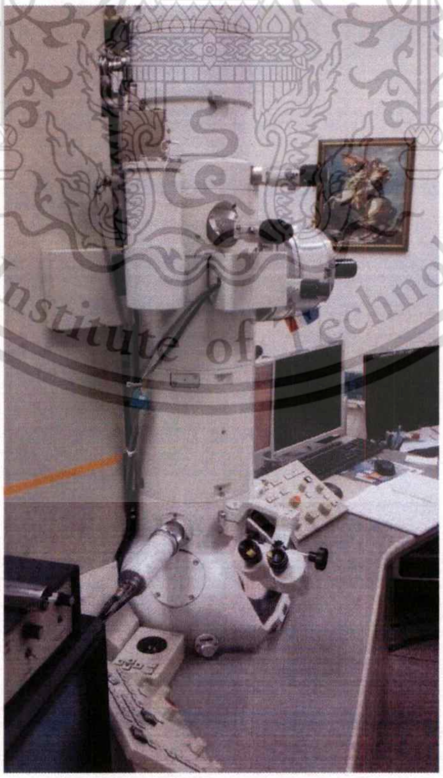


Figure 4-4. Transmission electron microscope machine

The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEM can reveal the finest details of internal structure - in some cases as small as individual atoms.

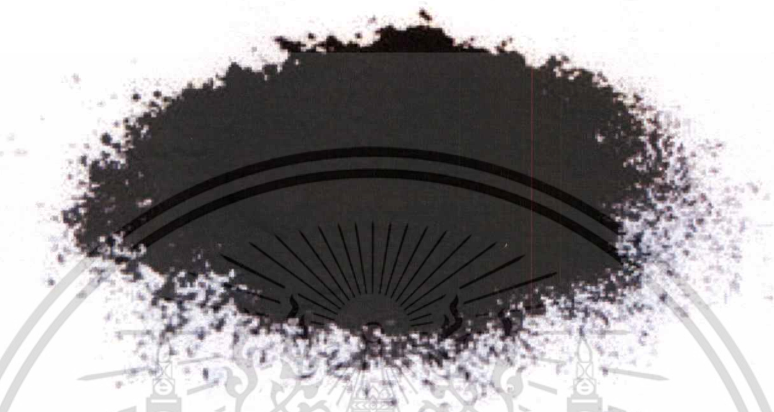


Figure 4-5. Commercial carbon black powder

The objective is to compare morphology between diesel engine soot and commercial Carbon Black. Figure 4-5 shows the powder of commercial carbon black and Figure 4-6 shows the preparation in copper grid.

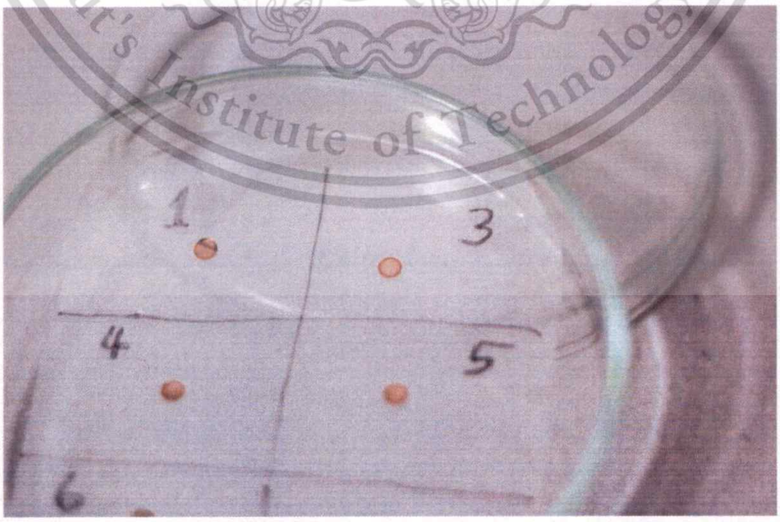


Figure 4-6. Carbon black powder and soot prepared in copper grid

The investigation by transmission electron microscope is a study of physical properties of both carbon black and soot. It presents the physical shape of single particle and also presents the complexity of their agglomerate. This is just only physical properties study.

For chemical properties, it is not conducted in this thesis. However, more studies are processed from the public literature reviews.

Maricq [40], in 2007, has written “Review Chemical Characterization of particulate emissions from diesel engine” and published in Journal of Aerosal Science. He investigated diesel particulate matter (PMs) and explained the composition model of its. It shows that diesel PM consists of main particle (soot, pure carbon composition) and other elements which are from the combustion process such as unburned hydrocarbon, sulfur, and metallic ash. This information is noticed that the soot particle which kept from diesel engine exhaust system is not purity by carbon element but it may have other elements contaminated at surrounding of soot particle. The model of Maricq is shown in Figure 4-7 [40].

Karin *et al.* [41] investigated chemical composition of diesel particulate matter (PMs) from different engine conditions and different fuel, and compared with commercial carbon black named N330. They found that the estimated carbon and hydrocarbon content inside PMs are analyzed by CHN analysis, as shown in Figure 4-8. Carbon fraction inside commercial carbon black is higher than that of diesel and biodiesel engine PMs. From their results, it showed that, at engine operating with high load, engine PMs has composition of carbon and hydrogen of 81% and 1.1% respectively. For carbon black, it consists carbon at 93.9% and hydrogen at only 0.5%. This is highly significant difference between commercial carbon black and diesel engine PMs.

Finally, the information above indicated that carbon black is more purity in carbon composition than PMs. It is the very advantage to use carbon black as a representative of diesel engine soot for this thesis study because it can be neglected the effect from chemical reaction with hydrogen in any test.

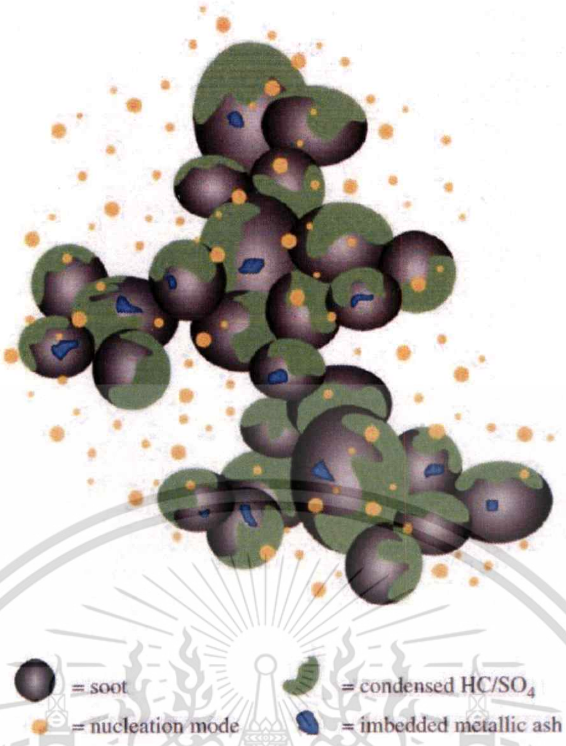


Figure 4-7. Diesel particulate matter composition model [40]

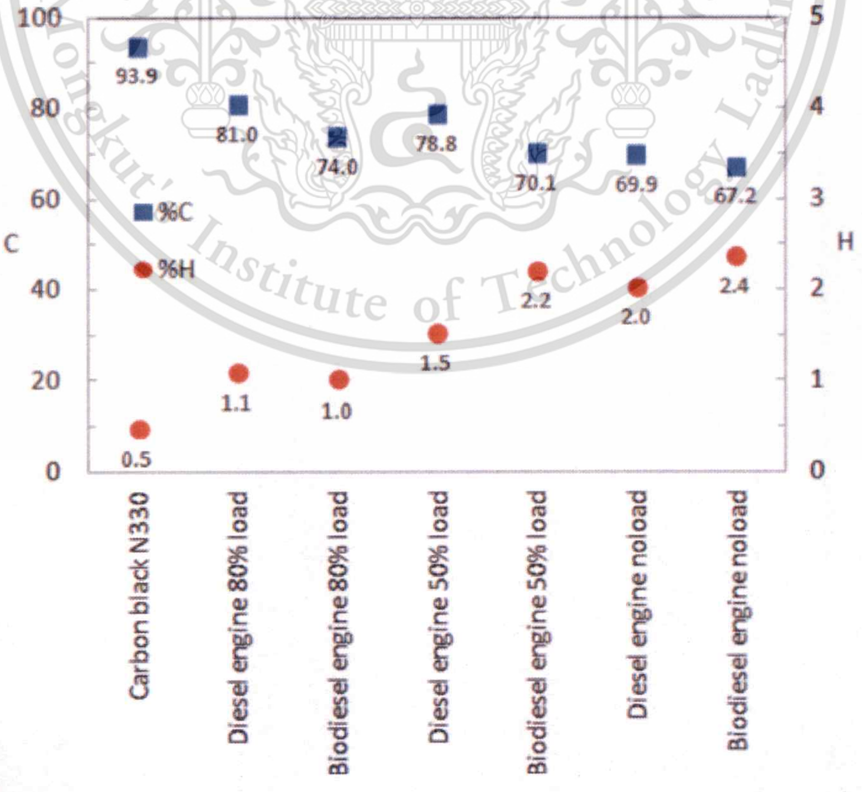


Figure 4-8. CHN analysis of diesel engine soot and carbon black [41]

4.3 The Study of Soot Particle Distribution in Liquid

The main purpose of this test is to analyze the statistical association between carbon black distribution and lubricating oil additive by means of Laser particle size detector.

In this case study, there are 2 major conditions for testing.

1) Behavior of soot dispersing in typical liquid
    - Dispersing in water
    - Dispersing in palm oil
    - Dispersing in formulated oil
2) Behavior of soot dispersing in commercial formulated oils which have different content of additives.

To study in the above conditions, several tools are used.

1) Particle size distribution is investigated by high resolution optical microscope and laser diffraction technique tool.
2) Formulated oil properties are tested as same as the test in the case study 1 (The detail is in topic 4.1). Viscosity, oxidation, nitration, and contamination are investigated.
3) Oil additives in formulated oil are investigated by X-ray fluorescence tool (XRF).

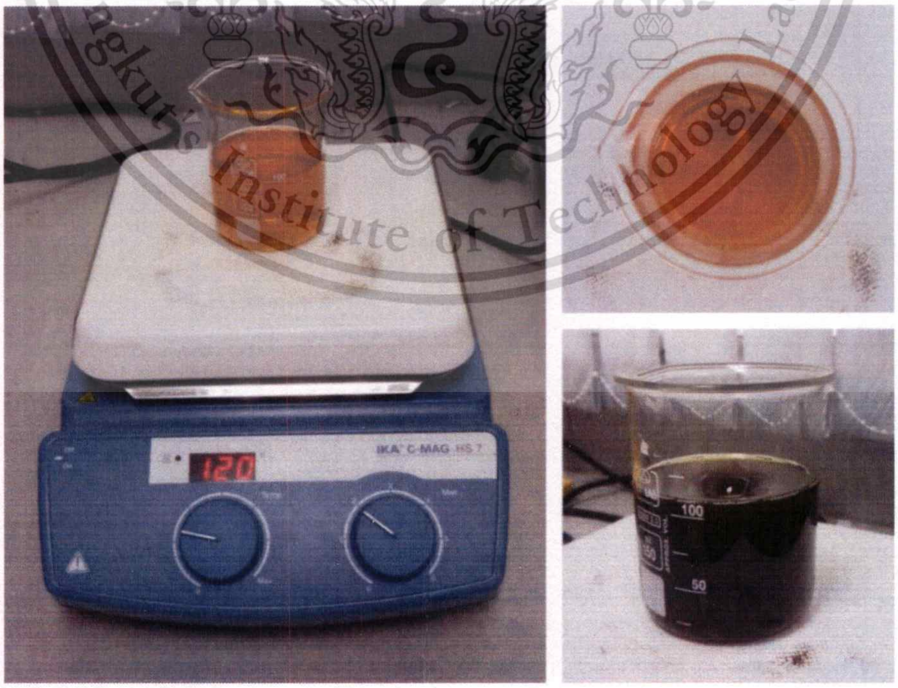


Figure 4-9. Experimental oil samples preparation by hotplate with magnetic stirer

Figure 4-9 shows apparatus for preparing liquid samples. All of samples (water, palm oil, and 2 formulated oils) are prepared volume of 100 ml and heat at 100ºC then mixed with carbon black long last 15 minutes. Each liquid is varying the amount of carbon black contamination from 0.25% to 2.0% by weight. Thus, there are all 16 liquid samples for testing.

The first test, all samples are observed by high resolution optical microscope to see the behavior of carbon black in all liquid and to compare the level of agglomerate particle.

Then, all samples are investigated particle size distribution by laser diffraction technique. The results will show the difference of the ability of dispersing particle or separating particle.

Laser particle size detection, sometimes called as laser diffraction, is a widely used particle sizing technique for ranging the materials from hundreds of nanometers up to several millimeters in size. Laser diffraction measures particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles, as illustrated below. The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter.

Laser diffraction measures particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Diffracted and refracted light is useful for this purpose; absorbed and reflected light works against this purpose and must be taken into account during measurement and size calculation. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles.

The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern, using the Mie theory of light scattering. The particle size is reported as a volume equivalent sphere diameter.

The second test, there are a trying to study the ability of additive in modern oil so more samples are tested with laser diffraction technique and checked additive by XRF.

There are 6 lubricating oil samples prepared for testing, lubricant A, B, C, D, E, and F. They all are formulated oils for heavy duty diesel truck engine and certificated viscosity grade as SAE 15W-40. The objective is to measure and classify additive elements in lubricating oil by means of X-ray Fluorescence spectrometer.

Figure 4-10. Heavy duty truck diesel engine lubricating oils (SAE 15W-40)

Figure 4-11. Lubricating oil samples prepared for XRF testing

X-ray fluorescence (XRF) is a powerful analytical instrumental method used in a wide variety of industries to determine the elemental composition of various materials. In oil analysis especially, XRF techniques have gained wide acceptance. Among other applications, XRF is used to determine Sulphur in petroleum products and residual catalysts, monitor additives in lubricating oils, analyze regular wear metal in lubricants and analyze wear debris [42].

The oil samples were mixed with a suitable solvent and introduced into the plasma of the spectrometer. The plasma is generated by a powerful radio frequency discharge and very high temperatures. When the different elements are subjected to such high temperatures, they will emit light of different frequencies. The intensity of each frequency is proportional to the concentration of each element in the oil.

Finally, after the lubricant additive element has been known, they will have been classified to indicate the function of the found additives by relying on the reasonable information powered by Evan [42] on Table 4-1.

Table 4-1. General element sources typically analyzed using XRF [42]

General element	Contamination sources
Iron (Fe)	Cylinder liners, crankshafts, gear, shafts ,valves, anti-friction bearings, rust, radiator water
Chromium (Cr)	Cylinder liners, rings, shafts, anti-friction bearings, internal coolant leak, dirt entry, coatings
Nickel (Ni)	Anti-friction bearings, gears, turbine components, valve and valve guides, coatings, fuel contaminant
Molybdenum (Mo)	Piston rings, synchro rings, oil additives, greases, solid additive (anti-friction), internal coolant leak
Vanadium (V)	Turbine blades, valves, fuel contaminant
Manganese (Mn)	Shafts, valves, anti-friction bearings, dirt entry
Titanium (Ti)	Turbine components, springs, valves, ceramics, dirt entry
Aluminum (Al)	Pistons, plain bearings, torque convertors, thrust washers, bushes, housings, pumps, greases, dirt entry
Copper (Cu)	Plain bearings, bushes, thrust washers, any components made from "yellow metal alloys" (such as bronze, phosphor bronze or brass), worm gears, clutch packs, brakes, cooling system, oil additives, assembly greases
Tin (Sn)	Plain bearings, piston flashing, solder, cooling system
Lead (Pb)	Plain bearing, bushes, clutch packs, cooling system, solder, oil additives, petrol additives, combustion by-products, greases, coatings
Magnesium (Mg)	Oil additives, sea water, coatings, engine blocks, housings/casings
Calcium (Ca)	Oil additives, greases, sea water
Zinc (Zn)	Oil additives, brass components, cooling system
Phosphorus (P)	Oil additives, bronze components
Sulphur (S)	Oil additives, base oil component
Barium (Ba)	Oil additives
Boron (B)	Oil additives, internal coolant leak
Lithium (Li)	Greases
Sodium (Na)	Internal coolant leak, oil additives, greases, dirt entry, sea water
Silicon (Si)	Dirt entry, oil additives, internal coolant leak, greases, assembly compounds, pistons, silicon/aluminum alloys

4.4 The Study of Effect of Soot Contamination in Oil on Metal Wear and friction by Means of Four-ball Tribology Test

The Four-ball testing is one of the tribology test methods. This test method can be used to determine the relative wear preventive properties of lubricating fluid in sliding contact under the prescribed test conditions. No attempt has been made to correlate this test with balls in rolling contact [43].

The illustration of principle for a Four-ball set-up is presented in Figure 4-12 and Figure 4-13. The Four-ball tribology test is a versatile test for evaluating seizure and wear. The upper holder has one rotating steel ball, which is loaded against lower three stationary steel balls. All contact areas are drowned in the testing lubricant. The load can be applied by using deadweight or through a hydraulic system. The rotation is central along the symmetry axis of both the upper and the lower holders. Circular wear scars will appear on the lower balls, while a circular wear track will appear on the upper ball.

The main purpose of this test is to measure wear and friction due to carbon black by means of Four-ball testing.

In Four-ball tribology testing, to study the impact of soot on metal wear, four lubricating oil samples were prepared. Two samples are fresh oil from lubricant A and B, other two samples are the oil which were contaminated with carbon black at 1% weight concentration.

There were 4 lubricating oil samples prepared for testing as following.

- New lubricant A
- New lubricant B
- New lubricant A added carbon black 1% (wt.)
- New lubricant B added carbon black 1% (wt.)

Lubricant A and B are formulated oils for heavy duty diesel truck engine and certificated viscosity grade as SAE 15W-40.

Four-ball test machine has load cell sensor on driving shaft. During the test, resistant force which occurring is recorded. So friction torque during test can be measured and can be calculate more or convert to friction force and also friction coefficient. After test, wear will occur on all steel ball, where wear scar appears 3 lower ball and wear track appears on upper ball, as model is shown in Figure 4-14. The prepared oil samples are shown in Figure 4-15 and the prepared steel balls are shown in Figure 4-16.

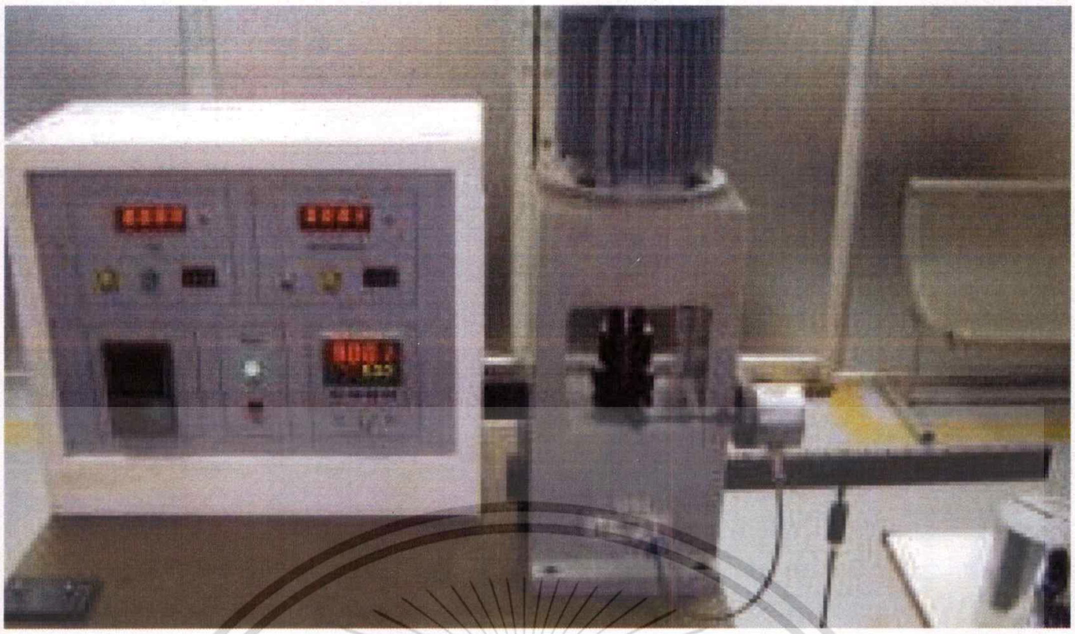


Figure 4-12. Four-ball tribology test machine

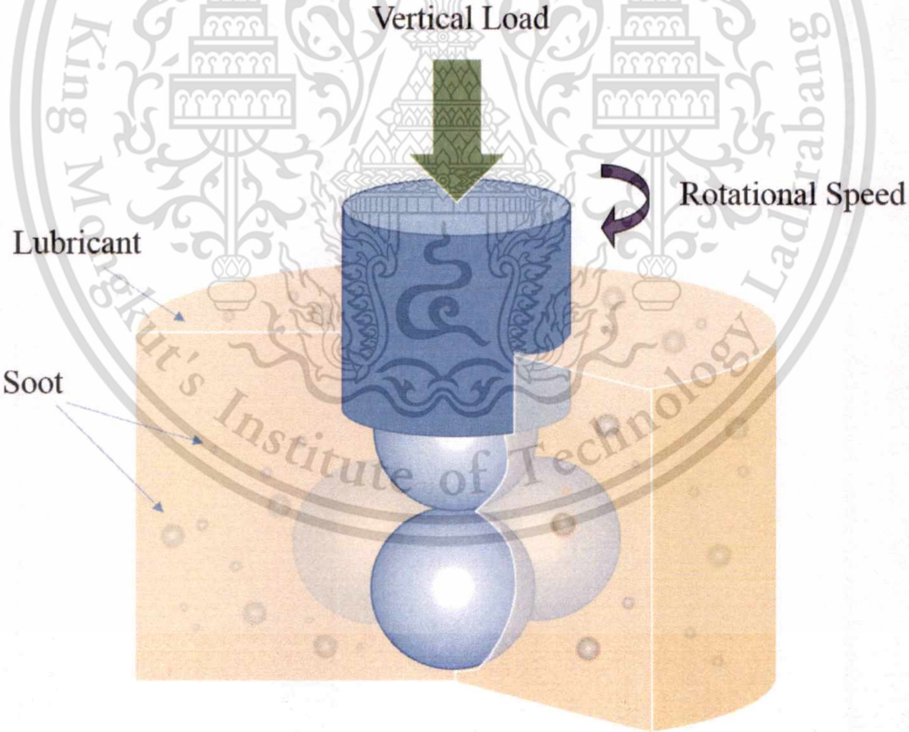


Figure 4-13. Schematic of Four-ball tribological test

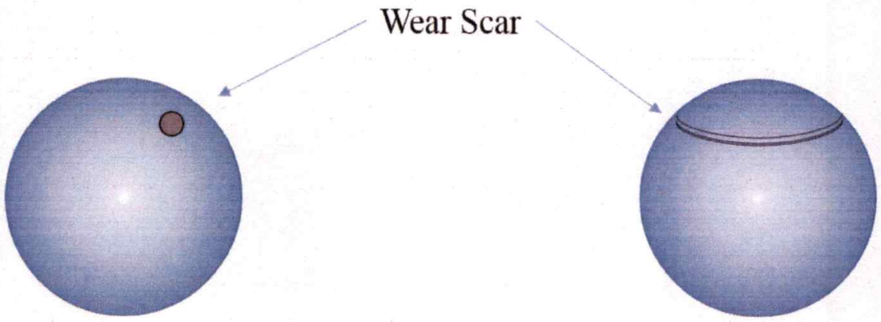


Figure 4-14. Wear scar on steel ball from Four-ball tribology test

Figure 4-15. Lubricating oil samples for Four-ball tribology testing (a) new lubricant A (b) new lubricant B (c) new lubricant A added carbon black 1% (wt.) (d) new lubricant B added carbon black 1% (wt.)

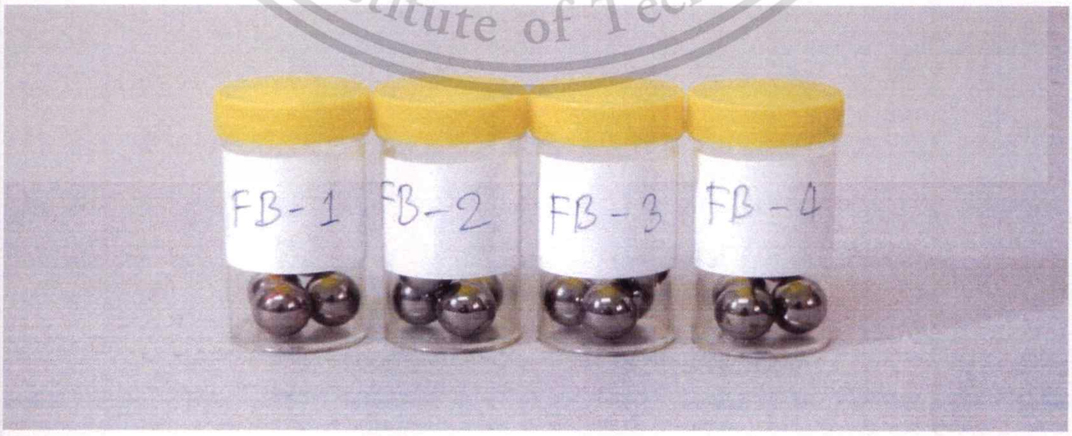


Figure 4-16. Steel balls prepared for Four-ball tribology testing

The four lubricating oil samples were tested via using this tribology test method as follow the ASTM standard number D-4172. Three 12.7 mm diameter steel balls are clamped together and covered with the lubricating oil sample to be evaluated. A fourth 12.7 mm diameter steel ball, referred to as the top ball, is pressed with a force of 392 N into the cavity formed by the three clamped balls for three-point contact. The temperature of the test sample is regulated at 75°C and then the top ball is rotated at 1200 rpm for 60 min.

The testing results are compared by using the average size of the scar diameters worn on the three lower clamped balls, during testing, friction torque is also measured. The wear scar results are observed by Optical Microscope (OM), firstly.

After inspect by OM, wear that appear on both upper balls and lower balls are also inspected more by convert the captured images from optical microscope to black and white color and gray scale color for helping investigation morphology on wear scar.

Moreover, 3D image rendering system is used to investigate wear shape and measure surface roughness. This test will help us to know more details in wear mechanism which occurred during test especially the test with soot contamination oil samples.

The Bottom Line

Now, all details of each designed case study have been already explained. Then, next chapter will be the results of each experiments and also the analysis information of that data. Every investigating result will help us to clarify and understand the characteristic of soot and carbon black, and will be also reach a knowledge about the behavior among particulates, metal wear, and lubricating oil additives.

CHAPTER 5

RESULTS AND DATA ANALYSIS

On This chapter, all results from each case study are shown. There are all case studies which are already descripted in previous chapter. The results are separated into 10 topics.

5.1 Amount of Soot Contamination in Diesel Engine Used Oil

After investigated used oil which are sampled from passenger car and truck. There are 17 samples of diesel engine used oil, 15 samples from passenger car and 2 samples from heavy duty truck. Moreover, in a group of passenger car, they can be separated into 3 groups by engine size classifying, 2,000 cc, 2,500 cc, and 3,000 cc. For truck engine, its size is 7,684 cc. The oil interval changes of passenger car differ from truck where truck has more long last interval change than passenger car. Passenger car normally changes oil when oil age reach 10,000 km and 25,000 km for truck (see detail in Appendix A).

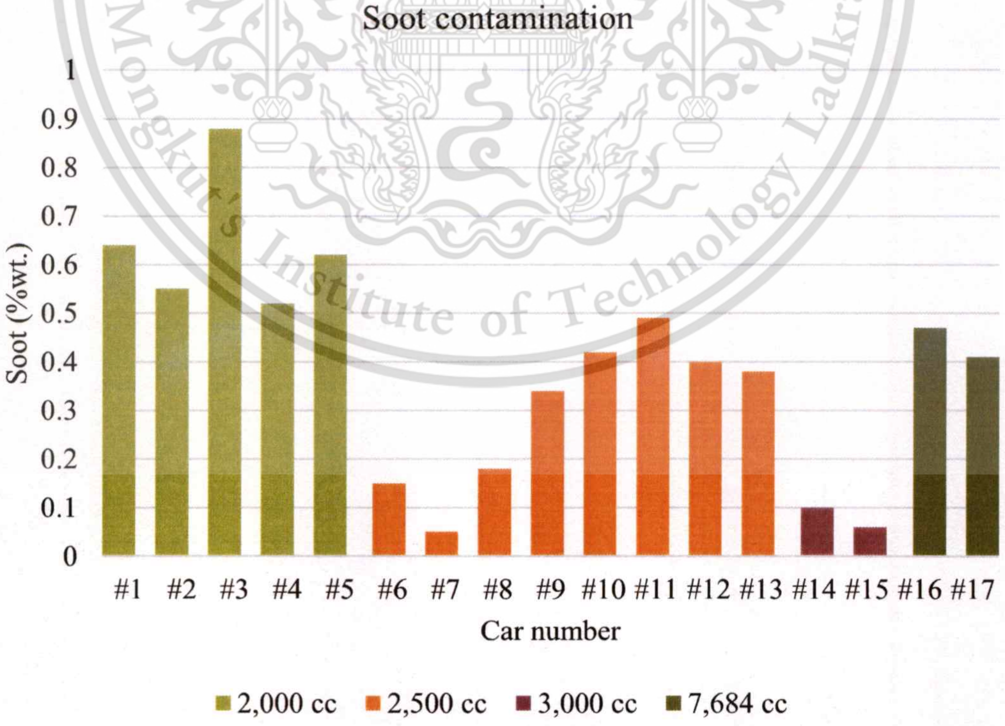


Figure 5-1. Soot contamination in diesel engine used oil

This case is trying to investigate the amount of soot that contaminate in diesel engine oil at after end of interval change. The results are shown in Figure 5-1. There are 5 samples which kept from 2,000 cc engine and their average value of soot contamination is 0.64% by weight. For 2,500 cc engine, 8 samples have the average soot of 0.30%. They are 0.08% and 0.44% of soot contamination from 3,000 cc and 7,684 cc engine, respectively.

Table 5-1. Average soot contamination in diesel engine passenger car and truck

Group	Engine size	Amount	Average soot contamination (% wt.)
1	2,000 cc	5	0.642
2	2,500 cc	8	0.301
3	3,000 cc	2	0.080
4	7,684 cc	2	0.440
Total	All	17	0.392

It is an average value of soot contamination in all samples of 0.39% by weight. All of the average value are presented in Table 5-1. This results indicated that, among oil using through end of oil life, soot contaminated in oil is less than 1% by weight. From literature reviews, in past century, the amount of soot founded in engine reached in range of 3-5%. This may be the effect by fuel technology and engine development by manufacturer that trying to reduce the producing of particulate matter in the engine.

The results have been noticed that the amount of soot in small engine is higher than large size engine. It may be because small engine has to operate in higher speed than large engine to reach maximum torque and power during running. Then it produced soot more times than the larger size engine. In case of truck engine, it is the largest engine in this study and it normally operated at high load situation so it may produce more soot by the increasing of fuel-air ratio during running at high load to reach high performance. Furthermore, truck also has longer period of oil change interval, then it has longer lasting for collecting soot in oil than the smaller size engine.

5.2 Viscosity Changing of Used Oil

This case is trying to investigate the level of viscosity of diesel engine oil at after end of interval change. The results are shown in Figure 5-2 and Figure 5-3. In case of viscosity test at 40°C, the viscosity in all samples fall in range of 61.8 – 70.6 cSt. The average value is 67.1 cSt. The samples from truck are not inspected in this test. It shows that the values of all group are very close to each other. It is just small difference (see detail in Appendix A).

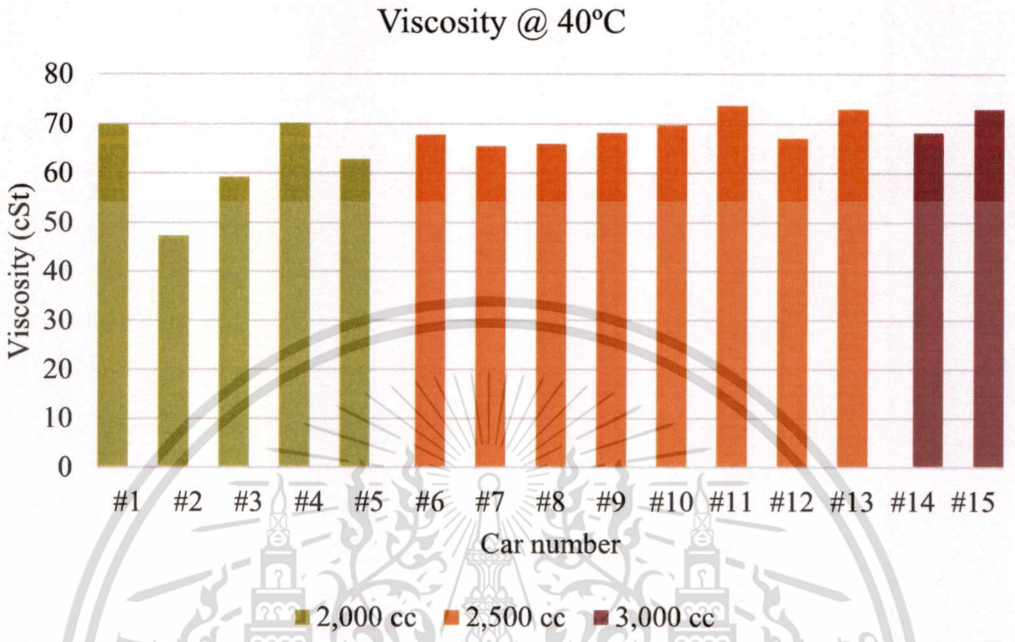


Figure 5-2. Viscosity at 40 Celsius of diesel engine used oil

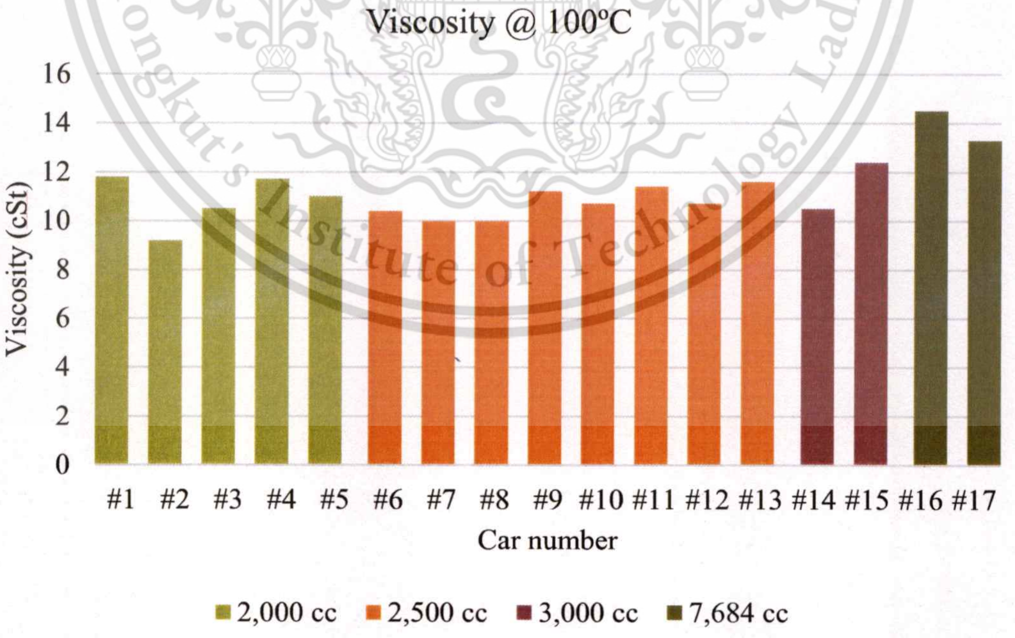


Figure 5-3. Viscosity at 100 Celsius of diesel engine used oil

In case of viscosity test at 100ºC, the viscosity of all group fall in range of 10.7 – 13.9 cSt, where samples from truck is the highest value in this test. The average viscosity is 11.7 cSt. All parameters are concluded in Table 5-2.

Table 5-2. Average viscosity of diesel engine passenger car and truck

Group	Engine size	Amount	Viscosity @ 40°C (cSt)	Viscosity @ 100°C (cSt)
1	2,000 cc	5	61.88	10.84
2	2,500 cc	8	68.89	10.75
3	3,000 cc	2	70.60	11.45
4	7,684 cc	2	-	13.90
Total	All	17	67.12	11.73

5.3 Increasing of Oxidation of Used Oil

This case is trying to investigate the level of oxidation in diesel engine used oil. The results are shown in Figure 5-4 and Table 5-3 (see detail in Appendix A).

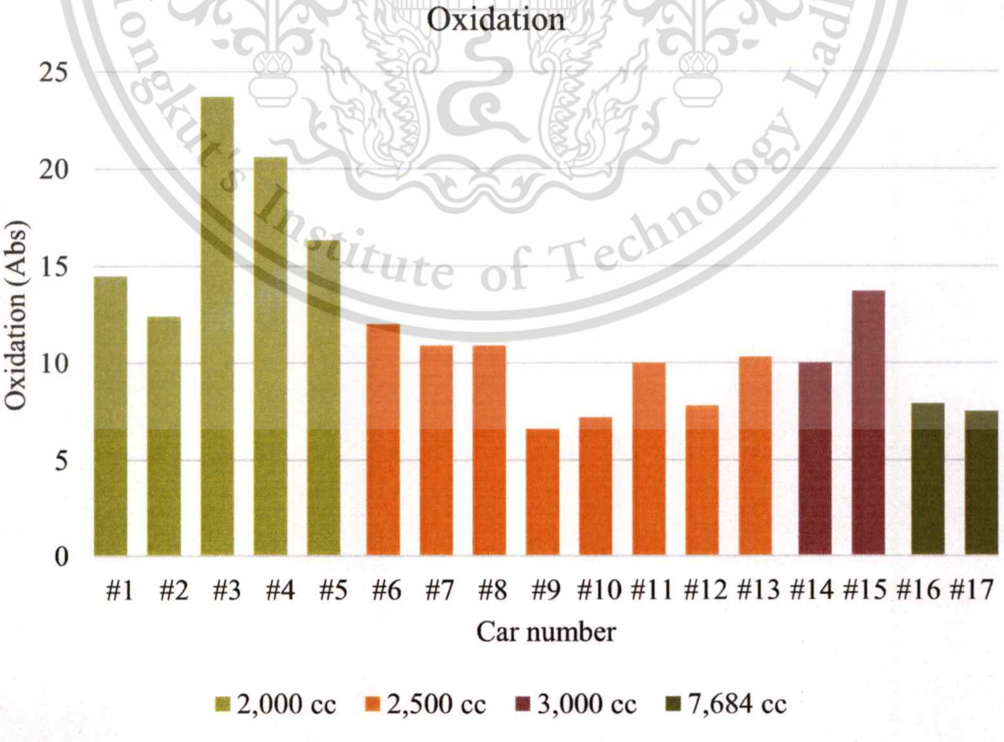


Figure 5-4. Oxidation in diesel engine used oil

Table 5-3. Average oxidation in diesel engine passenger car and truck

Group	Engine size	Amount	Oxidation (Abs)
1	2,000 cc	5	17.50
2	2,500 cc	8	9.45
3	3,000 cc	2	11.85
4	7,684 cc	2	7.70
Total	All	17	11.63

For oxidation test, it shows that the all average value is 11.6 absorbance, where group 1 (engine size 2,000 cc) is the highest level of oxidation at 17.5 absorbance. It has been noticed that this group is also producing highest soot contamination in used oil. Other groups are same level at about 10 absorbance.

5.4 Increasing of Nitration of Used Oil

This case is trying to investigate the level of nitration in diesel engine used oil. The results are shown in bar chart in Figure 5-5 and the average values of each car group are shown in Table 5-4 (see detail in Appendix A).

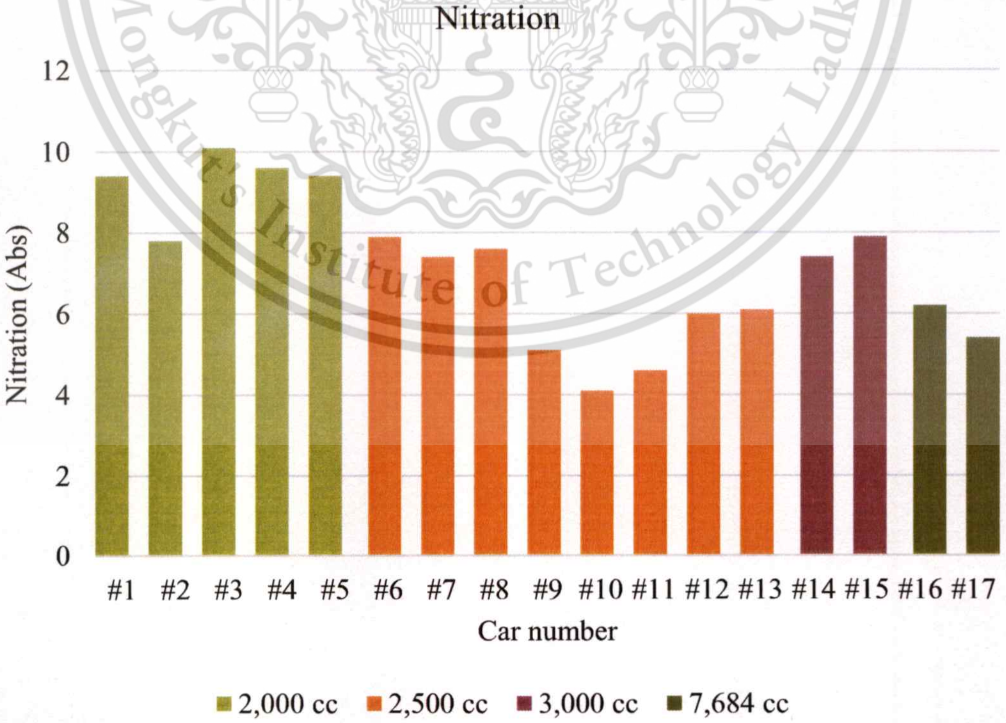


Figure 5-5. Nitration in diesel engine used oil

Table 5-4. Average nitration in diesel engine passenger car and truck

Group	Engine size	Amount	Nitration (Abs)
1	2,000 cc	5	9.26
2	2,500 cc	8	6.10
3	3,000 cc	2	7.65
4	7,684 cc	2	5.80
Total	All	17	7.20

For nitration test, the results are shows the same tendency as oxidation. It shows that the all average value is 7.2 absorbance, where the highest level of nitration of 9.3 absorbance is from group of small size engine, which are the group of highest percentage of soot contamination in used oil.

5.5 Decreasing of Total Base Number of Used Oil

This case is trying to investigate the level of total base number which remaining in diesel engine used oil. The results are shown in chart in Figure 5-6 and also shown the average value in Table 5-5 (see detail in Appendix A).

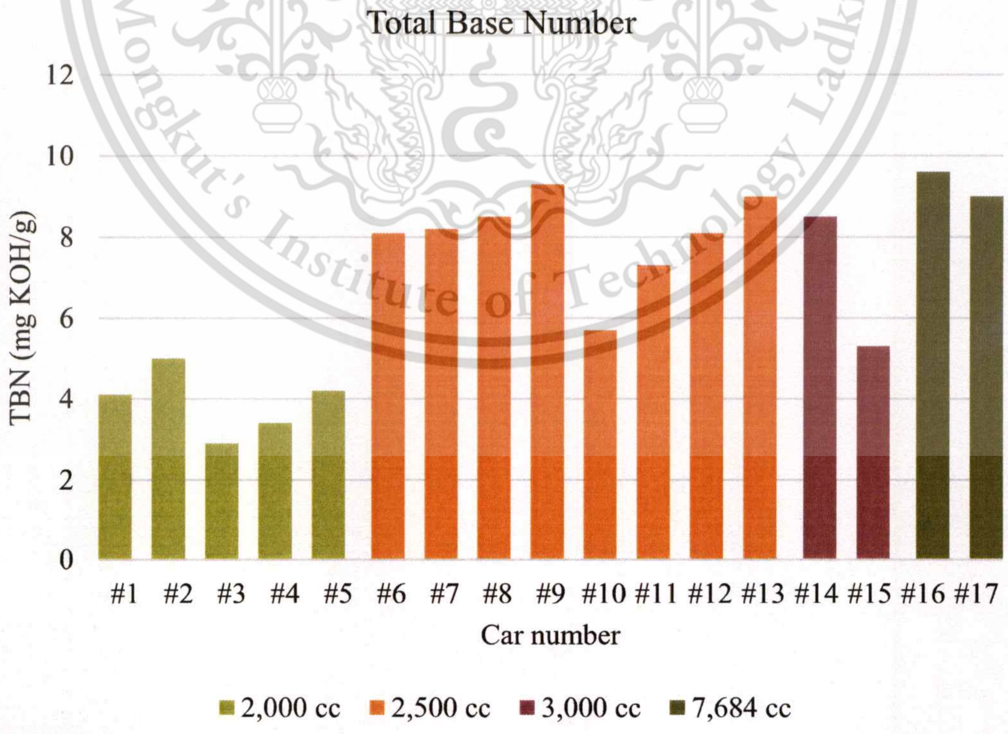


Figure 5-6. Total base number of diesel engine used oil

Table 5-5. Average total base number in diesel engine passenger car and truck

Group	Engine size	Amount	Total base number (mg KOH/g)
1	2,000 cc	5	3.92
2	2,500 cc	8	8.03
3	3,000 cc	2	6.90
4	7,684 cc	2	9.30
Total	All	17	7.04

The total base number (TBN) is measured of the oil's condition and a high TBN indicates a good condition. Fresh oil may contain basic additives such as detergents and dispersants, giving a high TBN. These basic additives are added to the lubricant to neutralize acidic components that may form in the lubricant. Therefore, the TBN will gradually be lowered when these additives are consumed, usually followed by oxidation and an increase in soot contamination. Consequently, the TBN is a good indicator of the remaining life of engine oils, express by Torbake [14].

The results show that the 2,000 cc engine has minimum value of total base number which relate to high nitration, oxidation, and soot contamination. When soot contaminate in lubricating oil, detergent react with them by surround soot particle and prevent them to agglomerate [14], then make the level of total base number decrease.

5.6 Metal Particle Contamination in Used Oil

Metal particle contamination in used oil is a measurement the volume of metal element in used oil. There are 2 classified groups, small particle size (smaller than 5 πm) and large particle size (larger than 5 µm), as shown in Table 5-6 (see detail in Appendix A).

Table 5-6. Average metal particle in diesel engine passenger car and truck

Group	Engine size	Car No.	Amount	Small particle (ppm)	Large particle (ppm)
1	2,000 cc	1-5	5	87.30	62.92
2	2,500 cc	6-13	8	36.40	20.08
3	3,000 cc	14-15	2	38.35	7.65
4	7,684 cc	16-17	2	9.45	4.55
Total	All		17	42.88	23.80

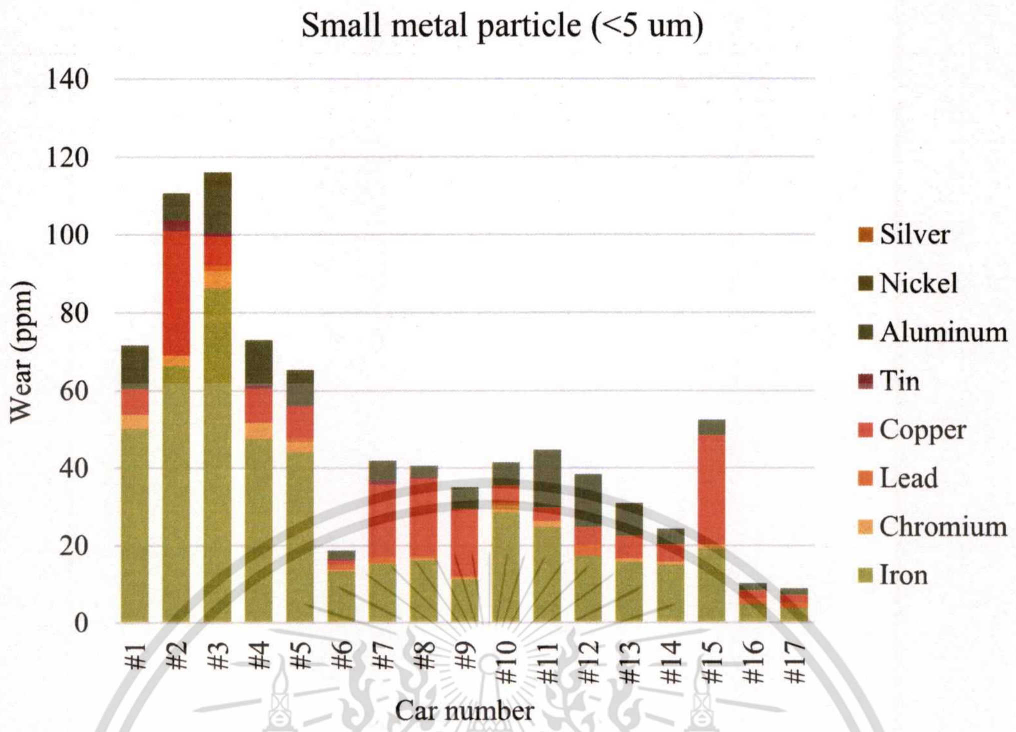


Figure 5-7. Small metal particle contamination in diesel used oil

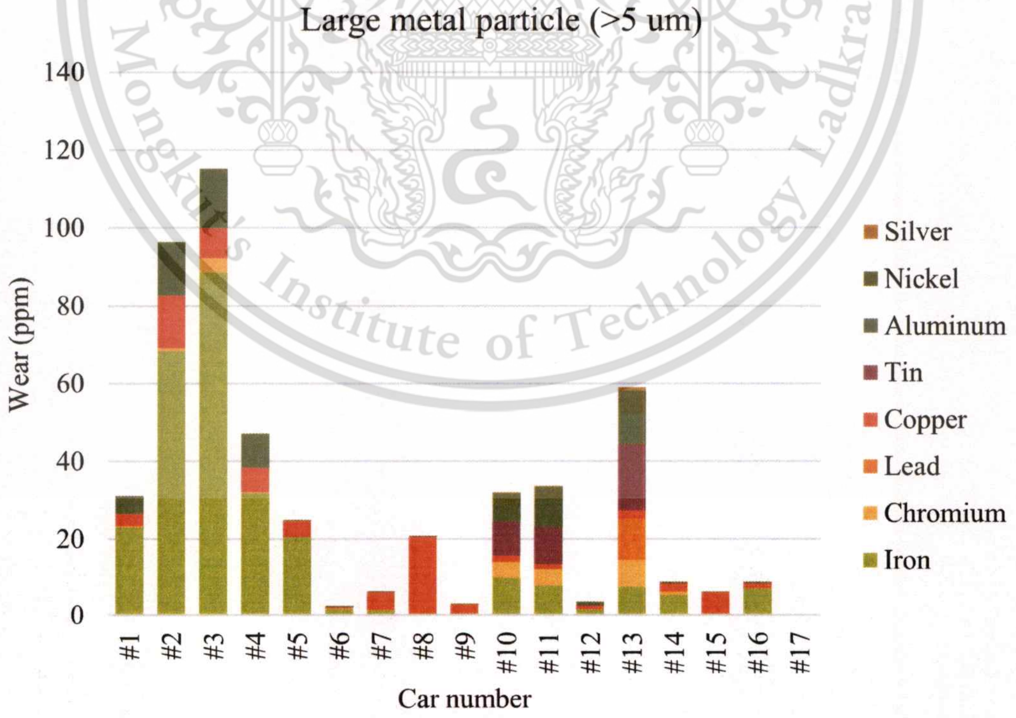


Figure 5-8. Large metal particle contamination in diesel engine used oil

Figure 5-7 and Figure 5-8 show the volume of small metal elements and large metal elements, respectively, which both small and large particle are from wear of engine parts. Group 1 (2,000 cc engine), number 1-5, has maximum volume at 87.3 ppm. It is higher than others for double.

According to previous study, it shows that group 1 car has produced high soot contamination. It has been noticed that when soot is more produced, more wear is occurred. Soot may cause in producing more wear. This is supported by the result test of Gautam *et al.* [18] that lubricant with soot contamination makes more wear than without, this is tested by ball-on-flat tribology test. Hu *et al.* [12] concluded that the average wear scar diameters of steel ball have increased among soot content increasing.

Figure 5-9, 5-10, 5-11, and 5-12, present the proportion of metal element particle contaminating in used oil and classified by group of engine's size, 2,000 cc, 2,500 cc, 3,000 cc, and 7,684 cc respectively. The results show that iron is the highest percentage and followed by copper and aluminum respectively because most of engine parts are made by iron, especially in the parts which have more rubbing surface areas, such as a cylinder wall area.

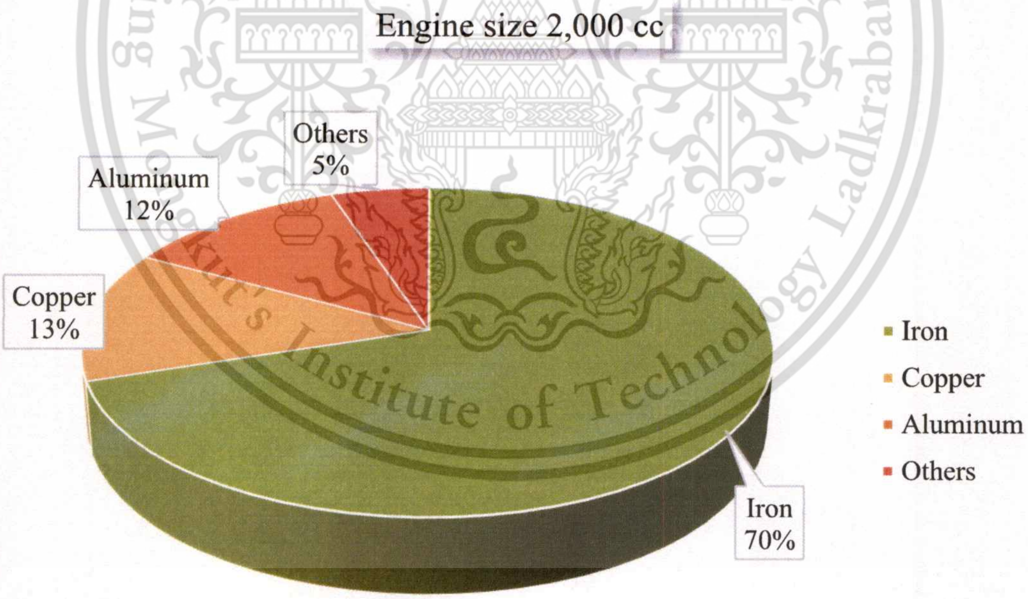


Figure 5-9. Total metal wear particle in used oil of 2,000 cc diesel engine

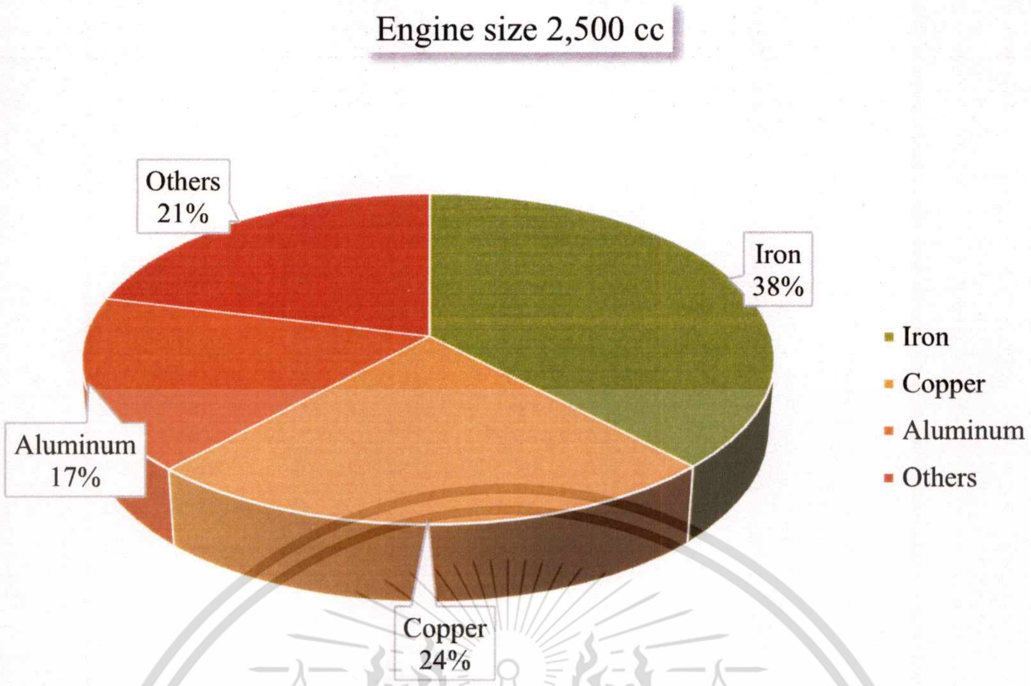


Figure 5-10. Total metal wear particle in used oil of 2,500 cc diesel engine

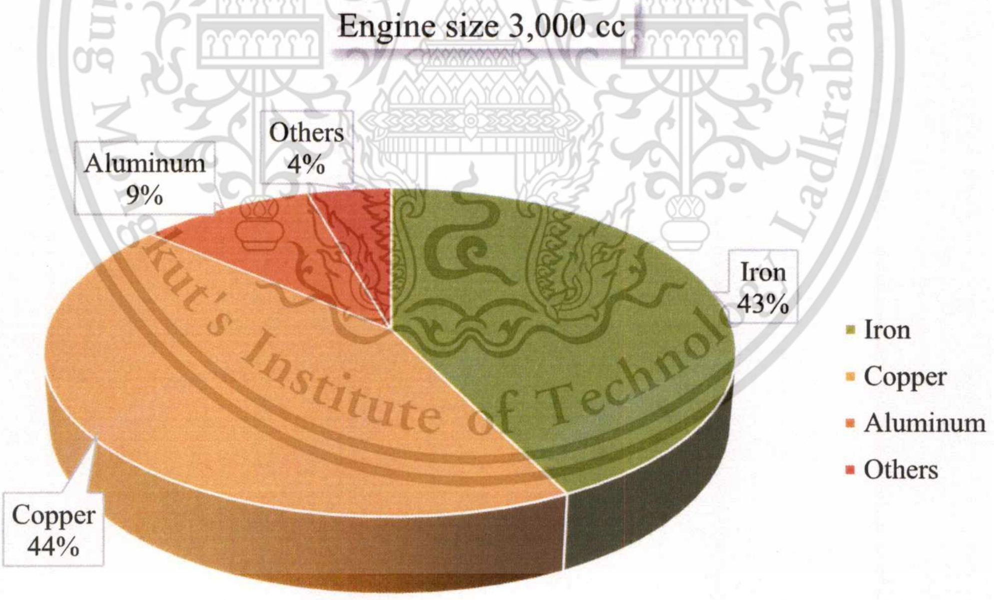


Figure 5-11. Total metal wear particle in used oil of 3,000 cc diesel engine

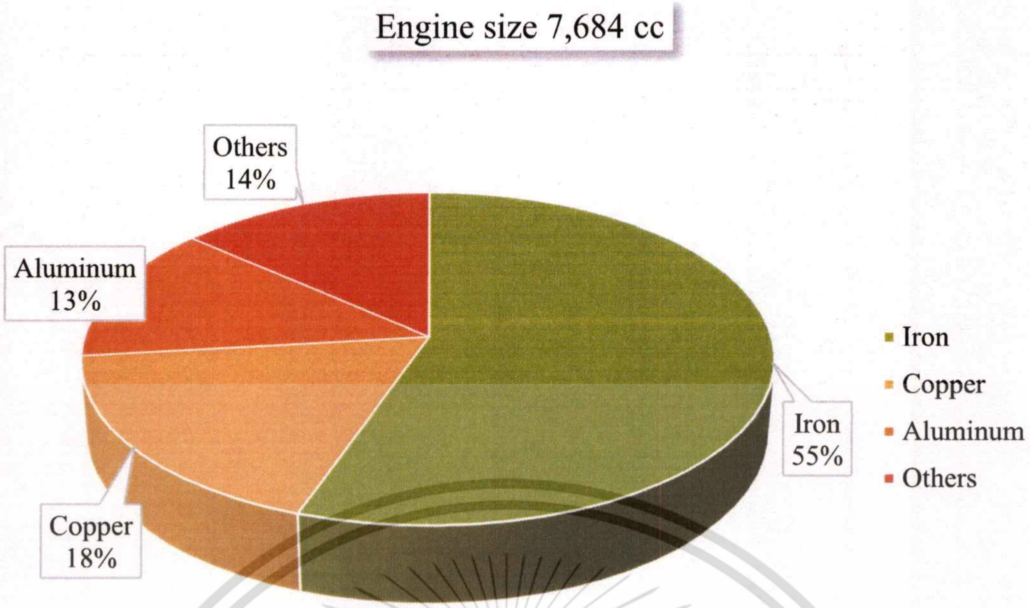


Figure 5-12. Total metal wear particle in used oil of 7,684 cc diesel truck engine

Base on the results from 5.1 to 5.6, it indicated that the level of total base number strongly relates to the amount of soot contamination. When soot increases, TBN decreases.

The level of soot relates to level of wear where soot increases, wear also increases.

Oxidation and nitration value are direct-variation with soot content and they are also direct-variation with operating time of engine. However, the test results appear to be no clear relationship between the soot content and oxidation and nitration.

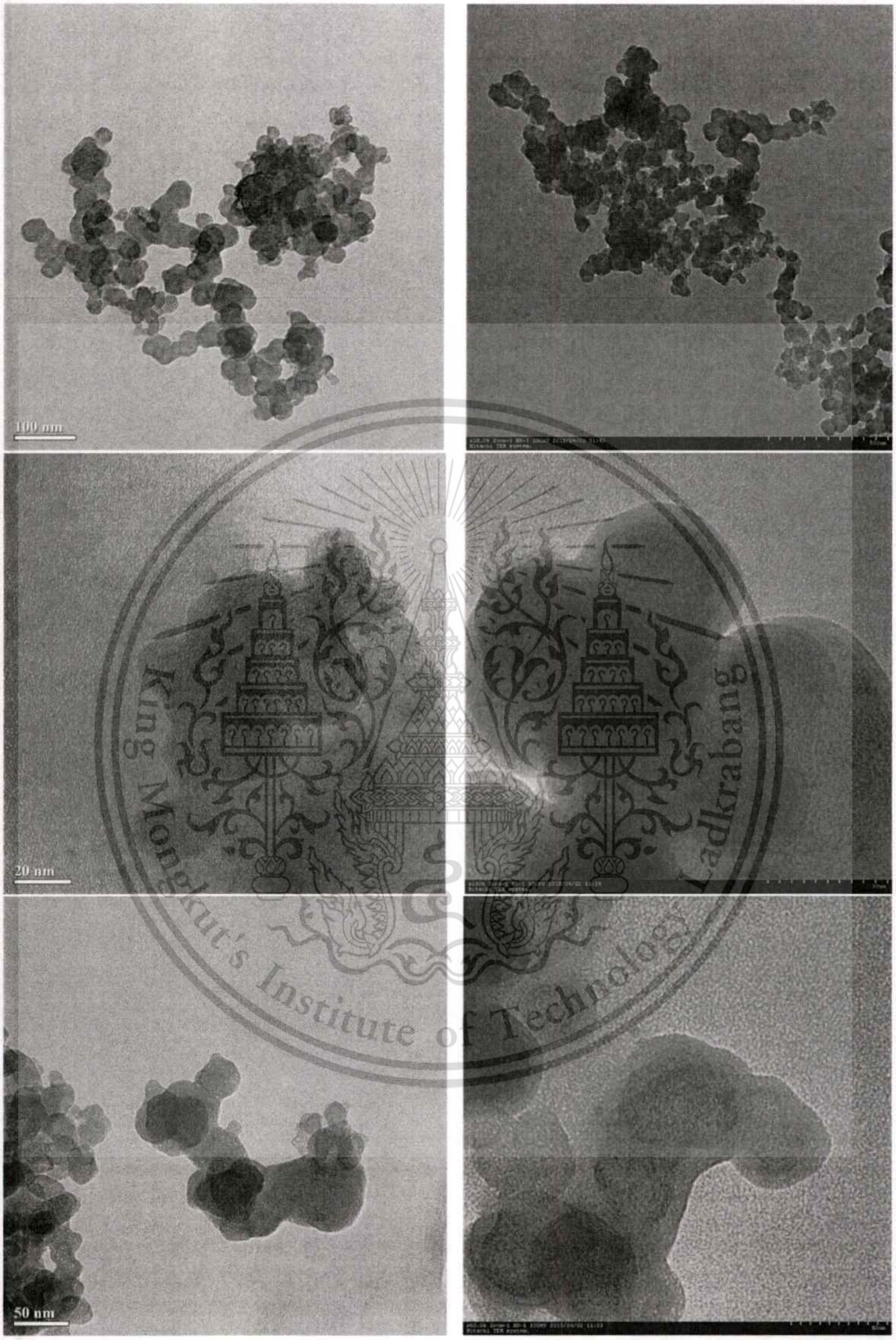


Figure 5-13. Morphological differences of soot and carbon black (left) Diesel engine exhaust soot (right) commercial carbon black

5.7 Comparison of Diesel Engine Soot and Commercial Carbon Black

After Transmission Electron Microscope (TEM) has been conducted to capture the images of particulates both soot particles from exhaust system in diesel engine and commercial carbon black particles, some images are shown in Figure 5-13. The samples were prepared by using the ethanol solvent extraction technique and were put on the copper grid plates.

There are all 68 images captured of the diesel soot and 47 images for commercial carbon black. The images shown in Figure 5-13 (left) present typical single soot and agglomerates from diesel engine exhaust system, and Figure 5-13 (right) present carbon black. Most of the images captured is in high magnification, so there are only some images that shown clumped particulates. The agglomerate size is 200 nm up to 500 nm in both soot and carbon black.

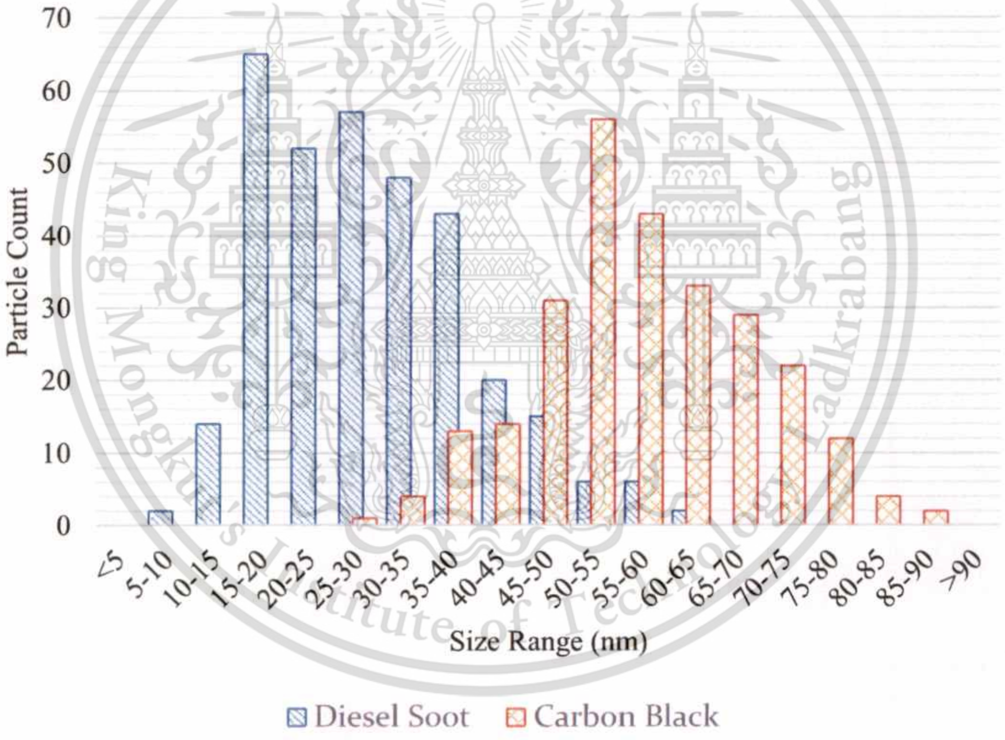


Figure 5-14. Size distribution of primary particles of diesel soot and commercial carbon black

These images of primary particle are quite difficult to measure the primary size of single particle because they are stacking together, so we cannot determine diameter of all particulates. The idea is just only measuring some of them that stay at border and clearly appear. Figure 5-14 presents the distribution of primary single size which plotted in histogram bar chart. There are in range of 5 nm to 90 nm. The highest peak of diesel soot and carbon black sizes are 15-20 nm and 50-55 nm, respectively. Most of soot are clearly presented smaller size than carbon black. More TEM image of soot and carbon black are shown in Appendix B.

Finally, more than 500 particles were investigated the primary size, 330 and 264 particle counts are from diesel soot images and carbon black images, respectively. The maximum diesel soot size is 62 nm and carbon black size is 87 nm. The minimum of diesel soot is also smaller than carbon black, 8 nm for diesel soot and 30 nm for carbon black. Then, the mean values of diesel soot and carbon black are 30 nm and 58 nm, respectively (more image in Appendix B).

Table 5-7. Statistical data of diesel soot and carbon black

Statistical Data	Soot and Simulant	
	Diesel Soot	Carbon Black
Particle Count	330	264
Maximum	62.1 nm	87.3 nm
Minimum	8.1 nm	29.5 nm
Average	29.5 nm	57.8 nm
Standard Deviation	10.8	11.3

The statistical data has been concluded in Table 5-7. It showed that the commercial carbon black, representing to typical soot, average size is double to the average of diesel engine exhaust system soot. It could be an effect from carbon black production process. When carbon black is produced in low temperature and low pressure atmosphere, it may become larger in size than the particle which is conducted in combustion chamber.

5.8 Soot Particle Distributing in Liquid

Figure 5-15, 5-16, 5-17, and 5-18 are shown the dispersing of carbon black in water, palm oil, lubricant A, and lubricant B respectively. The gray color scale on each figure show the percentage of mixing carbon black into liquid samples. There are the percentage in range of 0.25%, 0.5%, 1.0%, and 2.0% by weight.

Results of the particle-dispersing observation by optical microscope are accordance with assumption before the experiment that soot dispersion is not similar at different liquid significantly. Piles of black particle obviously seen in Fig. 5-15 is the accumulated carbon black which represent the soot particle in water. Additionally, the result presents the carbon black accumulates more clearly if its percentage by weight increases. However, the accumulation may not be strong because this situation is occurred in ambient air pressure and the temperature is not too high comparing to hard carbon which produced in combustion chamber of engine.

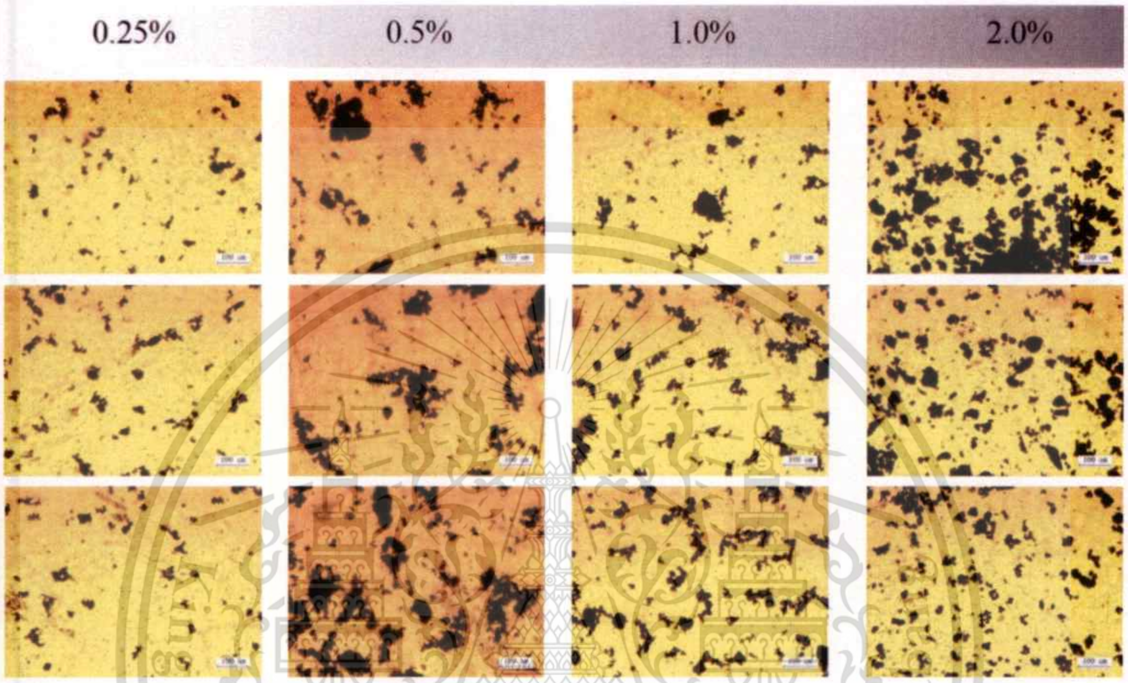


Figure 5-15. Carbon black disperse in water

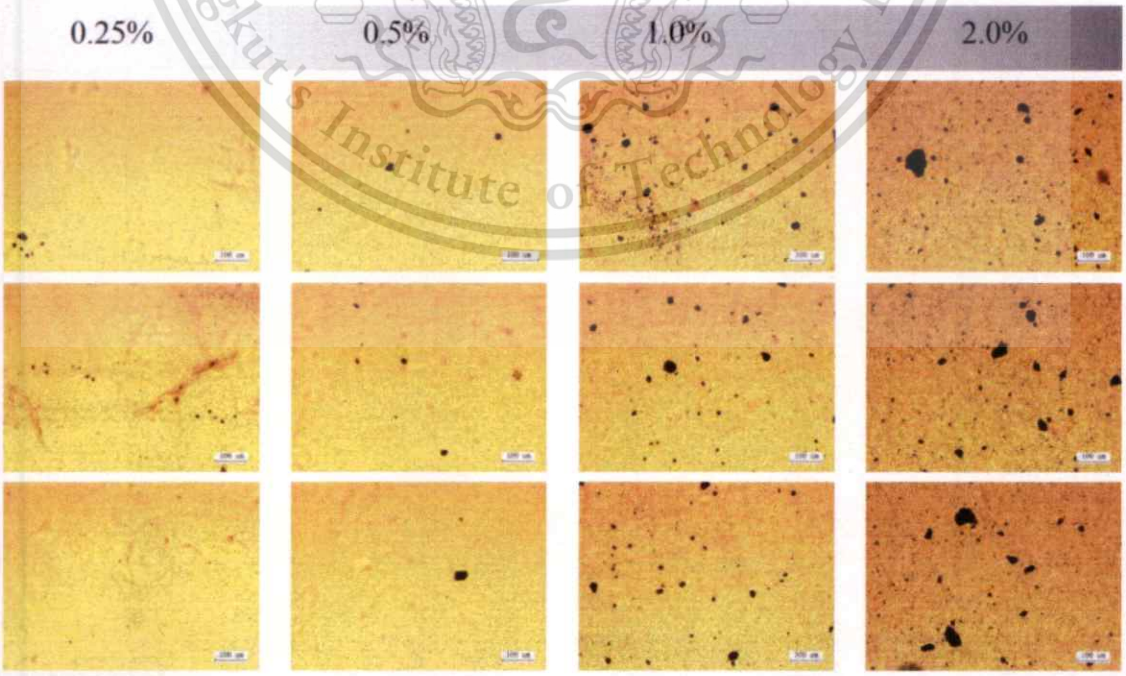


Figure 5-16. Carbon black disperse in palm oil

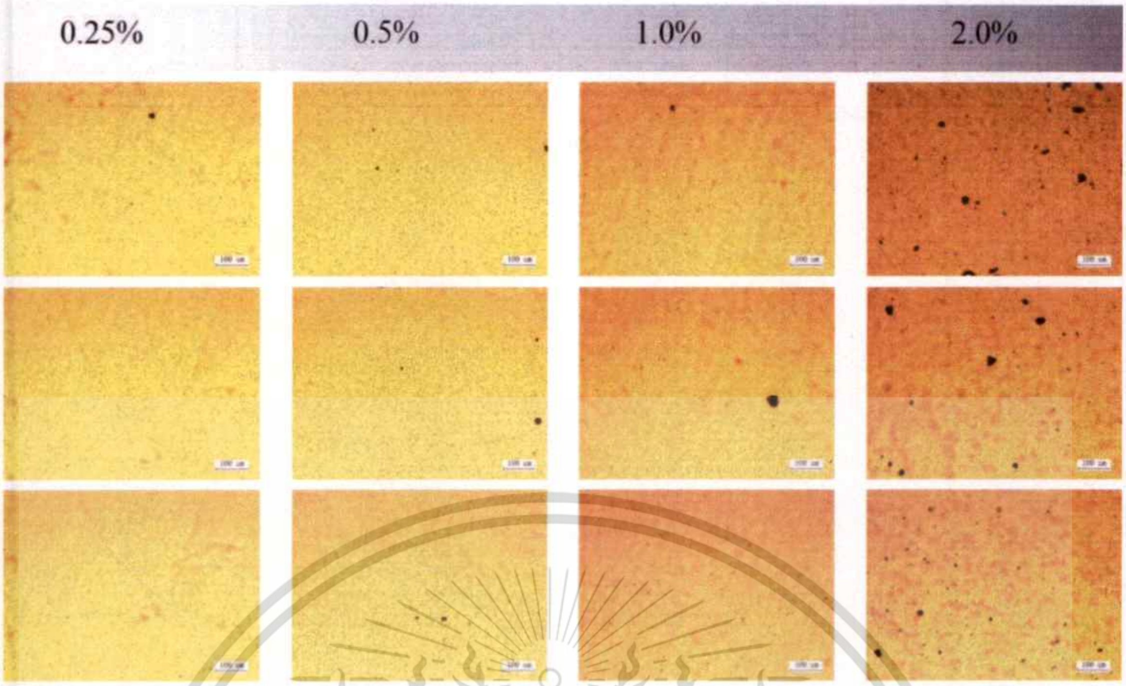


Figure 5-17. Carbon black disperse in formulated oil lubricant A

Figure 5-18. Carbon black disperse in formulated oil lubricant B

Moreover, as the other liquid sample shown in Fig 5-16, the observation results of carbon black dispersion in palm oil present it is worse if an amount of carbon black increases. Comparing between the two liquid, carbon black dispersion in palm oil, which is more similar chemical characteristic with oil lubricant than water, is quite batter than the previous one. As expected, when looking at the sample of the carbon black-dispersing results in formulated oil lubricant A and B (Fig. 5-17 and 5-18), theirs dispersing is significantly better than in water and oil because an oil lubricant has an additive that help to disperse soot particle. It is obviously different if the samples of liquid have much carbon back particle. At 2% carbon black, the dispersion in the oil lubricants is better than the others clearly.

When comparing between formulated oil lubricant A and B, the carbon black dispersion in oil lubricant A is worse than the other observed by color tone of the figures. The dark tone represents the dispersion of carbon black is quite great until a light is hard to lay through the lubricant. For this reason, it can be concluded that the lubricant B is better than the lubricant A.

After investigate the distribution of carbon black in liquid by using optical microscope, this case study is also investigated liquid sample mixed carbon black by laser diffraction technique. The results are shown in Figure 5-19 to 5-28.

Figure 5-19 shows size distribution of carbon black powder mixing in palm oil at 0.25% and 1% by weight. In case of mixing at 0.25%, there are small particles which have the size of 10 nm to 60 nm. The bigger size particles, they may be the agglomerate, are size of 100 nm to 50 μm where the highest peak is at 5 μm.

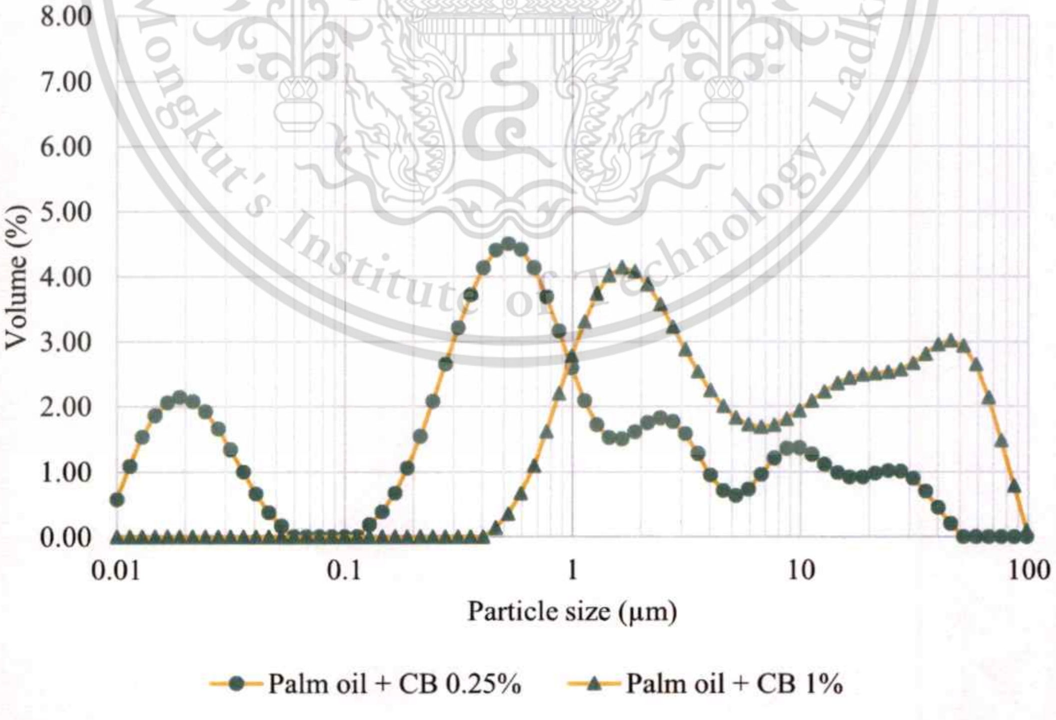


Figure 5-19. Carbon black particle distributing in palm oil

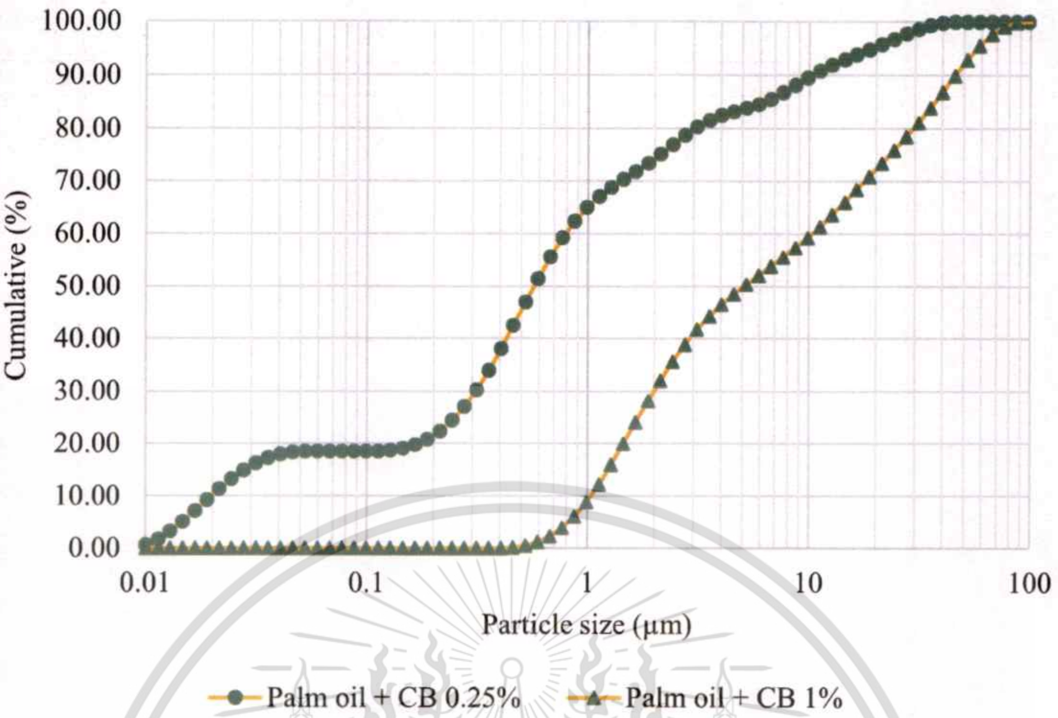


Figure 5-20. Cumulative of carbon black particle distributing in palm oil

In case of mixing at 1%, there are not small particles in nanoscale. The sizes are in range of 400 nm to 100 μm. Figure 5-20 shows the cumulative percentage of particle size of carbon black in palm oil. It shows that there is just only the test with 0.25% concentration which can maintain or keep particle small, which are size of 10 nm to 60 nm, it is about 20% cumulative (see laser particle size report of palm oil in Appendix C).

Another two tests are the test with commercial formulated oil, lubricant A and B. The results of the test with lubricant A is shown in Figure 5-21 and 5-22. They show that lubricant A can keep carbon black particle small at all concentration percentages. Even though it was mixed at 2%, it maintains the particle in size of 10 nm to 60 nm at about 5%. Moreover, it has been noticed that at the level of 1% mixing, lubricant A makes additive the most active compared to other levels of concentration. It can keep small particle reach to 18% cumulative (see laser particle size report of lubricant A in Appendix C).

Figure 5-23 and 5-24 show the results from the test with lubricant B. They present the same trend as lubricant A. In all level of mixing with carbon black, lubricant B can keep particle small and the remaining are agglomerate. Furthermore, lubricant B is also the most additive active at 1% carbon black mixed (see laser particle size report of lubricant B in Appendix C).

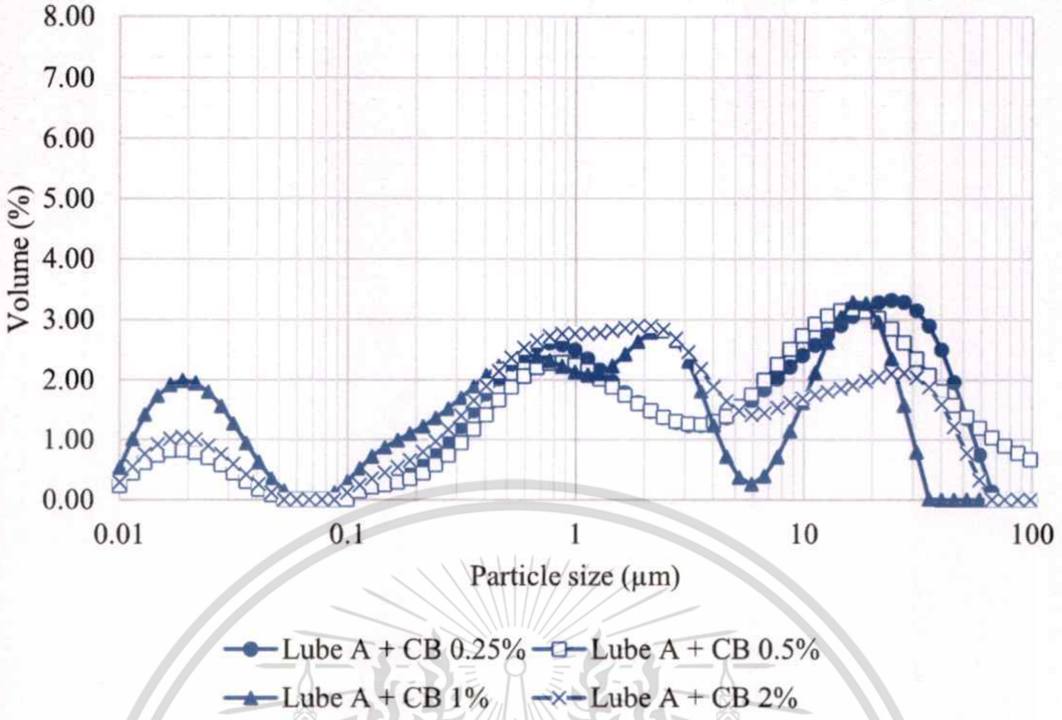


Figure 5-21. Carbon black particle distributing in lubricant A

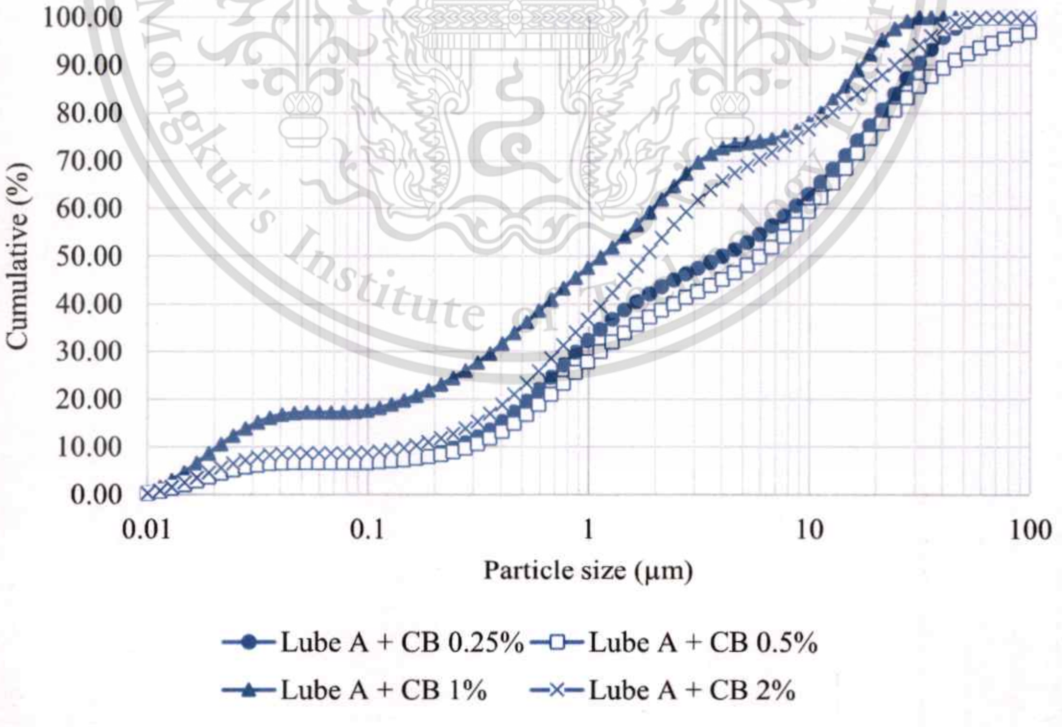


Figure 5-22. Cumulative of carbon black particle distributing in lubricant A

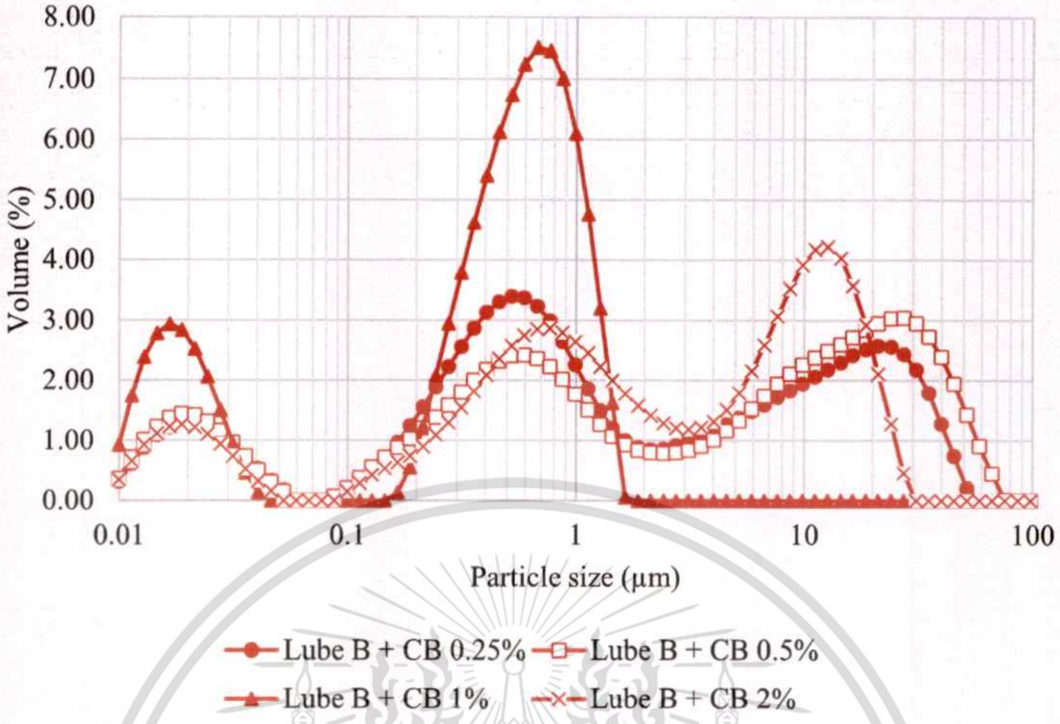


Figure 5-23. Carbon black particle distributing in lubricant B

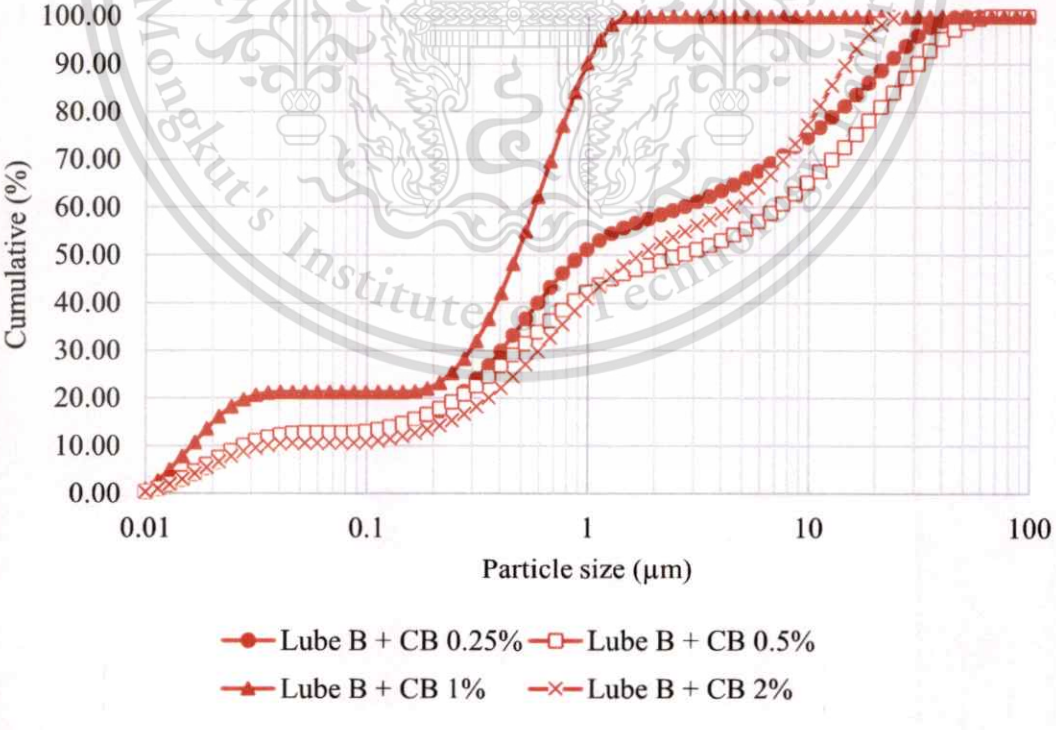


Figure 5-24. Cumulative of carbon black distributing in lubricant B

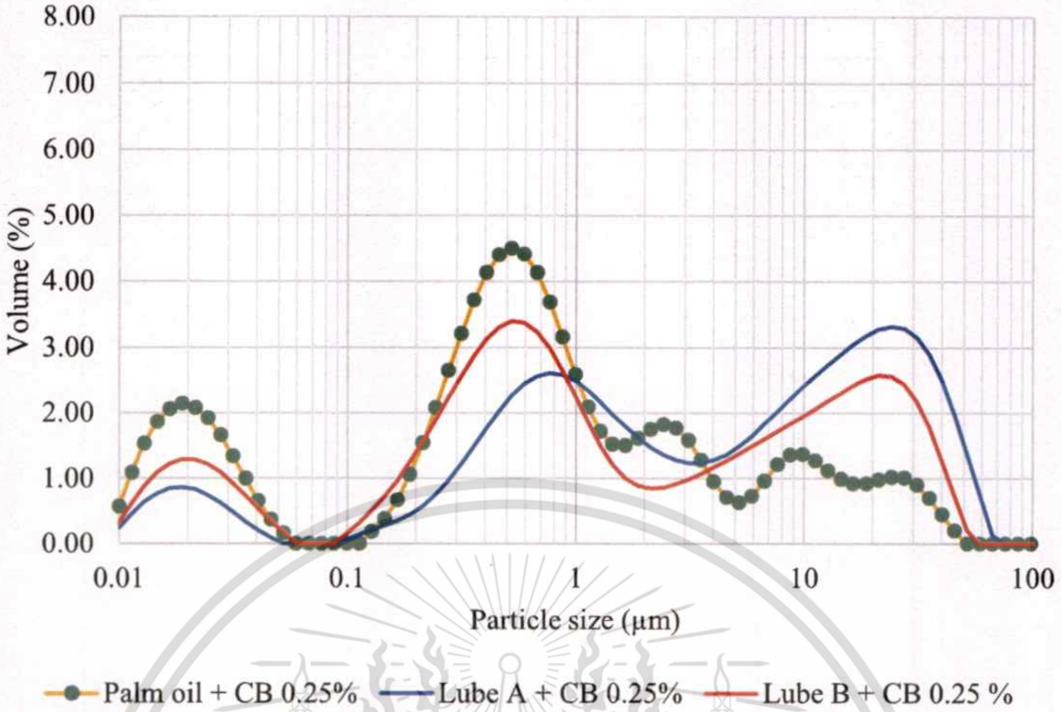


Figure 5-25. Carbon black 0.25% by weight distributing in liquid

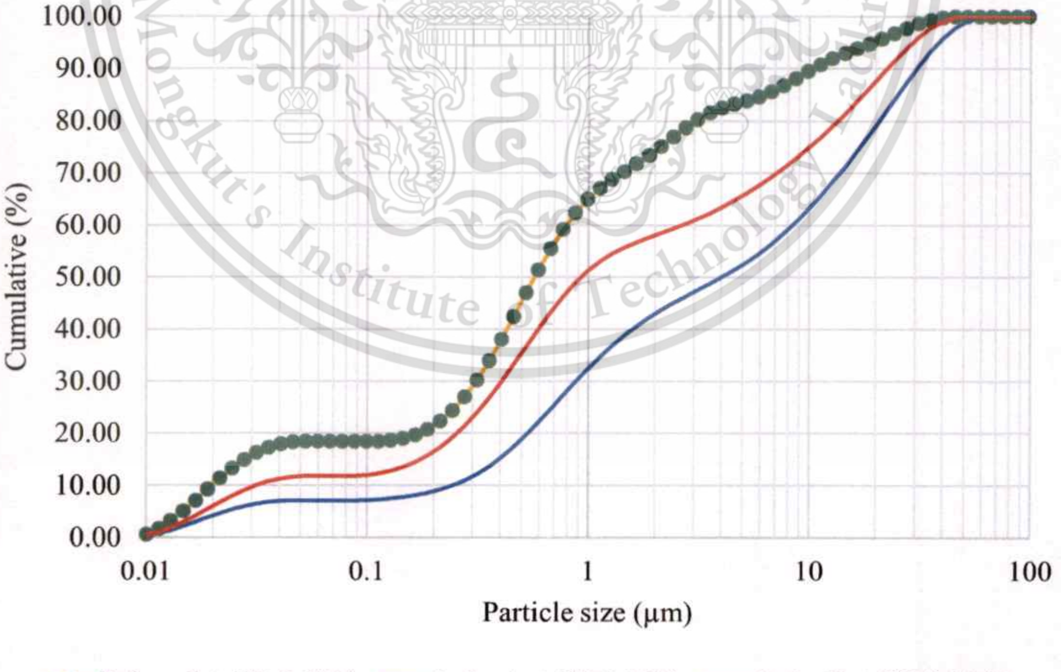


Figure 5-26. Cumulative of carbon black 0.25% by weight distributing in liquid

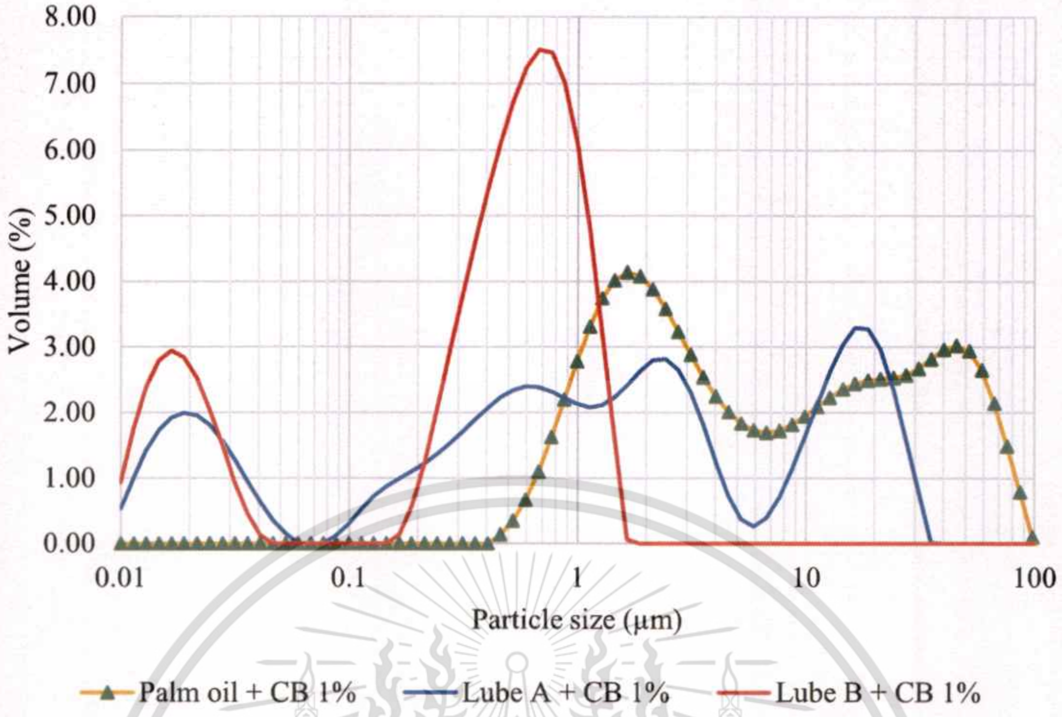


Figure 5-27. Carbon black 1% by weight distributing in liquid

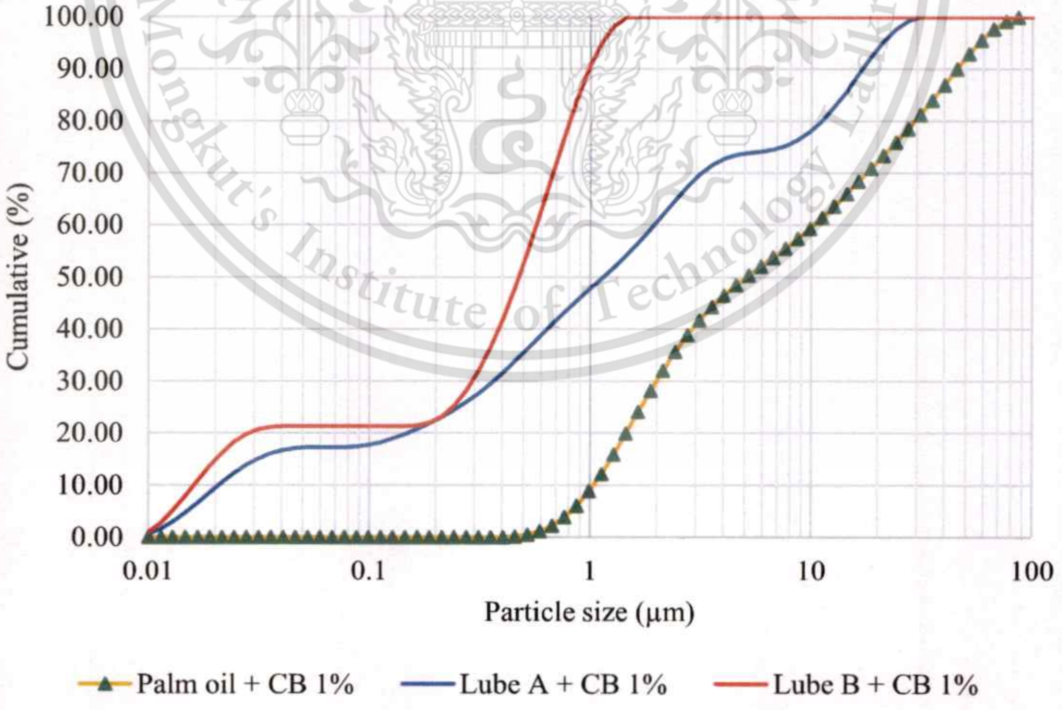


Figure 5-28. Cumulative carbon black 1% by weight distributing in liquid

Figure 5-25 and Figure 5-26 are repeating result from earlier one. They show the results of testing with palm oil, lubricant A, and lubricant B, but picked up only the mixing at 0.25% by weight. It shows that palm oil makes the best result by keeping carbon black particle small in size of lower than 100 nm at about 20% cumulative. Lubricant B is also giving a better result than lubricant A.

Figure 5-27 and 5-28 present the results of testing at 1% carbon black mixing concentration by weight. It shows the significant result that palm oil cannot maintain small particle and let them agglomerate to be larger size. Moreover, lubricant B is the best one that can keep particle small at about 24% over lubricant A at near 18% cumulative.

After investigate carbon black size distribution in liquid, the results indicated that properties of oil are the dominant for dispersing soot. Moreover, oil additives are also having an effect to prevent agglomeration of soot particle. Then more fundamental information about oil additives is need.

This thesis is designed to study the effect of oil additives on the ability of dispersing soot. Thus, more commercial formulated oils are prepared to investigate particle size distribution by using laser diffraction technique.

Before doing dispersing test, all formulated oils are inspected several oil properties to make sure that they are same conditions but just only oil additives different.

Table 5-8. Oil properties of diesel engine lubricant grade SAE 15W-40

Oil condition		Lubricant (SAE 15W-40)					
		Lube A	Lube B	Lube C	Lube D	Lube E	Lube F
Viscosity @40 C	cSt	104.2	110.1	108.9	107.5	106.7	109.5
Viscosity @100 C	cSt	13.8	15.0	14.6	14.4	14.6	14.4
Oxidation	Abs	4.0	6.6	7.0	12.1	5.9	5.0
Nitration	Abs	5.5	3.5	3.4	6.9	3.5	4.0
TAN	mg KOH/g	0.91	1.58	1.63	0.92	1.81	2.20
TBN	mg KOH/g	8.2	9.2	9.8	9.4	8.1	7.7

Table 5-8 shows oil properties of 6 diesel engine lubricating oil which are same viscosity grade as standard SAE 15W-40. There are several condition for investigating such as viscosity, oxidation, nitration, total acid number, and total base number (see details commercial oil properties in Appendix D).

Oil additives in all 6 formulated oils are analyzed by using X-ray fluorescence (XRF). The results are shown in Figure 5-29 and 5-30. The summary of that data are presented in Table 5-9 (see details of XRF results in Appendix E).

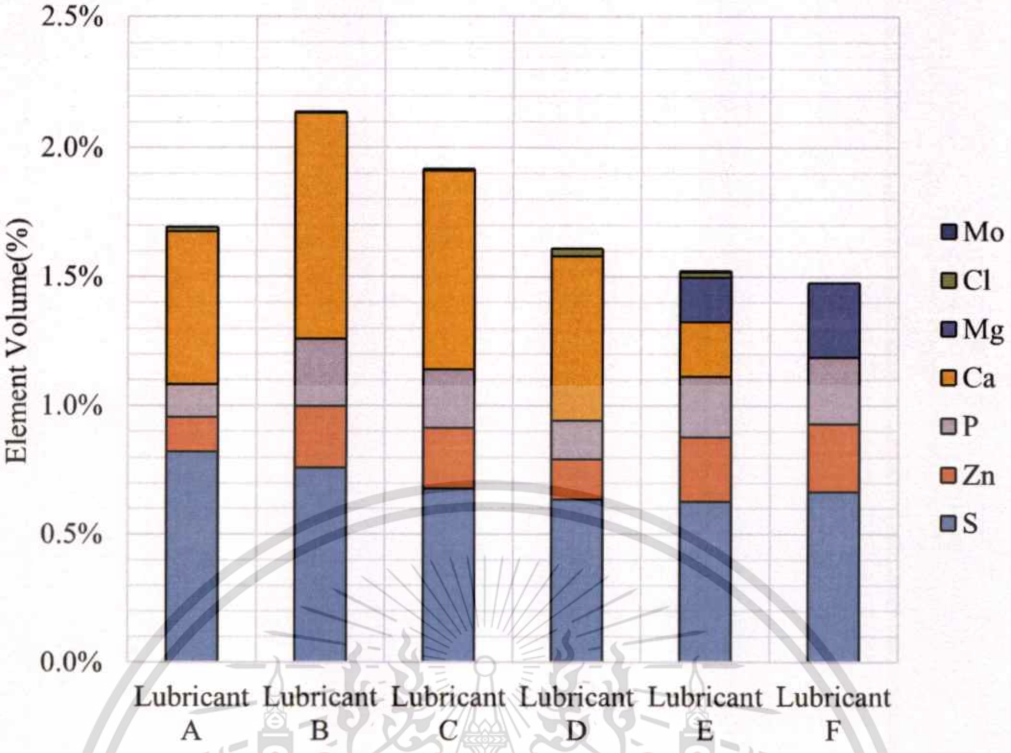


Figure 5-29. Stacked bar chart of total additive element volume

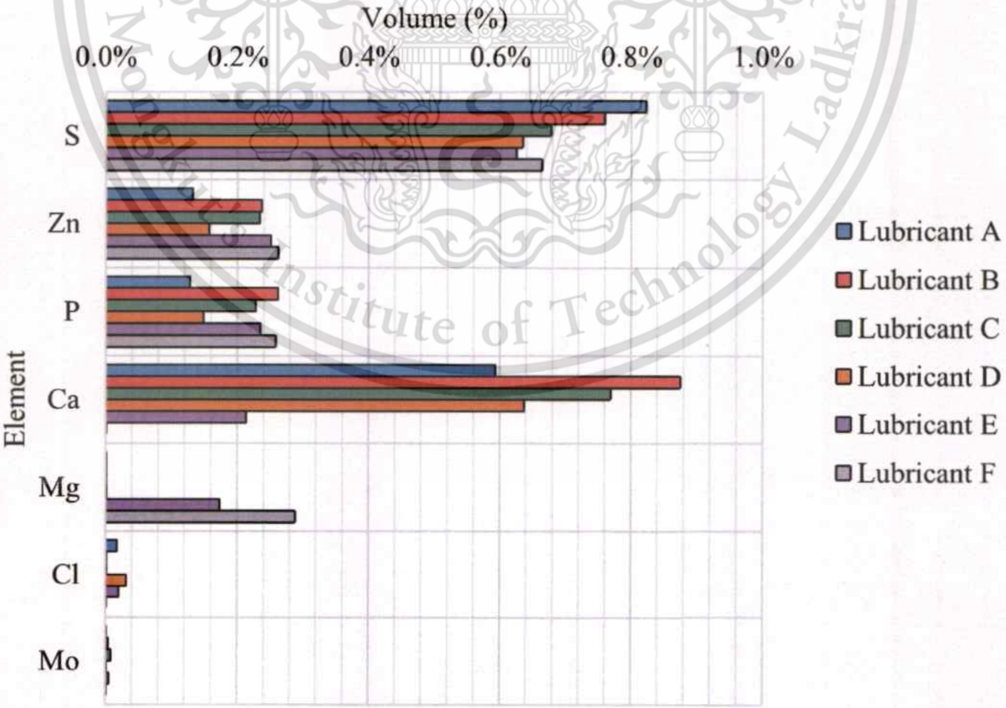


Figure 5-30. Clustered bar chart of additive element volume

Table 5-9. Additive element volume of lubricating oils analyzed using XRF

Lubricating Oil	Element Volume (%)						
	S	Ca	Zn	P	Mg	Cl	Mo
Lubricant A	0.822	0.593	0.132	0.128	-	171 ppm	-
Lubricant B	0.760	0.875	0.237	0.262	-	-	38.2 ppm
Lubricant C	0.678	0.769	0.234	0.228	-	-	79.0 ppm
Lubricant D	0.635	0.637	0.157	0.149	-	308 ppm	-
Lubricant E	0.625	0.213	0.251	0.235	0.173	195 ppm	49.3 ppm
Lubricant F	0.664	-	0.263	0.259	0.289	-	-

Table 5-9 shows the volume of oil additive elements of 6 commercial formulated oil which are analyzed by using XRF tool. Whereas lubricant A is the most contain Sulphur and lubricant B has Calcium more than others. However, lubricant B is the most contain all element additive than others (more than lubricant A), as shown in Figure 5-19.

According to Table 4-1 [42], the sources of each element can be classified as following:

Sulphur (S) is a natural constituent of base oil, so it appears in almost all oil samples. Highly refined and synthetic base stocks may contain no or very little Sulphur. Sulphur is also found in many additives, including anti-wear, anti-oxidant, extreme pressure, corrosion inhibitor and metal deactivator additives.

Calcium (Ca) is often found in conjunction with magnesium and forms the detergent and corrosion inhibitor part of the additive package.

Zinc (Zn) is found in chemicals used to make anti-wear, anti-oxidant, detergent and corrosion inhibitor additives.

Phosphorus (P) is a non-metal and is found in many additives. These include: anti-wear, anti-oxidant, extreme pressure, corrosion inhibitor, friction modifiers, metal deactivator, and biocide chemicals.

Magnesium (Mg) is used in the formulation of detergents and corrosion inhibitors.

Molybdenum (Mo) is seen as an additive in engine oils as part of the anti-oxidant package. Molybdenum disulphide (Mo-Di) is an aftermarket additive than can be added to lubricants by the end user. Mo-Di is an anti-friction compound that has been used in lubricants for almost a century.

Chlorine (Cl) is not found that used in any lubricant additive purposes. Then, it may be coming from the production process and refining process of lubricant, so it may also conclude that chlorine is a contamination part of the lubricant.

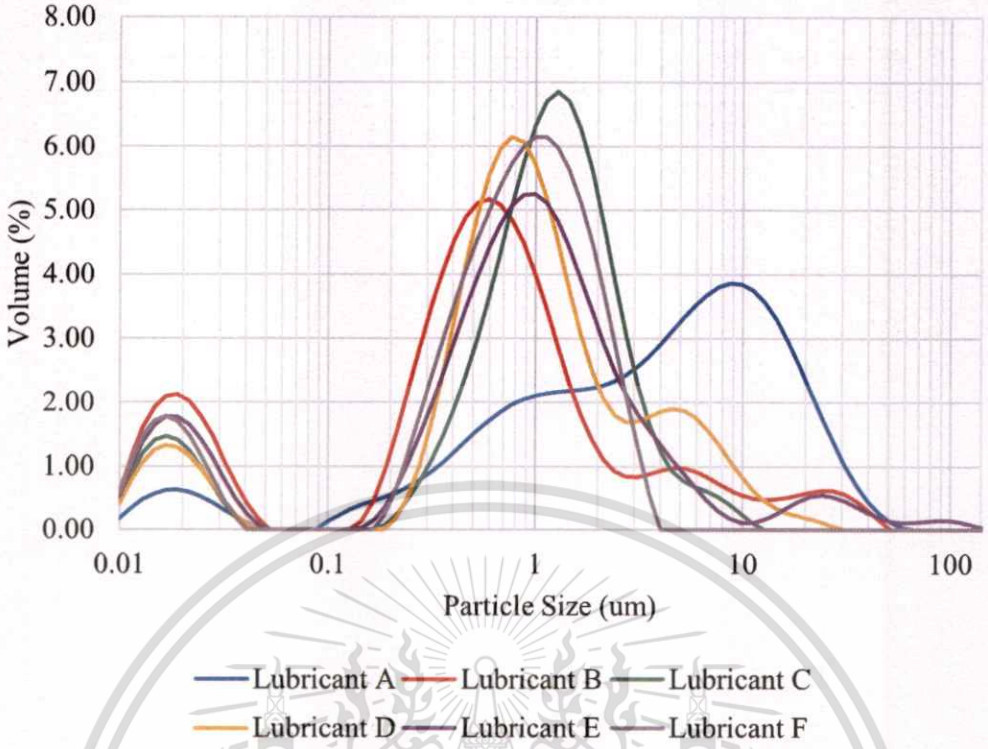


Figure 5-31. Particle size distribution of carbon black dispersing in lubricant

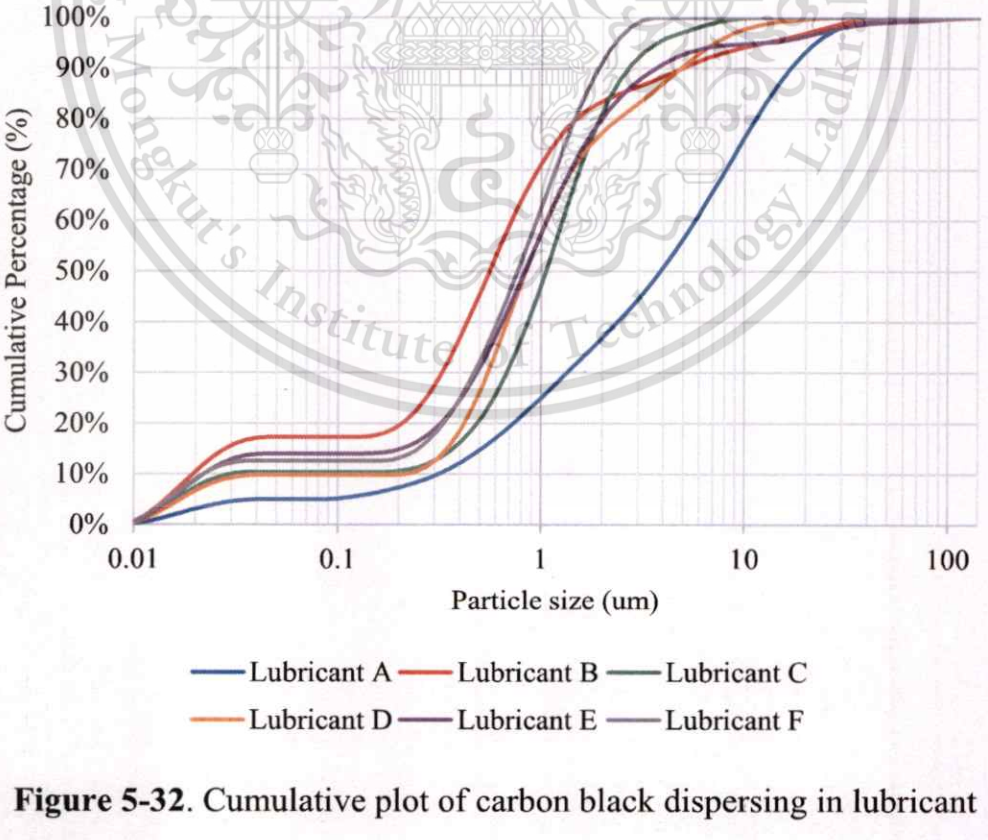


Figure 5-32. Cumulative plot of carbon black dispersing in lubricant

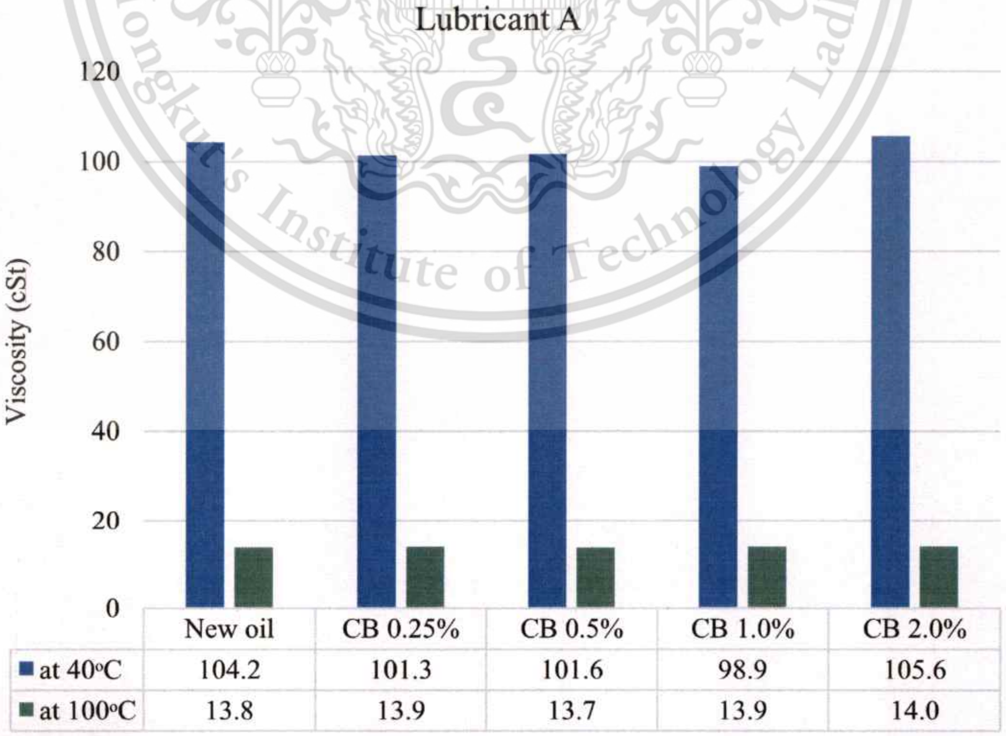
Figure 5-31 and 5-32 are shown the results of the study of effect of oil additives on the ability of dispersing carbon black in 6 formulated oils (see laser particle size report of commercial lubricant in Appendix F).

It has been noticed that lubricant A has large carbon black particle more than others and lubricant B is the most contain small carbon black particle.

Torbake [14] reported that most of all additives have polar moiety and hydrocarbon chain. They can react with all polar particle that contaminated in oil and soot or carbon black are also the polar particle. This can be supported to the results of particle size distribution test which lubricant B can keep carbon black in small size than others because it is the highest containing of oil additives.

5.9 Effect of Soot Contamination in Oil on Metal Wear

The objective of using lubricating oil is to get advantage from ability of film layer forming by lubricant, whereas film thickness is depended on viscosity at operating temperature. Then the viscosity of lubricant A and B are investigated for estimating oil film thickness of each lubricant. The viscosity of lubricant A and B are shown in Figure 5-33 and 5-34, respectively.



	New oil	CB 0.25%	CB 0.5%	CB 1.0%	CB 2.0%
■ at 40°C	104.2	101.3	101.6	98.9	105.6
■ at 100°C	13.8	13.9	13.7	13.9	14.0

Figure 5-33. Viscosity of lubricant A mixed with carbon black

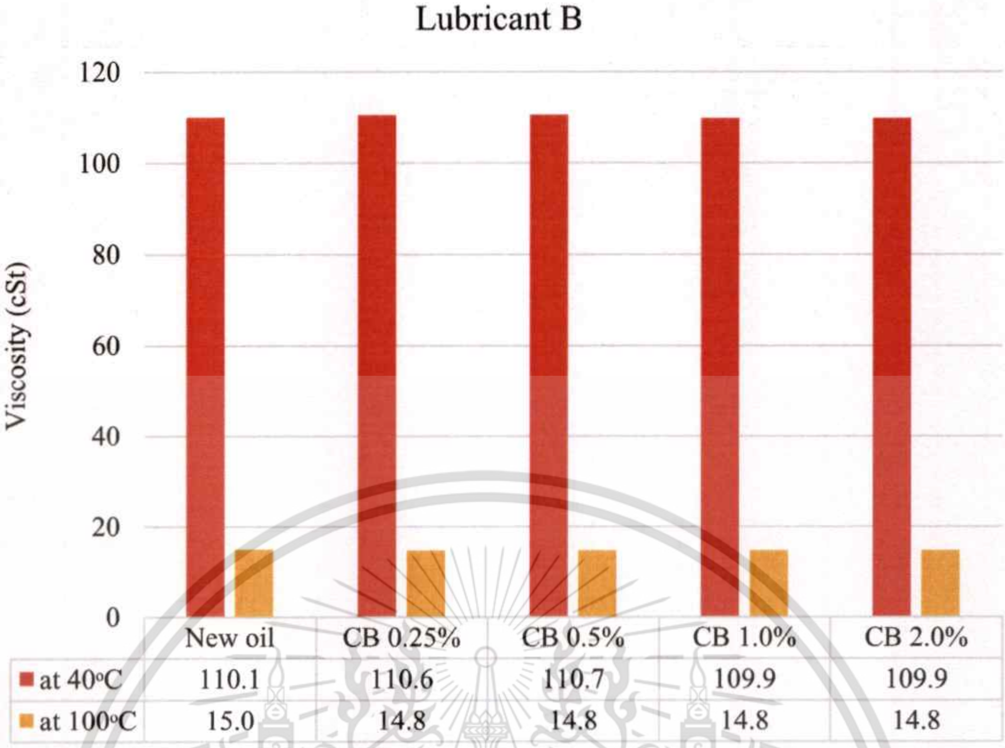


Figure 5-34. Viscosity of lubricant B mixed with carbon black

Minimum film thickness is calculated by equation (3.6) which several parameters are required as following:

$$\frac{h_0}{R'} = 3.63\left(\frac{U\eta_0}{E'R'}\right)^{0.68}(\alpha E')^{0.49}\left(\frac{W}{E'R'^2}\right)^{-0.073}(1 - e^{-0.68k})$$

h_0	is the minimum film thickness [m].
U	is the entraining surface velocity = 0.23 [m/s]
η_0	is the viscosity at atmospheric pressure of the lubricant = 60.9 [Pa·s].
E'	is the reduced Young's modulus = 2.308 x 10^{11} [Pa].
R'	is the reduced radius of curvature = 1.5875 x 10^{-3} [m].
α	is the pressure-viscosity coefficient = 2.332 x 10^{-8} [m^2/N].
W	is the contact load = 159.9 [N].
k	is the ellipticity parameter = 1.0339

After calculation, the oil film thickness of lubricant A and B are shown in Table 5-10.

Table 5-10. Estimation of oil film thickness of lubricant A and B

Cases	Oil film thickness h_0 (nm)
Lubricant A	302
Lubricant A + CB 1% wt.	294
Lubricant B	319
Lubricant B + CB 1% wt.	311

From Table 5-10, the values of oil film thickness of all cases are hardly different at about 300 nm.

Lubricant A and B with and without carbon black 1% by weight are brought to test four-ball tribology test under controlled condition, 60 minutes duration, apply load 392 N, speed 1200 rpm, and temperature at 75°C.

The wear scar diameter was measured under microscope. Figure 5-35 shows the microscopy image of wear scars found on three lower balls and one upper ball after 60 min running time in lubricant A without carbon black and Figure 5-36 shows for lubricant A with carbon black. The results showed that wear diameter of four metal balls in case of testing with soot are larger than wear diameter of four balls without soot. Similarly, wear diameter of four balls in lubricant B with soot are larger than wear diameter of four balls without soot, as shown in Figure 5-37 and Figure 5-38. Wear edge shape of balls in lubricant A are quite smoother than shape of balls in lubricant B. The average wear diameter of balls in case of testing in lubricant A is 493 microns and in lubricant A with soot is 537 microns. In case of lubricant B, the average of wear diameters are 531 and 597 microns for case without soot and with soot respectively. Even though they are same viscosity grade, wear shapes are a little bit different.

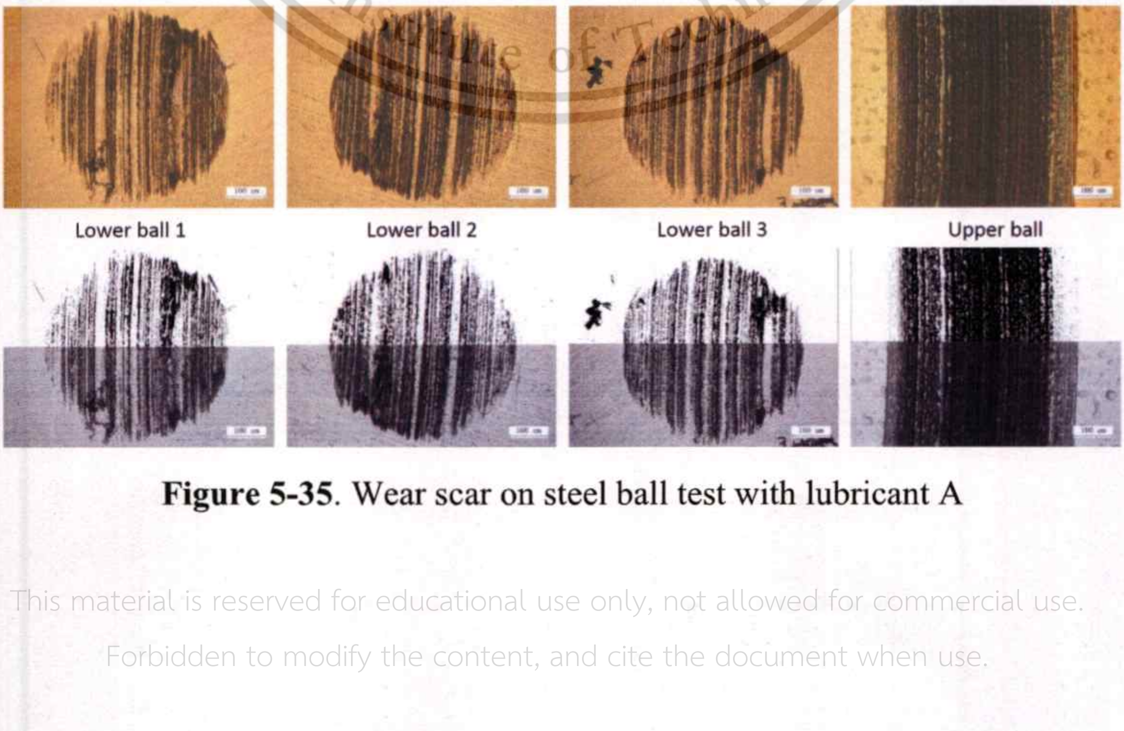


Figure 5-35. Wear scar on steel ball test with lubricant A

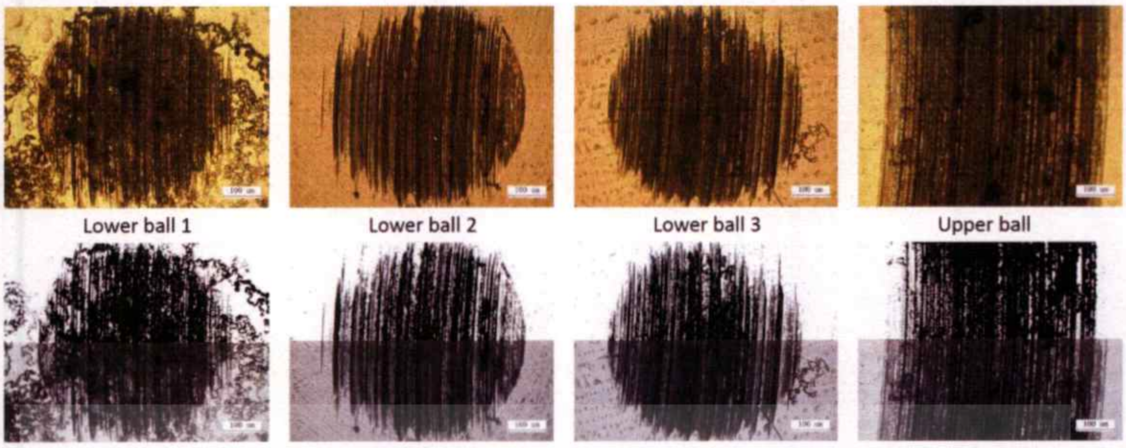


Figure 5-36. Wear scar on steel ball test with lubricant A mixed carbon black

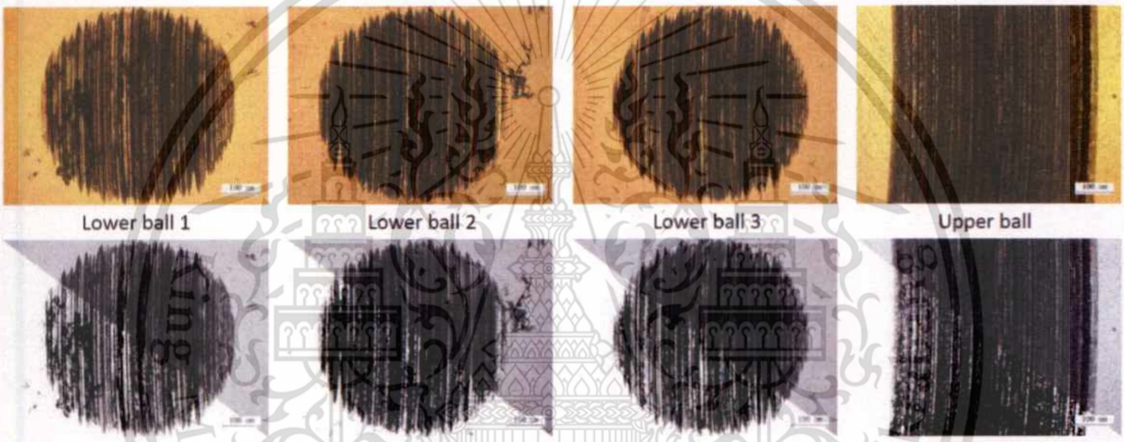


Figure 5-37. Wear scar on steel ball test with lubricant B

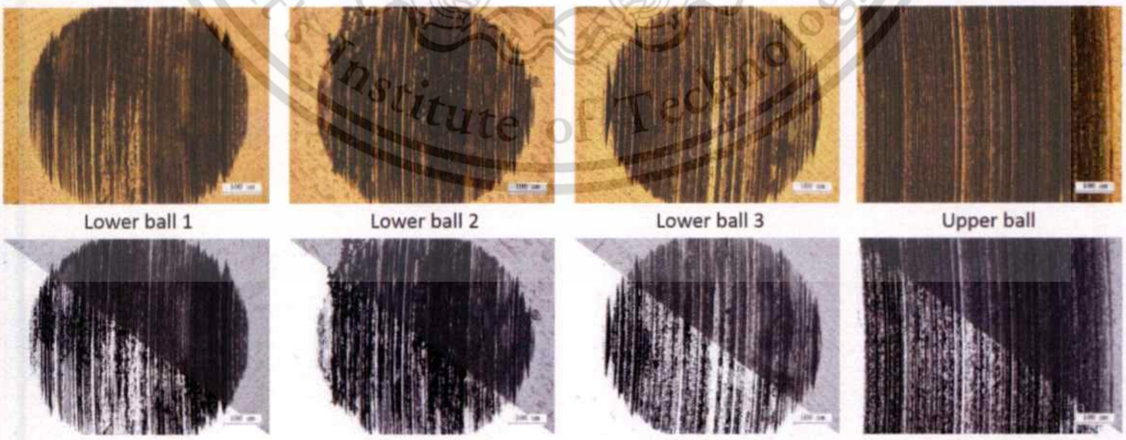


Figure 5-38. Wear scar on steel ball test with lubricant B mixed carbon black

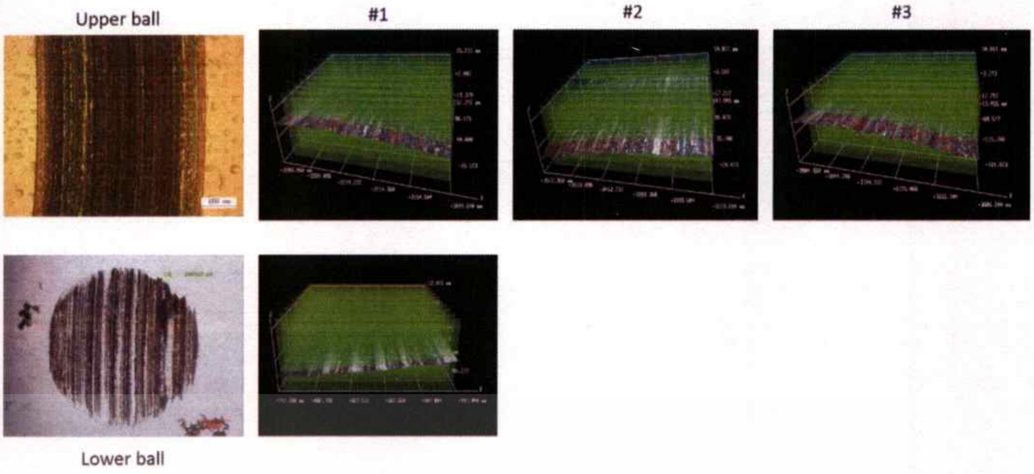


Figure 5-39. Roughness on steel ball test with lubricant A

Figure 5-40. Roughness on steel ball test with lubricant A mixed carbon black

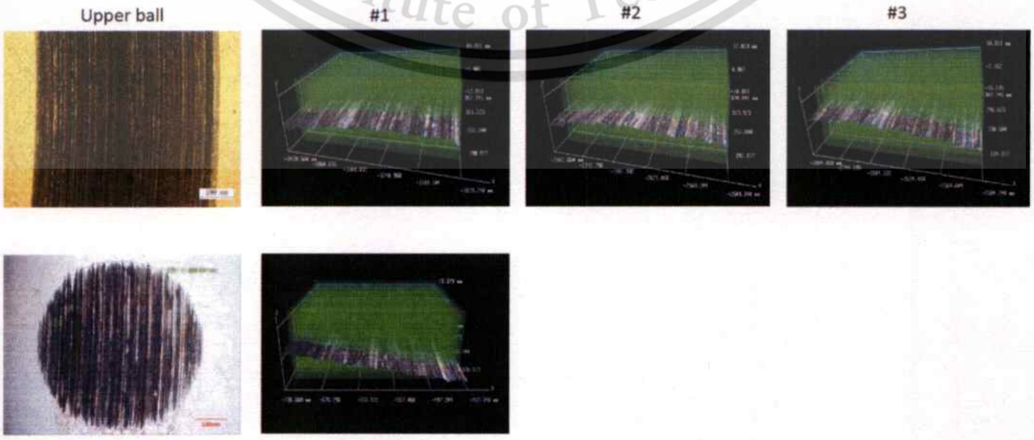


Figure 5-41. Roughness on steel ball test with lubricant B

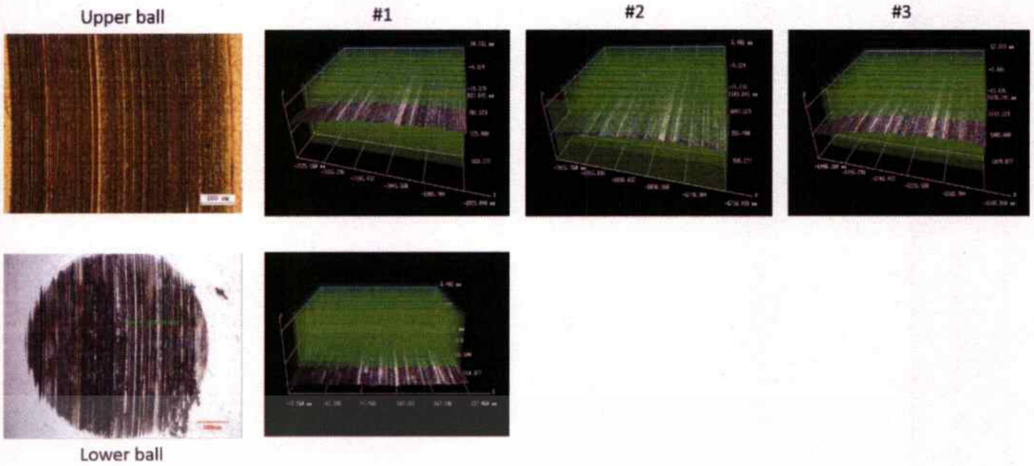


Figure 5-42. Roughness on steel ball test with lubricant B mixed carbon black

Table 5-11 presents the count of wear track which occur on wear scar on steel ball. The track density on lower ball of the test with lubricant A with and without carbon black 1% wt. are 237 and 261 line per millimeters respectively. The track density on lower ball of the test with lubricant B with and without carbon black 1% wt. are 279 and 301 line per millimeters respectively (see high resolution image of wear scar in Appendix G).

Roughness on wear scar of lower ball of the test with lubricant A is 0.07 μm. It is lower than the test with lubricant A mixed carbon black at 0.19 μm. The results are different from the test with lubricant B. Roughness on wear scar of lower ball of the test with fresh lubricant B is higher than the test with contaminated lubricant B which are 0.15 and 0.03 μm respectively (see 3D rendering image of wear scar in Appendix H).

Table 5-11. Summary of investigation on wear scar

		Lube A	Lube A+CB	Lube B	Lube B+CB
Wear diameter	Upper ball	468	575	538	650
(um)	Lower ball	493	537	531	597
Track density	Upper ball	244	230	312	317
(line/mm)	Lower ball	237	261	279	301
Roughness	Upper ball	0.10	0.16	0.12	0.09
(um)	Lower ball	0.07	0.19	0.15	0.03

Figure 5-43 shows that both lubricant A mixed carbon black 1% by weight and lubricant B mixed carbon black 1% by weight make more wear than case of fresh oil. William [99] suggests that the too large particle cannot enter to the contact surface zone. Thus, the carbon black, which is smaller than minimum oil film thickness (300 nm), is introduced to the rubbing zone and then make wear on metal surface.

From the experiment 5.8 soot particle distributing in liquid, indicated that 9% of carbon black in lubricant A is smaller than 300 nm and 25% for lubricant B. It means carbon in lubricant B can be introduced to rubbing zone more than carbon black in lubricant A. This related to the results of experiment 5.9, wear diameter increased 44 μm for lubricant A testing and 66 μm for lubricant B testing.

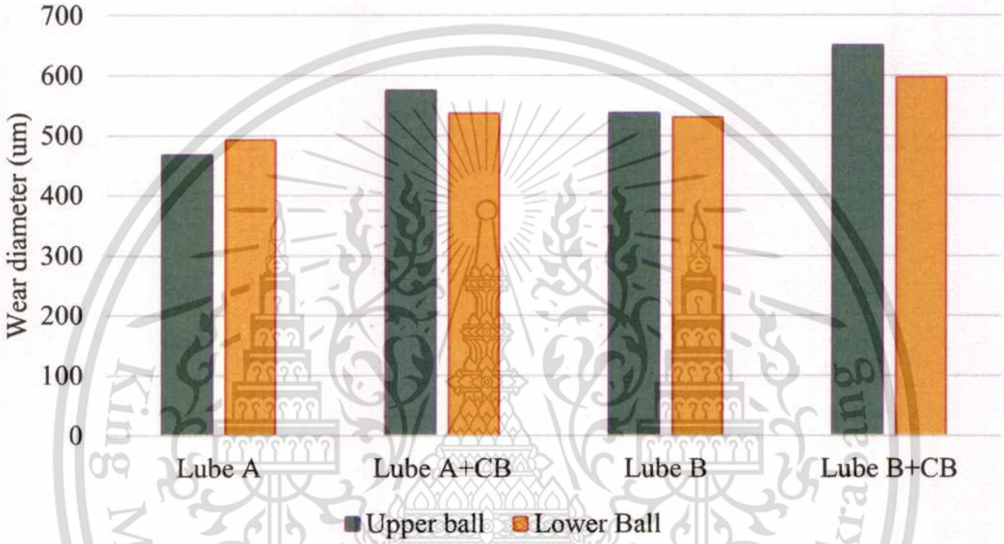


Figure 5-43. Wear scar diameter on lower and upper steel ball

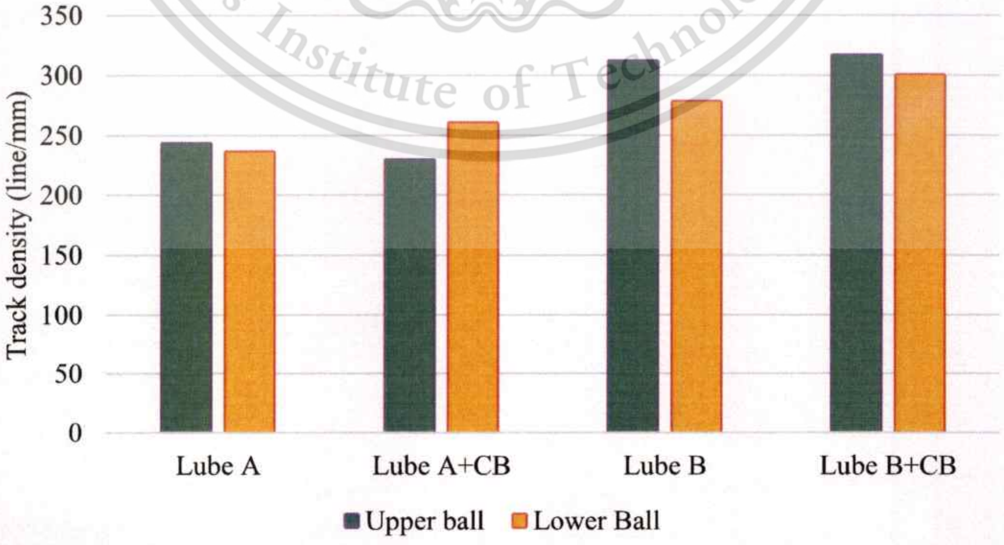


Figure 5-44. Wear track density on lower and upper steel ball

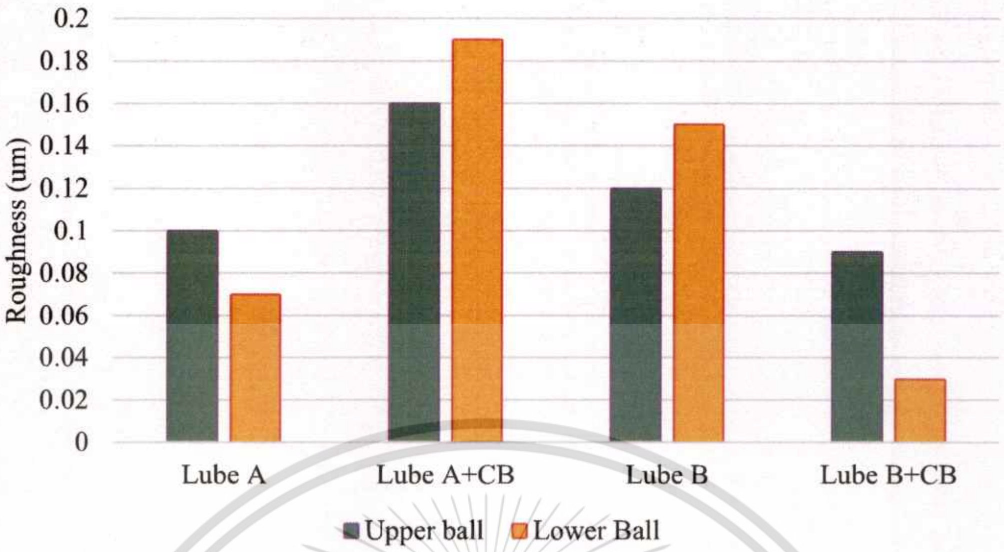


Figure 5-45. Roughness of wear scar on lower and upper steel ball

Figure 5-39, 5-40, 5-41, and 5-42 show the surface image from 3D rendering optical microscope. They are helping to inspect morphology of wear scar surface and helping to understand wear mechanism of four-ball tribology system (two sphere steel ball geometry contact). Furthermore, this tool is also providing the roughness value which is a good information for calculating and helping defining the lubrication regime of the test.

Figure 5-45 presents roughness on wear scar on steel ball. It shows that lubricant B mixed CB testing (which contain carbon black size smaller than 300nm of 25% by volume) has lower roughness than the test with fresh lubricant B from 0.15 to 0.03 μm. However, in case of the test with lubricant A, roughness is increase from 0.07 to 0.19 μm. It may be the effect from the amount of small particle (smaller than minimum film thickness) which lubricant A mixed CB contain just only 9% by volume. Whereas 9% containing may not enough to scratch and reduce roughness at contact surface.

Figure 5-44 present track count on wear scar on steel ball. Both lubricant A and B, when mixing with carbon black, track density increased on wear scar. For lubricant A testing, it increased 24 lines from 237 lines. For lubricant B testing, it also increased 22 lines from 279 lines. However, the wear track is investigated by human observation from optical microscope image so it may not count the track accurately.

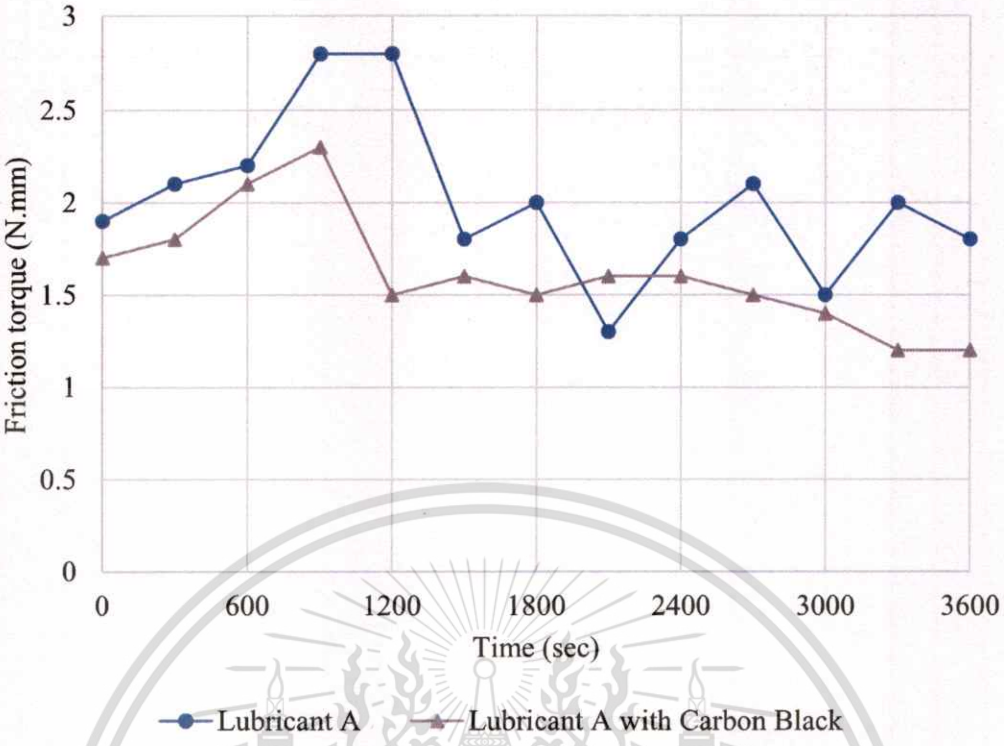


Figure 5-46. Friction torque of lubricant A case tested using Four-ball tribometer

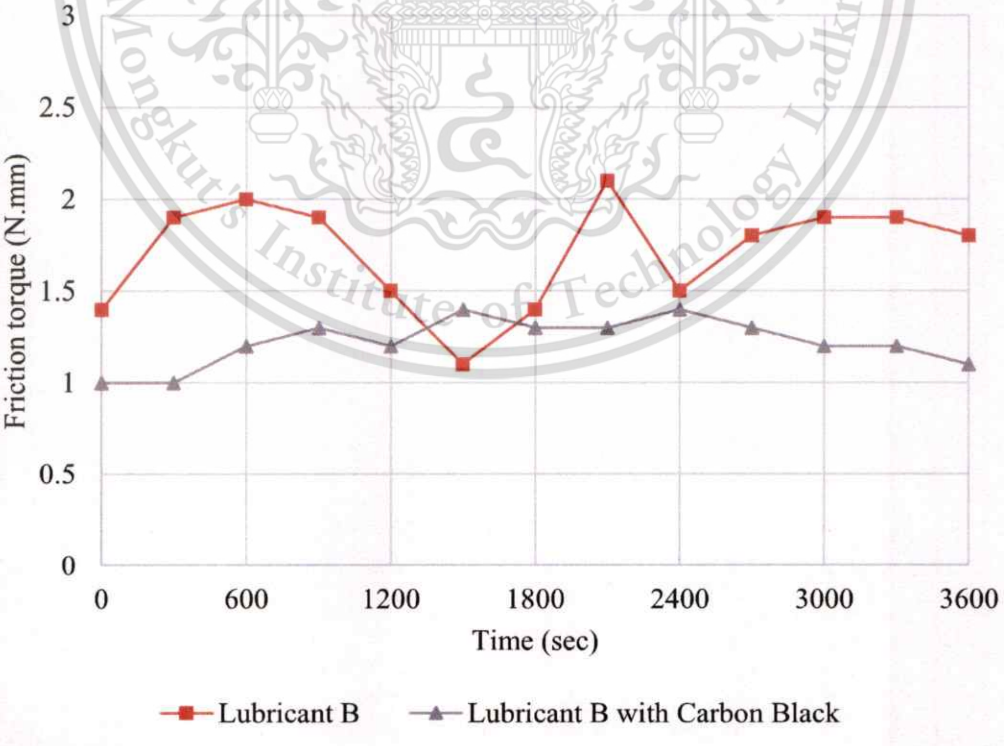


Figure 5-47. Friction torque of lubricant B case tested using Four-ball tribometer

5.10 Effect of Soot Contamination in Oil on Friction

Figure 5-46 and Figure 5-47 show the friction torque. The value of friction torque is very low. The samples with soot seem to be lower friction torque than the sample without soot in both cases. The average friction torque in testing with lubricant A is 2.008 N.mm and the average friction torque in testing in lubricant A with soot is 1.615 N.mm. In lubricant B, the average friction torque in case none soot and mixed with soot are 1.708 and 1.223 N.mm respectively.

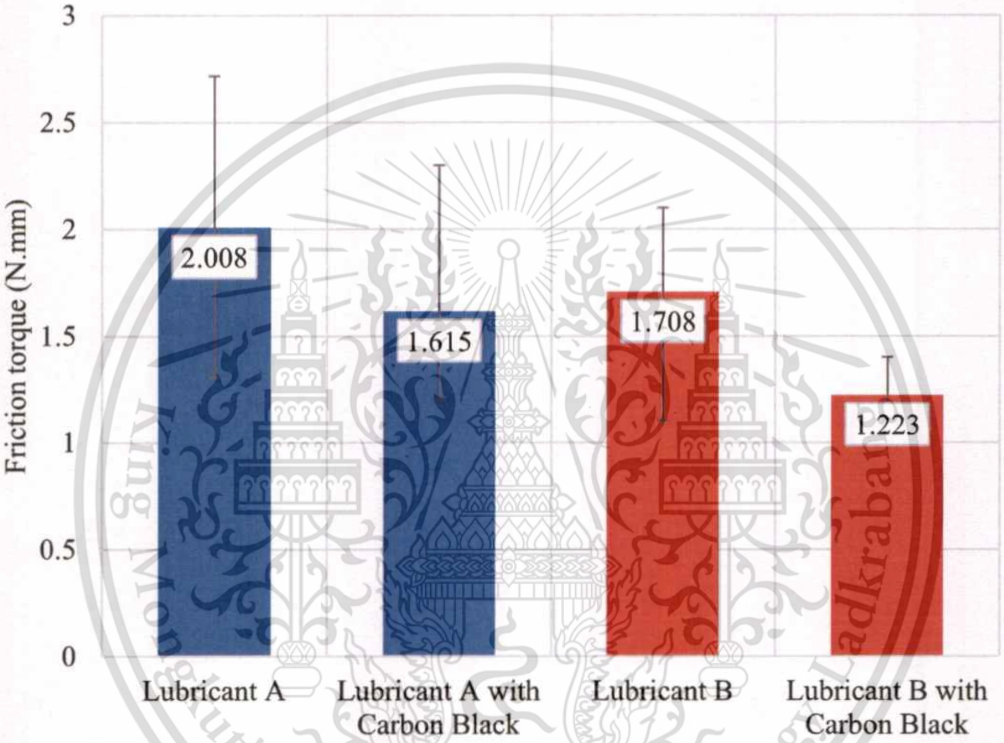


Figure 5-48. Average friction torque

From Figure 5-48, the values of friction torque are calculated for friction coefficient by equation below (derived by four-ball geometry) [44]:

$$\mu = 2.227 \frac{\tau}{W}$$

Where

μ is friction coefficient
τ is friction torque [kg·cm]
W is normal load to contact surface = 40 [kg]

Film parameter can be calculated by equation (3.1) in chapter 3 and the values are shown in Table 5-12.

Table 5-12. Summary of friction coefficient and film parameter

	Friction coefficient	Film parameter
Lubricant A	0.110	2.47
Lubricant A+CB	0.088	1.18
Lubricant B	0.093	1.66
Lubricant B+CB	0.067	3.27

Table 5-12 presents the decreasing of friction coefficient when carbon black is mixed to lubricant in both case of A and B. Carbon black in lubricating oil may act as a rolling element and result in reducing friction between metal surfaces, however, this suggestion is still not inspected in this thesis. Another idea is that carbon black may react with lubricating oil by both physical and chemical reaction and result in increasing oil film thickness between contact surfaces.

Film parameter indicates the lubrication regime of four-ball test. Where film parameter value is under 1 refer that the situation is in boundary lubrication regime, 1-3 refer to mixed lubrication regime, and more than 3 refer to hydrodynamic lubrication regime (related to Figure 3-3 [14]).

Form Table 5-12, it reported that the four-ball situation is in mixed lubrication regime except the case of testing with lubricant B mixed with carbon black, it referred to full film or hydrodynamic lubrication regime.

According to Figure 3-4 [32], this may refer that this test can represent the system of valve train and piston ring system which are in mixed lubrication regime.

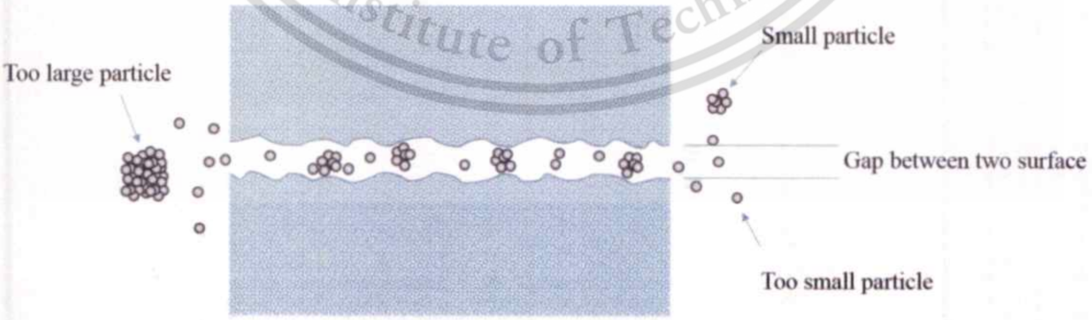


Figure 5-49. Model of carbon black particles introduced to gap between two metal surfaces

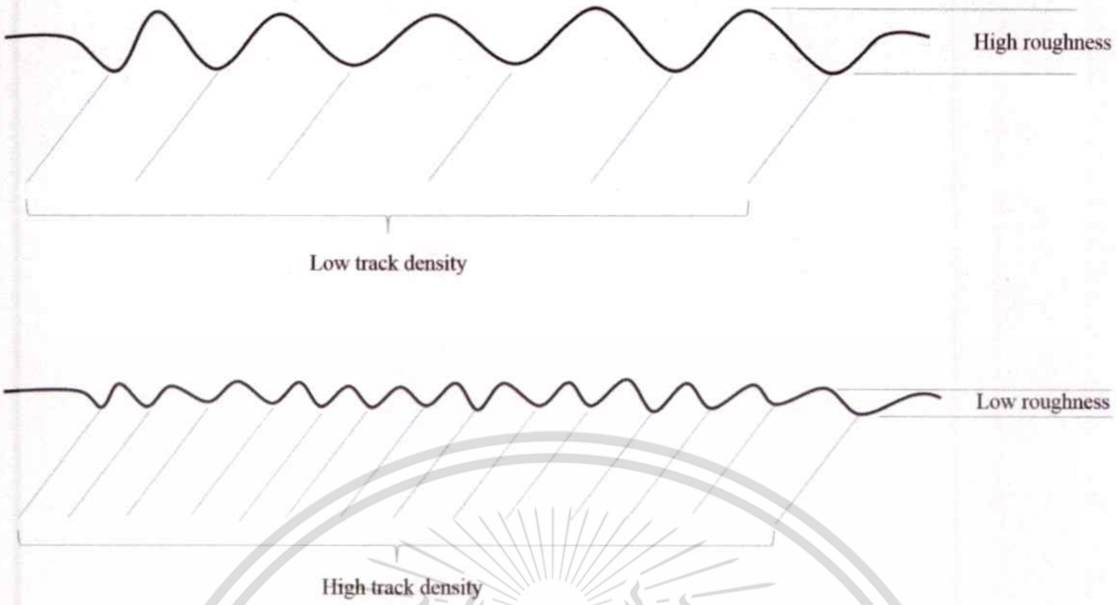


Figure 5-50. Model of wear scar scratched by carbon black (upper) high roughness and low track density (lower) low roughness and high track density

After analyze all of the data, they may be explained that soot or carbon black which are mixed into tested lubricants, the too small particles may not affect to the metal surfaces. The too large particles may also escape out from scrubbing areas because they cannot enter to that clearance. They are limited by the gap length between two metal surfaces which defined by oil film thickness. There are just only the proper particles which near to film thickness can be introduced to the gap and scratch the metal surfaces and make them wear. This is demonstrated by a drawing in Figure 5-49.

The gap height is calculated from equation (3.6). It shows the oil film thickness is about 300 nm. Then particles which can be introduced to this gap are the particle size of lower than 300 nm. In case of the test with lubricant A mixed carbon black 1% by weight, there are only 9% of all which are smaller than the limit. Moreover, in case of lubricant B, there are reached to 25%. That mean lubricant B is more containing the particles which have dominant effect on scratching than lubricant A (see data and explanations in section 5.9).

Figure 5-50 demonstrates two forms of wear scar that occurred in this four ball test. Related to the results in section 5.9, lubricant A which contains the proper particles at 9% make metal surfaces scratched, where the roughness of wear scars are 0.16 μm and 0.19 μm (on upper ball and lower ball respectively) and wear track density are 230 and 261 lines per millimeter (on upper ball and lower ball respectively). On the other hand, lubricant B contains the dominant particle at 25% can make higher probability for scratching metal surfaces, so wear track density is higher than the test with lubricant A (317 and 301 lines per millimeter for upper ball and lower ball respectively), but these dominant particles are also reducing the metal surface peak areas then roughness of this case are lower than the case of lubricant A (0.09 μm and 0.03 μm for upper ball and lower ball respectively). These situations are demonstrated by this illustration in Figure 5-50, where upper model shows schematic of high roughness and low wear track count which refer to wear scar on steel ball tested with lubricant A mixed carbon black, and lower model shows schematic of low roughness and high wear track count which refer to the test with lubricant B mixed carbon black (mixing at same concentration but different in amount of dominant-effected particles).

In conclusion, all of the results have been already analyzed. It shows that the situation of four-ball test is in mixed lubrication regime. Thus, this system can be used to simulate the mechanism of gear and valve train system in the engine. The relationship between soot and wear and friction are very complicated. There are only the suggestion ideas trying to explain the behavior of soot. However, more fundamental knowledge is still in need. More experimental works are required to investigate.

The Bottom Line

The next chapter is the final chapter in the thesis. Chapter 1-3 give the information about the significant of this study and provide public literature reviews and theories which related. Chapter 4 and 5 provide the experimental process and the results that help to understand about the behavior of soot contamination in lubricating oil and their effect on metal wear and friction. Next will be the conclusion of which this thesis has conducted.

CHAPTER 6

CONCLUSION

According to the study of the impact of soot on lubricating oil properties and on metal wear, it can be concluded as following:

In case of investigating lubricant from passenger car and truck, it has been showed that soot was contaminating in range of 0.05-0.88% by weight in diesel engine used oil. It is less than 1% by this study. Moreover, the results also induced to show that soot may be the cause of decreasing total base number of oil by absorb oil additives, and increasing metal wear from engine parts.

Carbon black can be used to be a simulant of soot because the both have a similar morphology. However, they still have small difference in the view point of the particle diameter size of which the average sizes are 29.5 nm and 57.8 nm for soot and carbon black, respectively.

Oil additives have a significant effect on dispersing soot in lubricant oil. However, it cannot be concluded clearly that which additive make the most effect. The tested results presented the difference of soot particle size distribution in liquid that there are highly agglomerated in water, and smaller level of agglomeration in palm oil, and well dispersing in formulated oil.

Based on the four-ball tribology test, soot in lubricating oil may act as a rolling element and result in reducing friction between metal surfaces, however, this suggestion is still not inspected in this thesis. Another idea is that soot may react with lubricating oil by both physical and chemical reaction and result in increasing oil film thickness between contact surfaces. Furthermore, high soot contaminating has an effect on increasing more wear by increase more area of abrasive mechanism and increase probability in scratching process between metal surfaces.

Finally, this thesis found the most significant result that the appropriate particle size, which is near to oil film thickness between metal surface contacts, is the dominant cause of making wear. The too large particle size compared to oil film thickness will escape out and too small particle size will not effect on wear. Furthermore, high level of proper particle size contaminated in oil will increase probability of rubbing process then make contact surfaces smoother or make lower in roughness.

REFERENCES

[1] G.T. Kalghatgi: Combustion Chamber Deposits in Spark-Ignition Engines – A Literature Review: SAE Technical Paper 952443, (1995)

[2] A.D.H. Clague, J.B. Donnet, T.K. Wang, and J.C.M. Peng: A Comparison of Diesel Engine Soot with Carbon Black: Carbon, 30, p.1553-1565 (1999).

[3] K.O. Lee, R. Cole, R. Sekar, M.Y. Choi, J.S. Kang, C.S. Bae, and H.D. Shin: Morphological Investigation of the Microstructure, Dimensions, and Fractal Geometry of Diesel Particulates: Proceeding of the Combustion Institute, 29, p.647-653 (2002).

[4] M. Soejima, Y. Ejima, K. Uemori, and M. Kawasaki: Studies on Friction and Wear Characteristics of Cam and Follower: Influences of Soot Contamination in Engine Oil: JSAE Review, 23, p.113-119 (2002).

[5] K. Park, D.B. Kittelson, and P.H. McMurry: Structural Properties of Diesel Exhaust Particles Measured by Transmission Electron Microscopy – Relationships to Particle Mass and Mobility: Aerosol Science and Technology, 38, p.881-889 (2004).

[6] J. Zhu, K.O. Lee, A. Yozgatligil, and M.Y. Choi: Effects of Engine Operating Conditions on Morphology, Microstructure, and Fractal Geometry of Light-Duty Diesel Engine Particulates: Proceedings of the Combustion Institute, 30, p.2781-2789 (2005).

[7] H. Bhowmick, S.K. Majumdar, and S.K. Biswas: Influence of Physical Structure and Chemistry of Diesel Soot Suspended in Hexadecane on Lubrication of Steel-on-steel Contact: Wear, 300, p.180-188 (2013).

[8] A.L. Rocca, G.D. Liberto, P.J. Shayler, and M.W. Fay: The Nanostructure of Soot-in-oil Particles and Agglomerates from an Automotive Diesel Engine: Tribology International, 61, p.80-87 (2013).

[9] Y. Wang, X. Liang, G. Shu, X. Wang, X. Sun, and C.Liu: Effect of Lubricant Oil Additive on Size Distribution, Morphology, and Nanostructure of Diesel Particulate Matter: Applied Energy, 130, p.33-40 (2014).

[10] I.M. Kennedy: Models of Soot Formation and Oxidation: Progress in Energy and Combustion Science, 23, p.95-132 (1997).

[11] G. Mascolo, R. Rausa, G. Bugnoulo, G. Mininni, and L. Tinucci: Thermal Degradation of Synthetic Lubricants under Oxidative Pyrolytic

Conditions: Journal of Analytical and Applied Pyrolysis, 75, p.167-173 (2006).

[12] E. Hu, X. Hu, T. Liu, L. Fang, K.D. Dearn, and H. Xu: The Role of Soot Particles in the Tribological Behavior of Engine Lubricating Oils: Wear, 304, p.152-161 (2013).

[13] D. Uy, M.A. Ford, D.T. Jayne, A.E. O'Neill, L.P. Haack, J. Hangas, M.J. Jagner, A. Sammut, and A.K. Gangopadhyay: Characterization of Gasoline Soot and Comparison to Diesel Soot: Morphology, Chemistry, and Wear: Tribology International, 80, p.198-209 (2014).

[14] M. Torbacke, A.K. Rudolphi, and E. Kassfeldt: Lubricants: Introduction to Properties and Performance: John Wiley & Sons, First Edition, (2014).

[15] D.A. Green, R. Lewis, and R.S. Dwyer-Joyce: Wear Effects and Mechanisms of Soot-contaminated Automotive Lubricants: Proceedings of the Institution of Mechanical Engineers, Journal of Engineering Tribology, 220, p.156-169 (2006).

[16] P. Ramkumar, L. Wang, T.J. Harvey, R.J.K. Wood, K. Nelson, E.S. Yamaguchi, J.J. Harrison, and H.E.G. Powrie: The Effect of Diesel Engine Oil Contamination on Friction and Wear: Proceedings of World Tribology Congress, 3, p.537-538 (2005).

[17] E.S. Yamaguchi, M. Untermann, S.H. Roby, P.R. Ryson, and S.W. Yeh: Soot Wear in Diesel Engines: Proceedings of the Institution of Mechanical Engineers, 220, p.463-469 (2006).

[18] M. Guatam, K. Chitoor, M. Durbha, and J.C. Summers: Effect of Diesel Soot Contaminated Oil on Engine Wear – Investigation of Novel Oil Formulations: Tribology International, 32, p.687-699 (1999).

[19] P. Diatto, M. Anzani, L. Tinucci, G. Tripaldi, and A. Vettor: Investigation on Soot Dispersant Properties and Wear Effects in the Boundary Lubrication Regime: Lubrication at the Frontier, 1, p.809-819 (1999).

[20] J.J. Truhan, J. Qu, and P.J. Blau: The Effect of Lubricating Oil Condition on the Friction and Wear of Piston Ring and Cylinder Liner Materials in a Reciprocating Bench Test: Wear, 259, p.1048-1055 (2005).

[21] J.S. McQueen, H. Gao, E.D. Black, A.K. Gangopadhyay, and R.K. Jensen: Friction and Wear of Tribofilms Formed by Zinc Dialkyl Dithiphosphate Antiwear Additive in Low Viscosity Engine Oils: Tribology International, 38, p.289-297 (2005).

[22] Y.Y. Wu, W.C. Tsui, and T.C. Liu: Experimental Analysis of Tribological Properties of Lubricating Oils with Nanoparticle Additives: Wear, 262, p.819-825 (2007).

[23] M. Dienwiebel, and K. Pohlmann: Nanoscale Evolution of Sliding Metal Surfaces during Running-in: Tribol Lett, 27, p.255-260 (2007).

[24] S. Aldajah, O.O. Ajayi, G.R. Fenske, and I.L. Golblatt: Effect of Exhaust Gas Recirculation (EGR) Contamination of Diesel Engine Oil on Wear: Wear, 263, p.93-98 (2007).

[25] S. Antusch, M. Dienwiebel, E. Nold, P. Albers, U. Spicher, and M. Scherge: On the Tribochemical Action of Engine Soot: Wear, 269, p.1-12 (2010).

[26] M.A. Abdullah, S.A. Saleman, N. Tamaldin, and M.S. Suhaimi: Reducing Wear and Friction by Means of Lubricants Mixtures: Procedia Engineering, 68, p.338-344 (2013).

[27] S. George, S. Ball, V. Guatam, and M. Guatam: Effect of Diesel Soot on Lubricant Oil Viscosity: Tribology International, 40, p.809-818 (2007).

[28] C. Esangbedo, A.L. Boehman, and J.M. Parez: Characteristics of Diesel Engine Soot that Lead to Excessive Oil Thickening: Tribology International, 47, p.194-203 (2012).

[29] S. Daido, Y. Kodama, T. Inohara, N. Ohyama, and T. Sugiyama: Analysis of Soot Accumulation inside Diesel Engines: JSAE Review, 21, p.303-308 (2000).

[30] P.R. Ryason, I.Y. Chan, and J.T. Gilmore: Polishing Wear by Soot: Wear, 137, p.15-24 (1990).

[31] M. Ratoi, and H.A. Spikes: The Influence of Soot and Dispersant on ZDDP Film Thickness and Friction: Lubrication Science, 17, p.25-43 (2004).

[32] S.Q.A. Rizvi: A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design: ASTM International, p.4-6 (2009).

[33] Y. Wang, Q.J. Wang: Encyclopedia of Tribology: Springer Science & Business, p.2110-2111 (2013).

[34] P.A. Lakshminarayanan, N.S. Nayak: Critical Component Wear in Heavy Duty Engines: Wiley, (2011).

[35] G.W. Stachowiak, A.W. Batchelor: Engineering Tribology: Elsevier Inc., p.293-365 (2013).

[36] ASTM D445-15a, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity), ASTM International, West Conshohocken, PA, 2015, www.astm.org

[37] ASTM E2412-10, Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry, ASTM International, West Conshohocken, PA, 2010, www.astm.org

[38] ASTM D4739-11, Standard Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration, ASTM International, West Conshohocken, PA, 2011, www.astm.org

[39] ASTM D6595-16, Standard Test Method for Determination of Wear Metals and Contaminants in Used Lubricating Oils or Used Hydraulic Fluids by Rotating Disc Electrode Atomic Emission Spectrometry, ASTM International, West Conshohocken, PA, 2016, www.astm.org

[40] M.M. Maricq: Chemical characterization of particulate emissions from diesel engines – A review: Aerosol Science, 38, p.1079-1118 (2007).

[41] P. Karin, M. Borhanipour, Y. Songsaengchan, S. Laosuwan, C. Charoenphonphanich, N. Chollacoop, and K. Hanamura: Oxidation kinetics of small CI engine's biodiesel particulate matter: International Journal of Automotive Technology, 16, p.211-219 (2015).

[42] J.S. Evan: Where does all that Metal Come from: Technical Bulletin, 47, p.1-6 (2010).

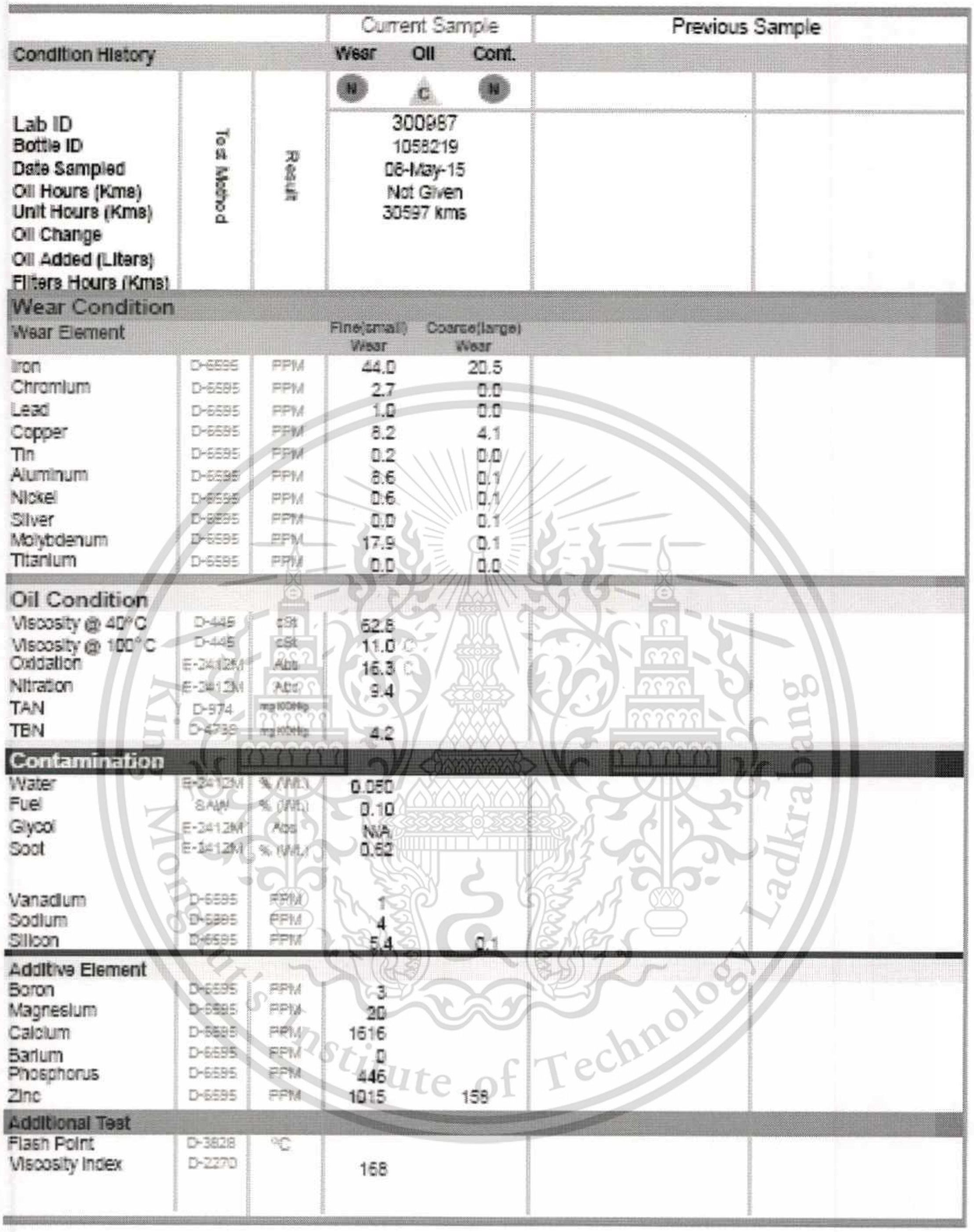
[43] ASTM D4172-94(2016): Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method): ASTM International, West Conshohocken, PA, 2016, www.astm.org

[44] ASTM D5183-05(2016), Standard Test Method for Determination of the Coefficient of Friction of Lubricants Using the Four-Ball Wear Test Machine, ASTM International, West Conshohocken, PA, 2016, www.astm.org

APPENDIX A

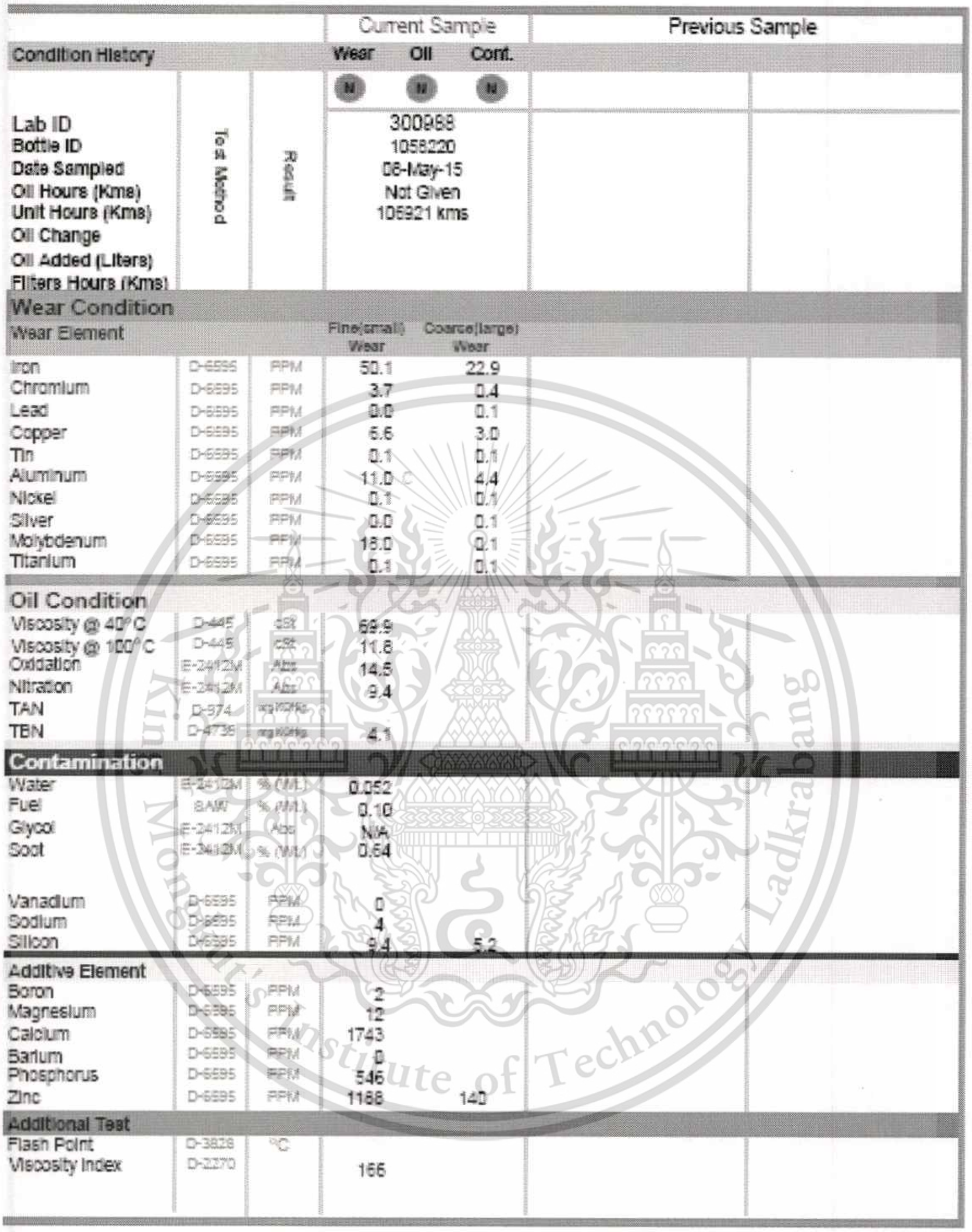
Physical and Chemical Properties of Used Oil from Diesel Engine Passenger Car

Used oil properties of car number 1 (engine size 2,000 cc)



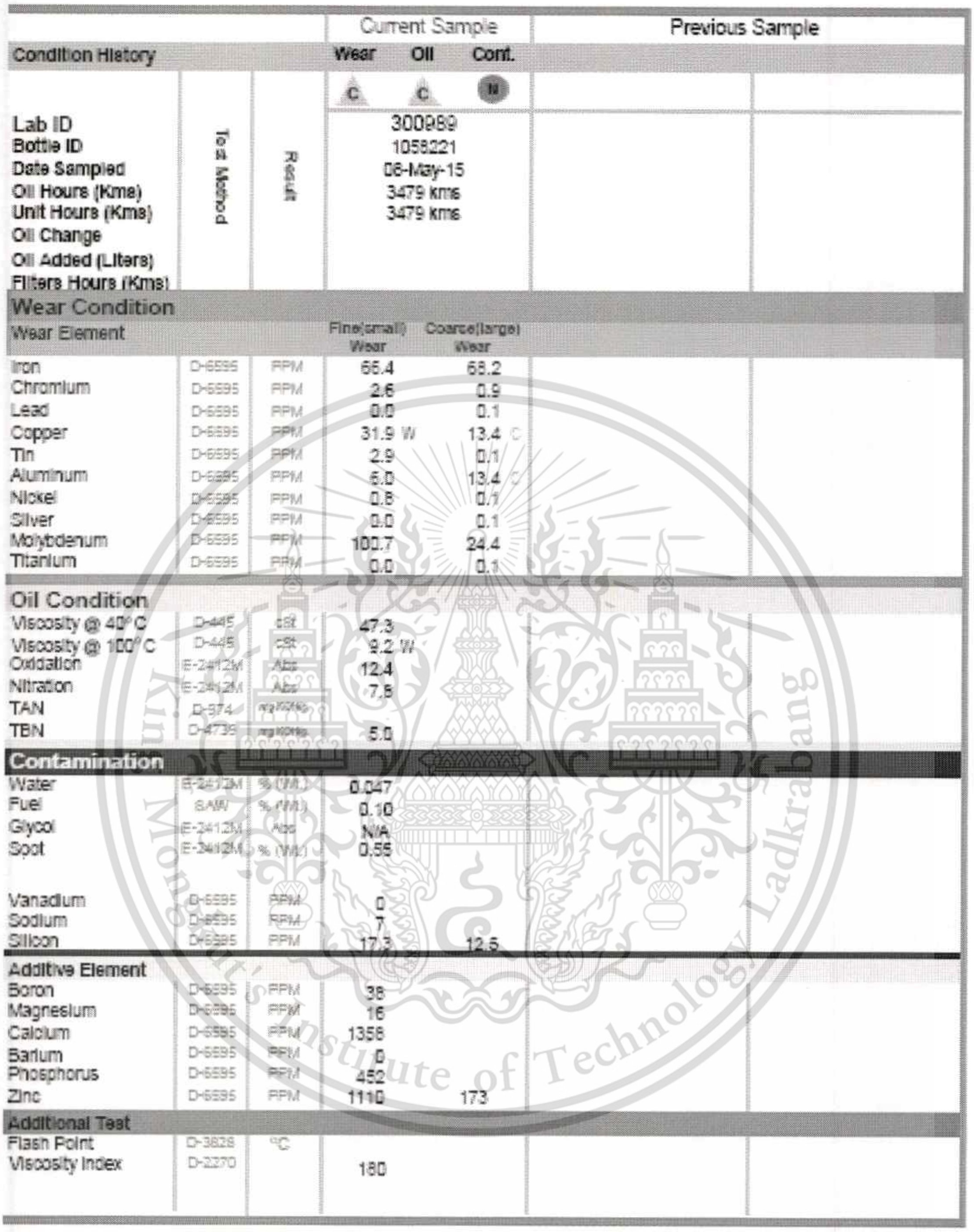
	Test Method	Result	Current Sample			Previous Sample	
Condition History			Wear	Oil	Cont.		
			● N	▲ C	● N		
Lab ID			300987				
Bottle ID			1058219				
Date Sampled			08-May-15				
Oil Hours (Kms)			Not Given				
Unit Hours (Kms)			30597 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear	Coarse(large) Wear			
Iron	D-6595	PPM	44.0	20.5			
Chromium	D-6595	PPM	2.7	0.0			
Lead	D-6595	PPM	1.0	0.0			
Copper	D-6595	PPM	8.2	4.1			
Tin	D-6595	PPM	0.2	0.0			
Aluminum	D-6595	PPM	8.6	0.1			
Nickel	D-6595	PPM	0.6	0.1			
Silver	D-6595	PPM	0.0	0.1			
Molybdenum	D-6595	PPM	17.9	0.1			
Titanium	D-6595	PPM	0.0	0.0			
Oil Condition							
Viscosity @ 40°C	D-445	cSt	62.8				
Viscosity @ 100°C	D-445	cSt	11.0 C				
Oxidation	E-2412M	Abs	16.3 C				
Nitration	E-2412M	Abs	9.4				
TAN	D-974	mgKOH/g					
TBN	D-4739	mgKOH/g	4.2				
Contamination							
Water	E-2412M	% (Wt.)	0.050				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.62				
Vanadium	D-6595	PPM	1				
Sodium	D-6595	PPM	4				
Silicon	D-6595	PPM	5.4	0.1			
Additive Element							
Boron	D-6595	PPM	3				
Magnesium	D-6595	PPM	20				
Calcium	D-6595	PPM	1616				
Barium	D-6595	PPM	0				
Phosphorus	D-6595	PPM	446				
Zinc	D-6595	PPM	1015	158			
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		168				

Used oil properties of car number 2 (engine size 2,000 cc)



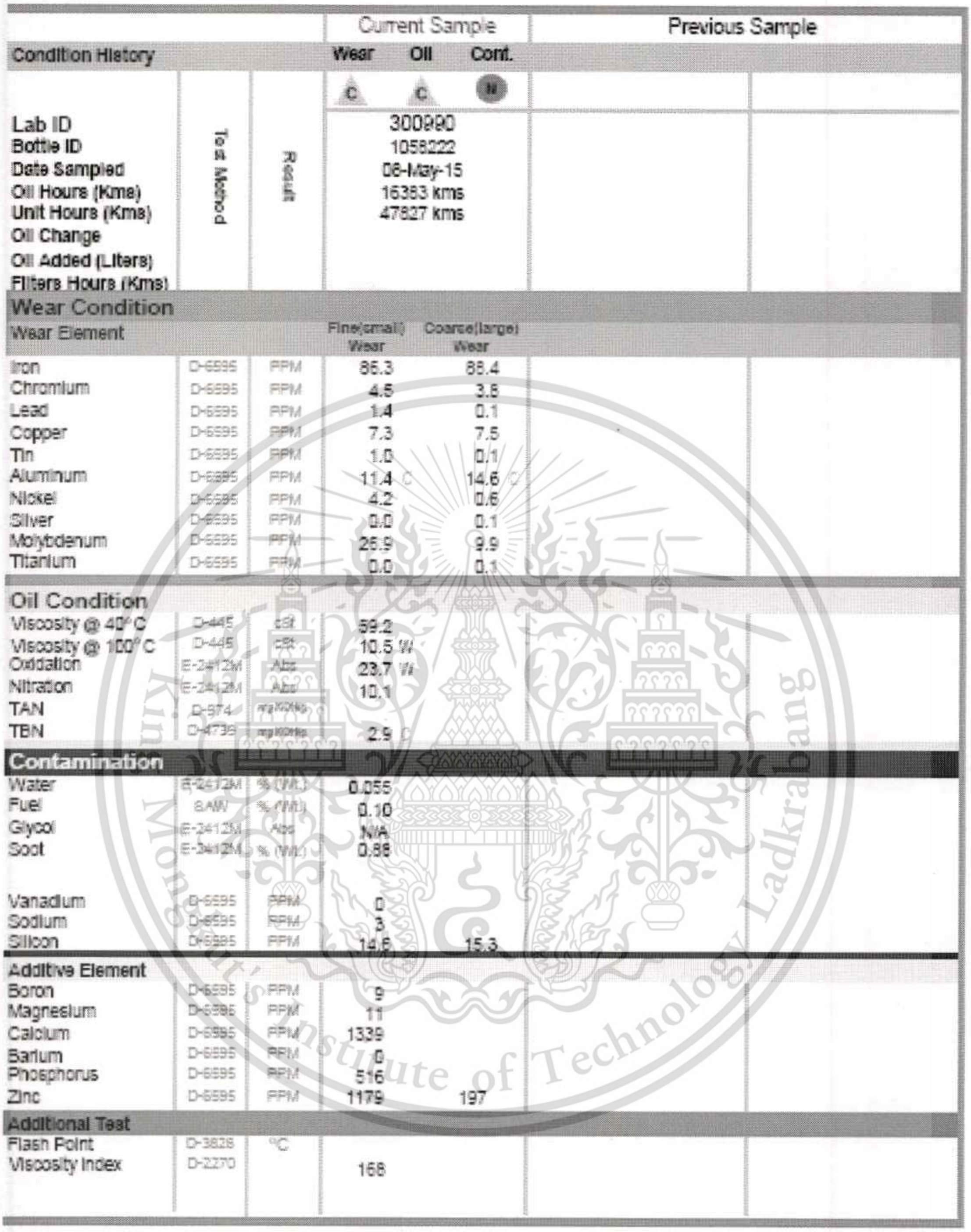
			Current Sample		Previous Sample	
Condition History			Wear Oil Cont.			
			N N N			
	Test Method	Result				
Lab ID			300988			
Bottle ID			1058220			
Date Sampled			08-May-15			
Oil Hours (Kms)			Not Given			
Unit Hours (Kms)			105921 kms			
Oil Change						
Oil Added (Liters)						
Filters Hours (Kms)						
Wear Condition						
Wear Element			Fine(small) Wear	Coarse(large) Wear		
Iron	D-6595	PPM	50.1	22.9		
Chromium	D-6595	PPM	3.7	0.4		
Lead	D-6595	PPM	0.0	0.1		
Copper	D-6595	PPM	6.6	3.0		
Tin	D-6595	PPM	0.1	0.1		
Aluminum	D-6595	PPM	11.0 C	4.4		
Nickel	D-6595	PPM	0.1	0.1		
Silver	D-6595	PPM	0.0	0.1		
Molybdenum	D-6595	PPM	18.0	0.1		
Titanium	D-6595	PPM	0.1	0.1		
Oil Condition						
Viscosity @ 40°C	D-445	cSt	69.9			
Viscosity @ 100°C	D-445	cSt	11.8			
Oxidation	E-2412M	Abs	14.5			
Nitration	E-2412M	Abs	9.4			
TAN	D-974	mg KOH/g				
TBN	D-4739	mg KOH/g	4.1			
Contamination						
Water	E-2412M	% (Wt.)	0.052			
Fuel	SAW	% (Wt.)	0.10			
Glycol	E-2412M	Abs	N/A			
Soot	E-2412M	% (Wt.)	0.64			
Vanadium	D-6595	PPM	0			
Sodium	D-6595	PPM	4			
Silicon	D-6595	PPM	9.4	5.2		
Additive Element						
Boron	D-6595	PPM	2			
Magnesium	D-6595	PPM	12			
Calcium	D-6595	PPM	1743			
Barium	D-6595	PPM	0			
Phosphorus	D-6595	PPM	546			
Zinc	D-6595	PPM	1188	140		
Additional Test						
Flash Point	D-3828	°C				
Viscosity Index	D-2270		166			

Used oil properties of car number 3 (engine size 2,000 cc)



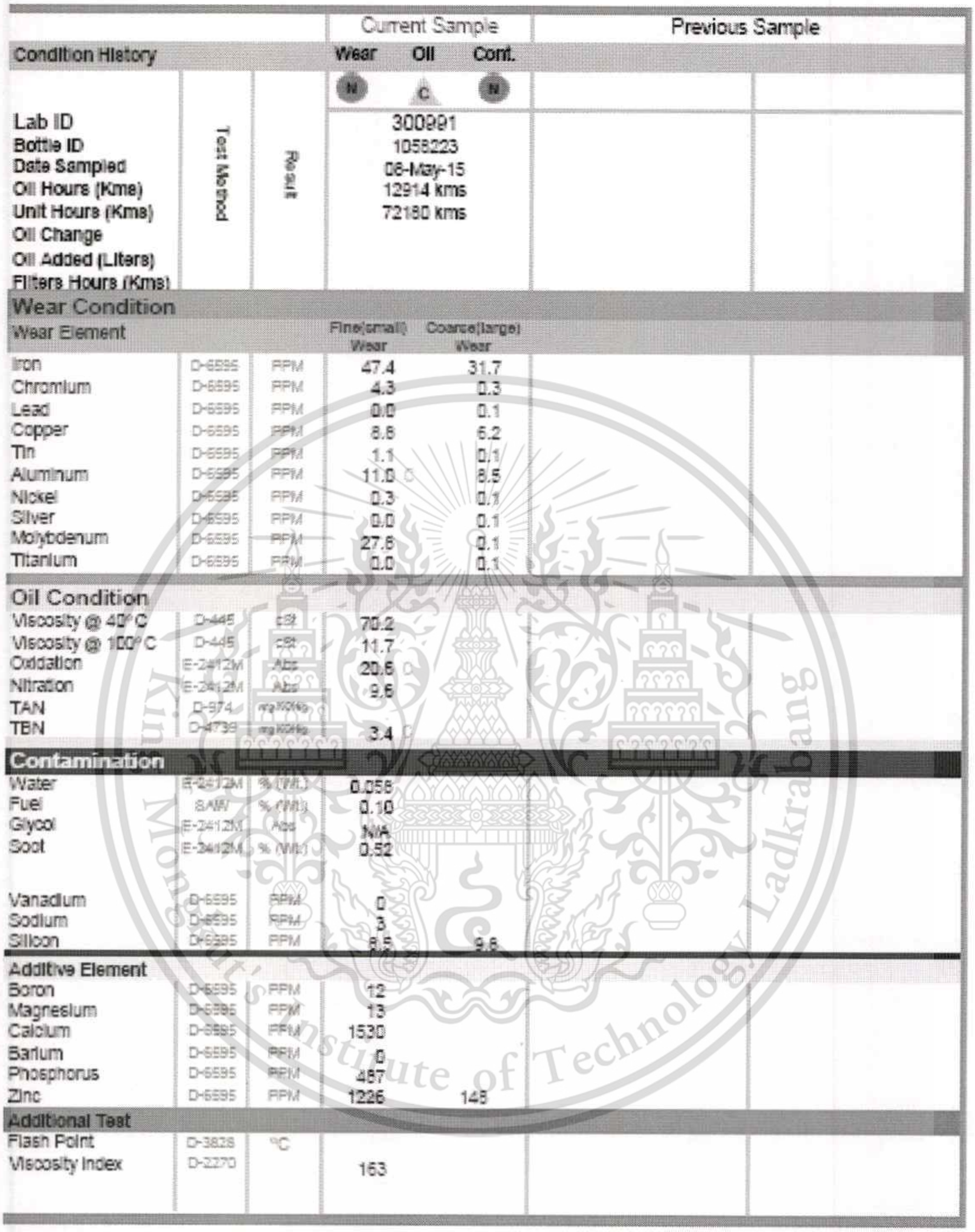
	Test Method	Result	Current Sample			Previous Sample	
Condition History			**Wear**	**Oil**	**Cont.**		
			C	C	N		
Lab ID			300989				
Bottle ID			1058221				
Date Sampled			06-May-15				
Oil Hours (Kms)			3479 kms				
Unit Hours (Kms)			3479 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear		Coarse(large) Wear		
Iron	D-6595	PPM	66.4		68.2		
Chromium	D-6595	PPM	2.6		0.9		
Lead	D-6595	PPM	0.0		0.1		
Copper	D-6595	PPM	31.9 W		13.4 C		
Tin	D-6595	PPM	2.9		0.1		
Aluminum	D-6595	PPM	6.0		13.4 C		
Nickel	D-6595	PPM	0.8		0.1		
Silver	D-6595	PPM	0.0		0.1		
Molybdenum	D-6595	PPM	100.7		24.4		
Titanium	D-6595	PPM	0.0		0.1		
Oil Condition							
Viscosity @ 40°C	D-445	cSt	47.3				
Viscosity @ 100°C	D-445	cSt	9.2 W				
Oxidation	E-2412M	Abs	12.4				
Nitration	E-2412M	Abs	7.8				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	5.0				
Contamination							
Water	E-2412M	% (Wt.)	0.047				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.55				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	7				
Silicon	D-6595	PPM	17.3		12.5		
Additive Element							
Boron	D-6595	PPM	38				
Magnesium	D-6595	PPM	16				
Calcium	D-6595	PPM	1358				
Barium	D-6595	PPM	0				
Phosphorus	D-6595	PPM	452				
Zinc	D-6595	PPM	1110		173		
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		180				

Used oil properties of car number 4 (engine size 2,000 cc)



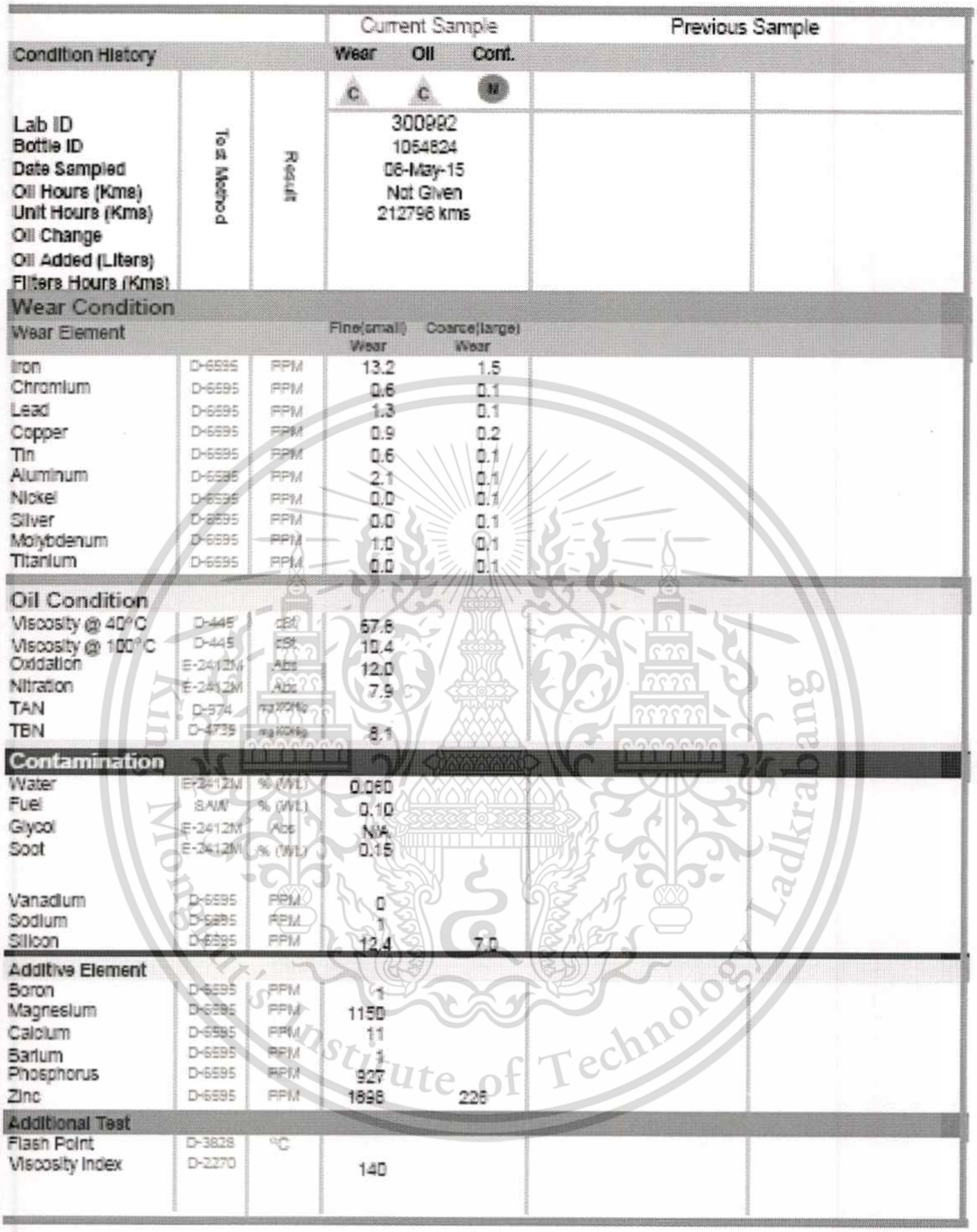
	Test Method	Result	Current Sample			Previous Sample	
Condition History			Wear	Oil	Cont.		
			C	C	N		
Lab ID			300990				
Bottle ID			1058222				
Date Sampled			06-May-15				
Oil Hours (Kms)			16383 kms				
Unit Hours (Kms)			47827 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear	Coarse(large) Wear			
Iron	D-6595	PPM	86.3	88.4			
Chromium	D-6595	PPM	4.5	3.8			
Lead	D-6595	PPM	1.4	0.1			
Copper	D-6595	PPM	7.3	7.5			
Tin	D-6595	PPM	1.0	0.1			
Aluminum	D-6595	PPM	11.4 C	14.6 C			
Nickel	D-6595	PPM	4.2	0.6			
Silver	D-6595	PPM	0.0	0.1			
Molybdenum	D-6595	PPM	26.9	9.9			
Titanium	D-6595	PPM	0.0	0.1			
Oil Condition							
Viscosity @ 40°C	D-445	cSt	59.2				
Viscosity @ 100°C	D-445	cSt	10.5 W				
Oxidation	E-2412M	Abs	23.7 W				
Nitration	E-2412M	Abs	10.1				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	2.9 C				
Contamination							
Water	E-2412M	% (Wt.)	0.055				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.88				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	3				
Silicon	D-6595	PPM	14.6	15.3			
Additive Element							
Boron	D-6595	PPM	9				
Magnesium	D-6595	PPM	11				
Calcium	D-6595	PPM	1339				
Barium	D-6595	PPM	0				
Phosphorus	D-6595	PPM	516				
Zinc	D-6595	PPM	1179	197			
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		168				

Used oil properties of car number 5 (engine size 2,000 cc)



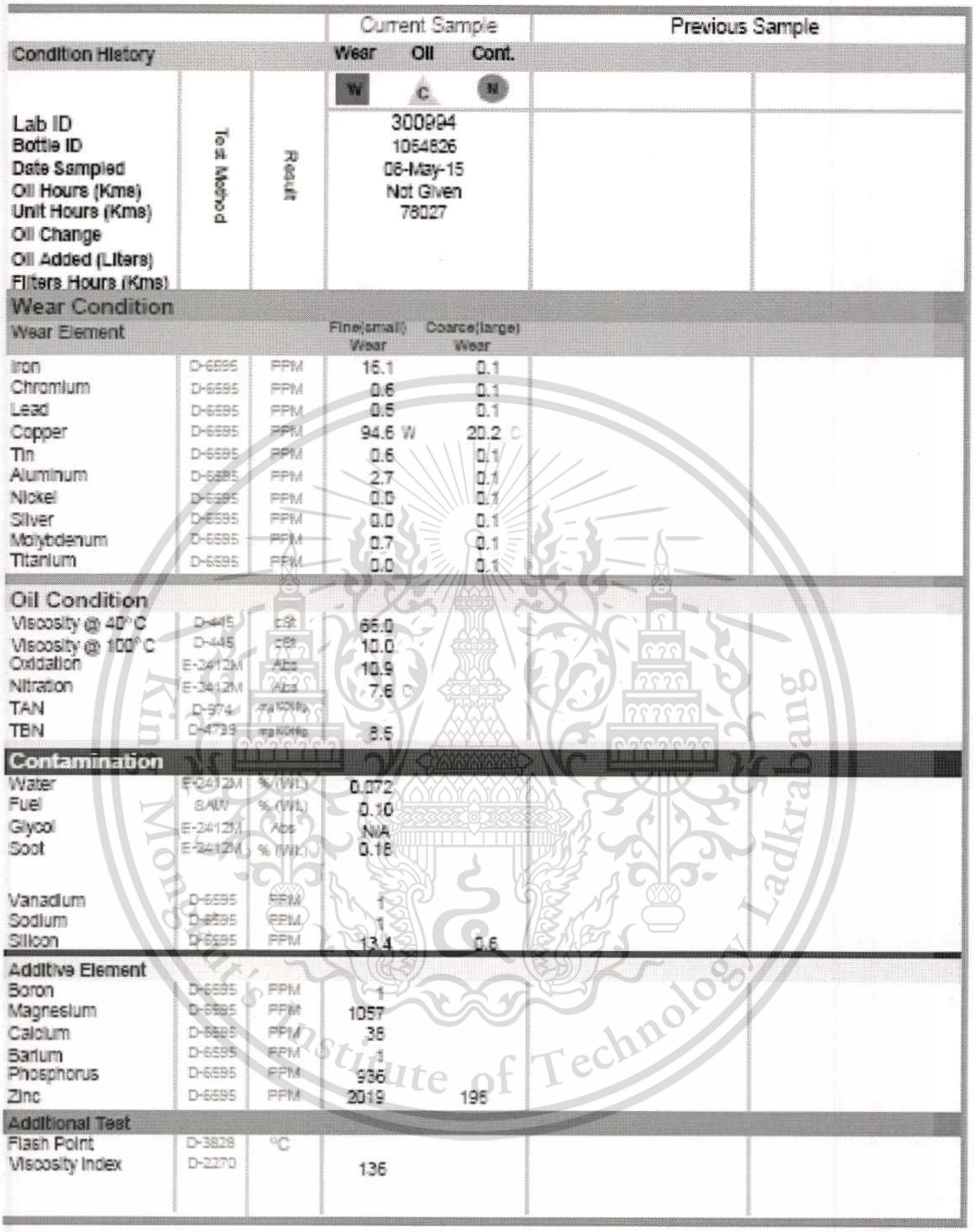
			Current Sample			Previous Sample	
Condition History			Wear	Oil	Cont.		
			N	C	N		
Lab ID Bottle ID Date Sampled Oil Hours (Kms) Unit Hours (Kms) Oil Change Oil Added (Liters) Filters Hours (Kms)	Test Method	Result		300991 1058223 08-May-15 12914 kms 72180 kms			
Wear Condition							
Wear Element			Fine(small) Wear		Coarse(large) Wear		
Iron	D-6595	PPM	47.4		31.7		
Chromium	D-6595	PPM	4.3		0.3		
Lead	D-6595	PPM	0.0		0.1		
Copper	D-6595	PPM	8.8		6.2		
Tin	D-6595	PPM	1.1		0.1		
Aluminum	D-6595	PPM	11.0 C		8.5		
Nickel	D-6595	PPM	0.3		0.1		
Silver	D-6595	PPM	0.0		0.1		
Molybdenum	D-6595	PPM	27.6		0.1		
Titanium	D-6595	PPM	0.0		0.1		
Oil Condition							
Viscosity @ 40°C	D-445	cSt	70.2				
Viscosity @ 100°C	D-445	cSt	11.7				
Oxidation	E-2412M	Abs	20.6 C				
Nitration	E-2412M	Abs	9.6				
TAN	D-974	mgKOH/g					
TBN	D-4739	mgKOH/g	3.4 C				
Contamination							
Water	E-2412M	% (Wt.)	0.058				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.52				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	3				
Silicon	D-6595	PPM	8.5		9.6		
Additive Element							
Boron	D-6595	PPM	12				
Magnesium	D-6595	PPM	13				
Calcium	D-6595	PPM	1530				
Barium	D-6595	PPM	0				
Phosphorus	D-6595	PPM	487				
Zinc	D-6595	PPM	1226		148		
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		163				

Used oil properties of car number 6 (engine size 2,500 cc)



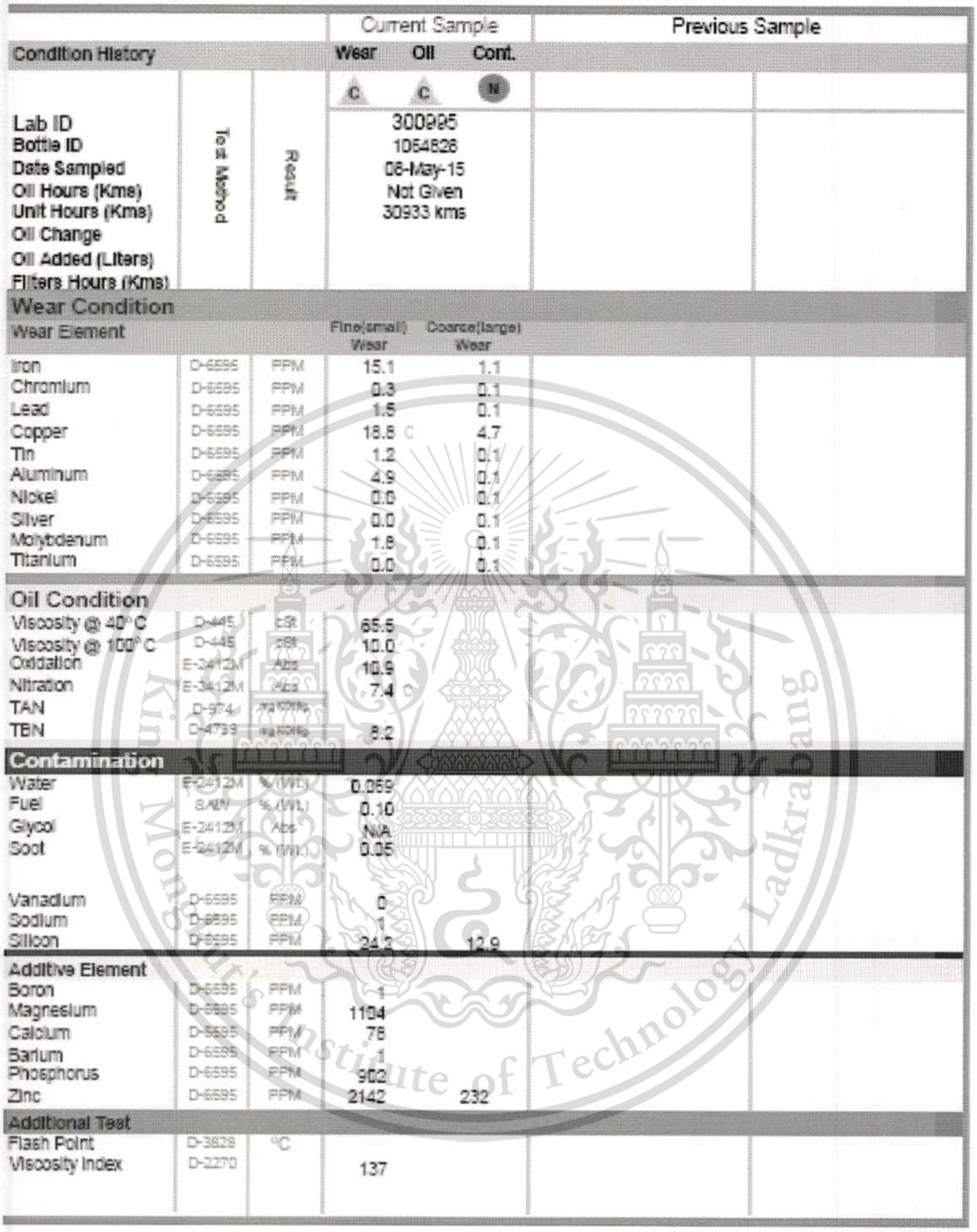
			Current Sample			Previous Sample	
Condition History			**Wear**	**Oil**	**Cont.**		
			C	C	N		
Lab ID	Test Method	Result		300992			
Bottle ID				1054824			
Date Sampled				08-May-15			
Oil Hours (Kms)				Not Given			
Unit Hours (Kms)				212796 kms			
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear		Coarse(large) Wear		
Iron	D-6595	PPM	13.2		1.5		
Chromium	D-6595	PPM	0.6		0.1		
Lead	D-6595	PPM	1.3		0.1		
Copper	D-6595	PPM	0.9		0.2		
Tin	D-6595	PPM	0.6		0.1		
Aluminum	D-6595	PPM	2.1		0.1		
Nickel	D-6595	PPM	0.0		0.1		
Silver	D-6595	PPM	0.0		0.1		
Molybdenum	D-6595	PPM	1.0		0.1		
Titanium	D-6595	PPM	0.0		0.1		
Oil Condition							
Viscosity @ 40°C	D-445	cSt	57.6				
Viscosity @ 100°C	D-445	cSt	10.4				
Oxidation	E-2412M	Abs	12.0				
Nitration	E-2412M	Abs	7.9				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	8.1				
Contamination							
Water	E-2412M	% (Wt.)	0.060				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.15				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	1				
Silicon	D-6595	PPM	12.4		7.0		
Additive Element							
Boron	D-6595	PPM	1				
Magnesium	D-6595	PPM	1150				
Calcium	D-6595	PPM	11				
Barium	D-6595	PPM	1				
Phosphorus	D-6595	PPM	927				
Zinc	D-6595	PPM	1098		225		
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		140				

Used oil properties of car number 7 (engine size 2,500 cc)



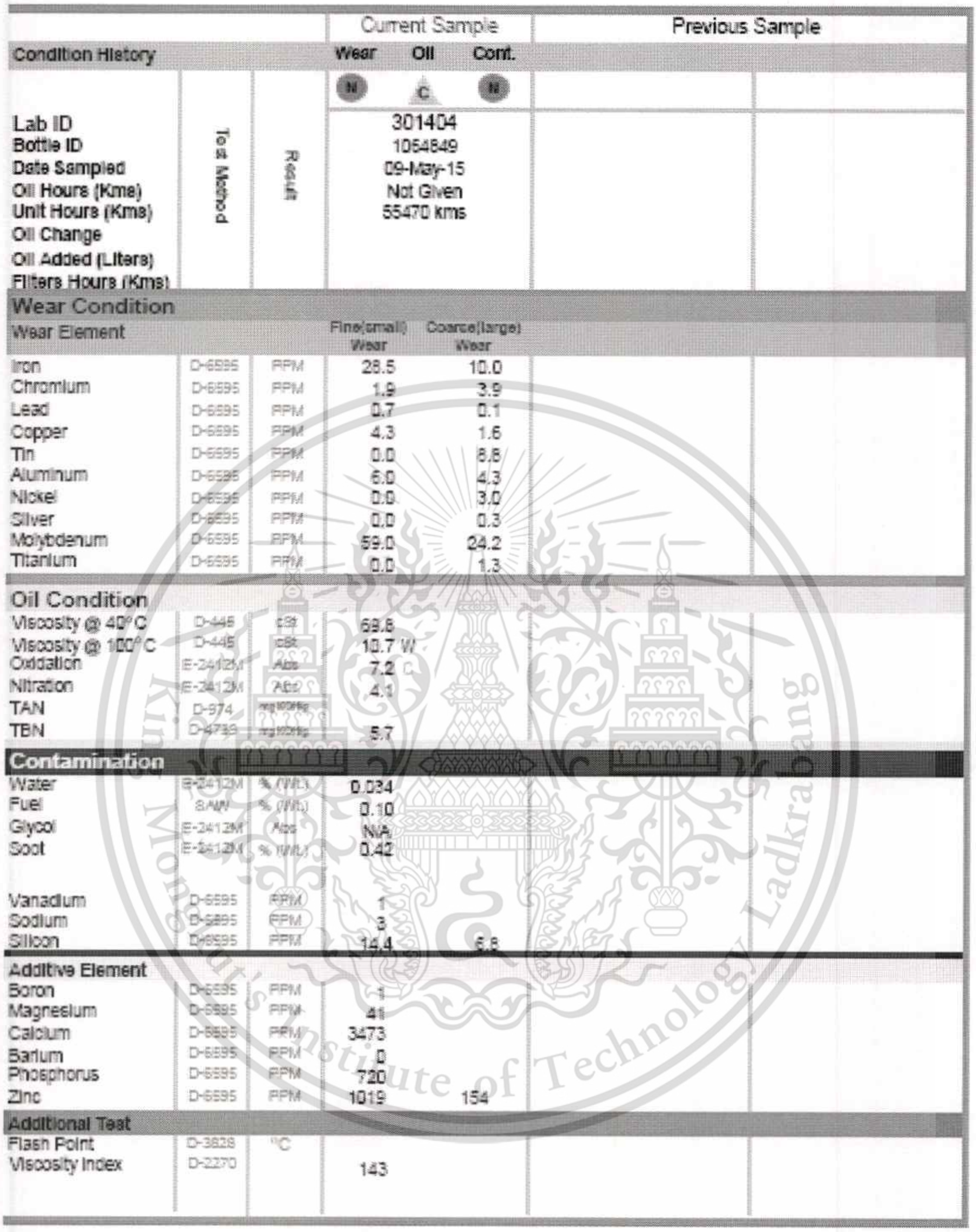
			Current Sample			Previous Sample	
Condition History			Wear	Oil	Cont.		
	Test Method	Result	W	C	N		
Lab ID			300994				
Bottle ID			1054826				
Date Sampled			06-May-15				
Oil Hours (Kms)			Not Given				
Unit Hours (Kms)			78027				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear	Coarse(large) Wear			
Iron	D-6595	PPM	16.1	0.1			
Chromium	D-6595	PPM	0.6	0.1			
Lead	D-6595	PPM	0.5	0.1			
Copper	D-6595	PPM	94.6 W	20.2 C			
Tin	D-6595	PPM	0.6	0.1			
Aluminum	D-6595	PPM	2.7	0.1			
Nickel	D-6595	PPM	0.0	0.1			
Silver	D-6595	PPM	0.0	0.1			
Molybdenum	D-6595	PPM	0.7	0.1			
Titanium	D-6595	PPM	0.0	0.1			
Oil Condition							
Viscosity @ 40°C	D-445	cSt	66.0				
Viscosity @ 100°C	D-445	cSt	10.0				
Oxidation	E-2412M	Abs	10.9				
Nitration	E-2412M	Abs	7.6 C				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	8.5				
Contamination							
Water	E-2412M	% (Wt.)	0.072				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.18				
Vanadium	D-6595	PPM	1				
Sodium	D-6595	PPM	1				
Silicon	D-6595	PPM	13.4	0.6			
Additive Element							
Boron	D-6595	PPM	1				
Magnesium	D-6595	PPM	1057				
Calcium	D-6595	PPM	38				
Barium	D-6595	PPM	1				
Phosphorus	D-6595	PPM	936				
Zinc	D-6595	PPM	2019	196			
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		136				

Used oil properties of car number 8 (engine size 2,500 cc)



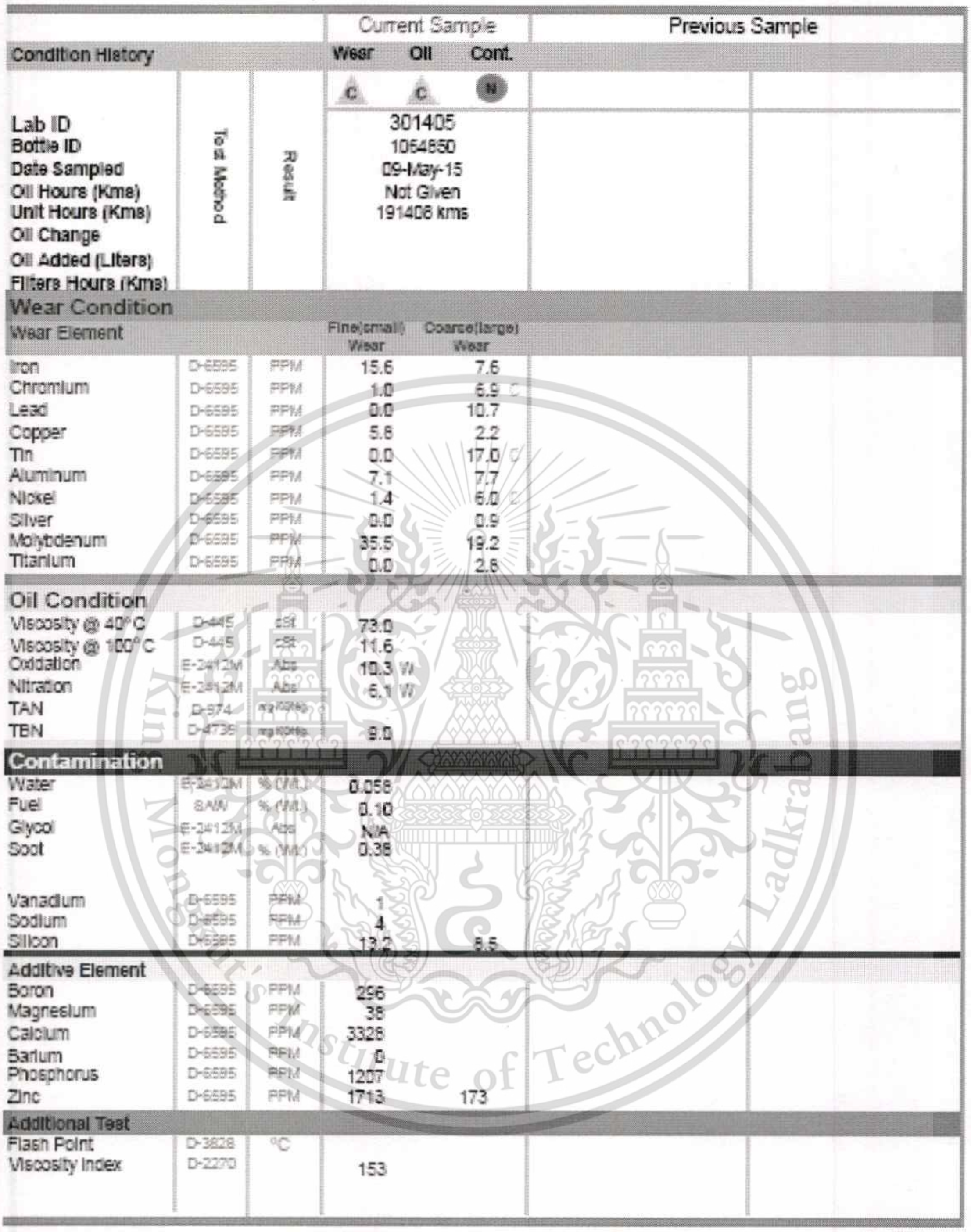
	Test Method	Result	Current Sample			Previous Sample	
Condition History			Wear	Oil	Cont.		
			C	C	N		
Lab ID			300995				
Bottle ID			1064826				
Date Sampled			06-May-15				
Oil Hours (Kms)			Not Given				
Unit Hours (Kms)			30933 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear		Coarse(large) Wear		
Iron	D-6595	PPM	15.1		1.1		
Chromium	D-6595	PPM	0.3		0.1		
Lead	D-6595	PPM	1.5		0.1		
Copper	D-6595	PPM	18.8 C		4.7		
Tin	D-6595	PPM	1.2		0.1		
Aluminum	D-6595	PPM	4.9		0.1		
Nickel	D-6595	PPM	0.0		0.1		
Silver	D-6595	PPM	0.0		0.1		
Molybdenum	D-6595	PPM	1.8		0.1		
Titanium	D-6595	PPM	0.0		0.1		
Oil Condition							
Viscosity @ 40°C	D-445	cSt	65.5				
Viscosity @ 100°C	D-445	cSt	10.0				
Oxidation	E-2412M	Abs	10.9				
Nitration	E-2412M	Abs	7.4 C				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	8.2				
Contamination							
Water	E-2412M	% (Wt.)	0.069				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.05				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	1				
Silicon	D-6595	PPM	24.2		12.9		
Additive Element							
Boron	D-6595	PPM	1				
Magnesium	D-6595	PPM	1104				
Calcium	D-6595	PPM	78				
Barium	D-6595	PPM	1				
Phosphorus	D-6595	PPM	902				
Zinc	D-6595	PPM	2142		232		
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		137				

Used oil properties of car number 9 (engine size 2,500 cc)



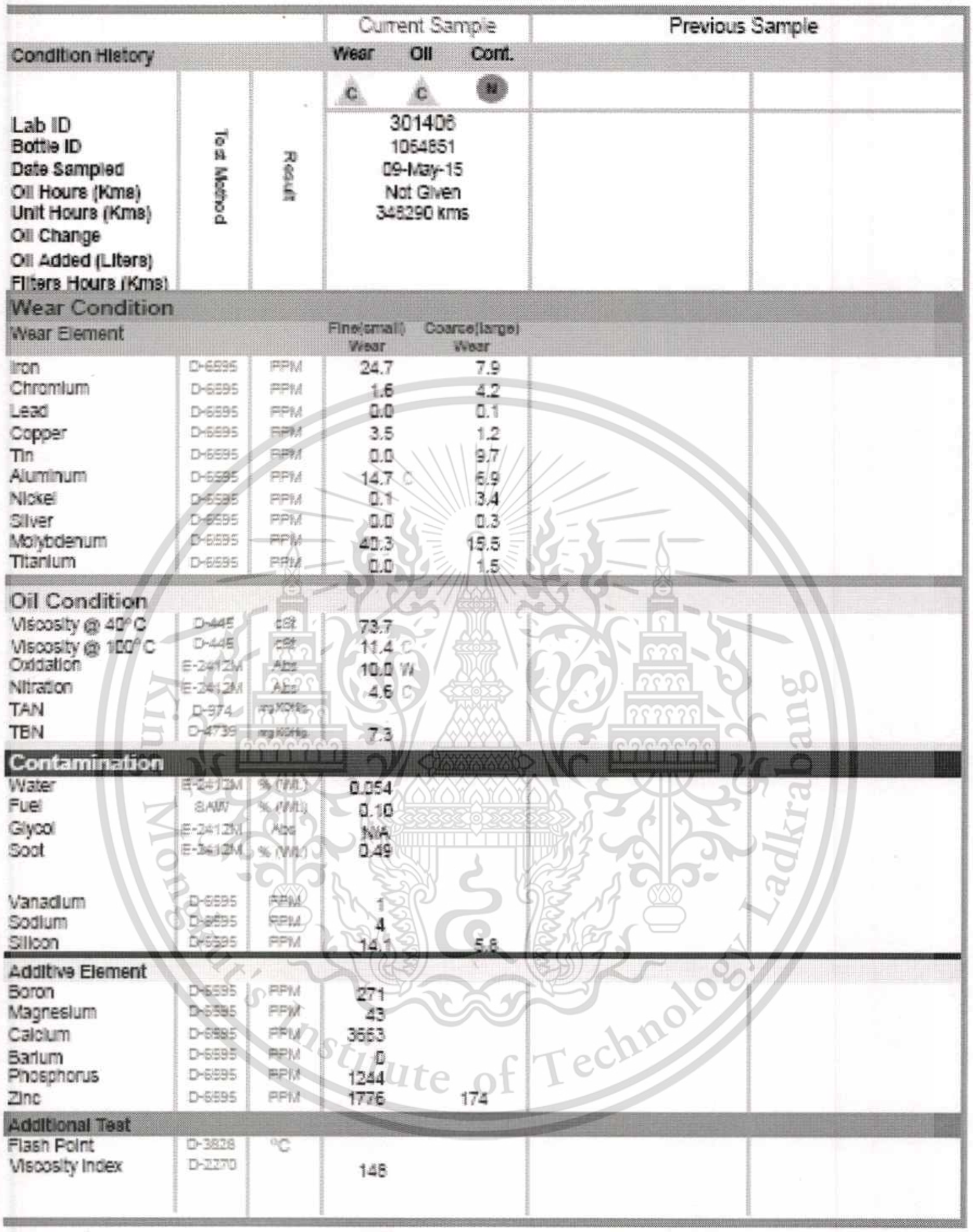
			Current Sample			Previous Sample	
Condition History			Wear	Oil	Cont.		
	Test Method	Result	N	C	N		
Lab ID			301404				
Bottle ID			1064849				
Date Sampled			09-May-15				
Oil Hours (Kms)			Not Given				
Unit Hours (Kms)			55470 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear	Coarse(large) Wear			
Iron	D-6595	PPM	28.5	10.0			
Chromium	D-6595	PPM	1.9	3.9			
Lead	D-6595	PPM	0.7	0.1			
Copper	D-6595	PPM	4.3	1.6			
Tin	D-6595	PPM	0.0	8.8			
Aluminum	D-6595	PPM	6.0	4.3			
Nickel	D-6595	PPM	0.0	3.0			
Silver	D-6595	PPM	0.0	0.3			
Molybdenum	D-6595	PPM	59.0	24.2			
Titanium	D-6595	PPM	0.0	1.3			
Oil Condition							
Viscosity @ 40°C	D-445	cSt	68.8				
Viscosity @ 100°C	D-445	cSt	10.7 W				
Oxidation	E-2412M	Abs	7.2 C				
Nitration	E-2412M	Abs	4.1				
TAN	D-974	mgKOH/g					
TBN	D-4739	mgKOH/g	5.7				
Contamination							
Water	E-2412M	% (Wt.)	0.034				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.42				
Vanadium	D-6595	PPM	1				
Sodium	D-6595	PPM	3				
Silicon	D-6595	PPM	14.4	6.8			
Additive Element							
Boron	D-6595	PPM	1				
Magnesium	D-6595	PPM	41				
Calcium	D-6595	PPM	3473				
Barium	D-6595	PPM	0				
Phosphorus	D-6595	PPM	720				
Zinc	D-6595	PPM	1019	154			
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		143				

Used oil properties of car number 10 (engine size 2,500 cc)



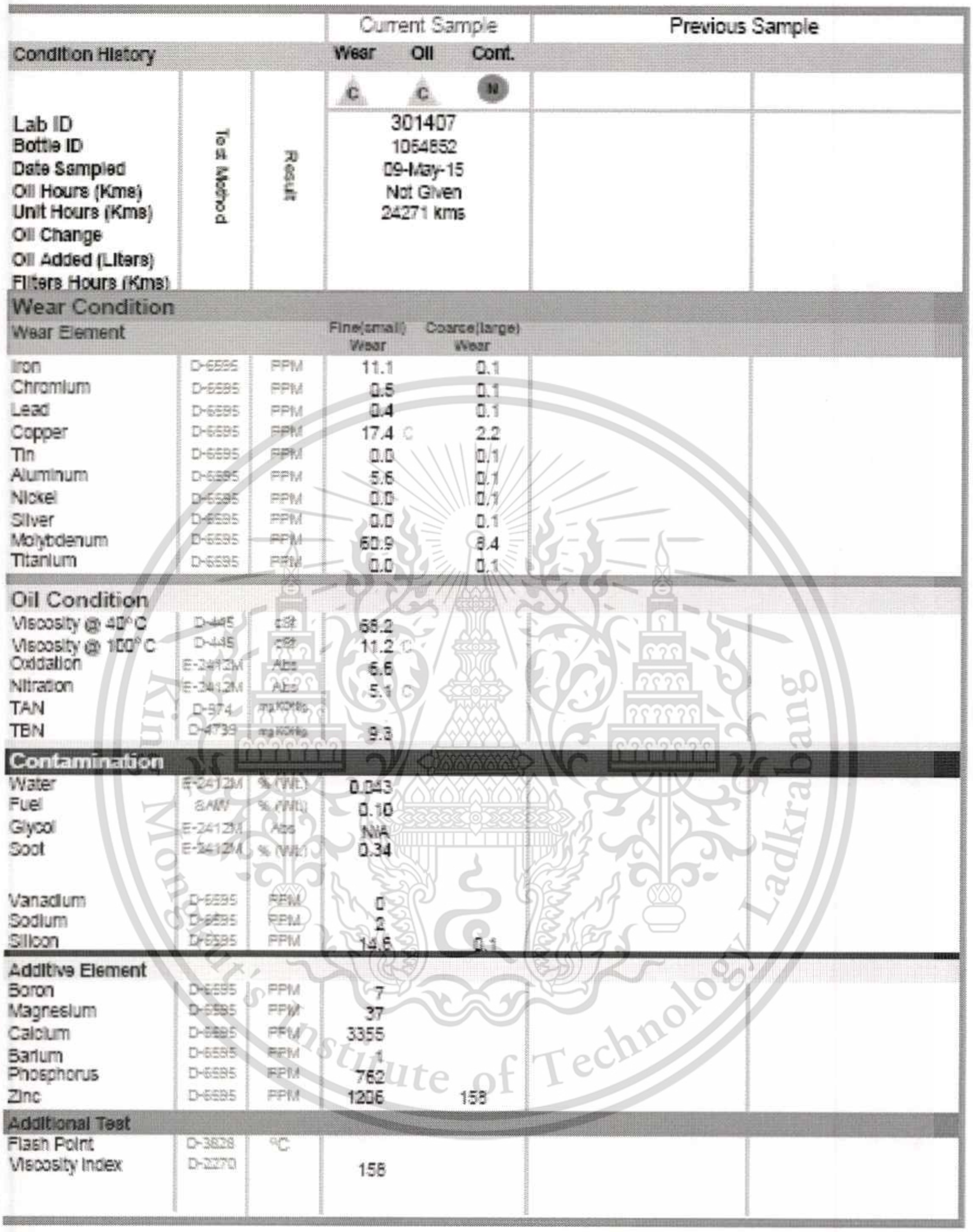
	Test Method	Result	Current Sample			Previous Sample	
Condition History			**Wear**	**Oil**	**Cont.**		
			C	C	N		
Lab ID			301405				
Bottle ID			1064650				
Date Sampled			09-May-15				
Oil Hours (Kms)			Not Given				
Unit Hours (Kms)			191406 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear	Coarse(large) Wear			
Iron	D-6595	PPM	15.6	7.6			
Chromium	D-6595	PPM	1.0	6.9 C			
Lead	D-6595	PPM	0.0	10.7			
Copper	D-6595	PPM	5.8	2.2			
Tin	D-6595	PPM	0.0	17.0 C			
Aluminum	D-6595	PPM	7.1	7.7			
Nickel	D-6595	PPM	1.4	6.0 C			
Silver	D-6595	PPM	0.0	0.9			
Molybdenum	D-6595	PPM	35.5	19.2			
Titanium	D-6595	PPM	0.0	2.6			
Oil Condition							
Viscosity @ 40°C	D-445	cSt	73.0				
Viscosity @ 100°C	D-445	cSt	11.6				
Oxidation	E-2412M	Abs	10.3 W				
Nitration	E-2412M	Abs	6.1 W				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	9.0				
Contamination							
Water	E-2412M	% (Vol.)	0.058				
Fuel	SAW	% (Vol.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Vol.)	0.38				
Vanadium	D-6595	PPM	1				
Sodium	D-6595	PPM	4				
Silicon	D-6595	PPM	13.2	8.5			
Additive Element							
Boron	D-6595	PPM	296				
Magnesium	D-6595	PPM	38				
Calcium	D-6595	PPM	3328				
Barium	D-6595	PPM	0				
Phosphorus	D-6595	PPM	1207				
Zinc	D-6595	PPM	1713	173			
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		153				

Used oil properties of car number 11 (engine size 2,500 cc)



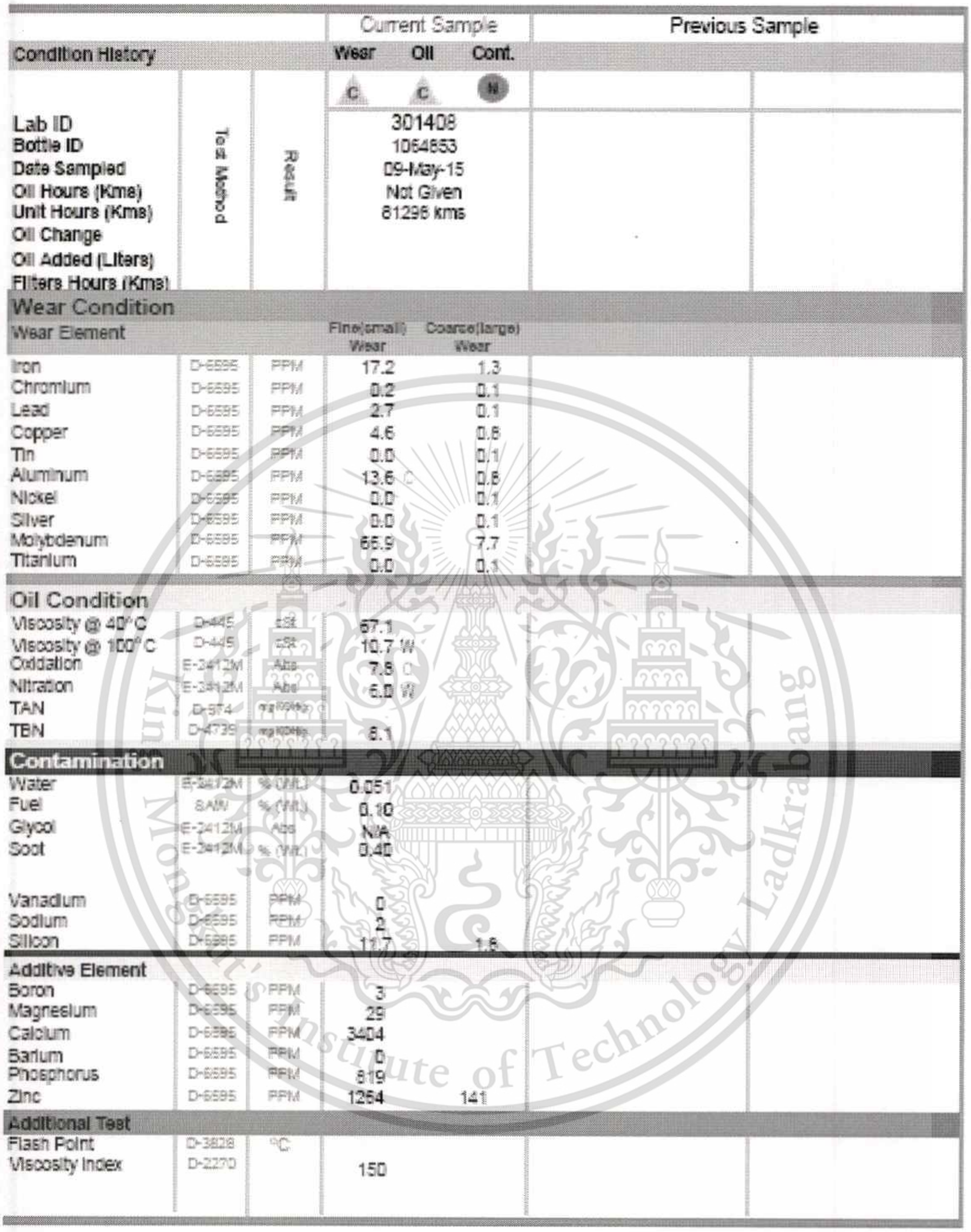
	Test Method	Result	Current Sample		Previous Sample	
Condition History			Wear Oil Cont.			
			C C N			
Lab ID			301406			
Bottle ID			1064651			
Date Sampled			09-May-15			
Oil Hours (Kms)			Not Given			
Unit Hours (Kms)			348290 kms			
Oil Change						
Oil Added (Liters)						
Filters Hours (Kms)						
Wear Condition						
Wear Element			Fine(small) Wear	Coarse(large) Wear		
Iron	D-6595	PPM	24.7	7.9		
Chromium	D-6595	PPM	1.6	4.2		
Lead	D-6595	PPM	0.0	0.1		
Copper	D-6595	PPM	3.5	1.2		
Tin	D-6595	PPM	0.0	9.7		
Aluminum	D-6595	PPM	14.7 C	6.9		
Nickel	D-6595	PPM	0.1	3.4		
Silver	D-6595	PPM	0.0	0.3		
Molybdenum	D-6595	PPM	40.3	15.5		
Titanium	D-6595	PPM	0.0	1.5		
Oil Condition						
Viscosity @ 40°C	D-445	cSt	73.7			
Viscosity @ 100°C	D-445	cSt	11.4 C			
Oxidation	E-2412M	Abs	10.0 W			
Nitration	E-2412M	Abs	4.6 C			
TAN	D-974	mg KOH/g				
TBN	D-4739	mg KOH/g	7.3			
Contamination						
Water	E-2412M	% (Wt.)	0.054			
Fuel	SAW	% (Wt.)	0.10			
Glycol	E-2412M	Abs	N/A			
Soot	E-2412M	% (Wt.)	0.49			
Vanadium	D-6595	PPM	1			
Sodium	D-6595	PPM	4			
Silicon	D-6595	PPM	14.1	5.8		
Additive Element						
Boron	D-6595	PPM	271			
Magnesium	D-6595	PPM	43			
Calcium	D-6595	PPM	3563			
Barium	D-6595	PPM	0			
Phosphorus	D-6595	PPM	1244			
Zinc	D-6595	PPM	1776	174		
Additional Test						
Flash Point	D-3828	°C				
Viscosity Index	D-2270		148			

Used oil properties of car number 12 (engine size 2,500 cc)



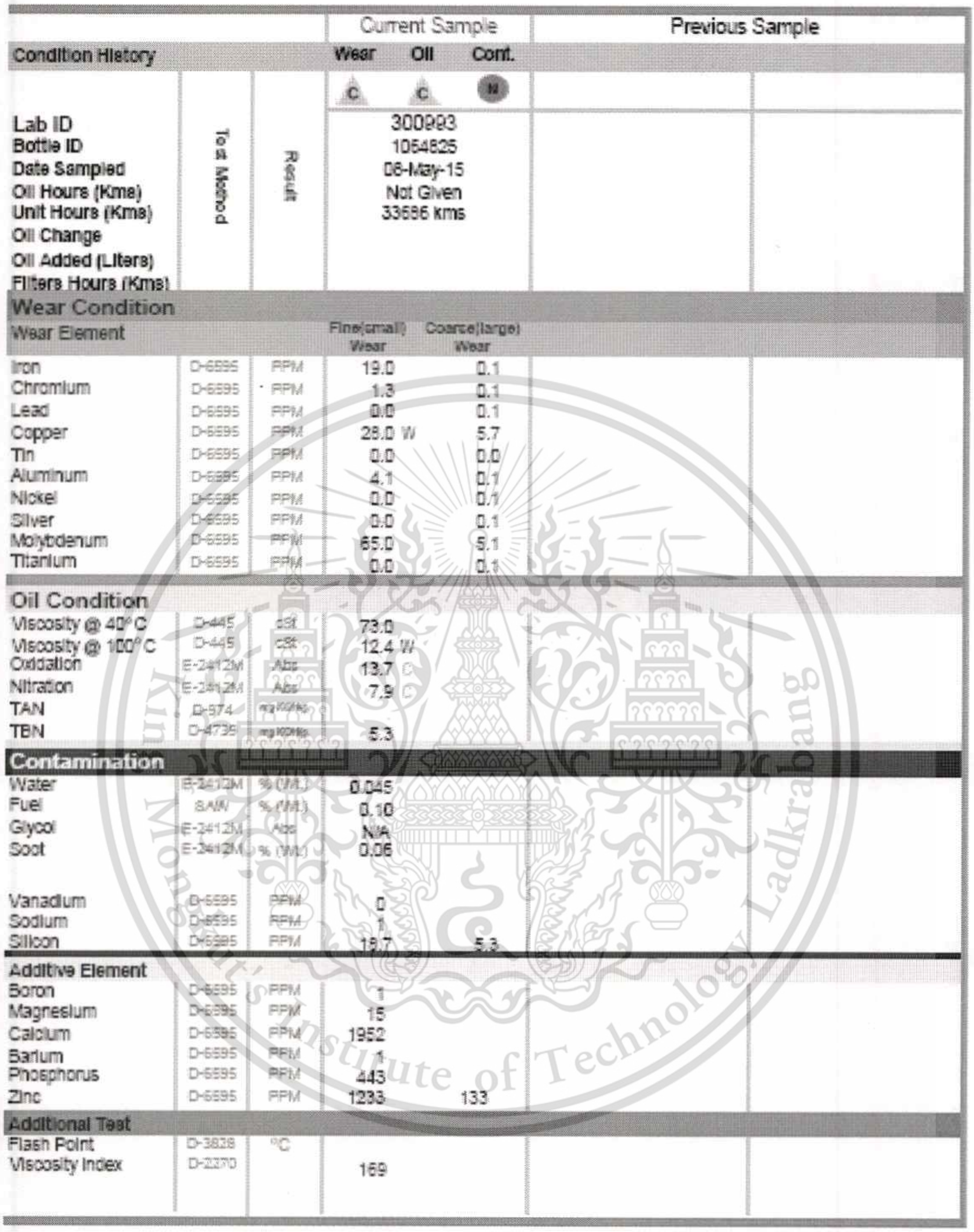
	Test Method	Result	Current Sample			Previous Sample	
Condition History			**Wear**	**Oil**	**Cont.**		
			C	C	N		
Lab ID				301407			
Bottle ID				1064852			
Date Sampled				09-May-15			
Oil Hours (Kms)				Not Given			
Unit Hours (Kms)				24271 kms			
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear		Coarse(large) Wear		
Iron	D-6595	PPM	11.1		0.1		
Chromium	D-6595	PPM	0.5		0.1		
Lead	D-6595	PPM	0.4		0.1		
Copper	D-6595	PPM	17.4 C		2.2		
Tin	D-6595	PPM	0.0		0.1		
Aluminum	D-6595	PPM	5.6		0.1		
Nickel	D-6595	PPM	0.0		0.1		
Silver	D-6595	PPM	0.0		0.1		
Molybdenum	D-6595	PPM	60.9		8.4		
Titanium	D-6595	PPM	0.0		0.1		
Oil Condition							
Viscosity @ 40°C	D-445	cSt	66.2				
Viscosity @ 100°C	D-445	cSt	11.2 C				
Oxidation	E-2412M	Abs	6.6				
Nitration	E-2412M	Abs	5.1 C				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	9.3				
Contamination							
Water	E-2412M	% (Wt.)	0.043				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.34				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	2				
Silicon	D-6595	PPM	14.6		0.1		
Additive Element							
Boron	D-6595	PPM	7				
Magnesium	D-6595	PPM	37				
Calcium	D-6595	PPM	3355				
Barium	D-6595	PPM	1				
Phosphorus	D-6595	PPM	762				
Zinc	D-6595	PPM	1206		158		
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		158				

Used oil properties of car number 13 (engine size 2,500 cc)



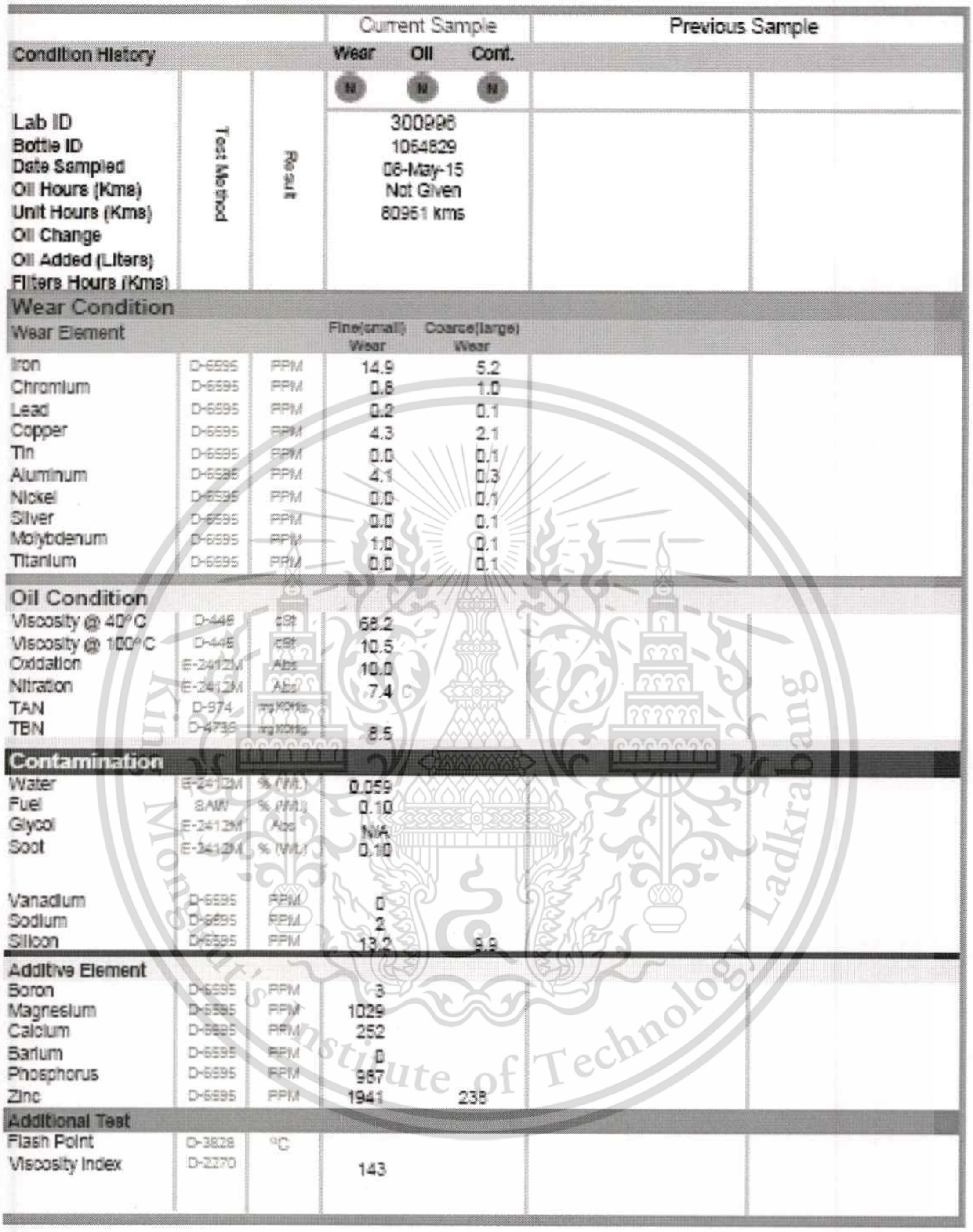
	Test Method	Result	Current Sample		Previous Sample	
Condition History			Wear Oil Cont.			
			C C N			
Lab ID			301408			
Bottle ID			1064653			
Date Sampled			09-May-15			
Oil Hours (Kms)			Not Given			
Unit Hours (Kms)			81296 kms			
Oil Change						
Oil Added (Liters)						
Filters Hours (Kms)						
Wear Condition						
Wear Element			Fine(small) Wear	Coarse(large) Wear		
Iron	D-6595	PPM	17.2	1.3		
Chromium	D-6595	PPM	0.2	0.1		
Lead	D-6595	PPM	2.7	0.1		
Copper	D-6595	PPM	4.6	0.6		
Tin	D-6595	PPM	0.0	0.1		
Aluminum	D-6595	PPM	13.6 C	0.6		
Nickel	D-6595	PPM	0.0	0.1		
Silver	D-6595	PPM	0.0	0.1		
Molybdenum	D-6595	PPM	65.9	7.7		
Titanium	D-6595	PPM	0.0	0.1		
Oil Condition						
Viscosity @ 40°C	D-445	cSt	67.1			
Viscosity @ 100°C	D-445	cSt	10.7 W			
Oxidation	E-2412M	Abs	7.8 C			
Nitration	E-2412M	Abs	6.0 W			
TAN	D-974	mgKOH/g				
TBN	D-4739	mgKOH/g	6.1			
Contamination						
Water	E-2412M	% (Vol.)	0.051			
Fuel	SAW	% (Vol.)	0.10			
Glycol	E-2412M	Abs	N/A			
Soot	E-2412M	% (Vol.)	0.40			
Vanadium	D-6595	PPM	0			
Sodium	D-6595	PPM	2			
Silicon	D-6595	PPM	11.7	1.6		
Additive Element						
Boron	D-6595	PPM	3			
Magnesium	D-6595	PPM	29			
Calcium	D-6595	PPM	3404			
Barium	D-6595	PPM	0			
Phosphorus	D-6595	PPM	819			
Zinc	D-6595	PPM	1264	141		
Additional Test						
Flash Point	D-3828	°C				
Viscosity Index	D-2270		150			

Used oil properties of car number 14 (engine size 3,000 cc)



			Current Sample			Previous Sample	
Condition History			Wear	Oil	Cont.		
	Test Method	Result	C	C	N		
Lab ID			300993				
Bottle ID			1064825				
Date Sampled			06-May-15				
Oil Hours (Kms)			Not Given				
Unit Hours (Kms)			33686 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear	Coarse(large) Wear			
Iron	D-6595	PPM	19.0	0.1			
Chromium	D-6595	PPM	1.3	0.1			
Lead	D-6595	PPM	0.0	0.1			
Copper	D-6595	PPM	28.0 W	5.7			
Tin	D-6595	PPM	0.0	0.0			
Aluminum	D-6595	PPM	4.1	0.1			
Nickel	D-6595	PPM	0.0	0.1			
Silver	D-6595	PPM	0.0	0.1			
Molybdenum	D-6595	PPM	65.0	5.1			
Titanium	D-6595	PPM	0.0	0.1			
Oil Condition							
Viscosity @ 40°C	D-445	cSt	73.0				
Viscosity @ 100°C	D-445	cSt	12.4 W				
Oxidation	E-2412M	Abs	13.7 C				
Nitration	E-2412M	Abs	7.9 C				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	5.3				
Contamination							
Water	E-2412M	% (Wt.)	0.045				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.06				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	1				
Silicon	D-6595	PPM	19.7	5.3			
Additive Element							
Boron	D-6595	PPM	1				
Magnesium	D-6595	PPM	15				
Calcium	D-6595	PPM	1952				
Barium	D-6595	PPM	1				
Phosphorus	D-6595	PPM	443				
Zinc	D-6595	PPM	1233	133			
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		169				

Used oil properties of car number 15 (engine size 3,000 cc)



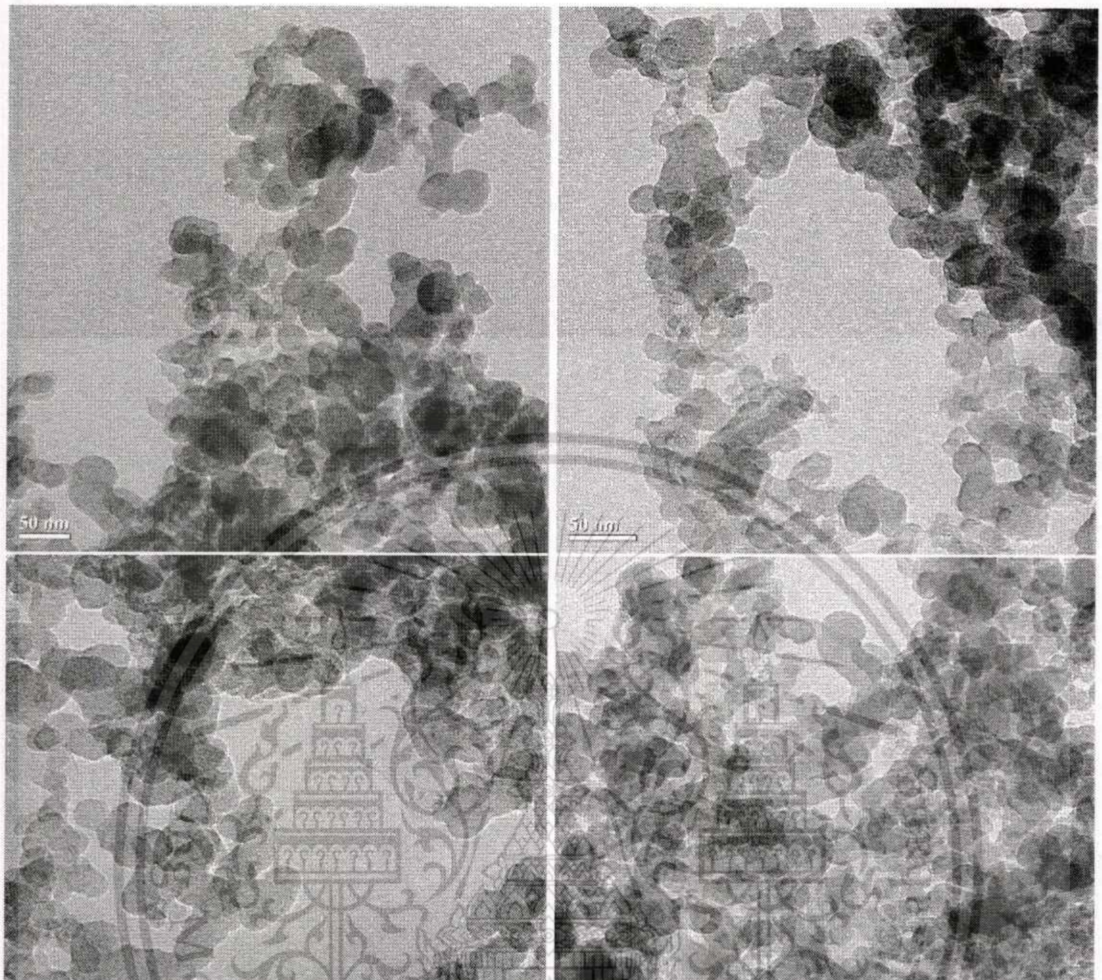
			Current Sample			Previous Sample	
Condition History			**Wear**	**Oil**	**Cont.**		
			N	N	N		
Lab ID	Test Method	Result	300996				
Bottle ID			1064829				
Date Sampled			06-May-15				
Oil Hours (Kms)			Not Given				
Unit Hours (Kms)			80951 kms				
Oil Change							
Oil Added (Liters)							
Filters Hours (Kms)							
Wear Condition							
Wear Element			Fine(small) Wear	Coarse(large) Wear			
Iron	D-6595	PPM	14.9	5.2			
Chromium	D-6595	PPM	0.6	1.0			
Lead	D-6595	PPM	0.2	0.1			
Copper	D-6595	PPM	4.3	2.1			
Tin	D-6595	PPM	0.0	0.1			
Aluminum	D-6595	PPM	4.1	0.3			
Nickel	D-6595	PPM	0.0	0.1			
Silver	D-6595	PPM	0.0	0.1			
Molybdenum	D-6595	PPM	1.0	0.1			
Titanium	D-6595	PPM	0.0	0.1			
Oil Condition							
Viscosity @ 40°C	D-445	cSt	68.2				
Viscosity @ 100°C	D-445	cSt	10.5				
Oxidation	E-2412M	Abs	10.0				
Nitration	E-2412M	Abs	7.4				
TAN	D-974	mg KOH/g					
TBN	D-4739	mg KOH/g	8.5				
Contamination							
Water	E-2412M	% (Wt.)	0.059				
Fuel	SAW	% (Wt.)	0.10				
Glycol	E-2412M	Abs	N/A				
Soot	E-2412M	% (Wt.)	0.10				
Vanadium	D-6595	PPM	0				
Sodium	D-6595	PPM	2				
Silicon	D-6595	PPM	13.2	9.9			
Additive Element							
Boron	D-6595	PPM	3				
Magnesium	D-6595	PPM	1029				
Calcium	D-6595	PPM	252				
Barium	D-6595	PPM	0				
Phosphorus	D-6595	PPM	967				
Zinc	D-6595	PPM	1941	238			
Additional Test							
Flash Point	D-3828	°C					
Viscosity Index	D-2270		143				

APPENDIX B

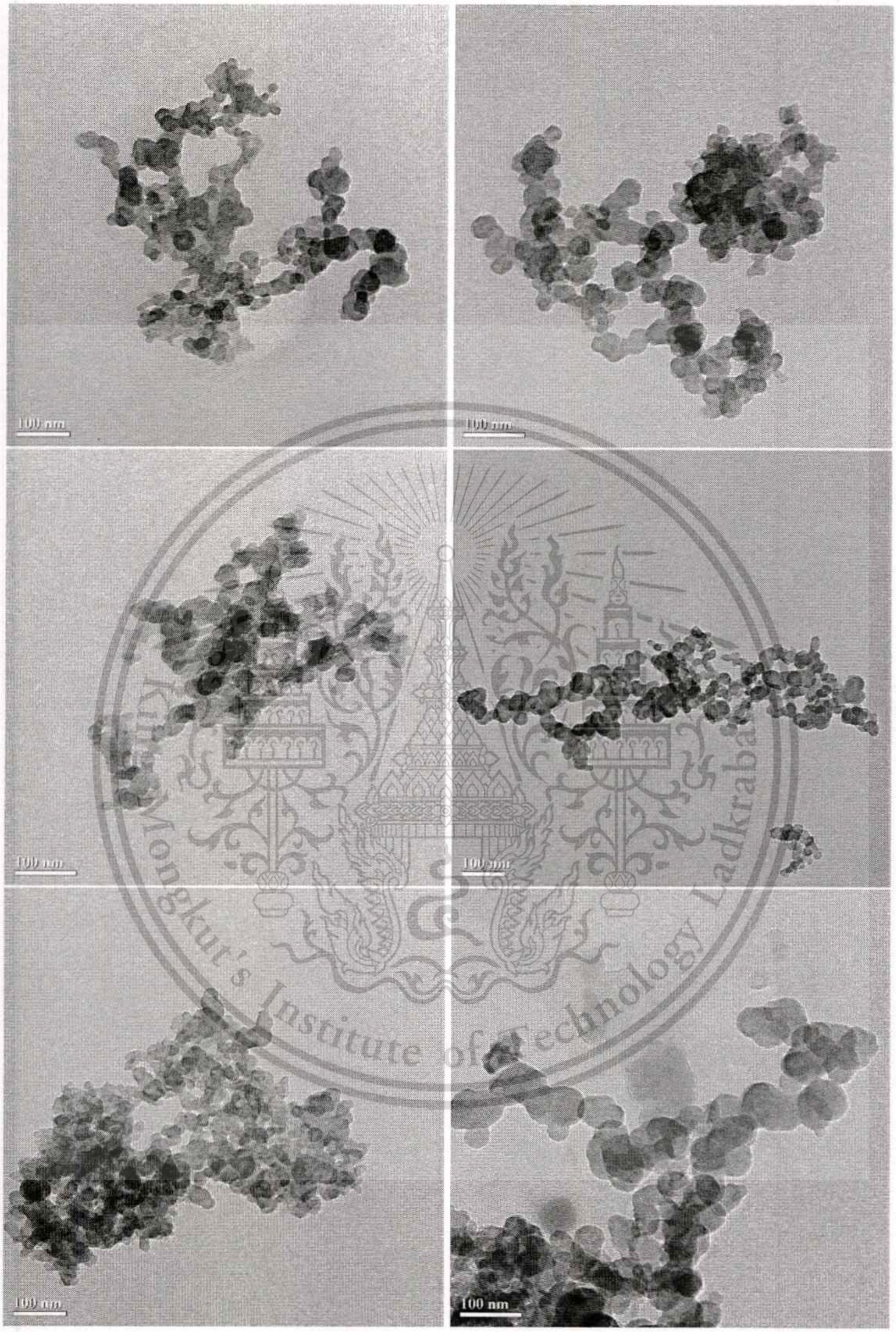
High Resolution Image of Diesel Engine Soot and Carbon Black analyzed by Transmission Electron Microscope (TEM)

*Remark: All images are in attached CD. This section shows some of example images.

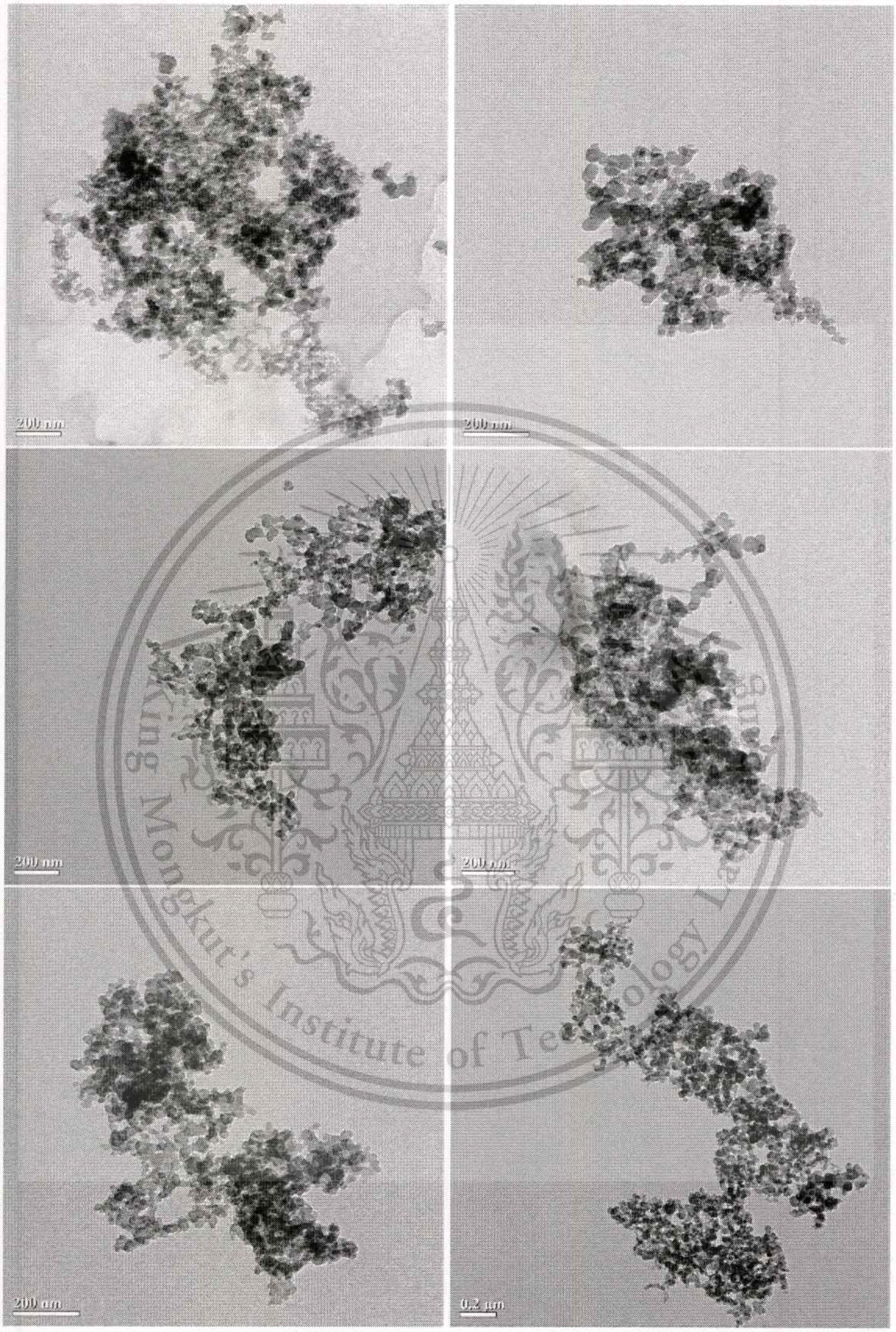
TEM image of diesel engine soot from exhaust pipe



Images captured at scale of 50 nanometers



Images captured at scale of 100 nanometers



Images captured at scale of 200 nanometers

TEM image of commercial carbon black

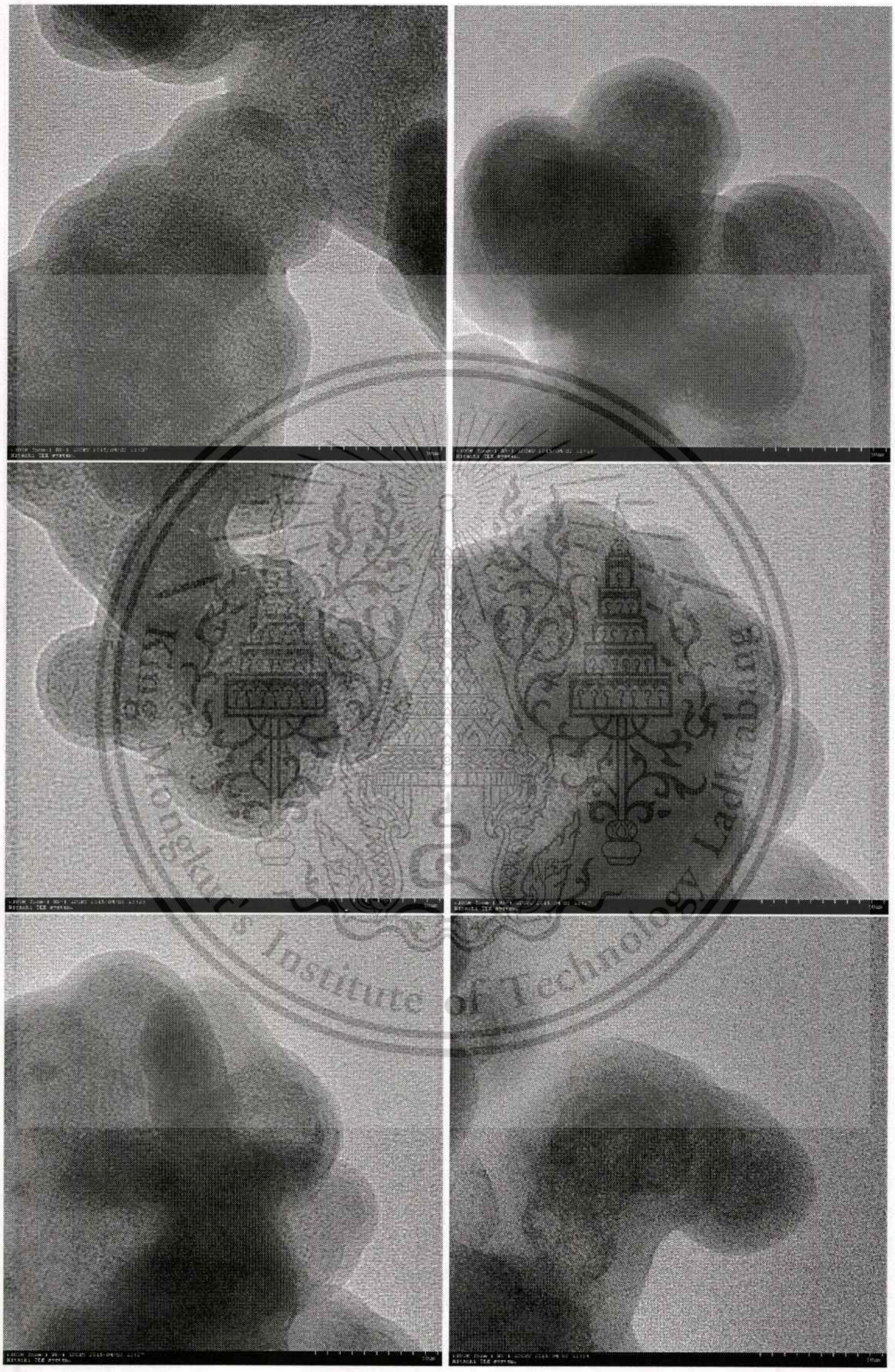


Image captured at magnification of 100,000x

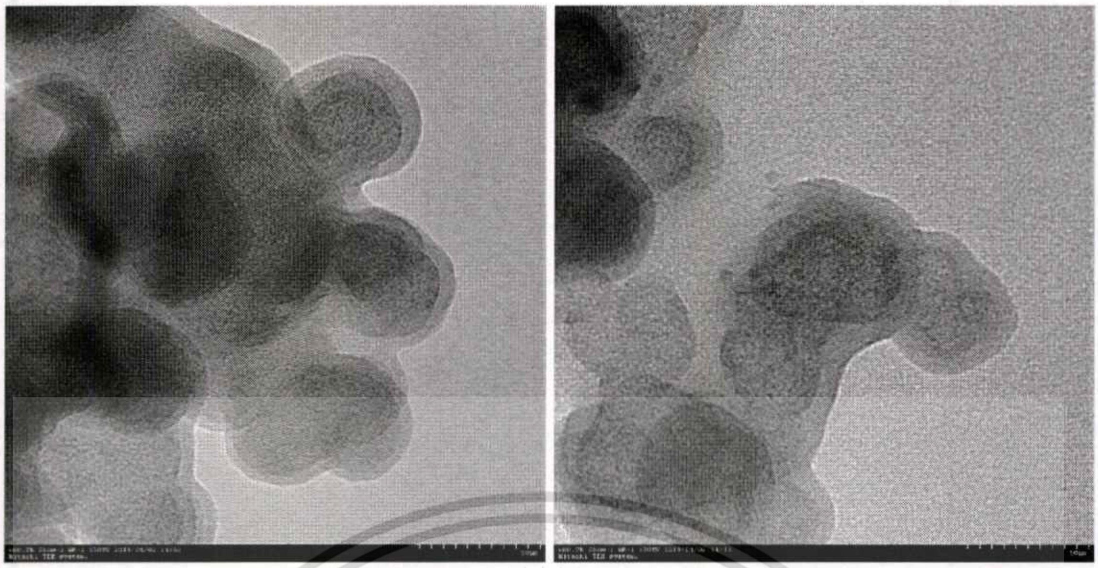


Image captured at magnification of 80,000x

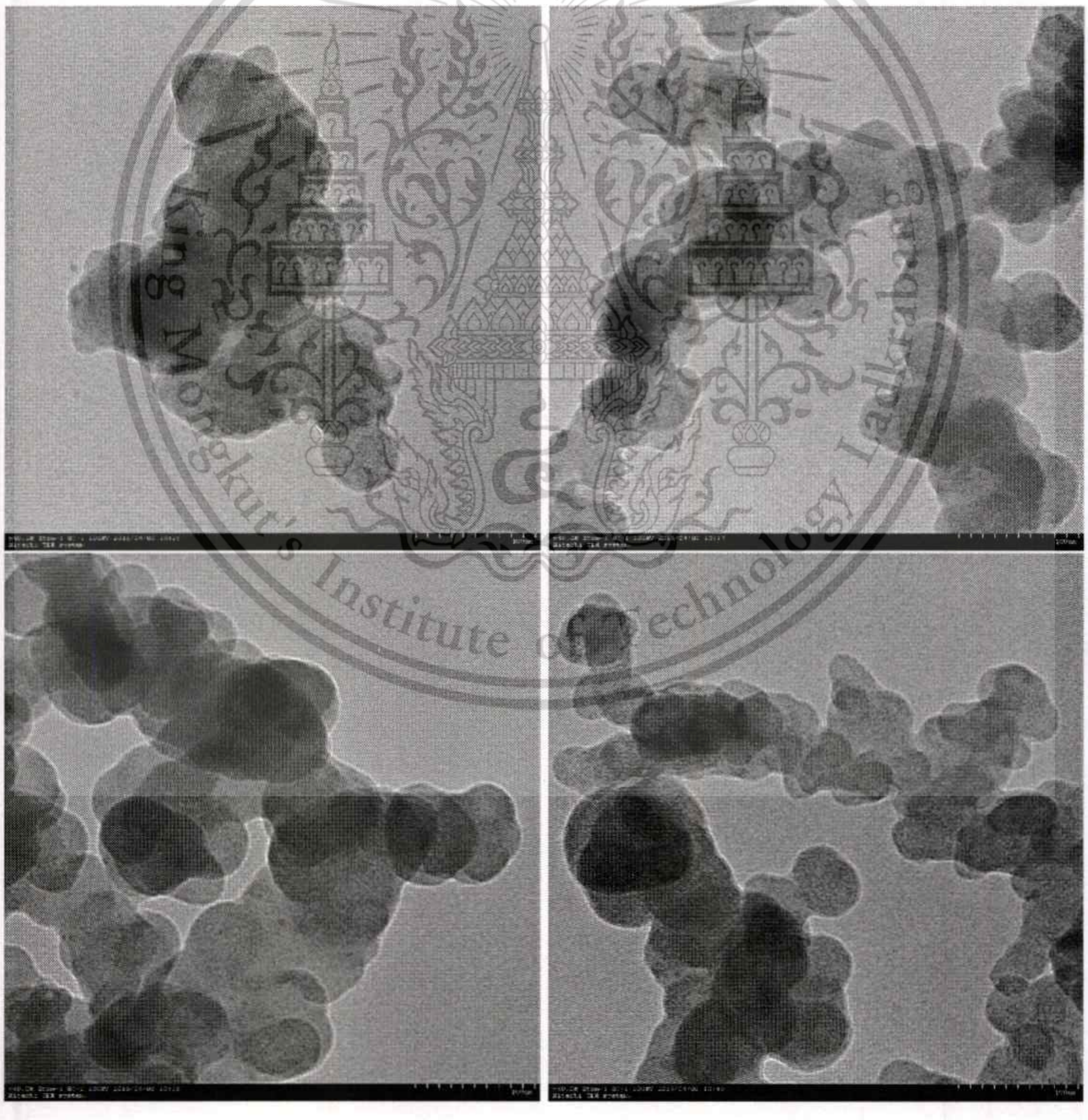


Image captured at magnification of 40,000x

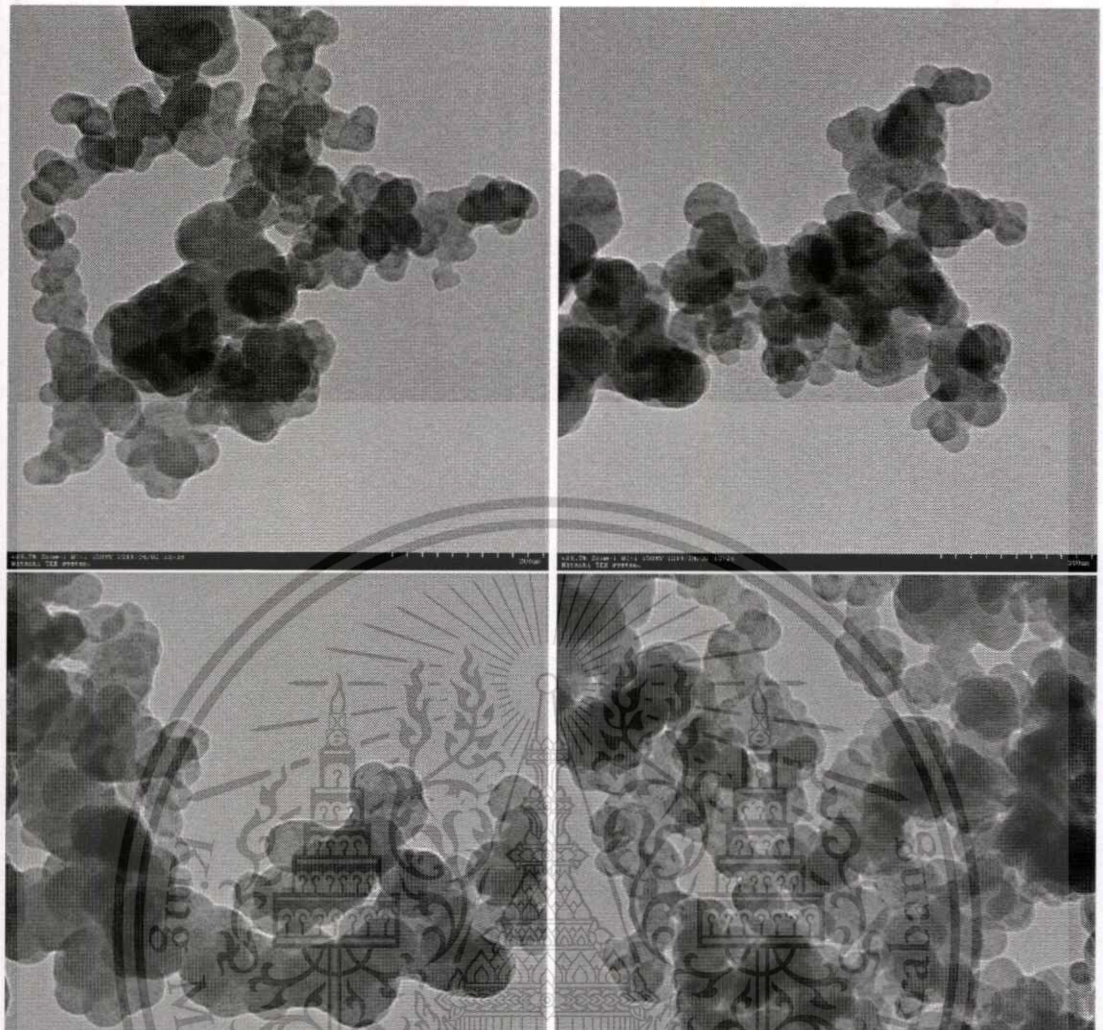


Image captured at magnification of 25,000x

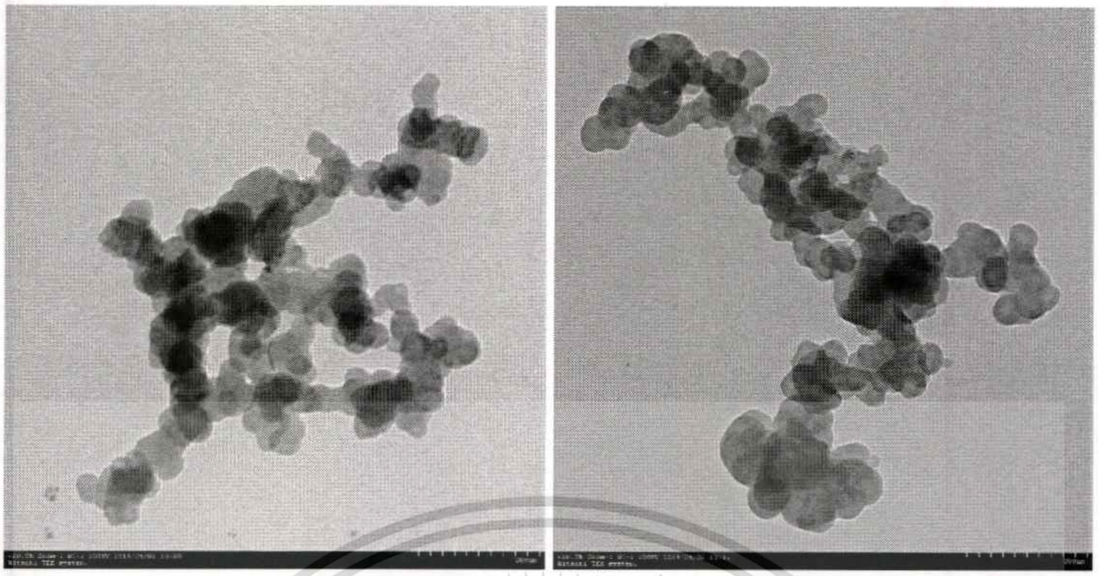


Image captured at magnification of 20,000x

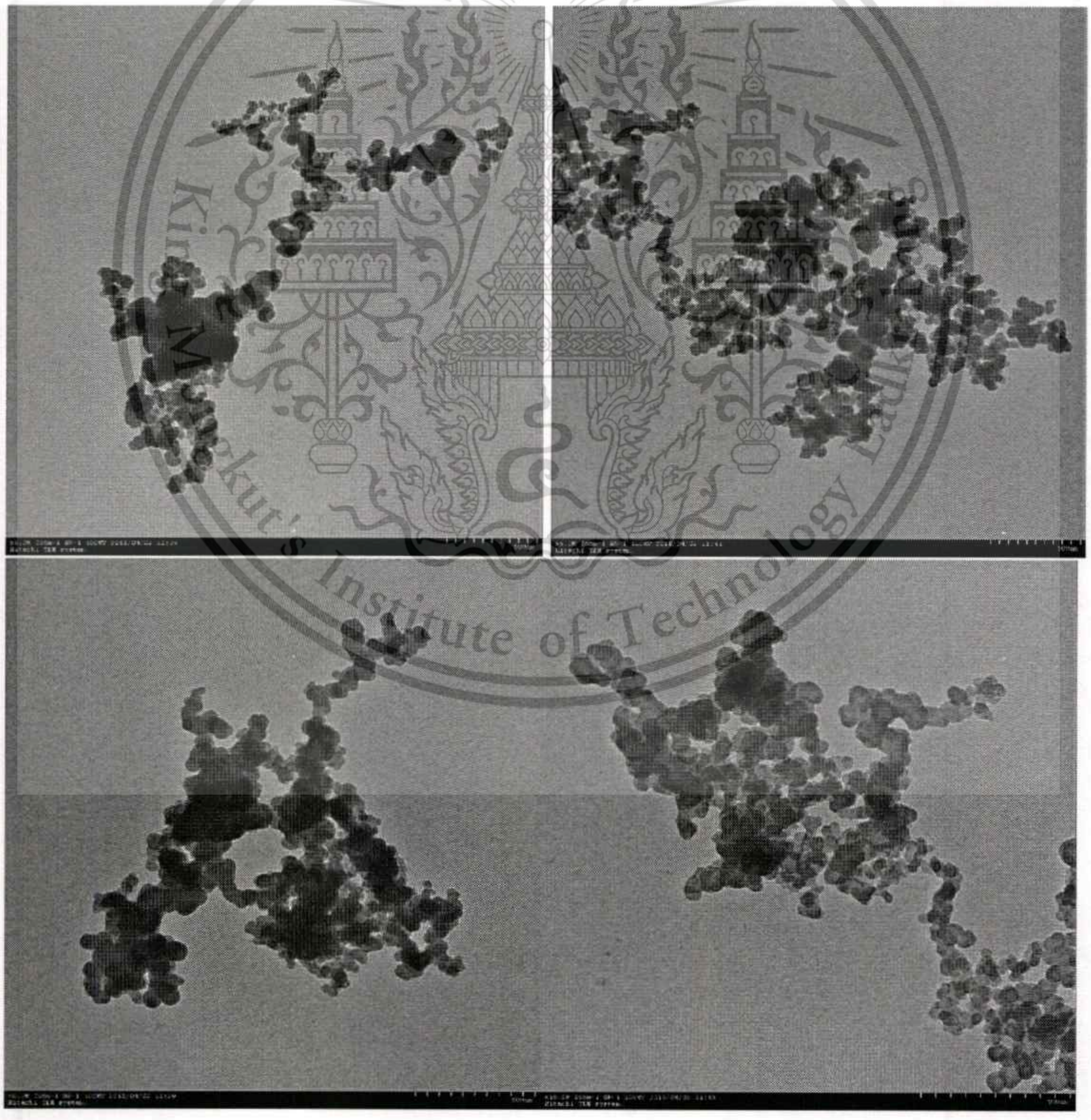


Image captured at magnification of 10,000x

APPENDIX C

Particle Size Distribution in Liquid Analyzed by Laser Diffraction Technique

Palm oil mixed carbon black 0.25% by weight

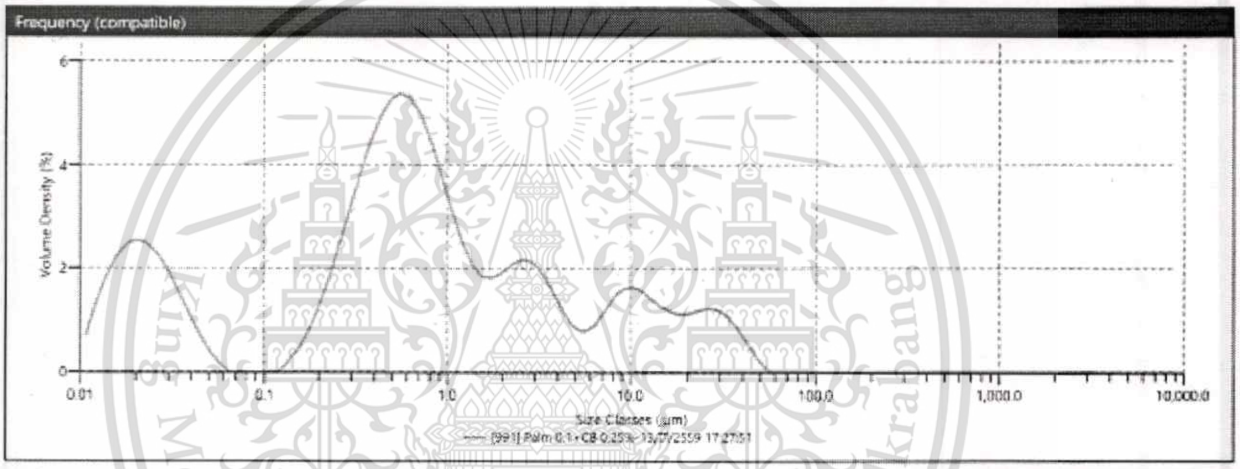
Sample Name Palm 0.1 + CB 0.25%
Measurement Date 13/7/2559
File Name 590507-9302

Instrument Type Mastersizer3000
Instrument Serial No. MAL1099267
Accessory Name Hydro MV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 16.96 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 3000 rpm
Particle Notes

Result Units Volume
Concentration 0.0008 %
Uniformity 5.220
Span 18.095
Specific Surface Area 29260 m²/kg
Weighted Residual 1.05 %
Dv (10) 0.0225 µm
Dv (50) 0.649 µm
Dv (90) 11.8 µm
D [4,3] 3.66 µm
D [3,2] 0.0976 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.57	0.0679	0.00	0.460	4.40	3.12	1.58	21.2	0.95	144	0.00	976	0.0
0.0114	1.09	0.0771	0.00	0.523	4.50	3.55	1.28	24.1	1.02	163	0.00	1110	0.0
0.0129	1.53	0.0876	0.00	0.594	4.41	4.03	0.95	27.4	1.01	186	0.00	1260	0.0
0.0147	1.86	0.0995	0.00	0.675	4.13	4.58	0.71	31.1	0.90	211	0.00	1430	0.0
0.0167	2.06	0.113	0.00	0.767	3.69	5.21	0.63	35.3	0.70	240	0.00	1630	0.0
0.0189	2.14	0.128	0.18	0.872	3.16	5.92	0.73	40.1	0.45	272	0.00	1850	0.0
0.0215	2.08	0.146	0.38	0.991	2.59	6.72	0.96	45.6	0.20	310	0.00	2100	0.0
0.0244	1.92	0.166	0.67	1.13	2.09	7.64	1.21	51.8	0.00	352	0.00	2390	0.0
0.0278	1.66	0.188	1.06	1.28	1.72	8.68	1.36	58.9	0.00	400	0.00	2710	0.0
0.0315	1.34	0.214	1.54	1.45	1.52	9.86	1.37	66.9	0.00	454	0.00	3080	0.0
0.0358	1.00	0.243	2.08	1.65	1.50	11.2	1.27	76.0	0.00	516	0.00	3500	
0.0407	0.66	0.276	2.65	1.88	1.61	12.7	1.12	86.4	0.00	586	0.00		
0.0463	0.37	0.314	3.21	2.13	1.75	14.5	0.99	98.1	0.00	666	0.00		
0.0526	0.16	0.357	3.72	2.42	1.82	16.4	0.92	111	0.00	756	0.00		
0.0597	0.00	0.405	4.13	2.75	1.77	18.7	0.92	127	0.00	859	0.00		

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590507-9302

Mastersizer - v3.40
Page 1 of 1

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Palm oil mixed carbon black 1.00% by weight

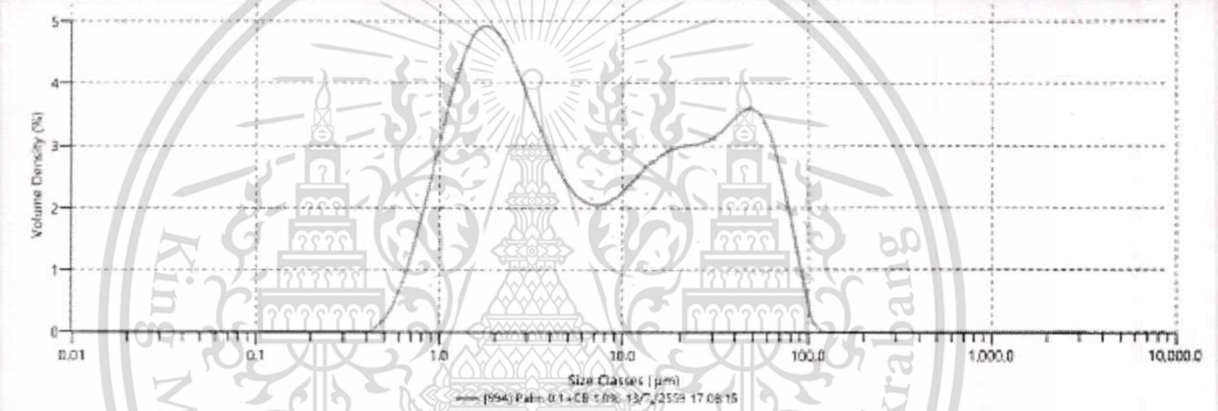
Sample Name	Palm 0.1+CB 1.0%
Measurement Date	13/7/2559
File Name	590507-9302

Instrument Type	Mastersizer3000
Instrument Serial No.	MAL1099267
Accessory Name	Hydro MV

Particle Name	Carbon black
Particle Refractive Index	1.840
Particle Absorption Index	3.000
Dispersant Name	n-Hexane
Dispersant Refractive Index	1.380
Analysis Model	General Purpose
Scattering Model	Mie
Laser Obscuration	25.35 %
Ultrasound Achieved	0 %
Stirrer Speed Achieved	2000 rpm
Particle Notes	

Result Units	Volume
Concentration	0.0093 %
Uniformity	2.588
Span	8.801
Specific Surface Area	930.1 m²/kg
Weighted Residual	1.27 %
Dv (10)	1.18 μm
Dv (50)	5.78 μm
Dv (90)	52.0 μm
D [4,3]	17.2 μm
D [3,2]	3.07 μm

Frequency (compatible)



Result

Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In
0.0100	0.00	0.0679	0.00	0.460	0.14	3.12	2.88	21.2	2.51	144	0.00	976	0.00
0.0114	0.00	0.0771	0.00	0.523	0.35	3.55	2.54	24.1	2.53	163	0.00	1110	0.00
0.0129	0.00	0.0876	0.00	0.594	0.67	4.03	2.25	27.4	2.57	186	0.00	1260	0.00
0.0147	0.00	0.0995	0.00	0.675	1.10	4.58	2.01	31.1	2.67	211	0.00	1430	0.00
0.0167	0.00	0.113	0.00	0.767	1.62	5.21	1.83	35.3	2.81	240	0.00	1630	0.00
0.0189	0.00	0.128	0.00	0.872	2.20	5.92	1.73	40.1	2.96	272	0.00	1850	0.00
0.0215	0.00	0.146	0.00	0.991	2.78	6.72	1.69	45.6	3.02	310	0.00	2100	0.00
0.0244	0.00	0.166	0.00	1.13	3.31	7.64	1.72	51.8	2.94	352	0.00	2390	0.00
0.0278	0.00	0.188	0.00	1.28	3.74	8.68	1.81	58.9	2.65	400	0.00	2710	0.00
0.0315	0.00	0.214	0.00	1.45	4.02	9.86	1.94	66.9	2.14	454	0.00	3080	0.00
0.0358	0.00	0.243	0.00	1.65	4.14	11.2	2.09	76.0	1.48	516	0.00	3500	
0.0407	0.00	0.276	0.00	1.88	4.08	12.7	2.23	86.4	0.79	586	0.00		
0.0463	0.00	0.314	0.00	2.13	3.88	14.5	2.36	98.1	0.10	666	0.00		
0.0526	0.00	0.357	0.00	2.42	3.58	16.4	2.44	111	0.00	756	0.00		
0.0597	0.00	0.405	0.00	2.75	3.23	18.7	2.49	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

590507-9302

Created: 10/5/2559
Printed: 15/7/2559 10:59

Lubricant A mixed carbon black 0.25% by weight

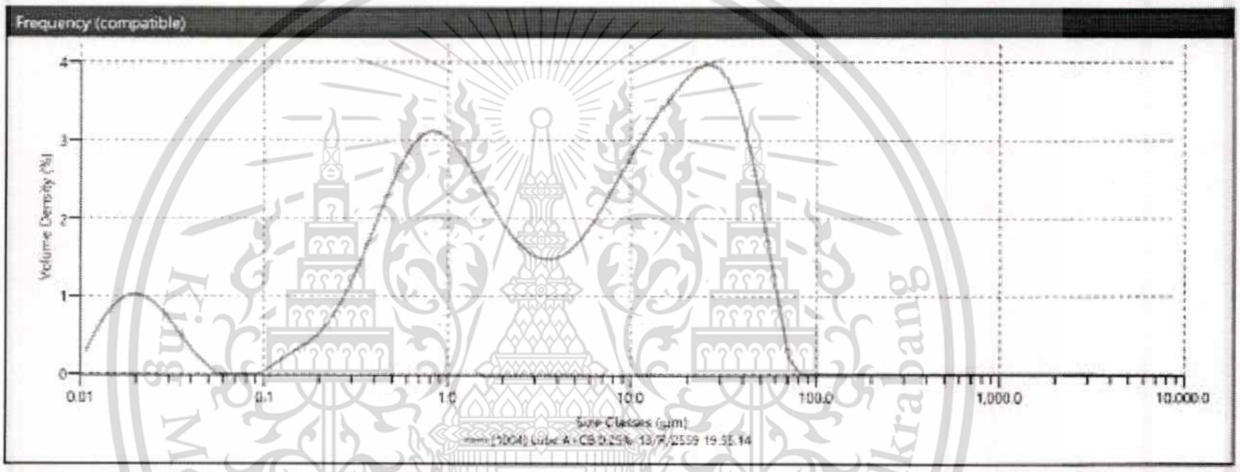
Sample Name Lube A+CB 0.25%
Measurement Date 13/7/2559
File Name 590507-9302

Instrument Type Mastersizer3000
Instrument Serial No. MAL1099267
Accessory Name Hydro MV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 22.82 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 2500 rpm
Particle Notes

Result Units Volume
Concentration 0.0023 %
Uniformity 2.350
Span 7.526
Specific Surface Area 12200 m²/kg
Weighted Residual 0.94 %
Dv (10) 0.280 µm
Dv (50) 4.58 µm
Dv (90) 34.7 µm
D [4,3] 11.9 µm
D [3,2] 0.234 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.24	0.0679	0.00	0.460	2.02	3.12	1.23	21.2	3.28	144	0.00	976	0.00
0.0114	0.46	0.0771	0.00	0.523	2.26	3.55	1.23	24.1	3.32	163	0.00	1110	0.00
0.0129	0.54	0.0876	0.00	0.594	2.44	4.03	1.28	27.4	3.29	186	0.00	1260	0.00
0.0147	0.77	0.0995	0.06	0.675	2.56	4.58	1.36	31.1	3.15	211	0.00	1430	0.00
0.0167	0.85	0.113	0.14	0.767	2.61	5.21	1.49	35.3	2.89	240	0.00	1630	0.00
0.0189	0.86	0.128	0.21	0.872	2.58	5.92	1.64	40.1	2.49	272	0.00	1850	0.00
0.0215	0.83	0.146	0.28	0.991	2.49	6.72	1.83	45.6	1.96	310	0.00	2100	0.00
0.0244	0.74	0.166	0.35	1.13	2.34	7.64	2.02	51.8	1.35	352	0.00	2390	0.00
0.0278	0.62	0.188	0.44	1.28	2.16	8.68	2.21	58.9	0.74	400	0.00	2710	0.00
0.0315	0.48	0.214	0.57	1.45	1.97	9.86	2.40	66.9	0.13	454	0.00	3080	0.00
0.0358	0.33	0.243	0.75	1.65	1.79	11.2	2.57	76.0	0.00	516	0.00	3500	
0.0407	0.20	0.276	0.96	1.88	1.62	12.7	2.74	86.4	0.00	586	0.00		
0.0463	0.09	0.314	1.21	2.13	1.47	14.5	2.90	98.1	0.00	666	0.00		
0.0526	0.00	0.357	1.48	2.42	1.36	16.4	3.05	111	0.00	756	0.00		
0.0597	0.00	0.405	1.76	2.75	1.28	18.7	3.16	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

590507-9302
Created: 10/5/2559
Printed: 15/7/2559 11:05

Lubricant A mixed carbon black 0.50% by weight

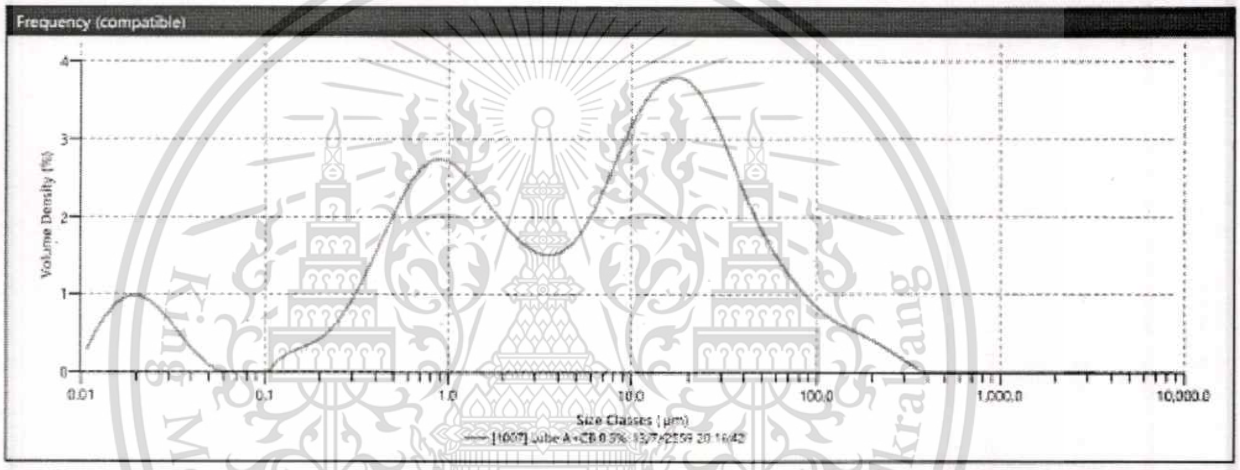
Sample Name	Lube A+CB 0.5%
Measurement Date	13/7/2559
File Name	590507-9302

Instrument Type	Mastersizer3000
Instrument Serial No.	MAL1099267
Accessory Name	Hydro MV

Particle Name	Carbon black
Particle Refractive Index	1.840
Particle Absorption Index	3.000
Dispersant Name	n-Hexane
Dispersant Refractive Index	1.380
Analysis Model	General Purpose
Scattering Model	Mie
Laser Obscuration	22.89 %
Ultrasound Achieved	0 %
Stirrer Speed Achieved	2500 rpm
Particle Notes	

Result Units	Volume
Concentration	0.0027 %
Uniformity	2.587
Span	6.989
Specific Surface Area	11440 m^2/kg
Weighted Residual	0.73 %
Dv (10)	0.326 µm
Dv (50)	6.77 µm
Dv (90)	47.6 µm
D [4,3]	19.1 µm
D [3,2]	0.250 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.23	0.0679	0.00	0.460	1.65	3.12	1.26	21.2	3.02	144	0.46	976	0.00
0.0114	0.44	0.0771	0.00	0.523	1.86	3.55	1.25	24.1	2.84	163	0.41	1110	0.00
0.0129	0.62	0.0875	0.00	0.594	2.06	4.03	1.30	27.4	2.61	186	0.36	1260	0.00
0.0147	0.74	0.0995	0.00	0.675	2.20	4.58	1.39	31.1	2.34	211	0.29	1430	0.00
0.0167	0.81	0.113	0.14	0.767	2.27	5.21	1.55	35.3	2.07	240	0.22	1630	0.00
0.0189	0.82	0.128	0.21	0.872	2.28	5.92	1.75	40.1	1.81	272	0.15	1850	0.00
0.0215	0.78	0.146	0.25	0.991	2.24	6.72	1.99	45.6	1.57	310	0.08	2100	0.00
0.0244	0.70	0.166	0.29	1.13	2.15	7.64	2.25	51.8	1.37	352	0.00	2390	0.00
0.0278	0.58	0.188	0.35	1.28	2.02	8.68	2.50	58.9	1.19	400	0.00	2710	0.00
0.0315	0.44	0.214	0.44	1.45	1.88	9.86	2.73	66.9	1.03	454	0.00	3080	0.00
0.0358	0.30	0.243	0.56	1.65	1.74	11.2	2.92	76.0	0.89	516	0.00	3500	
0.0407	0.17	0.276	0.74	1.88	1.60	12.7	3.06	86.4	0.77	586	0.00		
0.0463	0.08	0.314	0.94	2.13	1.48	14.5	3.15	98.1	0.66	666	0.00		
0.0526	0.00	0.357	1.17	2.42	1.37	16.4	3.17	111	0.58	756	0.00		
0.0597	0.00	0.405	1.41	2.75	1.30	18.7	3.13	127	0.51	859	0.00		

Lubricant A mixed carbon black 1.00% by weight

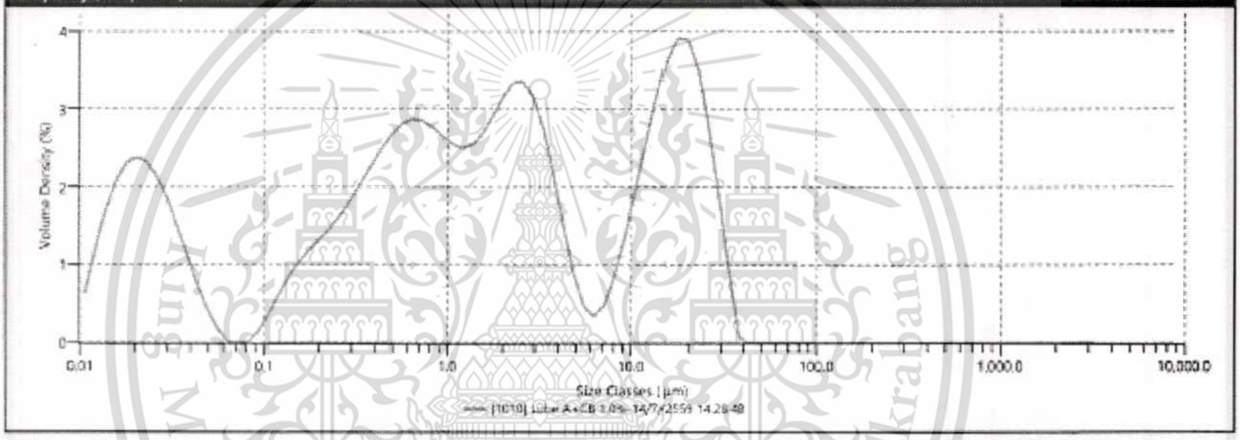
Sample Name Lube A+CB 1.0%
Measurement Date 14/7/2559
File Name 590507-9302

Instrument Type Mastersizer3000
Instrument Serial No. MAL1099267
Accessory Name Hydro MV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 24.19 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 2500 rpm
Particle Notes

Result Units Volume
Concentration 0.0014 %
Uniformity 3.939
Span 14.911
Specific Surface Area 27030 m²/kg
Weighted Residual 2.01 %
Dv (10) 0.0236 µm
Dv (50) 1.30 µm
Dv (90) 19.4 µm
D [4,3] 5.49 µm
D [3,2] 0.106 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.53	0.0679	0.00	0.460	2.23	3.12	2.31	21.2	2.96	144	0.00	976	0.00
0.0114	1.01	0.0771	0.00	0.523	2.34	3.55	1.81	24.1	2.35	163	0.00	1110	0.00
0.0129	1.42	0.0876	0.12	0.594	2.40	4.03	1.24	27.4	1.57	186	0.00	1260	0.00
0.0147	1.73	0.0995	0.30	0.675	2.39	4.58	0.72	31.1	0.79	211	0.00	1430	0.00
0.0167	1.92	0.113	0.52	0.767	2.32	5.21	0.37	35.3	0.01	240	0.00	1630	0.00
0.0189	1.99	0.128	0.72	0.872	2.22	5.92	0.26	40.1	0.00	272	0.00	1850	0.00
0.0215	1.95	0.146	0.87	0.991	2.13	6.72	0.39	45.6	0.00	310	0.00	2100	0.00
0.0244	1.80	0.166	0.99	1.13	2.08	7.64	0.71	51.8	0.00	352	0.00	2390	0.00
0.0276	1.56	0.188	1.10	1.28	2.11	8.68	1.14	58.9	0.00	400	0.00	2710	0.00
0.0315	1.27	0.214	1.22	1.45	2.23	9.86	1.62	66.9	0.00	454	0.00	3080	0.00
0.0358	0.94	0.243	1.36	1.65	2.42	11.2	2.12	76.0	0.00	516	0.00	3500	
0.0407	0.63	0.276	1.52	1.88	2.63	12.7	2.62	86.4	0.00	586	0.00		
0.0463	0.35	0.314	1.70	2.13	2.79	14.5	3.04	98.1	0.00	666	0.00		
0.0526	0.15	0.357	1.89	2.42	2.81	16.4	3.29	111	0.00	756	0.00		
0.0597	0.00	0.405	2.07	2.75	2.65	18.7	3.27	127	0.00	859	0.00		

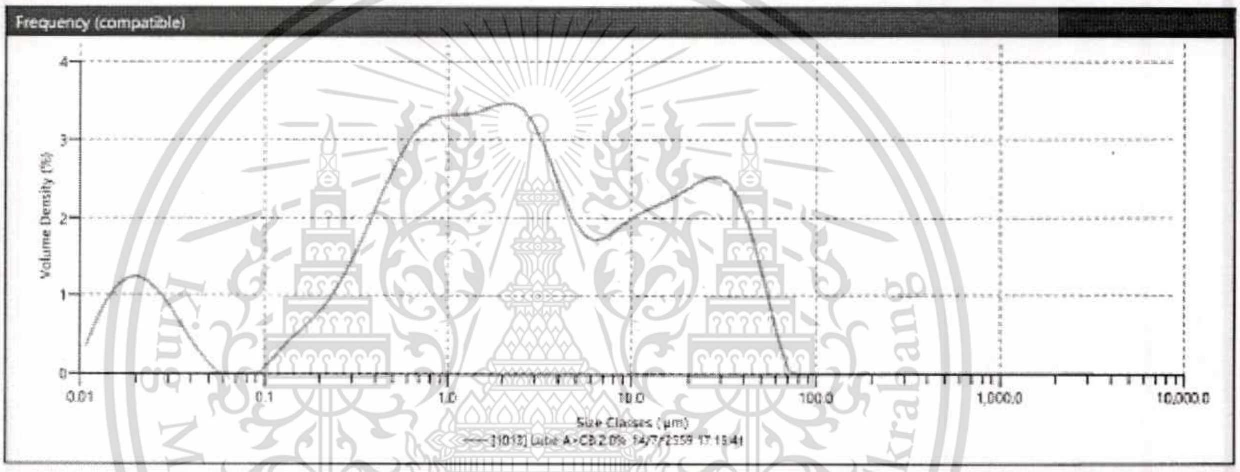
Lubricant A mixed carbon black 2.00% by weight

Sample Name	Lube A+CB 2.0%
Measurement Date	14/7/2559
File Name	590507-9302

Instrument Type	Mastersizer3000
Instrument Serial No.	MAL1099267
Accessory Name	Hydro MV

Particle Name	Carbon black
Particle Refractive Index	1.840
Particle Absorption Index	3.000
Dispersant Name	n-Hexane
Dispersant Refractive Index	1.380
Analysis Model	General Purpose
Scattering Model	Mie
Laser Obscuration	24.54 %
Ultrasound Achieved	0 %
Stirrer Speed Achieved	2500 rpm
Particle Notes	

Result Units	Volume
Concentration	0.0021 %
Uniformity	3.556
Span	13.218
Specific Surface Area	14760 m^2/kg
Weighted Residual	0.89 %
Dv (10)	0.175 µm
Dv (50)	2.05 µm
Dv (90)	27.3 µm
D [4,3]	8.04 µm
D [3,2]	0.194 µm



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.29	0.0679	0.00	0.460	2.14	3.12	2.46	21.2	2.05	144	0.00	976	0.00
0.0114	0.55	0.0771	0.00	0.523	2.36	3.55	2.18	24.1	2.10	163	0.00	1110	0.00
0.0129	0.76	0.0876	0.00	0.594	2.53	4.03	1.89	27.4	2.11	186	0.00	1260	0.00
0.0147	0.92	0.0995	0.12	0.675	2.65	4.58	1.64	31.1	2.04	211	0.00	1430	0.00
0.0167	1.01	0.113	0.24	0.767	2.72	5.21	1.48	35.3	1.85	240	0.00	1630	0.00
0.0189	1.04	0.128	0.35	0.872	2.76	5.92	1.41	40.1	1.59	272	0.00	1850	0.00
0.0215	1.00	0.146	0.45	0.991	2.76	6.72	1.44	45.6	1.21	310	0.00	2100	0.00
0.0244	0.90	0.166	0.54	1.13	2.76	7.64	1.53	51.8	0.77	352	0.00	2390	0.00
0.0278	0.76	0.188	0.65	1.28	2.77	8.68	1.62	58.9	0.33	400	0.00	2710	0.00
0.0315	0.59	0.214	0.79	1.45	2.81	9.86	1.69	66.9	0.00	454	0.00	3080	0.00
0.0358	0.42	0.243	0.97	1.65	2.85	11.2	1.75	76.0	0.00	516	0.00	3500	
0.0407	0.26	0.276	1.17	1.88	2.89	12.7	1.80	86.4	0.00	586	0.00		
0.0463	0.12	0.314	1.40	2.13	2.89	14.5	1.85	98.1	0.00	666	0.00		
0.0526	0.00	0.357	1.65	2.42	2.83	16.4	1.91	111	0.00	756	0.00		
0.0597	0.00	0.405	1.90	2.75	2.68	18.7	1.98	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

590507-9302

Created: 10/5/2559
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Lubricant B mixed carbon black 0.25% by weight

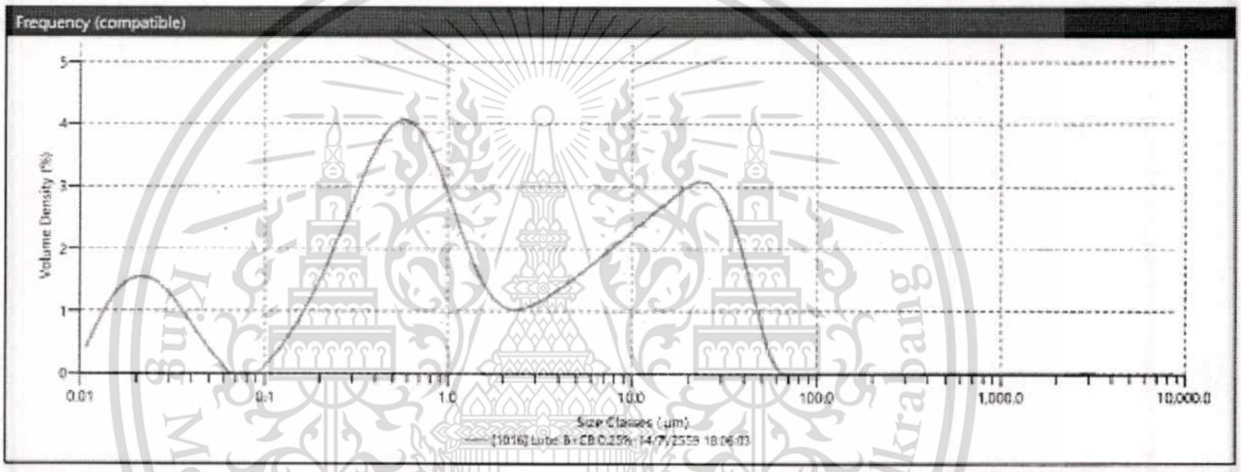
Sample Name	Lube B+CB 0.25%
Measurement Date	14/7/2559
File Name	590507-9302

Instrument Type	Mastersizer3000
Instrument Serial No.	MAL1099267
Accessory Name	Hydro MV

Particle Name	Carbon black
Particle Refractive Index	1.840
Particle Absorption Index	3.000
Dispersant Name	n-Hexane
Dispersant Refractive Index	1.380
Analysis Model	General Purpose
Scattering Model	Mie
Laser Obscuration	20.30 %
Ultrasound Achieved	0 %
Stirrer Speed Achieved	2000 rpm
Particle Notes	

Result Units	Volume
Concentration	0.0012 %
Uniformity	6.805
Span	24.283
Specific Surface Area	19070 m²/kg
Weighted Residual	1.31 %
Dv (10)	0.0360 µm
Dv (50)	1.05 µm
Dv (90)	25.6 µm
D [4,3]	7.56 µm
D [3,2]	0.150 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.32	0.0679	0.00	0.460	3.31	3.12	0.99	21.2	2.58	144	0.00	976	0.00
0.0114	0.62	0.0771	0.00	0.523	3.40	3.55	1.07	24.1	2.56	163	0.00	1110	0.00
0.0129	0.88	0.0876	0.00	0.594	3.38	4.03	1.17	27.4	2.44	186	0.00	1260	0.00
0.0147	1.09	0.0995	0.16	0.675	3.24	4.58	1.27	31.1	2.18	211	0.00	1430	0.00
0.0167	1.22	0.113	0.32	0.767	2.99	5.21	1.38	35.3	1.79	240	0.00	1630	0.00
0.0189	1.29	0.128	0.51	0.872	2.69	5.92	1.49	40.1	1.28	272	0.00	1850	0.00
0.0215	1.29	0.146	0.73	0.991	2.26	6.72	1.60	45.6	0.75	310	0.00	2100	0.00
0.0244	1.22	0.166	0.97	1.13	1.86	7.64	1.72	51.8	0.21	352	0.00	2390	0.00
0.0278	1.10	0.188	1.25	1.28	1.50	8.68	1.83	58.9	0.00	400	0.00	2710	0.00
0.0315	0.93	0.214	1.56	1.45	1.21	9.86	1.94	66.9	0.00	454	0.00	3080	0.00
0.0358	0.74	0.243	1.89	1.65	1.00	11.2	2.06	76.0	0.00	516	0.00	3500	
0.0407	0.54	0.276	2.23	1.88	0.89	12.7	2.18	86.4	0.00	586	0.00		
0.0463	0.34	0.314	2.56	2.13	0.85	14.5	2.30	98.1	0.00	666	0.00		
0.0526	0.18	0.357	2.87	2.42	0.86	16.4	2.42	111	0.00	756	0.00		
0.0597	0.00	0.405	3.13	2.75	0.92	18.7	2.52	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

590507-9302

Created: 10/5/2559
Printed: 15/7/2559 11:13

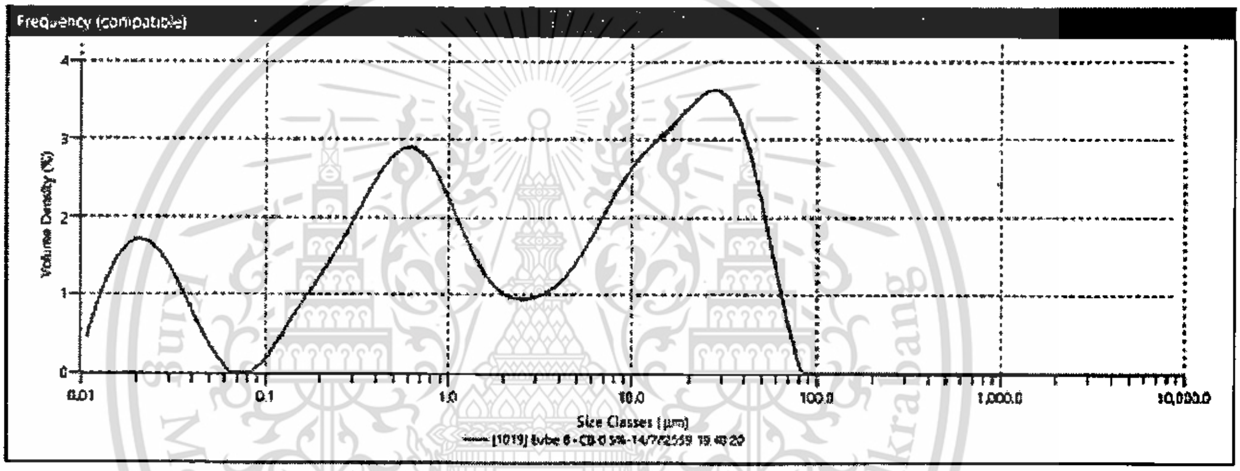
Lubricant B mixed carbon black 0.50% by weight

Sample Name Lube B+CB 0.5%
Measurement Date 14/7/2559
File Name 590507-9302

Instrument Type Mastersizer3000
Instrument Serial No. MAL1099267
Accessory Name Hydro MV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 22.34 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 3000 rpm
Particle Notes

Result Units Volume
Concentration 0.0015 %
Uniformity 3.633
Span 11.782
Specific Surface Area 20120 m²/kg
Weighted Residual 0.88 %
Dv (10) 0.0313 µm
Dv (50) 2.98 µm
Dv (90) 35.1 µm
D [4,3] 11.4 µm
D [3,2] 0.142 µm



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.37	0.0679	0.00	0.460	2.32	3.12	0.84	21.2	2.95	144	0.00	976	0.0
0.0114	0.72	0.0771	0.00	0.523	2.41	3.55	0.91	24.1	3.03	163	0.00	1110	0.0
0.0129	1.01	0.0876	0.07	0.594	2.42	4.03	1.01	27.4	3.04	186	0.00	1260	0.0
0.0147	1.23	0.0995	0.21	0.675	2.36	4.58	1.16	31.1	2.95	211	0.00	1430	0.0
0.0167	1.38	0.113	0.38	0.767	2.23	5.21	1.33	35.3	2.73	240	0.00	1630	0.0
0.0189	1.44	0.128	0.56	0.872	2.02	5.92	1.53	40.1	2.39	272	0.00	1850	0.0
0.0215	1.42	0.145	0.72	0.991	1.77	6.72	1.74	45.6	1.94	310	0.00	2100	0.0
0.0244	1.32	0.165	0.85	1.13	1.51	7.64	1.94	51.8	1.43	352	0.00	2390	0.0
0.0278	1.17	0.188	1.03	1.28	1.27	8.68	2.11	58.9	0.91	400	0.00	2710	0.0
0.0315	0.97	0.214	1.21	1.45	1.07	9.86	2.26	66.9	0.45	454	0.00	3080	0.0
0.0358	0.74	0.243	1.39	1.65	0.93	11.2	2.38	76.0	0.04	516	0.00	3500	
0.0407	0.51	0.276	1.59	1.88	0.84	12.7	2.49	86.4	0.00	586	0.00		
0.0463	0.31	0.314	1.80	2.13	0.80	14.5	2.60	98.1	0.00	666	0.00		
0.0525	0.15	0.357	2.00	2.42	0.79	16.4	2.72	111	0.00	756	0.00		
0.0597	0.00	0.405	2.18	2.75	0.80	18.7	2.84	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

590507-9302
Created: 10/5/2559
Printed: 15/7/2559 11.13

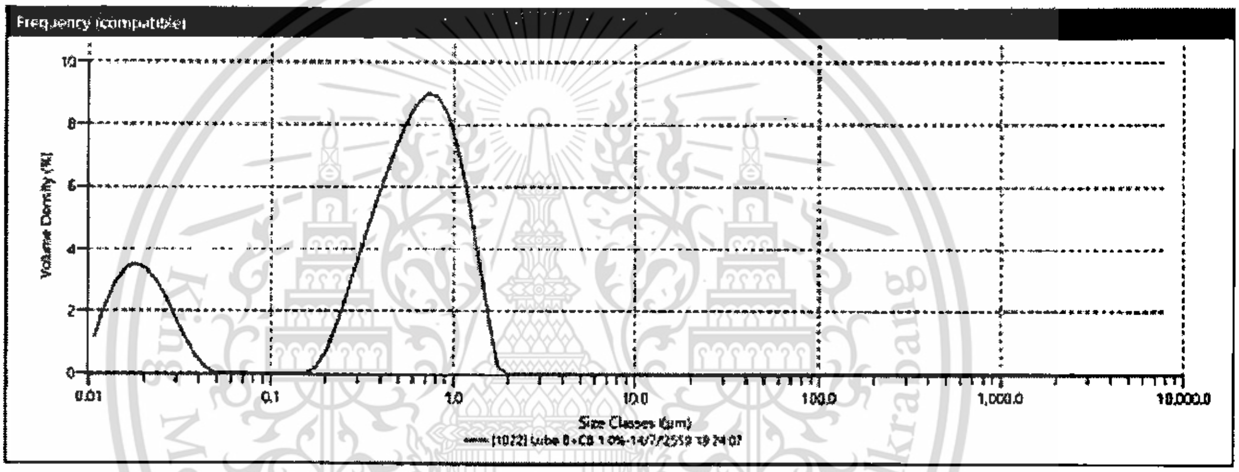
Lubricant B mixed carbon black 1.00% by weight

Sample Name Lube B+CB 1.0%
Measurement Date 14/7/2559
File Name 590507-9302

Instrument Type Mastersizer3000
Instrument Serial No. MAL1098267
Accessory Name Hydro MV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 10.70 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 3000 rpm
Particle Notes

Result Units Volume
Concentration 0.0004 %
Uniformity 0.611
Span 2.033
Specific Surface Area 37540 m²/kg
Weighted Residual 2.20 %
Dv (10) 0.0183 μm
Dv (50) 0.541 μm
Dv (90) 1.12 μm
D [4,3] 0.562 μm
D [3,2] 0.0761 μm



Result

Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In
0.0100	0.83	0.0679	0.00	0.460	6.13	3.12	0.00	21.2	0.00	144	0.00	976	0.0
0.0114	1.76	0.0771	0.00	0.523	6.75	3.55	0.00	24.1	0.00	163	0.00	1110	0.0
0.0129	2.39	0.0876	0.00	0.594	7.24	4.03	0.00	27.4	0.00	186	0.00	1260	0.0
0.0147	2.79	0.0995	0.00	0.675	7.51	4.58	0.00	31.1	0.00	211	0.00	1430	0.0
0.0167	2.94	0.113	0.00	0.767	7.46	5.21	0.00	35.3	0.00	240	0.00	1630	0.0
0.0189	2.84	0.128	0.00	0.872	7.01	5.92	0.00	40.1	0.00	272	0.00	1850	0.0
0.0215	2.53	0.146	0.00	0.991	6.10	6.72	0.00	45.6	0.00	310	0.00	2100	0.0
0.0244	2.06	0.166	0.14	1.13	4.77	7.64	0.00	51.8	0.00	352	0.00	2390	0.0
0.0278	1.51	0.188	0.56	1.28	3.20	8.68	0.00	58.9	0.00	400	0.00	2710	0.0
0.0315	0.95	0.214	1.24	1.45	1.63	9.86	0.00	66.9	0.00	454	0.00	3080	0.0
0.0358	0.47	0.243	2.05	1.65	0.05	11.2	0.00	76.0	0.00	516	0.00	3500	
0.0407	0.14	0.276	2.95	1.88	0.00	12.7	0.00	86.4	0.00	586	0.00		
0.0463	0.00	0.314	3.80	2.13	0.00	14.5	0.00	98.1	0.00	666	0.00		
0.0526	0.00	0.357	4.63	2.42	0.00	16.4	0.00	111	0.00	756	0.00		
0.0597	0.00	0.405	5.41	2.75	0.00	18.7	0.00	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

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Lubricant B mixed carbon black 2.00% by weight

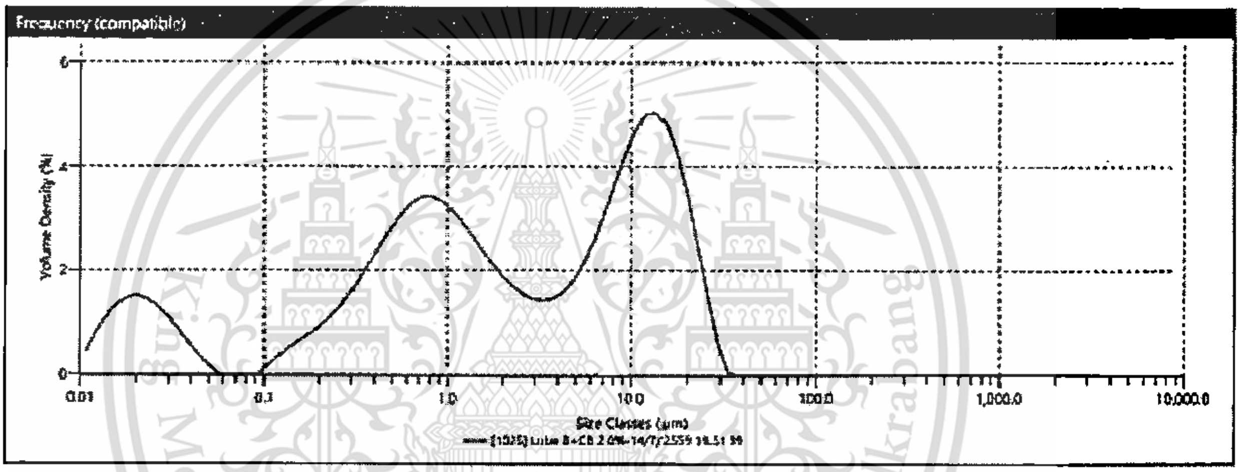
Sample Name Lube B+CB 2.0%
Measurement Date 14/7/2559
File Name 590507-9302

Instrument Type Mastersizer3000
Instrument Serial No. MAL1093267
Accessory Name Hydro MV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.390
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 17.14 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 2000 rpm
Particle Notes

Result Units Volume
Concentration 0.0812 %
Uniformity 2.689
Span 8.460
Specific Surface Area 17620 m²/kg
Weighted Residual 1.17 %
Dv (10) 0.0399 µm
Dv (50) 1.96 µm
Dv (90) 16.6 µm
D [4,3] 5.90 µm
D [3,2] 0.162 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.35	0.0679	0.00	0.460	2.36	3.12	1.19	21.2	2.11	144	0.00	976	0.0
0.0114	0.66	0.0771	0.00	0.523	2.58	3.55	1.22	24.1	1.25	163	0.00	1110	0.0
0.0129	0.93	0.0876	0.00	0.594	2.75	4.03	1.32	27.4	0.46	186	0.00	1260	0.0
0.0147	1.12	0.0995	0.15	0.675	2.85	4.58	1.51	31.1	0.00	211	0.00	1430	0.0
0.0167	1.23	0.113	0.29	0.767	2.87	5.21	1.79	35.3	0.00	240	0.00	1630	0.0
0.0189	1.27	0.128	0.43	0.872	2.80	5.92	2.16	40.1	0.00	272	0.00	1850	0.0
0.0215	1.22	0.146	0.54	0.991	2.65	6.72	2.59	45.6	0.00	310	0.00	2100	0.0
0.0244	1.11	0.166	0.64	1.13	2.46	7.64	3.07	51.8	0.00	352	0.00	2390	0.0
0.0278	0.94	0.188	0.75	1.28	2.23	8.68	3.53	58.9	0.00	400	0.00	2710	0.0
0.0315	0.74	0.214	0.90	1.45	2.00	9.86	3.92	66.9	0.00	454	0.00	3080	0.0
0.0358	0.53	0.243	1.09	1.65	1.76	11.2	4.17	76.0	0.00	516	0.00	3500	
0.0407	0.33	0.276	1.30	1.88	1.56	12.7	4.22	86.4	0.00	586	0.00		
0.0463	0.16	0.314	1.55	2.13	1.42	14.5	4.03	98.1	0.00	666	0.00		
0.0526	0.00	0.357	1.82	2.42	1.29	16.4	3.58	111	0.00	756	0.00		
0.0597	0.00	0.405	2.09	2.75	1.21	18.7	2.82	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

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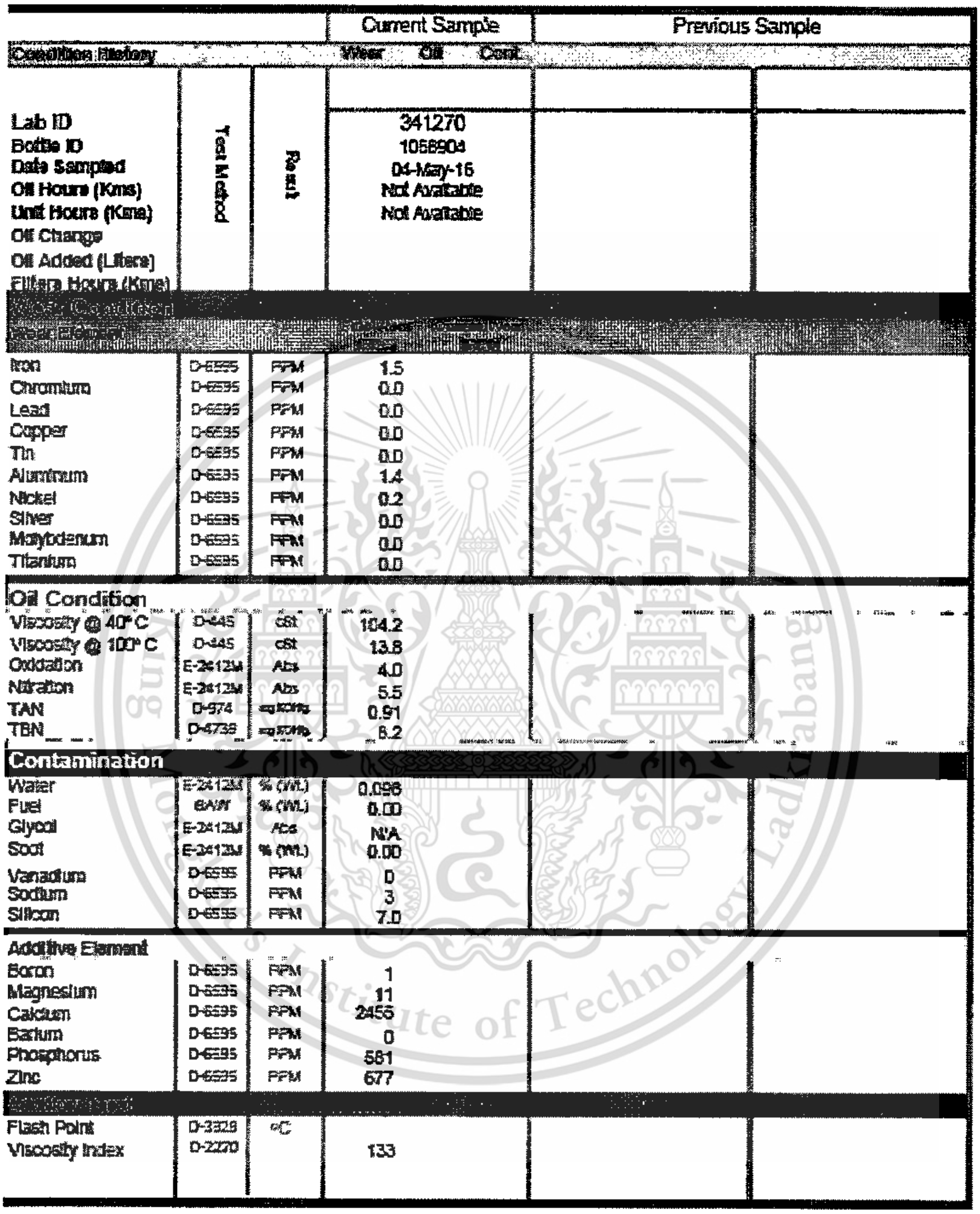
APPENDIX D

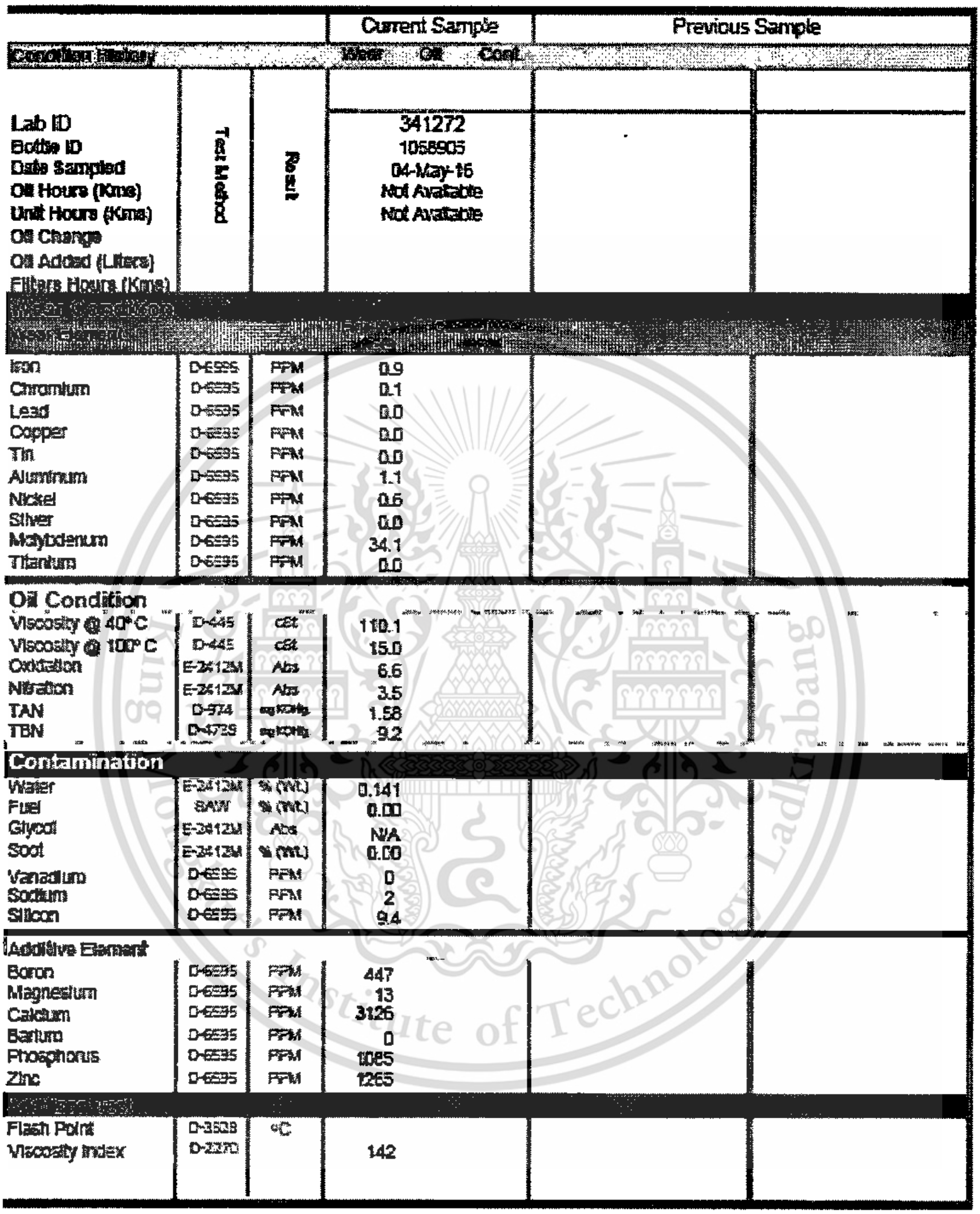
Physical and Chemical Oil Properties Reports of New Formulated Oils

Oil properties of lubricant A



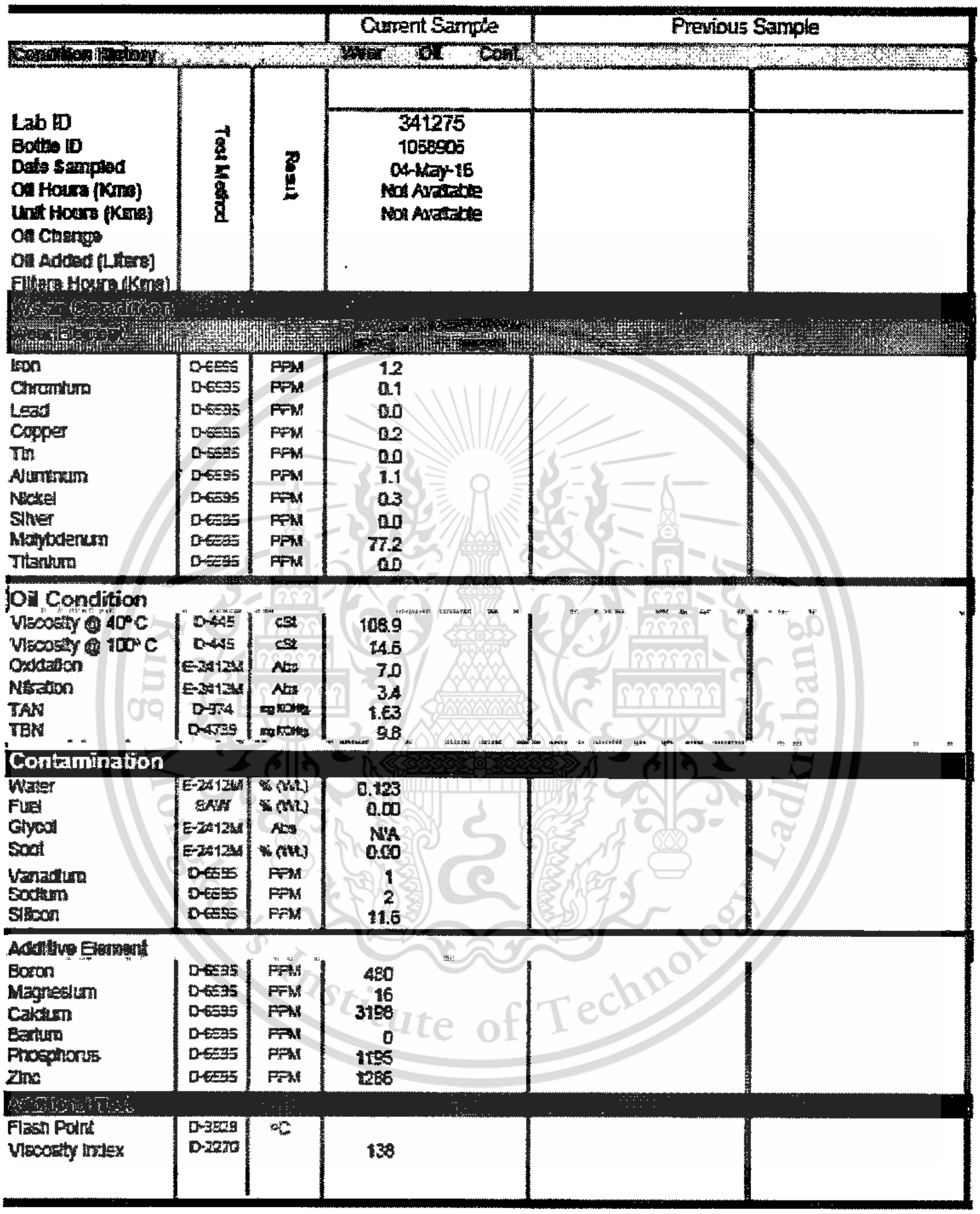
			Current Sample	Previous Sample	
Condition History			Wear Oil Cont.		
	Test Method	Result			
Lab ID			341270		
Bottle ID			1058904		
Date Sampled			04-May-16		
Oil Hours (Kms)			Not Available		
Unit Hours (Kms)			Not Available		
Oil Change					
Oil Added (Liters)					
Filters Hours (Kms)					
Wear Condition					
Wear Element					
Iron	D-6595	PPM	1.5		
Chromium	D-6595	PPM	0.0		
Lead	D-6595	PPM	0.0		
Copper	D-6595	PPM	0.0		
Tin	D-6595	PPM	0.0		
Aluminum	D-6595	PPM	1.4		
Nickel	D-6595	PPM	0.2		
Silver	D-6595	PPM	0.0		
Molybdenum	D-6595	PPM	0.0		
Titanium	D-6595	PPM	0.0		
Oil Condition					
Viscosity @ 40° C	D-445	cSt	104.2		
Viscosity @ 100° C	D-445	cSt	13.8		
Oxidation	E-2412M	Abs	4.0		
Nitration	E-2412M	Abs	5.5		
TAN	D-974	mgKOH/g	0.91		
TBN	D-4739	mgKOH/g	8.2		
Contamination					
Water	E-2412M	% (Wt.)	0.098		
Fuel	GAW	% (Wt.)	0.00		
Glycol	E-2412M	Abs	N/A		
Soot	E-2412M	% (Wt.)	0.00		
Vanadium	D-6595	PPM	0		
Sodium	D-6595	PPM	3		
Silicon	D-6595	PPM	7.0		
Additive Element					
Boron	D-6595	PPM	1		
Magnesium	D-6595	PPM	11		
Calcium	D-6595	PPM	2456		
Barium	D-6595	PPM	0		
Phosphorus	D-6595	PPM	581		
Zinc	D-6595	PPM	677		
[illegible]					
Flash Point	D-3828	°C			
Viscosity Index	D-2270		133		

Oil properties of lubricant B



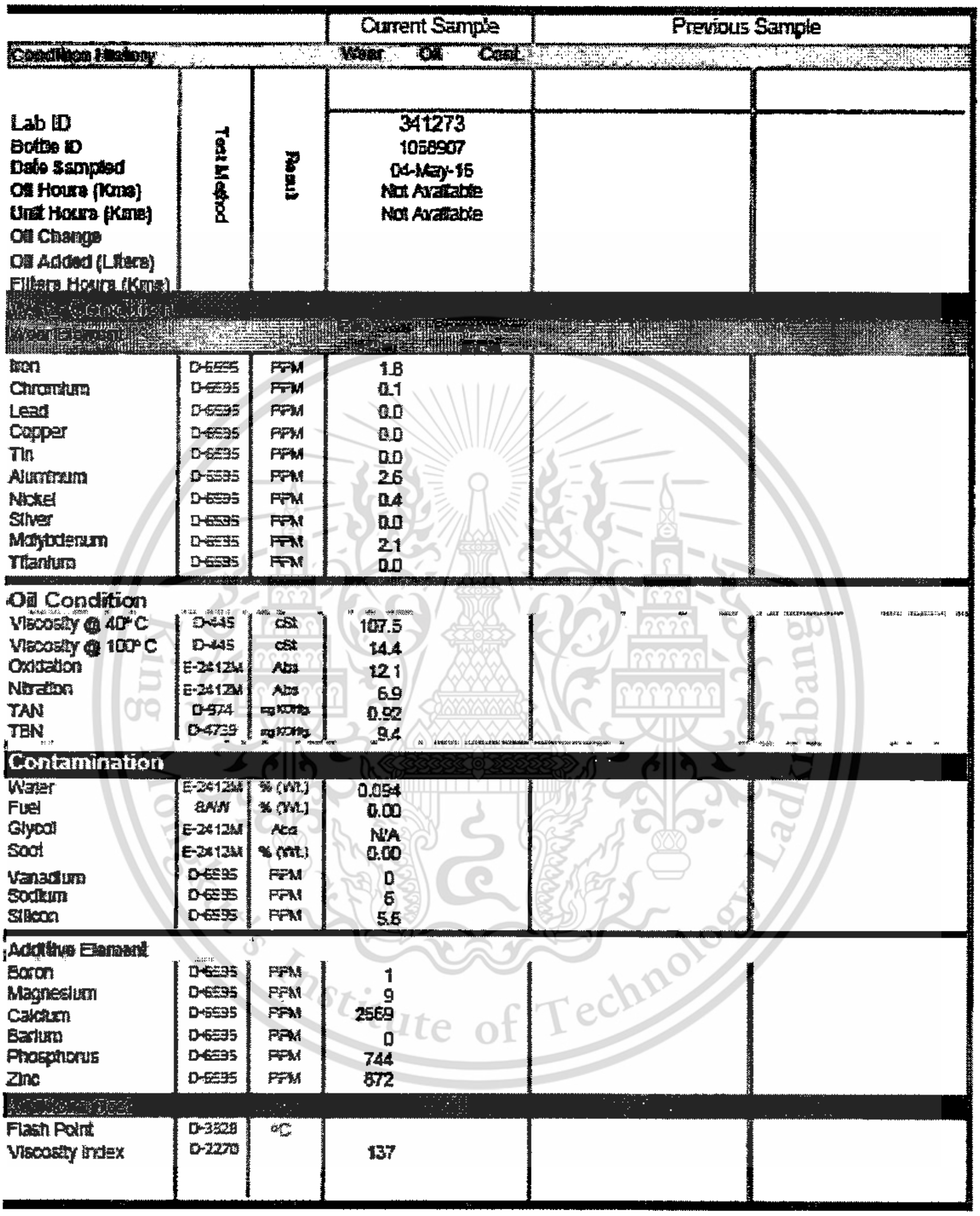
			Current Sample	Previous Sample	
Condition History			Wear Oil Cont.		
	Test Method	Result			
Lab ID			341272		
Bottle ID			1058905		
Date Sampled			04-May-16		
Oil Hours (Kms)			Not Available		
Unit Hours (Kms)			Not Available		
Oil Change					
Oil Added (Liters)					
Filters Hours (Kms)					
Wear Condition					
Wear Elements					
Iron	D-6595	PPM	0.9		
Chromium	D-6595	PPM	0.1		
Lead	D-6595	PPM	0.0		
Copper	D-6595	PPM	0.0		
Tin	D-6595	PPM	0.0		
Aluminum	D-6595	PPM	1.1		
Nickel	D-6595	PPM	0.6		
Silver	D-6595	PPM	0.0		
Molybdenum	D-6595	PPM	34.1		
Titanium	D-6595	PPM	0.0		
Oil Condition					
Viscosity @ 40° C	D-445	cSt	110.1		
Viscosity @ 100° C	D-445	cSt	15.0		
Oxidation	E-2412M	Abs	6.6		
Nitration	E-2412M	Abs	3.5		
TAN	D-974	mg KOH/g	1.58		
TBN	D-4739	mg KOH/g	9.2		
Contamination					
Water	E-2412M	% (Wt.)	0.141		
Fuel	SAW	% (Wt.)	0.00		
Glycol	E-2412M	Abs	N/A		
Soot	E-2412M	% (Wt.)	0.00		
Vanadium	D-6595	PPM	0		
Sodium	D-6595	PPM	2		
Silicon	D-6595	PPM	9.4		
Additive Element					
Boron	D-6595	PPM	447		
Magnesium	D-6595	PPM	13		
Calcium	D-6595	PPM	3126		
Barium	D-6595	PPM	0		
Phosphorus	D-6595	PPM	1085		
Zinc	D-6595	PPM	1265		
[illegible]					
Flash Point	D-3828	°C			
Viscosity Index	D-2270		142		

Oil properties of lubricant C



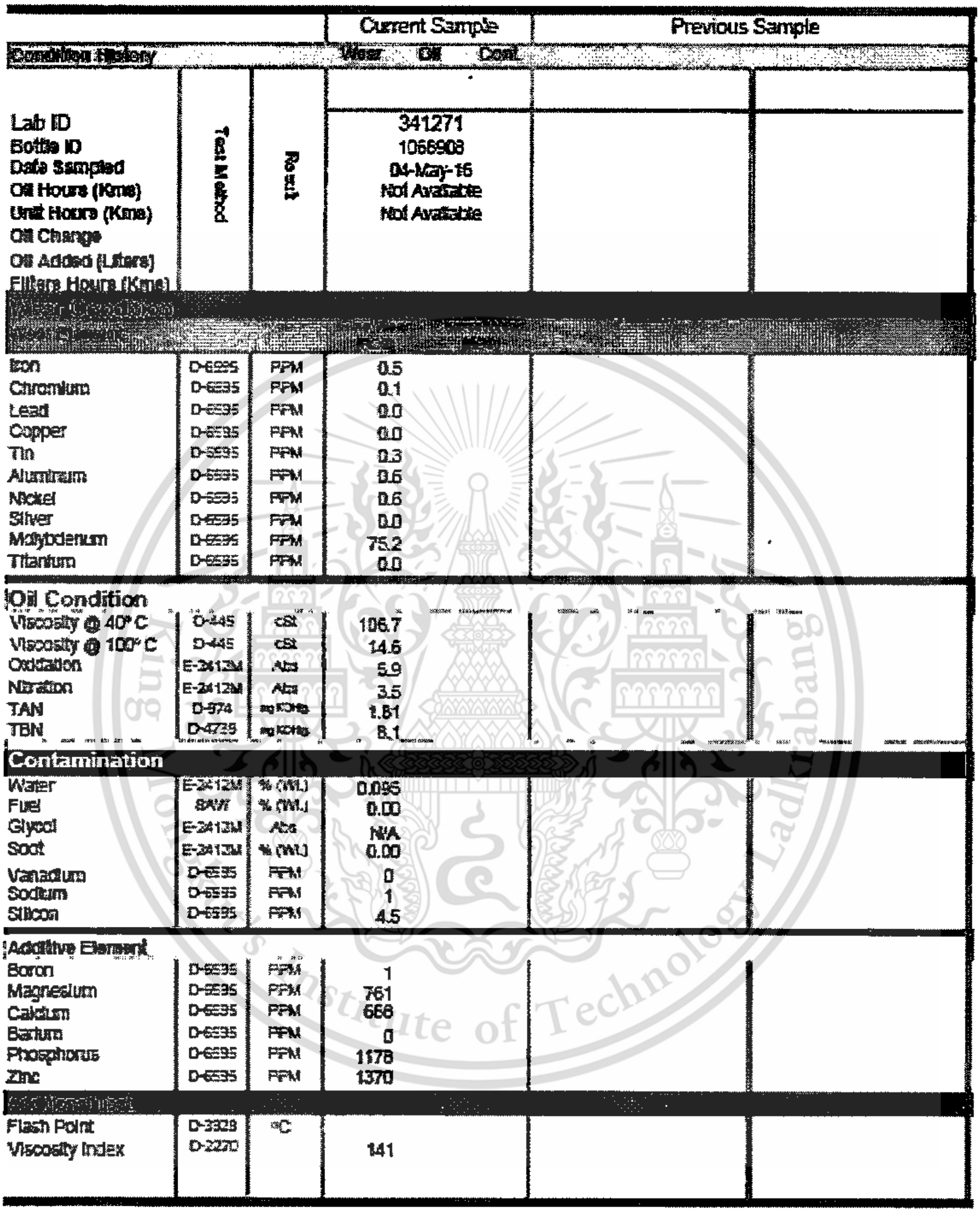
	Test Method	Result	Current Sample	Previous Sample	
Condition History			Wear Oil Cont.		
Lab ID			341275		
Bottle ID			1058905		
Date Sampled			04-May-16		
Oil Hours (Kms)			Not Available		
Unit Hours (Kms)			Not Available		
Oil Change					
Oil Added (Liters)					
Filters Hours (Kms)					
Wear Condition					
Wear Element					
Iron	D-6595	PPM	1.2		
Chromium	D-6595	PPM	0.1		
Lead	D-6595	PPM	0.0		
Copper	D-6595	PPM	0.2		
Tin	D-6595	PPM	0.0		
Aluminum	D-6595	PPM	1.1		
Nickel	D-6595	PPM	0.3		
Silver	D-6595	PPM	0.0		
Molybdenum	D-6595	PPM	77.2		
Titanium	D-6595	PPM	0.0		
Oil Condition					
Viscosity @ 40° C	D-445	cSt	108.9		
Viscosity @ 100° C	D-445	cSt	14.6		
Oxidation	E-2412M	Abs	7.0		
Nitration	E-2412M	Abs	3.4		
TAN	D-974	mg KOH/g	1.63		
TBN	D-4739	mg KOH/g	9.8		
Contamination					
Water	E-2412M	% (Wt.)	0.123		
Fuel	SAW	% (Wt.)	0.00		
Glycol	E-2412M	Abs	N/A		
Soot	E-2412M	% (Wt.)	0.00		
Vanadium	D-6595	PPM	1		
Sodium	D-6595	PPM	2		
Silicon	D-6595	PPM	11.6		
Additive Element					
Boron	D-6595	PPM	480		
Magnesium	D-6595	PPM	16		
Calcium	D-6595	PPM	3198		
Barium	D-6595	PPM	0		
Phosphorus	D-6595	PPM	1195		
Zinc	D-6595	PPM	1286		
Additional Test					
Flash Point	D-3828	°C			
Viscosity Index	D-2270		138		

Oil properties of lubricant D



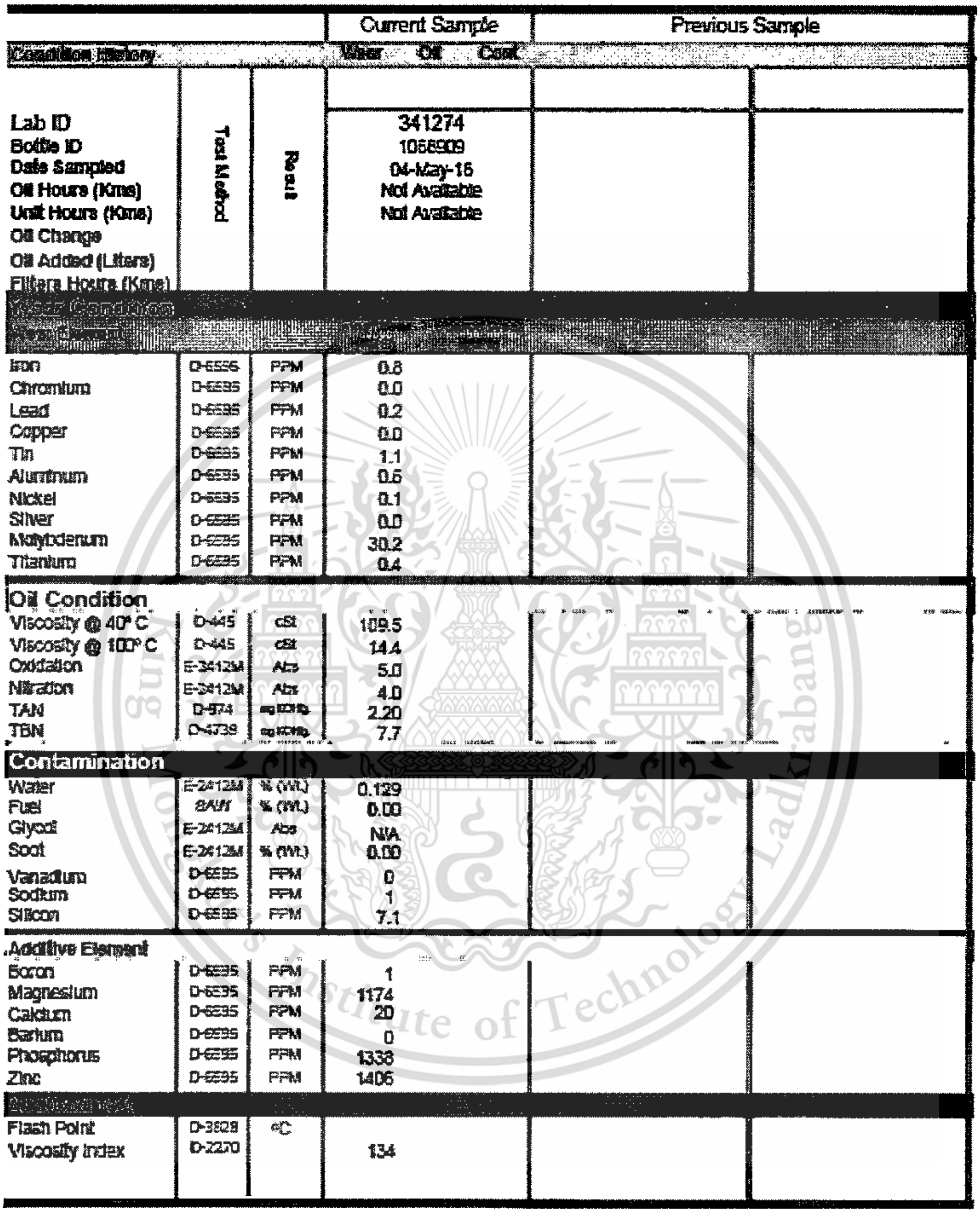
	Test Method	Result	Current Sample	Previous Sample	
Condition History			Wear Oil Cont		
Lab ID			341273		
Bottle ID			1058907		
Date Sampled			04-May-16		
Oil Hours (Kms)			Not Available		
Unit Hours (Kms)			Not Available		
Oil Change					
Oil Added (Liters)					
Filters Hours (Kms)					
Wear Condition					
Wear Element					
Iron	D-6595	PPM	1.8		
Chromium	D-6595	PPM	0.1		
Lead	D-6595	PPM	0.0		
Copper	D-6595	PPM	0.0		
Tin	D-6595	PPM	0.0		
Aluminum	D-6595	PPM	2.6		
Nickel	D-6595	PPM	0.4		
Silver	D-6595	PPM	0.0		
Molybdenum	D-6595	PPM	2.1		
Titanium	D-6595	PPM	0.0		
Oil Condition					
Viscosity @ 40° C	D-445	cSt	107.5		
Viscosity @ 100° C	D-445	cSt	14.4		
Oxidation	E-2412M	Abs	12.1		
Nitration	E-2412M	Abs	6.9		
TAN	D-974	mgKOH/g	0.92		
TBN	D-4739	mgKOH/g	9.4		
Contamination					
Water	E-2412M	% (Wt.)	0.094		
Fuel	SAW	% (Wt.)	0.00		
Glycol	E-2412M	Abs	N/A		
Soot	E-2412M	% (Wt.)	0.00		
Vanadium	D-6595	PPM	0		
Sodium	D-6595	PPM	6		
Silicon	D-6595	PPM	5.6		
Additive Element					
Boron	D-6595	PPM	1		
Magnesium	D-6595	PPM	9		
Calcium	D-6595	PPM	2569		
Barium	D-6595	PPM	0		
Phosphorus	D-6595	PPM	744		
Zinc	D-6595	PPM	872		
Additional Test					
Flash Point	D-3828	°C			
Viscosity Index	D-2270		137		

Oil properties of lubricant E



			Current Sample	Previous Sample	
Condition History			Wear Oil Cont.		
	Test Method	Result			
Lab ID			341271		
Bottle ID			1066908		
Date Sampled			04-May-16		
Oil Hours (Kms)			Not Available		
Unit Hours (Kms)			Not Available		
Oil Change					
Oil Added (Liters)					
Filters Hours (Kms)					
[illegible]					
[illegible]					
Iron	D-6595	PPM	0.5		
Chromium	D-6595	PPM	0.1		
Lead	D-6595	PPM	0.0		
Copper	D-6595	PPM	0.0		
Tin	D-6595	PPM	0.3		
Aluminum	D-6595	PPM	0.6		
Nickel	D-6595	PPM	0.6		
Silver	D-6595	PPM	0.0		
Molybdenum	D-6595	PPM	75.2		
Titanium	D-6595	PPM	0.0		
Oil Condition					
Viscosity @ 40° C	D-445	cSt	106.7		
Viscosity @ 100° C	D-445	cSt	14.6		
Oxidation	E-2412M	Abs	5.9		
Nitration	E-2412M	Abs	3.5		
TAN	D-974	mg KOH/g	1.81		
TBN	D-4739	mg KOH/g	8.1		
Contamination					
Water	E-2412M	% (Wt.)	0.096		
Fuel	SAW	% (Wt.)	0.00		
Glycol	E-2412M	Abs	N/A		
Soot	E-2412M	% (Wt.)	0.00		
Vanadium	D-6595	PPM	0		
Sodium	D-6595	PPM	1		
Silicon	D-6595	PPM	4.5		
Additive Element					
Boron	D-6595	PPM	1		
Magnesium	D-6595	PPM	761		
Calcium	D-6595	PPM	668		
Barium	D-6595	PPM	0		
Phosphorus	D-6595	PPM	1178		
Zinc	D-6595	PPM	1370		
[illegible]					
Flash Point	D-3828	°C			
Viscosity Index	D-2270		141		

Oil properties of lubricant F



			Current Sample	Previous Sample	
Condition History			Wear Oil Cont		
	Test Method	Result			
Lab ID			341274		
Bottle ID			1066909		
Date Sampled			04-May-16		
Oil Hours (Kms)			Not Available		
Unit Hours (Kms)			Not Available		
Oil Change					
Oil Added (Liters)					
Filters Hours (Kms)					
Wear Condition					
[illegible]					
Iron	D-6595	PPM	0.8		
Chromium	D-6595	PPM	0.0		
Lead	D-6595	PPM	0.2		
Copper	D-6595	PPM	0.0		
Tin	D-6595	PPM	1.1		
Aluminum	D-6595	PPM	0.6		
Nickel	D-6595	PPM	0.1		
Silver	D-6595	PPM	0.0		
Molybdenum	D-6595	PPM	30.2		
Titanium	D-6595	PPM	0.4		
Oil Condition					
Viscosity @ 40° C	D-445	cSt	109.5		
Viscosity @ 100° C	D-445	cSt	14.4		
Oxidation	E-2412M	Abs	5.0		
Nitration	E-2412M	Abs	4.0		
TAN	D-974	mg KOH/g	2.20		
TBN	D-4739	mg KOH/g	7.7		
Contamination					
Water	E-2412M	% (Wt.)	0.129		
Fuel	SAW	% (Wt.)	0.00		
Glycol	E-2412M	Abs	N/A		
Soot	E-2412M	% (Wt.)	0.00		
Vanadium	D-6595	PPM	0		
Sodium	D-6595	PPM	1		
Silicon	D-6595	PPM	7.1		
Additive Element					
Boron	D-6595	PPM	1		
Magnesium	D-6595	PPM	1174		
Calcium	D-6595	PPM	20		
Barium	D-6595	PPM	0		
Phosphorus	D-6595	PPM	1338		
Zinc	D-6595	PPM	1406		
[illegible]					
Flash Point	D-3828	°C			
Viscosity Index	D-2270		134		

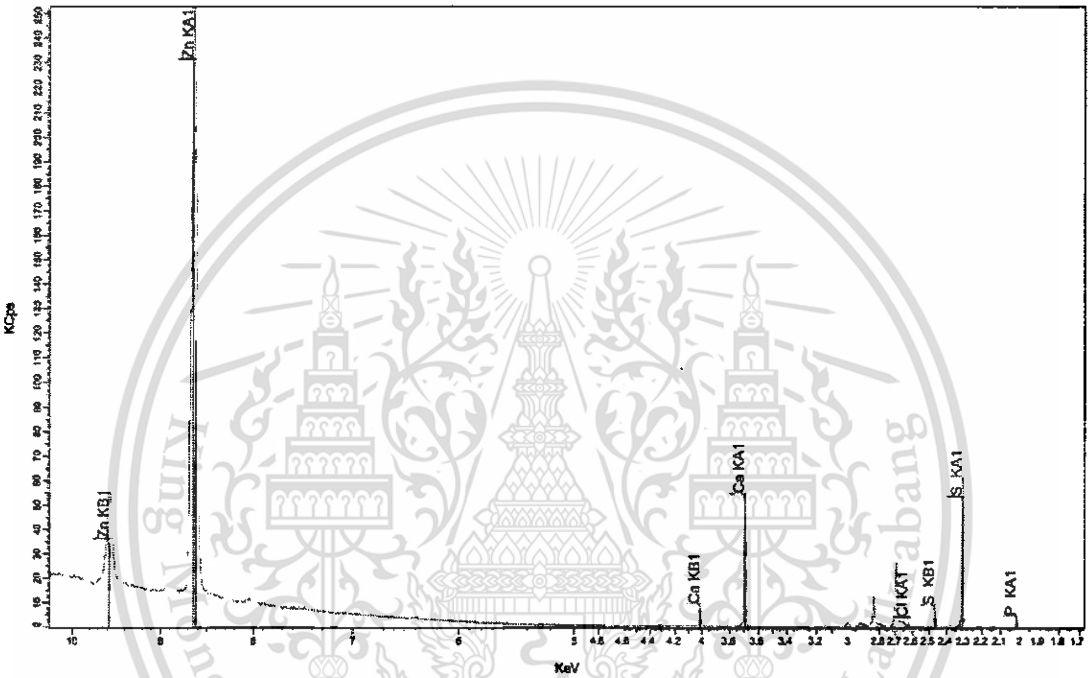
APPENDIX E

Additive Elements in Formulated Oils Analyzed by X-ray Fluorescence Spectrometer

No.	List	Page
1	New Lubricant A	135
2	New Lubricant B	136
3	New Lubricant C	137
4	New Lubricant D	138
5	New Lubricant E	139
6	New Lubricant F	140

Additives elements in lubricant A

Instrument Type	X-ray Fluorescence Spectrometer
Model	Bruker Model S8 Tiger
Measurement Method	Best Detection-He34mm
Calculation Method	Theoretical Formulas, "Fundamental Parameter Calculations"

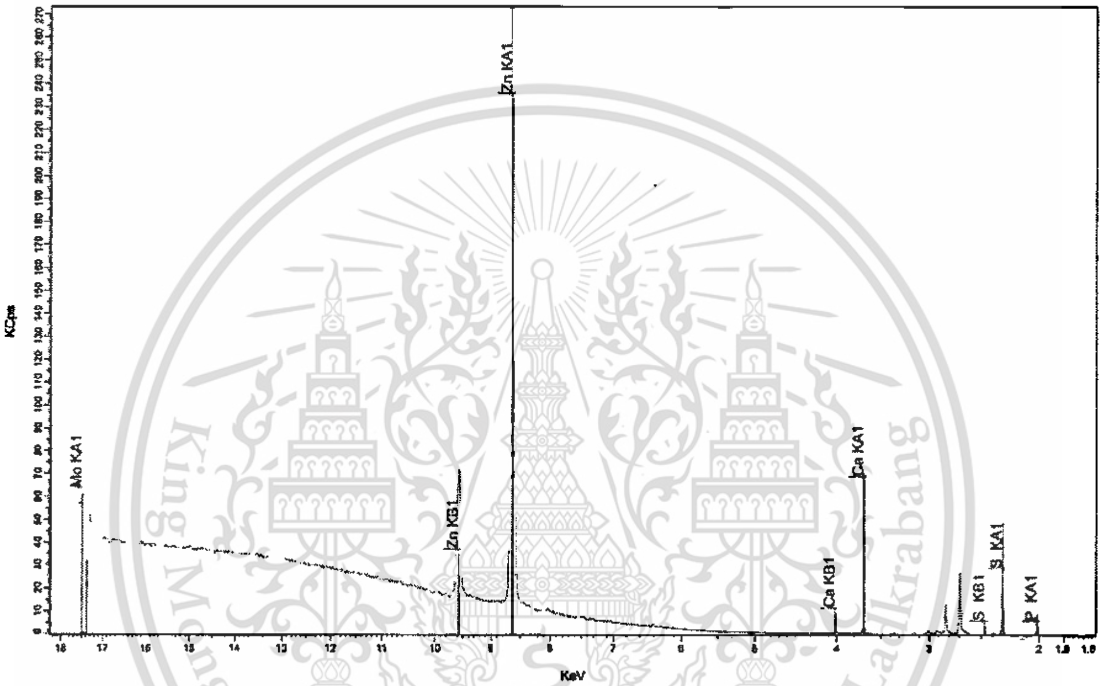


Result: LUBRICANT A

Element		Volume
SULPHUR	S	0.822 %
CALCIUM	Ca	0.593 %
ZINC	Zn	0.132 %
PHOSPHORUS	P	0.128 %
CHLORINE	Cl	171.0 ppm
Summary		1.7 %

Additives elements in lubricant B

Instrument Type	X-ray Fluorescence Spectrometer
Model	Bruker Model S8 Tiger
Measurement Method	Best Detection-He34mm
Calculation Method	Theoretical Formulas, "Fundamental Parameter Calculations"

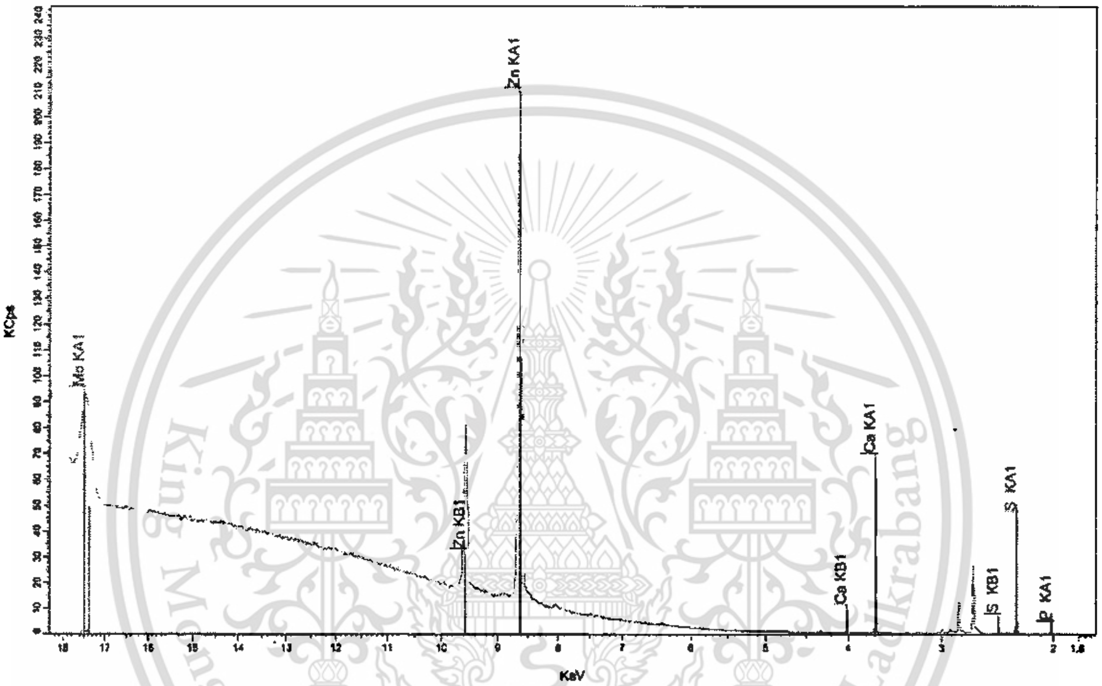


Result: LUBRICANT B

Element		Volume
CALCIUM	Ca	0.875 %
SULPHUR	S	0.760 %
PHOSPHORUS	P	0.262 %
ZINC	Zn	0.237 %
MOLYBDENUM	Mo	38.2 ppm
Summary		2.1 %

Additives elements in lubricant C

Instrument Type	X-ray Fluorescence Spectrometer
Model	Bruker Model S8 Tiger
Measurement Method	Best Detection-He34mm
Calculation Method	Theoretical Formulas, "Fundamental Parameter Calculations"

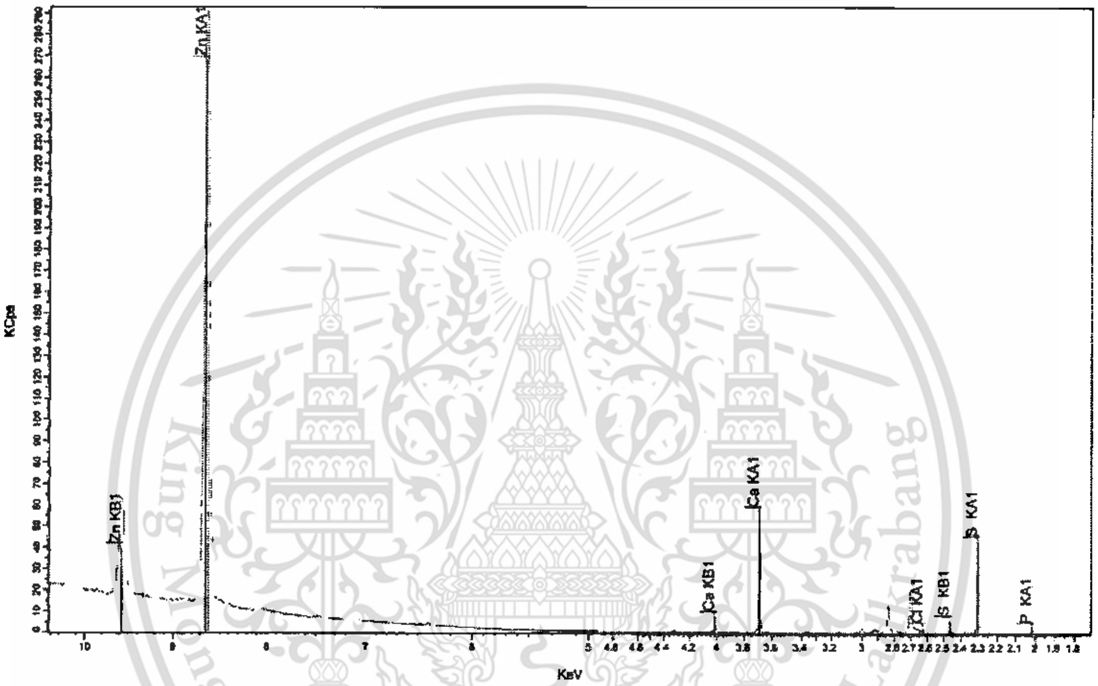


Result: LUBRICANT C

Element		Volume
CALCIUM	Ca	0.769 %
SULPHUR	S	0.678 %
ZINC	Zn	0.234 %
PHOSPHORUS	P	0.228 %
MOLYBDENUM	Mo	79.0 ppm
Summary		1.9 %

Additives elements in lubricant D

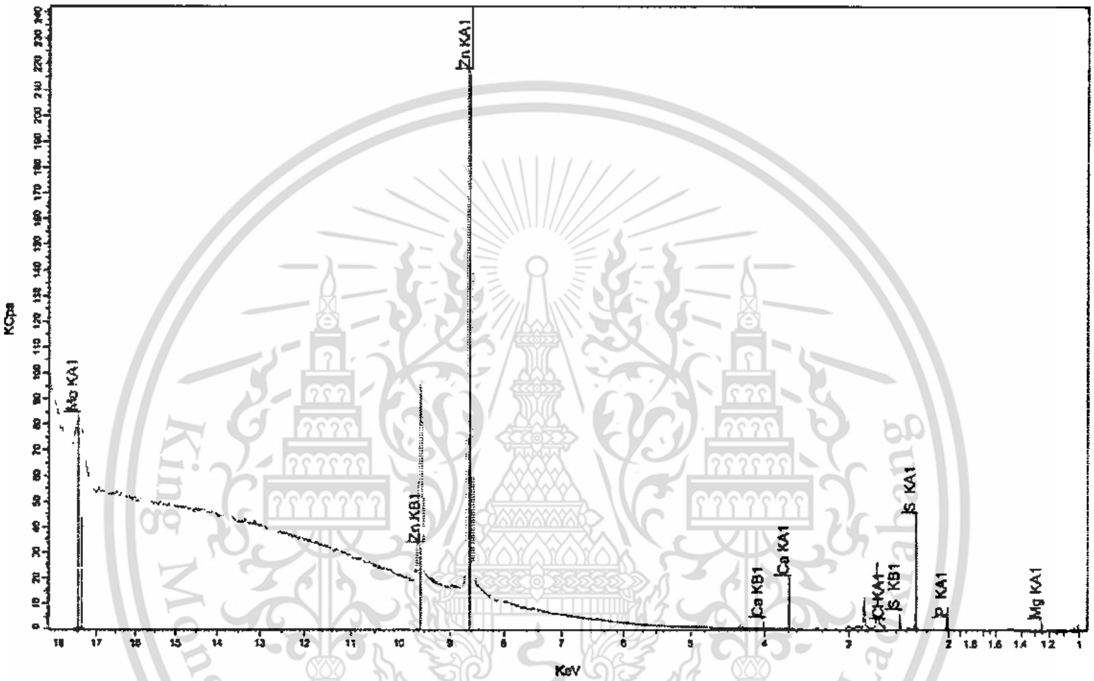
Instrument Type	X-ray Fluorescence Spectrometer
Model	Bruker Model S8 Tiger
Measurement Method	Best Detection-He34mm
Calculation Method	Theoretical Formulas, "Fundamental Parameter Calculations"



Result: LUBRICANT D		
Element		**Volume**
CALCIUM	Ca	0.637 %
SULPHUR	S	0.635 %
ZINC	Zn	0.157 %
PHOSPHORUS	P	0.149 %
CHLORINE	Cl	308 ppm
Summary		1.6 %

Additives elements in lubricant E

Instrument Type	X-ray Fluorescence Spectrometer
Model	Bruker Model S8 Tiger
Measurement Method	Best Detection-He34mm
Calculation Method	Theoretical Formulas, "Fundamental Parameter Calculations"

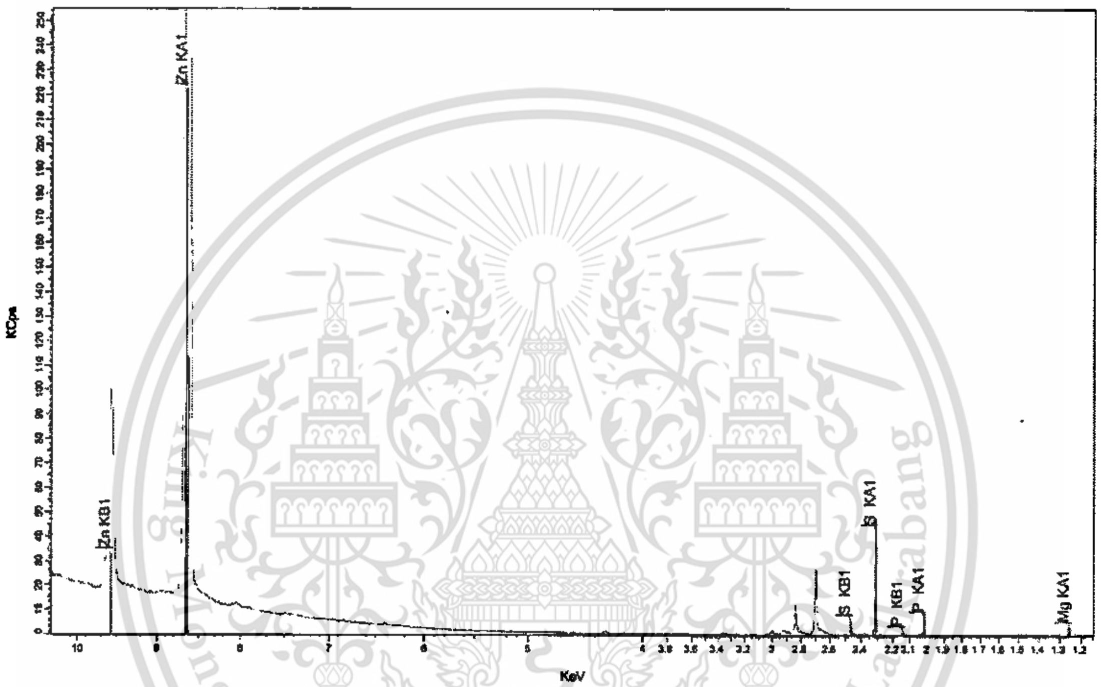


Result: LUBRICANT E

Element		Volume
SULPHUR	S	0.625 %
ZINC	Zn	0.251 %
PHOSPHORUS	P	0.235 %
CALCIUM	Ca	0.213 %
MAGNESIUM	Mg	0.173 %
CHLORINE	Cl	195.0 ppm
MOLYBDENUM	Mo	49.3 ppm
Summary		1.5 %

Additives elements in lubricant F

Instrument Type	X-ray Fluorescence Spectrometer
Model	Bruker Model S8 Tiger
Measurement Method	Best Detection-He34mm
Calculation Method	Theoretical Formulas, “Fundamental Parameter Calculations”



Result: LUBRICANT F

Element		Volume
SULPHUR	S	0.664 %
ZINC	Mg	0.289 %
PHOSPHORUS	Zn	0.263 %
CALCIUM	P	0.259 %
Summary		1.5 %

APPENDIX F

Particle Size Distribution in Formulated Oil Analyzed by Laser Diffraction Technique

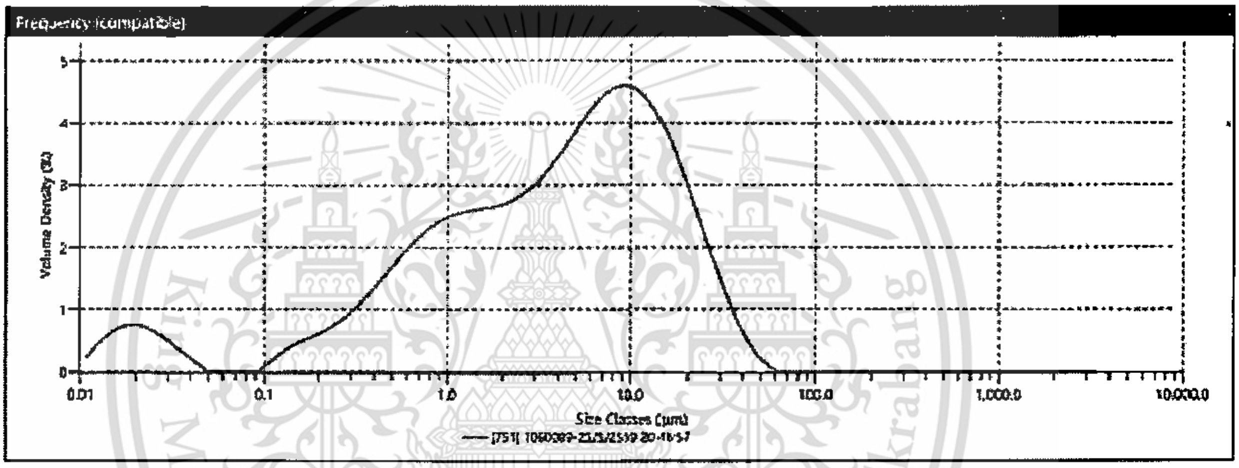
Lubricant A mixed carbon black 1% by weight

Sample Name	1060089
Measurement Date	25/5/2559
File Name	5591471

Instrument Type	Mastersizer3000
Instrument Serial No.	MAL1099267
Accessory Name	Hydro SV

Particle Name	Carbon black
Particle Refractive Index	1.840
Particle Absorption Index	3.000
Dispersant Name	n-Hexane
Dispersant Refractive Index	1.380
Analysis Model	General Purpose
Scattering Model	Mie
Laser Obscuration	15.53 %
Ultrasound Achieved	0 %
Stirrer Speed Achieved	1000 rpm
Particle Notes	

Result Units	Volume
Concentration	0.0018 %
Uniformity	1.346
Span	4.225
Specific Surface Area	9253 m²/kg
Weighted Residual	0.31 %
Dv (10)	0.359 µm
Dv (50)	4.34 µm
Dv (90)	18.7 µm
D [4,3]	7.34 µm
D [3,2]	0.309 µm



Result

Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In
0.0100	0.18	0.0679	0.00	0.460	1.38	3.12	2.63	21.2	2.13	144	0.00	976	0.00
0.0114	0.34	0.0771	0.00	0.523	1.55	3.55	2.80	24.1	1.72	163	0.00	1110	0.00
0.0129	0.48	0.0876	0.03	0.594	1.70	4.03	2.99	27.4	1.34	186	0.00	1260	0.00
0.0147	0.57	0.0995	0.12	0.675	1.84	4.58	3.19	31.1	0.98	211	0.00	1430	0.00
0.0167	0.62	0.113	0.22	0.767	1.95	5.21	3.39	35.3	0.67	240	0.00	1630	0.00
0.0189	0.63	0.128	0.32	0.872	2.03	5.92	3.57	40.1	0.41	272	0.00	1850	0.00
0.0215	0.59	0.146	0.39	0.991	2.09	6.72	3.72	45.6	0.21	310	0.00	2100	0.00
0.0244	0.52	0.166	0.45	1.13	2.13	7.64	3.82	51.8	0.08	352	0.00	2390	0.00
0.0278	0.43	0.188	0.51	1.28	2.16	8.68	3.85	58.9	0.02	400	0.00	2710	0.00
0.0315	0.32	0.214	0.58	1.45	2.18	9.86	3.82	66.9	0.00	454	0.00	3080	0.00
0.0358	0.21	0.243	0.67	1.65	2.21	11.2	3.70	76.0	0.00	516	0.00	3500	
0.0407	0.12	0.276	0.78	1.88	2.24	12.7	3.50	86.4	0.00	586	0.00		
0.0463	0.03	0.314	0.91	2.13	2.29	14.5	3.23	98.1	0.00	666	0.00		
0.0526	0.00	0.357	1.05	2.42	2.37	16.4	2.90	111	0.00	756	0.00		
0.0597	0.00	0.405	1.21	2.75	2.45	18.7	2.57	127	0.00	859	0.00		

5591471

Lubricant B mixed carbon black 1% by weight

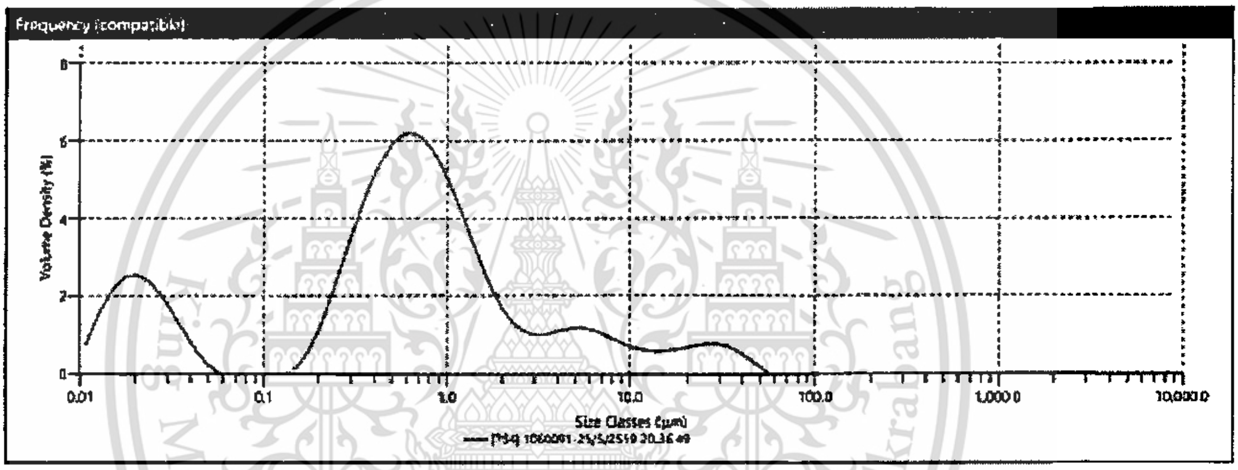
Sample Name 1060091
Measurement Date 25/5/2559
File Name S591471

Instrument Type Mastersizer3000
Instrument Serial No. MAL1099267
Accessory Name Hydro SV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 16.37 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 1000 rpm
Particle Notes

Result Units Volume
Concentration 0.0038 %
Uniformity 3.579
Span 8.866
Specific Surface Area 28980 m²/kg
Weighted Residual 0.61 %
Dv (10) 0.0223 µm
Dv (50) 0.631 µm
Dv (90) 5.61 µm
D [4,3] 2.54 µm
D [3,2] 0.0988 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.60	0.0679	0.00	0.460	4.90	3.12	0.82	21.2	0.59	144	0.00	976	0.0
0.0114	1.14	0.0771	0.00	0.523	5.12	3.55	0.87	24.1	0.62	163	0.00	1110	0.0
0.0129	1.59	0.0876	0.00	0.594	5.18	4.03	0.93	27.4	0.63	186	0.00	1260	0.0
0.0147	1.91	0.0995	0.00	0.675	5.09	4.58	0.95	31.1	0.58	211	0.00	1430	0.0
0.0167	2.09	0.113	0.00	0.767	4.85	5.21	0.95	35.3	0.40	240	0.00	1630	0.0
0.0189	2.12	0.128	0.00	0.872	4.49	5.92	0.93	40.1	0.34	272	0.00	1850	0.0
0.0215	2.07	0.146	0.16	0.991	4.01	6.72	0.84	45.6	0.17	310	0.00	2100	0.0
0.0244	1.80	0.166	0.47	1.13	3.45	7.64	0.74	51.8	0.00	352	0.00	2390	0.0
0.0278	1.50	0.188	0.93	1.28	2.87	8.68	0.63	58.9	0.00	400	0.00	2710	0.0
0.0315	1.14	0.214	1.53	1.45	2.30	9.86	0.55	66.9	0.00	454	0.00	3080	0.0
0.0358	0.76	0.243	2.19	1.65	1.79	11.2	0.49	76.0	0.00	516	0.00	3500	
0.0407	0.45	0.276	2.86	1.88	1.38	12.7	0.47	86.4	0.00	586	0.00		
0.0463	0.20	0.314	3.50	2.13	1.09	14.5	0.48	98.1	0.00	666	0.00		
0.0526	0.00	0.357	4.07	2.42	0.90	16.4	0.51	111	0.00	756	0.00		
0.0597	0.00	0.405	4.55	2.75	0.82	18.7	0.55	127	0.00	859	0.00		

Lubricant C mixed carbon black 1% by weight

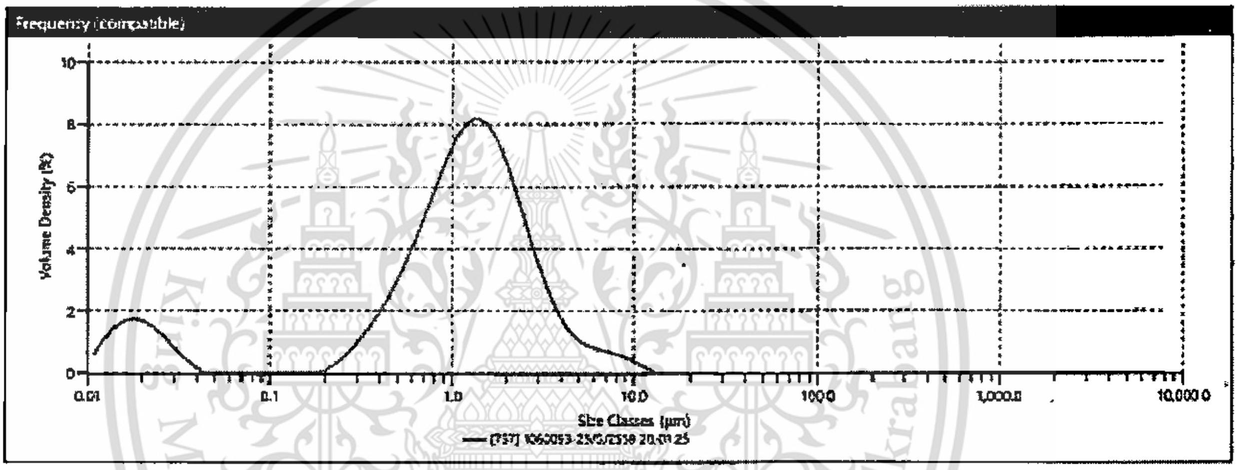
Sample Name	1060093
Measurement Date	25/5/2559
File Name	SS91471

Instrument Type	Mastersizer3000
Instrument Serial No.	MAL1099267
Accessory Name	Hydro SV

Particle Name	Carbon black
Particle Refractive Index	1.840
Particle Absorption Index	3.000
Dispersant Name	n-Hexane
Dispersant Refractive Index	1.380
Analysis Model	General Purpose
Scattering Model	Mie
Laser Obscuration	23.53 %
Ultrasound Achieved	0 %
Stirrer Speed Achieved	1000 rpm
Particle Notes	

Result Units	Volume
Concentration	0.0019 %
Uniformity	0.780
Span	2.506
Specific Surface Area	19070 m²/kg
Weighted Residual	0.85 %
Dv (10)	0.0336 µm
Dv (50)	1.20 µm
Dv (90)	3.03 µm
D [4,3]	1.54 µm
D [3,2]	0.150 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.47	0.0679	0.00	0.460	2.40	3.12	2.28	21.2	0.00	144	0.00	976	0.0
0.0114	0.89	0.0771	0.00	0.523	2.97	3.55	1.66	24.1	0.00	163	0.00	1110	0.0
0.0129	1.21	0.0876	0.00	0.594	3.62	4.03	1.20	27.4	0.00	186	0.00	1260	0.0
0.0147	1.41	0.0995	0.00	0.675	4.32	4.58	0.90	31.1	0.00	211	0.00	1430	0.0
0.0167	1.47	0.113	0.00	0.767	5.05	5.21	0.73	35.3	0.00	240	0.00	1630	0.0
0.0189	1.41	0.128	0.00	0.872	5.74	5.92	0.64	40.1	0.00	272	0.00	1850	0.0
0.0215	1.24	0.146	0.00	0.991	6.32	6.72	0.58	45.6	0.00	310	0.00	2100	0.0
0.0244	0.99	0.166	0.00	1.13	6.71	7.64	0.50	51.8	0.00	352	0.00	2390	0.0
0.0278	0.70	0.188	0.06	1.28	6.86	8.68	0.40	58.9	0.00	400	0.00	2710	0.0
0.0315	0.43	0.214	0.23	1.45	6.72	9.86	0.26	66.9	0.00	454	0.00	3080	0.0
0.0358	0.20	0.243	0.47	1.65	6.29	11.2	0.12	76.0	0.00	516	0.00	3500	
0.0407	0.00	0.276	0.76	1.88	5.62	12.7	0.00	86.4	0.00	586	0.00		
0.0463	0.00	0.314	1.08	2.13	4.80	14.5	0.00	98.1	0.00	666	0.00		
0.0526	0.00	0.357	1.46	2.42	3.91	16.4	0.00	111	0.00	756	0.00		
0.0597	0.00	0.405	1.90	2.75	3.04	18.7	0.00	127	0.00	859	0.00		

Lubricant D mixed carbon black 1% by weight

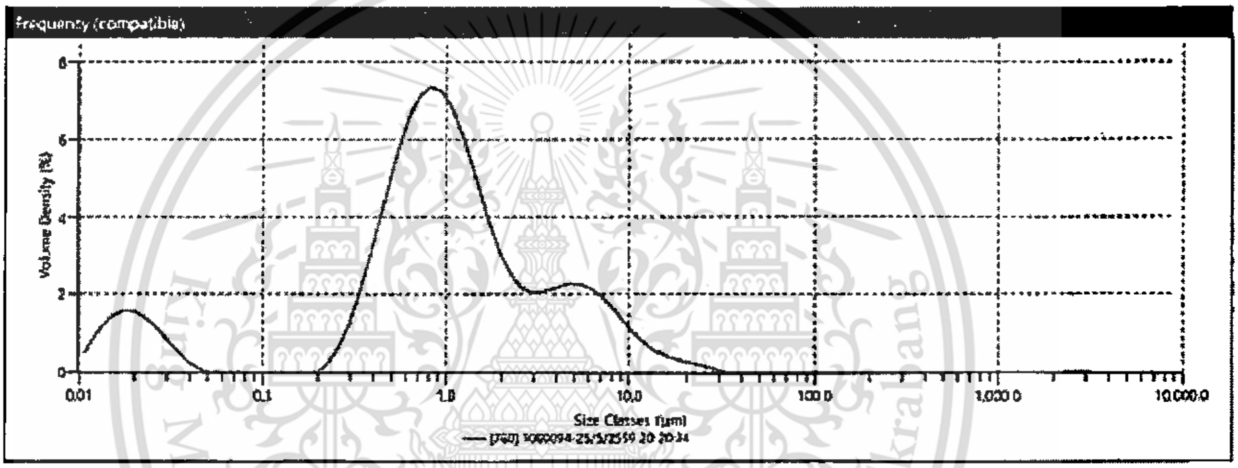
Sample Name 1060094
Measurement Date 25/5/2559
File Name 5591471

Instrument Type Mastersizer3000
Instrument Serial No. MAL1099267
Accessory Name Hydro SV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 13.89 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 1000 rpm
Particle Notes

Result Units Volume
Concentration 0.0310 %
Uniformity 1.624
Span 5.503
Specific Surface Area 17950 m²/kg
Weighted Residual 0.48 %
Dv (10) 0.247 μm
Dv (50) 0.959 μm
Dv (90) 5.52 μm
D [4,3] 2.05 μm
D [3,2] 0.159 μm

Frequency (compatible)



Result

Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In	Size (μm)	% Volume In
0.0100	0.41	0.0679	0.00	0.460	4.13	3.12	1.71	21.2	0.17	144	0.00	976	0.00
0.0114	0.77	0.0771	0.00	0.523	4.90	3.55	1.76	24.1	0.12	163	0.00	1110	0.00
0.0129	1.05	0.0876	0.00	0.594	5.54	4.03	1.87	27.4	0.06	186	0.00	1260	0.00
0.0147	1.24	0.0995	0.00	0.675	5.96	4.58	1.91	31.1	0.00	211	0.00	1430	0.00
0.0167	1.32	0.113	0.00	0.767	6.14	5.21	1.88	35.3	0.00	240	0.00	1630	0.00
0.0189	1.29	0.128	0.00	0.872	6.06	5.92	1.77	40.1	0.00	272	0.00	1850	0.00
0.0215	1.16	0.146	0.00	0.991	5.72	6.72	1.59	45.6	0.00	310	0.00	2100	0.00
0.0244	0.97	0.166	0.00	1.13	5.38	7.64	1.36	51.8	0.00	352	0.00	2390	0.00
0.0278	0.73	0.188	0.00	1.28	4.50	8.68	1.10	58.9	0.00	400	0.00	2710	0.00
0.0315	0.48	0.214	0.18	1.45	3.77	9.86	0.85	66.9	0.00	454	0.00	3080	0.00
0.0358	0.26	0.243	0.51	1.65	3.08	11.2	0.64	76.0	0.00	516	0.00	3500	
0.0407	0.10	0.276	1.00	1.88	2.49	12.7	0.47	86.4	0.00	586	0.00		
0.0463	0.00	0.314	1.65	2.13	2.06	14.5	0.35	98.1	0.00	666	0.00		
0.0526	0.00	0.357	2.43	2.42	1.80	16.4	0.27	111	0.00	756	0.00		
0.0597	0.00	0.405	3.28	2.75	1.70	18.7	0.22	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

Created: 10/5/2559
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Lubricant E mixed carbon black 1% by weight

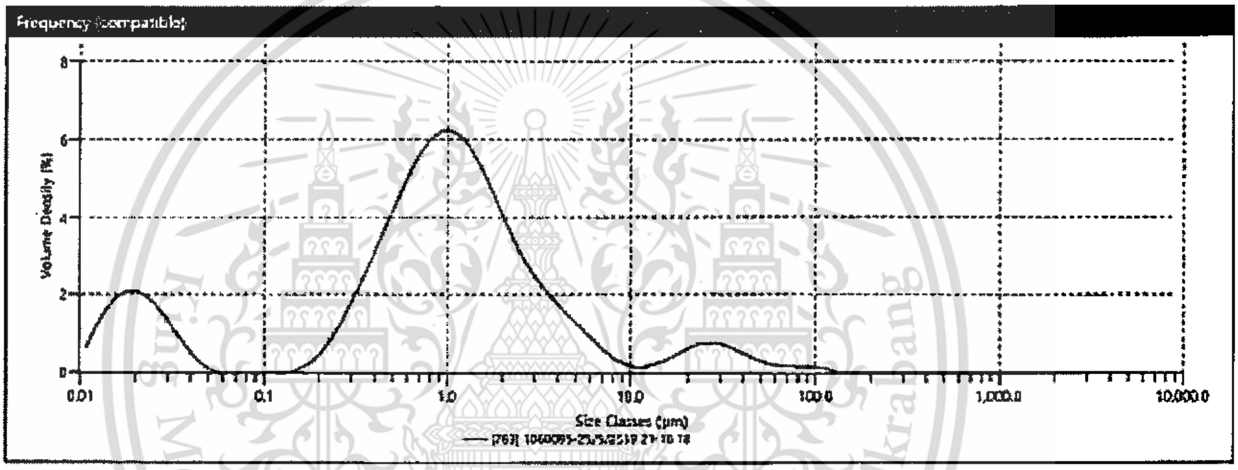
Sample Name 1060095
Measurement Date 25/5/2559
File Name 5591471

Instrument Type Mastersizer3000
Instrument Serial No. MAL1099267
Accessory Name Hydro SV

Particle Name Carbon black
Particle Refractive Index 1.840
Particle Absorption Index 3.000
Dispersant Name n-Hexane
Dispersant Refractive Index 1.380
Analysis Model General Purpose
Scattering Model Mie
Laser Obscuration 23.92 %
Ultrasound Achieved 0 %
Stirrer Speed Achieved 1000 rpm
Particle Notes

Result Units Volume
Concentration 0.0015 %
Uniformity 3.040
Span 4.652
Specific Surface Area 23460 m²/kg
Weighted Residual 0.40 %
Dv (10) 0.0254 µm
Dv (50) 0.958 µm
Dv (90) 4.48 µm
D [4,3] 3.35 µm
D [3,2] 0.122 µm

Frequency (compatible)



Result

Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.51	0.0679	0.00	0.460	3.41	3.12	1.82	21.2	0.61	144	0.00	976	0.00
0.0114	0.97	0.0771	0.00	0.523	3.90	3.55	1.57	24.1	0.65	163	0.00	1110	0.00
0.0129	1.35	0.0876	0.00	0.594	4.36	4.03	1.34	27.4	0.63	186	0.00	1260	0.00
0.0147	1.61	0.0995	0.00	0.675	4.74	4.58	1.12	31.1	0.57	211	0.00	1430	0.00
0.0167	1.74	0.113	0.00	0.767	5.03	5.21	0.90	35.3	0.47	240	0.00	1630	0.00
0.0189	1.74	0.128	0.05	0.872	5.19	5.92	0.68	40.1	0.37	272	0.00	1850	0.00
0.0215	1.63	0.146	0.07	0.991	5.20	6.72	0.48	45.6	0.27	310	0.00	2100	0.00
0.0244	1.42	0.166	0.18	1.13	5.06	7.64	0.30	51.8	0.19	352	0.00	2390	0.00
0.0278	1.14	0.188	0.37	1.28	4.77	8.68	0.18	58.9	0.15	400	0.00	2710	0.00
0.0315	0.83	0.214	0.64	1.45	4.37	9.86	0.12	66.9	0.14	454	0.00	3080	0.00
0.0358	0.52	0.243	1.02	1.65	3.89	11.2	0.12	76.0	0.13	516	0.00	3500	
0.0407	0.27	0.276	1.44	1.88	3.38	12.7	0.18	86.4	0.12	586	0.00		
0.0463	0.09	0.314	1.89	2.13	2.90	14.5	0.28	98.1	0.11	666	0.00		
0.0526	0.00	0.357	2.38	2.42	2.47	16.4	0.40	111	0.08	756	0.00		
0.0597	0.00	0.406	2.89	2.75	2.11	18.7	0.52	127	0.00	859	0.00		

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Mastersizer - v3.40
Page 1 of 1

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Lubricant F mixed carbon black 1% by weight

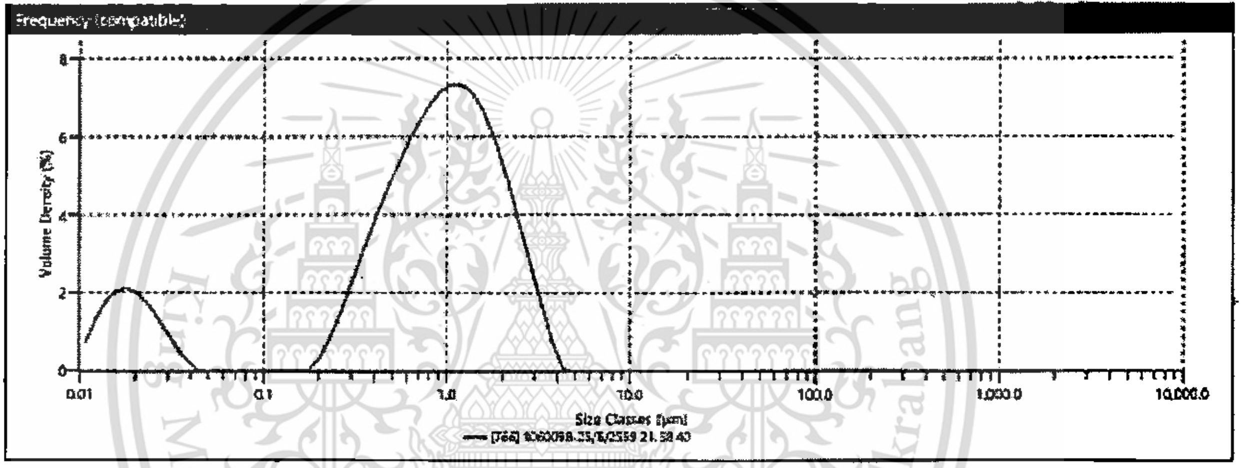
Sample Name	1050098
Measurement Date	25/5/2559
File Name	SS91471

Instrument Type	Mastersizer3000
Instrument Serial No.	MAL1098267
Accessory Name	Hydro SV

Particle Name	Carbon black
Particle Refractive Index	1.840
Particle Absorption Index	3.000
Dispersant Name	n-Hexane
Dispersant Refractive Index	1.380
Analysis Model	General Purpose
Scattering Model	Mie
Laser Obscuration	16.52 %
Ultrasound Achieved	0 %
Stirrer Speed Achieved	1000 rpm
Particle Notes	

Result Units	Volume
Concentration	0.0010 %
Uniformity	0.709
Span	2.471
Specific Surface Area	23260 m²/kg
Weighted Residual	1.16 %
Dv (10)	0.0249 µm
Dv (50)	0.872 µm
Dv (90)	2.18 µm
D [4,3]	1.04 µm
D [3,2]	0.123 µm

Frequency (compatible)



Result

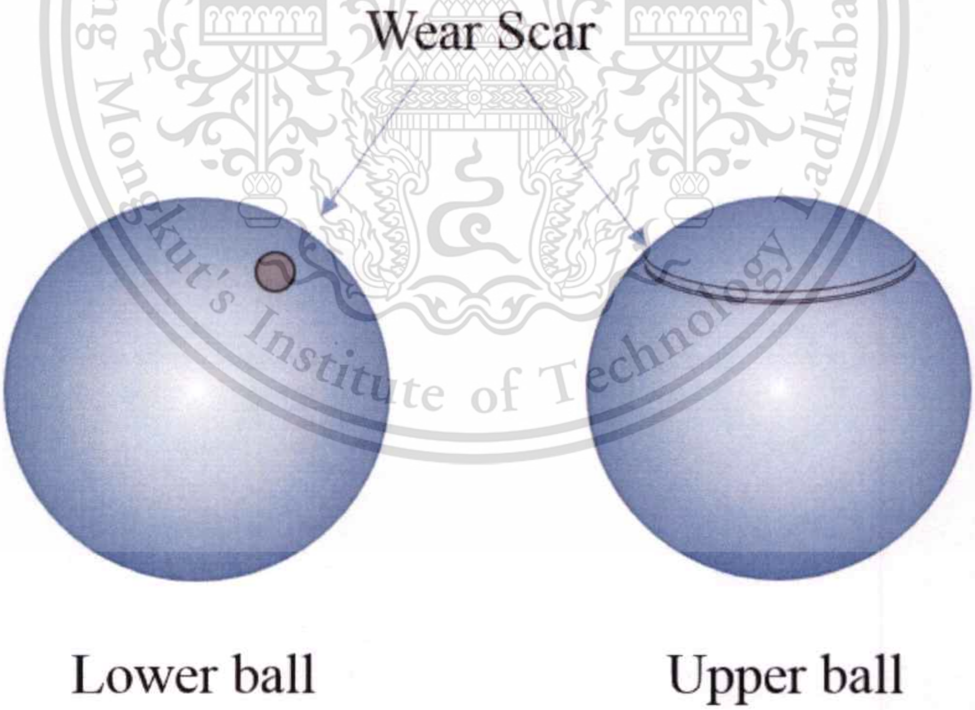
Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In	Size (µm)	% Volume In
0.0100	0.58	0.0679	0.00	0.460	4.06	3.12	1.34	21.2	0.00	144	0.00	976	0.0
0.0114	1.09	0.0771	0.00	0.523	4.54	3.55	0.57	24.1	0.00	163	0.00	1110	0.0
0.0129	1.48	0.0876	0.00	0.594	4.96	4.03	0.00	27.4	0.00	186	0.00	1260	0.0
0.0147	1.71	0.0995	0.00	0.675	5.39	4.58	0.00	31.1	0.00	211	0.00	1430	0.0
0.0167	1.79	0.113	0.00	0.767	5.73	5.21	0.00	35.3	0.00	240	0.00	1630	0.0
0.0189	1.70	0.128	0.00	0.872	5.99	5.92	0.00	40.1	0.00	272	0.00	1850	0.0
0.0215	1.48	0.146	0.00	0.991	6.13	6.72	0.00	45.6	0.00	310	0.00	2100	0.0
0.0244	1.17	0.166	0.00	1.13	6.13	7.64	0.00	51.8	0.00	352	0.00	2390	0.0
0.0278	0.82	0.188	0.23	1.28	5.95	8.68	0.00	58.9	0.00	400	0.00	2710	0.0
0.0315	0.48	0.214	0.65	1.45	5.60	9.86	0.00	66.9	0.00	454	0.00	3080	0.0
0.0358	0.21	0.243	1.19	1.65	5.30	11.2	0.00	76.0	0.00	516	0.00	3500	
0.0407	0.00	0.276	1.79	1.88	4.46	12.7	0.00	86.4	0.00	586	0.00		
0.0463	0.00	0.314	2.39	2.13	3.72	14.5	0.00	98.1	0.00	666	0.00		
0.0526	0.00	0.357	2.98	2.42	2.92	16.4	0.00	111	0.00	756	0.00		
0.0597	0.00	0.405	3.54	2.75	2.11	18.7	0.00	127	0.00	859	0.00		

APPENDIX G

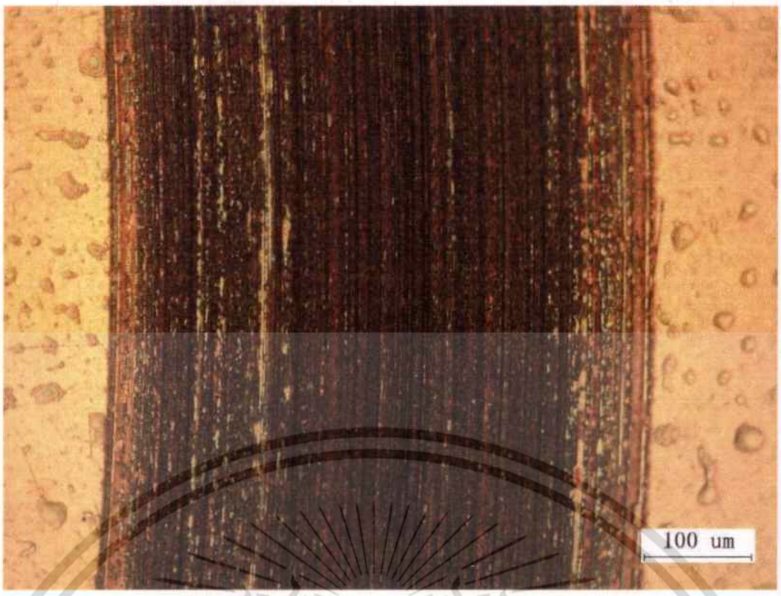
Wear Scar on Steel Balls Analyzed by High Resolution Optical Microscope

No.	Result List	Page
1	Steel ball testing with lubricant A	149
2	Steel ball testing with lubricant A mixed carbon black 1% wt.	150
3	Steel ball testing with lubricant B	151
4	Steel ball testing with lubricant B mixed carbon black 1% wt.	152

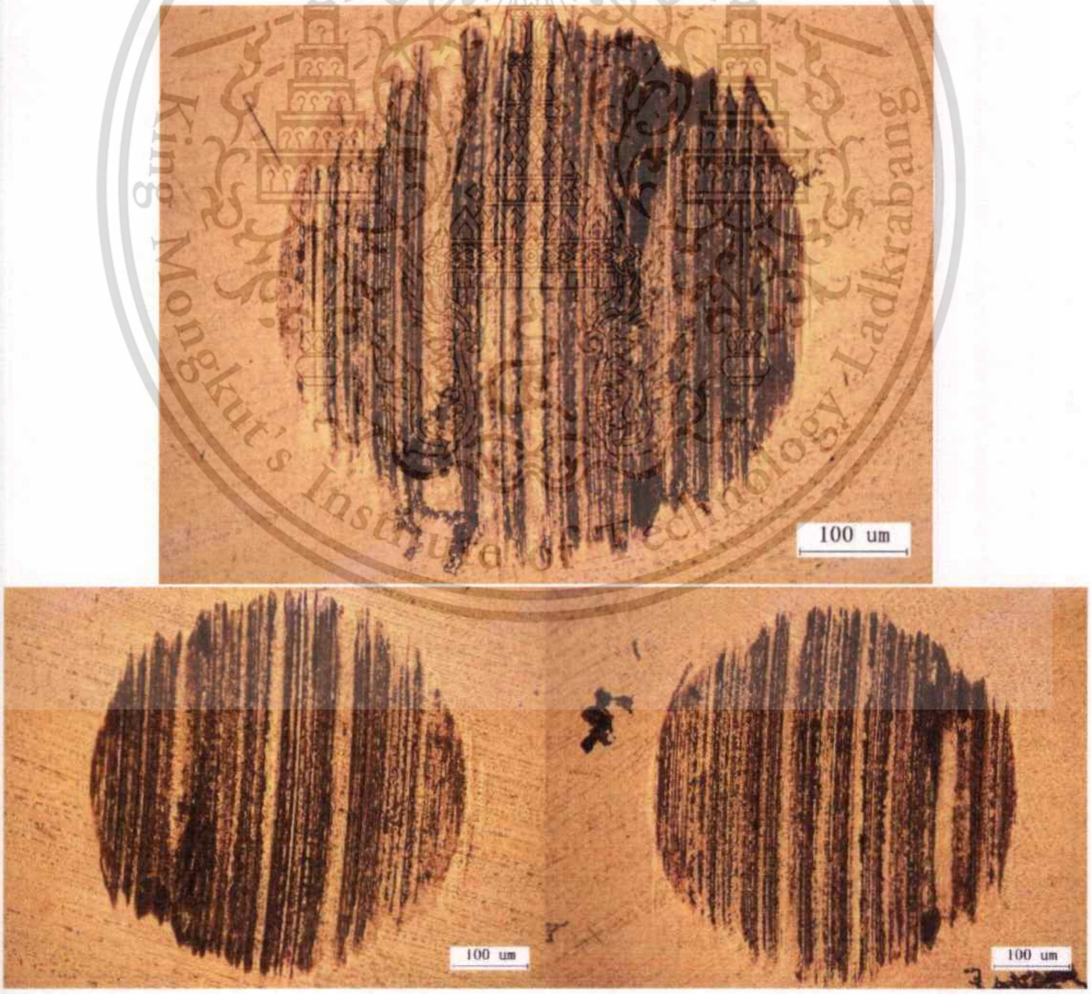
According to the four balls testing standard (ASTM D4172), the samples are tested at 75°C. The normal load applied is 392 N. Running time is 60 minutes. Below figure shows the wear position on the after tested steel ball. On the lower ball, wear is occurred like spot point. On the upper ball, wear is occurred like circular track.



Wear scar on steel ball tested with lubricant A

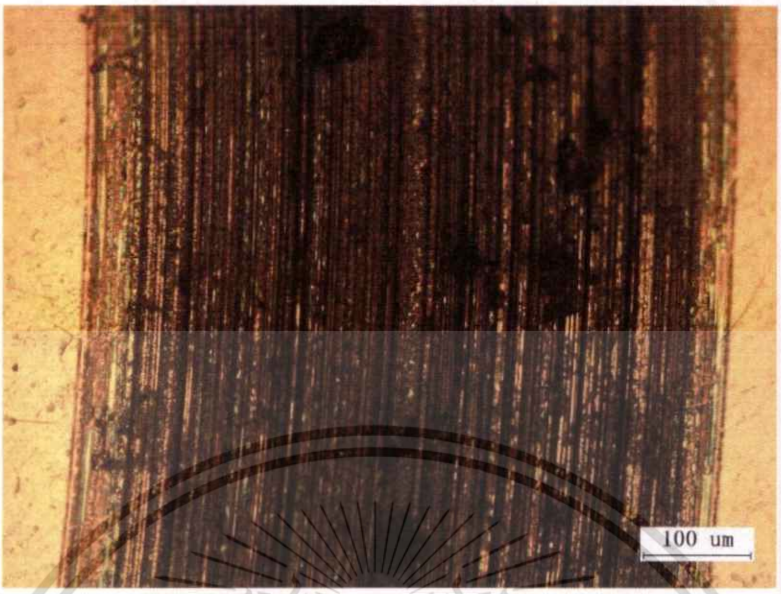


Wear track on upper ball

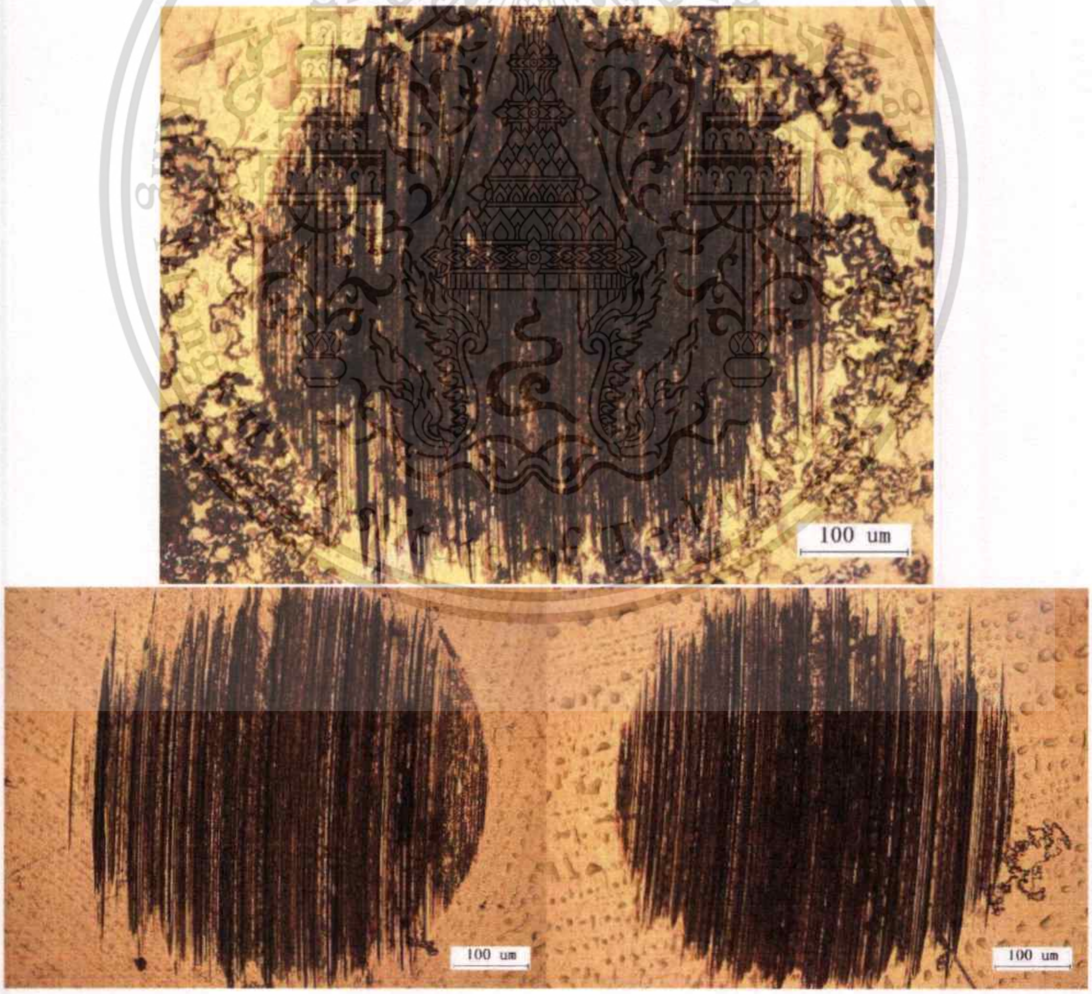


Wear scar on 3 lower balls (upper) ball #1, (lower left) ball #2, (lower right) ball#3

Wear scar on steel ball tested with lubricant A mixed carbon black

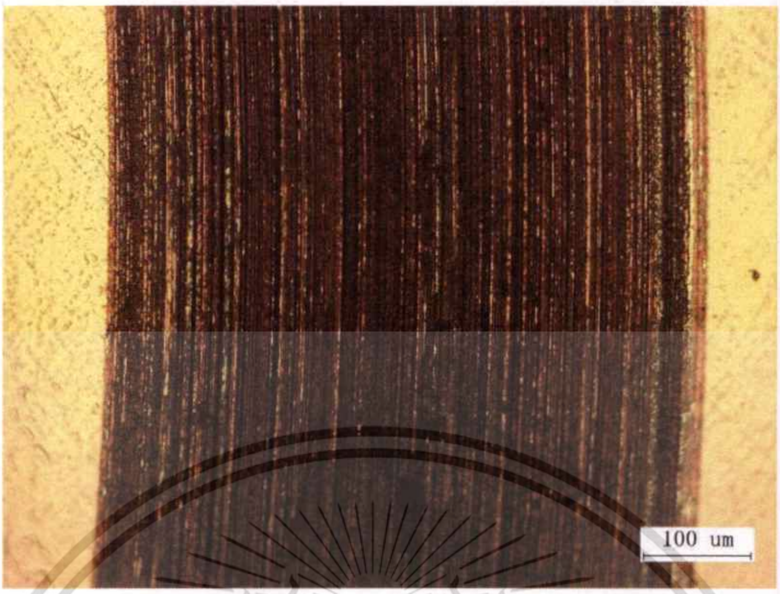


Wear track on upper ball

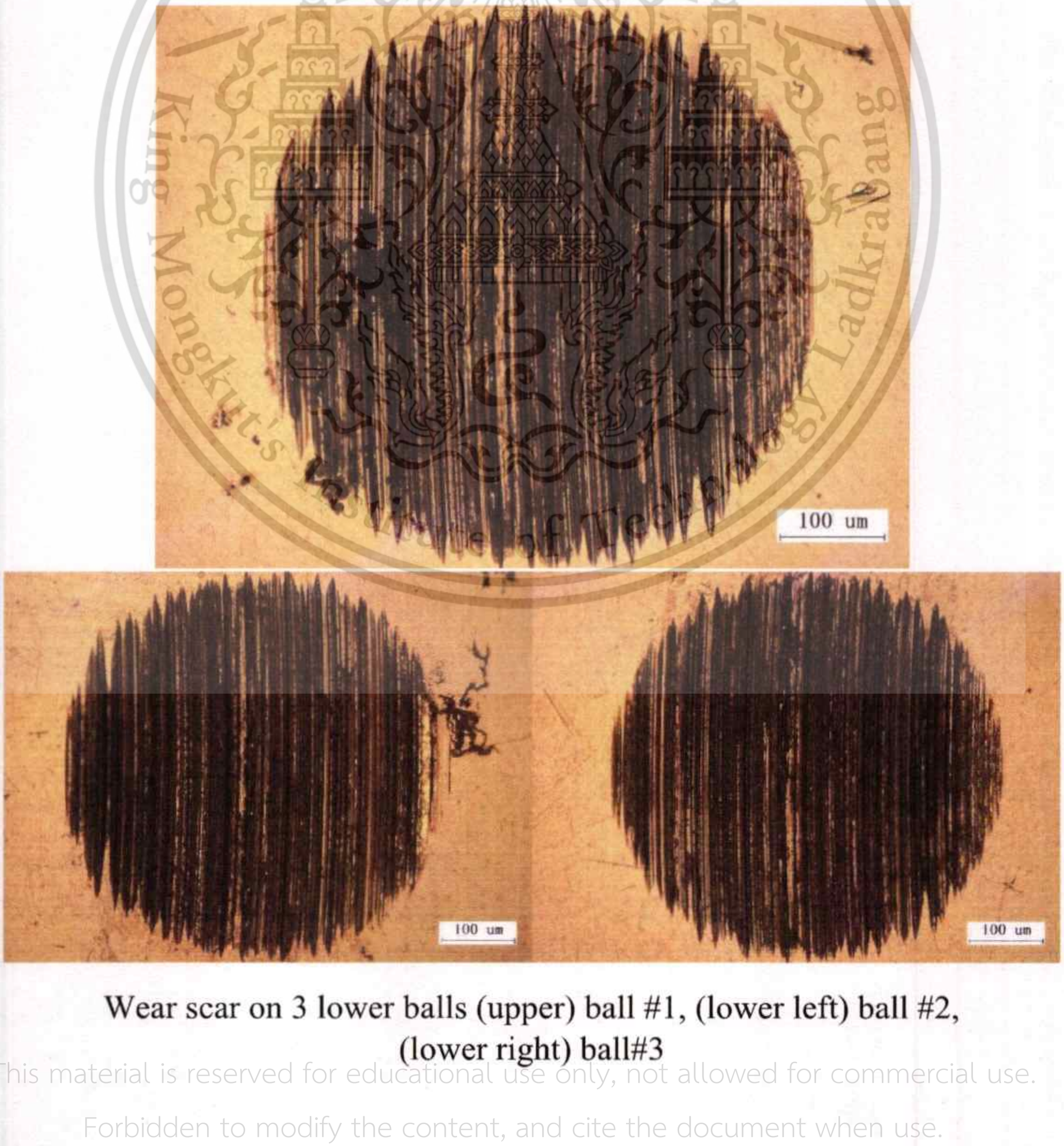


Wear scar on 3 lower balls (upper) ball #1, (lower left) ball #2, (lower right) ball#3

Wear scar on steel ball tested with lubricant B

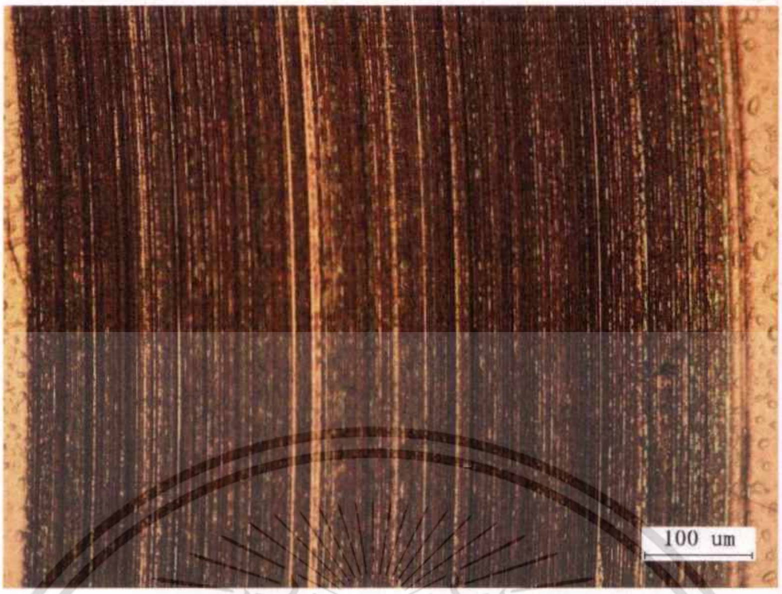


Wear track on upper ball

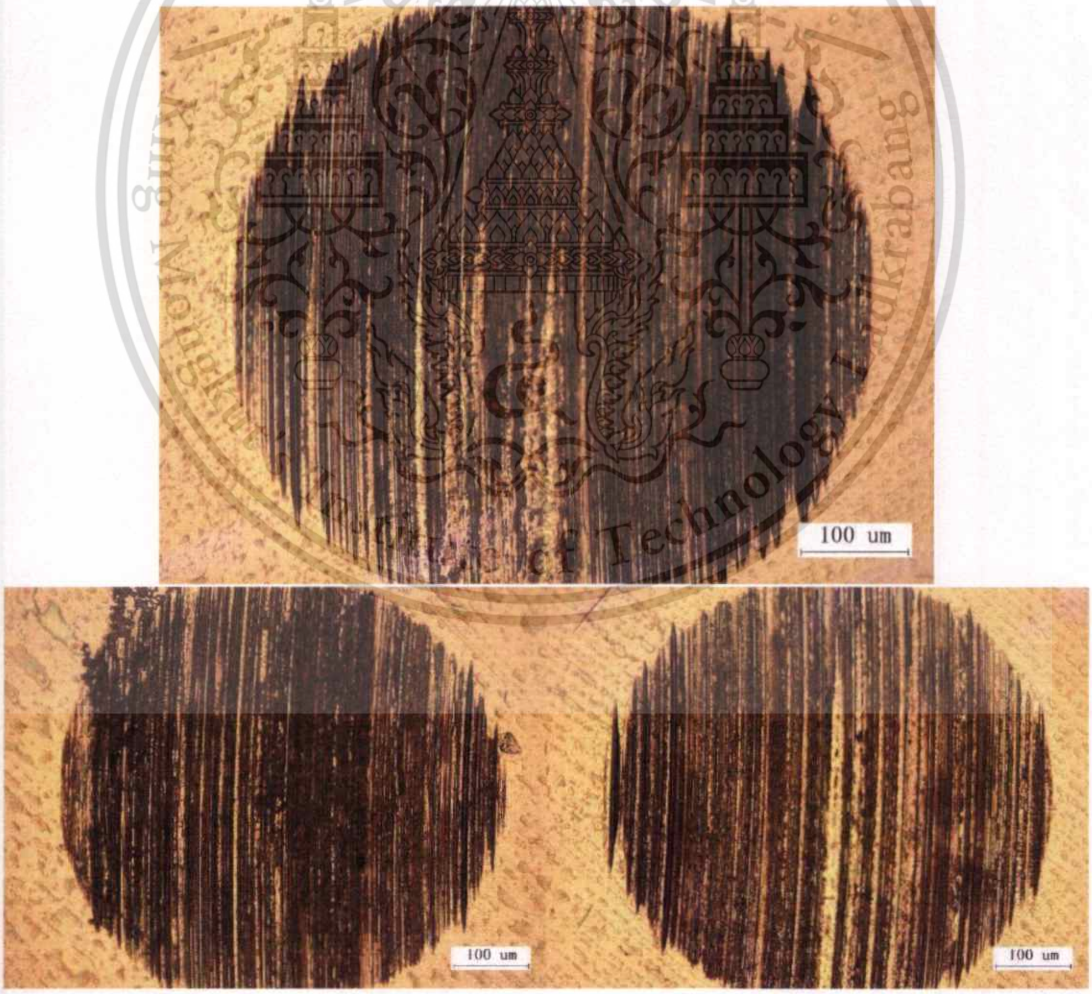


Wear scar on 3 lower balls (upper) ball #1, (lower left) ball #2, (lower right) ball#3

Wear scar on steel ball tested with lubricant B mixed carbon black



Wear track on upper ball



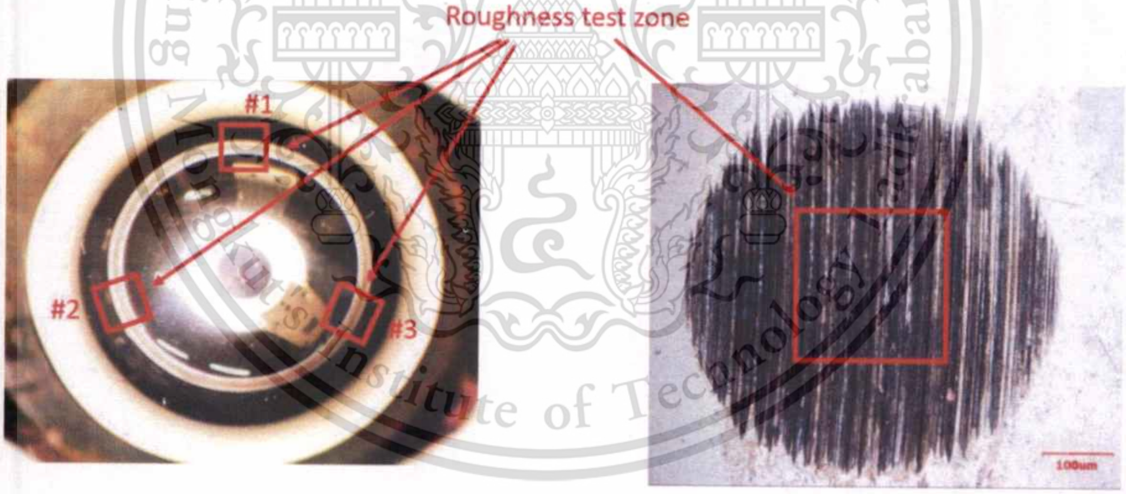
Wear scar on 3 lower balls (upper) ball #1, (lower left) ball #2, (lower right) ball#3

APPENDIX H

Roughness Test on Wear of Steel Balls Results

No.	Result List	Page
1	Steel ball testing with lubricant A	154
2	Steel ball testing with lubricant A mixed carbon black 1% wt.	155
3	Steel ball testing with lubricant B	156
4	Steel ball testing with lubricant B mixed carbon black 1% wt.	157

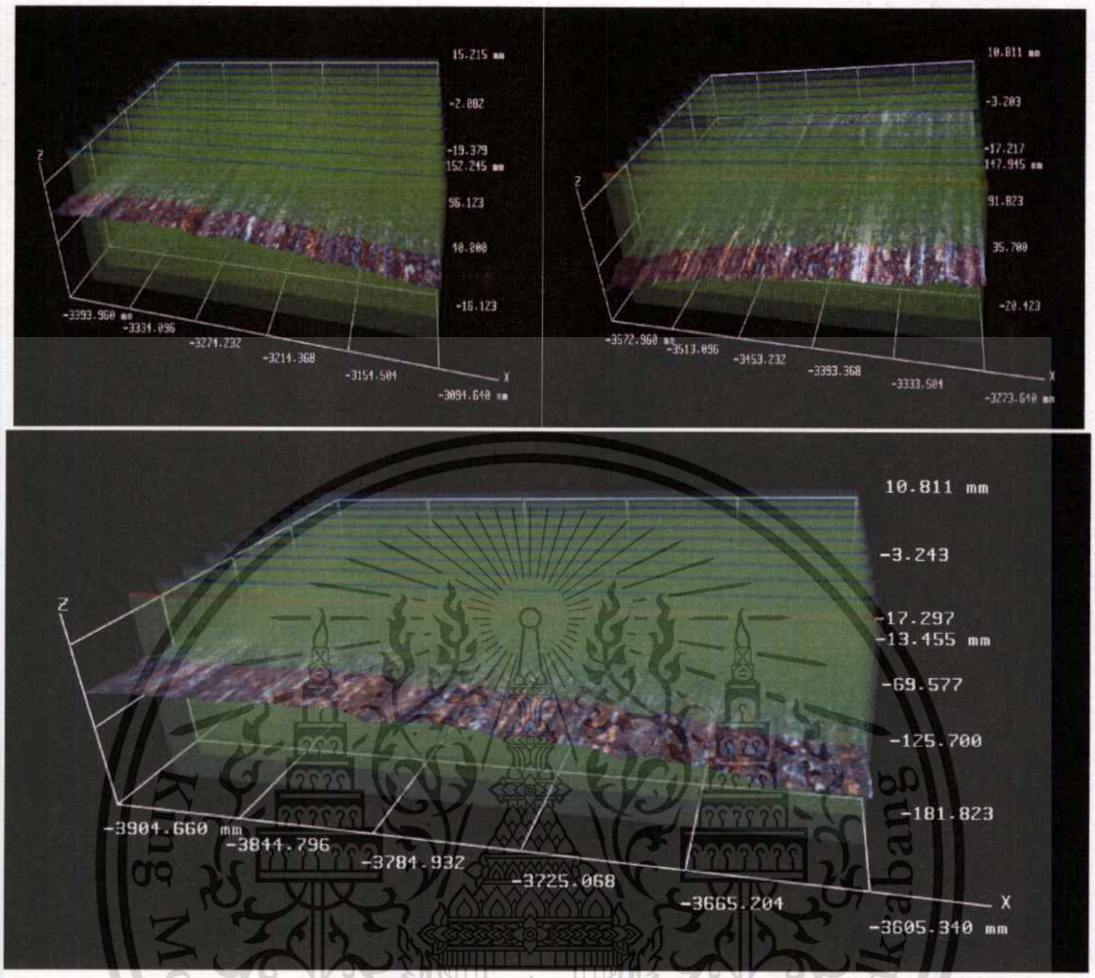
This objective is to measure the surface roughness of the balls after wear resistance testing according to ASTM D4172. The roughness was measured by optical microscopy in 3D mode. The wear scar presenting on the upper ball was circle. Thus, three areas as shown in left figure were analyzed the surface roughness. The analyzed area of the lower ball was shown in right figure.



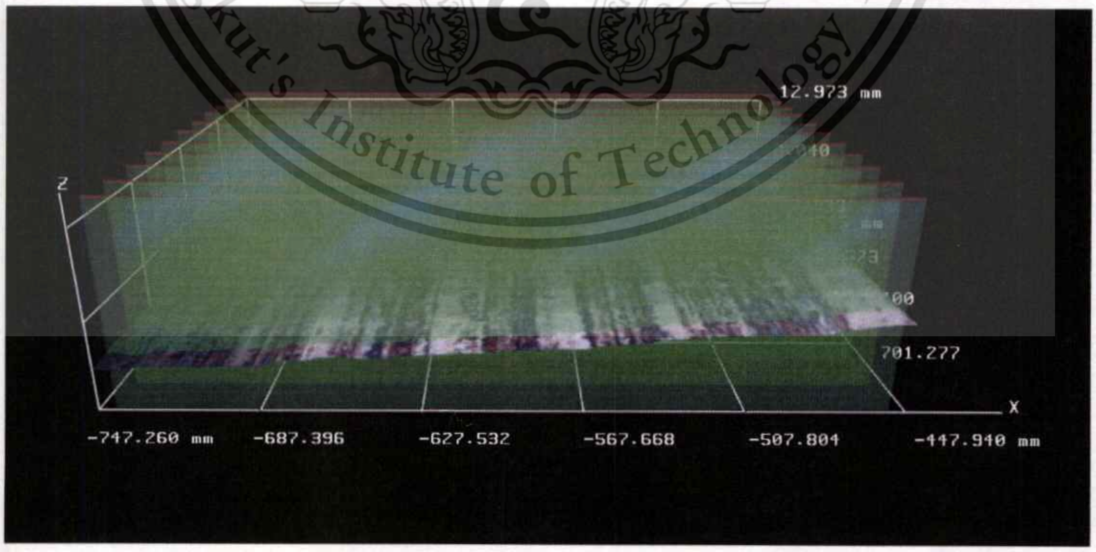
Upper ball

Lower ball

Roughness test of steel balls from testing with lubricant A

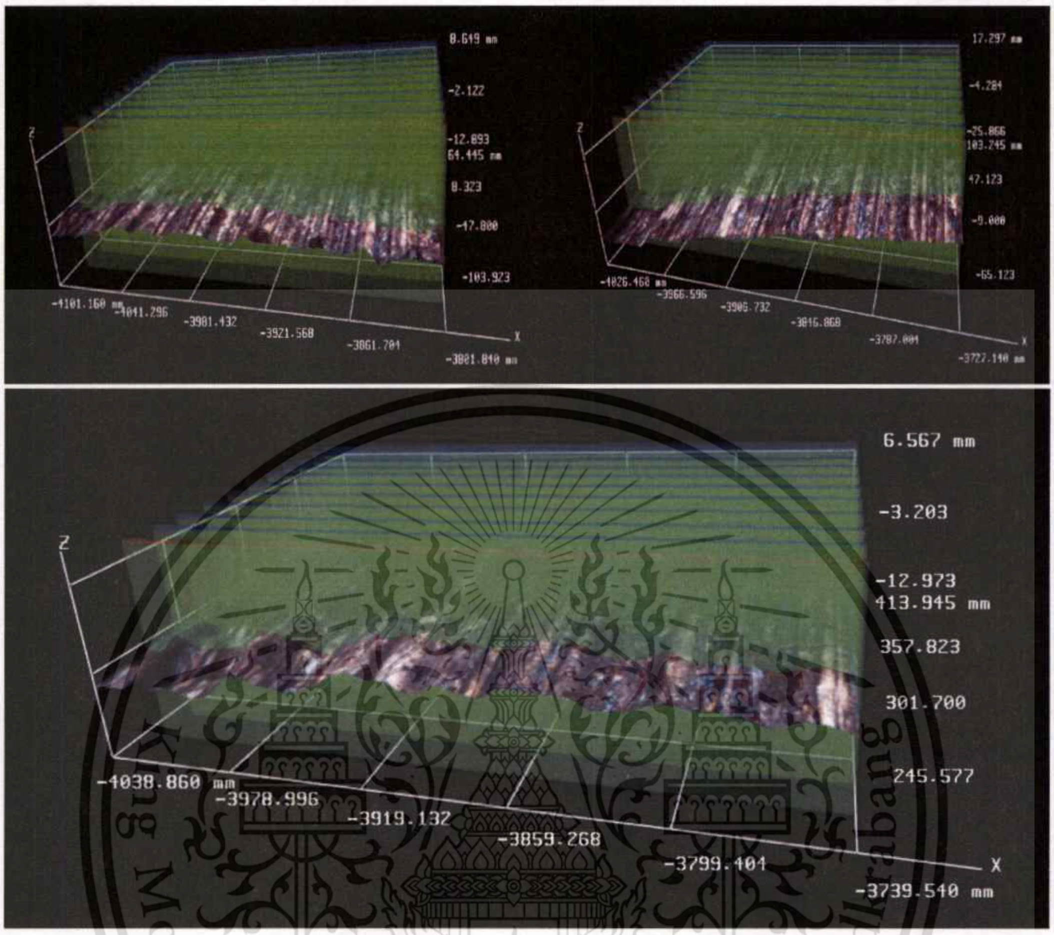


3D image roughness test of upper ball from 3 positions

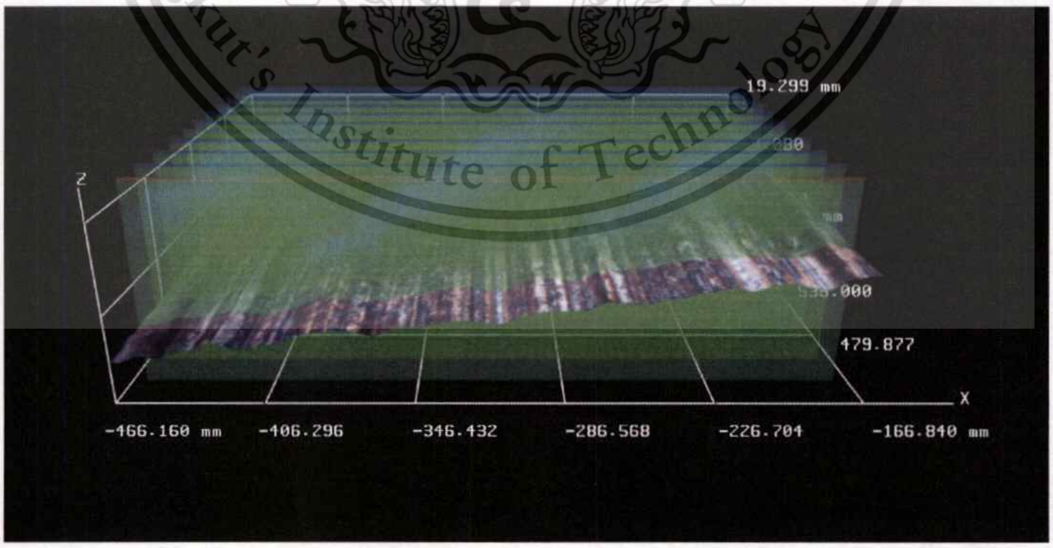


3D image roughness test of lower ball (ball #3)

Roughness test of steel balls from testing with lubricant A mixed carbon black

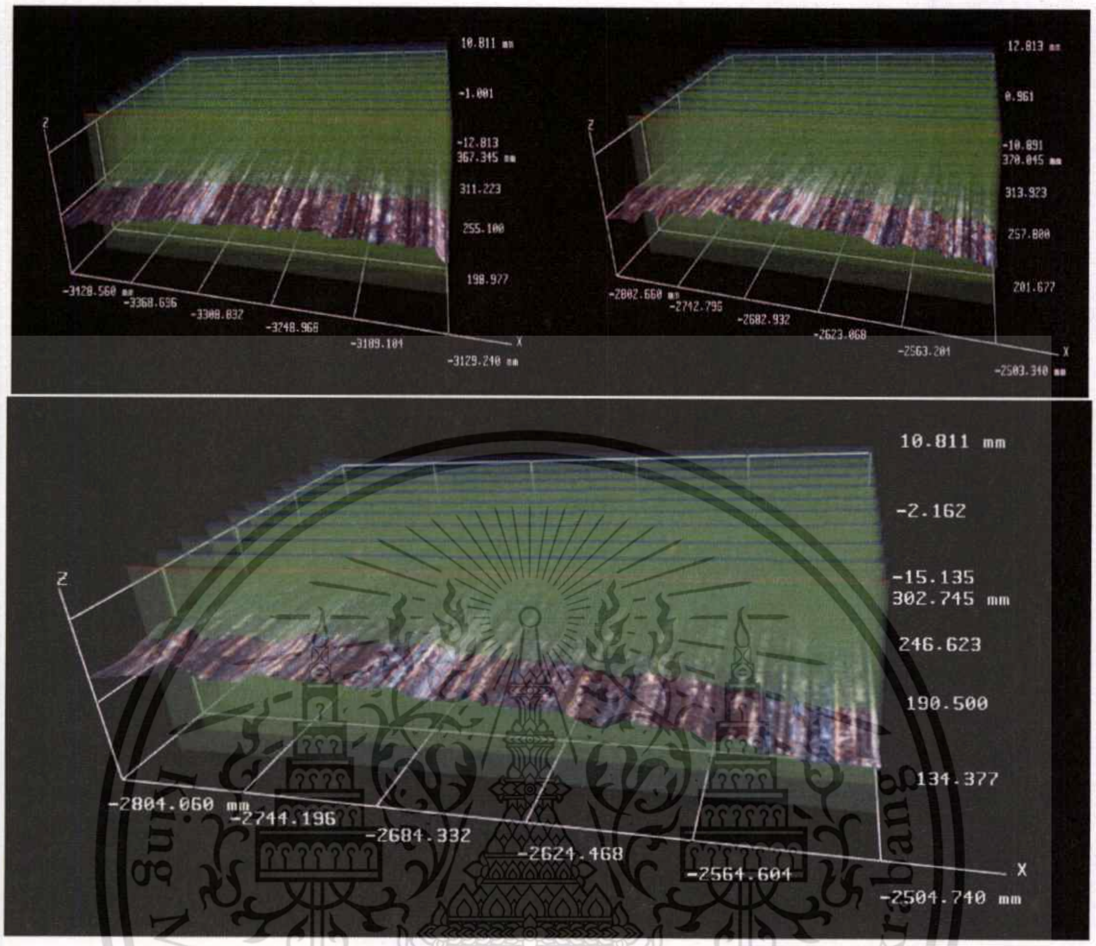


3D image roughness test of upper ball from 3 positions

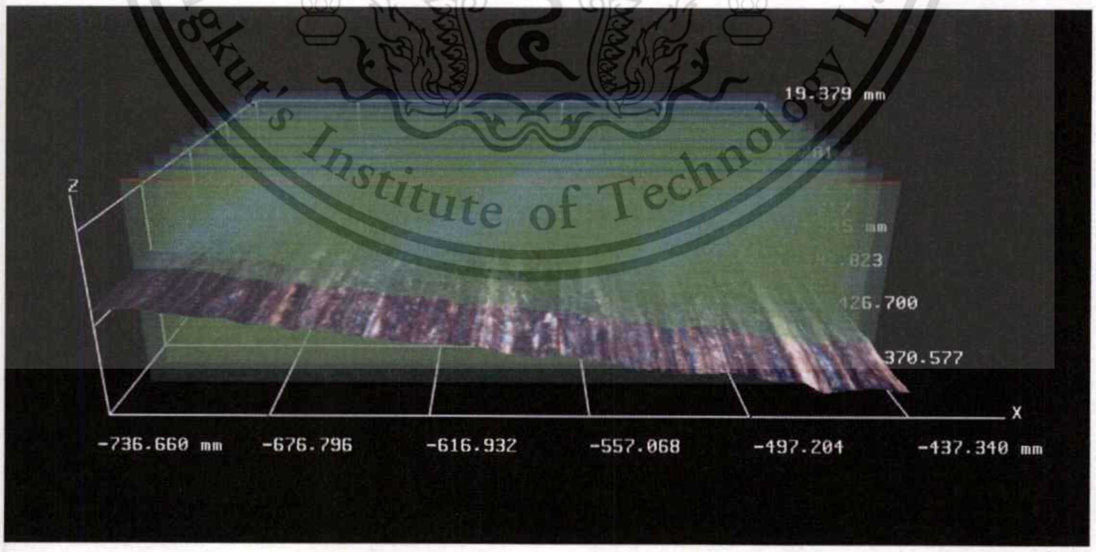


3D image roughness test of lower ball (ball #2)

Roughness test of steel balls from testing with lubricant B

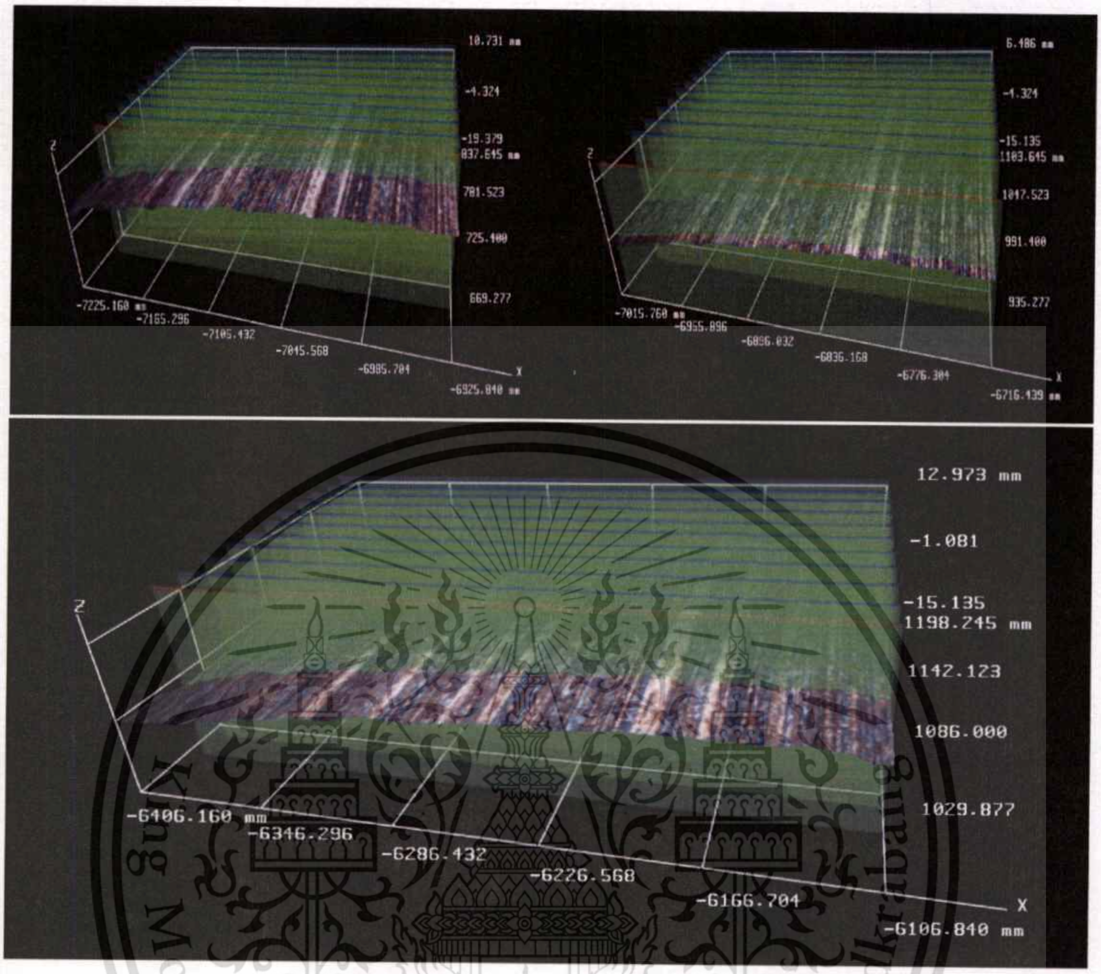


3D image roughness test of upper ball from 3 positions

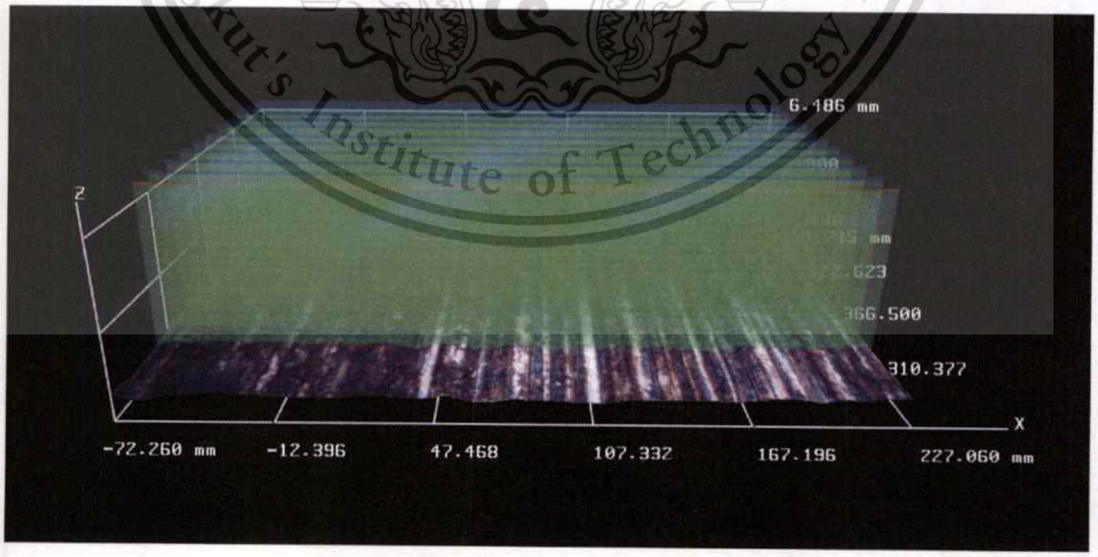


3D image roughness test of lower ball (ball #3)

Roughness test of steel balls from testing with lubricant B mixed carbon black



3D image roughness test of upper ball from 3 positions



3D image roughness test of lower ball (ball #2)

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Impact of Soot in Engine Lubricating Oil on Metal Wear using Four-Ball Testing

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ABSTRACT: This paper is a study of the characteristics of soot in the internal combustion engine affecting on the abilities of lubricating oil and leads to result in engine components wear. The tribological behavior was studied by means of a four-ball tribometer with friction and wear measured. This test method can be used to determine the relative wear preventive properties of lubricating fluid in sliding contract under the prescribed test conditions. Soot particle contamination was simulated using carbon black (CB). The candidate lubricants were two formulated engine lubricants for heavy duty diesel engine which have the viscosity grade as SAE 15W-40 and also blended with carbon black. Effects of oils with different additive on size distribution, morphology, and nanostructure of particles were studied. Transmission Electron Microscopy (TEM) was employed to study the morphology and nanostructure parameters of carbon black particles and agglomerated carbon black. The tribometer ball wear surfaces were analyzed by Optical Microscopy (OM). The results show that each lubricating oils blended with carbon black exhibits higher wear on tribometer ball than without carbon black. However, the contaminated lubricating oils seem to be lower friction than fresh oils.

KEY WORDS:heat engine, lubricating oil, tribology, Soot, Carbon Black, Four-Ball tribotest (A1)

1. INTRODUCTION

Soot particulate has a detrimental effect on the life of internal combustion engines. It has been disputed for a long time about soot behavior and continues to be of high interest to car manufacturers. Internal combustion engine produce soot as a result of incomplete fuel combustion. Ideally, complete combustion in cylinder would only produce carbon dioxide and water, but no engine is completely efficient.

Because of the way that fuel is injected and ignited, soot formation occurs more commonly in diesel than in gasoline engines. Unlike gasoline engines where the fuel/air mixture is ignited with a spark, fuel and air entering the diesel cylinder ignite spontaneously from the high pressure in the combustion chamber. The fuel and air mixture in diesel engines typically do not mix as thoroughly as they do in gasoline engines. This creates fuel-dense pockets that produce soot when ignited. While the majority of soot easily escapes through the exhaust, some gets past the piston rings and ends up in the lubricant oil.

From a number of literatures, we have been found the fact that the properties of soot particulate very much depend upon the thermodynamics of combustion in the engine. The structural complexity of soots varies depending on the type of engine and its operating conditions. Wentzel et al.(1) studied the primary particles of diesel engine under a single operating condition; only 5-7 aggregates were measured, and the average diameter of the primary particles was 23 nm. Park et al.(2) investigated the particle matter emissions of a four-cylinder diesel engine and calculated the average primary particle diameter as 32 nm. Lee et al.(3) concluded that the diameter changes at the range of 28-34 nm. Zhu et al.(4) found that the range is 20-35 nm with a nearly normal distribution. Wang et al.(5) studied the effect of lubricant oil additive on size distribution of diesel particulate matter, and they also found that the particle diameters are 20-25 nm.

The primary soot particles are 98 percent carbon by weight and typically spherical in shape. While most are only around 0.03 microns in size, they often clump together to form larger particles. Individual soot particles pose little risk to engine parts, but clumps of soot can cause damage. Dispersant additives in recent engine oils keep the individual soot particles from forming damaging clumps.

Until now, many conflicting, incomplete ideas and explanations about the properties and effects of soot particulates on the wear mechanism have been published. Some authors showed that soot is not abrasive but adsorb anti-wear additives, thus diminishing anti-wear properties. However, Ryason et al.(6) concluded that soot particles are abrasive because they were found to generate grooves and breakouts in metal surfaces. Ratoi and Spikes(7) showed that dispersed carbon black rapidly abraded

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additive reaction films. Gautam et al.(8) found more wear with soot contamination in the oil than without. Aldajah et al.(9) and Yamaguchi et al.(10) found that the presence of soot particles reduces the thickness of anti-wear films and act as an abrasive element. Truhan et al.(11) concluded their study that the chemical activity of soot particles and their reaction with additive prevents the formation of liquid boundary layers on metal surfaces.

Based on all conclusions from studied literatures, excessive soot levels in the oil could overwhelm the dispersant additives in engine oils. As the dispersants become depleted, the soot particles clump together, attach themselves to engine surfaces and lead to reduce lubrication due to impeded oil flow through the engine as well as through the oil filter. Esangbedo et al.(12) studied the characteristics of diesel engine soot that lead to excessive oil thickening. They concluded that severe oil thickening during a heavy duty diesel engine test is linked to soot agglomeration in the engine oil. The ineffectiveness of dispersant to retard particle growth is attributed to poor soot functionalization.

High oil soot levels can also lead to be a higher lubricant viscosity which impedes oil flow and increase engine wear. George et al.(13) found that the soot contaminating in lubricant change the chemical properties resulting in the lubricant creasing to perform its function. This causes an increase in viscosity of the engine oil causing pumpability problems. The performance of anti-wear lubricant additives can also be negatively impacted and lead to increase wear and premature engine failure.

Torbacke et al.(14) has written an introduction to tribological test methods that there are many reasons for carring out tribological tests or tribotest. One reason is to study the wear and friction mechanisms appearing in specific tribological applications. Other reasons are ranking of materials and lubricant for existing equipments or selection of materials and lubricant for new applications. Tribotesting may also be performed for general, application independent, characterization of wear and friction.

To understand how soot behave to engine metal suface, tribological test has been an our focus.

It can be concluded from the literature that the wear mechanism induced by the presence of soot is not fully understood yet. More fundamental knowledge is needed. Thus, the properties of soot and their influence on wear and also friction were in the focus of our studies.

Table 1 Properties of Experimental Lubricant

Properties	Unit	Experimental Lubricant	
		A	B
Oil Condition			
- Viscosity@40°C	[cSt]	111.9	101.8
- Viscosity@100°C	[cSt]	14.3	14.4
- Oxidation	-	6.0	4.4
- Nitration	-	3.3	3.9
- TBN	[mg KOH/g.]	10.7	10.4
- Flash Point	[°C]	200	210
Contamination			
- Water	[% Wt.]	0.080	0.072
- Fuel	[% Wt.]	0.00	0.00
- Soot	[% Wt.]	0.00	0.00

2. EXPERIMENTS

2.1 Experimental Lubricants

In this study, there were two lubricating oils used for the tribological tests, lubricant A and lubricant B, which are different by the factors of additive elements from each other. They are the formulated lubricants for using in heavy duty diesel engine which has the standard viscosity grade as SAE 15W-40. Before going to test, note that these oils were tested to get the several properties as presented the results in Table 1. For oil conditions, the viscosity value was conducted by ASTM standard method number D-445, total base number and flash point value were investigated by D-4739 and D-5828 respectively. Additionally, Fourier Tranform Infrared Spectroscopy (FTIR) was used for detecting oxidation and also nitration. For oil contamination, water, fuel and important soot were also tested by the method of FTIR and has been shown the results in form of percentage of weight concentration.

As shown in Table 1, two experimental lubricants have a little difference in all oil properties, thus they might be assumed as they are only different in additive elements and they are fresh clean oils and also have no soot contamination at initial.

In Four-ball tribological testing, to study the impact of soot on engine wear, four lubricating oil samples were prepared. Two samples are fresh oil from lubricant A and B, another two samples are the oils which was contaminated with carbon black at 1% by weight concentration.

2.2. Soot Concentration in Practical Condition

To determine the value of soot contamination in real situations, lubricant A was studied by testing in practical heavy duty diesel truck. The truck was not attempted to control the environmental conditions such as age of engine, route, driver's behavior and so on, because the objective of this case study is to determine the possibility of soot contamination.

While the practical test was operating, lubricating oils from truck's engine were sampled 100 cc for investigating soot contamination by using FTIR. The results of this real condition test would show the amount of soot concentration during truck working and at end of 30,000 km.

2.3 Carbon Black Properties

Nowaday, a wide variety of synthetic carbon black very different in size and structure are commercially available. In this study, a commercial carbon black was used as representative of practical soot particulate. Furthermore, size distribution, morphology and nanostructure of carbon black particles were studied. Transmission Electron Microscope (TEM) was employed to investigate morphology and nanostructure parameters of primary carbon black particles and also agglomerate particles. The main target is to define the major size of these commercial carbon black particulates.

2.4 Four-Ball Tribology Test

The Four-Ball testing is one of the tribological test methods. This test method can be used to determine the relative wear preventive properties of lubricating fluid in sliding contact under the prescribed test conditions. No attempt has been made to correlate this test with balls in rolling contact[15]. The illustration of principle for a Four-Ball set-up is presented in Figure 1.

As Figure 1, The Four-Ball tribotest is a versatile test for evaluating seizure and wear. The upper holder has one rotating steel ball, which is loaded against three stationary lower steel balls. All contact areas are drowned in the test lubricant. The load can be applied by using deadweight or through a hydraulic system. The rotation is central along the symmetry axis of both the upper and the lower holders. Circular wear scars will appear on the lower balls, while a circular wear track will appear on the upper ball.

In this study, four lubricating oil samples (fresh lubricant A, fresh lubricant B, contaminated lubricant A with carbon black, contaminated lubricant B with carbon black) were tested via using this tribotest method as follow the ASTM standard number D-4172.

Three 12.7 mm diameter steel balls are clamped together and covered with the lubricating oil sample to be evaluated. A fourth 12.7 mm diameter steel ball, referred to as the top ball, is pressed with a force of 392 N into the cavity formed by the three clamped balls for three-point contact. The temperature of the test sample is regulated at 75°C and then the top ball is rotated at 1200 rpm for 60 min. Lubricating oil samples are compared by using the average size of the scar diameters worn on the three lower clamped balls and friction torque is also measured. The wear scar results are observed by Optical Microscopy (OM).

3. RESULTS AND DISCUSSION

In this section, there are the results divided by aims of study and tools used. As of testing in practical engine, the results has been shown in topic soot in used lubricating oil. Nanostructure of carbon black was performed by using TEM. Finally, there were the discussions of tribological test results.

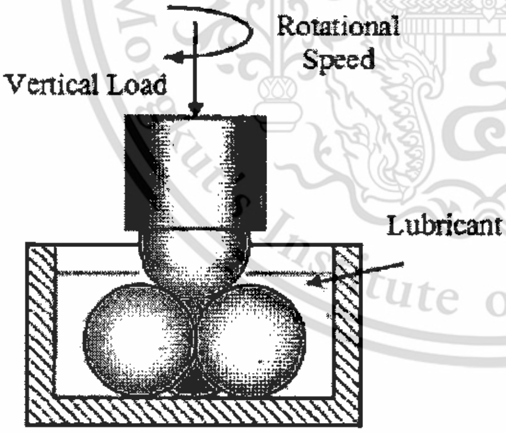

Fig.1 Four-Ball tribotest schematic

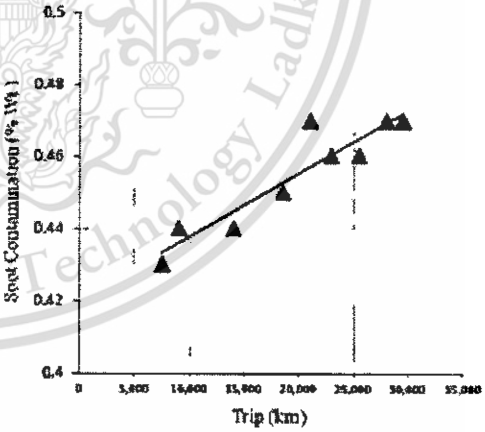

Fig.2 Soot contamination in heavy duty diesel engine

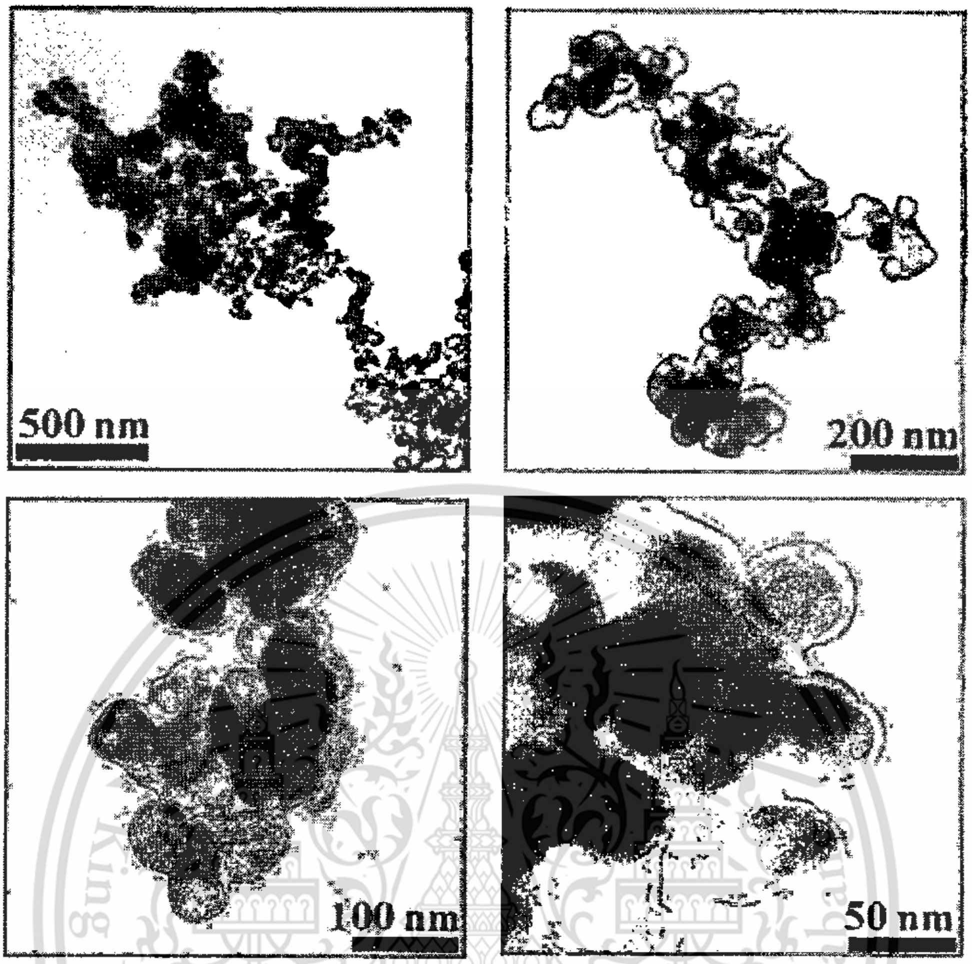

Fig.3 TEM image at varity of magnification

3.1 Soot in Used Lubricating Oil

After testing lubricant A on heavy duty diesel engine truck long lasting 30,000 km, the results have been shown on the graph in Figure 2. The graph showed the amount of soot that concentrate in lubricating oil over the period of route trip. For lubricant A, it was grow up from 0.43 at first sampling (at 8,000 km) to 0.47 %wt at the end of test (about 30,000 km). Soot in lubricant might come from both inside operating in engine and outside such as air. However, the main target of this case study is to determine the amount of soot after running by pratical engine and it has been already exhibited the fact that soot was around 0.40 -0.50 in percentage by weight concentration.

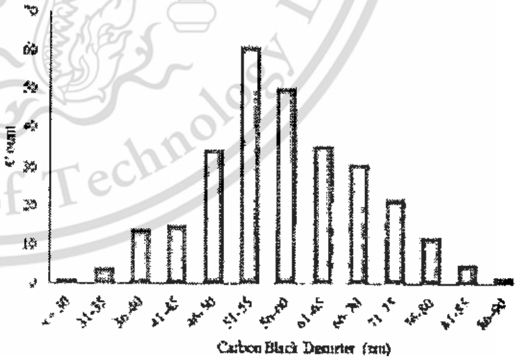

Fig.4 Carbon black size distribution

3.2 Transmission Electron Microscope (TEM)

The images shown in Figure 3 illustrate typical soot agglomerates from commercial carbon black sample prepared using the ethanol solvent extraction technique and put it on copper grid plate. The agglomerates have a branching structure and typically fall in the size range 30-700 nm. Figure 3 consisted of 4 types of image which vary by the magnificant of microscope. The most rough one was captured the outlook view of large soot or carbonblack agglomerates with a scale at 500 nm.

These images of carbon black are quite difficult to measure the primary size of single particle because they are stacking together, so we cannot determine diameter of all particulate. The idea is just only measure some of them that stay at border and clearly appear.

Finally, 286 primary carbon black particulates were measured and the result of all measuring has been plot on bar chart as a histogram graph in Figure 4. An average size is 58 nm. The minimum size and maximum size are 30 nm and 87 nm respectively with stadard deviation of 11 nm. The highest peak on histogram graph is at the rage of 51 - 55 nm in size. As of dividing size range with standard deviation value, the major particles are fallen in the size range 46 - 70 nm which are accounted for 74% of 286 particulate samples. Moreover, a number of smaller size and bigger size than major one are 14% and 12% respectively. This result differed from all reviewed literatures in the introduction section. They all got the primary size of soot near to 30 nm which contradict to this result showing that major size is near to 58 nm. It could be an effect from carbon black production process. When carbon black is produced in high temperature and high pressure atmosphere, it may become smaller in size than the particle which is conducted in room atmosphere.

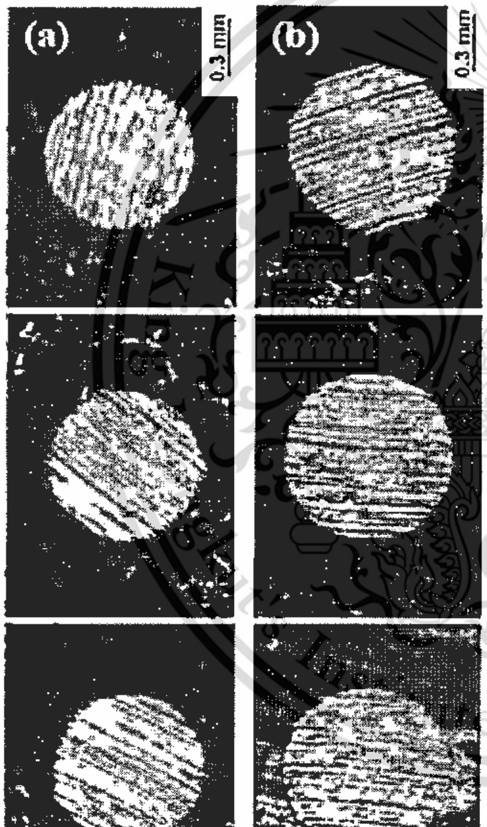

Fig.5 Wear on metal balls testing in (a) lubricant A, (b) lubricant A with carbon black

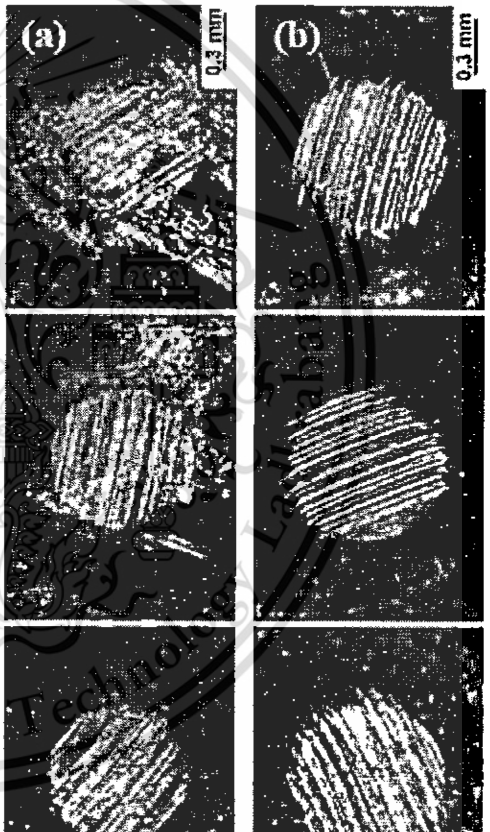

Fig.6 Wear on metal balls testing in (a) lubricant B, (b) lubricant B with carbon black

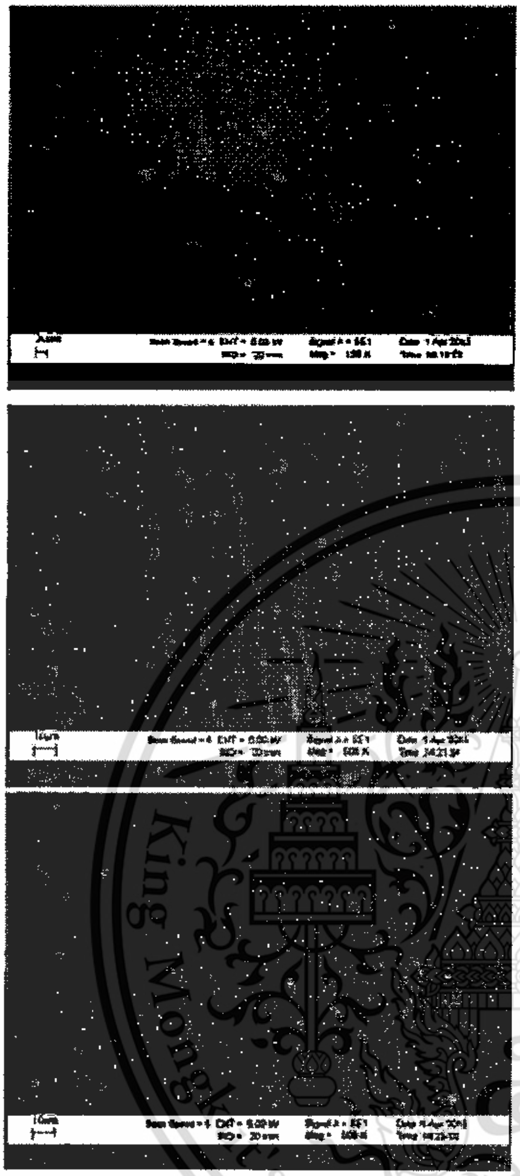

Fig. 7 SEM image of wear on metal ball

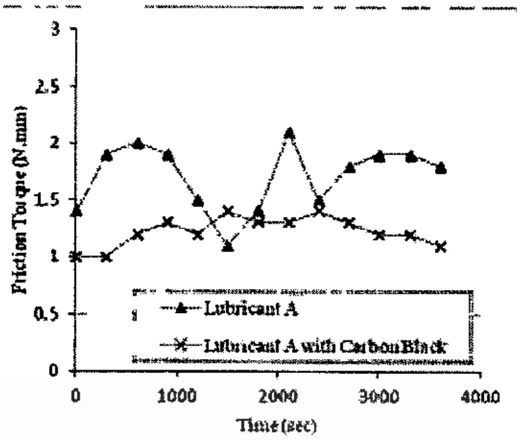

Fig. 8 Friction torque on testing with lubricant A

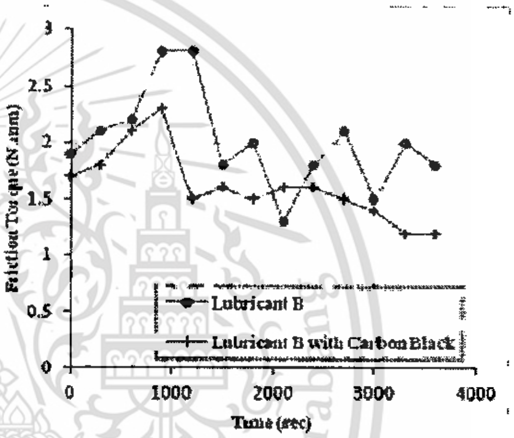

Fig. 9 Friction torque on testing with lubricant B

3.3 Wear and Friction

The wear scar diameter was measured under microscope, at 30X magnification. Figure 5 shows the microscopy image of wear scars found on three lower balls after 60 min running time in lubricant A without carbon black (on left hand side) and lubricant A with carbon black (on right hand side). The results showed that wear diameter of three metal balls in case of testing with soot are larger than wear diameter of three balls without soot. Similarly, wear diameter of three balls in lubricant B with soot are larger than wear diameter of three balls without soot, as shown in Fig. 6. Wear edge shape of balls in lubricant A are quite smoother than shape of balls in lubricant B. The average wear diameter of balls in case of testing in lubricant A is 786.3 microns and in lubricant A with soot is 877.3 microns. In case of lubricant B, the average of wear diameters are 723.5 and 790.6 microns for case without soot and with soot respectively. Eventhough they are same vicosity grade, wear shapes are a little bit different.

In addition, Scanning Electron Microscopy (SEM) was used to characterize shape of wear with 130X and 500X magnification for more deeply understanding. Figure 7 shows SEM image of one ball sample after test. It has presented the width of each wear tracks apploximately 5-10 microns.

Figure 8 and Figure 9 show the friction torque. The value of friction torque is very low. The sample with soot seem to be lower friction torque than the sample without soot for both cases. The average friction torque in testing in lubricant A is 1.708 N.mm and the average friction torque in testing in lubricant A with soot is 1.223 N.mm. In lubricant B, the average friction torque in case none soot and mixed with soot are 2.008 and 1.615 N.mm respectively.

4. CONCLUSIONS

Carbon black was contaminated in two conventional 15W-40 engine lubricating oils and tested in Four-Ball Tribotest for evaluate wear behavior. The results showed that carbon black could lead to resulted in increase wear diameter. However, carbon black might act as a sphere ball between metal surfaces and it might cause lower friction. The impact of soot concentration and soot diameter on wear phenomina and friction would be further investigation.

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REFERENCES

(1) M. Wentzel, H. Gorzawski, K.H. Naumann, H. Saathoff, S. Weinbruch: Transmission Electron Microscopical (TEM) and Aerosol Dynamical Characterization of Soot Aerosols: Aerosol Science, 34, p.1347-1370 (2003).

(2) K. Park, D.B. Kittelson, P.H. McMurry: Structural Properties of Diesel Exhaust Particles Measured by Transmission Electron Microscopy - Relationships to Particle Mass and Mobility: Aerosol Science and Technology, 38, p.881-889 (2004).

(3) K.O. Lee, R. Cole, R. Sekar, M.Y. Choi, J.S. Kang, C.S. Bae, H.D. Shin: Morphological Investigation ofthe Microstructure, Dimensions, and Fractal Geometry of Diesel Particulates: Proceedings of the Combustion Institute, 29, p.647-653 (2002).

(4) J. Zhu, K.O. Lee, A.Yozgatligil, M.Y. Choi: Effects of Engine Operating Conditions on morphology, Microstructure, and fractal geometry of Light-Duty Diesel Engine Particulates: Proceedings of the Combustion Institute, 30, p.2781-2789 (2005).

(5) Y. Wang, X. Liang, G. Shu, X. Wang, X. Sun, C. Liu: Effect of Lubricant Oil Additive on Size Distribution, Morphology, and Nanostructure of Diesel Particulate Matter: Applied Energy, 130, p.33-40 (2014).

(6) P.R. Ryason, I.Y. Chan, J.T. Gilmore: Polishing Wear by Soot: Wear, 137, p.15-24 (1990).

(7) M. Ratoi, H.A. Spikes: The Influence of Soot abd Dispersant on ZDDP Film Thickness and Friction: Lubrication Science, 17, p.25-43 (2004).

(8) M. Gautam, K. Chitoor, M. Durbha, J.C. Summers: Effect of Diesel Soot Contaminated Oil on Engine Wear - Investigation of Novel Oil Formulations: Tribology International, 32, p.687-699 (1999).

(9) S. Aldajah, O.O. Ajayi, G.R. Fenske, I.L. Golblatt: Effect of Exhaust Gas Recirculation (EGR) Contamination of Diesel Engine Oil on Wear: Wear, 263, p.93-98 (2007).

(10) E.S. Yamaguchi, M. Untermann, S.H. Roby, P.R. Ryason, S.W. Yeh: Soot Wear in Diesel Engines: Proc. IMechE, 220, p.463-469 (2006).

(11) J.J. Truhan, J. Qu, P.J. Blau: The Effect of Lubricating Oil Condition on the Friction and Wear of Piston Ring and Cylinder Liner Materials in a Reciprocating Bench Test: Wear, 259, p.1048-1055 (2005).

(12) C. Esangbedo, A.L. Boehman, J.M. Perez: Characteristics of Diesel Engine Soot that Lead to Excessive Oil Thickening: Tribology International, 47, p.194-203 (2012).

(13) S. George, S. Ball, V. Gautam, M. Gautam: Effect of Diesel Soot on Lubricant Oil Viscosity: Tribology International, 40, p.809-818 (2007).

(14) M. Torbacke, A.K. Rudolphi, E. Kassfeldt: Lubricants:Introduction to Properties and Performance: John Wiley & Sons, First Edition (2014).

(15) Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method): An American National Standard.