The Effect of Surfactant in Lubrication

By

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Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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Approved by,

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified source or persons.

JUMAATUL SAADIAH BT IMAM MAAROF

ABSTRACT

The Effect of Surfactant in Lubrication has been chosen as the title for final year project. The main objective of this project is to find the alternatives to regenerate the used lube oil so that the regenerated oil will have a middle quality between the new oil and used one. Besides that it is necessary to study the can-be-measured chemical and physical properties of the lube oil such as volatility, Total Acid Number (TAN), density, viscosity, detergency and dispersancy. The properties of used lube oil will be determined and it will be compared to the properties of new lube.

Through out this project paper, the definition of lubrication and surfactant will be defined in detail. It covered the principle of lubrication, explanations about the main components exist in lubricant, the system of surfactant in lubrication, how the good lubricant is defined and lastly the several alternatives to generate the used oil. Generally there are two main methods to regenerate the used lube oil. First is by reconditioning and second is by re-refining. Reconditioning is a mechanical separation to remove the solid contaminant from the used oil. Meanwhile re-refining is a method which intent to turn the used oil to the base oil.

To meet the project's objectives, 3 tests/experiments have been done to analyze the properties of the lube oil. There are Total Acid Number (TAN) test, viscosity test and density test. The methodology of the tests can be reviewed in Chapter 3. The 3 tests were done onto 3 different types of lube oil (used and unused). According to the result of the experiments, 2 samples indicate the viscosity and density of the lube oil will decrease after being used. Meanwhile for the TAN test, 2 samples show the greater value of used oil compared to unused.

The expected result for oil regeneration is the value of regenerated oil will lie between the values of used's and unused's. However based on the tests done onto the regenerated oil (mixture of used and unused oil), the result failed to develop a trend which can be referred to. The failure perhaps because of error occurred during the experiment, sample's problem and inappropriate test which under certain circumstances the test can not detect the improvement/change of the lube oil.

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First and foremost, I would like to express my "syukur" to ALLAH S.W.T. for giving me strength, hope and spirit to do this project with patience and joy. Without HIS help, I will not be able to complete my project within the time given.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Lubrication has been practiced for thousand years ago. Since 17^{th} century the science began with the development of bearings and axles. Only in the early 21^{st} century the application on automobile and steam engine started to become one of attractive technology due to the wide application.[1] Rapid advancement in automotive and instrumentations leads the growth of lubricating technology. Since lubricant is the key component in the lubrication system, many researchers interested in finding the alternatives on how to manipulate the lubricant compound in order to maximize its performance by inventing new formulation. Two basic components in lubricant are based oil and chemical additive. The additive behaves like a surfactant and it is used to overpower the performance of based oil. Besides focusing on the way how to improve the lubricant technology, peoples are not supposed to take the generation of used lube oil for granted. The high price of oil and the increasing of concern toward the environmental effect have resulted in effort for regeneration of used lube oil. An effort should be given to find the alternatives way to treat the hazardous waste. The used lube oil can be reduced, reused, regenerated or recycled in order to control the disposal.

1.2 Problem Statement

Oil and other petroleum-based motor products are a complex mixture of several hundred different organic chemicals, petroleum hydrocarbons, additives, and contaminants with varying physical, chemical, and toxicological properties. Many of these chemicals are toxic or carcinogenic and thus pose a threat to human health through skin contact or consumption of contaminated drinking water supplies. The lubricant oil, after being used in the car's engine has picked up concentrated levels of potentially toxic elements such as chromium, lead, phosphorous, magnesium copper, zinc, silicon, iron, and calcium. Thus by regenerating the used oil into once-again reusable lubricant oil offers a significant means of reducing pollution and protects the environment. The quality of reusable lubricant oil will be not as good as the new lubricant oil however it will be better than the used lubricant oil. The reusable lubricant oil can be applied to the lubricating system which requires less efficiency such as simple cutting machine. Various methods applicable to perform the regeneration process. Besides removing soot and other contaminant, it is necessary to study the affect of surfactant towards the used lube oil.

1.3 Objectives and Scope of Work

Generally the objectives of the project are:

- To study the measurable properties of lubricant oil such as viscosity, volatility, density and Total Acid Number (TAN).
- To compare the performance of measurable properties of used and unused lubricant oil.
- To find appropriate additive for used lube oil regeneration.
- To regenerate the used lube oil that has middle quality between used and unused lubricant oil, so that it will be used for simple lubrication system.

The first stage of study will focus on the identifying the measurable properties of used and unused lubricant oil. Then it will proceed to the determination of appropriate method that can be used to enhance the quality of used lubricant oil.

CHAPTER 2
LITERATURE REVIEW

2.1 Lubrication

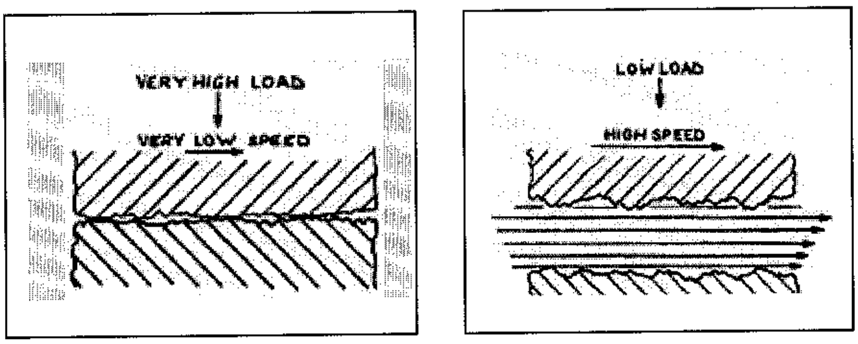
Lubrication system consists of two surfaces under load with the lubricant place in between.[1] When there are two surfaces under load slide over each other, there will be a friction which resists the sliding action. Two principles applied in the lubrication system: fluid to generate hydrodynamic and hydrostatic pressure to support the load thus avoiding contact between the surfaces (hydrodynamic lubrication) and the second principle is when the contact is inevitable; chemistry is used to generate a sacrificial film to protect the surfaces from shear stresses which effected by rubbing and abrasion (boundary lubrication). [1],[2]

2.1.1 Hydrodynamic Lubrication

Hydrodynamic lubrication happen when the motions of the surfaces are relatively quickly provided sufficient lubricant is present. Thus, the oil will drag between the surfaces. One surface is forced move smoothly of the other due to the upward lift generated by pressure within the lubricant film. The generation of sufficient lift results the surfaces are separated enough to ensure no surfaces contact happen. The regime is also known as elastohydrodynamic regime (Figure 2.1(b)). Within this regime the ability of the fluid to support the load is directly related to the viscosity and the relative speed.[1],[2]

2.1.2 Boundary Lubrication

Under the high load/low speed condition, boundary chemical film from chemical additive are used to generate protective thin film to protect the surfaces from inevitable rough contact. The chemical film created because the temperature is high enough to allow the reaction between lubricant (additive) and the metal surfaces. Commonly the boundary lubrication occurs when the lubricant starts to fill the space between the surfaces and at the moment the load supported by the surfaces is high (Figure 2.1(a)).[1],[2]



(a) (b)

Figure 2.1 Lubrication system (a) Boundary Lubrication (b) Hydrodynamic Lubrication

2.2 Lubricant

Lubricant is defined as the substance introduced between two moving surfaces to reduce the friction and wear between them. Almost 90% of the lubricant is based oil and remaining is the chemical additive. The physical properties (i.e viscosity, density, heat capacity and volatility) and chemical properties (i.e detergency, dispersancy, antiwear and antioxidant) are controlled by the composition of the based oil and some others are controlled by the chemical additive exist in the lubricant.[1]

2.2.1 Based Oil

Based oils are a mixture of various fractions from the crude oil refining process. The primary function of the refineries is to add value to crude oil by splitting it into a number of fractions. Heat is applied to the crude oil within a distillation column to separate its main component parts. The lightest fraction of petroleum gases is removed at the upper end of the distillation column while the heavy sticky residue from the bottom ends.[3] Base oil most often gained from petroleum fraction or mineral oil derived which has properties of high viscosity, low volatility and ability to dissolve the existing chemical additives as well inert toward metal surfaces, gasket and rubber seals. The basestock must be viscous enough to maintain a lubricant film under operating conditions but should be as fluid as possible to remove heat and to avoid loss due to viscous drag. It also must have the properties of high stability under thermal and oxidative stresses and capable to control friction and wear by itself. They generally consist of molecules containing 18-40 carbon atoms in three basic hydrocarbon types which are paraffins, aromatics and naphthenes.[1] The molecular structure can be shown as below

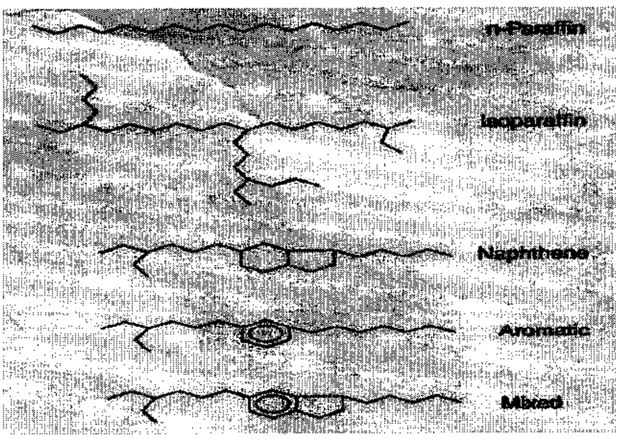


Figure 2.2 Molecular structures of base oil molecules[1]

These basestock also contain a small percentage of compounds containing hetereoatoms such as sulfur, nitrogen or oxygen. Even though the fraction is small, they have significant influence on the basestock stability and lubricating properties. The hetereoatoms consist of sulfur containing compound, nitrogen containing compound and oxygen containing compound. Sulfur containing compound typically are alkyl, cyclic and aromatic thiols, alkyl sulfides, alkyl-cyclo alkyl sulfides and cyclic sulfides. The nitrogen compounds are typically quinolines and pyridine alkyl substituent (basic nitrogen) and pyrroles, indoles, carbozoles (non-basic nitrogen). Meanwhile the oxygen compound is normal and branched acids, acids containing a cyclic group (acidic oxygen) and 1-, 2- or 3- and 4-methyldibenzofurans (neutral oxygen). Some of these compound posses antioxidant and antiwear functions and some of them are pro-oxidants and corrosive.[1]

2.2.2 Chemical Additive

Chemical additive is used to overpower the base oils to produce specific desirable characteristic. Basestock is behaving like the solvent for the additives. The most commonly additives found in industrial are detergent, friction-reducing additives, dispersant, antioxidant, anti form additives, pour point depressant, antiwear and extreme pressure additive, polymer thickeners and corrosion protection.

2.2.2.1 Detergent

Detergent is used to hold the acid-neutralizing compound in solution in the oil. It will interact with varnish or sludge to neutralize and solubilise. The alkaline property will react with the strong acid which form during the combustion of the fuel and will cause corrosion to the engine internal.[2] Overbased detergents are salts of alkaline metal such as calcium and magnesium that contain high alkaline metal. They have a good detergent properties and an excellent ability to neutralize strong acids. Basically compound used in detergent are metallo-organic compound of sodium, calcium and magnesium phenolates, phosphonates and sulphonates.[3]

2.2.2.2 Dispersant

Dispersant keep dirty and combustion products in suspension in the body of the oil thus prevent deposition of sludge or lacquer. Dispersant react in the oil and after certain time it depleted. That is the reason why regular oil changes are heavily contaminated system.[2] Compound used in dispersant formulation are alkylsuccimides and alkylsuccinic esters.[3]

2.2.2.3 Antioxidant

With presence of water, the oxidation will occur in the lubricant. The oxidation process cause formation of gum, lacquers and sludge thus increase acidity. Antioxidant inhibits the oxidation and some antioxidant also function at temperature above 100^0C by deactivating metal surfaces.[4] Zeodialkyldithiophosphate (ZDTP), hindered phenol, aromatic amines and suphurised phenols are example of chemical compound used in dispersant.[3]

2.2.2.4 Anti foam additive

Anti foam additive such as silicon polymers is a substance that prevent foaming. Air trapped in lubricating oil can cause starvation due to the presence of air bubbles at the contacting surfaces. The situation may lead to the failure of moving components.[2] The chemical compound used in antifoam are silicon polymers and organic copolymers.[3]

2.2.2.5 Pour point depressant

High viscosity mineral oils contain paraffin waxes that start crystallization at low temperature. The process will make the viscosity of the oil increase rapidly and lead to the faster crystallization as the temperature further decrease. Pour point depressant often prevent this rapid viscosity increase by suppress the agglomeration of the wax crystal.[2] Chemical compound exist in this type of additive are alkylated naphthalene and aromatic hydrocarbons.[3]

2.2.2.6 Anti wear and extreme pressure additive

The wear of contacting surfaces can be reduced by using these additives. Most common anti wear additives are zinc and phosphorus based for instance zinc dithiophosphates, acid phosphates, organic sulfur and chlorine compound, sulphurised fats, sulfides and disulfides.[3] Meanwhile the extreme pressure additive performs the similar task. It made from varying proportions of chemically bound sulphur and phosphorus. They bind with exposed metal surfaces to form low rupture strength films that limit damage from micro-seizure if the oil film ruptures.[2]

2.2.2.7 Polymer thickeners

These types of additives are used if the viscosity characteristic of oil at different temperature needs to be altered. Multigrade oils with few exceptions contain polymer to thicken a monograde oil of a lighter grade and give it multigrade properties i.e. they are able to function better at much lower temperature. The multigrade oils also can be used in emergency equipment due to the excellent viscosity/temperature characteristic.[2]

2.3 Surfactant in Lubrication

Surfactant is known as wetting agent where it has capability to reduce the surface tension of a liquid. Surfactant molecules posses hydrophilic head group (water seeking) which favor to water molecules and oliophilic tails (oil favor) which associate with oil. Molecules containing both types of components are said to be amphiphilic. For that reason they neither are nor preferred to be in either phase hence, they form aggregate which located at the phase boundary between the oil and water phase. That happens at low concentration of amphiphilic. Surfactants will favor on the surface. As the surface becomes crowded with surfactant more molecules will arrange into micelles. At some concentration the surface fully associate with surfactant and any further additions must arrange as micelles.[1],[5] The system can be explained as below.

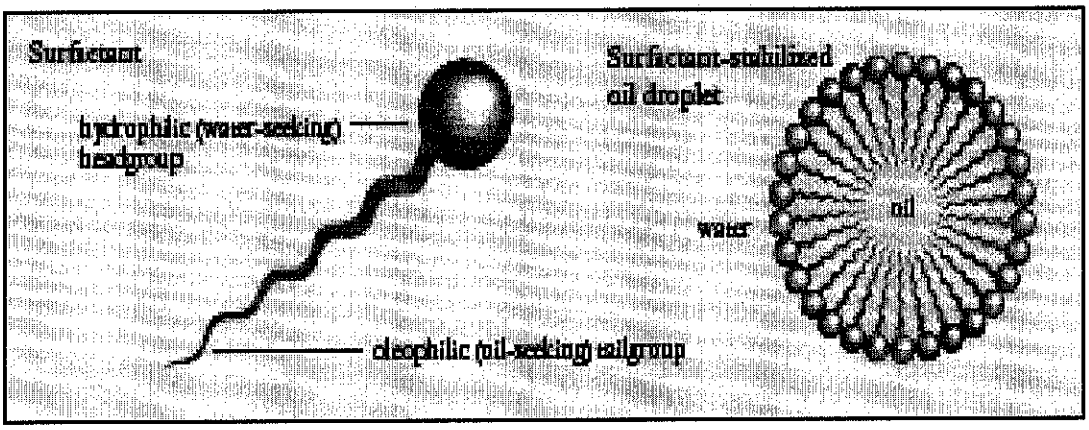


Figure 2.3 Surfactants consist of two parts; the water-seeking hydrophilic head group and an oil-seeking oleophilic tail group. This allows them to stabilize oil droplets.[5]

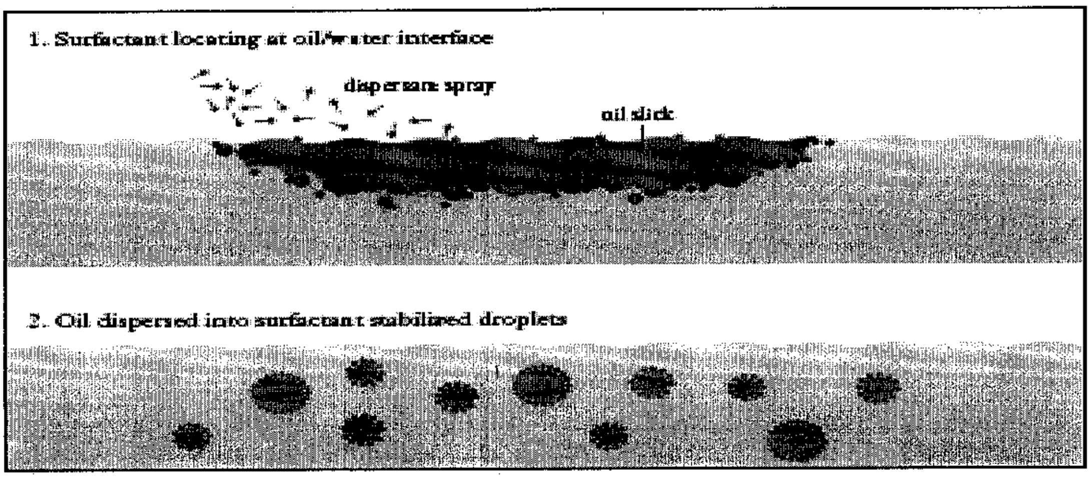


Figure 2.4 Surfactant locating at oil/water interface, and oil dispersed into surfactant-stabilized droplets.[5]

In most cases, the chemical additive in lubricant behaves like surfactants due to the polar functional groups exist in the substance. Chemical additives will form aggregate in the base oil. The additive molecules will deplete either by adsorption or reaction and as the lubrication process continue, the quantity of the molecule going to decrease thus lowering the performance of the lubricant. Figure 2.5 shows the molecules in the circle represent the individual micelle. These molecules freely compete for the solid surface via absorption. The micelles will dissociate to release more free molecules.[1] This is the concept on how the lubricant can maintain the functionality through it life.

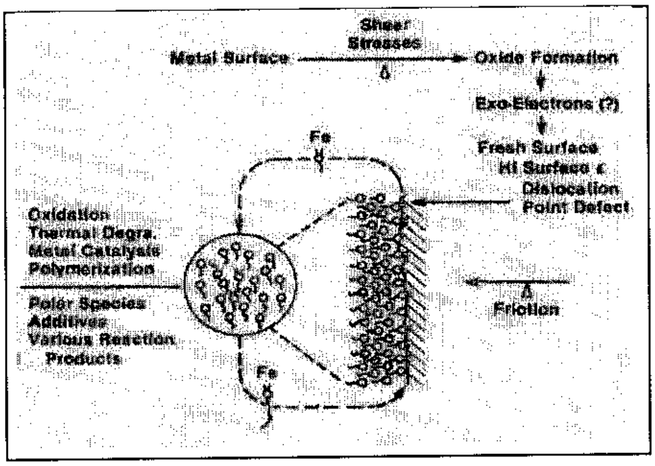


Figure 2.5 Qualitative model of lubricant molecules in solution.[1]

2.4 Good Lubricant

The effectiveness of a lubricant is depends on the compatibility between the lubricant and the system where the lubricant is used. In certain applications, safety issues are extremely important such as where there is a potential fire hazard, the use of an aqueous-based lubricant will allow optimum fire protection.[6] In general, the characteristic of good lubricant is described below.

2.4.1 Good Lubricity

Since lubrication system consists of various components that contain surfaces that are in close contact and move in relation to each other. Thus, the most important feature of a good lubricant it must has a capability to protect system against wear and lubricate the surfaces.[7]

2.4.2 Stable viscosity

Viscosity is a lubricant property that varies with temperature and pressure. Lubricant having large changes of viscosity with temperature is commonly referred as low viscosity index and those having small changes of viscosity with temperature are known as high viscosity index lubricant. Lubricant which has high viscosity index is desired in lubrication. [7]

2.4.3 Chemical and physical stability

The characteristics of a lubricant should remain unchanged during an extended useful life. Since many aspects of stability are chemical in nature, the temperatures to which the lubricant will be exposed are an important criterion in the selection of a lubricant. [7]

2.4.4 System compatibility

The lubricant oil should be inert to materials used in or near the lubricated equipment. If the lubricant in anyway attacks, destroys, dissolves or changes parts of the lubrication system, the system may lose its functional efficiency and may start malfunctioning. [7]

2.4.5 Good heat dissipation

Pressure drops, mechanical friction, fluid friction, leakages, all generate heat. The lubricant must carry the generated heat away and readily dissipate it to the atmosphere or coolers. [7]

2.4.6 Flash point

The flash point of lubricant oil is defined as the temperature at which flashes will be generated when the oil is brought into contact with any heated matter. [7]

2.4.7 Fire resistant

The lubricant oil are petroleum derivatives and thus for critical applications, artificial or synthetic hydraulic fluids are used which have high fire resistances. Various grades of fluids with high water content are also available nowadays for oil hydraulic systems. [7]

2.4.8 Prevent rust formation

Moisture and oxygen cause rusting of iron parts in the system that can lead to abrasive wear of system components and also act as catalyst to increase the rate of oxidation of the oil. Lubricant with rust inhibitors minimizes rust formation in the system. [7]

2.4.9 Low in volatility

The lubricant should have low vapor pressure or high boiling point characteristic. The vapor pressure of the lubricant varies with temperature and hence the operating temperature range of the system is important in determining the suitability of the lubricant. [7]

2.4.10 Low coefficient of expansion

The lubricant oil should have a low coefficient of expansion to minimize the total volume of the system required at the operating temperature. [7]

2.5 Fundamental Process of Lubricant Ageing

2.5.1 Water and untreated acid.

Total Acid Number measures the rate of decomposition by indicating the amount of acid present. It is expressed as the number of milligrams of potassium hydroxide (KOH) needed to neutralize 1 gram of lubricant. The standard acid number for new lube oil commonly is less than 1 mg KOH/gram. Increase TAN normally is due to the depletion of additive. Meanwhile the existence of water will raise the viscosity value and the performance of lubricant additive will be ineffective.[8]

2.5.2 Heat

Heat can be absorbed by the lubricant if the fluid has high air content. The surging pressure experienced by the fluid will compress and expand the air, heating it, resulting in high lubricant temperature. As a general rule, every 10°C increase in operating temperature over the "nominal" level would reduce the useful life of the lubricant by half.[9]

2.5.3 Contaminant

Contaminant in lubricant can be introduces or self generated. When a system has been run for a reasonable period, the majority of solid contaminants will be in the form of small platelets, created by bedding-in and the normal wear process, the bulk of which are between 5 and 15 microns in size. Because of their size and shape, they can take a long time to settle. The other common form of self generated contaminant is that the local cold welding microscopic surface particles will be torn off when they move in relation to each other releasing wear particles. Lubricating system can also be contaminated by ingression through the oil film on seals. Worn seals will increase this possibility.[8]

2.5.4 Viscosity

Viscosity is the prime physical property of a lubricant. It implies the ability of lubricants internal resistance to flow or in other words how thick or thin the lubricant is. The change value of viscosity may indicate oxidation of the oil, presence of insoluble like soot, contamination with water or fuel, or the use of the wrong lubricant.[7]

2.5.5 Fuel dilution

When excessive fuel dilution occurs, the effectiveness of the lubricant is reduced. As the fuel thins the lubricant, the viscosity goes down and may allow increased wear which in turn may cause overheating. Oil needs to keep the metal parts separated, to provide sealing from combustion products and transfer heat from the engine for cooling. When the oil is diluted by the fuel, its ability to perform is diminished and the effects can lead to engine failure.[4]

2.6 Used Oil Regeneration

All the factors of lubricant aging of course affect the performance and quality of lubricant. Thus, the properties of used lube oil are very poor. Therefore, several methods available to regenerate the used lube oil.

2.6.1 Reconditioning

Basically the methods used in purposed to remove the solid, suspended particles and water from the used lube oil. The process of is known as reconditioning. Reconditioning in general is a preliminary step in the purification before other methods are employed. For reconditioning, there are a number of mechanical separation process which can be operated individually or by combination.[8]

2.6.1.1 Screening

In the screening process, perforated metal plate is used where the contaminated oil is passing through the plate to retain the coarser impurities and relieve the filter section.[8]

2.6.1.2 Settling

Settling used the gravity to separate the impurities of higher specific gravity than the oil such as fine metallic particles, water and sludge. The oil will be heated to 80^0C to reduce viscosity and increase separation.[8]

2.6.1.3 Filtration

Filtration is to remove the finest floating impurities in the oil which cannot be retained by screening and precipitation. The process can be through paper, cloth, fine metal gauge, sintered ceramic plate or through a bed of inert substances.[8]

2.6.1.4 Vacuum Dehydration

Vacuum dehydration is a process in which water and other volatile impurities like un burnt fuel and solvents are removed by distillation under vacuum. Water and oil are immiscible liquids. If not agitated water introduced into a lubricating oil separates readily by gravity in the settling process. However, any kind of agitation can break up the body of water into small droplets which become dispersed in the oil and are then not readily separated by gravity. Presence of surface active compounds may also stabilize the emulsion of oil and water. In the vacuum dehydrating unit the oil is heated to a comparatively low temperature under vacuum to drive off the moisture and volatiles. The use of vacuum permits volatilization at low temperature thus avoiding oxidation of the oil. Vacuum dehydration also removes low molecular weight acids and volatile components which are responsible for odor. Vacuum dehydration is often combined with settling, filtration or centrifugal separation. In some cases the water is removed by settling and vacuum dehydration followed by filtration or centrifugation to remove solid particles and suspended matter. Contact filtration may also be employed after dehydration or contacting maybe done under vacuum in a single vessel thus serving both the purposes of vacuum dehydration and adsorbent contacting. In other cases the oil is first filtered through specially designed filter packs or the solid impurities are removed by centrifuging and then the oil is subjected to vacuum treatment which dehydrates and degasses the oil completely.[8]

2.6.2 Re-refining

Re-refining is a more drastic process and not only removes solid matter, water, gases etc. but also acids, soluble products of deterioration, asphaltenes, unsaturated compounds, sulphur, colour compounds and odour forming substances. The re-refining processes are similar to the refining processes employed in the refining of reduced petroleum stocks or lubricating base stocks. The re-refined products are almost like new oils from the refineries and can be considered as a new base oils for the manufacture of lubricating oils. Re-refining methods are not so widely used as conditioning methods.

Generally, reconditioning is sufficient but if the oil has been badly oxidised and additives completely depleted then refining methods maybe considered. Re-refining involves high capital and operating costs and is economical only when large quantities of used oils are readily available. Re-refining is always preceded by some sort of preliminary purifying methods such as settling, filtration or centrifuging and vacuum dehydration. Various methods are employed for the re-refining of used lubricating oils such as (a) chemical treatment (b) solvent extraction (c) clay contacting or adsorbent treatment (d) distillation or fractionation (e) hydrotreating. These methods are usually not used alone; more often two or more methods are combined in the re-refining process. Chemical treatment involves treatment with acids such as sulphuric acid and oleum or with alkalies such as soda ash, caustic soda, trisodium phosphate etc. Solvent extraction can be done with propane or isopropyl alcohol. Adsorbent treatment involves mixing a precalculated amount of an adsorbent to the oil, heating and agitating the mixture and then after a specified interval of time fIltering oil. Distillation or fractionation is carried out under vacuum and is usually done when the oil to be re refined is a mixture of various types of oils from different origin and it is desired to separate the various bases in terms of viscosity or boiling points.[8]

2.6.2.1 Conventional Acid Clay Process

In the conventional acid clay process the used lubricating oil is settled or filtered after collection and dehydrated. The oil is then treated with concentrated sulphuric acid to remove polymers, asphalts, degraded additives and other products of degradation. The sludge formed is allowed to settle and removed. The oil is neutralised with activated clay at elevated temperatures. The clay also bleaches the oil and adsorbs certain impurities not removed by acid treatment. The clay-oil slurry is filtered to remove clay and other solids. If the raw material contains more than one grade of lube oil products, the reclaimed oil has to be steam striped or fractionated under vacuum to obtain different bases. As in case of original refining the spindle or neutral base stocks may be given a clay finishing treatment and the bright stock may be acid-clay treated. However, this often not necessary. The different bases are then doped with required amount of additives to produce different lubricating oils. The conventional process has been very popular because of low initial investment and simple knowhow. However, new problems have made it less attractive. Acid sludge disposal has become a problem because of tough environmental laws. The high additive concentration of modem multigrade oils has decreased the regeneration yield, at the same time increasing the chemical consumption, asphaltic impurities are not so easily removed by acid treatment as by solvent extraction. This has become a problem with higher mileage motor oils because they become more and more asphaltic on prolonged use. Oil clay waste disposal is also a problem.[8]

2.6.2.2 Distillation-cum-hydrotreating Process

In this process the dehydrated used lube oil is flashed in a high vacuum distillation column to produce desired lube base stocks. Light ends are removed from the top and contaminants e.g. metals, polymerisation products, asphaltenic materials etc. go with the residue. The distillate lube oil is mixed with hydrogen gas, heated in a furnace and is passed through a fixed catalyst bed in the reactor. Final product quality is controlled by the operating conditions used. The hydrogen gas is continuously circulated by means of a compressor. The oil may be further stripped/fractionated to obtain different base stocks. Finally, additives are incorporated in the base stocks.[8]

2.6.2.3 Nigos Reconditioner

This plant consists of a main tank in which the oil is heated upto a temperature of 150_oC. The heating can be done externally by fuel or internally by immersion heaters. The oil is then treated with a patented powder in a ratio depending upon the acidity of oil but usually a ratio of 1:3 is employed. The mixture is agitated and heating is stopped after mixture is uniform in nature. Airtight covers are put on the tank and air is put via an air inlet tube to a maximum pressure of 2 kg/cm_2. The bottom of tank contains especially designed membranes through which the oil is filtered and it issues through the clean oil outlet. The plant removes all suspended matter, moisture and other dissolved impurities including acids. The oil can be filtered continuously and the complete plant is portable.[8]

2.6.2.4 Propane Extraction-cum-acid Clay Process

In this process the dehydrated oil is mixed with liquid propane and sent to the extractor. Propane containing dissolved oil is sent overhead while residues, containing às phaltometallic materials are taken off at the bottom. Propane is separated from the oil in two-stage columns and sent to the propane liquification unit for recycling. The clean oil is sent to the subsequent acid and clay treating units and finally stripped/fractionated to obtain the desired products to be blended with required additives.[8]

CHAPTER 3

METHODOLOGY /PROJECT WORK

The purpose of the tests is to study the properties of used lube oil by making unused oil properties as the reference. The used oil and unused oil are come form the same type/brand of lubricant. Three types of lubricant available and for the used lubricant, they are collected from 3 different cars (Proton Wira) at 15000 km mileage-change-oil.

3.1 Density Test

The densities of the sample are tested by using picnometer 25 ml at 25^0C (room temperature)

Procedure:

1. The mass of the picnometer was taken and label as M1
2. The sample then pours into the picnometer and the mass of picnometer together with the sample is taken and label as M2
3. Then the density is calculated by virtue of

   Density: Mass/Volume
4. The steps above were repeated for the 6 samples.

3.2 Viscosity Test

In order to perform the experiment, the Brookfield viscometer model 2000 is used. The operation is pictured in Figure 4.2.

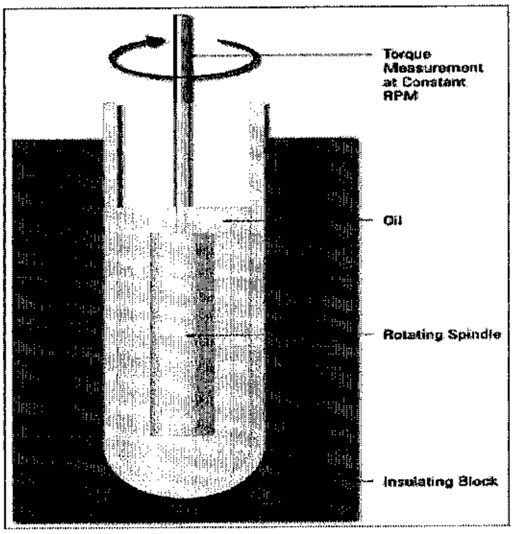


Figure 4.2 Rotary Viscometer

Since the equipment used to test the viscosity has no heating probe, the test was run at room temperature (25^0C).

Procedure:

1. The experiment was done by try and error
2. There are two variables which are speed and spindle that need to be manipulated in order to get the highest percentage.
3. So that, in order to get the highest percentage which produces the best viscosity value, the appropriate spindle and speed must be selected.

3.3 Total Acid Number (TAN)

Chemical Used:

- i. Sample: 6 samples of lubricant
- ii. Solvent: Toluene
- iii. Chemical Indicator: Phenolphthalein
- iv. Chemical for titration: 0.1 mol of KOH

Procedure:

1. 1.0 gram of lubricant taken.
2. 0.5 ml of toluene and 2 drops of phenolphthalein added to the lubricant sample.
3. The mixture was titrated by using 0.1 mol of KOH
4. The volume of KOH used to titrate 1.0 gram of lubricant taken.

Calculation of 0.1 mol KOH

250 ml of 0.1 mol KOH

MW of KOH: 56.11 g/mol

Mass of KOH: 0.1 mol/L x 56.11 g/mol x 250 ml x 1L/1000 ml = **1.402g**

Thus, 1.40275 g of KOH dissolved into 250 of distilled water used to titrate the lubricant.

Calculation for mass of KOH used

(Sample calculation):

Gram of KOH = 56.11 g/mol x 0.6167 ml x 0.1 mol/L x 1L/1000 ml

= **0.00346 gram**

CHAPTER 4

RESULT AND DISCUSSION

4.1 Total Acid Number (TAN)

Total Acid Number (TAN) is a method to determine the acidic constituents in new and used petroleum products. The TAN is defined as the number of milligram of potassium hydroxide (KOH) required to neutralize 1 gram of lubricant. The solvent mixture of toluene and phenolphthalein indicator solution is added to the sample. The KOH used to titrate the sample is at 0.1 M concentration.

Calculation of 0.1 mol KOH

250 ml of 0.1 mol KOH

MW of KOH: 56.11 g/mol

Mass of KOH: 0.1 mol/L x 56.11 g/mol x 250 ml x 1L/1000 ml = **1.402g**

Thus, 1.40275 g of KOH dissolved into 250 of distilled water used to titrate the lubricant.

The samples are titrated to the end-point color change. For the new oil, the color will turn to pink while the color of used oil will change to light brown. The result of the experiment can be reviewed at the next page.

4.1.1 Result:

Volume of KOH used to titrate 20mL of lubricant (mL)	Sample 1		Sample 2		Sample 3	
	New	Used	New	Used	New	Used
Reading 1	0.7000	1.4000	1.1000	0.3000	2.0500	11.5000
Reading 2	0.6000	1.5000	0.6000	0.9000	0.3500	7.1000
Reading 3	0.5500	1.1000	0.7500	1.1000	1.0000	5.0000
Average	0.6167	1.3333	0.8167	0.7667	1.1333	7.8667
TAN (mass of KOH per 1 gram of lubricant)	0.00346	0.00748	0.00458	0.00430	0.00636	0.04415

Table 4.1 Result for TAN

(Sample calculation):

Calculation for mass of KOH used

Gram of KOH = 56.11 g/mol x 0.6167 ml x 0.1 mol/L x 1L/1000 ml

= **0.00346 gram**

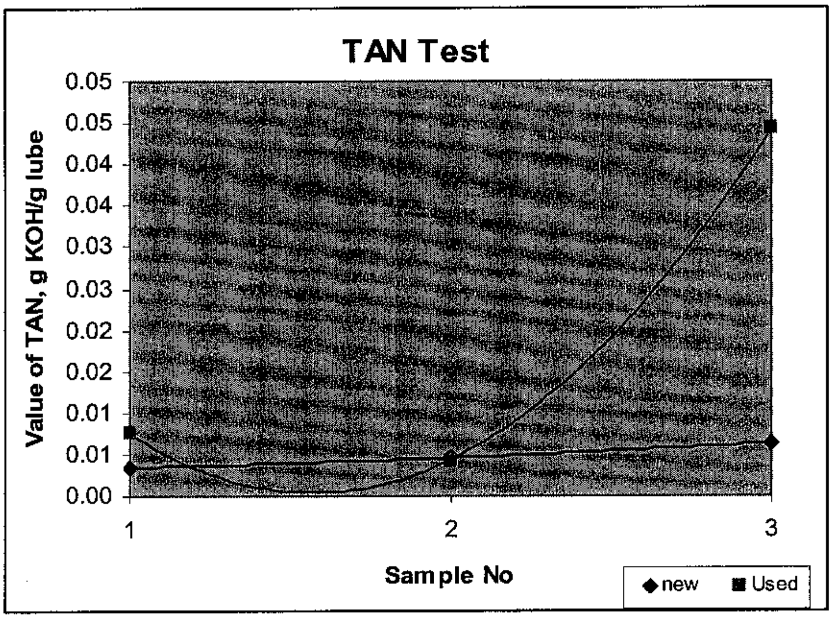


Figure 4.1 Plot of TAN versus number of sample

4.1.2 Discussion

Result shows that the Total Acid Number for used lube oil is greater than the new oil except for the sample 2. The new oil often has a lower level of acids compared to the used oil. Many factors contribute toward the increment of acid level such as high temperature, wear-particles and additive depletion. The root cause of the high level of TAN is explained below.

4.1.2.1 Combustion

Acids are formed within the lube by several sources. In most all forms of fuel for internal combustion engines, trace amounts of sulfur are present. Sulfuric acid is formed within the lube oil when sulfur molecules react with oxygen in the combustion chamber to form sulfur oxides. These sulfur oxides are then blown past the rings and enter the oil. Here the sulfur oxides mix with moisture to form the highly corrosive sulfuric acid. It is next to impossible to remove trace amounts of sulfur from fuels by filtration.

4.1.2.2 Oxidation

Lube oils react with oxygen which exists in atmosphere to produce organic oxidation products that are acidic in nature. The reaction is slow at normal temperature and it will not give significant effect to the oil condition. At high temperature reaction rates are much higher since reaction will go faster as temperature increase. During the lubrication process, the metal surfaces will slide over each other and producing heat. At that particular condition, temperatures can be very much higher than the surrounding metal. The reaction between oil and oxygen will be faster assisted by the combustion and wear products in solution in the oil. Many of these direct or primary oxidation products combine with other materials such as wear metals, solid contamination, and moisture, to form second and third derivative products.

Oxidation is greatly stimulated by the contamination solids and moisture. Heat will be hold by the solid, thereby increasing the lube oil temperature around the solid contamination. This condition acts to accelerate oxidation. Combine this effect with the presence of moisture (H_2O) from normal condensation, and the oxidation process accelerates even faster. When moisture is present in the lubrication system, the level of oxygen available to mix with hydrocarbons in the lube oil is raised dramatically. The presence of normal solid and moisture contamination, combined with maximum operating load of the equipment, will produce high oil oxidation rates, even with normal oil temperatures.

4.1.2.3 Nitration

Nitration as well can cause the formation of acid in oil. The combustion chambers of engines provide one of the few environments where there is sufficient heat and pressure to break the atmospheric nitrogen molecule down to two atoms that can react with oxygen to form nitrous oxides (NOx). When nitrogen oxide products enter the lube oil through normal blow-by, they react with moisture present in the lube and become very acidic and rapidly accelerate the oxidation rate of the oil

By existence of detergent additive the acidic product will be neutralized and reduce the acid amount the lube oil. However the reaction is not easy and some how they both tend to co-exist.

A high value of TAN indicates the detergent additives become depleted. Due to additive depletion the acidic product can not be neutralized and increase the TAN value. Nevertheless there are a few type of lubricant supplied at high TAN number because of some reason. The value however will drop as the additives are depleted with use, then slowly rise again as the effects of ageing become apparent.

High value of TAN will cause the formation of gums and lacquers on metal surfaces and it will increase the viscosity. Furthermore with the existence of water the system will easily corrosive.

4.1.2 Error

However the experiment was exposed to several errors that make the value of TAN are not accurate. The significant error that produces major uncertainty is the setting of end point color change. It was difficult to determine the end point of used lube oil due to the dark color. The color obtained for the 3 types of used lube oil are different. Thus it creates uncertainty at which stage should be the neutralization process stopped.

4.2 Viscosity

There is no property more critical to effective component lubrication than base oil viscosity. Generally, viscosity is a fluid's resistance to flow (shear stress) at a given temperature. Sometimes, viscosity is erroneously referred to as thickness (or weight). Viscosity can be measured and reported as dynamic (absolute) viscosity or as kinematic viscosity. Oil of the correct viscosity will provide optimum film strength in bearing clearance with minimum friction losses and leakage. Lubricating system keeps friction between surfaces to a minimum and assists in dissipating the heat developed. The temperature must be defined to interpret the viscosity reading. Typically, viscosity is reported at 40°C or 100°C

The equipment is used to determine absolute viscosity which has unit of cP. Absolute viscosity measurement has historically been used for research applications, quality control and grease analysis within the field of machinery lubrication. The absolute viscosity determines the film thickness provided by the oil. Kinematic viscosity is merely a convenient attempt to estimate the degree of film thickness the oil can provide, but has less significance if the oil is non-Newtonian. Table 4.2 provides the Newtonian information. While Table 4.3 shows the viscosity at the standard temperature of 100°C.

The result of the experiment is as shown in Table 4.5. To determine the viscosity the most suitable spindle type and an appropriate speed of spindle need to be selected to produce the highest percentage.

Oil Type or Condition	Viscosity Behavior
New Base Oils R & O Oils Non-VI Improved Oil	Newtonian
Aged Non-VI Improved Oil Contaminated Oil Moderately Oxidized Oil	Leans Toward Newtonian
Heavily Oxidized Oil Aged VI Improved Oil	Leans Toward Non-Newtonian
New VI Improved Oils Water-Oils Emulsions Grease	Non-Newtonian

Table 4.2 Type of oil/condition according to the viscosity behavior

SAE Viscosity Grade	Viscosity cSt at 100^0C	
	Min	Pumpable
0W	3.8	-35
5W	3.8	-30
10W	4.1	-25
15W	5.6	-20
20W	5.6	-15
25W	9.3	-10
20	5.6	Max <9.3
30	9.3	Max <12.5
40	12.5	Max <16.3
50	16.3	Max <21.9

Table 4.3 Viscosity at the standard temperature of 100°C

4.2.1 Result:

	Sample 1		Sample 2		Sample 3	
	New	Used	New	Used	New	Used
Absolute Viscocity (cP)	176.8	170.2	187.4	264.3	242.4	107.9
Kinematic Viscosity (cSt)	192.17	185.0	203.7	287.0	263.5	117.3
Speed of spindle (rpm)	30	20	30	20	20	50
Type of spindle	S61	S61	S61	S61	S61	S61
%	88.3	85.2	93.7	88.0	80.8	90

Table 4.4 Result for viscosity

Sample calculation for kinematic viscosity:

(The specific gravity of mineral oils varies from 0.86 to 0.98, thus take the average 0.92)[11]

cSt = cP/ SG

= 176.8 / 0.92

= 192.17

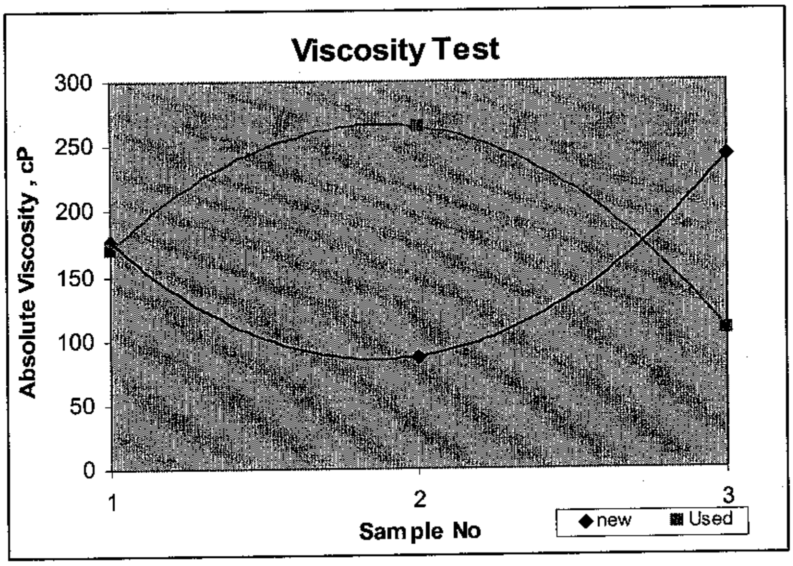


Figure 4.3 Plot of viscosity versus number of sample

From the test done onto the new and used lube oil, the result shows that the viscosity for the sample 1 and 3 are reduced after being used. Unlike Sample 2 which shows the viscosity of used oil is greater than the new.

Generally, the viscosity change in lube oil is due to several factors. Changes in the viscosity indicate the degree of aging, by-product contamination, dilution, the possibility of mixed products, and other abnormalities that affect the serviceability of the lubricant.

The value is possible to fall due to distillate fuel oil dilution, by topping up with an incorrect oil grade, or shear of polymer additives.

Meanwhile the viscosity may increase due to excessive soot loading (insoluble content) or if the centrifuge or filters are not operating correctly. For all oils, ageing caused by oxidation and thermal degradation may lead to thickening and an increase in viscosity.

4.3 Density

Density is the mass of a unit volume of a substance. The parameter is used in lubrication to identify oil fractions, and to measure kinematic viscosity (absolute viscosity divided by density). Also, density is in the equations for the calculation of temperature rise in an oil film, and the equation for Reynolds Number (which determines if flow of an oil film is laminar or turbulent). The density of mineral oil lubricants varies from 0.86 to 0.98 g ml^{-1}.

The equipment used to test density is picnometer. Experimental result shows that the density of all sample are decrease except for sample 1. The change in density in lube oil is related to the viscosity.

4.3.1 Result:

	Sample 1		Sample 2		Sample 3	
	New	Used	New	Used	New	Used
Mass of empty container (g), m_1	19.7562	19.3686	19.5431	19.2474	19.2212	19.8884
Mass of empty container + oil (g), m_2	42.7197	42.9421	42.486	41.7191	42.3241	42.0826
Mass of oil (g), $(m_2 - m_1)$	22.9635	23.5735	22.9429	22.4717	23.1029	22.1942
Volume (mL)	25	25	25	25	25	25
Density $(m_2 - m_1)$/volume, (g/mL)	0.91854	0.94294	0.917716	0.898868	0.924116	0.887768

Table 4.5 Result for density

Sample calculation for density:

Density = Mass of oil/Volume of picnometer = 22.9635 g / 25ml = 0.91854 g/m

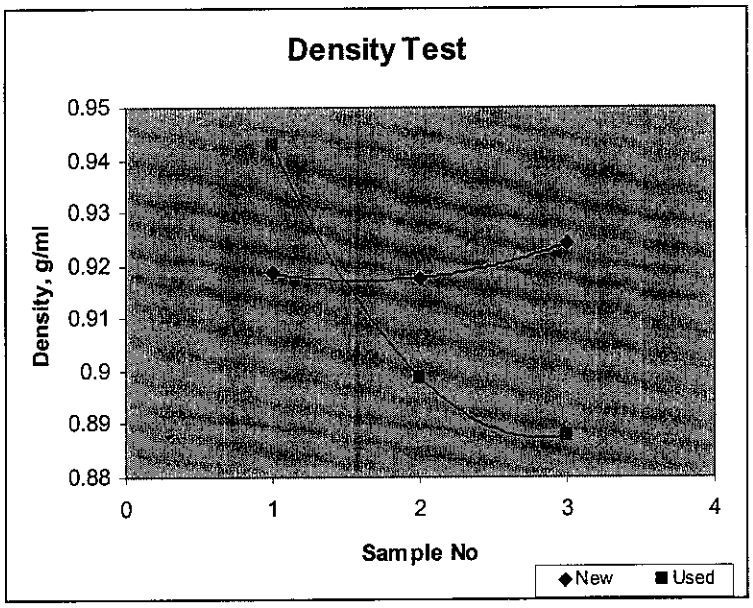


Figure 4.4 Plot of density versus number of sample

The molecules in oil are in a state of constant motion. As the temperature of the oil increases the molecules vibrate at higher amplitudes, they take up more space, and the volume of the oil increases. At constant mass, as the volume increases, the density of the oil decreases due to reverse relationship between the two. The change in volume, dV, is proportional to the volume of the liquid, V, and the change in temperature, dt. The constant of proportionality is known as the coefficient of thermal expansion and is given the letter alpha, α. The units of α are 1/temperature and the higher the value the more a liquid will expand with a given temperature increase.

4.4 Regeneration of Used Lube Oil

For regeneration purpose the experiment is done as follow:

1. 50% of used lube oil is added into 50% of new lube oil.
2. Then the mixture is heated about one hour at 150^0C to ensure they mix well.
3. The viscosity, TAN and density of the mixture then is tested according to the method that has been explained in Chapter 3.

The expected result is all the properties of the mixture are lie between the properties value of new oil and used oil. The result of the experiment can be reviewed at the next section.

4.4.1 Result and discussion

Total Acid Number (TAN) Test	
Volume of KOH used to titrate 1mL of lubricant (mL)	
Reading 1	1.00
Reading 2	1.20
Reading 3	0.90
Average	1.03
TAN (mass of KOH per 1 gram of lubricant)	0.0058

Viscosity Test	
Absolute Viscosity (cP)	93.2
Kinematic Viscosity (cSt)	101.3
Speed of spindle (rpm)	60
Type of spindle	S61
%	93.60%

Density Test	
Mass of empty container (g), m_1	19.611
Mass of empty container + oil (g), m_2	42.730
Mass of oil (g), $(m_2 - m_1)$	23.119
Volume (mL)	25.000
Density $(m_2 - m_1)$/volume, (g/mL)	0.925

Table 4.6 Result for TAN, viscosity and density for used oil regeneration

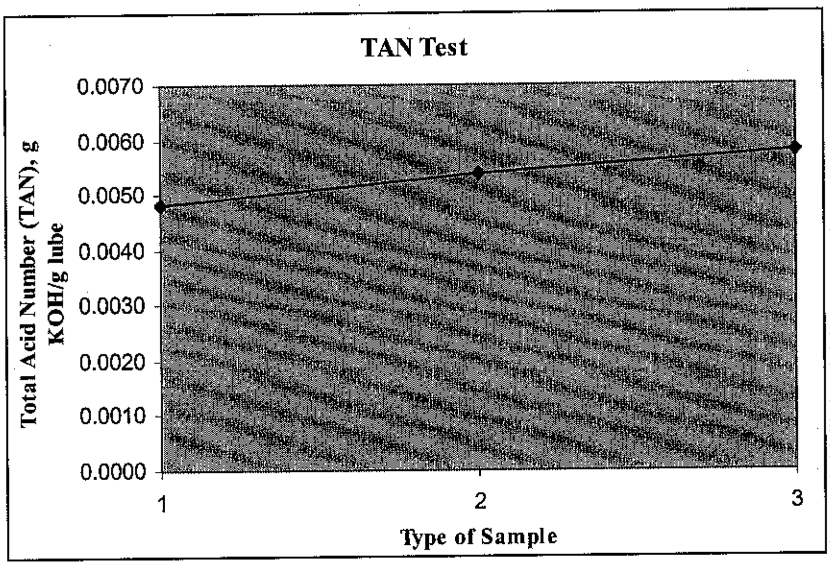


Figure 4.5 Plot of TAN vs type of sample

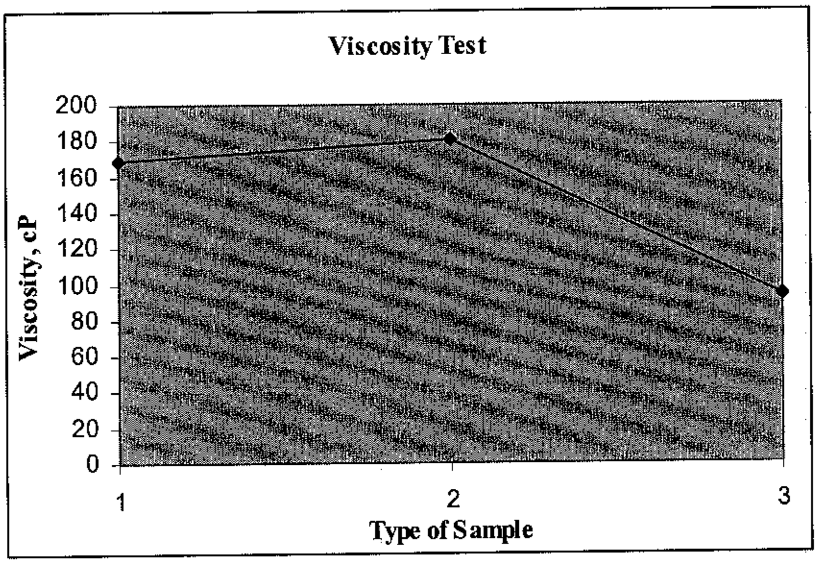


Figure 4.6 Plot of viscosity vs type of sample

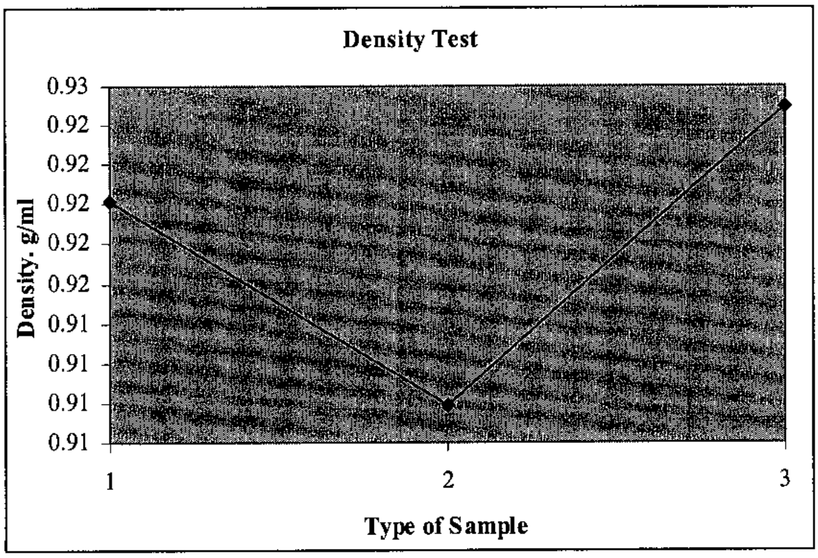


Figure 4.7 Plot of density vs type of sample

Reference:
Type of Sample
1 – New Lube Oil
2 – Used Lube Oil
3 – 50% New Lube Oil + 50% Used Lube Oil

Figure 4.5, 4.6 and 4.7 shows the properties comparison between the three types of sample which are new lube oil, used lube oil and the mixture of 50% of new lube oil and 50% of used lube oil. According to the plots obtained, no one of the tests complies with the objective. The property values of the mixture (50% New Lube Oil + 50% Used Lube Oil) do not lie between the property values of new and used lube oil (average value determined from the 3 samples).

For the TAN and density tests, the mixture's value is slightly higher than the new and used oil. Meanwhile, for the viscosity test the mixture value is lower than the two types of reference oil.

From the experiment done there are three points can be discussed. First is the experimental error. For instance the TAN test. The uncertainties happen because the exact end point of neutralization can not be determined due to the different color change of each sample. For the viscosity test, the value for the mixture (50% New Lube Oil +

50% Used Lube Oil) is very low compared to the new and used oil perhaps because of the heating effect. The test was run before the sample is cooled down to room temperature.

The second point is all the three types of test are not feasible to make the comparison. Since the viscosity and density are physical properties, therefore the comparison can not be done. In general, by mixing 50% of new lube oil and 50% of used lube oil, the properties of new lube oil will tend to improve the properties of used lube oil. However the improvement can not be detected by performing the three types of tests (viscosity, density and TAN). The more appropriate test perhaps can be applied for instance the test that can investigate the chemical properties of the lube oil.

Third point is the error created from the samples itself. Obviously from the experiments done, the reading for Sample 2 was slightly inconsistent. There is possibility where the problem was created from the source of the sample for instance the sample was obtained from the car which has engine problem or the oil has not been change for long time.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This study is to investigate the effect of surfactant in lubrication. The physical properties that have been studied on are the Total Acid Number (TAN), viscosity and density. In the literature review conducted earlier, it is believed that as the additive depleted in lubricant, the performance of the oil will be reduced. Two methods required to regenerate the used lube oil. At lower stage reconditioning take place and it need further treatment which re-refining is necessary to turn the used lube oil to base oil. Only after that the base oil can be added with the additives.

Based on experiments, it can be concluded that the results show the differences of value between used and unused oil and the different value between them involved many factor i.e viscosity of used oil can be greater and lower than unused oil. As well as the properties of regenerated used oil can not be compared due to inconsistent result and limited properties.

This project has potential to be very valuable toward human and environmental safety. Thus, it is recommended to extent the project to the next semester. This project can be continued by finding other alternatives (experimentally) on how to regenerate the used oil such as varying the percent of mixture so that the result can be analyzed better or by using surfactant to regenerate the used oil. More experiment need to be conducted to test the properties of the lubricant oil such as engine metal (iron, chromium, lead, copper etc) and contaminant (silicon, sodium etc), additive (zinc, phosphorous etc). Thus the comparison will be done better.

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