

DEVELOPMENT AND CHARACTERIZATION OF  
LUBRICATING OIL FROM A PETROLEUM  
BASED OIL

A THESIS

*Presented to*

The Postgraduate School  
Federal University of Technology, Minna.

*By*

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(M. ENG/SEET/2001/723)

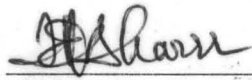
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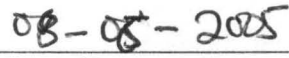
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## DECLARATION

I, Kefas Haruna Mavakumba, declare that this thesis is solely the result of my work and has never been submitted anywhere for any degree. All literature cited has been duly acknowledged in the references.



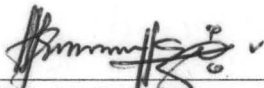
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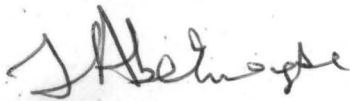
This thesis entitled DEVELOPMENT AND CHARACTERIZATION OF LUBRICATING OIL FROM A PETROLEUM BASED OIL by Kefas Haruna Mavakumba, meets the regulations governing the award of the degree of Master of Engineering (Chemical Engineering) of Federal University of Technology, Minna, and is approved for its contributions to knowledge and literal presentations.



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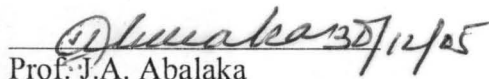
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## DEDICATION

This piece of work is specially dedicated to my dear wife, Sis. Hopeful Haruna and my father, Mr. Kefas A., for their care, love and understanding.

## ACKNOWLEDGEMENT

My profound gratitude and appreciation goes to the Almighty God for His protection and guidance over me and for making the programme a reality.

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## ABSTRACT

Lubricating oils were developed from a petroleum base oil (500N HVI oil) using simplex lattice design. Subsequently, the developed samples were characterized and the following properties were determined according to ASTM standard methods as follows: Kinematic viscosities (at 40°C and 100°C), specific gravity, API gravity, viscosity index, flash point, pour point, total base number and appearance. The lubricant were further designed using 2<sup>3</sup> factorial by subjecting them to various process variables namely temperature, pressure and time and subsequently modelled by regression.

The result showed that the oils are of the motor oil grades of SAE 30, SAE 40 and SAE 20W50 based on their viscosities. Samples 5 and 6 of the SAE 20W50 grade were the best since they have specifications very close to acceptable standards worldwide with viscosity indices of 126 and 124 respectively.

The results for the sample that gave the best results showed that temperature alone has significant effect on the viscosity of the component while time and the interactions between the process variables have no significant effect.

The regression model relating process variables and viscosity of all the lubricants samples showed that the approximating functions are first order type, and the models for the samples that gave the best results are given as follows:

$$V_5 = 328.8091667 - 3.06991667p_1 - 0.35166667p_2 - 0.15083333p_3 \\ + 0.000666667p_1p_2 + 0.000333333 p_1p_3 + 0.045 p_2p_3$$

$$V_6 = 318.2783333 - 2.97133333p_1 - 0.51666667p_2 - 0.25833333p_3 \\ + 0.002166667p_1p_2 + 0.001583333 p_1p_3 + 0.055 p_2p_3$$

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## ABBREVIATIONS

ASTM	American Society for Testing and Materials
HVI	High Viscosity Index
LVI	Low Viscosity Index
MVI	Medium Viscosity Index
SAE	Society of Automative Engineers
BS	Bright Stock
LPFO	Low Pour Fuel Oil
HPFO	High Pour Fuel Oil
CD	Cylinder Oil
VI	Viscosity Improver
API	American Petroleum Institute
S.G	Specific Gravity
cSt	Centistoke
TBN	Total Base Number
CV	Coefficient of Variation
R <sup>2</sup>	Regression Square
ANOVA	Analysis of Variance
V	Viscosity
W	Winter
N	Neutral
P	Pale
TAN	Total Acid Number
NIS	Nigerian Industrial Standard
SS	Sum of Square
DF	Degree of Freedom
SON	Standard Organization of Nigeria

## NOTATIONS

$^{\circ}\text{C}$	Degree Celsius
$^{\circ}\text{F}$	Fahrenheit
$P_1$	Temperature
$P_2$	Pressure
$P_3$	Time
$\text{mgKOH/g}$	Milligram Potassium Hydroxide per gram
$\text{mm}^2/\text{s}$	Millimetre Square per Second

## CHAPTER ONE

### 1.0 INTRODUCTION

Lubrication is simply the use of a material to improve the smoothness of movement of one surface over another, and the material, which is used in this way, is called a lubricant. Lubricants are usually liquids or semi-liquids, but may be solids or gases or any combination of solids, liquids and/or gases (Lansdown, 1982).

No surface, however polished, is ideally smooth. Though modern machinery is capable of producing finishes that approach perfection. When one surface moves over another, there is always some resistance to movement, and the resisting force is called friction. This friction, if low and steady, there will be smooth, easy sliding. At the other extreme, the friction may be so great, or so uneven that movement becomes impossible and the surfaces can overheat or seriously damage.

The overall importance of lubrication is to ensure that the economic and design of equipment, machinery and plant are achieved at minimum costs through the following functions.

1. To maintain oil film between moving parts so as to minimize the frictional effect of metal contact.
2. To act as a cooling medium by absorbing dissipation excessive heat generation.
3. To remove dirt from engine parts thus keeping them clean and efficient.

Lubricating oil must perform the above functions in an automobile engine and apart from these functions, it must also protect the metal as much as possible from rusting, corrosion, surface damage and wear.

The characteristics and performance of lubricating oils depend on the crude oil source, refining method, base stocks and chemical additives



incorporated. Basically, there are two types of lubricant are normally used for engine lubrication, namely petroleum based-fluid and synthetic ones. However, petroleum products have been found to excel as lubricants. They have high wetting ability as well as maintain high viscosity characteristics required of a lubricating film. Petroleum lubricant also possesses many essential additional properties such as good water resistance, inherent rust preventive characteristics, material adhesiveness, relatively good thermal stability and the ability to transfer frictional heat from lubricating parts. Colours of lubricating oils vary from colourless to dark red and this has no bearing upon the usefulness of an oil for a given application, although it has been believed by some laymen that pale colour indicates high quality. Colour is important in certain applications, such as the textile industry, where a dark coloured oil in a bolt of cloth would be objectionable (Popovich, 1959).

The basic petroleum lubricant simply referred to as base oil is a complex mixture of hydrocarbon molecules and is derived from the refining of crude petroleum residue from vacuum distillation that has a boiling point of 700-1000 °F. It is available in a great variety of types and grades, i.e. (100N, 150N, 250N and BS).

### **1.1 Background of the Study**

At present, most lubricants designs are carried out based on simplistic unifactor approach and the implication is that the effects of lubricant quality are not realised and hence, the lubricants are far from being optimum. Considering the geometric increase in the number of automobile engines, the oil designer, therefore, is faced with problem of developing oils that can perform optimally under a wide variety of operating conditions. The essence of this study

therefore is to use a statistical design means to obtain a lubricant with optimum performance.

## **1.2 Aims and Objectives**

The aim of this project is to develop lubricating oil from a petroleum source. Specifically, the aim is to develop and design a lubricant that has optimum lubrication performance, by incorporating various additives based on simplex lattice design.

## **1.3 Approach**

The following procedures were used to obtain the lubricating oils with improved qualities. In view of achieving the above objective, the following approaches were used.

1. A high viscosity index oil (500N) obtained from vacuum distillation unit of the Kaduna refinery was used as the base oil for the formulation. This choice became inevitable due to its kinematic viscosity among other high viscosity index oil.
2. Designing of the base oil by incorporating various additives. The additives used were viscosity index improver (ethylene-propylene copolymer) and Paranox 5501 additive (its constituents are contained in the Appendix).
3. Designing of the formulated oils from step 2 above using a statistical approach typical of simplex lattice design.
4. Finally, the application of the design lubricants to an improvised system was investigated by  $2^3$  factorial design (Scheffe, 1963).

## CHAPTER TWO

### 2.0

### LITERATURE REVIEW

#### 2.1 Lubrication

The act of lubrication probably dates from the invention of the wheel and axle. Carts were first built with crudely fashioned wooden axles and bearings. In due time, it was discovered that a lump of fat from a slain animal, smeared on the dry and squeaking parts served to make the wheel run smoothly and quietly. Without benefit of modern concepts of that greased surfaces would move over one another more easily than ungreased surfaces.

Later, iron and brass replaced wood as materials of construction for the early moving machinery. The need for more suitable lubricants than crude fat began to emerge. All the fatty and oily materials previously adopted were of vegetable or animal origin, used singly or in compounded form. Among these oils were olive oils, tallow, rape oil, and castor oil. Oils from marine life, such as whales, porpoises and menhaden, were also used.

Petroleum oils did not come into general use as machine lubricants until the middle of the 19<sup>th</sup> century in 1845. It was alleged that the progressive owner of a cotton spinning mill in Pittsburgh, Pa, was induced to try a sample of mineral oil obtained from a salt well drilled in Tarentum, Pa, on the Allegheny River. He experimented with it very cautiously using a blend of petroleum with the sperm oil, which has been employed for the lubrication of the spindles. The record showed that the blend was much better than the straight sperm oil. For ten years, he kept the secret from his competitors. It was not till 1859, when

Colonel Edwin L. Drake drilled the first oil well coincidentally, that petroleum oils began to take the place of non-mineral.

The art of lubrication made slow progress during the late half of the 19<sup>th</sup> century because lubrication requirements of the early types of engines were easily met. Progress, however, was inevitable, and automobile engineers were in the vanguard. Standards of accuracy became more rigid, leading to the possibility of greater operating speeds and higher power output. New types of machine tool were being developed and somewhere along this line that machinery men began to encounter lubrication troubles. A general-purpose oil which had served well enough in simpler days could not meet the new conditions of higher speeds, pressures and temperature. The problem of friction began to assume paramount importance, and operational failures traceable to wear, became more frequent. Thus, the necessity for new types of lubricant became obvious.

In due course, research was initiated in which chemists, physicists, engineers, oil refiners and metallurgists took part. This program gained momentum and, at the present time, is being carried out on a vast scale. The aim of the present day oil research laboratory is to keep a breast of the demands of the designers and users of engines and machinery for lubricants which will afford efficient protection under the diverse and severe operational conditions now encountered. Difficult problems are being solved and the empirical art of lubrication has now earned the dignified status of a science.

## 2.2 Mechanism of Lubrication

The basic purpose of lubrication is to maintain between the surfaces something which will keep them from rubbing together and injuring one another. A good example is shown by two optically flat pieces of glass or metal. When the surfaces are extremely clean, these will cohere very tightly when pressed together, but if rubbed with even fingers before being placed in contact, they will not cohere. The reason is, of course, that in the first case there is little or nothing between the surfaces, while in the second, the fingers have left a greasy film which acts as a lubricant. For industrial bearings something more is needed than the film left by clean fingers and this something is usually a layer of liquid oil. As the bearing fit is made more precise, the load heavier and the temperature higher, the layer of oil becomes thinner (Gruce, 1967).

Friction is of course a common element in daily life. One can walk up a steep ramp without slipping back because of high friction between shoe soles and ramp surfaces. One can slide down a ski run because friction between packed snow and skis is low. One can express the amount of frictional resistance to motion in terms of the coefficient of friction, which is the ratio of frictional force opposing the motion to the load at right angles to the surfaces.

This ratio is very roughly constant for any one pair of surfaces. For lubricated metal of ordinary smoothness and cleanness exposed to the atmosphere, it may have a value of about 1, and for the same metals contaminated by handling, the value will be about 0.3 to 1. For well designed and well lubricated systems the coefficient may be as low as 0.005, and under very special conditions, value as low as 0.000005 has been attained.

By contrast, the coefficient for clean metal surfaces in a vacuum may be as high as 100-200 or more. These variations show that there are differences in kind as well as in amount of lubrication. When the surfaces are very smooth and a layer of fluid is kept between them, they do not touch and, for this condition, they play no vital part in the lubrication.

### **2.3 Composition of Lubrication Oil Base Stocks**

The identification of constituent is unfeasible, due to the fact that the number of individual molecular species in lubrication oil base stock is extremely large. Chemically, labelled distillates consist of complicated hydrocarbons of paraffins, naphthenes and aromatic structure, with a number of carbon atoms per molecule ranging from 22 to 34. Apart from these three types of hydrocarbon, there may be small quantities of compounds present which also contain other atoms, such as oxygen, sulphur, phosphorus and nitrogen. (These compounds are sometimes referred as asphaltenes).

The various hydrocarbon groups differ considerably with respect to their suitability as lubricating oils.

- (i) The paraffins have very good viscosity temperature characteristics. However, the straight chain paraffins occurring in the label cannot be used owing to their high melting points. They must be removed by dewaxing to reduce the pour point.
- (ii) The isoparaffins have much lower melting points but are generally present only as minor constituents of label.

- (iii) Aromatic hydrocarbons have poor viscosity temperature characteristics and are the least suitable for use.
- (iv) Hydrocarbons consisting of naphthenic rings and long isoparaffinic side chains are the most desirable components for the lubricating oils. Properties such as specific gravity, viscosity and viscosity index may give rough indication of chemical composition of lubricating oil. When a comparison is made with the hydrocarbon varying in type but with an equal number of carbon atoms, it appears that, the specific gravity increases in the order, paraffins, naphthenes, and aromatic. The viscosity index decreases in the order, paraffins, naphthenes, and aromatics.

### 2.3.1 Types and grades of lubricating oil

Lubricating oils can be divided into two main groups from a manufacturing point of view. These are the distillate oils and bright stocks.

**Distillate oils:** The distillate lubricating oils can be subdivided into the following:

- Low viscosity index (LVI) oils;
- Medium viscosity index (MVI) oils;
- High viscosity index (HVI) oils;

Medium viscosity index oils are produced from both naphthenic and paraffinic distillates and are referred to as MVIN (naphthenic) and MVIP (paraffinic) oil. The MVIP oils are obtained from paraffinic label distillates by dewaxing

followed by acid treatment. They are used as general purpose lubricants for application where the low viscosity index oil is a disadvantage.

HVI oils are prepared by solvent extraction and dewaxing of paraffinic distillates. Solvent extraction improves not only the viscosity index but also the oxidation and colour stability. HVI oils are used whenever an oil with good viscosity temperature and oxidation characteristics is needed, such as in motor oils and turbine oils. For the purpose of this project, the HVI oil will be used as base stock for the formulation of the lube oil.

**Bright stock:** They are usually obtained by propane desalphalting extraction and dewaxing of paraffinic short residues. In view of their limited tendency to evaporate and their high viscosity, bright stocks are used as cylinder oils, but their main application is as blending components in the heavier motor and diesel oils.

Viscosity in a nutshell is the useful parameter for the identifying of the various grades of lubricating oils as regards to the environment condition. There are several grades of single-viscosity oils. They are rated for winter and for other seasons. Winter grade oils include SAE 5W, SAE 20W, etc. The Society of Automotive Engineers (SAE) developed the grading system. The 'W' stands for winter. A low viscosity oil is thin while high viscosity oil is thick. SAE 5 is lighter than SAE 10 and so on. To improve oil performance, additives like viscosity index improvers are added. Oil possessing this quality



resists thinning when temperature increases and thickening when it decreases. The kind of such oil have an inscription like SAE 5W-10, SAE 10W-40, or SAE 30W-50. This oil is generally referred to as a multi-grade oil meaning that at low temperature, the oil behaves like SAE 20 and as the oil heats up, it behaves like SAE 40 (SAE 20W-40). In practical engine operation, there is protection of a thick oil when the engine heats up to highway or cruising speed. The relative change of oil viscosity with changes in temperature is called Viscosity Index (VI).

Table2.1: Viscosity of Oils for Various Applications.

Application	Viscosity in centistokes at 25°C (77°F)	Primary function
Engine oils		
SAE 10W	60-90	Lubricates piston rings, cylinders, valve gear, bearings, cool piston, prevent deposition on metal surfaces
SAE 20	90-180	
SAE 30	180-280	
SAE 40	280-450	
SAE 50	450-800	
Gear oil		
SAE 80	100-400	Prevents metal contact and wear of spur-gears, hypoid gears, work gears, cool gear cases
SAE 90	400-1000	
SAE 140	1000-2200	
Aviation engine oils	220-700	Same as engine oils
Torque converter fluid	80-140	Lubricate, transmit power
Hydraulic brake fluid	35	Transmit power
Refrigerator oils	30-260	Lubricates compressor pump
Steam-turbine oil	55-300	Lubricates reduction gearing, cool
Steam cylinder oil	1500-3300	Lubricates in presence of steam at high temperature

## 2.4 Production of Lubricating Oil

The process for the production of lubricating oil involves the following stages:

- i. Preparation of the feedstock. Production of the initial oil fractions.
- ii. Production of the components and incorporation of additives for production of commercial grades of oils.

The residue from topped crude oil that is left after the removal of straight run gasoline; kerosene and gas oil by a topping operation is the basic stock for lubricant manufacture. The residues include the wax portion, raffinate portions, extract portion, and the asphalts. The basic stock is further processed by physical separations which include solvent extraction, wax removal and filtration, chemical processing methods such as hydrofinishing.

The imported heavy crude oil from Venezuela and Saudi Arabia provide the base stock distillates in the vacuum distillation unit from the atmospheric distillation unit residue at Kaduna Refinery while the slurry is further stripped as feed stock into the petrochemical plant. The base stock distillates are treated to improve and enhance their triphysical properties while the vacuum residue is deasphalted in a propane deasphalting unit by adding propane as solvent to remove resins and asphaltic tar. The raffinate is propane deasphalted oil comprising of saturates and structures of mononuclear, dinuclear and polynuclear aromatics.

The deasphalted oil is subjected to furfural extraction process to separate aromatic compounds from non-aromatic compounds to give freedom from

sludge in high temperature operation. Many solvents, such as phenol, creosol and propane (duo-sol), liquid sulphur dioxide, benzene have been employed. This is achieved by adding furfural as solvent in particular to the mixture of deasphalted oil and distillate from the vacuum tower to improve the base stock viscosity, increase its viscosity index, thermal and oxidation stability. The wax crystals in the base stocks are removed by the process of MEK dewaxing. The process filters are used to remove the long chain paraffin wax in the presence of methylethyl ketone and toluene as solvents to reduce the pour and flash point characteristics of the resulting base oils. The wax from the rotary dewaxing filter is removed and then hydrogenated in the presence of wolfram-cobalt catalyst to manufacture food grade wax.

In some premium base manufacturing, the dewaxed base oil is further subjected to hydrofinishing. This operation is necessary to improve their colour oxidation, thermal stability and to remove the traces of moisture which make the oil hazy rather than bright. The heavy residual from all the stages of base oil manufacturing are then blended in a specific ratio in the asphaltic blower to make the different penetration grades of bitumen.

The residue from the atmospheric distillation tower is heated in a furnace and flows to the flash zone of the vacuum distillation unit to separate the heavier hydrocarbon groups into high, medium and low viscosity index lubricating base oils. The high viscosity index oils (HVI) are the 100 neutral, 150 neutral, 250 neutral, 500 neutral and bright stocks (BS) while the low viscosity base oils are the 100 P, 1200 P and cylinder oil (CD) (Table 2.2). The

process of vacuum distillation controls the physical properties of the distillates like viscosity, flash point and carbon residue to prevent thermal cracking as their hot vapour condense as per the boiling range. The residue from this process is then used as blend stock for low pour fuel oil (LPFO) and high pour fuel oil (HPFO) and formation for asphalt feedstock .

Table 2.2: Nigerian National Petroleum Corporation Specification for Lube Base Oils (SON, 1995).

Characteristics	HVI					LVI				Test	
	100N	150N	250N	500N	BS	100P	500P	1200P	Cylinder Oil (CO)		
Specific gravity at 60/60°F	Report	Report	Report	Report	Report	Report	Report	Report	Report	Report	ASTMD 1298
Kinematic viscosity	3.9-4.3	4.9-5.5	6.9-7.7	10.8-12	30.5-32.5	4.0-4.2	10.5-11.2	16.5-18.5	40-44		ASTMD
Viscosity Index (minimum)	95	95	95	95	95	75	75	75	75		ASTMD
Pour point (maximum) °C	-9	-9	-9	-9	-9	-9	-9	-9	-9	-9	ASTMD
Flash point (minimum)	193	20	210	221	226	165	210	215	270		ASTMD
Colour (maximum)	1	1	1-2	2	3.5-4.5	1	2	2-3	5		ASTMD
Colour stability 100°C	1	1	1	1	1	1	1	1	1		ASTMS
Appearance	Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright	Clear & bright

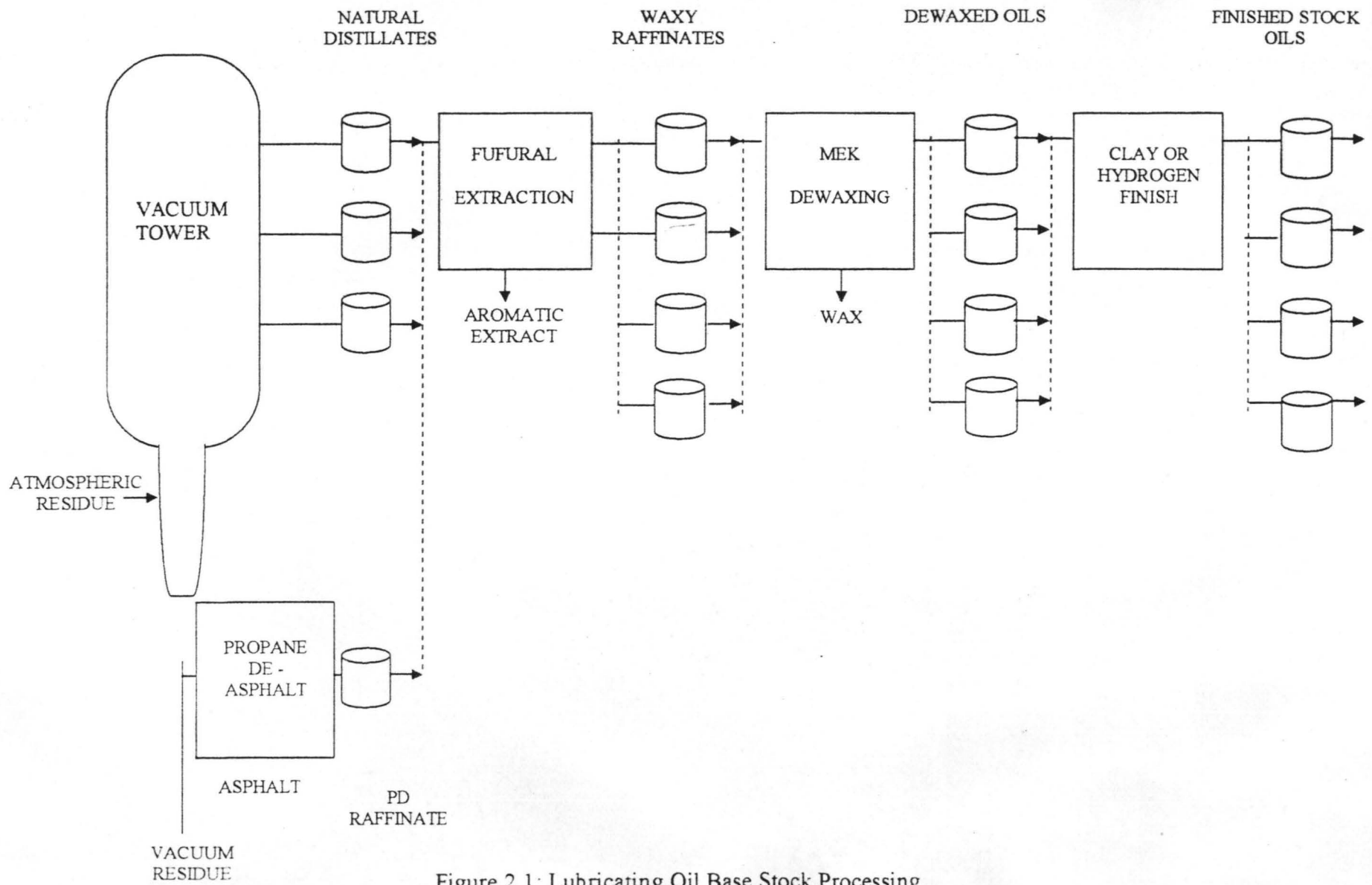


Figure 2.1: Lubricating Oil Base Stock Processing

## 2.5 Formulation and Treatment of Lubricating Oil

Lubricating oils are formulated and blended to meet specific needs and exact application. There is no single formulations for the manufacture of lubricating oils but the international bodies maintain products that must meet or in some cases exceed set down standards parameters in specifications, characteristics and categorisation for universal acceptability by engine builders in their selection, recommendations and applications.

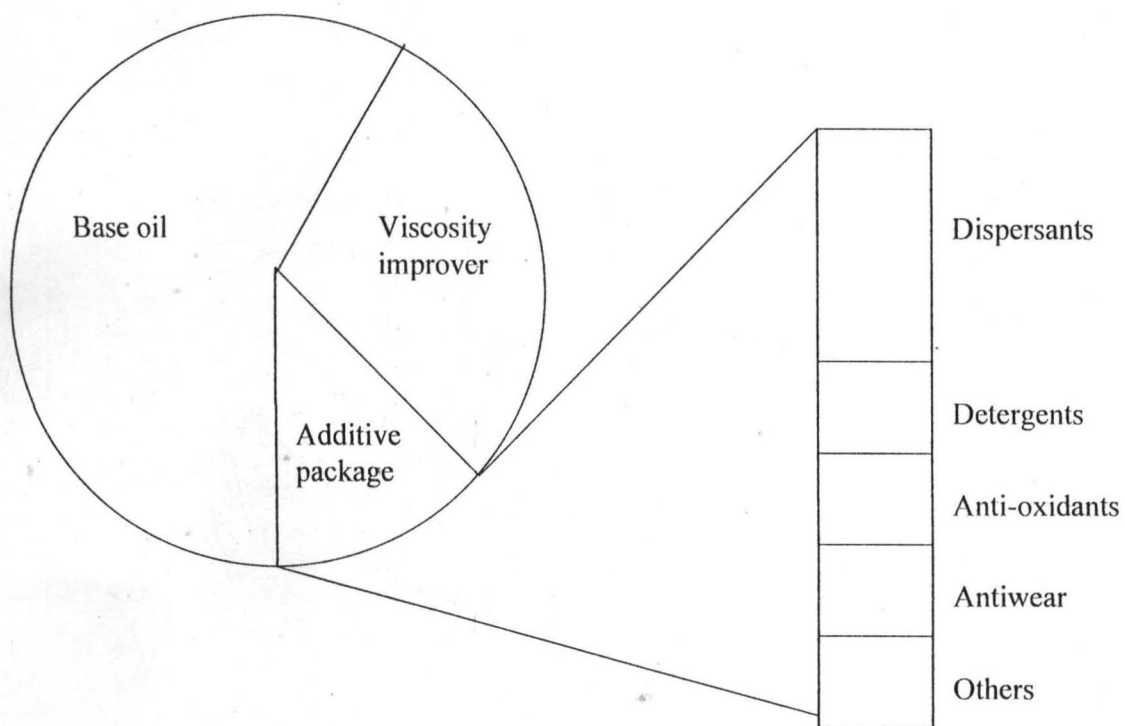


Figure 2.2: Engine Oil Formulation



From the chart in Figure 2.2, it means that about 60% of the total blend stands for the base oils, while 27.8% is for the viscosity improver and 13.9% for the additive package. For the additive package, the breakdown is 6.7, 2.6, 1.9, 1.5 and 1.3 percent for dispersants, detergents, antioxidants, antiwear and others respectively.

Lubricating oils are either mineral or synthetic based. The mineral oils are manufactured by blending mineral base oils with chemical additives while the term synthetic base are used to describe fluids that are produced by chemically combining individual low molecular weight compounds into a unified entity. They are man-made specifically tailored to have controlled molecular structure with predictable properties. It is important, due to the purpose of this introduction, to state that synthetic base fluids are classified into the following.

**Organic esters:** These are compounds obtained by reaction of an alcohol with an acid. They are used for manufacture of aircraft jet engine lubricants. Almost all gas turbine engines are lubricated by them. Examples are dibasic acids esters, polyesters (now preferred).

**Phosphate esters:** These are produced by reaction between alcohol and phosphate acid, and are widely used for their outstanding fire resistance. They are good lubricants, but are limited to temperatures not much over 100°C because of poor thermal stability. They also attack many paints, plastics, and rubber. They are used for the manufacture of hydraulic fluid for commercial aircraft, fire resistant fluid oils, etc.

**Silicones:** These are generally used for their good high temperature properties, but they have several other advantages. They are chemically quite inert, repel water, are non-toxic and electrically insulating. They can be obtained in a very wide range of viscosities; but are not good boundary lubricants for steel against steel.

**Chlorinated and fluorinated compounds:** These include the chlorinated biphenyls, fluorocarbons, chlorosilicones and fluorosilicones. They have good chemical inertness, which gives them good fire resistance, and generally good thermal stability, especially with the fluorocarbons and fluorosilicones. They are not particularly good lubricants and their prices are generally high.

**Polyglycols:** They have major advantage, in that when they are heated above their maximum temperatures of about 200°C they decompose cleanly. They are therefore used at temperatures which are so high that any liquid lubricant must decompose, such as 400°C or higher, because they will not leave the deposits of coke or ash which would be left by other lubricants. Some of them are water soluble or water insoluble and are used in the manufacture of brake/clutch fluids, metal working fluid, rubber bearing lubricants, heat transfer fluid, refrigeration compressor oils.

**Synthesized hydrocarbons:** They are pure hydrocarbons manufactured from raw materials derived from crude oil such as olefin oligomers, alkylated aromatic polybutenes, cycloaliphatics.

Other types of lubricating fluids are as follows:

- Polyphenyl esters for the manufacture of heat transfer fluids, radiation resistant greases
- Emulsions, examples are soluble oils used as coolants in metal working, in grinding, drilling, boring, turning, milling, etc.

The overall advantages of using synthetic lubricants and other fluids in place of a mineral oil include their outstanding flow characteristics at extremely low temperatures, stability at extremely low temperatures, stability at extremely high temperature, lower flammability and extended range of service interval. They also provide enhanced oxidation stability, corrosive protection, superior rust protection and viscosity index (VI) improver when compared with mineral base lubricants. Other advantages are extended lubricant life resulting in low lubrication cost and overall maintenance cost, improved system cleanliness with no sludge and deposit build up.

As automotive and industrial lubrication requirement becomes more severe with the progressive development of engines and general machinery it becomes necessary firstly to improve the quality of lubricating oil by new methods of refining and eventually to use additives either to reinforce existing qualities or to confer additional properties.

### **2.5.1 The Important Properties of Oils**

The most important single property of lubricating oil is its viscosity. Many other properties are important for other reasons.

In practice, many other factors must be taken into account, to make sure that the oil continues to lubricate properly over a long period, or to make sure that nothing also goes wrong with the system and so on. The following are some of these other factors:

- i. Thermal or temperature stability: If an oil becomes hot in use, then it is important that the heat does not make it breakdown so that it ceases to lubricate properly.
- ii. Chemical stability: Oil can be chemically attacked by oxygen from the air, or by water, or by other substances with which it comes into contact. Such attack can also make it unsuitable for use. Chemical stability means the ability to resist chemical attack, and must be assessed in relation to the substances which the oil expected to contact. Chemical stability is related to thermal stability, because the speed of a chemical reaction increases as the temperature increases.
- iii. Compatibility: This is a more general term referring to any interaction between the oil and other materials present. For example, an oil may cause the rubber of a seal to swell or shrink, or to soften or harden.
- iv. Corrosiveness: Corrosion is a particular type of incompatibility, in which the oil, or something in the oil, attacks a metal component in the system. An oil which is completely non-corrosive when new may become corrosive after a period of use.

- v. Thermal or heat conductivity: This is important where the oil is required to conduct heat away from the bearing.
- vi. Heat capacity (specific heat): In an oil-circulation system the amount of heat which the oil can carry away from the bearing depends on the rate of flow and on the specific heat.
- vii. Flammability: It is obviously important that the oil should not catch fire under the conditions under which it is used. This is particularly important in some industries such as aviation and coal-mining. Flammability means the same as inflammability.
- viii. Toxicity: This is a very broad term meaning almost every aspect in which a substance affects health. The health problems which arise from their use tend to be long term rather than immediate. Acute (i.e. rapid or immediate) toxicity is more likely to arise from more reactive additives than from base oils, especially where these are present in high concentrations, such as in soluble oils and some diesel-engine lubricating oils. Some of the long-term effect health problems include cancer, and dermatitis, but lubricant manufacturers have made great efforts to identify and remove the dangerous components.
- ix. Availability: It is obvious that oil must be available before it can be used, but where a piece of equipment is to be used in different parts of the world, availability may become both important and difficult.

- x. Price: Again, it is obvious that price is an important aspect of lubricating oil, or of almost anything else, but it is not a simple matter. A single bearing failure in a critical position may cost more than a company's whole lubricant bill for a year. So while price competition cannot be ignored, the choice of the right type of oil should never be abandoned for price reasons alone. Only where different oils meet the same specifications can a choice be based on price alone, and even then it is important to make sure that the specification is relevant to the application for which the oil is being selected.

### **2.5.2 Types and Functions of Additives**

A straight mineral oil regardless of how well refined does not provide satisfactory lubrication for engines. Chemical substances known as additives have been discovered to boost the properties, specification and characteristics of oils, to enable them perform various functions in the finished product. These chemical additives include the following;

#### **Viscosity Index Improver**

The viscosity of a liquid is a measure of its resistance to flow, the higher its viscosity, the less easily it flows. As temperature is increased, the viscosity of petroleum oils decreases. The rate at which viscosity changes with temperature is expressed as the Viscosity Index (V.I.). The V.I., an empirical number

calculated from the observed viscosities of a lubricant at two widely separated temperatures, in fact indicate the resistance of a lubricant to viscosity change with temperature. The higher the V.I. value, the greater the resistance of the lubricant to thicken at low temperatures and thin out at high temperatures.

Viscosity Index improvers are high molecular weight polymers which are added to lubricating oils to modify the viscosity. Temperature relationship of the base oils makes them conform more closely to the ideal lubricant, i.e., one whose viscosity remains unaltered by changes in temperature. These polymers include polyisobutylene, polymethacrylate, polyalkylstyrene, ethylene-propylene copolymers, olefin copolymers and acrylate polymers.

### **Detergent and Dispersant**

To prevent insoluble contaminants from agglomerating and forming carbon, varnish and sludge deposits, additives are used to keep them finely dispersed throughout the oil. These additives can be divided into two classes.

Detergents are generally metallic soaps of oil soluble organic acid. The metals, most commonly used as calcium, barium and magnesium, organic groups include sulfonates, phenates and thiophenates, salicylates and phosphonates. These metallic compounds function in oil somewhat as soap or washing detergents function in water. Particles are coated and kept in fine suspension. You may have noticed that detergent-containing motor oils become very black in a very short time in service; this is a natural result of the action of the detergent in dispersing soot and dirt so that it is not deposited in the engine.

Dispersants in the petroleum industry are defined as additives capable of keeping the precursor and components of "low temperature sludge" in fine suspensions. Dispersants are usually complex ashless nitrogen compounds, ashless (non-metallic) chemicals such as polyisobutanyl-succinimides, metallic and polyisobutyenyl succinic esters. Although they have been used traditionally for low temperature dispersancy, recent developments have been extending their high temperature capability.

### **Antioxidants**

Lubricants used in engines come in contact with air at high temperatures. Metal surfaces and fine metal particles are present which can act as catalysts and promote oxidation reactions that convert petroleum compounds into harmful acidic materials, heavy oxidised molecules that increase the oil viscosity and some oil-insoluble sludge. Also formed are resins, lacquers and oil-soluble oxy-products.

Antioxidants are added to petroleum oils to slow down or eliminate these oxidation reactions. Thus the oil is given a much longer, safer life to fulfil its duties of lubrication, protecting the surfaces against corrosion and carrying away excess heat from bearing surfaces. Antioxidants commonly used are sulfurized esters, sulfurized terpenes, sulfurised olefins (paraffin wax olefins), aromatic sulfides, alkyl sulfides, organic phosphites, dithiophosphates, amines, phenols and hindered phenols.



### **Antiwear**

When lubricated surfaces are completely separated by the lubricant film, negligible wear will occur and friction at constant load will be a function of the viscosity of the lubricant at the prevailing operating temperature and the speed. This is hydrodynamic lubrication. As pressure increases or speed decreases, or temperature rises, the lubricant film is squeezed out. When the film is so thin that high points on the opposing surfaces begin to rub, friction increases sharply and wear of the rubbing surfaces occurs. This is boundary lubrication. If lubricating oils are to reduce friction and prevent wear, special agents must be added to improve performance in boundary lubrication. Compound used as anti wear or as oiliners are esters fatty alcohols, phosphates, thiophosphates, phosphites, zinc diethyl dithio phosphate, rape seed oil, methyl stearate and dithiocarbonates.

### **Antirust agents**

An "antirust agent" is the name given to an additive that protects ferrous (iron) parts against rusting, when it is added to petroleum oils. Anti rust additives must have an affinity (or be attracted) to iron metallic surfaces and be able to repel water, or hold water so that the surfaces are protected from corrosion. These compounds include alkylated phenoxyl, alkylene oxides, alkaline earth sulphonates, alkenyl succinic acid and other derivatives of fatty and organic acids.

### **Corrosion inhibitors**

These are additives that protect corrosion-susceptible non-ferrous metal components of an engine from acidic attack. They help to neutralise the organic acid that develop in the oil and those induced by contaminants in the oils by chemically bonded on the engine parts to form a protective film to reduce corrosive wear. These inhibitors include highly alkaline materials such as zinc diethyl dithiophosphate, other sulphurs and phosphorus containing materials.

Table 2.3: Additives Used for Specific Equipment (Lansdown, 1982).

S/n	Equipment	Additives used
1	Petrol engine	Anti-oxidant, corrosion inhibitor, viscosity index improver, detergent/dispersant, anti-wear.
2	Diesel engines	Anti-oxidant, corrosion inhibitor, detergent/dispersant, anti-wear, anti-foam, basic additives (to neutralize acids)
3	Steam turbines, compressors	Anti-oxidant, corrosion inhibitor, anti-emulsifier
4	Gears, spur or bevel	Anti-wear, anti-oxidant, anti-foam, sometimes corrosion inhibitor
5	Gears, spiral bevel or hypoid	Extreme pressure, anti-foam, anti-oxidant
6	Gears, worm	Friction reducer, anti-oxidant, corrosion inhibitor
7	Machine-tool slide ways	Friction controller, anti-oxidant, corrosion inhibitor
8	Hydraulic systems	Anti-oxidant, anti-wear, antifoam, corrosion inhibitor, pour-point dispersant, viscosity index improver

### 2.5.3 Physicochemical properties of lubricating oil

These include the following:

**Kinematic viscosity:** This is the most widely used measurement in petroleum industry and is defined as the product of measured flow time and the calibration constant of the viscometer. Many petroleum and non-petroleum products are used as lubricants and the correct operation of the equipment depends upon the appropriate viscosity of the liquid used. In addition, the viscosity of many petroleum and non-petroleum products is important for the estimation of the optimum storage, handling operational conditions.

**Viscosity index (VI):** It is calculated from its viscosities in centistokes at 40 and 100°C. This is a dimensionless value used to denote viscosity change with temperature, normally ranging from 0 to 100 and above. If oil has a VI of 0, its viscosity changes rapidly with temperature. If it has VI of 100, its viscosity changes less with temperature.

**Density:** The density of lubricating oil is defined as the mass per unit volume at a standard temperature.

**Specific gravity:** The specific gravity is defined as the ratio of the weight of a unit volume of lubricating oil to the weight of an equal volume of water at a prescribed temperature. The widely used is the American Petroleum Institute (API) gravity value.

$$\text{API Gravity} = \frac{141.5}{\text{S.G. } 60/60 \text{ } ^\circ\text{F}} - 131.5$$

**Flash point:** This is the temperature at which lubricants releases a sufficient concentration of vapour at its surface to ignite when an open flame is applied to it. Flash point aids in evaluating fire resistant properties and like the pour point, flash point may in some instance become the major factor in selecting the proper lubricant, especially in lubricating machinery handling highly flammable materials

**Pour point:** This is the lowest temperature ( $15^{\circ}\text{C}$ ) at which the oil is observed to flow when cooled.

**Freezing point:** This is the temperature ( $5^{\circ}\text{C}$ ) at which solid crystal separates from lubricating oil.

**Carbon residue:** This is to determine the degree of reforming and carbon forming tendency of lubricating oil. Carbon residue is the amount of deposit (in 5 to 10 percentage by weight) after evaporation and pyrolysis of the product under prescribed conditions.

**Sulphate ash:** This is the residue, in percentage by weight remaining after burning the product, treating the deposit with sulphuric acid and burning this treated residue again to increase the non-combustible metallic components of the lubricating oil.

**Colour stability:** The colour of lubricating oil varies from colourless to dark red. Lubricating oil must have reasonable colour stability, so that no great discolouration may occur during storage. Colour stability is usually determined in an accelerated stability test by heating the oil for certain time at  $100^{\circ}\text{C}$ .

**Total acid number:** This is a measure of the amount of acid in oil expressed in terms of the quantity of a standard base required to neutralise a specific volume of oil.

**Total base number:** This is a measure of the alkalinity of the oil used and is defined as the rate of consumption of the alkaline content of the additive composition of the oil. New and used petroleum products can contain basic constituents that are present as additives. The relative amount of this material can be determined by titration with acid.

**Fire point:** This is the temperature at which the product will ignite and burn continuously when an open flame is applied on the lubricating oil.

**Cloud point:** This is the minimum temperature at which haze first appears to form wax crystals when the product is cooled.

Table 2.4: NIS Requirement for Engine Lubricating Oil (SON, 1995).

Characteristics	Specifications		
	Single grade	Single grade	Multi grade
	SAE 30	SAE 40	SAE 20W50
Appearance	Bright and clear	Bright and clear	Bright and clear
Specific gravity at 15°C	0.87-0.898	0.899-0.910	0.893-0.889
Kinematic viscosity at 100°C, cSt (mm <sup>2</sup> /s)	10.2-12.9	13.5-16.8	17.1-22.0
Viscosity index (VI) (min)	95	95 – 110.0	125
Total base no. MgKOH/g, (min)	5.0	5.0	5.0
Water content, %vol (max.)	0.025	0.025	0.025
Flash point, COC, °C (min)	204	204	204
Pour point, °C (max)	-18	-9	-23

## 2.6 Effect of Temperature and Pressure on the Viscosity of Lubricating Oils

The viscosity of most liquids changes with change in temperature. Oils of different chemical nature change viscosity to different extents when warmed through the same temperature ranges, but oils of approximately the same chemical nature but of different molecular weight (boiling point) will show different viscosity changes over the same range. In general, oils of more

Aromatic character decrease in viscosity faster for a given rise in temperature than do the paraffinic oils and oils of higher molecular weight. They similarly show greater change in viscosity per degree rise in temperature than do the lighter, less viscous oils of lower molecular weight. There has not been a strong theoretical basis relating temperature and viscosity. Most of the charts available is ASTM Viscosity – temperature charts (D341) and others are based on Walter equation (Gruce, 1967).

The effect of pressure on viscosity of lubricating oils is appreciable, although so far, it does not seem to have been applied very seriously by engineers. However; since the imposition of higher pressure causes increase of viscosity, this influence has been invoked as an explanation for another phenomenon. It is known that the working of an ordinary cylindrical journal in a sleeve bearing develops a high-pressure zone in the oil field which does the lubricating. It has been suggested that the increase in viscosity is responsible for effects now included under the mysterious name “oliness”. This rise in viscosity is attributed to increase in pressure in both cases, it can be said that moderate changes of viscosity are approximately proportional to changes of density, whether this later are caused by changes in temperature or of pressure. The change of viscosity with pressure change is influenced appreciably by the chemical structures of the compound or mixture of compound under study. For instance, as molecular weight or boiling point change their systematic change of



viscosity – pressure coefficient, but this varies as the chemical structure changes.

## 2.7 Statistical Design

This design, such as simplex lattice design is another method of designing lubricating oils. In order that the optimum performance of a lubricant be attained, product enhancement measures are therefore most effective at the designing stage using statistical modelling, typical of simplex-lattice design. To accommodate a polynomial region, a natural choice for a design would be one whose points are spread evenly over the whole simplex factor space. An ordered arrangement consisting of a uniformly spaced distribution of points on a simplex is known as a lattice. The name is used here simply to make reference to an array of points. The lubricant components in every blend or mixture are to satisfy the constraints;

$$x_i \geq 0, x_1 + x_2 + x_3 + \dots + x_q = 1.0,$$

where  $x_i$  (component proportion) can take the values from zero to unity, and all blends among the ingredients are possible.

The number of design points in the  $[q,m]$  simplex lattice is

$$\binom{q+m-1}{m} = \frac{(q+m-1)!}{m!(q-1)!}$$

Where  $m!$  is “M factorial” and

$$m! = m(m-1)(m-2)\dots(2)(1)$$

The symbol  $\binom{a}{b}$  is the combinational symbol for the number of ways “a” things can be taken “b” at a time and

$$\binom{a}{b} = \frac{(a!)}{b!(a-b)!}$$

In the {3,3} simplex-lattice which will be used for the design, for example, the number of points is

$$\binom{3+3-1}{3} = 10 \text{ points}$$

In the {q,m} simplex-lattice then, the points correspond to pure or single-component mixtures, to binary or two-component mixtures, to ternary or three component blends and so on, up to mixtures consisting of at most all "m" components. In table 2.5 below is indicated, the number of points in a {q,m} simplex-lattice for values of q and m for  $3 \leq q \leq 10$ ,  $1 \leq m \leq 4$ .

Table 2.5: Number of Points in the {q,m} Simplex-Lattice for  $3 \leq q \leq 10$ ,  $1 \leq m \leq 4$  where Number of Levels for each Components is m+1.

Degree of model	Number of components								
	M	q = 3	4	5	6	7	8	9	10
1		3	4	5	6	7	8	9	10
2		6	10	15	21	28	36	45	55
3		10	20	35	56	84	120	165	220
4		15	35	70	126	210	330	495	715

### 2.7.1 Factorial design ( $n^k$ ) lubricant composition

Factorial design is a statistical approach, which allows for simultaneous variation of process variables and more importantly all possible combinations of these variables at all chosen levels of investigation. Great number of variations are possible depending on the nature of the source of crude lubricant and method of application.

The number of possible combinations, "N" of these process-variables is given by  $N = n^k$ , where "n" stands for the number of possible levels of each variables and "k" for the number of process-variables that are to be considered for any particular experiment. The possible levels are usually obtained by using unifactor approach that is by varying one factor at a time while the other factors are fixed and the level that gives the best range of performance is chosen.

In the present study, a two level factorial experiment was considered, i.e.,  $N = 2^k$ . The process variables that are normally considered for lubricating oil application usually include temperature, pressure and time. The present factor in design expression,  $N = n^k$ , therefore is  $2^3 = 8$ , resulting in eight different operating conditions at which the oil would be subjected to.

## CHAPTER THREE

### 3.0 MATERIALS AND METHODS

#### 3.1 Instrumentation and Equipment

The following list of equipment and materials were used for the project (Table 3.1 and 3.2).

Table 3.1: List of Equipment

Equipment	Source	Code
Pilot blending machine	Prolabo, France	
Hydrometer	England	
Hydrometer cylinder	England	ISO 4788
Canon-Fenske routine viscometer	Technico, England	BS188ISO3105
PMT Tanson viscometer bath	Zoetermicer, Holland	
Sucker (Iso versinic)	Germany	
Seta-loc cloud and pour point refrigerator	Survey, U.K.	
Cleveland semi automatic apparatus (Cleveland open cup)	GmbH, Germany	
Potentiograph apparatus	Metrohm Herison, Switzerland	E536
Hydrostatic bench	Armfield, England	9092

Table 3.2: List of materials

Materials	Source	Code
500N	Venezuela	
Paranox	Paris	NOX 5501
Shelvis (copolymer)	Spain	SV 261
Petroleum spirit	Dagenham, England	
Paraffin oil	Nigeria	
Chlorobenzene	NAAFCO, Nigeria	
Acetic acid	Essex, England	6911
Perchloric acid	Unipetrol, Kaduna	
Methanol	Nigeria	

### 3.2 Formulation of the Lubricating Oils

The various lubricating samples were formulated using the pilot blending plant at Unipetrol laboratory, Kaduna, Nigeria. The various components (base oil, viscosity improver and additive package) of each sample were weighed in a 400 ml beaker using an electronic balance. During the formulation, each sample in the beaker was vigorously stirred to attain homogeneity and was at the same time heated at temperature of not more than 60°C using a heating mantle of the blending machine. The time for the blending for each sample was about five minutes. Immediately, a homogeneous mixture was attained, the sample was removed, cooled and analysed.

### 3.3 Characterisation of the Formulated Lubricating Oils

The physicochemical properties of the formulated lubricants were determined according to American Standard for Testing Materials (SON, 1995).

#### 3.3.1 Determination of kinematic viscosity at 100 and 40°C

A clean dry calibrated Canon Fenske viscometer with required estimated viscosity and flow time of not less than 200 seconds was used in determining the viscosity of the samples. The sample was then introduced into the capillary of the viscometer using suction. For the kinematic viscosity at 40°C, the temperature of the bath was allowed to reach 40°C and the viscometer was inserted into the bath. Suction was used to adjust the head level of the test sample to a position in the capillary arm of the instrument about 5mm ahead of the first timing mark. When the sample was flowing freely, the time was measured in seconds, for the oil to pass from the first timing mark to the second and the result recorded. This procedure was also repeated for kinematic viscosity at 100°C and the result recorded. The kinematic viscosity was calculated by multiplying the time with the tube constant, i.e.

$$N \times t \quad \text{-----} \quad 3.1$$

Where

N = tube constant

t = time in seconds for sample to pass through upper timing mark and lower timing mark

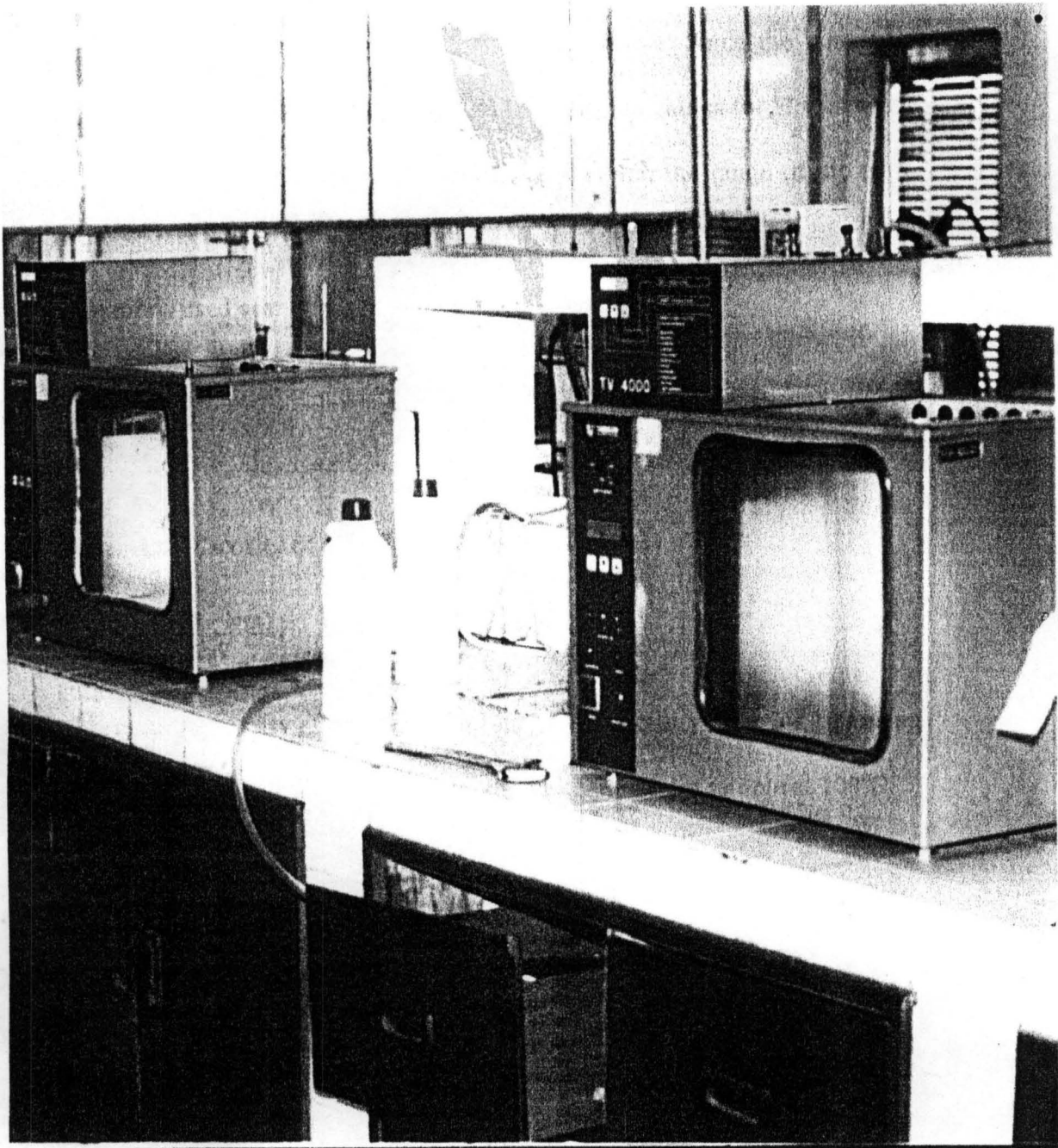


Plate I: Kinematic Viscosity Apparatus

### 3.3.2 Determination of viscosity index from kinematic viscosities at

#### 40 and 100°C

The procedure used to determine the viscosities index of the lubricants was that for oils of viscosity index of 100 and above. Since the kinematic viscosity of the oils at 100°C was less than 70 cSt, the values for H was taken from the table and measured values that are not within the range of the table and were interpolated.

The equations used are shown below (SON,1995);

$$Y^N = \frac{H}{U} \quad \text{-----3.2}$$

where

Y = kinematic viscosity of the oil sample at 110°C, cSt.

$$N = \frac{(\text{Log}H - \text{Log}U)}{\text{Log}Y} \quad \text{-----3.3}$$

H = kinematic viscosity at 40°C of an oil having a viscosity index of 100 using procedure A, and having the same kinematic viscosity as the sample at 100°C.

U = kinematic viscosity at 40°C of the sample (i.e. H>U)

$$\text{Viscosity index} = \{[\text{antilog}N]-1\}/0.00715\}+100 \quad \text{-----3.4}$$



### 3.3.3 Determination of specific gravity at 15°C

The sample was transferred into clean hydrometer cylinder without splashing air bubbles formation. The cylinder containing the sample was placed in a vertical position in a location free from air currents. The hydrometer was then lowered gently into the sample ensuring that the stem was not wetted. When the hydrometer was at rest floating freely away from the walls of the cylinder, the estimated reading of the hydrometer scale was recorded as the specific gravity. The correct hydrometer reading was the point on the meter at which the principal surface of the liquid cuts the scale ensuring horizontal value. The hydrometer was removed and the sample stirred continuously with the thermometer with the mercury thread fully immersed. The temperature of the sample was then recorded. The specific gravity of the lubricant was calculated using the formula below (SON, 1995);

$$\text{Specific gravity (15°C)} = (T - 15) 0.00062 + X \quad \text{-----3.5}$$

Where

T = temperature of sample

X = hydrometer reading

0.00062 = constant

### 3.3.4 Determination of API gravity

All API gravities were calculated using the formula,

$$\text{API Gravity} = \frac{141.5}{\text{S.G. } 60/60^{\circ}\text{F}} - 131.5 \quad \text{-----3.6}$$

Where

S.G. 60/60<sup>0</sup>F = specific gravity of samples at 60<sup>0</sup>F.

### 3.3.5 Determination of flash point (Cleveland open cup method)

The cup was filled with the sample so that the top of the meniscus was exactly at the filling line. The test flame was lighted and adjusted to a diameter of 3.2 to 4.8 mm. Heat was applied initially at the rate of 14 to 17 °C/min. When the sample was approximately 56°C below the expected flash point, the heat was reduced so that the rate of temperature rise of the last 28°C before the flash point was 5 to 6 °C/min. At 28 °C below the expected flash point, the test flame was applied and continued at every 2 °C rise thereafter. The test flame was passed across the center of the cup at right angles to the diameter and was not more than 3 mm above the upper edge of the cup in one direction only. The flash point was recorded at the temperature at which an instantaneous flash occurs on application of the flame.

### 3.3.6 Determination of pour point

The seta-loc cloud and pour point refrigerator was used to determine the pour point. The sample was poured into the test jar to the level mark. The test jar was closed with the cork carrying high-pour thermometer. The position of

the cork with the thermometer was adjusted so to fit tightly (the thermometer and the jar are co-axial) and the thermometer bulb was immersed so that the beginning of the capillary was 3 mm below the surface of the oil. The disk was placed at the bottom of the jacket and the gasket around the test jar 25 mm from the bottom. The test jar was inserted in the jacket and placed in the cooling medium without disturbing the oil as well as not shifting the thermometer.

The appearance of oil was examined when the oil temperature was 9 °C above the expected hour. At each test thermometer, the oil was removed and the jar tilted to see if there was any movement of oil. Where there was movement of oil, the jar was replaced in the jacket and the test was repeated at the next temperature 3 °C lower. This test was continued until the oil showed no movement each time the jar was tilted in a horizontal position. The reading was observed from the thermometer and recorded as maximum pour point. A 3 °C was added to the temperature recorded and result reported as the pour point.

### **3.3.7 Determination of total base number**

The potentiograph apparatus was used to determine the total base number of lubricant samples. Approximately 6.0 g of sample was weighed as required from its expected base number. The potentiograph was adjusted in accordance with manufacturer's instruction and titrated at a speed of 1.0 ml/min. On the completion of the titration, the beaker was removed and the electrode and

burette tip were rinsed with water, then again with solvent. A blank titration was made for each sample using 120 ml of titration solvent. The endpoint was interpreted from the graph obtained. The base number was calculated as follows;

$$\text{Base Number (mgKOH/g)} = \frac{\{[E-F]M_a \times 56.1\}}{S} \quad \text{-----}3.7$$

where

E is the volume of  $\text{HClO}_4$  (ml) used to titrate the sample to end point

F is the volume corresponding to E for blank titration

$M_a$  is molarity of  $\text{HClO}_4$  solution and

S is sample weight in grammes

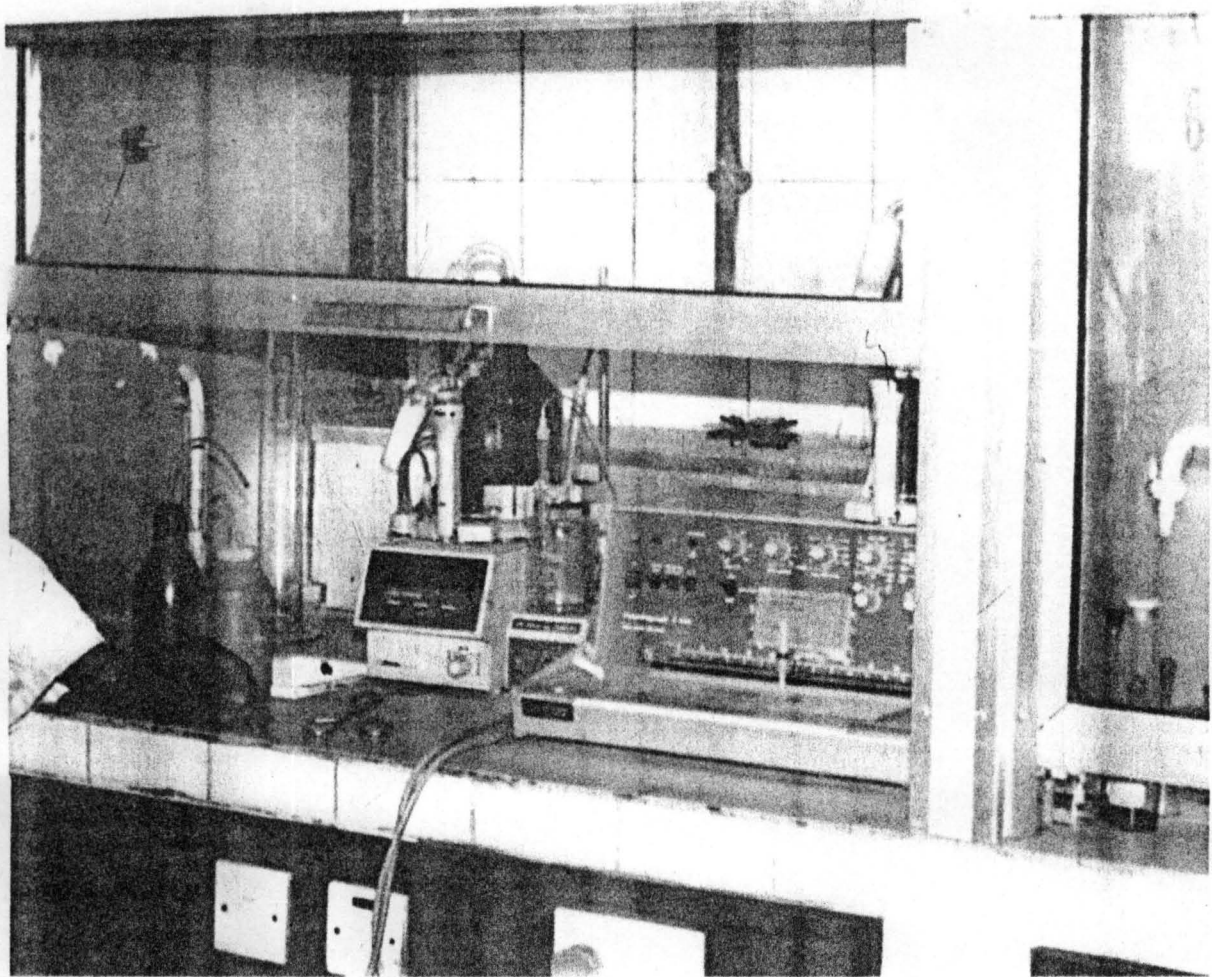


Plate II: Total Base Number Apparatus

### 3.3.8 Determination of water content

The beaker and thermometer were weighed and the reading was taken then 20ml of the lubricating oil sample was added and reweighed. The weighed sample was placed on a heating mantle and heated to a temperature above 100°C with continuous stirring. At 110°C, the sample was left on the heating mantle for one minute. This is to allow water to evaporate out of lubricating oil sample. The sample was removed, allowed to cool and was reweighed. The water content was calculated using the formula,

$$\% \text{ water} = \frac{V}{W} \times 100 \quad \text{-----}3.8$$

Where,

V is the difference in weight before and after heating the sample and

W is the initial weight of sample

### 3.3.9 Determination of appearance

Visual method was used to determine the appearance of the samples. Each sample of the lubricating oil in measuring cylinder was held up to the light and was visually examined for haze or lack of clarity. Subsequently, vortex was produced by swirling the oil sample and the bottom of the vortex was examined for particulate matter. The result was recorded as bright and clear or not clear.

Table 3.3 Various Tests and Test Methods used for Characterization of oil.

Test	Test Method
Specific Gravity	ASTM D 1298
Appearance	ASTM D 4176/1
Kinematic Viscosity at 40°C and 100°C	ASTM D 445
Viscosity Index	ASTM D 2270
Flash Point	ASTM D 92
Pour Point	ASTM 97
Total Base Number	ASTM D 2896

### 3.4 $2^3$ – Factorial Design

The lubricants formulated were studied using a two level factorial design, resulting in eight operating conditions at which blends were subject to process variables namely temperature, pressure and time. The viscosities were determined at various combinations of process variables using statistical design.

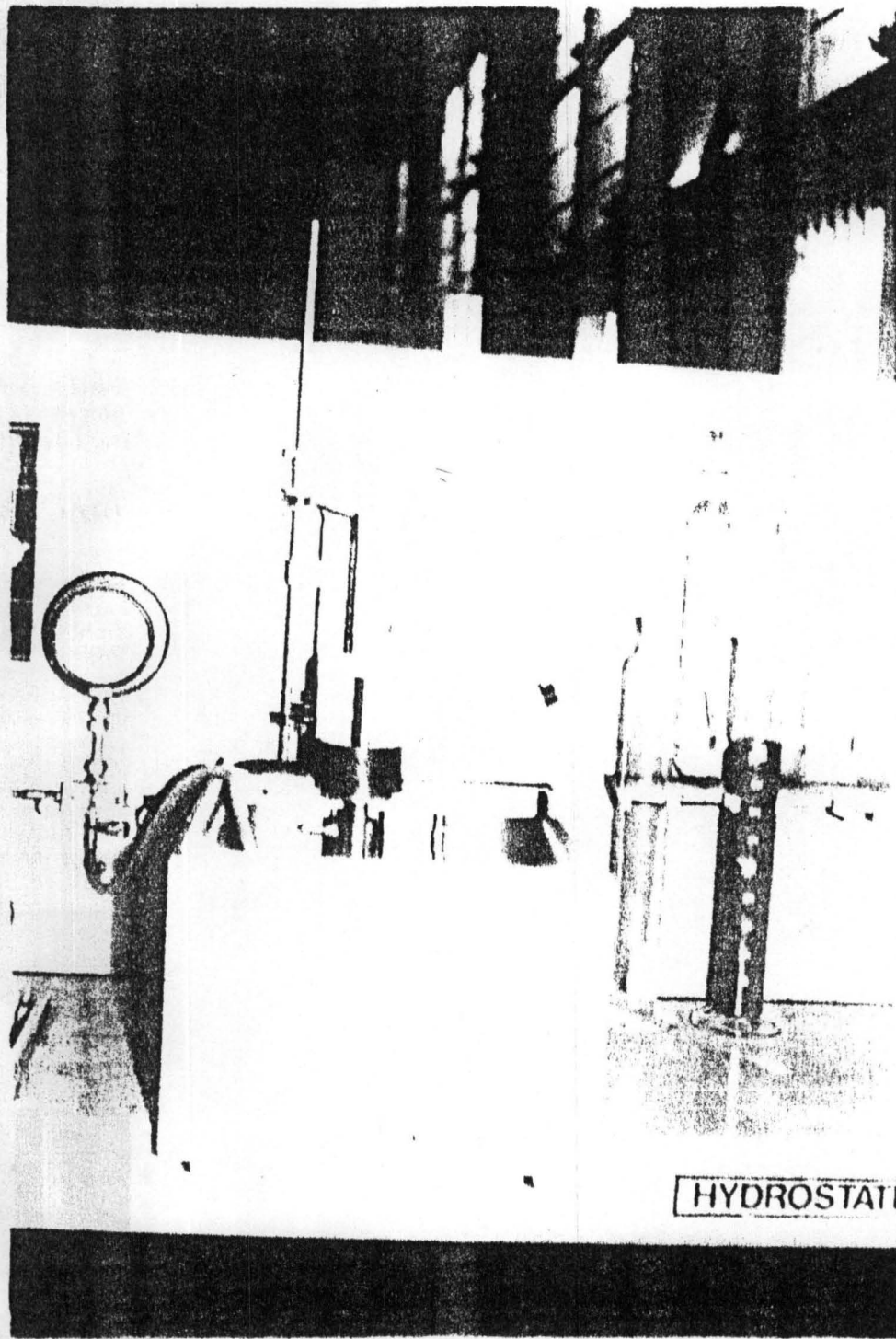


Plate III: Lubricating Oil Test Apparatus



## CHAPTER FOUR

### 4.0 RESULTS

Table 4.1: Physicochemical Properties of Lubricants

Lubricant number	I			II			III			IV			V			VI			VII			VIII			IX			X					
Composition	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	X <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>			
	1	0	0	.873	.127	0	.86	.14	0	.835	.10	.065	.82	.12	.06	.85	.08	.07	.87	.07	.06	.88	.06	.06	.873	.065	.06	.871	.068	.06			
Lubricant properties																																	
Appearance	Bright & clear			Bright & clear			Bright & clear			Bright & clear			Bright & clear			Bright & clear			Bright & clear			Bright & clear			Bright & clear			Bright & clear			Bright & clear		
Specific gravity at 15 °C	0.8814			0.8906			0.892			0.8897			0.8921			0.8884			0.8889			0.8885			0.8887			0.8888					
API gravity	29.0			27.4			27.1			27.5			27.1			27.8			27.7			27.8			27.7			27.7					
Kinematic viscosity at 40 °C, cSt	93.37			140.41			145.99			202.83			206.39			199.43			182.64			175.96			172.22			175.27					
Kinematic viscosity at 100 °C, cSt	10.88			14.71			15.25			20.90			21.63			20.97			19.26			18.78			18.59			19.07					
Viscosity index	100			104			106			122			126			124			120			120			121			124					
Total base number, mg KOH/g	0			8.78			9.77			6.89			9.36			5.64			4.85			4.19			4.49			4.72					
Flash point, °C	242			228			230			230			236			232			226			230			234			236					
Pour point, °C	-7			-8			-9			-7			-9			-10			-10			-11			-8			-8					
Water content, %vol	Nil			Nil			Nil			Nil			Nil			Nil			Nil			Nil			Nil			Nil					

x<sub>1</sub>: 500N (base oil), x<sub>2</sub>: Poranox 5501 (additive package), x<sub>3</sub>: SV 261 (viscosity improver)

The Table 4.2: Various Combinations Used for the Statistical Design

Process variables			I	II	III	IV	V	VI	VII	VIII	IX	X																			
P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>1</sub>	x <sub>2</sub>																		
Temperature	Pressure	Time	1	0	0	.873	.127	0	.86	.14	0	.835	.10	.065	.82	.12	.06	.85	.08	.07	.87	.07	.06	.88	.06	.06	.873	.065	.06	.871	.068
(°C)	(bar)	(hr)	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity	Viscosity																		
			(cSt)	(cSt)	(cSt)	(cSt)	(cSt)	(cSt)	(cSt)	(cSt)	(cSt)	(cSt)	(cSt)																		
40	1	4	91.70	138.44	144.05	201.42	205.31	198.47	180.98	174.52	171.07	174.35																			
100	1	4	10.22	13.91	15.12	20.44	21.25	20.63	18.39	18.06	18.12	18.73																			
40	2	4	91.53	137.27	143.40	201.35	205.18	198.19	180.91	174.49	171.01	174.29																			
100	2	4	10.11	13.87	15.06	20.41	21.13	20.62	18.35	18.04	18.09	18.69																			
40	1	6	91.43	137.40	143.06	201.24	205.14	198.12	180.88	174.43	170.98	174.25																			
100	1	6	10.09	13.84	15.02	20.39	21.09	20.61	18.35	17.62	18.08	18.67																			
40	2	6	91.36	137.04	142.43	201.20	205.07	198.09	180.81	174.39	170.93	174.19																			
100	2	6	10.05	13.76	14.97	20.36	21.09	20.57	18.30	17.48	18.05	18.64																			

$$\sum_{i=1}^3 x_i = 1$$

Table 4.3: Probability Greater than F for Oil Samples and Process Variables

Lubricant Number	I	II	III	IV	V	VI	VII	VIII	IX	X
	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F	Pr > F
Process Variables										
P <sub>1</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
P <sub>2</sub>	0.0489	0.3028	0.0046	0.112	0.1180	0.4208	0.0277	0.2840	0.0374	0.0335
P <sub>3</sub>	0.0303	0.3375	0.0030	0.0443	0.0792	0.3145	0.0219	0.0587	0.0255	0.0205
P <sub>1</sub> P <sub>2</sub>	0.2048	0.3454	0.0054	0.3440	0.4097	0.5236	0.1257	0.5635	0.1257	0.1257
P <sub>1</sub> P <sub>3</sub>	0.0760	0.4216	0.0036	0.0826	0.4097	0.4043	0.0577	0.0859	0.0704	0.0704
P <sub>2</sub> P <sub>3</sub>	0.1112	0.5314	0.2048	0.5000	0.2048	0.5760	0.5000	0.4471	0.5000	0.5000

Table 4.4: Regression Model Equation for the Lubricating Oil Samples

Lubricant Sample	I	II	III	IV	V	VI	VII	VIII	IX	X
Source										
Intercept	147.0654167	225.79125	234.2229167	322.6720833	328.8091667	318.278333	289.7129167	278.2220833	273.3529167	278.45375
P <sub>1</sub>	-1.36279167	-2.101875	-2.18804167	-3.02045833	-3.06991667	-2.97133333	-2.71204167	-2.59295833	-2.55104167	-2.595625
P <sub>2</sub>	-0.3625	-2.1975	-1.0675	-0.10916667	-0.35166667	-0.51666667	-0.07416667	0.1575	-0.08416667	-0.08916667
P <sub>3</sub>	-0.21541667	-0.78791667	-0.79625	-0.13208333	-0.15083333	-0.25833333	-0.06458333	0.13625	-0.06125	-0.06875
P <sub>1</sub> P <sub>2</sub>	0.00075	0.01175	0.00975	0.000416667	0.000666667	0.002166667	0.000416667	-0.00075	0.000416667	0.000416667
P <sub>1</sub> P <sub>3</sub>	0.001041667	0.004541667	0.007375	0.000958333	0.000333333	0.001583333	0.000458333	-0.003375	0.000375	0.000375
P <sub>3</sub> P <sub>3</sub>	0.0425	0.1925	0.0075	0.0075	0.045	0.055	-0.0025	-0.0325	0.0025	0.0025

## CHAPTER FIVE

### 5.0 DISCUSSION OF RESULTS

The values of the properties of the samples as obtained from the analysis of the physicochemical properties were given in tabulated Table 4.1. From the table, the appearances of the samples are bright and clear and are in conformity with the literature value (SON, 1995) as seen in Table 2.4.

The specific gravity value of the samples measured at 15°C are as follows 0.8814, 0.8806, 0.892, 0.8897, 0.8921, 0.8884, 0.8889, 0.8885, 0.8887 and 0.8888 for sample 1 - 10 respectively. These values also conform with the literature values (Table 2.4) except for samples II and III which are a little bit low but are still considered reasonable. This discrepancy may be attributable to little error in the experimental procedure.

The API gravity of the samples determined given in Table 4.1 conform with the literature, which are within the range of 24 – 30, confirming the results of the specific gravity, but why there is no deviation in case of samples II and III could not be explained.

The kinematic viscosity of the samples which is a major grading property of lubricants was used in classifying the lubricants into grades. From Table 4.1, the lubricants values fall within the various range of the literature value. For instance, sample I fall within the SAE 30 range, samples II and III fall within the SAE 40 and sample IV – X fall within the SAE 20W50 multigrade oil.

The viscosity index of the samples are 100, 104, 106, 122, 126, 124, 120, 120, 121 and 124 for I – X, respectively. The values for samples I, II, III and V

fall above the minimum value of Table 2.4.while the others are a little bit low the literature minimum value but are still considered reasonable. This discrepancy is attributable to the amount of viscosity improver and additive used in their formulation. The viscosity index of sample V is of the highest value and this means that the lubricant tend to display less change in viscosity with temperature increase and this implies that it has the best performance amongst others. Samples IV-X have higher viscosity indices because of the viscosity improver added in their formulation which boost their viscosities.

The result of the total base number (TBN) of the oils are given in Table 4.1. When compared with literature values in Table 2.4, the values of sample II, III, IV, V and VI are above the minimum literature of value. The value of sample VII and X, which are 4.85 and 4.72 mgKOH/g respectively, are not far from the literature value of 5.0 mgKOH/g. The values, which are a little bit low are those of samples VIII and IX, which are 4.19 and 4.49 mgKOH/g respectively. This attributed to the amount of additive used in formulating them. The TBN value of sample I is zero (mgKOH/g) and this is due to complete absence of additive in it. The implication of TBN below minimum value is that the lubricant can easily degrade when in service.

The results of the flash point of the lubricants are given in Table 4.1. It can be seen that these values are above the minimum literature value of 204 and 220°C (SON, 1995). These values indicate that the lubricants do not have highly volatile and flammable material in them.

The pour points of the lubricants are given in Table 4.1. These pour point values indicate the lowest temperature at which the oils could be used in any application. From the present study, it is understandable that some of the lubricants (IV-X) have high pour point values. This is attributable to the amount of wax present in the oil.

The water content of the lubricants is zero % volume. The literature value is 0.025% vol, maximum. This value indicated the complete absence of water in the formulated lubricants.

Table 4.2 shows the various combinations formed using  $2^3$  factorial design.

Table 4.3 shows the probability greater than "F" results extracted from the analysis of variance procedure obtained using table 4.2, that is, the effect of process variables (temperature, pressure and time) on their interactions on the viscosity of the lubricants.

From table 4.3, the results of the samples I, VII, IX and X show that temperature, pressure, and time have significant effect on the viscosity of the components while the interaction between temperature and pressure, temperature and time, pressure and time have no significant effect on the lubricants.

The results of samples II, V, VI and VIII show that only temperature has significant effect on the viscosity of the lubricants while pressure, time and the interactions between the process variables have no significant effect.

The result of sample III shows that temperature, pressure and time and the interaction between temperature and pressure, temperature and time have significant effect on its viscosity, while the interaction between pressure and time has no significant effect.

The result of sample IV shows that temperature and time have significant effect on the viscosity of the lubricant while pressure and the interaction between the process variables have no significant effect on it.

From Appendix B, it can be seen that for all the lubricants, the coefficient of regression ( $R^2$ ) is 1.0 (100%) except for sample II which has  $R^2$  value of 0.99999 (99.999%). This shows a perfect correlation. That is, all the points lie exactly on a line, so there is perfect linear relationship between the variable (process variables and dependent variable) of the samples. The coefficient of variations (CV) for the lubricants is less than 1. This shows that it is significant which implies that there is a very small variation of the effects on viscosities of the mixture.

Table 4.4 shows the regression model analysis and the results of the parameter estimate of the process variable of lubricants and their interactions. From the table the value of the intercepts of the samples are 147.0654167, 225.79125, 234.2229167, 332.6720833, 328.8091667, 318.2783333, 289.7129167, 278.2220833, 273.3529167 and 278.45375 cSt respectively. This values signify the viscosity of each sample where the value of the process variables is zero.



The parameter estimates (coefficients) of the process variables of the lubricants are negative values except for sample VIII where that for pressure and time are positive values. The negative values show a decrease. The higher the values, the greater the decrease in viscosities of the samples when the process variables are applied. Also the parameter estimate of the interaction between the process variables shows positive values except for sample VIII which has negative values. The positive values show an increment in viscosity of the samples when they are applied.

The Appendix B also shows the effect of process variables and their interactions on the viscosity of the lubricants. From the table, the results of samples II, IV, V, VI, VIII and IX show that only temperature has significant effect on the viscosity of the lubricants. The results of samples I, VII and X show that temperature and time have significant effect while pressure and the interactions between the process variables have no significant effect on the viscosities. The result of sample III shows that only the interaction between pressure and time that has no significant effect while the process variable and the remaining interactions have significant effect on the viscosity of the lubricant.

From Appendix B the regression analysis data show that the coefficient of regression ( $R^2$ ) is 1.0 for samples III, VII, IX and X while for samples I, II, IV, V, VI and VIII is approximately 1 (0.9999). This result shows a very good correlation between the variables.

## CHAPTER SIX

### 6.0 CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

It can be concluded that the ten samples formulated (i.e. pure blend, binary blend and ternary blend.) met the viscosity requirements of the grades of motor oils SAE 30, SAE 40 and SAE 20W50. Out of these samples, samples V and VI of the SAE 20W50 multi-grade motor oil have the best performance, since their properties are very close to literature standards with viscosity index of 126 and 124 respectively.

The analysis of variance performed for the samples that gave the best result shows that only temperature has significant effect on the viscosities of the components. The coefficient of regression ( $R^2$ ) is 1 for all the samples which means that there is a very good correlation between the variables. On the other hand the  $R^2$  from the regression model analysis for the samples is approximately 1.0. For samples that gave the best results, the models are given as follows:

$$V_5 = 328.8091667 - 3.06991667p_1 - 0.35166667p_2 - 0.15083333p_3 \\ + 0.000666667p_1p_2 + 0.000333333 p_1p_3 + 0.045 p_2p_3 \text{ ----- } 6.1$$

$$V_6 = 318.2783333 - 2.97133333p_1 - 0.51666667p_2 - 0.25833333p_3 \\ + 0.002166667p_1p_2 + 0.001583333 p_1p_3 + 0.055 p_2p_3 \text{ ----- } 6.2$$

## 6.1 Recommendations

It is recommended that the present petroleum based lubricants be tested with a reciprocating internal combustion engine of spark and compression-ignition types, so as to ascertain its suitability and performance as a motor engine lubricating oil.

It is also recommended that the lubricants be applied and tested at higher process variables and level so as to get a maximum process variables and level at which the formulations will give best performance.

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## APPENDICES

### Appendix A: Composition of Additive

Table A1: Paranox 5501 Performance Package

Typical Inspections	PARANOX 5501	Lubricant Formulated with 12.7% mass PARANOX 5501
Kinematic viscosity at 40 <sup>0</sup> c, cSt	4600	-
Kinematic viscosity at 100 <sup>0</sup> c, cSt	180	-
Density at 15 <sup>0</sup> c, Kg/m <sup>3</sup>	965	-
Sulphated Ash, mass %	8.7	1.1
Total Base Number, MgKOH/g	69	8.8
Mineral Oil content, mass %	39	-
Boron, mass %	0.11	0.01
Calcium, mass %	1.56	0.20
Copper, mass %	Nil	Nil
Magnesium, mass %	0.36	0.05
Nitrogen, mass %	0.57	0.07
Phosphorus, mass %	0.78	0.10
Sulphur, mass %	2.46	0.31
Zinc, mass %	0.86	0.11

Appendix B: Analysis of Variance Procedure

Table B1: Analysis of Variance Procedure for the Three Process Variables and  
Dependant Variable of Lubricants

Dependent variable	Source	DF	Sum squares	of Mean square	F value	Pr > F	R-square	CV
1	Model	6	13247.93137	2207.98856	99999.99	0.0	1.000000	0.020875
	Error	1	0.00011	0.00011				
	Corrected total	7	13247.93149					

Dependent variable	Source	DF	Sum squares	of Mean square	F value	Pr > F	R-square	CV
2	Model	6	30600.74338	5100.12390	56471.96	0.0032	0.999997	0.39703
	Error	1	0.09031	0.09031				
	Corrected total	7	30600.83369					

Dependent variable	Source	DF	Sum squares	of Mean square	F value	Pr > F	R-square	CV
3	Model	6	32868.01627	5478.00271	99999.99	0.0	1.000000	0.00446
	Error	1	0.00001	0.00001				
	Corrected total	7	32868.01629					

Dependent variable	Source	DF	Sum of squares	Mean square	F value	Pr > F	R-square	CV
4	Model	6	65451.46277	10908.57713	99999.99	0.0	1.000000	0.009568
	Error	1	0.00011	0.00011				
	Corrected total	7	65451.46289					

Dependent variable	Source	DF	Sum of squares	Mean square	F value	Pr > F	R-square	CV
5	Model	6	67737.80970	11289.63495	99999.99	0.0	1.000000	0.01874
	Error	1	0.00045	0.00045				
	Corrected total	7	67737.81015					

Dependent variable	Source	DF	Sum of squares	Mean square	F value	Pr > F	R-square	CV
6	Model	6	63090.70675	10515.11779	99999.99	0.0	1.000000	0.090479
	Error	1	0.00980	0.00980				
	Corrected total	7	63090.71655					



Dependent variable	Source	DF	Sum squares	of Mean square	F value	Pr > F	R-square	CV
7	Model	6	52843.39848	8807.23308	99999.99	0.0	1.000000	0.003549
	Error	1	0.00001	0.00001				
	Corrected total	7	52843.39849					

Dependent variable	Source	DF	Sum squares	of Mean square	F value	Pr > F	R-square	CV
8	Model	6	49083.41337	8180.56890	99999.99	0.0	1.000000	0.040457
	Error	1	0.00151	0.00151				
	Corrected total	7	49083.41489					

Dependent variable	Source	DF	Sum squares	of Mean square	F value	Pr > F	R-square	CV
9	Model	6	46764.47807	7794.07968	99999.99	0.0	1.000000	0.003740
	Error	1	0.00001	0.00001				
	Corrected total	7	46764.47809					

Dependant	Source	DF	Sum of squares	Mean square	F value	Pr > F	R-square	CV
10	Model	6	48414.95818	8069.15970	99999.99	0.0	1.000000	0.003665
	Error	1	0.00001	0.00001				
	Corrected total	7	48414.95819					

Table B2: Analysis of Variance Procedure for Process Variables

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
1	p1	1	13247.85031	13247.85031	99999.99	0.0
	p2	1	0.10901	0.10901	169.00	0.0489
	p3	1	0.04961	0.04961	441.00	0.0303
	p1p2	1	0.00101	0.00101	9.00	0.2048
	p1p3	1	0.00781	0.00781	69.44	0.0760
	p2p3	1	0.00361	0.00361	32.11	0.1112

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
2	p1	1	30599.66911	30599.66911	99999.99	0.0
	p2	1	0.34031	0.34031	3.77	0.3028
	p3	1	0.26281	0.26281	2.91	0.3375
	p1p2	1	0.24851	0.24851	2.75	0.3454
	p1p3	1	0.14851	0.14851	1.64	0.4216
	p2p3	1	0.07411	0.07411	0.82	0.5314

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
3	p1	1	32866.63411	32866.63411	99999.99	0.0
	p2	1	0.24151	0.24151	19321.00	0.0046
	p3	1	0.57781	0.57781	46225.00	0.0030
	p1p2	1	0.17111	0.17111	13689.00	0.0054
	p1p3	1	0.39161	0.39161	31329.00	0.0036
	p2p3	1	0.00011	0.00011	9.00	0.2048

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
4	p1	1	65451.42901	65451.42901	99999.99	0.0
	p2	1	0.00361	0.00361	32.11	0.1112
	p3	1	0.02311	0.02311	205.44	0.0443
	p1p2	1	0.00031	0.00031	2.78	0.3440
	p1p3	1	0.00661	0.00661	58.78	0.0826
	p2p3	1	0.00011	0.00011	1.00	0.5000

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
5	p1	1	67737.76245	67737.76245	99999.99	0.0
	p2	1	0.01280	0.01280	28.44	0.1180
	p3	1	0.02880	0.02880	64.00	0.0792
	p1p2	1	0.00080	0.00080	1.78	0.4097
	p1p3	1	0.00080	0.00080	1.78	0.4097
	p2p3	1	0.00405	0.00405	9.00	0.2048

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
6	p1	1	63090.62420	63090.62420	99999.99	0.0
	p2	1	0.01620	0.01620	1.65	0.4208
	p3	1	0.03380	0.03380	3.45	0.3145
	p1p2	1	0.00845	0.00845	0.86	0.5236
	p1p3	1	0.01805	0.01805	1.84	0.4043
	p2p3	1	0.00605	0.00605	0.62	0.5760

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
7	p1	1	52843.37951	52843.37951	99999.99	0.0
	p2	1	0.00661	0.00661	529.00	0.0277
	p3	1	0.01051	0.01051	841.00	0.0219
	p1p2	1	0.00031	0.00031	25.00	0.1257
	p1p3	1	0.00151	0.00151	121.00	0.0577
	p2p3	1	0.0001	0.0001	1.00	10

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
8	p1	1	49083.14461	49083.14461	99999.99	0.0
	p2	1	0.00661	0.00661	4.37	0.2840
	p3	1	0.17701	0.17701	117.03	0.0587
	p1p2	1	0.00101	0.00101	0.67	0.5635
	p1p3	1	0.08201	0.08201	54.22	0.0859
	p2p3	1	0.00211	0.00211	1.40	0.4471

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
9	p1	1	46764.46531	46764.46531	99999.99	0.0
	p2	1	0.00361	0.00361	289.00	0.0374
	p3	1	0.00781	0.00781	625.00	0.0255
	p1p2	1	0.00031	0.00031	25.00	0.1257
	p1p3	1	0.00101	0.00101	81.00	0.0704
	p2p3	1	0.00001	0.00001	1.00	0.5000

Dependant variable	Source	DF	Anova SS	Mean square	F value	Pr>F
10	p1	1	48414.94031	48414.94031	99999.99	0.0
	p2	1	0.00451	0.00451	361.00	0.0335
	p3	1	0.01201	0.01201	961.00	0.0205
	p1p2	1	0.00031	0.00031	25.00	0.1257
	p1p3	1	0.00101	0.00101	81.00	0.0704
	p2p3	1	0.00001	0.00001	1.00	0.5000

v2	p1	p2	p3	p1p2	p1p3	p2p3
138.44	40	1	4	40	160	4
13.91	100	1	4	100	400	4
137.27	40	2	4	80	160	8
13.87	100	2	4	200	400	8
137.4	40	1	6	40	240	6
13.84	100	1	6	100	600	6
137.04	40	2	6	80	240	12
13.76	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999998524
R Square	0.999997049
Adjusted R Square	0.999979341
Standard Error	0.300520382
Observations	8

<i>ANOVA</i>					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	30600.74338	5100.123896	56471.9601	0.003221126
Residual	1	0.0903125	0.0903125		
Total	7	30600.83369			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	225.79125	2.255293734	100.1161164	0.0063586	197.1351488	254.4473512	197.1351488	254.4473512
p1	-2.101875	0.020952783	-100.314839	0.00634601	-2.368104204	-1.8356458	-2.368104204	-1.835645796
p2	-2.1975	1.191601105	-1.8441574	0.3163211	-17.33816274	12.94316274	-17.33816274	12.94316274
p3	-0.78791667	0.417556342	-1.8869709	0.3102372	-6.093450305	4.517616972	-6.093450305	4.517616972
p1p2	0.01175	0.007083333	1.658823529	0.34536803	-0.078251898	0.101751898	-0.078251898	0.101751898
p1p3	0.004541667	0.003541667	1.282352941	0.42164104	-0.040459282	0.049542616	-0.040459282	0.049542616
p2p3	0.1925	0.2125	0.905882353	0.5314125	-2.507556939	2.892556939	-2.507556939	2.892556939



v3	p1	p2	p3	p1p2	p1p3	p2p3
144.05	40	1	4	40	160	4
15.12	100	1	4	100	400	4
143.4	40	2	4	80	160	8
15.06	100	2	4	200	400	8
143.06	40	1	6	40	240	6
15.02	100	1	6	100	600	6
142.43	40	2	6	80	240	12
14.97	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	1
R Square	1
Adjusted R Square	0.999999997
Standard Error	0.003535534
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	32868.01628	5478.002713	438240217	3.65653E-05
Residual	1	1.25E-05	1.25E-05		
Total	7	32868.01629			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	234.2229167	0.026532867	8827.651856	7.21165E-05	233.8857861	234.5600473	233.8857861	234.5600473
p1	-2.18804167	0.000246503	-8876.31708	7.17212E-05	-2.191173775	-2.18490956	-2.191173775	-2.184909558
p2	-1.0675	0.014018837	-76.147546	0.008359865	-1.245625444	-0.88937456	-1.245625444	-0.889374556
p3	-0.79625	0.004912428	-162.088904	0.003927546	-0.858668043	-0.73383196	-0.858668043	-0.733831957
p1p2	0.00975	8.33333E-05	117	0.005441062	0.008691154	0.010808846	0.008691154	0.010808846
p1p3	0.007375	4.16667E-05	177	0.003596684	0.006845577	0.007904423	0.006845577	0.007904423
p2p3	0.0075	0.0025	3	0.204832765	-0.024265376	0.039265376	-0.024265376	0.039265376

v4	p1	p2	p3	p1p2	p1p3	p2p3
201.42	40	1	4	40	160	4
20.44	100	1	4	100	400	4
201.35	40	2	4	80	160	8
20.41	100	2	4	200	400	8
201.24	40	1	6	40	240	6
20.39	100	1	6	100	600	6
201.2	40	2	6	80	240	12
20.36	100	2	6	200	600	12

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999999999
R Square	0.999999998
Adjusted R Square	0.999999988
Standard Error	0.010606602
Observations	8

ANOVA					
	df	SS	MS	F	Significance F
Regression	6	65451.46278	10908.57713	96965130	7.77352E-05
Residual	1	0.0001125	0.0001125		
Total	7	65451.46289			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	322.6720833	0.079598602	4053.740565	0.00015705	321.6606915	323.6834751	321.6606915	323.6834751
p1	-3.02045833	0.00073951	-4084.40514	0.00015587	-3.029854658	-3.01106201	-3.029854658	-3.011062008
p2	-0.10916667	0.04205651	-2.5957139	0.23410225	-0.643542999	0.425209665	-0.643542999	0.425209665
p3	-0.13208333	0.014737283	-8.96252969	0.07073868	-0.319337462	0.055170795	-0.319337462	0.055170795
p1p2	0.000416667	0.00025	1.666666667	0.34404174	-0.002759871	0.003593204	-0.002759871	0.003593204
p1p3	0.000958333	0.000125	7.666666667	0.0825712	-0.000629935	0.002546602	-0.000629935	0.002546602
p2p3	0.0075	0.0075	1	0.5	-0.087796127	0.102796127	-0.087796127	0.102796127

v5	p1	p2	p3	p1p2	p1p3	p2p3
205.31	40	1	4	40	160	4
21.25	100	1	4	100	400	4
205.18	40	2	4	80	160	8
21.13	100	2	4	200	400	8
205.14	40	1	6	40	240	6
21.09	100	1	6	100	600	6
205.07	40	2	6	80	240	12
21.09	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999999997
R Square	0.999999993
Adjusted R Square	0.999999953
Standard Error	0.021213203
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	67737.8097	11289.63495	25088077.7	0.000152824
Residual	1	0.00045	0.00045		
Total	7	67737.81015			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	328.8091667	0.159197205	2065.420478	0.00030823	326.7863831	330.8319503	326.7863831	330.8319503
p1	-3.06991667	0.00147902	-2075.64251	0.00030671	-3.088709316	-3.05112402	-3.088709316	-3.051124017
p2	-0.35166667	0.084113019	-4.1808827	0.14946128	-1.420419331	0.717085998	-1.420419331	0.717085998
p3	-0.15083333	0.029474565	-5.11740654	0.12285466	-0.52534159	0.223674923	-0.52534159	0.223674923
p1p2	0.000666667	0.0005	1.333333333	0.40966553	-0.005686408	0.007019742	-0.005686408	0.007019742
p1p3	0.000333333	0.00025	1.333333333	0.40966553	-0.002843204	0.003509871	-0.002843204	0.003509871
p2p3	0.045	0.015	3	0.20483276	-0.145592255	0.235592255	-0.145592255	0.235592255

v6	p1	p2	p3	p1p2	p1p3	p2p3
198.47	40	1	4	40	160	4
20.63	100	1	4	100	400	4
198.19	40	2	4	80	160	8
20.62	100	2	4	200	400	8
198.12	40	1	6	40	240	6
20.61	100	1	6	100	600	6
198.09	40	2	6	80	240	12
20.57	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999999922
R Square	0.999999845
Adjusted R Square	0.999998913
Standard Error	0.098994949
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	63090.70675	10515.11779	1072971.2	0.000738978
Residual	1	0.0098	0.0098		
Total	7	63090.71655			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	318.2783333	0.742920289	428.4151855	0.00148599	308.8386765	327.7179902	308.8386765	327.7179902
p1	-2.97133333	0.006902093	-430.49743	0.0014788	-3.059032365	-2.8836343	-3.059032365	-2.883634301
p2	-0.51666667	0.392527423	-1.31625623	0.41361161	-5.5041791	4.470845767	-5.5041791	4.470845767
p3	-0.25833333	0.137547971	-1.87813263	0.31147545	-2.006038532	1.489371865	-2.006038532	1.489371865
p1p2	0.002166667	0.002333333	0.928571429	0.52356774	-0.027481017	0.031814351	-0.027481017	0.031814351
p1p3	0.001583333	0.001166667	1.357142857	0.40427058	-0.013240509	0.016407175	-0.013240509	0.016407175
p2p3	0.055	0.07	0.785714286	0.57603082	-0.834430521	0.944430521	-0.834430521	0.944430521

v7	p1	p2	p3	p1p2	p1p3	p2p3
180.98	40	1	4	40	160	4
18.39	100	1	4	100	400	4
180.91	40	2	4	80	160	8
18.35	100	2	4	200	400	8
180.88	40	1	6	40	240	6
18.35	100	1	6	100	600	6
180.81	40	2	6	80	240	12
18.3	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	1
R Square	1
Adjusted R Square	0.999999998
Standard Error	0.003535534
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	52843.39848	8807.233079	704578646.3	2.88377E-05
Residual	1	1.25E-05	1.25E-05		
Total	7	52843.39849			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	289.7129167	0.026532867	10919.02023	5.83037E-05	289.3757861	290.0500473	289.3757861	290.0500473
p1	-2.71204167	0.000246503	-11002.0491	5.78637E-05	-2.715173775	-2.70890956	-2.715173775	-2.708909558
p2	-0.07416667	0.014018837	-5.29050085	0.118929493	-0.252292111	0.103958777	-0.252292111	0.103958777
p3	-0.06458333	0.004912428	-13.1469284	0.048330397	-0.127001376	-0.00216529	-0.127001376	-0.002165291
p1p2	0.000416667	8.33333E-05	5	0.125665916	-0.000642179	0.001475513	-0.000642179	0.001475513
p1p3	0.000458333	4.16667E-05	11	0.057715877	-7.10896E-05	0.000987756	-7.10896E-05	0.000987756
p2p3	-0.0025	0.0025	-1	0.499999999	-0.034265376	0.029265376	-0.034265376	0.029265376

v8	p1	p2	p3	p1p2	p1p3	p2p3
174.52	40	1	4	40	160	4
18.06	100	1	4	100	400	4
174.49	40	2	4	80	160	8
18.04	100	2	4	200	400	8
174.43	40	1	6	40	240	6
17.62	100	1	6	100	600	6
174.39	40	2	6	80	240	12
17.48	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	0.999999985
R Square	0.999999969
Adjusted R Square	0.999999784
Standard Error	0.038890873
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	49083.41338	8180.568896	5408640.59	0.000329141
Residual	1	0.0015125	0.0015125		
Total	7	49083.41489			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	278.2220833	0.291861542	953.2673657	0.00066783	274.5136467	281.93052	274.5136467	281.93052
p1	-2.59295833	0.002711537	-956.26899	0.00066573	-2.627411525	-2.55850514	-2.627411525	-2.558505142
p2	0.1575	0.154207202	1.021353076	0.49327516	-1.801879885	2.11687988	-1.801879885	2.116879885
p3	0.13625	0.054036703	2.521434364	0.24036955	-0.550348471	0.82284847	-0.550348471	0.822848471
p1p2	-0.00075	0.000916667	-0.81818182	0.56345104	-0.012397304	0.0108973	-0.012397304	0.010897304
p1p3	-0.003375	0.000458333	-7.36363636	0.08592887	-0.009198652	0.00244865	-0.009198652	0.002448652
p2p3	-0.0325	0.0275	-1.18181818	0.44707065	-0.381919133	0.31691913	-0.381919133	0.316919133

	v9	p1	p2	p3	p1p2	p1p3	p2p3
	171.07	40	1	4	40	160	4
	18.12	100	1	4	100	400	4
	171.01	40	2	4	80	160	8
	18.09	100	2	4	200	400	8
	170.98	40	1	6	40	240	6
	18.08	100	1	6	100	600	6
	170.93	40	2	6	80	240	12
	18.05	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	1
R Square	1
Adjusted R Square	0.999999998
Standard Error	0.003535534
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	46764.47808	7794.079679	623526374.3	3.06548E-05
Residual	1	1.25E-05	1.25E-05		
Total	7	46764.47809			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	273.3529167	0.026532867	10302.42649	6.17932E-05	273.0157861	273.6900473	273.0157861	273.6900473
p1	-2.55104167	0.000246503	-10348.9138	6.15156E-05	-2.554173775	-2.54790956	-2.554173775	-2.547909558
p2	-0.08416667	0.014018837	-6.00382681	0.10507111	-0.262292111	0.093958777	-0.262292111	0.093958777
p3	-0.06125	0.004912428	-12.4683773	0.050949693	-0.123668043	0.001168043	-0.123668043	0.001168043
p1p2	0.000416667	8.33333E-05	5	0.125665916	-0.000642179	0.001475513	-0.000642179	0.001475513
p1p3	0.000375	4.16667E-05	9	0.070446575	-0.000154423	0.000904423	-0.000154423	0.000904423
p2p3	0.0025	0.0025	1	0.500000001	-0.029265376	0.034265376	-0.029265376	0.034265376

v10	p1	p2	p3	p1p2	p1p3	p2p3
174.35	40	1	4	40	160	4
18.73	100	1	4	100	400	4
174.29	40	2	4	80	160	8
18.69	100	2	4	200	400	8
174.25	40	1	6	40	240	6
18.67	100	1	6	100	600	6
174.19	40	2	6	80	240	12
18.64	100	2	6	200	600	12

SUMMARY OUTPUT

<i>Regression Statistics</i>	
Multiple R	1
R Square	1
Adjusted R Square	0.999999998
Standard Error	0.003535534
Observations	8

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	6	48414.95818	8069.159696	645532775.7	3.01277E-05
Residual	1	1.25E-05	1.25E-05		
Total	7	48414.95819			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	278.45375	0.026532867	10494.67233	6.06612E-05	278.1166194	278.7908806	278.1166194	278.7908806
p1	-2.595625	0.000246503	-10529.7769	6.0459E-05	-2.598757108	-2.59249289	-2.598757108	-2.592492892
p2	-0.08916667	0.014018837	-6.36048979	0.099277076	-0.267292111	0.088958777	-0.267292111	0.088958777
p3	-0.06875	0.004912428	-13.9951173	0.045411526	-0.131168043	-0.00633196	-0.131168043	-0.006331957
p1p2	0.000416667	8.33333E-05	5	0.125665916	-0.000642179	0.001475513	-0.000642179	0.001475513
p1p3	0.000375	4.16667E-05	9	0.070446575	-0.000154423	0.000904423	-0.000154423	0.000904423
p2p3	0.0025	0.0025	1	0.500000001	-0.029265376	0.034265376	-0.029265376	0.034265376



Appendix C: Procedures for Calculations of Physicochemical Properties.

Kinematic Viscosity

This was calculated by multiplying the time with the tube constants.

i.e.  $N \times t$  (sec)

Table C1: Procedures for the calculation of Kinematic Viscosity at 100°C and 40°C

SAMPLES NO	CONSTANTS (N)		TIME (t)		KINEMATIC VISCOSITY	
	40°C	100°C	40°C	100°C	40°C	100°C
I	0.2382	0.04414	589.46	333.32	140.41	14.71
II	0.54215	0.03807	374.13	548.94	202.83	20.90
III	0.2382	0.04414	391.96	246.40	93.37	10.88
IV	0.47487	0.035972	307.44	424.06	145.99	15.25
V	0.53477	0.042632	385.94	507.5	206.39	21.63
VI	0.47487	0.042632	419.97	491.88	199.43	20.97
VII	0.53477	0.03807	341.53	505.91	182.64	19.26
VIII	0.54215	0.035972	324.56	522.08	175.96	18.78
IX	0.53477	0.036736	322.04	506.06	172.22	18.59
X	0.47487	0.042632	369.09	447.32	172.27	19.07

### Specific Gravity

$$\text{Specific Gravity (15}^{\circ}\text{c)} = (T - 15) 0.00062 + X$$

Table C2: Procedures for calculation of specific gravity

SAMPLE NO	I	II	III	IV	V	VI	VII	VIII	IX	X
T( $^{\circ}$ C)	24.0	29.3	25.4	26.3	26.5	26.9	27.7	28.8	29.1	29.2
X	0.885	0.881	0.875	0.885	0.885	0.88	0.881	0.88	0.88	0.88
Specific gravity	0.8906	0.8897	0.8814	0.8920	0.8921	0.8884	0.8889	0.8885	0.8887	0.8888

### Total Base Number

$$\text{Base Number Mg KOH/g} = [(E - F) \text{ MA} \times 56.1] / S$$

E is volume of HClO<sub>4</sub> used interpreted from graph

F for blank titration

MA is molarity of HClO<sub>4</sub>

S is weight in grammes.

Table C3: Procedures for TBN calculations

SAMPLE NO	I	II	III	IV	V	VI	VII	VIII	IX	X
Sample weight	6.301	5.7652	6.0651	6.5116	6.4177	8.2592	6.5682	6.096	6.0727	6.1314
Titrant (F)	199	144	4	228	193	168	123	94	100	106
Blank (E)	4	4	4	4	4	4	4	4	4	4
Molarity (MA)	0.1012001	0.1012001	0.1012001	0.1012001	0.1012001	0.1012001	0.1012001	0.1012001	0.1012001	0.1012001
X 0.05 factor	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
TBN MgKOH/g	8.78	6.89	0	9.77	8.36	5.64	4.85	4.19	4.49	4.72