TITLE PAGE

PROCESS DEVELOPMENT FOR THE PRODUCTION OF LUBRICATING

OIL ADDITIVE (CALCIUM LONG CHAIN ALKARYL SULFONATE)

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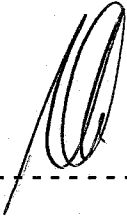THE AWARD OF BACHALOR OF ENGINEERING (B .ENG) IN THE

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APPROVAL PAGE

This research work has been read and approved having satisfied the requirement for the

award of the degree of Bachelor of Engineering in Chemical Engineering, School of

Engineering and Engineering Technology, Federal University of Technology, Minna.

-------------/------------------   03-11-2006

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EXTERNAL SUPERVISOR   DATE

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DECLARATION

I hereby declare that this project titled: Process development for the production of the lubricating oil additive, Calcium long chain alkaryl Sulfonate was carried out by me (Akanno Andrew Ndubuisi, 2000 / 9530EH) under the guidance and supervision of Engr.U.G Akpan of the department of Chemical Engineering Federal University of Technology, Minna. All the literature consulted in the course of the work has been duly acknowledged in the reference

02/11/06

DEDICATION

This project work is dedicated to my loving mother, Mrs. Josephine Akanno for all her encouragement and prayer.

ACKNOWLEDGEMENT

I must express my sincere adoration to GOD Almighty for giving me the strength and grace to see the end of this race.

I will also like to acknowledge my project supervisor Engr. U.G. Akpan for his encouragements and prayer.

My sincere gratitude goes to my mother Mrs. Josephine Akanno for her motherly role in my life, your love and kindness shall remain evergreen in my memory.

My sincere appreciation goes to the Management and staff of Oando Plc (lube blending plant) for providing me with the reagents I used for this work, and for allowing me access to their laboratory facilities, May God reward you.

My appreciation goes to my brother Chinedu Akanno, my classmate and friend Andrew Aba for their encouragement and belief in me.

The same appreciation goes to my best friend Ojochide Idakwo for being there for me when I needed someone to talk to. Thank you all and God bless.

ABSTRACT

This research work is aimed at developing a process for the production of the lubricating

oil additive, calcium long chain alkaryl sulfonate. The three reaction steps of sulphonation,

neutralization and overbasing involved in the production of the lubricating oil additive

were considered. In the sulphonation reaction step, refined base oil was substituted for the

unavailable deasphalted oil as the lube base stock, hence the results obtained were used to

establish the acid to base stock ratio, reaction temperature and time for the sulphonation

reaction; and the reaction temperature, time and the amount of calcium hydroxide required

in the neutralization step. The results showed that the properties of the base oil used is

quite different from those of deasphalted oil, hence the properties of the product obtained

will differ from those of the expected additive. The sulphonation reaction requires an acid

to lube base stock ratio of 1.3:1, and $1.3cm^3$ of the sulphonic acid produced requires 1g of

calcium hydroxide for complete neutralization. The overall reaction time is less than

60mins. In conclusion, this work provides a working document for the production of the

lubricating oil additive. Nonetheless, the deasphalted oil was not available at the time of

this work; it is recommended that before any full scale production, a laboratory scale be set

up to ascertain the correctness of the developed process.

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CHAPTER ONE

1.0 INTRODUCTION

Calcium long chain alkaryl sulfonate is one of the many additives applied in lubrication technology. It is unique and its application is vast. It is a compound with a long waxy soluble hydrocarbon chain attached to a polar end group. The polar end makes the molecule to exhibit electrically positive characteristics at one extremity and negative characteristics at the other. It is oil soluble at one end and water soluble at the other end. In lubricants, it acts as a detergent, as well as a dispersant, an emulsifier, a corrosion inhibitor and a friction modifier. This additive is used to blend diesel and gasoline engine oils as well as Automatic Transmission Fluid (A.T.F) for power steering. (http://www.chevron.com/products/oronite/references)

Calcium long chain alkaryl sulfonate is usually complexed with excess of calcium carbonate. The degree or extent of this complexing (dilution) determines their application. Packages with high concentration of the calcium salt is usually applied in diesel and gasoline engine oils (the salt functions as a detergent as well as a dispersant) (http://www.chevron.com/products/oronite/references)

This work focuses on developing a process for the production of the above mentioned lubricating oil additive, which is prepared via simple chemical reaction steps of sulphonation and neutralization.

Sulphonation which is essentially the reaction between an aromatic hydrocarbon and sulphuric acid has found applications in many industries like in detergent production. This process introduces a polar end group (SO_3H) into the hydrocarbon chain.

The polarized compound functions as an emulsifier and a friction modifier. The aromatic hydrocarbon used has a long waxy straight or branched alkyl chain which is partially soluble. It is obtained from the bottom of the vacuum distillation unit (VDU) from refining of paraffinic crude. This bottom is known as short residue (Chiyoda (1980) Kaduna refinery project; operating manual for process units-PDU volume xv).

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This short residue is usually deasphalted-using propane as solvent to obtain the aromatic hydrocarbons (lube base stock), which is known as deasphalted oil. Some of the properties of the lube stock is given in the discussion of results.

The next step of neutralization can be accomplished by adding calcium hydroxide to the sulphonic acid produced in the above process.

Neutralization is the reaction between an acid and an alkali metal base to give salt and water. This reaction has found wide application in different fields. The sulfuric acid produced from sulphonation is neutralized with $Ca(OH)_2$ to the corresponding salt and H_2O.

Calcium hydroxide also known as slaked lime or hydrated is soft white solid with a solubility of $0.185g/100Cm^3$ water. A suspension of fine calcium hydroxide particles in water called lime water is a medium strength base that reacts violently with acids and attacks many metals. Neutralization reaction is exothermic with a reaction temperature of about 40^0C. (Wilcox C.F. 1988, Jerry March, 1979).

1.1 Justification for the research

Although a process exists for the production of the lubricating oil additive, it is unavailable. It is held by the respective companies as a secret.

Africa and the Middle East accounts for about 5% of the world's lube oil production with about 15 lube oil refineries out of 133 in the entire world, with no lubricating oil additive company / plant existing anywhere in Africa. The research work is to serve as a working document for any person or group venturing into lubricating oil additive production in Africa.

1.2 Aims and Objectives

The research is undertaken to establish the following

i.   The properties of the suitable lubricating oil base stock.

ii.   The highest exothermic temperature for the sulphonation reaction.

iii.   The ratio of hydrocarbon to sulphuric acid required in the sulphonation reaction

iv. The temperature range for maximum yield of the desired product (essentially mono sulphonic acid)

v. The reaction time for sulphonation reaction

vi. The degree of stirring required

vii. The amount of $Ca(OH)_2$ required for neutralization i.e. ratio of sulphonic acid to $Ca(OH)_2$, and the reaction conditions.

viii. The ratio of the metal carbonate to alkaryl acid salt in the overbasing reaction. With the above, a process can then be developed (established) for the production of the additives.

1.3 Limitations

Although calcium long chain alkaryl sulfonate can be produced via simple chemical reaction steps of sulphonation and neutralization, the unavailability of deasphalted oil (lube base stock) at the time of conducting the research, militated against the practical aspect of the research.

Deasphalted oil is only obtained from refineries and as at the time of this research work, no refinery in the country was operating full in its capacity.

Lubricant blending plants employs refined deasphalted oil as the base oil (Bright stock) in lubricant blending / formulation.

The refining process involves two steps of

i. Solvent extraction to remove aromatics

ii. Solvent dewaxing, to remove the wax content

The process removes the inherent properties of deasphalted oil, producing refined base oil. Deasphalted oil is the appropriate lube base stock for lubricating oil additive production.

The oils obtained from this refining process, are in different grades from neutrals to Bright stocks. This was used in place of deasphalted oil as the lube base stock.

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CHAPTER TWO

LITERATURE REVIEW

2.1 Lubrication

Lubrication has always implied the use of lubricating oils usually formulated by blending appropriate quality lube base stocks and additives. (http://www.lubrication%20theory%20and%20practice.htm)

The main purpose of a lubricant is to form a layer between two moving surfaces so that the high solid friction is replaced by the internal friction of the lubricant. The viscosity of the lubricant is a measure of this internal friction. To ensure that this layer is maintained between the two solid surfaces a correct choice of lubricant has to be made, depending on the conditions of service and keeping in mind that higher viscosity results in higher power consumption. Thus a high-load low-speed bearing requires a high-viscosity lubricant, while a low-load high-speed bearing requires a low-viscosity lubricant. (Chiyoda (1980) Kaduna refinery project; operating manual for process units-PDU volume xv)

2.1.1 History of Lubrication Technology

More than 3, 000 years ago, lubrication technology has seen many phases of evolution. Early lubrication began with animal fats and oils, and slowly evolved to petroleum-based oils (Kramer et al, 2003). In the first phase, animal fats were used as lubricants. Ancient inscriptions dating back to 1400BC show beef and mutton fat (fallow) being applied to chariot axles. Little changed over the next 3,000 years except that the oils sometimes came from exotic animals such as whales (Kramer et al, 2003).

In 1852, petroleum-based oils became available. They were not widely accepted at first because they did not perform as well as many of the animal-based products. As the demand for automobiles grew, so did the demand for better lubricants. (David C. Kramer, Brent K. Lok, Russ R. Kurg and J.M. Rosenbaum (2003), Chevron Texaco Global lubricants. "The evolution of base oil technology industry focus" Machinery lubrication magazine)

2.1.2 Modern Lubrication Technology

In addition to minimizing friction and reducing wear between two surfaces in relative motion, a modern lubricant should have good oxidation stability, antiwear properties and should act as detergents by keeping contaminants in engine oils finely dispersed.(http://www.lubrication%20theory%20and%20practice.htm)

Many of these properties are inherent in the base oil from which lubricating oils are blended. In many cases, most of these properties are introduced into the lubricating oil during blending by addition of different kinds of additives (dopes). (Chiyoda (1980) Kaduna refinery project; operating manual for process units-PDU volume xv)

2.2 Formulation of Modern Lubricants

Designing a lubricant to perform the functions above in different systems is a complex task involving a careful balance of properties both in the base oil and the performance enhancing additives. Lubrication has always implied the use of lubricating oil usually formulated by blending appropriate quality base oil and additives. On an average, lubricating oils consist of at least 7% of chemical additives and at most 93% of base oil; hence the performance of a finished lubricant essentially depends upon the type and quality of base oil and additives. (http://www.lubrication%20theory%20and%20practice.htm)

One of the most rigorous and familiar example is the internal combustion engine in which the lubricant may be required to operate from sub-zero start up condition to a normal running temperature of about 150^0C - 200^0C. Here it is necessary to formulate lubricating oil in which the viscosity changes little with temperature. This property is achieved by refining and the addition of dopes (additives).(Chiyoda(1980) Kaduna refinery project; operating manual for process units-PDU volume xv)

2.3 Lubricating Oil Additives (LOA) Technology

Additives are chemical substances added to petroleum product to impart or improve certain properties. Common LOA are antifoam agent, anti-icing additives, corrosion inhibitors, demulsifiers, detergent, emulsifiers, extreme pressure (EP) additive, oilness

agent (Friction-modifiers), oxidation inhibitors, pour point depressant, rust inhibitor, and viscosity improver (http://www.chevron.com/products/oronite/references).

2.3.1 Antifoam agent

These are used to reduce foaming in lubricating oils by breaking up larger surface bubbles contained in the oil. Example is polysilicone (http://www.editionstechnip.com/sourcs/liste-IFP Fice.asp?cle=46020251&Annee=1991).

2.3.2 Corrosion inhibitors

They are polar compounds that wet metal surface preferentially, protecting it with a film of oil. Example is calcium long chain alkaryl sulfonate (http://www.editionstechnip.com/sourcs/liste-IFP Fice.asp?cle=46020251&Annee=1991)

2.3.3 Dispersants

These are calcium or barium salts that help keep materials in suspension in order to prevent deposit formation (http://www.chevron.com/products/oronite/references).

2.3.4 Detergent

These are polar compounds with a strong attraction for solid contaminants and they help to keep contaminants finely dispersed (http://www.chevron.com/products/oronite/references).

2.3.5 Emulsifier

They are polar molecules which are oil soluble at one end and water soluble at the other end. They help to form oil-water emulsions in lubricants (http://www.chevron.com/products/oronite/references)

2.3.6 Oilness agent (Friction –modifier)

They are molecules with a strong affinity for solid surfaces. Such molecules plate out to form a tenacious, friction-reducing film. They reduce the oils coefficient of friction mainly for fuel saving. Such additives have a long waxy soluble hydrocarbon chain attached to a polar end group (http://www.chevron.com/products/oronite/references).

2.3.7 Oxidation inhibitor

These additives may act as either a free radical inhibitor or as a peroxide decomposer since peroxides are involved in the oxidation mechanisms. Common antioxidants include zinc alkaryl dithiophosphate ($C_7 - C_{16}$) or zinc alkyl dithiophosphate ($C_3 - C_4$) and alkyl ($C_8 - C_9$) phenyl amine in aromatic solvents (http://www.chevron.com/products/oronite/references).

2.3.8 Pour point depressants

These are additives that improve the rheological properties of lubricants at low temperature by modifying and controlling wax crystals growth. e.g. polyalkyl ($C_{10} - C_{20}$) methacrylate (http://www.chevron.com/products/oronite/references).

2.3.9 Viscosity improver

These are additives with high molecular weight polymer that reduces the tendency of oil to change viscosity with temperatures (http://www.chevron.com/products/oronite/references).

2.4 Calcium long chain alkaryl sulfonate as an L.O.A. ($C_{11} - C_{50}$).

This is a compound with a long waxy soluble hydrocarbon chain attached to a polar end group. The polar end makes the molecule to exhibit electrically positive characteristics at one extremity and negative characteristics at the other.

Polarity gives the molecules a strong affinity for solid surfaces, such molecule plate out to form a tenacious friction – reducing film (oilness agent or friction-modifier) ((http://www.editionstechnip.com/sourcs/liste-IFP Fice.asp?cle=46020251&Annee=1991)

They are oil soluble at one end and water soluble at the other end. In lubricants they act as emulsifiers helping to form oil-water emulsions, i.e. they have good metal wetting properties.

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Calcium long chain alkaryl sulfonate is usually complexed with excess of calcium carbonate. The presence of this calcium salt in the molecule of the sulfonate makes it to function as a dispersant (http://www.epe.gov/chemtrk/pubs/summaries/alkylsulf/c13206rt.pdf#search=%22calcium%20long%20chain%20alkaryl%20sulfonate%22)

Calcium long chain alkaryl sulfonate acts as the following in lubricating oil.

1.   Friction modifier

2.   Emulsifier

3.   Detergent as well as

4.   Corrosion inhibitor (http://www.chevron.com/products/oronite/references).

2.4.1 Production technique for calcium long chain alkaryl sulfonate.

There is only one available route for the production of the above LOA.

It is prepared by the sulfonation of naturally occurring alkyl aromatic-rich fractions of heavy lubricating oil base stocks derived from petroleum streams (http://www.epe.gov/chemtrk/pubs/summaries/alkylsulf/c13206rt.pdf#search=%22calcium%20long%20chain%20alkaryl%20sulfonate%22).

Paraffinic base stocks are used because of its waxy nature. The alkyl substituent group may vary in number (e.g. mono or dialkyl), position (e.g. predominantly meta or para to the sulfonic acid position), chain length (e.g. C14 to C30) or in the degree of branching.

The sulfonation may be represented as

$$A \;\text{---}\!\!\left\langle\bigcirc\right\rangle + H_2SO_4 \,(aq) \rightarrow A \;\text{---}\!\!\left\langle\bigcirc\right\rangle\!\text{-}\, SO_3H + H_2O \;\text{----}\;(2.1)$$
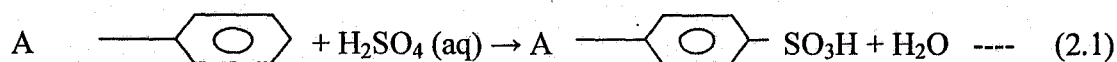
The process takes place in the base stock and thus the substrates are never isolated. Paraffinic base stocks are derived from the bottom of paraffinic crude oils. They are made up of about 90% saturates and 10% aromatics with more than 300 ppm sulphur. They also contain nitrogen and oxygen compounds as well as carbon and ash (Kramer et al, 2003).

Sulfonation introduces the polar group (SO$_3$H) into the chain of the hydrocarbon, hence producing sulfonic acid.

The sulfonic acid substituent can then be neutralized by alkali metal bases to form the corresponding alkali metal salt. Ca(OH)$_2$ is used, and the process can be represented as

A ——⟨O⟩ SO$_3$H + ½ Ca (OH)$_2$ (aq) → ½ (A ——⟨O⟩- SO$_3$)$_2$ Ca + H$_2$O---- (2.2)
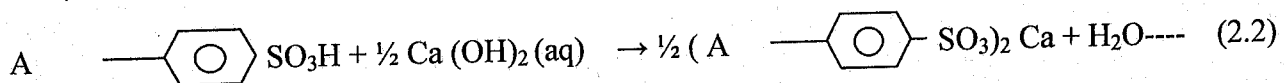
The calcium salt is then complexed (overbased) with an excess of calcium carbonate. The overbased products are produced in the presence of the alkaryl sulfonate by adding excess Ca(OH)$_2$ and carbon dioxide (10). The process is shown below as:

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3 + 2H_2O \text{ -------- } 2.3$$
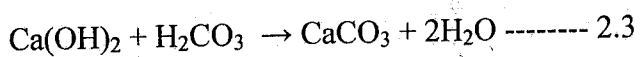
The over basing reaction forms the metal carbonate which exists in the alkaryl sulfonate as a reverse micelle (i.e. the metal carbonate is in the centre of the micelle with alkaryl sulfonate surrounding the carbonate). The ratio of metal carbonate to alkaryl sulfate can range from a low of 6:1 to a high of 30:1 (http://www.epe.gov/chemtrk/pubs/summaries/alkylsulf/c13206rt.pdf#search=%22calcium%20long%20chain%20alkaryl%20sulfonate%22).

The structure of the reverse micelle is shown below;
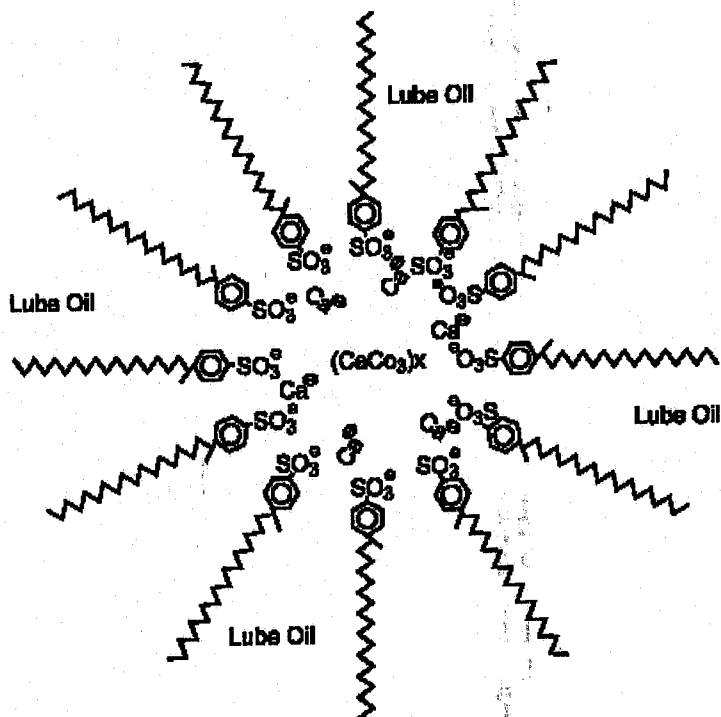
Fig. 1. Sulfonate reverse micelle structure

2.5   Sulfonation

This is used to obtain aromatic sulphonic acids. This can be by either directly sulfonating the aromatic hydrocarbons with sulphuric acid (Potapov and Tatarinchik, 1979) or by photosulfonation of the hydrocarbon. Acid concentration up to 98% or oleum (20% free SO_3) is usually employed in the former. The reaction is exothermic and also reversible hence it is necessary to drive the reaction to completion. (Potapov and Tatarinchik, 1979).

2.6   Neutralization

Neutralization is the reaction between an acid and an alkali metal base to give salt and water. This has wide applications in different fields. The sulfuric acid produced from sulfonation is neutralized with $Ca(OH)_2$ to give the corresponding salt and water.

2.7   Overbasing Reaction

The high acid concentration employed in the sulphonation reaction might make the salt formed to be acidic, hence the need to overbase the salt. The salt can be complexed or overbased with an excess of calcium carbonate. The overbased products are produced in the presence of the alkaryl sulfonic acid salt.

(http://www.epe.gov/chemtrk/pubs/summaries/alkylsulf/c13206rt.pdf#search=%22calcium%20long%20chain%20alkaryl%20sulfonate%22)

Overbased detergent additives are applied in lubrication of modern combustion engines. They neutralize the acidic products coming from combustion and fight corrosive wear.

CHAPTER THREE

3.0 MATERIAL AND METHOD

3.1 INSTRUMENTATION AND EQUIPMENT

Equipments employed in this research fall into two categories

    (a) Equipments for analysis of base oil

    (b) Equipment for reactions

The equipments required for analysis are given as follows

(i) Specific gravity

These includes

Hydrometer

Thermometers

(ii) Viscosity index

These includes

-   viscometer (calibrated viscometer of the glass capillary type)

-   viscometer holders

-   temperature controlled viscometer bath

-   timing device (stop watch)

(iii) Pour point

These includes

-   test jar (cylindrical of clear glass, flat bottom

-   thermometer

-   cork to fit the test jar

-   jacket (it is supported in a vertical position in the cooling bath).

- Gasket to fit snugly around the outside of the test jar and loosely inside the jacket.

- Cooling baths maintained at prescribed temperature with a firm support to hold the jacket vertical.

(iv) Flash point

The apparatus required is the Cleveland open cup apparatus.

This apparatus consists of the following

- test cup

- heating plate

- test flame application

- heater and supports

- thermometer

- test flame (natural gas i.e. methane flame and bottled gas (butane, propane) flame)

The equipment used for carrying out the various reaction include

(i) wide-necked flask

This served as the reactor. The various reactions were carried out in the flask.

(ii) Beakers

This is used for transferring reactant into flask. The beakers volume range are $50cm^3$, $100cm^3$ $150cm^3$,

(iii) Magnetic stirrer

This is a convenient stirring device which consists of an enclosed electric motor attached to a large bar magnet. In practice a second magnet (spin bar) is placed in the reaction flask, which rests on the stirrer enclosure; when the motor is turned on the enclosed magnet produces a rotating magnetic field that forces the spin bar to rotate magnetic field that forces the spin bar to rotate and stir the contents. (Chernir et al, 1987)

(iv)Funnel

The reaction is carried out in a fume chamber. The reaction set-up is shown below.
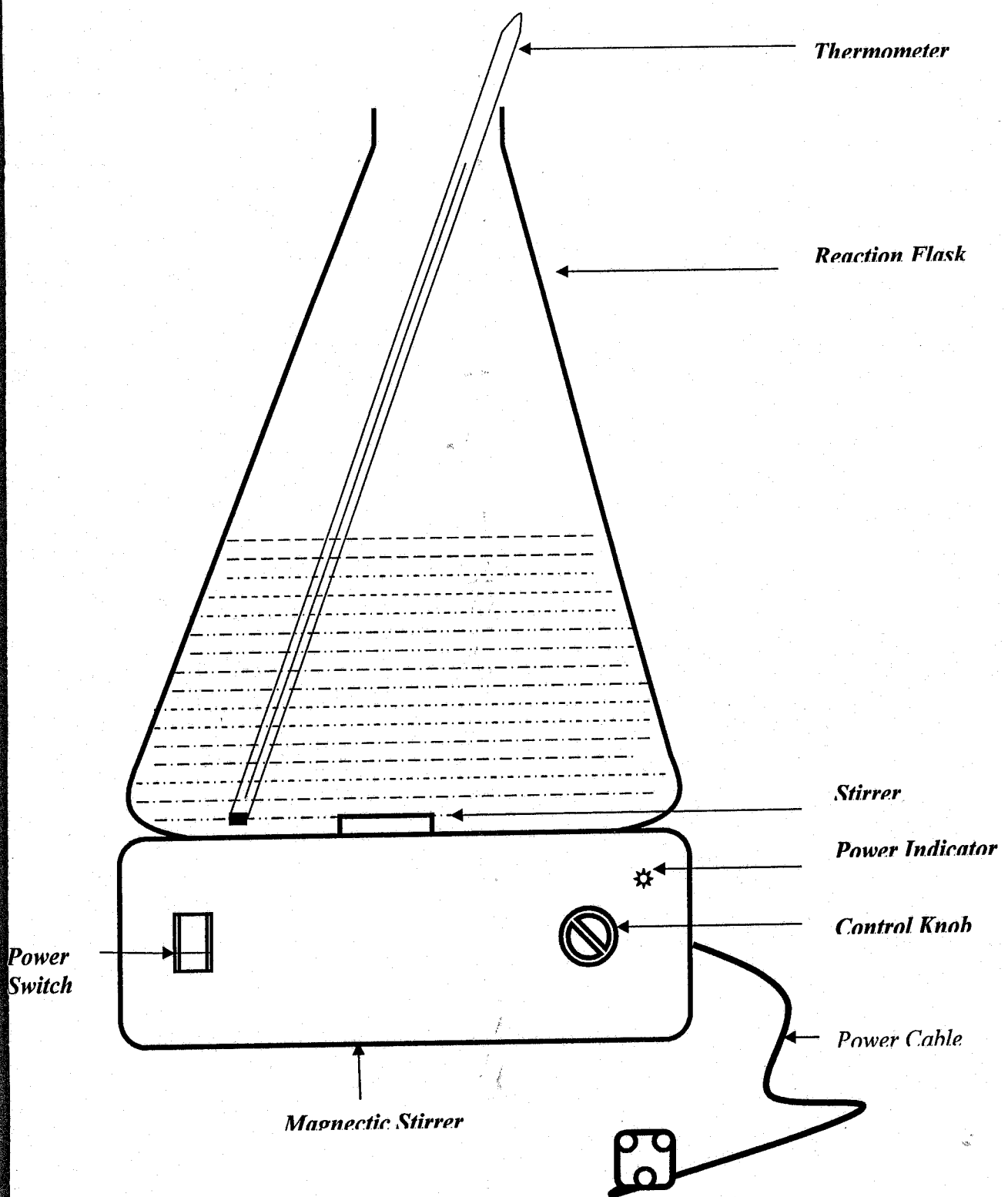
Fig. 3.1 The Reaction set – up showing the flask (Reactor) on the Stirrer

Labels in figure:
- Thermometer
- Reaction Flask
- Stirrer
- Power Indicator
- Control Knob
- Power Switch
- Power Cable
- Magnectic Stirrer
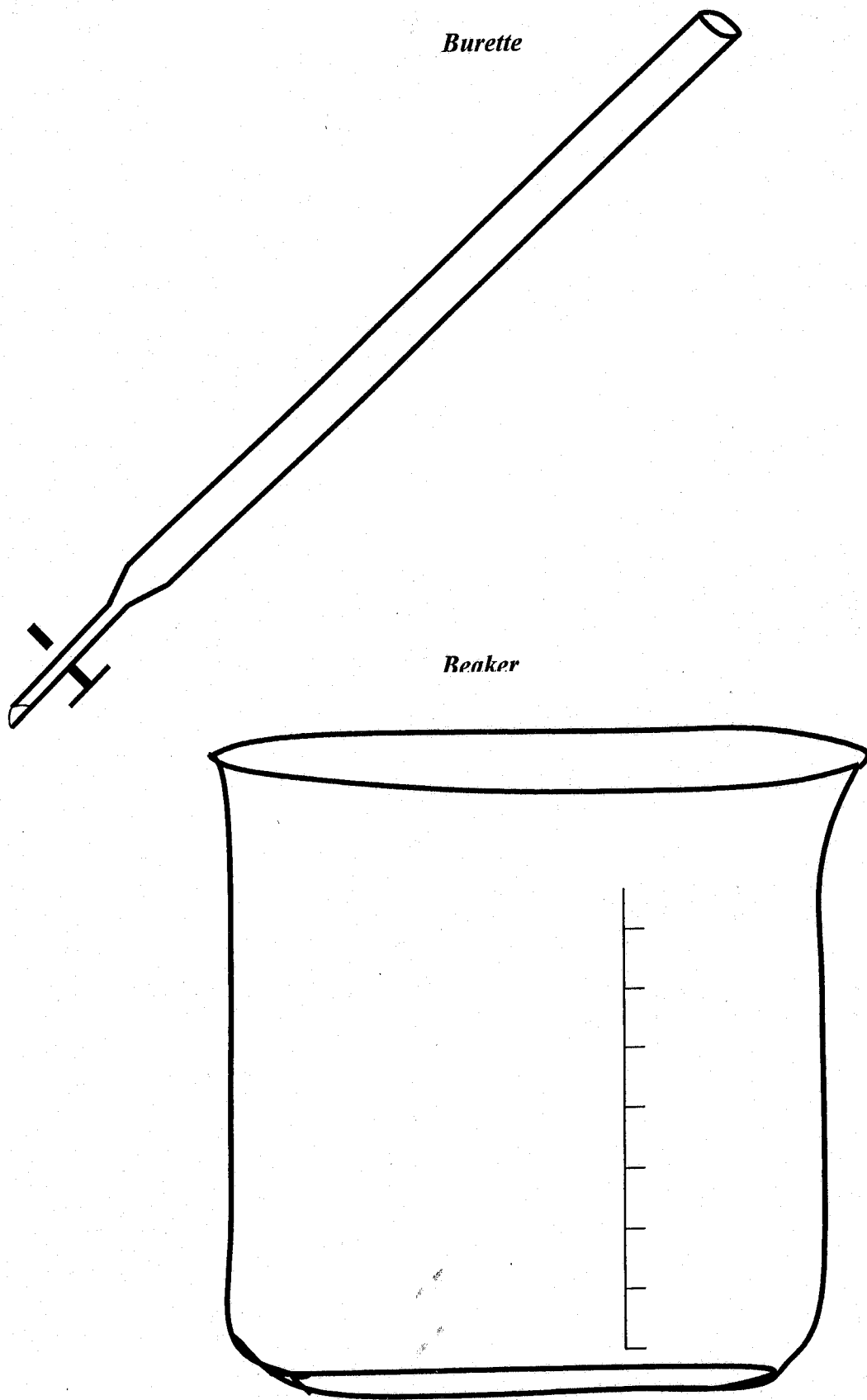
Burette

Beaker

Fig. 3.2 Diagram showing a burette and a beaker

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3.1.1. List of reagents

Table 3.1 List of reagents

Name	Source
Base Oil	Oando Plc (Lubricant blending plant)
98% Concentrated Sulphuric acid	Drury Chemicals Ltd
Calcium Hydroxide	Vickers Laboratories Ltd
Carbonic acid	F. U. T. Minna, Laboratory
Methyl orange	Bijos Chemicals

3.2 EXPERIMENTAL PROCEDURE

As stated in the introduction, refined lube base stock was substituted for the unavailable deasphalted oil.

This section is sub divided into

1. Test Procedure
2. Reaction procedure

3.2.1 TEST PROCEDURE

This gives the description of the tests carried out on the refined lube base stocks. The various grades of this lube oil include. –

- - SN 100, 150, 200, 350, 500, 600, 650 and

- BS 150

Three grades were obtained. These are SN 150, 500 and BS 150, and the following tests were carried out.

(i)   specific gravity

(ii)   viscosity index

(iii)   pour point

(iv)   colour and appearance

(v)   flash point

3.2.1.1 Specific gravity

This is done using the ASTM D 4052

Procedure

The temperature of the sample was adjusted to 15°C and transferred to a clean hydrometer cylinder without splashing. This is to avoid the formation of air bubbles. The cylinder containing the sample is placed in a vertical position in a location free from air currents. The hydrometer was gently lowered into the sample, taking care to avoid wetting the stem above the level to which it will be immersed in the liquid. The sample was stirred

continuously with the thermometer, until a steady temperature reading is observed. The temperature of the sample to the nearest 0.25 °C (0.5°F) was recorded.

The hydrometer was depressed about two scale divisions into the liquid and then released. The remainder of the stem of the hydrometer which is above the level of the liquid must be kept dry.

When the hydrometer has come to rest floating freely away from the walls of the cylinder, the hydrometer scale reading was estimated to the nearest 0.00001 relative density.

3.2.1.2 Viscosity index

This is done using ASTM D 2270

Procedure

The viscometer bath was adjusted to 100°C, and then maintained at this temperature.

A clean dry calibrated viscometer having a range covering the estimated kinematic viscosity was selected. Moist room air was carefully removed from the viscometer by applying vacuum to it. The sample was then drawn into the working capillary and timing bulb and then placed in the bath.

The sample was allowed to drain back. The head level of the test sample was adjusted to a position in the capillary arm about 7mm above the first timing mark using suction. With the sample flowing freely, the time required for the meniscus to pass from the first to the second timing mark was measured.

Calculate the kinematic viscosity, v, from the measured flow time t, and the viscosity constant c.

The above was repeated with viscometer maintained at 40°C

3.2.1.3 Pour point

This is done using ASTM D 97.

Procedure

The specimen was poured into the test jar to the level mark. The test jar was closed with the cork carrying the high pour thermometer. The position of the cork and thermometer was adjusted so that that cork fits tightly, (the thermometer and the jar are coaxial and the thermometer bulb is immersed so the beginning of the capillary is 3mm below the surface of the specimen (see that the disk, gasket and the inside of the jacket are clean and dry). The disk was placed in the bottom of the jacket with the gasket around the test jar, 25mm from the bottom. The test jar was then inserted in the jacket. The specimen was observed at intervals until the specimen has ceased to flow. The temperature reading on the thermometer was then recorded.

3.2.1.4 Colour and Appearance

This is done using ASTM D1500 and D 4176

3.2.1.5 Flash point

This was done using the ASTM D 92.

Procedure

The test cup was filled with the sample so that the top of the meniscus of the test specimen is exactly at the filling mark. The test cup was then placed on the center of the heater. The sample was heated initially to 100 °C, and the test flame was then applied to it. The test flame was passed across the center of the test cup at right angles to the diameter which passes through the thermometer.

The flash point is the lowest liquid temperature at which application of the test flame causes the vapors of the test specimen of the sample to ignite.

3.2.2 REACTION PROCEDURE

3.2.2.1 Sulphonation Reaction

The test results show that the properties of the base oil are similar; hence SN 150 will be used as the lube stock. SN 150 will be used as the lube stock.

Sulphonation Reaction 1

An ice bath was prepared for cooling. The reaction was set up as shown in figure 3.1. $50cm^3$ of the base stock (SN 150) was transferred into the flask. The magnetic stirrer was then inserted into the flask. $60cm^3$ of 98% concentrated H_2SO_4 (density 1.84 g / cm^3) was then added into the flask from the funnel. The mixture was stirred vigorously for 30minutes. The temperature rise with time was observed and tabulated.

At the end of the reaction, empty the product into a beaker and measure its volume and weight.

Sulphonation Reaction 2

Repeat the procedure in one with $80cm^3$ of the base stock (SN 150), and $100cm^3$ of the sulphuric acid. Stirring time is 30minutes

Sulphonation Reaction 3

Repeat the procedure in one with $150cm^3$ of the base stock (SN 150), and $200cm^3$ of the sulphuric acid. Stirring time is 60minutes

3.2.2.2 Neutralization Reaction

A 0.1248M $Ca(OH)_2$ solution was prepared(1.85g $Ca(OH)_2$ in $200cm^3$ of H_2O)

The sulphonic acid from step 1 was poured into the burette.

The $Ca(OH)_2$ solution was placed in the flask and drops of methyl orange were added

The stirrer and thermometer were inserted in the flask. The acid was added gradually from the burette, and the mixture was stirred vigorously until a colour change was observed.

The volume of acid used and the temperature of the final mixture were recorded. The reaction time was also recorded.

3.2.2.3 Overbasing Reaction

A 0.01248M Ca (OH)$_2$ solution was prepared (0.185g Ca(OH)$_2$ in 200cm^3 of H$_2$O)

The carbonic acid (H$_2$CO$_3$) was poured into the burette. 50cm^3 of the Ca(OH)$_2$ solution was placed in the flask and drops of methyl orange were added.

The stirrer and thermometer were inserted in the flask. The acid was added gradually from the burette, and the mixture was stirred vigorously until a colour change was observed.

The volume of acid used and the temperature of the final mixture were recorded. The reaction time was also recorded.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION OF RESULTS

4.1 RESULTS

The following results were obtained from the various test carried out on the different grade of base oil. This is tabulated below as;

Table 4.1 Results of the various grades of base oil tested.

Base oil

	SN 150	SN 500	BS 150
Specific gravity	0.8772	0.8881	0.9034
Viscosity index	102	92	98
Pour point oC	-15	-25	-19
Colour and appearance	Clear and bright	Clear and bright	Dark and clear
Flash point oC	200	244	290

The following results were obtained from the sulphonation reaction step

Reaction One

Reaction temperature rose from 26.6^0C to about 50^0C and remains steady at 50^0C. The reaction product was a black viscous liquid. After a period of time, the reaction mixture separated into two distinct phase (clear and a dark phase).

Reaction Two

The volume of the acid used was 95.978cm^3, while the volume of the base stock used was 73.829cm^3. The weight of sulphuric acid was 176.6g, while the weight of the base stock was 64.3g. At the end of the reaction the volume and weight of the product were 170cm3, 230.5g respectively. (Volume of dark phase was 122.5cm^3 and the volume of clear phase was 47.5cm^3)

Temperature rise with time

Table 4.2 Temperature rise with time for sulphonation reaction 2

Temperature rise ^{0}C	Time (s)
32	0
33	30
34	64
35	94
36	129
37	172
38	205
39	240
40	280
41	331
42	390
43	439
44	491
45	553
46	640
47	712
48	785
49	903
50	992
51	1148
52	1282
53	1458
54	1603
55	1882

Reaction Three

The volume of the acid used was 197.446cm^3, while the volume of the base stock used was 132.461cm^3. The weight of sulphuric acid was 363.3g, while the weight of the base stock was 115.4g. At the end of the reaction the volume and weight of the product were 329.5454cm3, 469.1g respectively. (Volume of dark phase was 243.1818cm^3 and the volume of clear phase was 86.3636cm^3)

Temperature rise

Table 4.3 Temperature rise with time for sulphonation reaction 3

Temperature rise ^0C	Time (s)
30	0
31	24
32	51
33	82
34	112
35	145
36	177
37	207
38	242
39	291
40	335
41	373
42	423
43	470
44	532
45	578
46	666
47	729
48	798
49	901
50	979
51	1112
52	1205
53	1350
54	1539
55	1714
56	1999
57	2280
58	3012

The following results were obtained from the neutralization reaction.

Indicator used = methyl orange

Colour in calcium hydroxide = yellow

Table 4.4 Results for the neutralization reaction

	Burette reading		Volume of acid used (cm^3)
	Initial (cm^3)	Final (cm^3)	
First	0.00	2.36	2.36
Second	5.34	7.94	2.60

The following results were obtained from the overbasing reaction.

Table 4.5 Results for the Overbasing reaction

	Burette reading		Volume of acid used (cm^3)
	Initial (cm^3)	Final (cm^3)	
First	0.00	249.55	249.55
Second	0.00	248.70	248.70

4.2 DISCUSSIONOF RESULTS

The properties of deasphalted oil is given in the table below

TABLE 4.6 the properties of deasphalted oil as given by ASTM

Specific gravity, d 70/4	0.885
Viscosity at 60°C cst	163
Viscosity at 100°C cst	34.5
Flash point PMcc	27.0
Conradson carbon %wt	1.6
Pour point °C	54
Sulpur %wt	2.70

d 70/4– represents density at 70 °F (21 °C) referred to water at 4 °C

PMcc – Pensky Martens closed cup apparatus (Source: Chiyoda (1980) Kaduna refinery

project; operating manual for process units-PDU volume xv)

Comparing the test results with the properties of deasphalted oil given above, we observe a

marked difference in the viscosity and pour point value.

4.2.1 Viscosity

Viscosity is an inherent property of a fluid which determines it flow characteristics. This is

one of the properties used in characterizing petroleum fractions. Viscosity index is

obtained by measuring the viscosity of a fluid at 40 °C and 100 °C; this is given in the

appendix. Table 4.6 shows that the viscosity of deasphalted oil decreased from 163 to 34.5

as the temperature was increased from 60 °C to 100 °C. The viscosity of BS 150 at a

temperature of 40°c is 478 cst; while for SN 150 and 500 are 30.30 and 97.45cst

respectively. The high viscosity of deasphalted oil (163cst) at a higher temperature of 60°C

compared with those of the base oils at 40°C indicates that the inherent property of

deasphalted oil which gives it the high resistance to flow has been removed during the

refining process as explained in the introduction. The viscosity – temperature

characteristics of the oils are the same. The result shows that the viscosity of the oils

decrease with increase in temperature.

4.2.2 Pour point

The pour point of deasphalted oil is 54 °C, while for the refined oils; the pour points are below 0 °C. From the introduction, one of the refining processes for the production of the refined base oils that was used in this work as the lube base stock, is solvent dewaxing. This removes the wax content of deasphalted oil. It involves chilling and precipitation of the oil in the presence of a solvent. The waxy nature of the deasphalted oil is one of the inherent properties required in the targeted lubricating oil additive.

4.2.3 Flash point

The flash point of the oils lies in the range between 200 and 300 °C. The test results showed that the properties of the refined base oils differ slightly from each other. For the reaction, SN 150 was chosen as the base stock.

4.2.4 Sulphonation reaction

This reaction was performed three times.

Reaction One.

This was used as a test reaction to obtain the volume ratio of sulphuric acid to lube base stock require in the sulphonation step. At the end of the reaction, the final temperature of the mixture was observed to be steady at 50 °C.

The product of the reaction was a black viscous liquid. This separated into two distinct phases (a clear phase and a dark phase) the dark phase represents the sulphonic acid formed while the clear phase is the excess spent sulphuric acid.

Reaction two.

From reaction two, the volume ratio of sulphuric acid to lube base stock was 1.3:1. The total volume of the reactant was 169.807 cm³. The volume of the product of reaction was approximately 169cm³.

The total mass of the reactants was 240.9g. At the end of the reaction, the mass of the product was 230.5g. This indicates a difference of 10.4g. This difference resulted mainly from loss of some portion of the reactants during transfer into the reaction flask.

Neglecting this difference, we can conclude that no portion of the reaction was lost in the course of the reaction. The volume of the sulphonic acid (dark phase) was 122.5cm^3, while the volume of the excess spent sulphuric acid was 46.5cm^3

A graph of the temperature rise against time was plotted as shown.

The rate of the temperature rise from 32 to 40 was very sharp, and slower from 40 to 55°C.

The stirring was vigorous and reaction time was approximately 30 minutes.
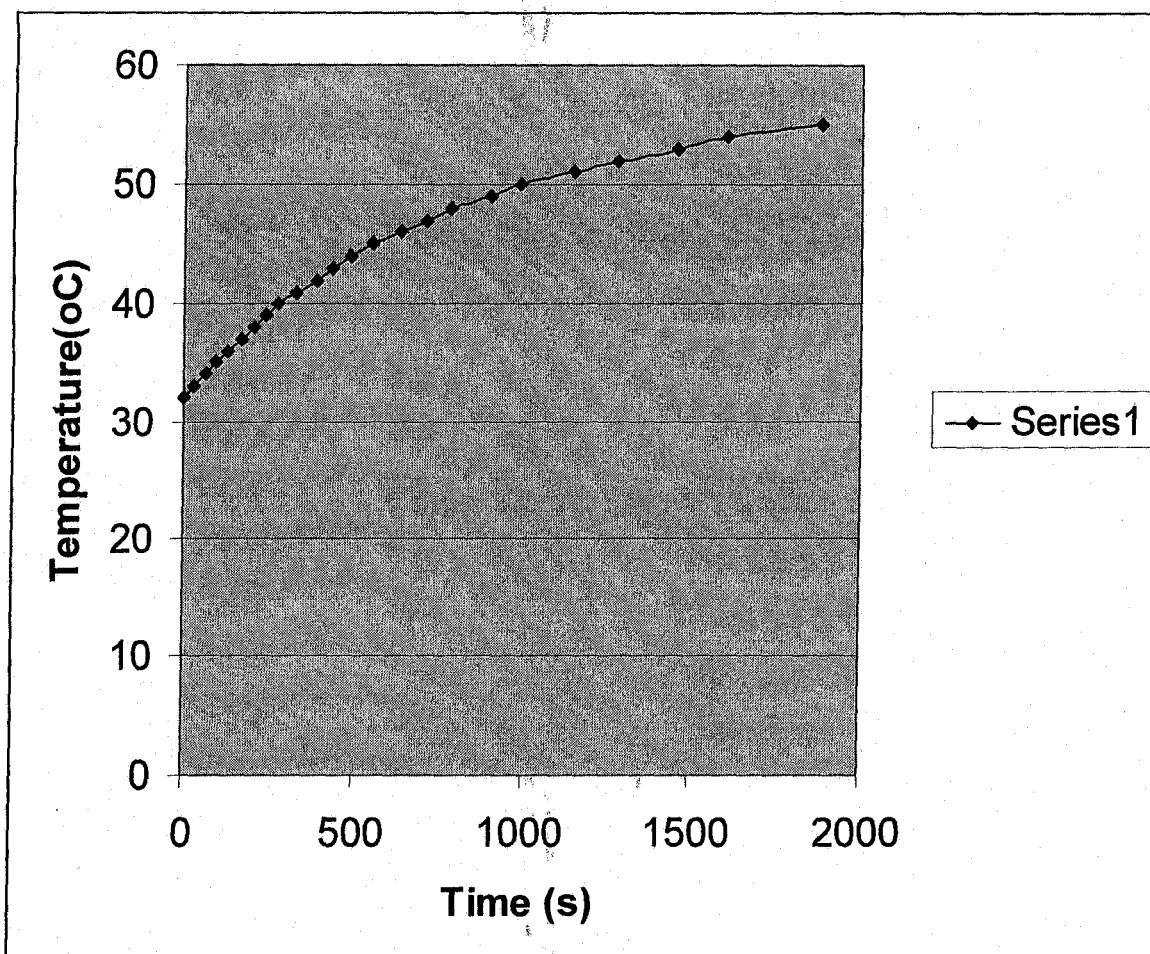
Fig 4.1 Graph of temperature rise against time for sulphonation reaction 2

Reaction three

From reaction three, the volume ratio of sulphuric acid to lube base stock was 1.49:1. The total volume of the reactants was 329.907cm^3. The volume of the product of reaction was approximately 329.5454cm^3. The total mass of the reactant was 478.7g. At the end of the reaction the mass of the product was 469.1g. This indicates a difference of 9.6g. This difference has been accounted for above.

The volume of the sulphonic acid (dark phase) was 243.1818cm^3, while the volume of the excess spent sulphuric acid was 86.3636cm^3. A graph of the temperature rise against time was also plotted.

Similarly, the rate of temperature was very sharp from 30 ^{o}C to 50 ^{o}C, and slower from 50 to 55 ^{o}C. The stirring was also vigorous and the reaction time was approximately 30minutes.

The completion of the reaction is indicated by the time at which the reaction temperature is steady even with prolonged stirring.

Hence the maximum exothermic temperature for the sulphonation reaction was 55 ^{o}C, and the temperature range for optimum yield of the desired product is 50 - 55 ^{o}C. In this temperature range the product formed is essentially the monosulphonic acid.
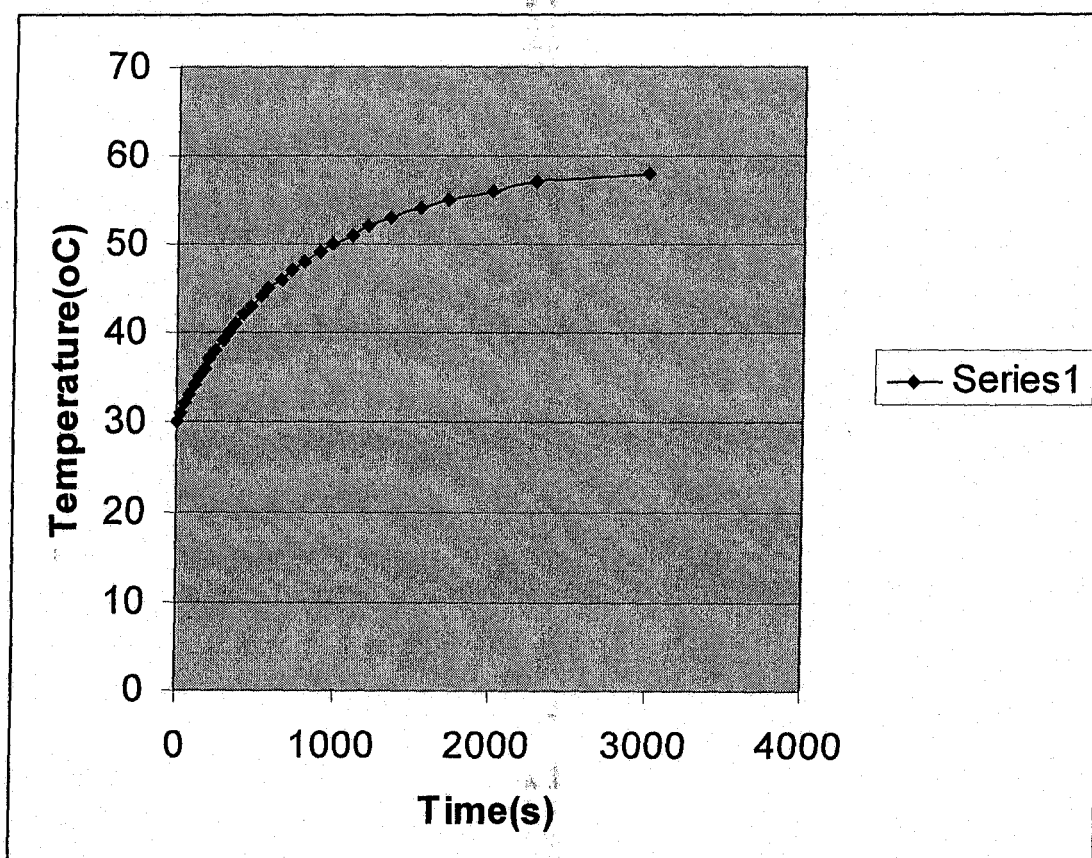

Fig 4.2 Graph of temperature rise against time for sulphonation reaction 3

4.2.5 Neutralization

For the first neutralization reaction, $2.36cm^3$ of the sulphonic acid was neutralized by 1.85g of calcium hydroxide.

On a second attempt, $2.60cm^3$ of the sulphonic acid was neutralized by 1.85g of calcium hydroxide. Taking the average of the two, we have that $2.48cm^3$ of the sulphonic acid will require 1.85g of calcium hydroxide for complete neutralization.

Hence we can infer that on an average, the ratio of sulphonic acid to calcium hydroxide required in the neutralization step is $1.3cm^3$ sulphonic acid to 1g calcium hydroxide.

The exothermic reaction temperature was 40 °C and reaction was very fast with vigorous stirring. The reaction time is less than 10minutes.

4.2.6 Overbasing reaction

In the first reaction, $249.55cm^3$ of carbonic acid was neutralized by 0.185g of calcium hydroxide.

On a second attempt, $248.70cm^3$ of carbonic acid was neutralized by 0.185g of calcium hydroxide. The average volume of carbonic acid required for complete neutralization of 0.185g of calcium hydroxide is $249.125cm^3$. The pH of the carbonic acid was measured as 3.6; hence the concentration of carbon dioxide in the acid is $0.00025mol/dm^3$. The overbasing reaction is usually carried out in the alkaryl acid salt formed in the neutralization reaction step.

As stated in the introduction, the degree or extent of overbasing of the alkaryl acid salt determines its application. For this work, the ratio of the calcium carbonate to the alkanyl acid salt was kept at 1:1.

For practical purposes; In the production of additive packages for use in blending diesel and gasoline engine oils, the calcium carbonate to alkaryl acid salt ratio can be as high as 30:1 while in the one for blending Automatic transmission fluid, this ratio can be between 1:1 to 6:1.
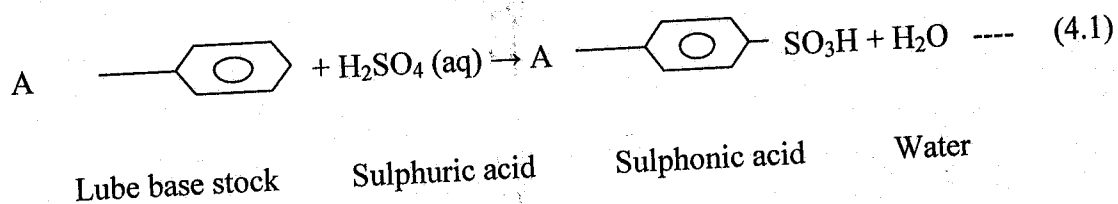
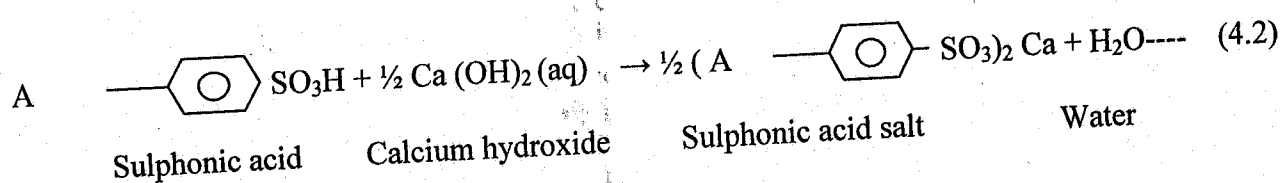# 4.3 Production of calcium long chain alkaryl sulfonate

4.3.1 Developed process

The raw materials required for the production of the above are 98% concentrated sulphuric acid, desaphalted oil (lube base stock), calcium hydroxide, carbonic acid of pH = 3.60

The deasphalted oil (lube base stock) is first sulphonated in a reaction step in which the ratio of sulphuric acid to lube base stock is about 1.3:1. The excess acid is allowed for complete sulphonation of the lube base stock. This ratio can be as high as 1.5:1, but for the sake of economy, the former ratio is used conveniently.

The reaction is exothermic with a maximum exothermic temperature of 55 °C and a reaction time of 30 minutes requiring vigorous stirring. The equation of the reaction can be represented as

$$A \quad \underset{\text{Lube base stock}}{\overline{\bigcirc}} + \underset{\text{Sulphuric acid}}{H_2SO_4 \,(aq)} \rightarrow A \quad \underset{\text{Sulphonic acid}}{\overline{\bigcirc} - SO_3H} + \underset{\text{Water}}{H_2O} \quad \text{----} \quad (4.1)$$

The sulphonic acid produced in addition with the excess spent sulphuric acid is then neutralized with calcium hydroxide in a reaction step in which the ratio of acid to calcium hydroxide is $1.3cm^3$ to 1g. The reaction is also exothermic with a maximum exothermic temperature of 40°C and reaction forms the alkaryl acid salt. The reaction is represented below as;

$$A \quad \underset{\text{Sulphonic acid}}{\overline{\bigcirc} SO_3H} + \underset{\text{Calcium hydroxide}}{\tfrac{1}{2} \, Ca(OH)_2 \,(aq)} \rightarrow \tfrac{1}{2} \, (A \quad \underset{\text{Sulphonic acid salt}}{\overline{\bigcirc} - SO_3)_2 \, Ca} + \underset{\text{Water}}{H_2O} \text{----} \quad (4.2)$$

The alkaryl acid salt is then complexed (overbased) with excess calcium carbonate. This involves adding excess calcium hydroxide and carbonic acid into the alkaryl acid salt to

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form calcium carbonate which exist in the alkaryl acid salt as a reverse micelle (as shown in the literature review). The ratio of the calcium carbonate to the alkaryl acid salt can range from as low as 6:1 to 30:1 depending on the application of the additive package. The reaction is represented as

$$Ca(OH)_2 \quad + \quad H_2CO_3 \quad \rightarrow \quad CaCO_3 \quad + \quad 2H_2O \text{ -------- 4.3}$$

Calcium hydroxide   Carbonic acid   Calcium carbonate   Water
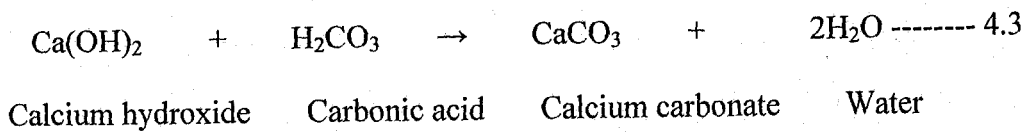
Some of the properties and applications of the finished additive packages are given below.

4.3.2 Additive package for diesel and gasoline engine oils

Applications: detergent, dispersant, antiwear agent, corrosion inhibitor and oxidation inhibitor.

Table 4.7 some physical and chemical properties of the expected additive packages as given by A.S.T.M.

Chemical

Calcium, mass/wt% (ASTM D4951/D4927)	2.62
Phosphorus, mass/wt%(ASTM D4951)	1.07
Zinc, mass/wt%(ASTM D4951)	1.17
Nitrogen, mass/wt%(ASTM D5291)	0.5
Sulfated Ash mass/wt%(ASTM D874)	10.44
Base Number, mgKOH/g (ASTM D2896)	75.4

Physical

Specific gravity at 15 °C(ASTM D4052)	0.98
Viscosity cst at 40 °C(ASTM D445)	3210
Viscosity cst at 100 °C(ASTM D445)	134

4.3.3 Additive package for Automatic transmission fluid

Applications: Friction-modifier, corrosion inhibitor and oxidation inhibitor.

Table 4.8 some physical and chemical properties of the expected additive packages as given by A.S.T.M.

Chemical

Calcium, mass/wt% (ASTM D4951/D4927)	0.25
Phosphorus, mass/wt%(ASTM D4951)	0.48
Zinc, mass/wt%(ASTM D4951)	0.53
Nitrogen, mass/wt%(ASTM D5291)	0.92

Physical

Specific gravity at 15 °C(ASTM D4052)	0.948
Viscosity cst at 40 °C(ASTM D445)	1820
Viscosity cst at 100 °C(ASTM D445)	165

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Investigation into the production of calcium long chain alkaryl sulfonate was conducted. Calcium long chain alkanyl sulfonate is a lubricating oil additive, it serve the following purposes in finished lubricant; as a detergent, a dispersant, a corrosion inhibitor, a friction-modifier, as well as an oxidation inhibitor.

A study of the three (3) reaction steps involved in the production of the additive reveals the following

(i)   Excess sulphuric acid is required for the complete sulphonation of the lube base stock

(ii)   The sulphonation reaction is essentially exothermic.

(iii)   The overall reaction time for the production of the additive is less than 60 minutes.

Hence from the discussion of results, the following conclusions were drawn,

(i)   The sulphonation reaction requires an acid to lube base stock ratio of 1.3:1. The reaction is exothermic; with a reaction temperature of 55 $^\circ$C and complete sulphonation was achieved in about 30 minutes with vigorous stirring of the reaction mixture.

(ii)   1.3cm^{3}of the sulphonic acid produced in (i) required 1g of calcium hydroxide for complete neutralization. The reaction is also exothermic, with a reaction temperature of 40 $^\circ$C and a reaction time of about 10 minutes.

(iii)   The alkaryl acid salt is complexed by adding excess calcium hydroxide and carbonic acid to form calcium carbonate which exists in the alkaryl acid salt as a reverse micelle. The ratio of calcium carbonate to alkaryl acid salt can range from as low as 6:1 to a high 30:1 depending on the application of the additive package.

5.2 Recommendations

Although the study of the reaction steps involved in the production of calcium long chain alkaryl sulfonate has been concluded, and a process has been developed for its production, a problem that militated against the study was the unavailability of deasphalted oil during the period of the research due to non-functional refineries.

Refined base oil was used as the lube base stock. The refining process involves the removal of most of the properties required in the final additive package. Hence the final product obtained at the end of the research lacked most of the properties listed in the discussion of result and in the literature review.

Therefore, going by the above and fact that the findings of the research works is to serve as a working document for any person venturing into lubricating oil additive production, it is hereby recommended that;

(i)   Before going into full production, a laboratory scale production be carried out using deasphalted oil as the lube base stock to ascertain the correctness of the developed process.

(ii)   Further research into lubricating oil additive production should be conducted. This is because lubricating oil additive technology is one aspect of lubrication technology in which very little work has been done.

PROCESS DEVELOPMENT FOR THE PRODUCTION OF

LUBRICATING OIL ADDITIVE

(CALCIUM LONG CHAIN ALKARYL SULFONATE)

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SEPTEMBER 2006.

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APPENDICES

Results for viscosity Index calculation

Table 4.9 Viscosity of base oils at 100°C and 40°C

Viscometer bath at 100°C

Base oil	Tube used	Tube constant	Observed time (s)	Calculated kinematic viscosity (cst)
SN 150	E-272	0.03999	130.6	5.22
SN 500	E-59	0.1103	97.18	10.72
BS 150	E-277	0.04414	721.22	31.83

Viscometer bath at 40°C

Base oil	Tube used	Tube constant	Observed time (s)	Calculated kinematic viscosity (cst)
SN 150	E-59	0.1108	273.48	30.30
SN 500	N 1035	1.287	75.72	97.45
BS 150	N 1035	1.287	371.41	478

The viscosity index can then be read be read from the viscosity index table (chart)

The viscosity index were obtained as

Base oil	Viscosity Index
SN 150	102
SN 500	92
BS 150	98

Sulphonation Reaction

Reaction two

Volume ratio = $\dfrac{\text{volume of sulphuric acid used}}{\text{Volume of lube base stock used}}$

Volume ratio = $\dfrac{95.978}{73.829}$ = 1.30

Reaction three

Volume ratio = $\dfrac{\text{volume of sulphuric acid used}}{\text{Volume of lube base stock used}}$

Volume ratio = $\dfrac{197.44}{132.461}$ = 1.49

The volumes indicated in the procedure differs from that in the results, this due to error in the measuring beaker used for measuring reagents