DECLARATION

I, ***DADA EBENEZER OLUJIMI,*** declare that this thesis is solely the result of my work and has never been submitted anywhere for any degree. All literature cited have been duly acknowledged in my references.

E. O. DADA   DATE

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E. O. DADA

05/09/2005

DATE

CERTIFICATION

This thesis entitled "***Development and Formulation of Shea Butter Based-Semi Solid Lubricant***", by Ebenezer Olujimi Dada 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 scientific contributions to knowledge and literary presentation.

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DEDICATION

Jehovah Elyon, you are the Most High God.

ACKNOWLEDGEMENT

The successful completion of this research work is not by my efforts alone but by God's grace and the contributions of my supervisor, lecturers, family members, friends, colleagues and well-wishers; therefore their contributions have to be acknowledged.

I would like to express my profound gratitude to my supervisor, Dr. M. O. Edoga, for the provision of relevant materials, guidance and most importantly, the creation of friendly environment. These, coupled with prompt attention encouraged me to work harder. I am really grateful.

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The Head of Department and all my colleagues (both Senior and Junior in the Department of Chemical Engineering, Lautech, I am indebted to you for your understanding and the comradeship.

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ABSTRACT

This work investigated the suitability of shea butter as a substitute for base oil derived from crude oil as the major component in the production of lubricants.

Shea butter was extracted via the use of soxhlet apparatus operated on the principles of solid/liquid indirect extraction from the seeds of shea tree. The extract was formulated into semi solid lubricants using simplex lattice design. The shea butter, in addition with other components-thickeners and additives was then used in producing lithium stearate grease. The thickener used was the simple soap- lithium stearate soap. Subsequently, the formulated samples were analysed for their physicochemical characteristics.

The results of the analysis of the physicochemical properties of the extracted shea butter showed that it possessed similar values for the parameters used in classifying 1000 pale oil as one of the 11 grades of the petroleum derived base oil. The dropping point temperatures of the produced samples of grease were found to be in conformity with the NLGI specification (177 – 204°C) for lithium grease. Also, the penetration values and NLGI consistency numbers of the produced samples of grease were found to be in conformity with the ASTM and NLGI specifications.

An Analysis of Variance (ANOVA) of process variables revealed that temperature, pressure and time affected the consistency of grease samples. The multiple regression analysis of these process variables revealed the extent of the effects of temperature, pressure and time on the consistency of the grease samples.

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DEVELOPMENT AND FORMULATION OF SHEA BUTTER BASED-SEMI SOLID LUBRICANT

A THESIS
PRESENTED TO

THE POSTGRADUATE SCHOOL
FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA

BY

DADA EBENEZER OLUJIMI
(M. ENG/SEET/2001/828)

In Partial Fulfilment of the Requirements for the Degree of Master of Engineering (Chemical Engineering)
Department of Chemical Engineering,
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AUGUST, 2005

ABBREVIATIONS/NOTATIONS

AOAC	Association of Official Analytical Chemists
ASAE	American Society of Agricultural Engineers
ASTM	American Society for Testing and Materials
cSt	Centistokes
FAO	Food and Agricultural Organisation
FIIRO	Federal Institute of Industrial and Research Oshodi
MEES	Microsoft Encarta Encyclopaedia Standard
NIS	Nigerian International Standards
NLGI	National Lubricating Grease Institute
VI	Viscosity Index
η	Absolute viscosity
τ	Shear stress
η_k	Kinematic viscosity
ρ	Density
Li	Lithium

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

The knowledge of lubrication as a catalyst of industrial revolution dates from the early history in Egypt, Greece, Rome and Persia where greases made of a combination of animal fats and calcium were used to lubricate chariot wheels (Benton, 1982).

The word lubricant, originally derived from a Latin word, "*lubricare*"- to make slippery, has as its principal function the reduction of friction and wear between contacting surfaces (Benton, 1982). However, depending on the application, lubricants may also have to fulfill other roles such as providing heat transfer (cooling) action, keeping contaminants in suspension, dispersing breakdown products, maintaining clean and deposit- free surfaces as well as preventing corrosion.

The use of various engines which contain several hundreds of moving parts that must be prevented from rubbing on one another requires the presence of a thin film of material – usually oil, in between them, this simply describes the lubricating action of lubricants. The absence of lubricants in such situations results into the rubbing of such parts on one another thus leading to severe wear (Spencer, 2002).

In addition, the resulting friction leads to heat generation which causes frequent expansion and contraction and eventual collapse of such parts.

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Lubricants perform three major functions in the life of every moving part of an engine. These include establishing a film of oil thick and strong enough to prevent metal to metal contact, acting as a coolant for the removal of heat generated by the engine and reducing friction and keeping any contaminant within the system in suspension (Eterigho, 2001).

Lubricants exist in the three states of matter – gases, liquids and solids. Any substance capable of preventing and controlling wear between sliding surfaces is a lubricant (Benton, 1982). Liquid lubricants include the familiar engine oils, gear oils as well as water-based emulsion used as coolants in metalworking, rolling and cutting operations. Greases can be defined, as semi solid/solid dispersions of a thickening agent in a liquid lubricant of which the ancient lubricants mentioned above are examples. Nowadays, thickening agents include metallic soaps, complex soaps and hydrophobic clays. The liquid lubricant can either be mineral or synthetic oil (Mang and Dresels, 1975).

Modern lubrication technology has developed from a multi-disciplinary approach involving chemists, colloidal and corrosion scientists, rheologists, physicists, and mathematicians all interacting with lubricant technologists and formulators.

Today's lubricants are complex mixtures of mineral or synthetic derived base fluids, combined with performance enhancing chemical

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additives to provide acceptable viscosity, dispersion, detergency, corrosion inhibition, thermal and oxidation stability.

Shea butter is obtained from shea nut which belongs to the family: *Sapotaceae*, genus: *Butyrosperum*, species: *Paradoxii/parki*. It is wide spread in the savanna and semi-arid areas of West Africa (Hammond *et al.*, 1997). Shea nut constitutes one of the major oil bearing agricultural seeds such as groundnut, palm fruits, cottonseeds, sun flower, melon seeds, etc. It contains 55% fat (Casten and Synder, 1985). Shea butter has many other economic importances and find various uses in chocolate, soap, cosmetic and lubricating industries (FAO, 1991).

In this present study, emphasis has been placed on the formulation and development of lithium stearate (soap) industrial grease with shea butter as the base fluid.

1.2 Aim and Objectives of the Study

The overall aim of this work is to formulate and produce semi solid lubricant that will meet international standard and specifications from natural (non-petroleum) oil, while the objectives are to:

i) Extract the natural oil (shea butter) from shea nut seeds employing the solid liquid (indirect leaching) extraction method via the use of soxhlet apparatus and subsequently characterising the shea butter using ASTM guidelines in order to find out its suitability as a base oil- one of the basic components of semi solid lubricants.

ii) Formulate semi-solid lubricant formulations from its components.

iii) Produce semi-solid lubricant using formulations as mentioned above.

iv) Subject the samples of the semi solid lubricant produced to standard tests using NLGI and ASTM guidelines in order to confirm their conformity with internationally acceptable specifications for semi solid lubricants.

1.3 Scope of the Study

This work is limited to the production of semi-solid lubricant using the extract (shea butter), lithium stearate soap and DF22 (chemical additive). The method of extraction process via the use of soxhlet apparatus was adopted because of its simplicity and also because of the greater yield of the oil in comparison to other methods of obtaining the oil from shea nut (Kar and Mital, 1981). Characterization of the extracted shea butter (base oil) and the formulated grease samples in accordance to ASTM and NLGI guidelines as well as testing of the developed grease samples with the view of knowing the effects of the test parameters such as temperature, pressure and time on the behaviour of the grease samples were also carried out.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Shea Nut Tree

The shea nut – *Butyrospernum paradoxii* tree, grows abundantly in the savannah and semi arid areas of West African countries with the highest density of shea trees in Mali, Burkina Faso, Togo, Benin, Nigeria and Sudan (not in order of production). In Nigeria, the spread of the tree is most predominant in the northern part of the country namely Bauchi, Niger, Adamawa, Benue and Kaduna States. In the western part, however, it is mainly found around Oyo and Ogun States while in the Eastern part is found around Ogoja province (Adgidzi, 1999).

Various names are given to Shea nut in Nigeria depending on the language of the people; the Hausas call it *kadanya*; Fulanis – *kareje*; Tivs – *chamman*; Yorubas - *emi-emi*; and the Ibos call it *osisi okwuma*.

The tree is a deciduous tree, 7-15m tall with deeply fissured bark splitting into rectangular scales. It has short shoots with leaf base scars and bears white fragrant flowers. The fruits are ellipsoidal, about 4-5cm long with fleshy pulp and usually one pulp seeded (Dakogol, 2001).

2.1.1 Shea nut seed

The seed is more or less ovoid, about 3.5cm long and 2.5cm broad with a shinning dark brown, hard shelly testa and a white scar down one side (Olajide *et al.*, 2002).

The kernels are about 50-58% shea butter depending on the method of extraction. A tree produces between 15-20kg of fresh fruits which correspond to 3-5kg of kernels.

2.1.2 Production of shea nut and its uses

Shea nut production in West Africa has been estimated at 0.5 million tons per year (Purseglove, 1984). The principal exporters being Nigeria, Mali, Togo, Benin and Burkina Faso.

Shea nut is principally used for the production of shea butter which is used as fat. It is also a source of edible oil in some areas.

2.2 Shea Butter

Shea butter is the natural fat obtained from shea nut. It has a characteristic mushroom odour and a creamy yellowish colour. Naturally, it has some anti-oxidant properties due to its richness in tocopherols (Fleury, 1981).

2.2.1 Production of shea butter

The extraction of shea butter is a very tedious process. Traditionally, the nuts are dried and shelled and then the kernels removed. The dried kernels are then pounded in mortar. The crushed substance called grits is roasted in a pot over fire. The roasted grits is then ground in a grinding stone into an oily paste. This paste is boiled in water for one hour and the oil floating on the surface of the water is skimmed off as given in Fig. 2.1.

During this last step some fibrous impurities settle at the bottom of the pot but not all the impurities settle, some still lock within the oil. The pre-treatment, drying and pounding differ from one region to another (Boateng, 1992). This, however, has a considerable influence on the final quality of the butter.

However, for laboratory extraction of shea butter, the extraction of the butter via soxhlet apparatus making use of organic solvents such as chloroform, benzene and normal hexane have been used. This apparatus operates on the principle of solid liquid indirect leaching. It gives the best yield and the purest form of the butter in comparison with the local methods. The nuts are dried and shelled and the kernels obtained. The kernels are

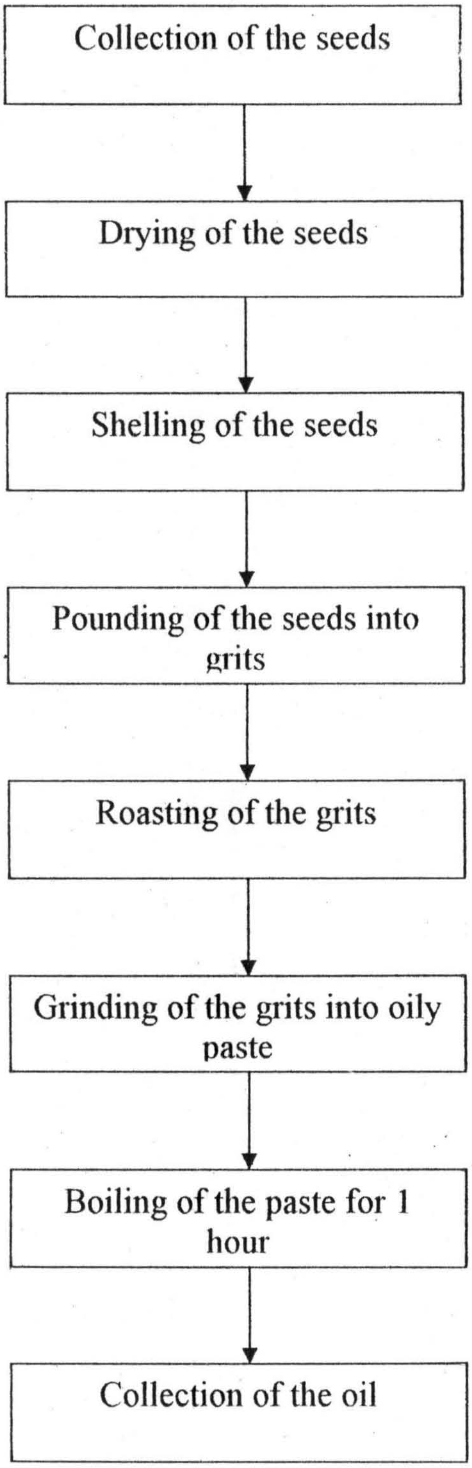


Fig. 2.1: Flow Chart of the Production of Shea Butter (Local Method)

then milled into finely ground form which is then put in the thimble of the apparatus where the condensing droplets of the organic solvents leach the oil out of the ground paste (Kar and Mital, 1981).

The oil is separated from solvent using a rotary evaporator under vacuum. The oil is further dried at 98°C to remove the residual solvent (AOAC, 1984).

2.2.2 Fatty acid composition of shea butter

The earlier work done by experts showed that the predominant fatty acids in shea butter are stearic and oleic acids. Hilditch and Williams (1964) reported 8.5%, 35.9%, 49.9% and 5.3% for palmitic, stearic, oleic and linoleic acids respectively, Badifu and Abah (1998) reported 4.2%, 47.5%, 41.8% and 6.5%, respectively, while Elemo *et al*., (2002) reported 9.7%, 32.0%, 51.1% and 3.82%, respectively. Badifu and Abah (1998) further reported the levels of saturation and unsaturation as 51.7% and 48.3%, respectively. Claiming this is responsible for the solid state of the butter at room temperature 33±1°C considering its smaller iodine value due to a higher saturation value. The more saturated a fat is, the smaller its iodine value and the greater the tendency to be solid at room temperature (Badifu and Abah, 1998).

2.2.3 Uses of shea butter

In Northern Nigeria, shea fat is commonly used as drying and cooking oil, it is also further used for its local medicinal value and in the treatment of cough and minor bone dislocation (Badifu, 1989).

In some other parts of West Africa, shea butter has industrial value. It serves as raw material in the production of local soaps. It can also be used as a substitute for cocoa butter for coating in chocolate manufacturing and cosmetic industries. The residue of the shea pulp after the extraction of butter can also be used for animal and poultry feed preparation (Adgidzi, 1999).

2.2.4 Suitability of shea butter

Shea butter is considered suitable for this study because of its rich concentration in fatty acids. The main fatty acid components (stearic and oleic acids) are long chain carboxylic acids which are not corrosive to skin and most metals. The acids have insignificant odour. Shea butter is also found to be compatible with most thickening agents used in the lubrication industry (Mital and Dove, 1971).

2.3 Lubrication

Lubrication is a means of preventing and / or reducing friction and maintaining its effects. When two substances rub each other, two things are noticeable:

- It takes energy to rub them together.
- The rubbing surfaces become hot.

Considering a boat being pushed along the beach into the sea, it takes much energy to be pushed, although the surface getting in contact with sand might not be felt getting hot as heat is dissipated rapidly. As the boat starts to float, it takes less energy and when fully floating it can be pushed easily because a lubricant-water inter-phase now exists between the sand and the boat. Lubrication, in addition, is also a process of reducing the energy required to move one substance over another by the introduction of lubricant into the adjoining space in between the two surfaces.

The knowledge of lubrication has helped to reduce considerably the problems posed by loss of useful energy due to friction developed in all surfaces in relative motion to one another. It has been estimated that about one third to one half of the total energy produced world wide is wasted by this opposing force of friction in all modern prime movers and industrial energy (Energy Today, 2002).

The overall importance of lubrication cannot be overemphasised but the ultimate aim of its correct and effective practice is to ensure that economic and design life of equipment, machinery and plant are achieved with minimum cost.

2.3.1 Lubrication application

The components of industrial machinery that require lubrication are those in relative motion such as bearings, gears, slides, guides, couplings pulleys, etc. These elements/components move in relation to one another, either by sliding, rolling, approaching, receeding, reciprocating or by combination of two or more of these motions. However, bearings find the widest use of grease in lubrication. It is important to state that improper, inadequate or excessive lubrication results in premature failure of machine elements resulting in high maintenance costs and thus lowering profitability in industries (Sasaki *et al.*, 1963).

2.3.2 Bearings

A bearing is a housing or support for a rotating part (a shaft rotating within a bearing) or one that moves linearly (moves axially within the bearing). A bearing may also restrain motion in some manner. Bearing are of two types: plain and rolling element (Hamrock, 1982).

Plain bearings

A plain bearing is the most basic type and contains no moving parts. It is based on the sliding motion between a stationary and a moving member. In most cases, a plain bearing is made of a material or alloy which is softer than that of the part that slides or moves against it. Thus, the bearing assumes most of the wear. Plain bearings that support load perpendicular to their axis of rotation are called journal bearings, while the ones that support load parallel to their axis of rotation are called thrust bearings.

Rolling element bearing

These have either balls or rollers which accommodate motion between the stationary and moving parts. The rollers can be spherical, cylindrical or tapered. Those with relatively long small diameter are called needle bearings. They are made of hard steel alloys because the small rolling elements must carry a wide range of loadings. The rolling elements are usually enclosed between rings called 'races'.

Rolling element bearings that support load perpendicular to their axis of rotation are called radial bearings. The lubricants in a rolling element perform the following functions: reduction of rolling and sliding friction, protection of the highly finished surfaces of the rolling elements and races against corrosion and pitting and acting as a sealant (Harris, 1990).

2.3.3 Types of lubrication

The mode of lubrication of a plain bearing depends on the conditions which affect the bearing's ability to develop a load carrying fluid film which can separate the journal and bearing surfaces. However, the principle governing the lubrication of rolling elements bearings differ from those of plain bearings.

Boundary lubrication

This is the type of lubrication in which there is no fluid film separating the journal and the bearing surfaces. This is often the situation when the shaft is at rest or low speed (during start-up). Under these conditions, lubrication depends on the nature of the contacting surfaces which are not completely separated and thus some metal to metal contact occurs. However, some lubricant decomposition products may be present on the contacting surfaces, so also, surface active additives form a thin, soft film on the metal surface which reduces friction (Moore, 1972).

Hydrodynamic lubrication

This is a situation in which a load-carrying film which can separate the journal and bearing surfaces is formed with a sufficient pressure. As speed increases, the wedging action of the lubricant moves in the direction of rotation. However, if loading on the bearing is increased sufficiently, the full fluid film that separates the journal and bearing may collapse and the situation reverts to boundary lubrication. As a result of this, lubricant of sufficient viscosity must be chosen for a specific job.

Elastohydrodynamic lubrication

In a fluid film plain bearing, the journal load is supported by a continuous hydrodynamic lubricant film which keeps the two contact surfaces separated.

In a rolling element-bearing unit, pressures are extremely high between the relatively small rolling elements and their raceways. Lubricants subjected to the high pressure within the contact area of a rolling element bearing were found to undergo a dramatic increase in viscosity (ASAE, 1986). This increase in viscosity enables the lubricant film to withstand the high contact stress while preventing contact between the rolling surfaces. The high contact pressure in a rolling element bearing also elastically deforms the rolling surface to enlarge the contact area which supports the load. The combination of surface deformation and hydrodynamic lubrication action produces a thin, elastohydrodynamic lubricant film which provides for lubrication within the contact zone of rolling element bearings (Moore, 1972).

2.4 Lubricants

These are substances applied to the bearings, guiding or contacting surface of machineries in order to reduce friction between the moving parts (Benton, 1982)

In the early days, the fatty oils derived from animals, fishes and vegetables could meet the modest demands made on them as lubricants, but the severe conditions under which modern machineries have to operate on can only be met satisfactorily by minerals and synthetic oils derived from crude oil and other means (Mang and Dresels, 1975).

Lubricants enable machineries to function continuously by preventing abrasion or seizing of metal parts caused by heating. Some lubricants are also coolants and this prevents material deformities caused by heat. Thin film lubricants are used for heavy load where internal frictions in the lubricant and the consequent loss of power have to be avoided (Mc Graw-Hill, 1982). Thick film lubricants are used in machineries in which moving parts or oscillating conditions are moderate.

2.5 Types of Lubricants

Lubricants may be broadly classified as: gases, liquids and semi-solids

2.5.1 Gaseous lubricants

Gases such as air and helium are used as medium to completely separate moving parts. Because of their very low viscosities, they give low friction and low heat generation. They are used for very high speed bearings.

2.5.2 Liquid lubricants

There are three categories of liquid lubricants.

Mineral oils – These are the almost automatic choice if a liquid lubricant is to be used as they are relatively cheap, available in a wide range of viscosities, compatible with seals, metals and paints. Their properties may be modified or enhanced with additives and they may be manufactured to closely controlled properties.

Aqueous lubricants – These are water lubricants which are mainly used because of the cooling properties of water and its resistance to burning. Their use is mainly limited to fluids for metal working and fire resistant hydraulic fluids. They may or may not contain mineral oil as an emulsion.

Synthetic lubricants – These are used in situations where mineral oils cannot be used. This is usually when the lubricant is required to operate at high temperature or where the lubricant must be fire resistant or in advanced automobile diesel engines. Examples of such lubricant are silicone fluids, organic esters, poly alkylene glycol derivatives (Grolier, 1994).

2.5.3 Semi-solid lubricants

These are lubricants which will not flow under their weight. They are also called greases and consist essentially of a thickener dispersed in a liquid often referred to as base oil. Their main advantage over liquid lubricant is that they have fewer tendencies to escape from bearings. They also act as seals which protect the bearings from contamination (Grolier, 1994).

2.6 Physicochemical Properties of Lubricants

These are the basic qualities or characteristics a substance must possess before it can function effectively and efficiently as a lubricant. They include the following:

2.6.1 Viscosity

This is the property of a fluid that tends to prevent it from flowing when subjected to an applied force. Highly viscous fluids resist flow more than less viscous fluids. The viscosity of a fluid decreases with a decrease in density which occurs when temperature increases. In a less dense fluid, fewer molecules are available per unit volume to transfer the motion from moving layer to the stationary layer. This in turn affects the speed of the different layers. Momentum is transferred less readily between the layers and thus viscosity falls (Badmus, 2003).

In a few liquids, the increased molecular speed just balances the decrease in density. Silicone oils for example change very little in their tendency to flow with changes in temperature. This effect stands out silicone oils as very good lubricant when machinery is subjected to great temperature changes.

Absolute viscosity

Isaac Newton showed that the absolute viscosity of a liquid, can be defined as

$$\eta = \frac{\tau}{S} \text{ .... Eq 2.1}$$

Where η = absolute viscosity, N.s m^{-2}

τ = Shear stress, Nm^{-2}

S = Shear strain rate, s^{-1}

But $\tau = \text{Shear stress} = \frac{\text{Force}}{\text{Area}}$ .... Eq 2.2

And S = shear strain rate = velocity gradient = $\frac{\text{velocity}}{\text{Distance}}$ ....Eq 2.3

$$\therefore \quad \eta = \frac{\tau}{S} = \frac{\frac{\text{Force}}{\text{Area}}}{\frac{\text{Velocity}}{\text{distance}}} = \frac{\text{Shear stress}}{\text{Shear strain rate}} \text{ .... Eq 2.4}$$

It follows from Equation 2.4 that the unit of viscosity must be the units of shear stress divided by units of shear strain rate.

In SI system, the unit of η is N.s m^{-2} Pa.s

In cgs system, the unit is dyne.c.cm^{-2} or poise and 10^{-2} poise = 1 cP

In English system, the unit is Ibf.s.ft^{-2}

Kinematic viscosity

In many situations, it is more convenient to use kinematic viscosity rather than absolute viscosity. It is defined as;

$$\eta_k = \frac{\text{Absolute viscosity}}{\text{Force density}} = \frac{\eta}{\rho} \text{ .... Eq 2.5}$$

The cgs unit of η_k is cm^2/s

The English unit is ft^2/hr

2.6.2 Viscosity index

All lubricants change viscosity with temperature, with viscosity increasing when cooled and decreasing when heated. Not all oils behave in the same way. Some reduce their viscosity much faster than others when heated. This property is important in selecting lubricant for various applications. For example, a lubricant should change its viscosity as little as possible so that it is not too thick when cold thereby making start-up to be very difficult and not too thin when hot thereby running off the surfaces (Spencer, 2002).

There is no absolute measure of this property but for comparison of different oil an arbitrary scale known as viscosity index (VI) has been devised. A low number indicates an oil which changes viscosity rapidly with temperature, whereas, a high number indicates an oil which changes viscosity little when heated or cooled. Viscosity index is not an indication of lubrication, an oil with a high viscosity index can be a low viscous lubricant whereas a heavy viscous lubricant used for lubricating steam cylinders may have a low viscosity index (Harris, 1990).

2.6.3 Pour point

Oils generally may become plastic solids when cooled as a result of partial separation of wax or congealing of hydrocarbons. The lowest temperature at which oil will just flow naturally by gravity without any agitation under prescribed conditions is known as the pour point. The conditions of the test bear little relation to operating conditions though they correlate to some extent with storage conditions. However, they give a guide to the behaviour of the oil to make sure that the temperature under operating conditions are about that specified as the pour point of the oil.

2.6.4 Flash point

This is the temperature at which the lubricant or any substance gives off sufficient vapour to form a flammable mixture with air. Flash point is however, of limited significance as far as lubrication is concerned. The end user might want to know the value for a particular product. The deterioration of the flash point in unused oil in a blending plant is a guide in detecting contaminant by volatile materials.

2.6.5 Moisture content

In almost all systems, traces of water in the lubricants arise from such sources as leaking oil coolers, engine cooling system leaks and in all types of machineries from atmospheric condensation. The presence of excessive amount of water will affect the viscosity of the oil. It may also give rise to emulsion formation, which inevitably causes failure of such systems. The water content should therefore not exceed the limit specified for the different grades of lubricants and applications. When a rise in water content is observed, the source of water contamination must be traced and rectified.

2.6.6 Density

This is a measure of the mass of a given volume of fluid at a standard temperature. It is usually expressed as kg/litre at 15°C. This term has replaced specific gravity. Though specific gravity is of no value in predicting the quality of a lubricant but it can be a useful indicator of the type of base oil and for detecting contamination between oils.

2.6.7 Appearance/colour

The colour of lubricant is of little significance as additives may change its appearance considerably. However, colour can be significant where the lubricant is used in a manufacturing process and not as a lubricant, for instance, in the cosmetic industry. When a difference in colour is observed, it implies there is a contamination.

2.7 Lubricating Grease

Grease may be defined as a semi fluid, semi solid lubricant produced by the dispersions of a thickening agent in a liquid-base oil with the addition of performance enhancing chemical substances (additives). They are non

Newtonian semi solid lubricants which will not flow under their own weight (Billet, 1979).

The basis for blending the component together however depend on the type of grease to be produced by the manufacturer. But generally, base oil takes the highest percentage of blending proportions because it imparts the lubricating ability into the grease structure. This is followed by the thickener, the amount of which determines how hard or soft the grease will be and the additive is just added to enhance the final qualities of the other two components.

In summary, lubricating grease is a chemical arrangement of the component particles of a thickening agent (mostly soaps) in a liquid (lubricant) blended with additives or modifiers to form a physical structure where nature and stability determine the appearance, texture and properties of the final product.

2.8 Grease Usage and Trends

Worldwide grease usage patterns are not static, nor is the technology of product development to meet changing, and increasingly stringent, application and environmental requirements. These influences and trends can only be expected to intensity in the foreseeable future. The result is an increasing use of higher gravity, higher priced products and a corresponding reduction in the use of lower price and performance greases (Luboil, 2001).

2.8.1 Worldwide usage

Central and Eastern Europe account for the majority of world wide grease usage (Figure. 2.2) followed by Asia/Pacific, North America, Western Europe, Central and South America, Africa and the Mid-East. A significant difference in types of products used exists between the major user regions. Western Europe and North America typically require higher quality products than the Central and Eastern European users. Africa uses specialised products (such as greases for mining equipment), and use of polyurea products predominates in Asia (MEES, 2004).

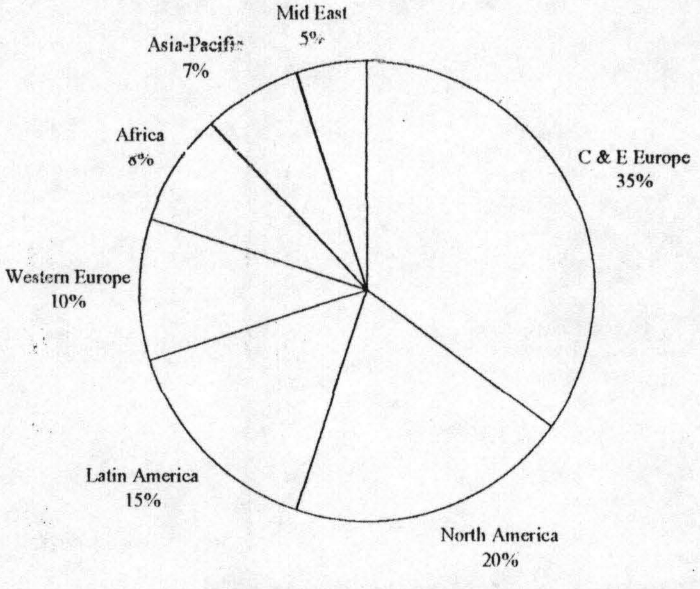


Fig 2.2: Worldwide distribution of grease usage

Throughout the world, industrial applications account for most of the grease used (Figure. 2.3). Of this usage, railroad, general manufacturing, steel production and mining predominate. (Figure. 2.4)

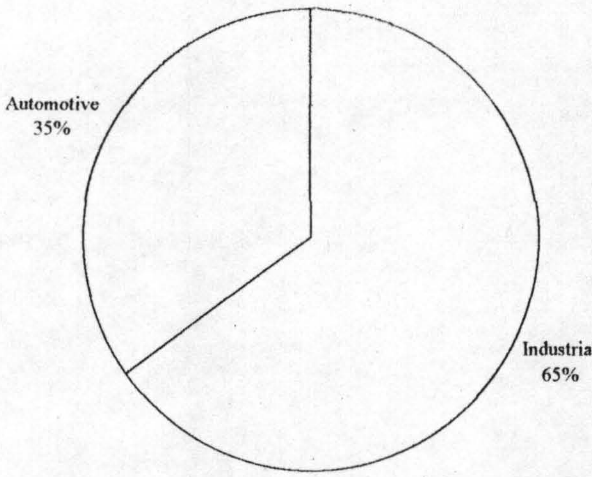


Fig 2.3: World grease market

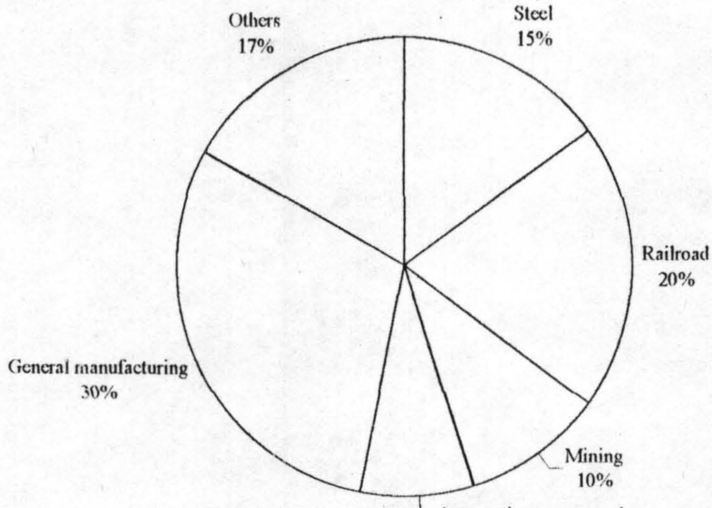


Fig 2.4: World industrial market

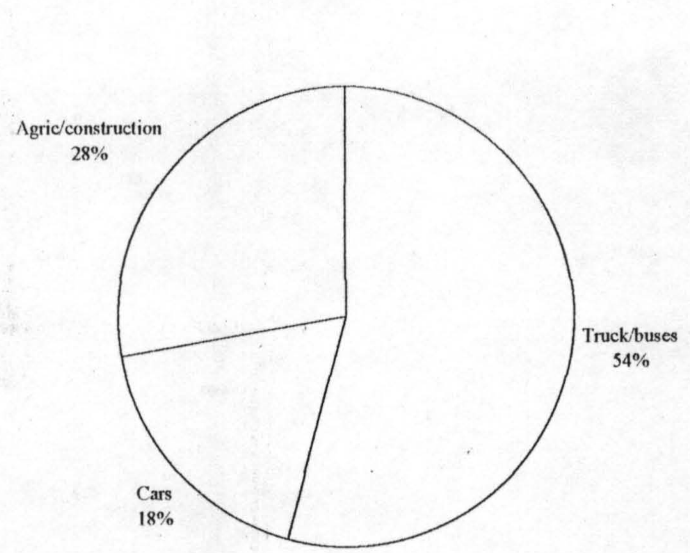


Fig 2.5: Worldwide automotive grease market

Among automotive applications, trucks and buses account for the majority of grease used (Figure. 2.5) followed by agricultural and construction equipment and passenger cars.

2.9 Lubricating Grease Components

Lubricating grease comprises of the basic components: a base fluid, a thickening agent and chemical additives. Different types and combinations of base fluids and thickeners along with supplemented structure modifiers and performance additives combine to give the final product its special lubricating properties (Bennett, 2004).

2.9.1 Base oil

This is the major component of lubricating grease and thus the most important in the foundation of grease. It exerts a considerable influence on the behaviour of the grease due to the viscosity it carries into the grease structure. In formulating grease, base oil's viscosity is usually chosen such that it is similar to that which would be normally chosen if the equipment were to be oil lubricated. The oxidation resistance of grease may be poor if its base oil component has a low viscosity index or large amount of sulphur or polynuclear aromatic molecules. Poor low temperature properties of a base oil do not always define the behaviour of the finished grease because certain thickeners may themselves function as pour point depressants.

Base oil can be of high viscosity index. This is when the viscosity index is greater than or equal to 95, or it can be classified as medium viscosity index oil if the viscosity index lies between 75 and 95.

Base oils are normally of mineral (petroleum) or synthetic origin although vegetable oils may be used for specialised applications. The classification below further distinguishes between the various forms of available base oils.

Mineral oils

These are produced by a number of processes depending on the refining of the crude oil. For this reason, the choice of crude is very important. Most favoured are paraffinic crudes which give good yield of high viscosity index stocks. Although, they contain a lot of wax. For certain applications, naphtenic crudes are preferred because they yield little wax and naturally have low pour points.

Synthetic oils

These oils are becoming increasingly important in the grease industry especially in greases designed for special extreme temperature applications. Synthetic oils can be of petroleum or vegetable oil feedstock. They include poly alpha olefins, diesters, halogenated ethers and all oils derived from either plants or animals, such as castor oil, shea butter, sesame oil and shale oil. They have viscosities in the range of the lower heavy viscosity index neutral mineral oils. Their viscosity indices and flash points are higher and their pour points are considerably lower. These make them valuable, useful and usable blending components when compounding oils for extreme service at both low and high temperatures.

Table 2.1 shows the NLGI approved grades of base oil with their properties.

Table 2.1: NLGI approved grades of lubricating base oil and specifications

Grades of oil	*100 Neutral oil 100N*	*150 Neutral oil 150N*	*250 Neutral oil 250N*	*500 Neutral oil 500N*	*Bright stock BS*	*100 pale oil 100p*	*400 pale oil 400p*	*500 pale oil 500p*	*1000 pale oil 1000p*	*1200 pale oil 1200p*	*Cylinder oil Cp*
Kinematic viscosity at 100°C, cSt	3.4- 4.2	4.8 – 5.4	6.7 – 7.5	10.6–11.8	29.4–31.4	3.9 – 4.2	7.2 – 7.9	10.2–10.9	11.5–12.7	15.9–17.9	38.5– 42.5
Viscosity index minimum	95	95	95	95	95	75	75	75	75	75	75
Pour point, °C (maximum)	- 7	- 9	- 9	- 9	- 9	- 9	- 9	- 9	- 9	- 9	- 9
Flash point, °C (minimum)	193	204	210	221	266	165	210	210	210	215	270
Appearance	Bright and clear	Bright and clear	Bright and clear	Bright and clear	Bright and clear	Bright and clear	Bright and clear	Bright and clear	Bright and clear	Bright and clear	Bright and clear

Source: Nigerian Industrial Standards Handbook NIS 213 1985

2.9.2 Thickeners

This is the second basic component of lubricating grease. It is used to describe the ingredients added to thicken the base oil into greases' structure. There are two broad categories of thickeners: organic and inorganic thickeners (Luboil, 2001).

Organic thickeners

Organic thickeners are further subdivided into soap based and non soap based thickeners.

Soap Based Thickeners:

These are thickeners that are formed as a result of saponification reaction. Saponification reaction is a reaction between fatty acid or esters of either an animal or vegetable origin and an alkali or an alkaline earth metal in presence of heat and pressure. The products formed are the soap and water. The water is subsequently evaporated in the course of the reaction.

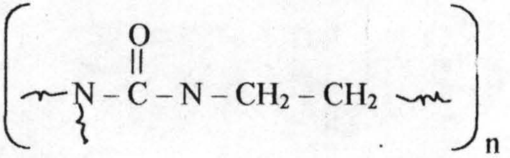
Simple soap thickeners – These are formed as described above. The alkali or alkaline earth metal is in its elemental form or occurs as an hydroxide or oxide. The mechanical stability and rheological properties of the finished grease result from the fibre structure provided by the metal soap.

Complex soap thickeners - These thickeners are formed by simultaneously reacting a fatty acid and derivative and another polar compound called a complexing agent with a basic component. For example, co-reacting 12-hydroxystearic acid and azelaic acid with lithium hydroxide produces a more intricate lattice structure than that of simple lithium soap. Complexing agents usually have a lower molecular weight than that of a fatty acid derivative. This category of thickeners assists in developing grease that can withstand the more extreme operating conditions of most modern production equipments.

Mixed soap thickeners – These thickeners are produced from either simple soap combinations or simple – complex soap combinations. The effect of this action is to enhance the structure and properties of the final product.

Non-soap thickeners

The most widely used non-soap organic thickeners are polyureas which are prepared by reacting isocyanates with amines. Chemically, the products can be represented as



$$\left(\sim N - \overset{O}{\overset{\|}{C}} - N - CH_2 - CH_2 \sim \right)_n$$

When acetate groups are incorporated in the polymer chain, the designation "polyurea-acetate complex" may be used. Due to its durability, this thickener is used in making greases frequently used in sealed-for-life bearings which are filled during assemblage permanently seated and operated without relubrication for the normal life of the equipment.

Other examples of thickeners in this category are salts of phosphoric acids, thiophosphoric acids, phosphonic acids and terpthalic acids.

Inorganic thickeners

These include primarily clays and silica.

Clays – Two clays of the montmorillonite group – bentonite and hectorite are the most important inorganic thickeners. Grease produced from those thickeners are functional over extremely wide temperature ranges because they lack melting points and resist other phase transformations. They are used for aerospace applications.

Silica – Silica based thickeners are prepared by treating finely dispersed sodium silicate with diisocyanates or epoxides. The resulting gel structure is amorphous rather than crystalline. Because of their tolerance for radiation, greases produced from this thickener containing aromatic base fluids are often used for lubricating rolling element bearings in nuclear power plants.

2.9.3 Additives

This is the third component of what makes up the grease structure. The properties and inherent abilities of the base oil and the thickener are usually inadequate to meet the arduous requirement of modern machinery and engines. Special substances, usually chemicals are thus incorporated into the grease structure in order to improve its chemical, structural and rheological properties and consequently enhance its performance.

Most of the additives involved are chemically active, i.e. they produce their effect through a chemical reaction either within the lubricant medium or on the metallic surface.

The category includes oxidation inhibitors, rust and corrosion preventors extreme pressure agents, antiwear agents and structure modifiers. However, there are some additives that are chemically inert; they only affect the physical property of the grease such as structure, rheology or water tolerance. Examples of such additives are viscosity modifiers, pour point depressants and antifoam agents.

Viscosity index improvers

They improve the viscosity index of base oils. The variation of viscosity with temperature is measured in terms of a number called the viscosity index. Usually between 70 and 100. this number can be boosted to 180 or more for grease in applications where extremely high temperature are encountered.

A high viscosity index shows that the grease is more resistant to change of viscosity with temperature. The use of viscosity index improver is favoured to prolonged refining process of oils.

Pour point depressants

These are substances added to the grease structure in order to lower the temperature at which the oil becomes unpumpable at low ambient temperature. Since wax is solid at normal temperature, then oil of a high proportion of wax will have a much higher pour point than a dewaxed one of the same viscosity.

Rather than simply removing all the wax from the oil, additives are used as pour point depressants because it is cheaper and more convenient to add them to continue refining the oil. The additives used as pour point depressants function by reducing the growth of wax crystals so that the particles of the wax remain so. Low pour points are at great importance in oils such as refrigerants and engine oil used in cold climate areas of the world.

Antioxidants

These additives inhibit oxidation of oils and prevent corrosion. Lubricating under oxidising conditions yield unstable materials called peroxides. Once formed, peroxides quickly decompose to form other materials which are even more susceptible to oxidation. The process is a chain reaction which is accelerated by increased temperature and which is catalysed by certain metals – particularly those present in soap based thickening agents. Antioxidants function by preferentially combining with the peroxides or radical species thereby terminating the free radical chain reaction. The natural oxidation resistance of a grease and the effect of the any given oxidation inhibitor depend on the type of thickener, the relative acidity or basicity of the system and the nature of the base oil component. Examples of antioxidant are phenols, aromatic amines, zinc dialkyl di-thiophosphates.

Detergents

Detergency is the ability of an oil to keep working surfaces of equipment clean by removing and holding in suspension particles, metal dusts and air borne dusts. Detergents are thus oil soluble metallic organic compounds of high molecular weights. They have affinity for dissolving carbonaceous deposits in ring grooves, piston surfaces and sludge deposits in internal combustion engines. Most detergents in use are metallic salts of calcium, magnesium or barium such as sulphonates or phosphanates.

Dispersants

Dispersancy is the ability of oil to prevent dirty particles and water forming into sludge by preventing the particles from coagulating and settling out. It takes place where the temperature is not quite so high for instance in an engine crank case where water can be present. Dispersants are very high molecular weight organic compounds that disperse and suspend the cold sludge forming materials in the oil from settling as engine deposits. An example is polyisobutynyl.

Antifoamants

In cases where there is air entrainment, i.e. suspended air bubbles in the body of the lubricant, this leads to malfunctioning of the system and eventual loss of pressure in critical circuits. Antifoam agents such as silicone polymers, polyacrylates and other organic polymeric materials help in inhibiting foaming by causing air bubble to coalesce, float to the surface and collapse thereby releasing the entrained air in the lubricant.

Rust inhibitors

The corrosion of iron and steel bearing components caused by the presence of atmospheric oxygen and water can lead to serious malfunctioning. Protection of metal surface from rusting is especially important in steel rolling mill applications where large volume of cooling water impinges on the bearings and where functioning grease (lubricants) are expected to absorb much of the water without loss in performance. Thickeners and structure modifiers often impart natural rust resisting properties, but supplemental rust inhibitors may be necessary if condition warrants. These are highly polar oil-metal surface to form a thin protective film which excludes air and water. Typical rust inhibitors include fatty amines, fatty amides, carboxylic acids, and sodium sulphonates.

Extreme pressure and antiwear agents

Greases are formulated with extreme pressure agents to prevent seizure under conditions of high temperature, heavy loading or extended periods of operation. These chemicals often contain sulphur, chlorine, phosphorus metals or their combinations. They function under boundary conditions where metal surfaces are in intimate contact. As the surfaces move against one another, collision of surface contacts produces localised temperature increments which activate the extreme pressure agents. Distinct chemical compounds form and immediately plate out on the metal surface as a thin film. Examples of extreme pressure agents are sulphurised olefins, metal di-thio carbonates and chlorinated paraffins, among others.

2.10 Functions of Grease

Generally, very good lubricating grease must be able to perform the following functions effectively:

- Reduction of friction and wear.
- Corrosion protection.
- Complete sealing off of bearings from water and contaminants.
- Maintenance of mobility under application condition.
- Moisture tolerance or repulsion.
- Leakage resistance.
- Consistent structure throughout service life.
- Avoidance of dripping and throw offs.

2.11 Properties of Grease

Lubricating grease must however possess some qualities before being able to perform the above functions very satisfactorily. These properties are highlighted below.

2.11.1 Consistency

The degree to which a plastic material such as grease resists deformation under the application of force is a measure of its hardness or softness. Grease consistency correlates to the firmness of the grease. Depending on the application they are designed for, greases can range from semi fluid consistency to almost solid. Grease is graded by its hardness, however, hardness does not depend on the viscosity.

Hardness is expressed in terms of ASTM penetration or NLGI consistency number. ASTM penetration is a numerical representation of an actual test of an object as it sinks into grease under specific test conditions. It is measured in tenths of a millimetre. NLGI uses consistency numbers 000 to 6 to classify the grease with the use of ASTM penetration text results. These numbers are in order of increasing consistency or hardness of the grease structure. The higher the ASTM penetration, the lower the consistency number. For instance, a grease having the consistency number 000 is soft like ice cream at room temperature (25°C) whereas a grease having the consistency number 6 is hard like butter just removed from a refrigerator (Schulz, 1972).

However, care must be taken in selecting the correct consistency for any application. If the grease is too hard, it may not flow adequately to the areas in need of lubrication and if it is too soft, it may leak away from the desired area. Consistency is determined with the ASTM cone penetration Test D-217. Table 2.2 shows the NLGI consistency number and ASTM penetration with which greases are classified.

Table 2.2: NLGI Consistency Number, ASTM Worked Penetration Range and Nature of Grease

NLGI Consistency Number	ASTM worked penetration range of 25°C (10ths of mm)	Nature of grease
000	445 – 475	Semi fluid, extremely soft
00	400 – 430	Semi fluid very soft
0	355 – 385	Very soft
1	310 – 340	Soft
2	265 – 295	Mild soft
3	220 – 250	Medium
4	175 – 205	Stiff
5	130 – 160	Very stiff
6	85 – 115	Brick grease

Source: Institute of Petroleum Handbook for Standard Methods for Analysis and Testing of Petroleum and Related Products 1993 Edition, Vol. I.

2.11.2 Dropping point temperature

This is the temperature at which grease structure becomes steadily softer and no longer function as a thickened lubricant.

The dropping point test ASTM D – 2265 and ASTM D – 566 are used to determine this temperature i.e. the temperature at which a drop of the grease falls from the article of the test apparatus. This temperature does not have a fixed value but differs with respect to the thickener used in the formulation of the grease. For regular greases, the range is between 80 – 200°C while for complex greases, the range is between 200 – 260 °C and above (See Table 2.3).

2.11.3 Oxidation stability

Since grease may be subjected to severe oxidising conditions during use, it must have good oxidation stability. Oxidation stability has to do with the performance of grease after being exposed to oxygen. Both the ASTM D – 942 (Bomb oxidation test) and high temperature bearing life test ASTM D – 3527 are used to measure the extent of greases' oxidation. It can either be categorised as being poor, good or excellent (See Table 2.3).

2.11.4 Water stability

Exposure to water may affect grease in several ways. First, it can cause grease to change its consistency, becoming softer or firmer. Also, it may change the greases' texture perhaps becoming less additive and it may form emulsion with the grease thus losing its lubricating effectiveness. The water washout test ASTM D – 1264 and water spray off Test ASTM D – 4049 measure the amount of grease washed away from various water washing and spraying conditions (See Table 2.3).

2.11.5 Load carrying capability

This is the ability of grease to maintain foreign body in suspension during operation without causing wearing effects on the contacting surfaces of the engine. The four ball wear test ASTM D – 2266 measures wear at light loads.

Table 2.3: Grease Application Guide

Properties	Aluminium grease	sodium grease	Calcium grease	Lithium grease	Aluminium complex grease	Calcium complex grease	Lithium complex grease	Polymer grease	Organo clay grease
Dropping point (°C)	110	163-177	96-104	≥ 260	≥ 260	≥ 260	≥ 260	≥ 243	≥ 260
Maximum usable temperature (°C)	79	121	93	135	177	177	177	177	177
Water resistant	Good to Excellent	Poor to Fair	Good to Excellent		Good to Excellent	Fair to Excellent	Good to Excellent	Good to Excellent	Fair to Excellent
Oxidation stability	Excellent	Poor to good	Poor to Excellent	Fair to Excellent	Fair to Excellent	Poor to Excellent	Fair to Excellent	Good to Excellent	Good
Appearance	Smooth and clear	Smooth and fibrous	Smooth and buttery	Smooth and buttery	Smooth and buttery	Smooth and buttery	Smooth and buttery	Smooth and buttery	Smooth and buttery
Protection against rust	Good to Excellent	Good to Excellent	Poor to Excellent	Poor to Excellent	Good to Excellent	Fair to Excellent	Fair to Excellent	Fair to Excellent	Poor to Excellent
Work stability	Poor	Fair	Fair to Good	Good to Excellent	Good to Excellent	Fair to Good	Good to Excellent	Poor to Good	Fair to Good

Source: ASTM Yearly Handbook, 1998.

2.12 Categories of Grease

Grease is categorised into two major groups depending on the type and nature of the thickening agent used in the formulation of such grease. Generally, there are soap based and non-soap based grease.

2.12.1 Soap based grease

This is the type of grease produced from soap based thickener. The thickener is a product of saponification reaction, i.e. the reaction between a fatty acid or an ester and an alkali or an alkaline earth metal or hydroxide under controlled conditions of temperature and pressure. The soap so produced (thickener) is then brought to react or heated with the base oil at 195°C for thirty minutes. The mixture is then left to cool to 85°C before the chemical additives are added. However, there are simple soap and complex soap grease depending on the thickener used as described under 2.8.2.

2.12.2 Non-soap based grease

This is the type of grease produced from non-soap based thickening agents. There are organic and inorganic non-soap greases.

Organic non-soap grease

This is the type of grease whose thickening agent is organic non soap based as described under 2.8.2. The process of the grease production follows the process described under 2.11.1.

Inorganic non-soap grease

This is the type of grease whose thickening agent is an inorganic non-soap based as described under 2.8.2.

2.13 Advantages of Lubricating Grease over Lubricating Oil

In lubricating any given substance, a fundamental choice must be made as to whether the lubricant will be a liquid or semi solid. The choice is made by the machine designer who appraises the expected operating conditions and the properties of available lubricants and decides on the lubrication system to be used.

There are several advantages of using grease over lubricating oil ranging from cost to efficiency, effectiveness and suitability.

Low speed combined with high pressure

Greases are usually the preferred lubricant when bearings are operating at speed below 100 rpm at high loads. If a very high viscous oil is used, an adequate lubricating film will be formed. However, such an oil has very poor pumpability and often cannot be employed. Lower viscous oil will not form an adequate lubricant film under these conditions.

However, because of the high apparent viscosity of grease at low speed, it forms a lubricant film of adequate thickness. Such a film despite the high load will lubricate successfully under this adverse condition.

When machine parts are badly worn

As an equipment grows in age, wear causes machine clearance to increase until adequate oil films can no longer be maintained in service. At this juncture, a change to grease is helpful, because, with increased clearance, shear rate of the moving mechanism decreases. At low shear rate, grease films are much thicker than oil films, providing adequate lubrication. This effect permits the machine to continue in service at least until a maintenance shut down can be scheduled.

When noise reduction is important

As machine wears out, gears, bearings and shafts loosen up. This leads to noisy operation. Under such circumstances the thick film provided by the grease cushions the excessive movement and significantly reduces the noise level.

Intermittent operation

The fact that oil drains away when a machine is stopped but grease does not drain away is significant. Also, when an equipment operates intermittently, change speed or reverse direction, on start up, bearings are dry until oil has been drawn in between the surfaces forming a lubricating film. Grease does not drain away when device is stationary on start up, a lubricating film forms immediately. In this manner, grease protects against wear that would be found with oil as the lubricant.

Scaling out of contaminants

Grease makes seals to be effective; it assists in keeping out contaminants. In mining operations, and steel mills, dust, dirt and water must be excluded. In paper mills, corrosive water and pulp are potential contaminants. In chemical plants and many other environments, corrosive gases and liquids must be kept out. If the corrosive contaminants enter the bearing cavity, grease is more protective of the metal surface than oil would be. When a machine is stopped, oil drains away but grease does not thus protecting the bearing surfaces against corrosion.

Suspension of solid additives

Some solids have lubricating properties in varying degrees when mixed with oils or greases. The mixture often performs better than the oil or grease alone does.

When mixed with oils, the solids tend to settle out leaving very little if any in suspension but exact opposite is the case in grease. Grease enjoys the advantages and services of these solids additives more than oils and thus lasts longer as a more effective lubricant.

Reduction in level of dripping and splashing

Since grease assists seals, it tends to stay in its housing therefore neither leaking nor dripping out. This becomes more obvious as seals wear out. This anti drip and anti splash action has obvious effects in cases where contamination must be avoided such as food processing and pharmaceutical industries.

Reduction in frequency of lubrication

Machine designs at time require the placement of bearings in places where they cannot be easily serviced without shutting down the plant. In these circumstances, grease provides lubrication for long period of time. Electric motors in plants are often lubricated annually or even less often. Under these circumstances, grease is preferred to lubricating oil.

Operating under extreme conditions

Under very severe operating conditions, greases are much more effective than oils.

High Temperature – Many industrial operations subject equipment and lubricants to very high operating temperatures. Kiln car and furnace door bearings are good examples. Oil lubrication tends to develop too thin film and poses a significant fire hazard. High temperature greases give satisfactory lubrication.

High Pressure – Under heavy loads, films in oil lubricated bearings are so thin that bearing service life tends to be short. The slightest particulate contamination can cause the film to rupture thus causing wear, whereas grease lubrication does not rupture easily under high pressure.

Shock Loading – This is an instantaneous and severe increase in stress. Such loadings tend to rupture a thin lubricant film leading to rapid wear. Greases appear to cushion against such sharp rupturing of the film. Shock loading is experienced in rolling mills when a thick slab hits rollers that have been preset to a less thickness.

2.14 Lubricating Grease Design

The formulation and development of lubricating grease involves a batch process that incorporates a technology bounded by saponification, dehydration, milling, de-aeration and filtering of the dispersed thickener in a base oil with the incorporation of performance enhancing chemical additives and modifiers.

The ability of lubricating grease to perform in so many differing applications under a wide variety of environmental and operating conditions is a testimony of its compositional flexibility.

The three major components of the structure of grease are 'cooked' together under the prescribed conditions giving rising to the final product which is then taken for analysis and characterisation.

2.15 Statistical Design-the Modelling Approach

In using the statistical approach in designing and analysing an experiment, it is necessary for the designer to have a clear idea of what is to be done, how the data is to be collected and at least a qualitative understanding of how theses data are to be analysed.

A design process involves series of tests in which purposeful changes are made to the input variables of a process or system so that observations can be made and reason for changes in the output response be identified.

The process or system is then represented by model equations. A process is visualised as a combination of methods and other resources that transform some inputs into those that have one or more observable responses.

Design methods have found broad application in many disciplines. It is used for improving the performance of a manufacturing process. Its application early in process development can result in improved process yields, reduced overall cost, development time and variability to target requirements (Montgomery, 1991). However, in achieving these, some analytical tools such as regression analysis, either multiple or single linear regression and analysis of variance are utilised.

In many problems involving design, there is possibility of two or more variables being related, it is therefore important to model and explore this relationship. For instance, consider a chemical process in which the yield of product is related to the operating temperature and other factors. It may be of interest to build a model equation relating yield to temperature and other factors. The model equations are used for prediction, process optimisation or process control. In general, suppose that there is a single dependent variable, in this case, yield which depends on some independent (regressor) variables, in this case, temperature and other factors. The relationship between these variables is characterised by a mathematical model called regression equation.

Analysis of variance (ANOVA) is the statistical technique that examines the variability of the observations within the independent variables as well as between different conditions that these variables are subject to (Norušis, 1992). Generally, analysis of variance in a design experiment helps to identify the extent to which or whether certain factors can affect an observable occurrence. In achieving this, a null hypothesis indicating that no significant changes occur in the values of dependent variables when independent variable are varied must be accepted or rejected. This however depends on the values of the **observed significance level** that are generated from the statistical analysis. The observed significance level is the probability that a difference at least as large as the one observed would have arisen if the variance is equal. It is obtained by comparing the calculated F value to the F distribution i.e. the distribution of the F- statistic when the null hypothesis is true. If the observed significance level is small, within the range $0< x \leq 0.05$, the null hypothesis i.e. all variances that are equal, can be rejected but if it is large the null hypothesis must not be rejected. i.e. there is no sufficient evidence to suspect that the variances are unequal.

CHAPTER THREE

3.0 EXPERIMENTAL PROCEDURE

3.1 Instrument and Equipment

Table 3.1 shows the list of equipment used in the course of this study, while Table 3.2 gives the list and grades of the chemical reagents used.

Table 3.1: List of Equipment.

Equipment	Source	Comment
Cleveland open cup (Semi automatic)	Walter Herzorg GMBH (Germany)	Determination of flash point
Seta lec cloud and Pour point refrigerator	Stanhope – seta (U.S.A)	Determination of pour point
Hydrometer	Pyrex Inc U.S.A	Determination of Density
Penetrometer	Thevenin and sons (U.K)	Determination of cone penetration
Dropping point Apparatus	Lopess and Watz (U.K)	Determination of dropping point temperature.
Soxhlet Apparatus	Lowensky KTBP (Switzerland)	Extraction of shea butter.
Cannon Fenske U-tube Viscometer	Pyrex Inc. (U.S.A)	Determination of kinematics Viscosity
Grease worker	Thevenin and sons (U.K)	Determination of prolonged work penetrations

Table 3.2: Chemicals and Reagents Used in the Experiment

Chemical and reagent	Formula	Comments
Normal Hexane	C_6H_{14}	Commercial reagent grade
Lithium Hydroxide	LiOH	Commercial reagent grade
Stearic Acid	$C_{17}H_{35}COOH$	Commercial reagent grade
Diethyl ether	$C_2H_5COC_2H_5$	Commercial reagent grade
Motor spirit	Alcoholic group	Commercial reagent grade
Petroleum spirit	organic alcohol	Commercial reagent grade
DF 22(Additive package)	See 3.7.	Commercial reagent grade

3.2 Collection and Treatment of Shea Nut Seeds.

Shea nut seeds were purchased from Bosso market in Bosso Local Government Area of Niger state, Nigeria. The nuts were screened to remove dirts and other particles after which the nuts were cracked to remove the shells. The seeds were then sun dried and subsequently oven dried at temperature of 100^0C for an hour. After the drying, the seeds were allowed to cool before weighing. The above procedure was repeated until a constant weight was obtained which ensured that the seeds were moisture free.

3.3 Extraction of Shea Butter

The moisture – free seeds were ground with the aid of pestle and mortar to fine state. The finely pounded shea nut paste was put into the thimble in an extraction chamber of sohxlet apparatus.

Two hundred millilitres (200ml) of normal hexane was charged into the round bottom flask of the soxhlet apparatus and mounted in the heating mantle of the apparatus (plate 1) and was heated at $55^{O}C$ in order to prevent loss of hexane vapour because the boiling point of N-hexane is $69^{0}C$ (Morrison and Boyd, 1973). The evaporating normal hexane was condensed into the thimble by the condenser where it leached the oil out of the paste. The oil rich solvent after reaching a level syphoned back automatically into the round button flask where the process described so far was repeated. After five cycles of syphoning, the thimble was discarded of its raffinate, while the solvent was evaporated leaving behind pure shea butter (oil). The above process was repeated until enough shea butter was obtained.

3.4 Analysis and Characterization of Shea Butter

The parameters with which base oil are identified as contained in Table 2.1 were subsequently determined for the extracted shea butter as follows:

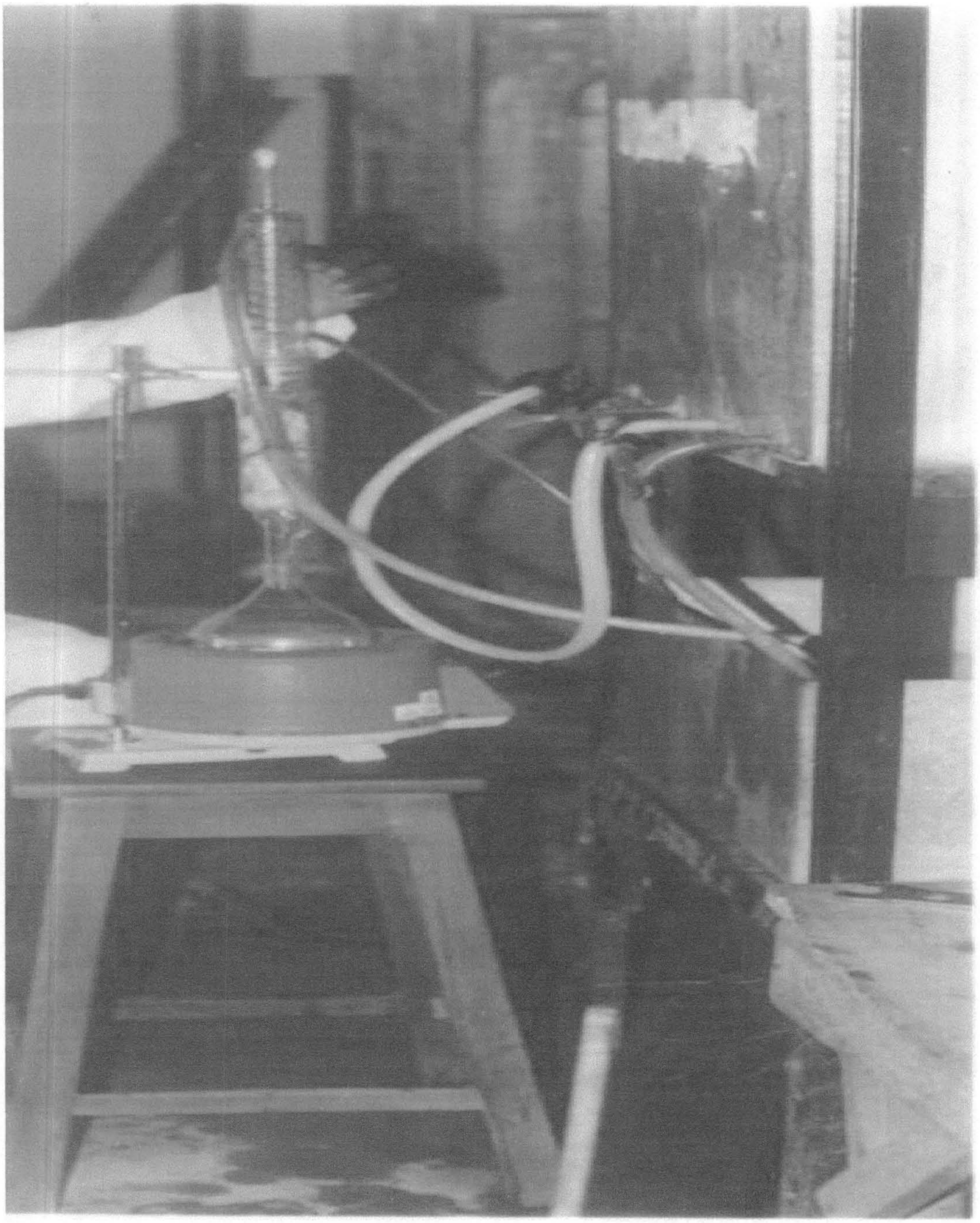


Plate 1 Soxhlet Apparatus

3.4.1. Determination of density

The equipment used for this analysis has been described and presented in Table 3.1. The determination of the density was carried out according to ASTM D-1298.

Sample of the specimen was transferred into a clean hydrometer cylinder without any splashing. The hydrometer cylinder was placed in vertical position in a place free from air current. The hydrometer was then lowered gently into the sample making sure that the stem was not wetted. A thermometer was placed inside the sample which was stirred continuously making sure that the stems were not wetted. The temperature was noted and recorded when a steady reading was observed.

The hydrometer was then depressed for about two scale division into the sample and then released. Thereafter, sufficient time was allowed for the hydrometer to come to rest floating freely and away from the walls of the cylinder. The hydrometer scale reading was estimated to the nearest 0.0001 and the reading was recorded as the density of the sample at $15^{O}C$.

3.4.2. Determination of flash point

The equipment used for this analysis was described and presented in Table 3.1 and the determination of the flash point was carried out according to ASTM D-92.

Twenty -five millilitres (25ml) of shea butter was poured into the test cup and was heated up, a thermometer held by a retort stand was inserted in the test cup with the tip of the thermometer slightly touching the sample in the test cup. At specific intervals, a test flame was passed across the vapour being let out of the shea butter in the test cup and the lowest temperature of the shea butter at which applications of the test flame caused the vapour of the butter to be ignited was noted on the thermometer. This was recorded as the flash point of the sample (see Plate 2).

3.4.3. Determination of pour point

The equipment used for this analysis was described and presented in Table 3.1 and the determination of the pour point was carried out according to ASTM D – 97.

The test jar was filled with shea butter to the marked level and closed tightly with a cork which held the appropriate calibrated thermometer. The jar was placed in the appropriate hole of the Seta lec refrigerator and was covered up. The specimen was observed at intervals of two minutes and the lowest temperature at which the specimen was observed to be able to flow was noted and recorded as the pour point of the sample (see Plate 3).

Plate 2. Cleveland Open Cup (Semi Automatic).

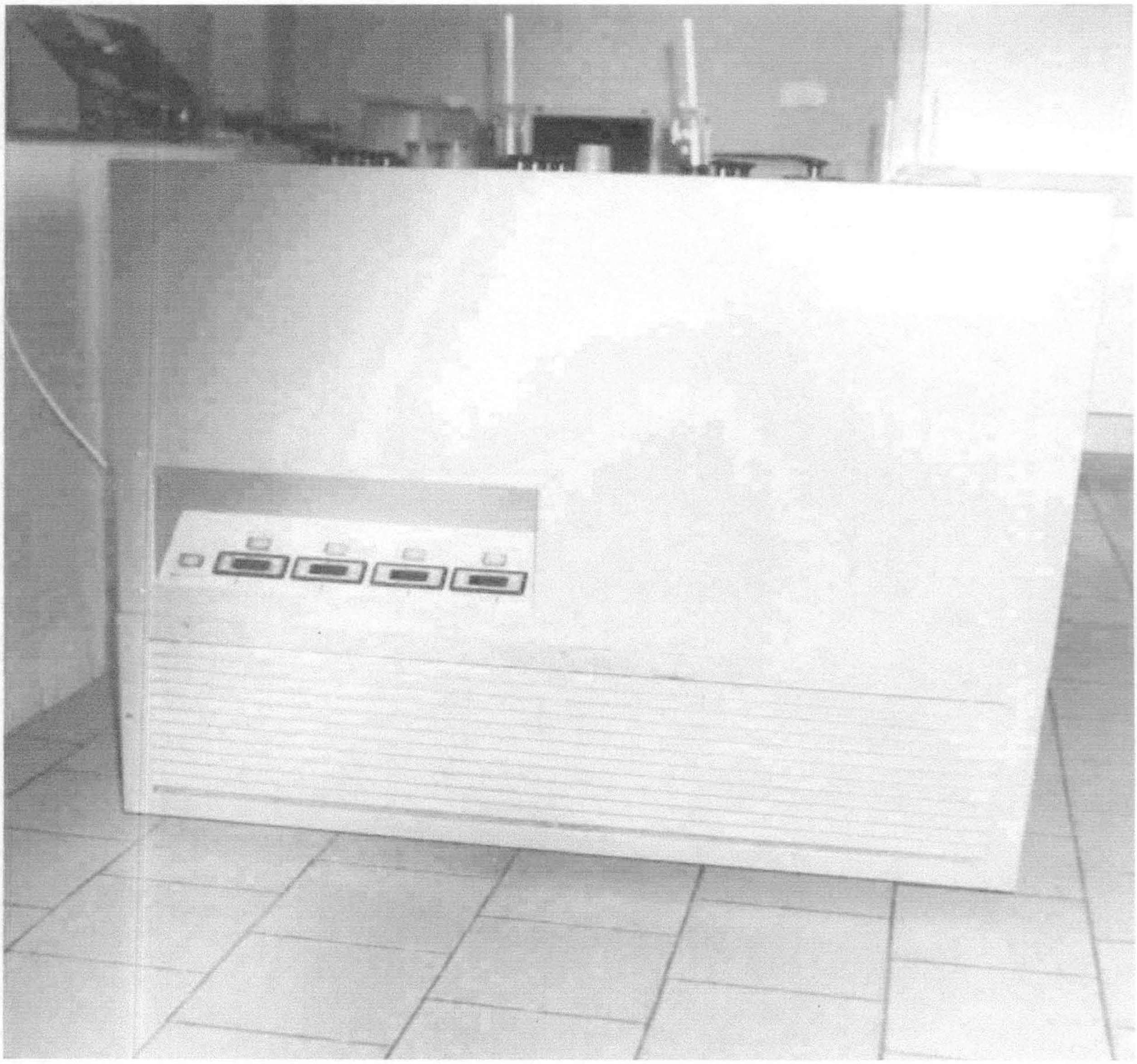


Plate 3. Seta-lec Cloud and Pour Point Refrigerator.

3.4.4. Determination of kinematic viscosity

The equipment used for this analysis was described and presented in Table 3.1. The determination of the kinematic viscosities at $40^{O}C$ and $100^{O}C$ was carried out according to ASTM D-445. The Cannon – Fenske U–tube viscometer to be used was initially washed thoroughly with motor spirit and dried with open air.

With the aid of suction pump, shea butter was drawn into the viscometer to reach the marked point. The viscometer was then fixed in the viscometer holder and the set up was then immersed vertically in the thermostat viscometer bath maintained at $40^{O}C$ for 30 minutes, this was in order for the set-up to attain the temperature of the bath. The shea butter was thereafter sucked into the viscometer in the bath with the aid of the suction pump and was left to fall freely. The period of falling was timed and was used to calculate the viscosity using the formula

$$V= CT \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Eq.3.1}$$

Where V= Viscosity

C= viscometer calibration constant

T= time of falling in seconds.

The above procedure was repeated using a constant temperature bath maintained at $100^{O}C$ for determination of viscosity at $100^{O}C$.

3.4.5. Determination of viscosity Index

The value of viscosity index of the sample was determined by reading it off from a table specially constructed for the purpose (See Appendix C). The kinematic viscosity at $100^{O}C$ was located in the table and traced down to the value of the kinematic viscosity at $40^{O}C$ and the value of the viscosity index at this instance is the value for the sample (ASTM, 1982).

3.4.6. Determination of appearance/ colour

This was determined by visual observation of the sample and comparing with the set standard according to ASTM D–417. The sample was put into a clean cylinder and checked visually for evidence of water or particulate contamination. The sample was then held up to the light and visually examined for haze or lack of clarity.

The sample inside the cylinder was subjected to swirling to produce a vortex and the bottom of the vortex was examined for any particulate matter. The visual clarity was noted and recorded.

3.5. Preparation of Thickening Agents

Saponification process

This is process where fats / fatty acids react with metals / metallic hydroxides to produce soap and water at prevailing conditions of temperature and pressure.

The water produced as a by-product of the reaction is evaporated due to very high reacting temperature of the mixture.

The soap produced under this manner is referred to as thickening agent in the lubrication industry.

In this study, the thickening agent used was Lithuim Stearate (Lithuim soap) which is a simple soap.

Lithium stearate was produced as a result of the reaction between lithium hydroxide and stearate acid as shown below:

Name	formular	moleculer weight
Lithium hydroxide	$LiOH$	24
Stearic Acid	$C_{17}H_{35}COOH$	284

The reaction is shown below:

Stearic Acid + Lithium Hydroxide = Lithium strearate + water

$$C_{17}H_{35}COOH + LiOH \longrightarrow C_{17}H_{35}COOLi + H_2O$$

See Appendix A for the stoichiometry of the reaction.

3.6 Composition of the Additive Package Used

The additive package used was sold under the commercial name DF22 and it had the following as its composition.

Basis 100% of additive

Components	%
Zinc di thio phosphate	-25%
Phenol	- 10%
Pyrolidone	- 6%
Aromatic amines	- 8%
Hexanol	- 6%
Hydrogen sulphite	- 7%
Phosphoric acid	- 12%
Butadiene	- 15%
Organic chlorine compound	- 6%
Methacrylates	- 5%

3.7 Formulation and Production of Grease

Formulation of ten different samples of grease was done in accordance to NLGI specifications. For each sample, proportions of base oil (shea butter), lithium stearate (thickening agent) and DF 22 (additive package) were varied. Table 3.3 shows the different proportions of components of the samples of the grease produced.

Table 3.3 Proportions of Components of Samples of Grease

Sample	Lithium sterate (Thickener) ‘g’	Base oil (Shea butter) ‘g’	Additive package ‘g’	Total ‘g’
I	38	61	1	100
II	37	59	4	100
III	33	66	I	100
IV	36	60	4	100
V	40	57	3	100
VI	50	50	0	100
VII	45	53	2	100
VIII	48	50	2	100
IX	30	68	2	100
X	42	56	2	100

The base oil and lithium sterate mixture was cooked at 200^{O}C with continuous stirring (Plate 4). The mixtures were mixed with respect to the proportions in Table 3.3 (see Appendix B for the saponification process for the preparation of the ten samples of the lithium stearate soap used for the production of the grease). Table 3.4 shows the empirical composition of the basic components of the developed grease samples.

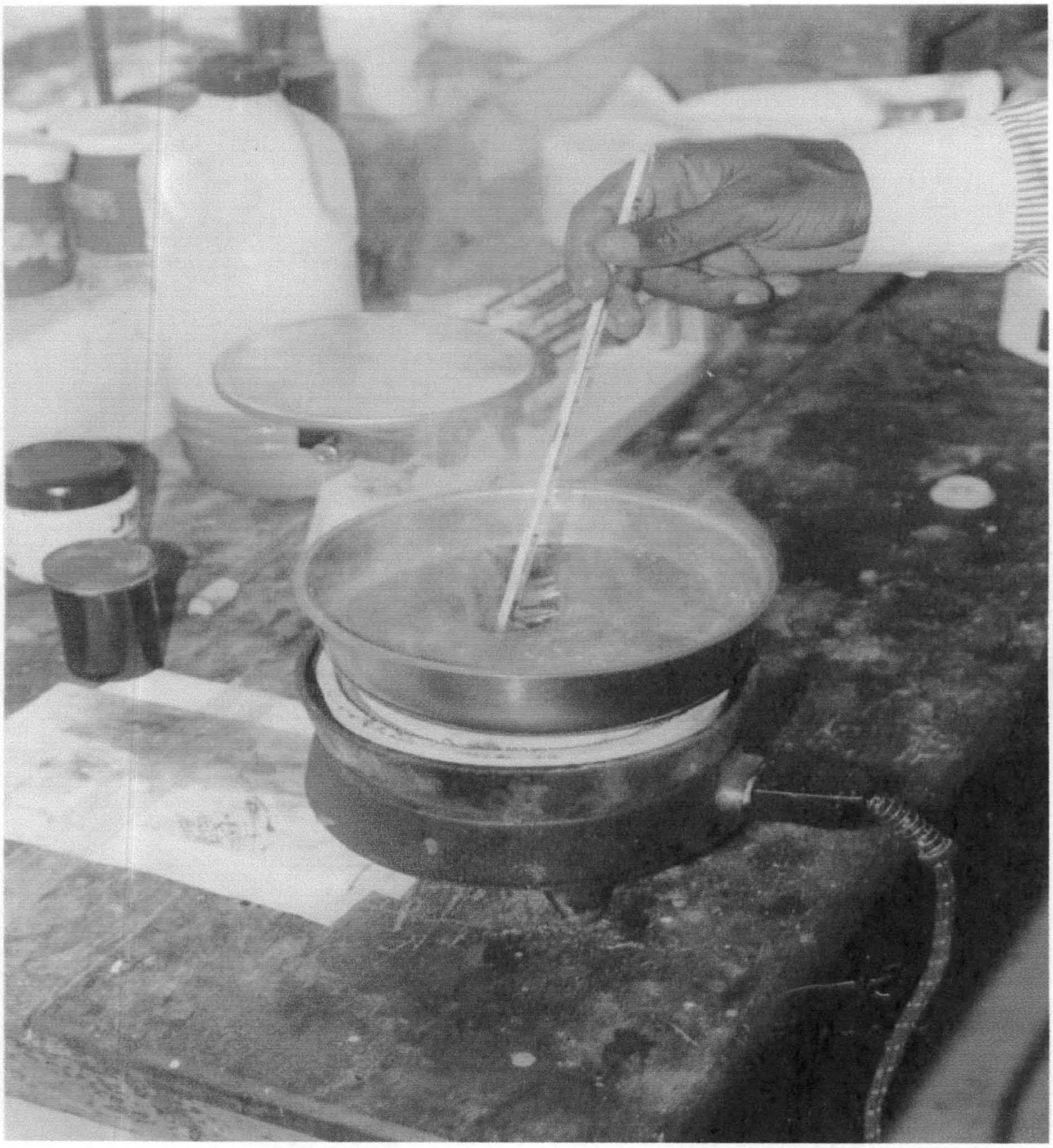


Plate 4. Production/Cooking of Grease

Table 3.4: Empirical Composition of Components of Developed Grease

Sample	Shea butter 'g'	Stearic acid 'g'	Lithium hydroxide 'g'	Water evaporated 'g'	Additive package 'g'	Total 'g'
I	61.00	37.21	3.14	2.35	1.00	100.00
II	59.00	36.23	3.06	2.29	4.00	100.00
III	66.00	32.32	2.73	2.05	1.00	100.00
IV	60.00	34.28	2.90	2.18	4.00	100.00
V	57.00	39.17	3.31	2.48	3.00	100.00
VI	50.00	48.97	4.14	3.11	0.00	100.00
VII	53.00	44.07	3.73	2.80	2.00	100.00
VIII	50.00	47.01	3.97	2.98	2.00	100.00
IX	68.00	29.38	2.48	1.86	2.00	100.00
X	56.00	41.13	3.48	2.61	2.00	100.00

The mixture of the base oil and the lithium stearate after being thoroughly cooked and stirred for 30 minutes at 200°C was allowed to cool to 85°C before the additive package was introduced into the mixture. The mixture was then further milled until it attained room temperature. At room temperature further milling of the mixture was done until a homogenous substance was obtained. The homogeneous substance obtained was the lithium stearate grease which was then taken for further analysis and characterization as highlighted below.

3.8 Analysis and Characterization of Grease

The analysis and characterization of the developed grease sample was based on ASTM specifications. The analysis carried out included the cone penetration consistency test (ASTM D–217), dropping point temperature test (ASTM D – 566) and Copper strip corrosion test (ASTM D – 130).

3.8.1 Determination of dropping point temperature

The equipment used for this analysis has been described and presented in Table 3.1 and the determination of the dropping point temperature was carried at according to ASTM D-566.

A thermometer was positioned such that the tip of its bulb was 3mm above the bottom of the grease cup with the aid of rubber cork. The second thermometer was suspended in the test tube such that its bulb was at approximately the same level as the bulb of the thermometer inside the grease cup. The wall of the grease cup had been earlier lined with a thin film of the sample whose dropping point temperature was to be determined through the use of a rod designed for that purpose. The thermometer and the cup were assembled in the test tube and the test tube was suspended in the oil bath. The oil bath was stirred occasionally and heated at the rate of $5^{O}C$ per minute. This continued gradually, until a drop of material (grease) fell from the orifice of the grease cup. The temperatures of the two thermometers were noted at this instance and the average was calculated as the dropping point temperature of the grease sample. The procedure was then repeated for the remaining samples of the grease (see Plate 5).

3.8.2 Determination of the consistency of the grease

The equipment used for this analysis has been described and presented in Table 3.1 and the determination of the consistency of grease was carried out according to ASTM D-217.

Sufficient amount of grease was put in the grease Jarring cup which was jarred severely in order to eliminate any air entrapped within the grease. The vent cork was released and retightened in order to ensure that appropriate pressure was maintained during the working of the grease. The grease was then subjected to 60 full double strokes of the plunger which was completed in one minute. This is referred to as **Grease Working**. The plunger was then removed and the grease cup was taken to the penetrometer table where the cone shaft of the penetrometer was released into the grease in the cup for 5 seconds during which it penetrated the grease. The penetration was read off from the penetrometer's indicator. This procedure was then repeated for the remaining samples of

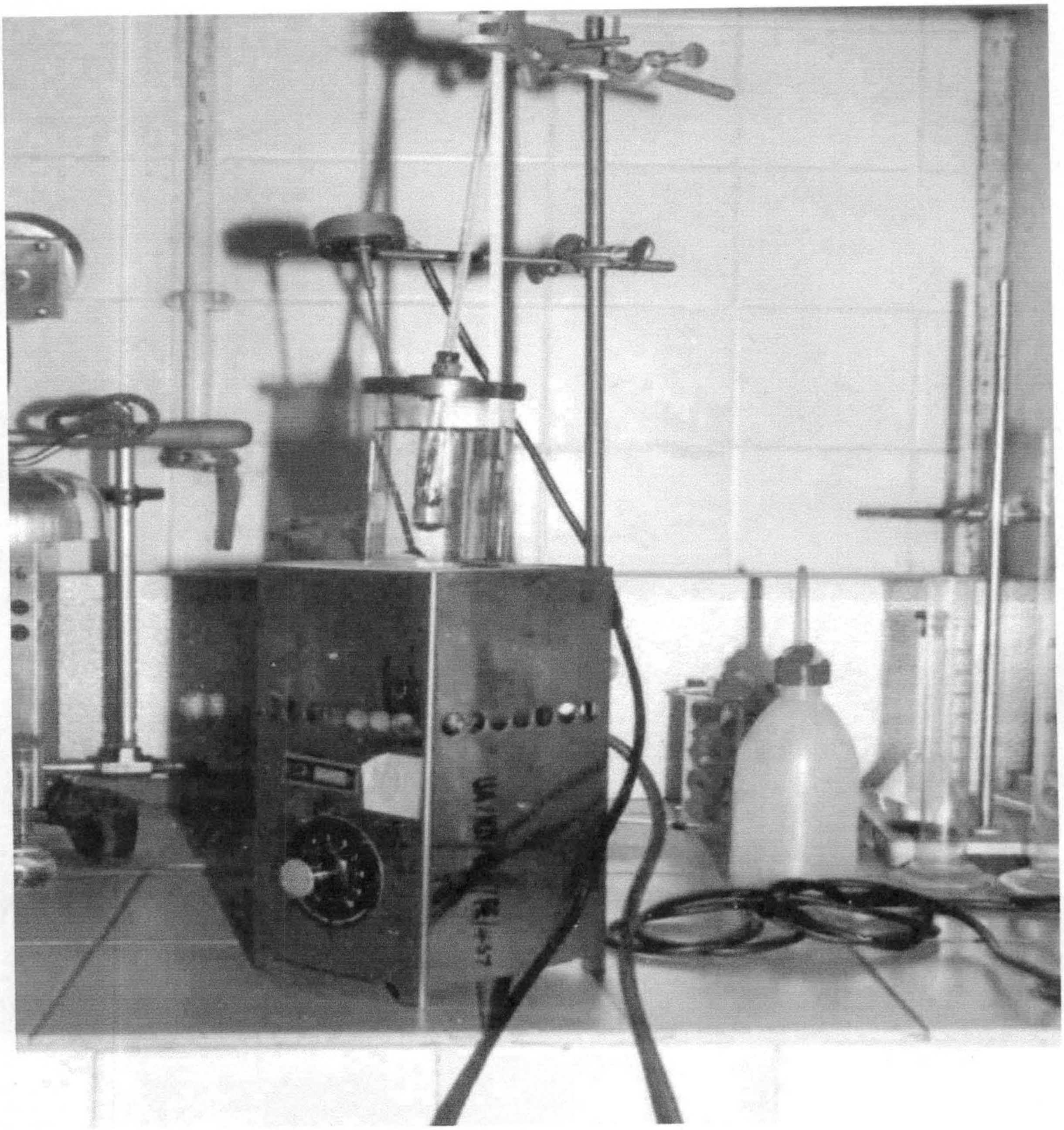


Plate 5. Dropping Point Apparatus.

the grease. The consistency numbers of the grease were then determined from the penetration (see Plate 6).

3.8.3 Prolonged worked penetration

With the use of the grease worker (Plate 7), the samples of the grease were subjected to different conditions of temperature, pressure and time (duration). The above procedure was repeated subjecting each sample of the grease to eight different working conditions of pressure, temperature and time (process variables) and their effects on the penetration of the grease samples were observed and recorded.

Plate 8 shows the plungers and jarring cups used during this process. This procedure was used to test and assess the efficiency of the developed grease samples.

3.8.4 Copper strip corrosion detection test

The procedure as contained in ASTM Test D – 130 was followed. Pieces of mechanically polished copper strips of uniform finish free surfaces were inserted 6 mm deep into the sample of the grease for 6 hours. At the end of 6 hours, the copper strips were removed and were wiped with cotton wool, washed with petroleum spirit and later by diethyl ether.

The surface conditions of the copper strips were then examined for the slightest changes of etchings, pitting and discolouration.

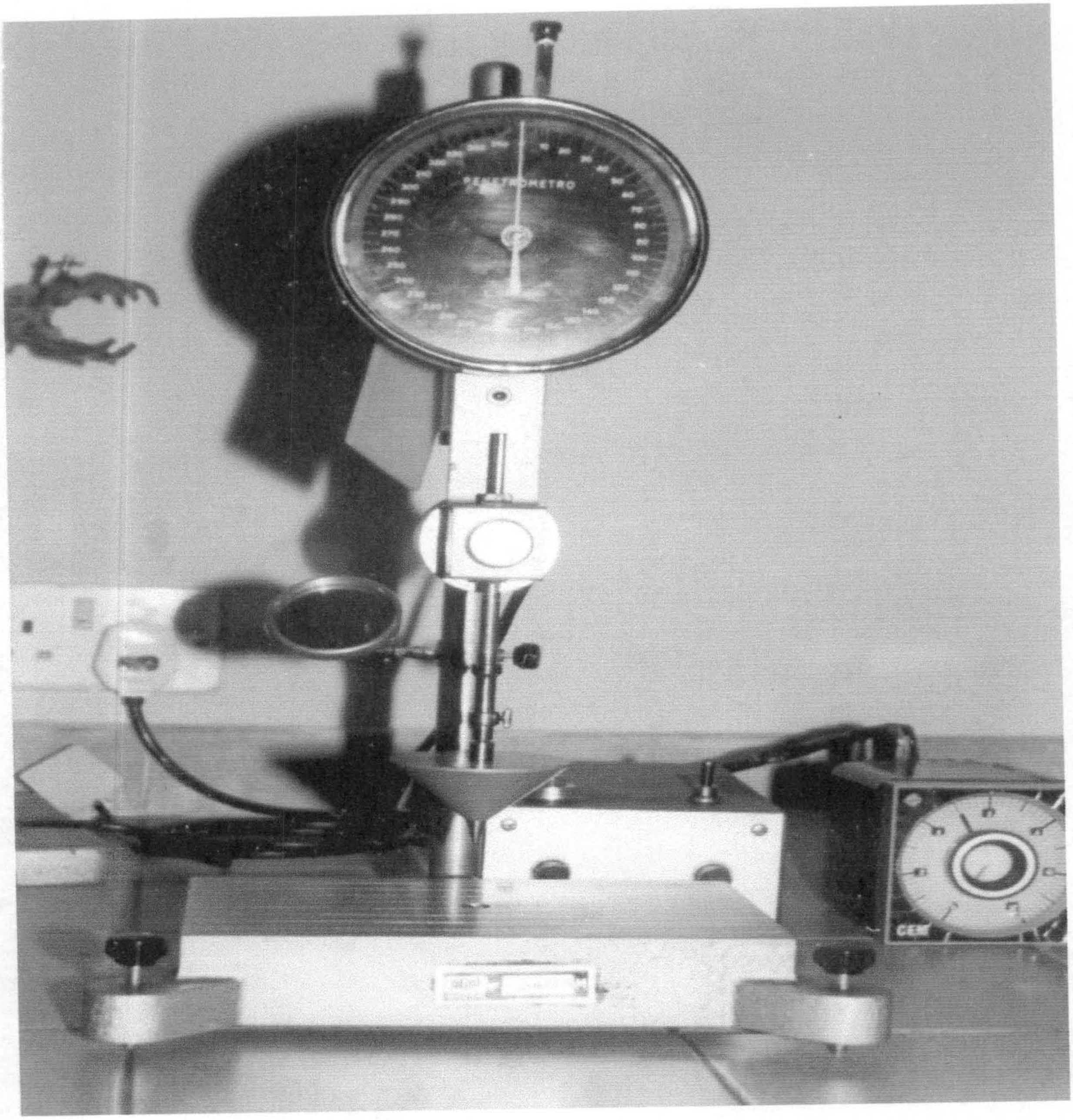


Plate 6. Penetrometer.

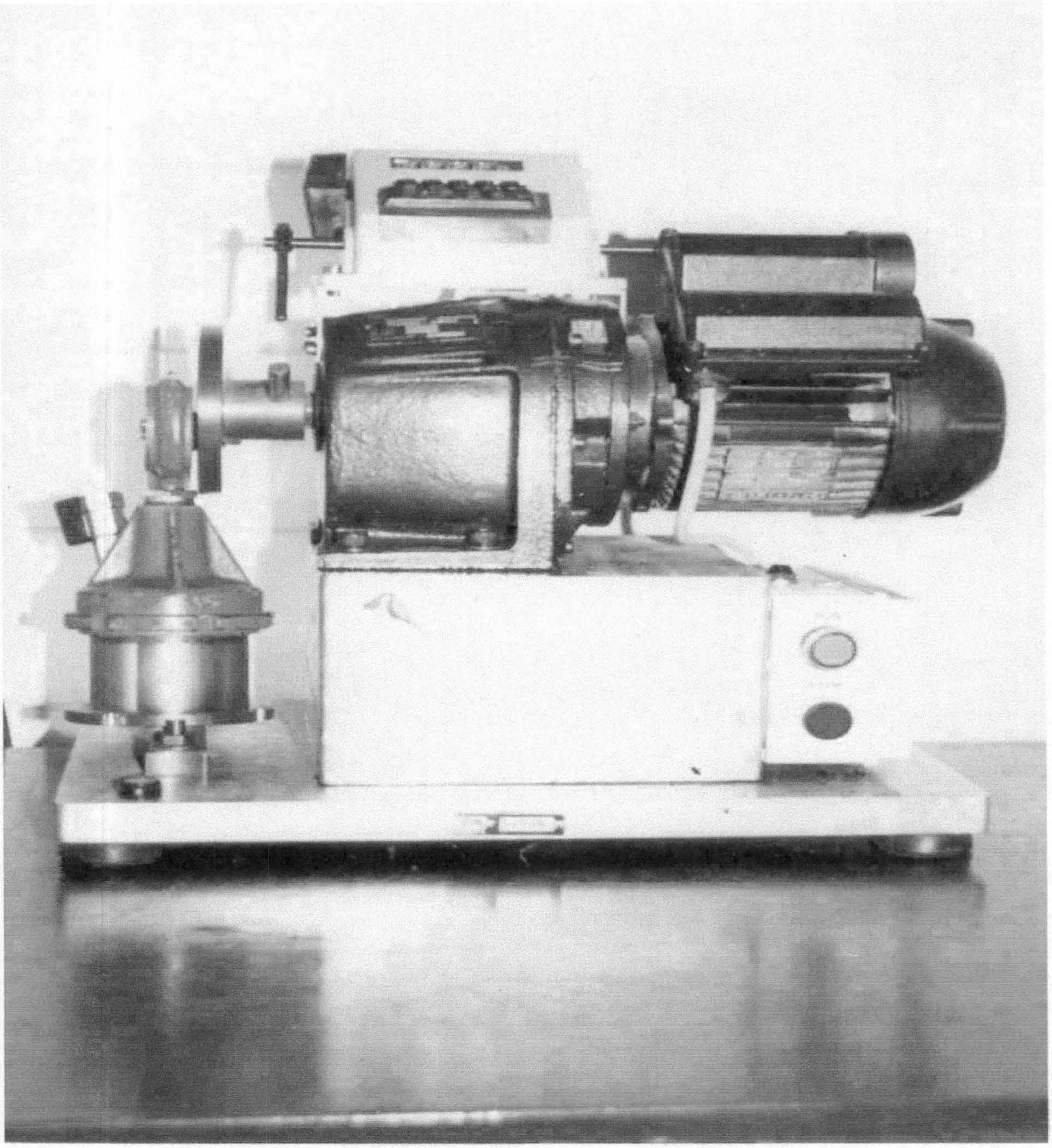


Plate 7. Grease Worker.

Plate 8. Plungers and Jarring Cups.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1. Physicochemical Properties of Shea Butter

Table 4.1 gives the results of the physicochemical analysis of the extracted shea butter. The density, flash point, pour point and viscosity index of the shea butter were 0.0009366kg/m^3; 242^{0}C, -9.5^{0}C and 151 respectively, and the appearance was bright and clear. The calculation of kinematics viscosities at 40^{0}C and 100^{0}C whose values are given in Table 4.1 is contained in Appendix D.

Table 4.1: Physicochemical Properties of Extracted Shea Butter

Properties	Test method	Unit	Result
Density	ASTM D-1298	Kg/m^3	0.0009336
Flash point	ASTM D –92	^{o}C	242
Pour point	ASTM D-97	^{o}C	-9.5
Kinematic viscosity at 40^{o}C	ASTM D-445	CSt	82.44
At 100^{o}C	ASTM D-445	CSt	12.60
VI	-	-	151
Appearance	ASTM D-417		Bright and clear

Table 4.2 gives the comparison between the properties of shea butter and 1000 pale grade of mineral base oil.

Table 4.2 Specification of Base Oil 1000pale Grade and Shea Butter.

Sample Properties	1000pale oil	shea butter
Flash point (0C) (minimum)	210	242
Pour point (C) (maximum)	-9	-9.5
Kinematic viscosity at 100 C (Cst)	11.5 – 12.7	12.60
Viscosity index (minimum)	75	151
Appearance	bright & clear	bright and clear

4.2 Physicochemical Properties of the Produced Grease

Table 4.3 gives the values of some of the physicochemical properties of the samples of the developed grease.

Table 4.3: Properties of Produced Samples of Grease

Sample	Drop pt Temp ^0C	Worked penetration (tenth of mm)	NLGI Consistency Number	Nature of structure
I	188	340	1	Soft grease
II	186	344	0	Very soft grease
III	181	369	0	Very soft grease
IV	183	350	0	Very soft grease
V	190	336	1	Soft grease
VI	197	225	3	Medium grease
VII	194	270	2	Mild soft grease
VIII	196	248	3	Medium grease
IX	178	380	0	Very soft grease
X	192	290	2	Mild soft grease

4.3 Corrosion Resistance of Grease

Table 4.4 gives the results of the corrosion resistance tests.

Table 4.4: Corrosion Resistance Test

Sample	Colour of copper strips before test	Conditions of Copper Strip after test	Comment
I	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
II	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
III	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
IV	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
V	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
VI	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
VII	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
VIII	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
IX	Reddish brown	No pittings, etchings nor discolouration	Non corrosive
X	Reddish brown	No pittings, etchings nor discolouration	Non corrosive

4.4 Prolonged worked penetration

Table 4.5 shows the result of the prolonged worked penetration of the samples of the developed grease after being subjected to the conditions discussed in section 3.8.3

4.5 Analysis of Variance (ANOVA)

The results contained in Table 4.5 were subjected to analysis of variance. This was done in order to know the extent of effect of changes in the values of each independent variable (temperature, pressure and time) on the dependent variable (consistency of the grease). Table 4.6 that shows the values of the observed significance level for the grease samples was extracted from the results of the analysis of variance (Appendix E).

4.6 Multiple Linear Regression Analysis

The results contained in Table 4.5 were in addition subjected to multiple linear regression analysis. This was done to find out the relationship between the consistency of the samples of developed grease (dependent variable) and the regressor variables (independent variables). Table 4.7, that shows the regression model equation coefficients for the grease samples, was extracted from the results of the multiple linear regression analysis (Appendix F).

Table 4.5: Various Combinations Used for the Statistical Design Test

			I $X_1 X_2 X_3$	II $X_1 X_2 X_3$	III $X_1 X_2 X_3$	IV $X_1 X_2 X_3$	V $X_1 X_2 X_3$	VI $X_1 X_2 X_3$	VII $X_1 X_2 X_3$	VIII $X_1 X_2 X_3$	IX $X_1 X_2 X_3$	X $X_1 X_2 X_3$
Process variables			0.38 0.61 0.01	0.37 0.59 0.04	0.33 0..66 0.01	0..35 0..60 0.05	0.40 0.57 0.03	0.50 0.50 0.0	0.45 0.53 0.02	0.48 0.50 0.02 /	0.30 0.68 0.02 /	0.42 0.56 0.02
T Temperature (°C)	P pressure (Bar)	t time (hr)	Proloned Worked Penetration (1/10th of mm)	Proloned Worked Penetration (1/10th of mm)	proloned worked penetration (1/10th of mm)	Proloned Worked Penetration (1/10th of mm)	Proloned Worked Penetration (1/10th of mm)	proloned worked penetration (1/10th of mm)	Proloned Worked Penetration (1/10th of mm)	Proloned Worked Penetration (1/10th of mm)	proloned worked penetration (1/10th of mm)	prolonged worked penetration (1/10th of mm)
130	10	4	340.4	344.1	369.2	350.2	336.3	225.5	270.8	248.2	80.8	90.2
135	10	4	340.6	344.4	370.1	350.5	336.5	225.6	271.2	248.6	381.3	290.5
130	20	4	341.1	344.8	370.6	350.9	336.7	225.8	271.4	248.9	381.6	290.8
135	20	4	341.2	344.9	370.9	357.0	336.8	226.0	271.7	249.1	381.9	291.1
130	10	6	341.6	345.2	371.1	357.4	337.2	226.4	271.9	249.3	382.4	291.3
135	10	6	341.9	345.4	371.3	351.5	337.4	226.7	272.2	249.7	382.8	291.6
130	20	6	342.3	345.9	371.7	357.8	337.7	226.8	272.5	249.9	383.2	291.9
135	20	6	342.6	346.3	371.9	357.9	338.2	226.9	272.7	250.3	383.9	292.1

x_1 = thickener (lithium sterate), x_2 = shea butter, x_3 = additive (DF22)

Table 4.6: Observed Significance Level Values.

	Samples									
Process variables	I	II	III	IV	V	VI	VII	VIII	IX	X
T	0.0704	0.2422	0.2284	0.2048	0.2422	0.2578	0.0	0.0903	0.1638	0.5077
P	0.0236	0.0903	0.1112	0.0635	0.1257	0.1444	0.0	0.0529	0.5057	0.0277
t	0.0125	0.0552	0.0731	0.0318	0.0604	0.0489	0.0	0.0289	0.0474	0.0148
TP	0.5000	0.9999	0.5000	0.5000	0.7048	0.7952	0.0	0.5000	0.8743	0.5000
Tt	0.2048	07048	0.4097	0.5000	0.5000	0.7952	0.0	0.5000	0.5060	0.5000
Pt	0.5000	0.5000	0.3440	0.2952	0.3743	0.7952	0.0	0.999	0.5000	0.5000

T= Temperature P =Pressure t =Time

Table 4.7: Regression Model Equation Coefficients for the Grease Samples

Grease	I	II	III	IV	V	VI	VII	VIII	IX	X
Intercept	331.300000	334.575000	355.725000	343.925000	327.100000	218.650000	260.40000	236.325000	364.225000	280.350000
T	0.045000	0.050000	0.08000	0.030000	0.050000	0.035000	0.060000	0.070000	0.095000	0.055000
P	0.067500	0.070000	0.08500	0.050000	0.050000	0.032500	0.055000	0.060000	0.082500	0.057500
t	0.637500	0.575000	0.65000	0.500000	0.525000	0.487500	0.525000	0.550000	0.837500	0.537500

T=temperature, P= pressure, t= time

4.7 Model Equations of the Samples of Developed Grease

The following model equations, which can be used to predict the consistency of each grease sample, have been developed from the coefficients enumerated in Table 4.7.

Sample I: $C_i = 331.3 + 0.045T + 0.0675P + 0.637t$

Sample II: $C_{ii} = 334.575 + 0.05T + 0.075P + 0.575t$

Sample III: $C_{iii} = 355.725 + 0.08T + 0.085P + 0.65t$

Sample IV: $C_{iv} = 343.925 + 0.03T + 0.05P + 0.5t$

Sample V: $C_v = 327.1 + 0.05T + 0.05P + 0.525t$

Sample VI: $C_{vi} = 218.65 + 0.035T + 0.0325P + 0.4875t$

Sample VII: $C_{vii} = 260.4 + 0.06T + 0.055P + 0.525t$

Sample VIII: $C_{viii} = 236.325 + 0.07T + 0.06P + 0.55t$

Sample IX: $C_{ix} = 364.226 + 0.095T + 0.0825P + 0.8375t$

Sample X: $C_x = 280.35 + 0.055T + 0.0575P + 0.5375t$

C = consistency of the grease

T = temperature

P = pressure

t = time

4.8 Discussion of Results

The physico-chemical properties of the present shea butter are given in Table 4.1. From the Table, the appearance of the shea butter was bright and clear which conformed to the literature standard (Table 2.1)

The value of the flash point was 242^{0}C which fell within the literature range of (165^{0}C – 300^{0}C) for all the grades of base oil being used in the industry. However, this high value of 242 ^{0}C indicated that the shea butter does not contain highly volatile and flammable materials (Harris, 1990).The value of the pour point, which was -9.5^{0}C, indicated the lowest temperature at which the shea butter can be used in any application. The maximum pour point for all grades of base oil is -9^{0}C (Table 2.1).The value of viscosity index which was 151 also showed conformity with all the grades of base oil in the literature, both heavy and light oils (Table 2.1). The minimum value is 75, this high value of viscosity index observed for the shea butter grease suggested that the shea butter-based lubricant will be mechanically and thermally stable as increase in temperature during service will have a very little significance. The kinematic viscosity of shea butter at 100^{0}C, which was 12.6 cSt, fell within the range standard (11.5cSt – 12.7cSt) for kinematic viscosity (1000pale oil), which is one of the grades of base oil derived from crude refining (NIS, 1985). The values of the dropping point temperature of the samples of the grease were 188, 186,181, 183, 190,197, 194, 196, 178 and

192^{0}C for samples I – X, respectively. The values are within the range standard (177-204^{0}C) for dropping point temperature for lithium grease (Bennett, 2004).

The values of the worked penetration of the samples of grease were given in Table 4.3. Samples II, III, IV and IX with 344 tenth of mm, 369 tenth of mm, 350 tenth of mm and 380 tenth of mm penetration, respectively, conform with the literature values for the **very soft grease** whose NLGI consistency number is 0 (Table 2.2).

Samples VII and X with 270 and 290 (tenth of mm) penetration, respectively, conform with the literature values for the **mild soft grease** whose NLGI consistency number is 2 (see Table 2.2). Samples I and V with 340 and 366 (tenth of mm) penetration, respectively, conform with the literature values for the **soft grease** whose NLGI consistency number is whose NLGI consistency number is 1 (Table 2.2). Samples VI and VIII with 225 and 248 (tenth of mm) penetration, respectively, conform with the literature values for the **medium grease** whose NLGI consistency number is 3 (Table 2.2).

The deduction from the above is that the amount of thickener in the formulation of grease determines the nature of the structure of the grease.

From the results in Table 4.3, sample IX formulated with the lowest amount of thickener (30g) had the highest penetration of 380 tenths of mm, which made the grease to be the softest, whereas, sample VI formulated with the highest amount of thickener (50g) had the least penetration of 225 tenths of mm with the sample being the hardest of all.

The result of the copper strip corrosion resistance tests of the grease samples showed that the grease samples were not corrosive and that the grease samples might protect against rust, which is a satisfactory attribute. The copper strips that were removed from the samples of grease showed no slightest changes of etchings, neither any pittings nor any discolouration which confirmed that the samples of the grease were non-corrosive.

Table 4.5 gives the various combinations formed using 2^3 factorial design and the results of the prolonged worked penetration when each of the grease sample was subjected to different conditions of pressure, temperature and time.

Table 4.6 shows the values of observed significant levels within and between the independent variables when the data in Table 4.5 were subjected to statistical analysis of variance. For any value less than 0.05, the null hypothesis must be rejected (Norušis, 1992). This means that there is a significant change in the value of the consistency of the grease when temperature, pressure and time were varied. From the table, the result for sample VII shows that temperature, pressure and time had significant effects on the prolonged worked penetration of the component. Also, the interactions between temperature and pressure, temperature and time as well as pressure and time had significant effect on the sample. The result of samples I and X shows that pressure and time had very significant effect on the prolonged worked penetration of the grease samples while temperature had less significant effect.

The results of samples IV, VI VII and XI show that only time had very significant effect on the prolonged worked penetration of the grease while pressure and temperature had less significant effect. This was so because the null hypothesis that says no significant effect on the consistency of the grease samples despite changes in the values of the independent variables had been rejected (Norušis, 1992).

From Appendix F, it can be seen that for all the grease samples the coefficient of regression square (R^2) were 0.999708, 0.994730, 0.991728, 0.998062, 0.993151, 0.994860, 1, 0.998529, 0.995833, 0.999600, respectively, for samples I – X. R-square (R^2) is the proportion of the variability in the data with the range $0 \leq R \leq 1$ which implies that larger values of R – square (R^2) are more desirable. These values of R- square demonstrate excellent correlations indicating that there were linear relationships between the independent variables and the dependent variable. The coefficient of variations for all the grease samples were 0.010354, 0.040977, 0.05702, 0.020137 and 0.041952, 0.046888, 0.028369, 0.046248 and 0.012142, respectively, for samples I – X. The coefficient of variation (CV) measures the residual variability in the data as a percentage of the mean of the dependent variable. In this case, the higher the value of this number, the less the tendency of being significant on the prolonged worked penetration (consistency) of the samples. For instance, the coefficient of variation of sample VII was 0 the lowest coefficient and sample III was 0.057202, the highest coefficient. The implication of this was that all the process variables and the interactions between the process variables had the most significant effect on sample VII while the process variables and the interaction between the process variables had the least significant effect on sample III.

From Table 4.7 which gives the regression analysis model equation coefficients, the values of the intercepts of the grease samples were 331.3000, 334.5750, 355.250, 343.9250, 327.1000, 218.6500, 260.4000, 236.3250, 364.2250 and 280.3500 tenths of mm respectively. These values predicted the values of the unworked penetration of each grease sample. The implication of this was that provided the samples were not subjected to working at the prescribed process conditions of temperature, pressure and time, the value of the intercept is the predictive value of the consistency of the sample. These values show a similar pattern to the values contained in Table 4.3 for the worked penetration of the grease samples.

The co-efficient of parameter estimates of the process variables of the grease were positive values which show increment and implying that the higher these values, the higher the values of the prolonged worked penetration of the sample of grease when the process variable were applied. From the table, time had higher co-efficient compared to those of pressure and temperature and this implied time had higher effect on the worked penetration of the grease than pressure or temperature.

CHAPTER FIVE

5.0. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

It can be concluded that the shea butter can be used as a substitute for base oil grade 1000pale oil because the results of the present study met the requirements of the base oil grade shown in the result section.

Furthermore, it can be concluded that the grease samples formulated from the shea butter in the present study met the ASTM and NLGI specifications of lubricating grease.

This present study has shown that the consistency of produced sample of grease can be affected by temperature, pressure and time with time having the most significant effect on the consistency of the grease samples and that temperature can only have significant effect on the consistency of the grease samples if the dropping point temperature is exceeded.

5.2 Recommendations

It is recommended that higher process variables values be applied in testing the grease so as to get a maximum condition at which the formulated grease will give the best performance.

It is also recommended that the grease be subjected to further testing in the automobile and manufacturing industry in order to ascertain its performance under wider application, in addition, the use of bleached shea butter is further suggested as a substitute for mineral base oil in order to find out its suitability.

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APPENDICES

APPENDIX A

Name	formular	moleculer weight
Lithium hydroxide	$LiOH$	24
Stearic Acid	$C_{17}H_{35}COOH$	284

The reaction is shown below:

Stearic Acid + Lithium Hydroxide = Lithuim strearate + water

$$C_{17}H_{35}COOH + LiOH \longrightarrow C_{17}H_{35}COOLi + H_2O$$

284g + 24g 290g + 18g

Stoichiometry

From the above, for stearic acid:

290g of soap can be produced by 284g of stearic Acid, thus 1g of soap will be produced by 284/290 of stearic acid.

i.e. 1g of soap will be produced by 0.9793 amount of stearic acid.

For lithium hydroxide:

290g of soap required 24g of Lithium Hydroxide. 1g of soap will required 24/290 amount of lithium Hydroxide. i.e. 1g of soap will require 0.0828 amount of Lithium Hydroxide.

Stearate Acid + Lithium Hydroxide = Lithuim strearate + water

Since 10g of lithium stearate requires 9.793g of stearate acid and 0.828g of lithium hydroxide, the mass of water given OH will be the excess of addition of amount of reactants on the product.

i.e. 9.793g of stearic acid + 0.828g of LiOH gives 10.62g of mixture of Lithuim stearate and water.

Therefore, the amount of water in the mixture is (10.62 - 10)g = 0.62g.

This amount was evaporated during the reaction.

APPENDIX B

Calculation of Compositions of Thickening Agents

The steps below were taken in calculating the amount of stearic acid and lithium dihydroxide required for the formation of the thickening agent needed for each sample of the produced grease.

Sample I

Basis: 100g of grease

Amount of thickening agent: 38g (Table 4.1)

Since 1g of soap requires 0.9793 of stearic acid (Appendix 1)

Then, 38g of soap will require (38 x 0.9793)g of stearic acid = 37.21g

Also, since 1g of soap requires 0.0828 of lithium hydroxide (Appendix 1)

Then 38g of soap will require (38 x 0.0828)g of lithium hydroxide = 3.44g

The excess of the addition of the stearic acid and lithium hydroxide on the amount of soap is the amount of water that will be evaporated off, i.e. (40.35 – 38)g = 2.35g

Sample II

Basis: 100g of grease

Amount of thickening agent = 37g

Stearic acid required = (37 x 0.97hb93)g = 36.23g

Lithium hydroxide required = (37 x 0.0828)g = 3.069g

Total 39.29g

Amount of water evaporated = (39.29 – 37)g = 2.29g

Sample III

Basis: 100g of grease

Amount of thickening agent = 33g

Stearic acid required = (33 x 0.9793)g = 32.32g

Lithium hydroxide required = (33 x 0.0828)g = 2..73 g
Total 35.05g

Amount of water evaporated = (35.05 – 33)g = 2.05g

Sample IV

Basis: 100g of grease

Amount of thickening agent = 35g

Stearic acid required = (35 x 0.9793)g = 34.28g

Lithium hydroxide required = (35 x 0.0828)g = 2.90 g
Total 37.18g

Amount of water evaporated = (37.18 – 35)g = 2.18g

Sample V

Basis: 100g of grease

Amount of thickening agent = 40g

Stearic acid required = (40 x 0.9793)g = 39.17g

Lithium hydroxide required = (40 x 0.0828)g = 3.31 g
Total 42.48g

Amount of water evaporated = (42.48 – 40)g = 2.48g

Sample VI

Basis: 100g of grease

Amount of thickening agent = 50g

Stearic acid required = (50 x 0.9793)g = 48.97g

Lithium hydroxide required = (50 x 0.0828)g = $\underline{4.14\text{ g}}$
Total $\underline{53.11\text{g}}$

Amount of water evaporated = (53.11 – 50)g = 3.11g

Sample VII

Basis: 100g of grease

Amount of thickening agent = 45g

Stearic acid required = (45 x 0.9793)g = 44.07g

Lithium hydroxide required = (45 x 0.0828)g = $\underline{3.73\text{ g}}$
Total $\underline{47.80\text{g}}$

Amount of water evaporated = (47.80 – 45)g = 2.80g

Sample VIII

Basis: 100g of grease

Amount of thickening agent = 48g

Stearic acid required = (48 x 0.9793)g = 47.01g

Lithium hydroxide required = (48 x 0.0828)g = $\underline{3.97\text{ g}}$
Total $\underline{50.98\text{g}}$

Amount of water evaporated = (50.98 – 48)g = 2.98g

Sample IX

Basis: 100g of grease

Amount of thickening agent = 30g

Stearic acid required = (30 x 0.9793)g = 29.38g

Lithium hydroxide required = (30 x 0.0828)g = 2.48 g

Total 31.86g

Amount of water evaporated = (31.86 – 30)g = 2.98g

Sample X

Basis: 100g of grease

Amount of thickening agent = 42g

Stearic acid required = (42 x 0.9793)g = 41.31g

Lithium hydroxide required = (42 x 0.0828)g = 3.48 g

Total 44.61g

Amount of water evaporated = (44.61 – 42)g = 2.61g

APPENDIX C

0 to 50 V. I.

V. I.	KINEMATIC VISCOSITY AT 100C. cSt									
	12.60	12.62	12.64	12.66	12.68	12.70	12.72	12.74	12.76	12.78
	KINEMATIC VISCOSITY AT 40C. cSt									
0	219.6	220.2	220.8	221.4	222.0	222.6	223.2	223.8	224.5	225.1
1	218.6	219.2	219.8	220.4	221.0	221.5	222.2	222.8	223.4	224.0
2	217.5	218.1	218.7	219.3	219.9	220.5	221.1	221.7	222.3	222.9
3	216.5	217.1	217.7	218.3	218.9	219.4	220.1	220.7	221.3	221.9
4	215.5	216.0	216.6	217.2	217.8	218.4	219.0	219.6	220.2	220.8
5	214.4	215.0	215.6	216.2	216.8	217.3	217.9	218.5	219.1	219.7
6	213.4	214.0	214.5	215.1	215.7	216.3	216.9	217.5	218.1	218.7
7	212.3	212.9	213.5	214.1	214.7	215.2	215.8	216.4	217.0	217.6
8	211.3	211.9	212.5	213.0	213.6	214.2	214.8	215.4	216.0	216.5
9	210.3	210.8	211.4	212.0	212.6	213.1	213.7	214.3	214.9	215.5
10	209.2	209.8	210.4	210.9	211.5	212.1	212.7	213.2	213.8	214.4
11	208.2	208.8	209.3	209.9	210.5	211.0	211.6	212.2	212.8	213.3
12	207.2	207.7	208.3	208.9	209.4	210.0	210.6	211.1	211.7	212.3
13	206.1	206.7	207.2	207.8	208.4	208.9	209.5	210.1	210.6	211.2
14	205.1	205.7	206.2	206.8	207.3	207.9	208.4	209.0	209.6	210.2
15	204.1	204.6	205.2	205.7	206.3	206.8	207.4	208.0	208.5	209.1
16	203.0	203.6	204.1	204.7	205.2	205.8	206.3	206.9	207.5	208.0
17	202.0	202.5	203.1	203.6	204.2	204.7	205.3	205.8	206.4	207.0
18	201.0	201.5	202.0	202.6	203.1	203.7	204.2	204.8	205.3	205.9
19	199.9	200.5	201.0	201.5	202.1	202.6	203.2	203.7	204.3	204.8
20	198.9	199.4	200.0	200.5	201.0	201.6	202.1	202.7	203.2	203.8
21	197.8	198.4	198.9	199.4	200.0	200.5	201.1	201.6	202.1	202.7
22	196.8	197.3	197.9	198.4	198.9	199.5	200.0	200.5	201.1	201.6
23	195.8	196.3	196.8	197.4	197.9	198.4	198.9	199.5	200.0	200.5
24	194.7	195.3	195.8	196.3	196.8	197.4	197.9	198.4	199.0	199.5
25	193.7	194.2	194.7	195.3	195.8	196.3	196.8	197.4	197.9	198.4
26	192.7	193.2	193.7	194.2	194.7	195.2	195.8	196.3	196.8	197.4
27	191.6	192.1	192.7	193.2	193.7	194.2	194.7	195.2	195.8	196.3
28	190.6	191.1	191.6	192.1	192.6	193.1	193.7	194.2	194.7	195.3
29	189.6	190.1	190.6	191.1	191.6	192.1	192.6	193.1	193.6	194.2

150 to 200 V. I.

V. I.	KINEMATIC VISCOSITY AT 100C. cSt									
	12.50	12.62	12.64	12.66	12.68	12.70	12.72	12.74	12.76	12.78
	KINEMATIC VISCOSITY AT 40C. cSt									
150	82.87	83.05	83.23	83.42	83.60	83.78	83.95	84.12	84.29	84.45
151	82.39	82.57	82.75	82.94	83.12	83.30	83.46	83.63	83.80	83.96
152	81.92	82.10	82.28	82.46	82.64	82.82	82.98	83.15	83.31	83.48
153	81.45	81.63	81.81	81.99	82.17	82.34	82.51	82.67	82.84	83.00
154	80.99	81.17	81.34	81.52	81.70	81.88	82.04	82.20	82.36	82.53
155	80.53	80.71	80.88	81.06	81.24	81.41	81.57	81.74	81.90	82.06
156	80.08	80.26	80.43	80.60	80.78	80.95	81.11	81.27	81.44	81.60
157	79.63	79.81	79.98	80.15	80.33	80.50	80.66	80.82	80.98	81.14
158	79.19	79.36	79.53	79.71	79.88	80.05	80.21	80.37	80.53	80.68
159	78.75	78.92	79.09	79.26	79.44	79.61	79.76	79.92	80.08	80.23
160	78.32	78.49	78.66	78.83	79.00	79.17	79.32	79.48	79.63	79.79
161	77.89	78.06	78.23	78.40	78.56	78.73	78.89	79.04	79.20	79.35
162	77.47	77.63	77.80	77.97	78.13	78.30	78.46	78.61	78.76	78.92
163	77.05	77.21	77.38	77.54	77.71	77.88	78.03	78.18	78.33	78.49
164	76.63	76.79	76.96	77.12	77.29	77.45	77.61	77.76	77.91	78.06
165	76.22	76.38	76.55	76.71	76.87	77.04	77.19	77.34	77.49	77.64
166	75.81	75.97	76.14	76.30	76.46	76.62	76.77	76.92	77.07	77.22
167	75.41	75.57	75.73	75.89	76.05	76.21	76.36	76.51	76.66	76.81
168	75.01	75.17	75.33	75.49	75.65	75.81	75.96	76.10	76.25	76.40
169	74.61	74.77	74.93	75.09	75.25	75.41	75.56	75.70	75.85	75.99
170	74.22	74.38	74.54	74.70	74.86	75.01	75.16	75.30	75.45	75.59
171	73.83	73.99	74.15	74.31	74.46	74.62	74.76	74.91	75.05	75.20
172	73.45	73.61	73.76	73.92	74.08	74.23	74.38	74.52	74.66	74.80
173	73.07	73.23	73.38	73.54	73.69	73.85	73.99	74.13	74.27	74.42
174	72.70	72.85	73.00	73.16	73.31	73.47	73.61	73.75	73.89	74.03
175	72.32	72.48	72.63	72.78	72.94	73.09	73.23	73.37	73.51	73.65
176	71.95	72.11	72.26	72.41	72.56	72.72	72.85	72.99	73.13	73.27
177	71.59	71.74	71.89	72.04	72.19	72.35	72.48	72.62	72.76	72.90
178	71.23	71.38	71.53	71.68	71.83	71.98	72.12	72.25	72.39	72.53
179	70.87	71.02	71.17	71.32	71.47	71.62	71.75	71.89	72.03	72.16

APPENDIX D

Calculation of Kinematic Viscosities

The kinematics viscosities at 40^0C and 100^0C as shown in Table 4.1 were calculated as shown below:

At 100^0C

The viscosity number, viscosity calibration constant are time of falling are 200/27773, 0.089904 and 140.16.

But viscosity = calibration constant x time of falling

$$V = C \times T$$

$$= 0.089904 \times 140.16$$

$$= 12.60$$

At 40^0C

The viscosity number, viscosity calibration constant and time of falling are 40/038, 1.2622118 and 65.32.

But viscosity = calibration constant x time of falling

i.e. $$V = C \times T$$

$$= 1.262118 \times 65.32$$

$$= 82.44$$

APPENDIX E

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                               SAS                                   19

                 Analysis of Variance Procedure
                    Class Level Information

                    Class    Levels    Values

                    P1            2    1 2

                    P2            2    1 2

                    P3            2    1 2

              Number of observations in data set = 8
                               SAS                                   20

                 Analysis of Variance Procedure

Dependent Variable: SAMP1
                                  Sum of            Mean
Source                  DF       Squares          Square   F Value        Pr > F

Model                    6    4.27750000      0.71291667    570.33        0.0320

Error                    1    0.00125000      0.00125000

Corrected Total          7    4.27875000

              R-Square          C.V.        Root MSE              SAMP1 Mean

              0.999708      0.010354        0.035355              341.462500


Source                  DF       Anova SS    Mean Square   F Value        Pr > F

P1                       1    0.10125000      0.10125000     81.00        0.0704
P2                       1    0.91125000      0.91125000    729.00        0.0236
P3                       1    3.25125000      3.25125000   2601.00        0.0125
P1*P2                    1    0.00125000      0.00125000      1.00        0.5000
P1*P3                    1    0.01125000      0.01125000      9.00        0.2048
P2*P3                    1    0.00125000      0.00125000      1.00        0.5000
                               SAS                                   21

                 Analysis of Variance Procedure

Dependent Variable: SAMP2
                                  Sum of            Mean
Source                  DF       Squares          Square   F Value        Pr > F

Model                    6    3.77500000      0.62916667     31.46        0.1356

Error                    1    0.02000000      0.02000000

Corrected Total          7    3.79500000
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                R-Square            C.V.         Root MSE              SAMP2 Mean

                0.994730        0.040977         0.141421              345.125000


ource                 DF        Anova SS      Mean Square    F Value        Pr > F

1                      1      0.12500000       0.12500000       6.25        0.2422
2                      1      0.98000000       0.98000000      49.00        0.0903
3                      1      2.64500000       2.64500000     132.25        0.0552
1*P2                   1      0.00000000       0.00000000       0.00        0.9999
1*P3                   1      0.00500000       0.00500000       0.25        0.7048
2*P3                   1      0.02000000       0.02000000       1.00        0.5000

                                     SAS                                        22

                         Analysis of Variance Procedure

ependent Variable: SAMP3
                                  Sum of             Mean
ource                 DF         Squares           Square    F Value        Pr > F

Model                  6      5.39500000       0.89916667      19.98        0.1696

Error                  1      0.04500000       0.04500000

Corrected Total        7      5.44000000

                R-Square            C.V.         Root MSE              SAMP3 Mean

                0.991728        0.057202         0.212132              370.850000


Source                DF        Anova SS      Mean Square    F Value        Pr > F

P1                     1      0.32000000       0.32000000       7.11        0.2284
P2                     1      1.44500000       1.44500000      32.11        0.1112
P3                     1      3.38000000       3.38000000      75.11        0.0731
P1*P2                  1      0.04500000       0.04500000       1.00        0.5000
P1*P3                  1      0.08000000       0.08000000       1.78        0.4097
P2*P3                  1      0.12500000       0.12500000       2.78        0.3440

                                     SAS                                        23

                         Analysis of Variance Procedure

Dependent Variable: SAMP4
                                  Sum of             Mean
Source                DF         Squares           Square    F Value        Pr > F

Model                  6      2.57500000       0.42916667      85.83        0.0824

Error                  1      0.00500000       0.00500000

Corrected Total        7      2.58000000

                R-Square            C.V.         Root MSE              SAMP4 Mean
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                0.998062         0.020137         0.070711              351.150000

Source                DF         Anova SS      Mean Square   F Value        Pr > F

P1                     1       0.04500000       0.04500000      9.00        0.2048
P2                     1       0.50000000       0.50000000    100.00        0.0635
P3                     1       2.00000000       2.00000000    400.00        0.0318
P1*P2                  1       0.00500000       0.00500000      1.00        0.5000
P1*P3                  1       0.00500000       0.00500000      1.00        0.5000
P2*P3                  1       0.02000000       0.02000000      4.00        0.2952

                                  SAS                                           24

                      Analysis of Variance Procedure

Dependent Variable: SAMP5
                                   Sum of             Mean
Source                DF          Squares           Square   F Value        Pr > F

Model                  6       2.90000000       0.48333333     24.17        0.1545

Error                  1       0.02000000       0.02000000

Corrected Total        7       2.92000000

                R-Square             C.V.         Root MSE               SAMP5 Mean

                0.993151         0.041952         0.141421               337.100000

Source                DF         Anova SS      Mean Square   F Value        Pr > F

P1                     1       0.12500000       0.12500000      6.25        0.2422
P2                     1       0.50000000       0.50000000     25.00        0.1257
P3                     1       2.20500000       2.20500000    110.25        0.0604
P1*P2                  1       0.00500000       0.00500000      0.25        0.7048
P1*P3                  1       0.02000000       0.02000000      1.00        0.5000
P2*P3                  1       0.04500000       0.04500000      2.25        0.3743

                                  SAS                                           25

                      Analysis of Variance Procedure

Dependent Variable: SAMP6
                                   Sum of             Mean
Source                DF          Squares           Square   F Value        Pr > F

Model                  6       2.17750000       0.36291667     32.26        0.1340

Error                  1       0.01125000       0.01125000

Corrected Total        7       2.18875000

                R-Square             C.V.         Root MSE               SAMP6 Mean

                0.994860         0.046888         0.106066               226.212500
```

```
Source                  DF        Anova SS    Mean Square   F Value     Pr > F

P1                       1      0.06125000     0.06125000      5.44     0.2578
P2                       1      0.21125000     0.21125000     18.78     0.1444
P3                       1      1.90125000     1.90125000    169.00     0.0489
P1*P2                    1      0.00125000     0.00125000      0.11     0.7952
P1*P3                    1      0.00125000     0.00125000      0.11     0.7952
P2*P3                    1      0.00125000     0.00125000      0.11     0.7952

                                     SAS                                    26

                        Analysis of Variance Procedure

Dependent Variable: SAMP7
                                    Sum of           Mean
Source                  DF         Squares         Square   F Value     Pr > F

Model                    6      3.00000000     0.50000000  99999.99     0.0

Error                    1      0.00000000     0.00000000

Corrected Total          7      3.00000000

                  R-Square            C.V.       Root MSE           SAMP7 Mean

                  1.000000               0              0           271.800000

Source                  DF        Anova SS    Mean Square   F Value     Pr > F

P1                       1      0.18000000     0.18000000  99999.99     0.0
P2                       1      0.60500000     0.60500000  99999.99     0.0
P3                       1      2.20500000     2.20500000  99999.99     0.0
P1*P2                    1      0.00500000     0.00500000  99999.99     0.0
P1*P3                    1      0.00500000     0.00500000  99999.99     0.0
P2*P3                    1      0.00000000     0.00000000  99999.99     0.0

                                     SAS                                    27

                        Analysis of Variance Procedure

Dependent Variable: SAMP8
                                    Sum of           Mean
Source                  DF         Squares         Square   F Value     Pr > F

Model                    6      3.39500000     0.56583333    113.17     0.0718

Error                    1      0.00500000     0.00500000

Corrected Total          7      3.40000000

                  R-Square            C.V.       Root MSE           SAMP8 Mean

                  0.998529        0.028369       0.070711           249.250000

Source                  DF        Anova SS    Mean Square   F Value     Pr > F
```

```
P1                      1      0.24500000      0.24500000       49.00        0.0903
P2                      1      0.72000000      0.72000000      144.00        0.0529
P3                      1      2.42000000      2.42000000      484.00        0.0289
P1*P2                   1      0.00500000      0.00500000        1.00        0.5000
P1*P3                   1      0.00500000      0.00500000        1.00        0.5000
P2*P3                   1      0.00000000      0.00000000        0.00        0.9999

                                   SAS                                           28

                  Analysis of Variance Procedure

Dependent Variable: SAMP9
                                   Sum of            Mean
Source                  DF        Squares          Square     F Value        Pr > F

Model                    6     7.46750000      1.24458333       39.83        0.1207

Error                    1     0.03125000      0.03125000

Corrected Total          7     7.49875000

              R-Square               C.V.        Root MSE                SAMP9 Mean

              0.995833           0.046248        0.176777                382.237500

Source                  DF       Anova SS     Mean Square     F Value        Pr > F

P1                      1      0.45125000      0.45125000       14.44        0.1638
P2                      1      1.36125000      1.36125000       43.56        0.0957
P3                      1      5.61125000      5.61125000      179.56        0.0474
P1*P2                   1      0.00125000      0.00125000        0.04        0.8743
P1*P3                   1      0.01125000      0.01125000        0.36        0.6560
P2*P3                   1      0.03125000      0.03125000        1.00        0.5000

                                   SAS                                           29

                  Analysis of Variance Procedure

Dependent Variable: SAMP10
                                   Sum of            Mean
Source                  DF        Squares          Square     F Value        Pr > F

Model                    6     3.12750000      0.52125000      417.00        0.0375

Error                    1     0.00125000      0.00125000

Corrected Total          7     3.12875000

              R-Square               C.V.        Root MSE               SAMP10 Mean

              0.999600           0.012142        0.035355                291.187500

Source                  DF       Anova SS     Mean Square     F Value        Pr > F

P1                      1      0.15125000      0.15125000      121.00        0.0577
P2                      1      0.66125000      0.66125000      529.00        0.0277
P3                      1      2.31125000      2.31125000     1849.00        0.0148
```

```
P1*P2                    1      0.00125000     0.00125000         1.00      0.5000
P1*P3                    1      0.00125000     0.00125000         1.00      0.5000
P2*P3                    1      0.00125000     0.00125000         1.00      0.5000

                                     SAS                                       30

                        Analysis of Variance Procedure

               Duncan's Multiple Range Test for variable: SAMP1

         NOTE: This test controls the type I comparisonwise error rate, not
               the experimentwise error rate

                       Alpha= 0.05  df= 1  MSE= 0.00125

                            Number of Means      2
                            Critical Range   0.318

         Means with the same letter are not significantly different.

                 Duncan Grouping              Mean         N  P1

                               A          341.5750         4  2
                               A
                               A          341.3500         4  1

                                     SAS                                       31

                        Analysis of Variance Procedure

               Duncan's Multiple Range Test for variable: SAMP2

         NOTE: This test controls the type I comparisonwise error rate, not
               the experimentwise error rate

                        Alpha= 0.05  df= 1  MSE= 0.02

                            Number of Means      2
                            Critical Range   1.271

         Means with the same letter are not significantly different.

                 Duncan Grouping              Mean         N  P1

                               A           345.250         4  2
                               A
                               A           345.000         4  1

                                     SAS                                       32

                        Analysis of Variance Procedure

               Duncan's Multiple Range Test for variable: SAMP3

         NOTE: This test controls the type I comparisonwise error rate, not
               the experimentwise error rate
```

APPENDIX F

```
------------------------------------------------------------------------------
Page   3  COMBINED DATA FOR ALL THE SAMPLE                             11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Variable(s) Entered on Step Number
   1..     P3
   2..     P2
   3..     P1
------------------------------------------------------------------------------
Page   4  COMBINED DATA FOR ALL THE SAMPLE                             11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X



Multiple R             .01328
R Square               .00018
Adjusted R Square    -.03929
Standard Error      51.96771

Analysis of Variance
                     DF      Sum of Squares       Mean Square
Regression            3            36.21100          12.07033
Residual             76        205248.89650        2700.64338

F =        .00447       Signif F =  .9996
------------------------------------------------------------------------------
Page   5  COMBINED DATA FOR ALL THE SAMPLE                             11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


------------------ Variables in the Equation ------------------

Variable              B        SE B       Beta         T  Sig T

P3              .582500    5.810167    .011499      .100  .9204
P2              .061000    1.162033    .006021      .052  .9583
P1              .057000    2.324067    .002813      .025  .9805
(Constant)   305.257500  309.851371                 .985  .3277


End Block Number   1   All requested variables entered.
------------------------------------------------------------------------------
Page   7  DATA FOR SAMPLE ONE ONLY                                     11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *


Listwise Deletion of Missing Data

Equation Number 1    Dependent Variable..   X

Block Number  1.  Method:  Enter      P1       P2       P3
------------------------------------------------------------------------------
Page   8  DATA FOR SAMPLE ONE ONLY                                     11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X
```

```
Variable(s) Entered on Step Number
   1..     P3
   2..     P2
   3..     P1
---------------------------------------------------------------------------------
Page   9   DATA FOR SAMPLE ONE ONLY                                       11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Multiple R           .99825
R Square             .99649
Adjusted R Square    .99387
Standard Error       .06124

Analysis of Variance
                    DF       Sum of Squares      Mean Square
Regression           3              4.26375          1.42125
Residual             4               .01500           .00375

F =      379.00000        Signif F =  .0000
---------------------------------------------------------------------------------
Page  10   DATA FOR SAMPLE ONE ONLY                                       11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


------------------ Variables in the Equation ------------------

Variable               B        SE B       Beta          T  Sig T

P3              .637500     .021651    .871699     29.445  .0000
P2              .067500     .004330    .461488     15.588  .0001
P1              .045000     .008660    .153829      5.196  .0065
(Constant)   331.300000    1.154610               286.937  .0000


End Block Number   1   All requested variables entered.
---------------------------------------------------------------------------------
Page  12   DATA FOR SAMPLE TWO ONLY                                       11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *


Listwise Deletion of Missing Data

Equation Number 1    Dependent Variable..   X

Block Number  1.  Method:  Enter        P1         P2         P3
---------------------------------------------------------------------------------
Page  13   DATA FOR SAMPLE TWO ONLY                                       11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Variable(s) Entered on Step Number
   1..     P3
   2..     P2
   3..     P1
---------------------------------------------------------------------------------
Page  14   DATA FOR SAMPLE TWO ONLY                                       11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *
```

```
Equation Number 1    Dependent Variable..   X


Multiple R            .99405
R Square              .98814
Adjusted R Square     .97925
Standard Error        .10607

Analysis of Variance
                     DF      Sum of Squares      Mean Square
Regression            3             3.75000          1.25000
Residual              4              .04500           .01125

F =      111.11111       Signif F =  .0003
------------------------------------------------------------------------------
Page  15   DATA FOR SAMPLE TWO ONLY                                     11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


------------------ Variables in the Equation ------------------

Variable                 B         SE B         Beta          T  Sig T

P3                 .575000      .037500      .834847     15.333  .0001
P2                 .070000      .007500      .508168      9.333  .0007
P1                 .050000      .015000      .181489      3.333  .0290
(Constant)      334.575000     1.999844                 167.301  .0000


End Block Number   1   All requested variables entered.
------------------------------------------------------------------------------
Page  17   DATA FOR SAMPLE THREE ONLY                                   11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *


Listwise Deletion of Missing Data

Equation Number 1    Dependent Variable..   X

Block Number  1.  Method:  Enter      P1       P2       P3
------------------------------------------------------------------------------
Page  18   DATA FOR SAMPLE THREE ONLY                                   11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Variable(s) Entered on Step Number
   1..    P3
   2..    P2
   3..    P1
------------------------------------------------------------------------------
Page  19   DATA FOR SAMPLE THREE ONLY                                   11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X

Multiple R            .97251
R Square              .94577
Adjusted R Square     .90510
Standard Error        .27157

Analysis of Variance
```

```
                       DF      Sum of Squares      Mean Square
Regression              3             5.14500          1.71500
Residual                4              .29500           .07375

F =       23.25424        Signif F =  .0054
------------------------------------------------------------------------------
Page  20   DATA FOR SAMPLE THREE ONLY                                  11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X

----------------- Variables in the Equation -----------------

Variable                B         SE B         Beta          T  Sig T

P3               .650000      .096014      .788241      6.770  .0025
P2               .085000      .019203      .515388      4.426  .0115
P1               .080000      .038406      .242536      2.083  .1057
(Constant)    355.725000     5.120364                  69.473  .0000

nd Block Number   1   All requested variables entered.
------------------------------------------------------------------------------
age  22   DATA FOR SAMPLE FOUR ONLY                                    11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

istwise Deletion of Missing Data

quation Number 1    Dependent Variable..   X

Block Number  1.  Method:  Enter      P1        P2        P3
------------------------------------------------------------------------------
Page  23   DATA FOR SAMPLE FOUR ONLY                                   11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X

Variable(s) Entered on Step Number
   1..     P3
   2..     P2
   3..     P1
------------------------------------------------------------------------------
Page  24   DATA FOR SAMPLE FOUR ONLY                                   11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


ultiple R            .99319
 Square              .98643
djusted R Square     .97626
tandard Error        .09354

nalysis of Variance
                       DF      Sum of Squares      Mean Square
egression               3             2.54500           .84833
esidual                 4              .03500           .00875

 =       96.95238        Signif F =  .0003
------------------------------------------------------------------------------
age  25   DATA FOR SAMPLE FOUR ONLY                                    11/3/ 4

         * * * *   M U L T I P L E   R E G R E S S I O N   * * * *
```

```
Equation Number 1    Dependent Variable..   X


------------------ Variables in the Equation ------------------

Variable               B          SE B        Beta          T  Sig T

P3               .500000       .033072     .880451     15.119  .0001
P2               .050000       .006614     .440225      7.559  .0016
P1               .030000       .013229     .132068      2.268  .0859
(Constant)    343.925000      1.763696                195.002  .0000


End Block Number   1   All requested variables entered.
--------------------------------------------------------------------------------
Page  27   DATA FOR SAMPLE FIVE ONLY                                   11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *


Listwise Deletion of Missing Data

Equation Number 1    Dependent Variable..   X

Block Number  1.  Method:  Enter       P1        P2        P3
--------------------------------------------------------------------------------
Page  28   DATA FOR SAMPLE FIVE ONLY                                   11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Variable(s) Entered on Step Number
   1..    P3
   2..    P2
   3..    P1
--------------------------------------------------------------------------------
Page  29   DATA FOR SAMPLE FIVE ONLY                                   11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X



Multiple R           .98447
R Square             .96918
Adjusted R Square    .94606
Standard Error       .15000

Analysis of Variance
                    DF      Sum of Squares      Mean Square
Regression           3             2.83000           .94333
Residual             4              .09000           .02250

F =      41.92593       Signif F =  .0018
--------------------------------------------------------------------------------
Page  30   DATA FOR SAMPLE FIVE ONLY                                   11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


------------------ Variables in the Equation ------------------

Variable               B          SE B        Beta          T  Sig T

P3               .525000       .053033     .868986      9.899  .0006
```

```
2                .050000        .010607      .413803       4.714   .0092
1                .050000        .021213      .206901       2.357   .0779
(Constant)    327.100000       2.828206                  115.656   .0000

nd Block Number   1   All requested variables entered.
------------------------------------------------------------------------------
age  32   DATA FOR SAMPLE SIX ONLY                                   11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *


istwise Deletion of Missing Data

quation Number 1    Dependent Variable..   X

lock Number  1.  Method:  Enter      P1        P2        P3
------------------------------------------------------------------------------
age  33   DATA FOR SAMPLE SIX ONLY                                   11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

quation Number 1    Dependent Variable..   X


ariable(s) Entered on Step Number
  1..    P3
  2..    P2
  3..    P1
------------------------------------------------------------------------------
age  34   DATA FOR SAMPLE SIX ONLY                                   11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

quation Number 1    Dependent Variable..   X



ultiple R           .99657
 Square             .99315
djusted R Square    .98801
tandard Error       .06124

nalysis of Variance
                    DF      Sum of Squares      Mean Square
egression            3             2.17375           .72458
esidual              4              .01500           .00375

 =     193.22222       Signif F =  .0001
------------------------------------------------------------------------------
age  35   DATA FOR SAMPLE SIX ONLY                                   11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

quation Number 1    Dependent Variable..   X


 ---------------- Variables in the Equation -----------------

 ariable              B         SE B        Beta          T  Sig T

3                .487500      .021651     .932012     22.517  .0000
2                .032500      .004330     .310671      7.506  .0017
1                .035000      .008660     .167284      4.041  .0156
onstant)      218.650000     1.154610                189.371  .0000

 d Block Number   1   All requested variables entered.
------------------------------------------------------------------------------
 ge  37   DATA FOR SAMPLE SEVEN ONLY                                 11/3/ 4
```

```
--------------------------------------------------------------------------------
Page  43   DATA FOR SAMPLE EIGHT ONLY                                    11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Variable(s) Entered on Step Number
   1..     P3
   2..     P2
   3..     P1
--------------------------------------------------------------------------------
Page  44   DATA FOR SAMPLE EIGHT ONLY                                    11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Multiple R             .99779
R Square               .99559
Adjusted R Square      .99228
Standard Error         .06124

Analysis of Variance
                   DF       Sum of Squares      Mean Square
Regression          3              3.38500          1.12833
Residual            4               .01500           .00375

F =      300.88889       Signif F =  .0000
--------------------------------------------------------------------------------
Page  45   DATA FOR SAMPLE EIGHT ONLY                                    11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X

------------------ Variables in the Equation ------------------

Variable                B          SE B       Beta          T  Sig T

P3               .550000      .021651    .843661     25.403  .0000
P2               .060000      .004330    .460179     13.856  .0002
P1               .070000      .008660    .268438      8.083  .0013
(Constant)    236.325000     1.154610               204.679  .0000

nd Block Number   1   All requested variables entered.
--------------------------------------------------------------------------------
age  47   DATA FOR SAMPLE NINE ONLY                                      11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *


istwise Deletion of Missing Data

quation Number 1    Dependent Variable..   X

lock Number  1.  Method:  Enter       P1        P2        P3
--------------------------------------------------------------------------------
ge  48   DATA FOR SAMPLE NINE ONLY                                       11/3/ 4

       * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

uation Number 1    Dependent Variable..   X
```

```
Variable(s) Entered on Step Number
   1..    P3
   2..    P2
   3..    P1
------------------------------------------------------------------------------
Page  49   DATA FOR SAMPLE NINE ONLY                                  11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Multiple R              .99499
R Square                .99000
Adjusted R Square       .98250
Standard Error          .13693

Analysis of Variance
                       DF       Sum of Squares      Mean Square
Regression              3            7.42375          2.47458
Residual                4             .07500           .01875

F =      131.97778       Signif F =  .0002
------------------------------------------------------------------------------
Page  50   DATA FOR SAMPLE NINE ONLY                                  11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


------------------ Variables in the Equation ------------------

Variable              B          SE B       Beta          T  Sig T

P3              .837500      .048412    .865038     17.299  .0001
P2              .082500      .009682    .426064      8.521  .0010
P1              .095000      .019365    .245309      4.906  .0080
(Constant)   364.225000     2.581787               141.075  .0000


End Block Number   1   All requested variables entered.
------------------------------------------------------------------------------
Page  52   DATA FOR SAMPLE TEN ONLY                                   11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *


Listwise Deletion of Missing Data

Equation Number 1    Dependent Variable..   X

Block Number  1.  Method:  Enter      P1        P2        P3
------------------------------------------------------------------------------
Page  53   DATA FOR SAMPLE TEN ONLY                                   11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X


Variable(s) Entered on Step Number
   1..    P3
   2..    P2
   3..    P1
------------------------------------------------------------------------------
Page  54   DATA FOR SAMPLE TEN ONLY                                   11/3/ 4

        * * * *   M U L T I P L E   R E G R E S S I O N   * * * *
```

```
      * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Listwise Deletion of Missing Data

Equation Number 1    Dependent Variable..   X

Block Number  1.  Method:  Enter       P1        P2        P3
----------------------------------------------------------------------
Page  38    DATA FOR SAMPLE SEVEN ONLY                           11/3/ 4

      * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X

Variable(s) Entered on Step Number
   1..    P3
   2..    P2
   3..    P1
----------------------------------------------------------------------
Page  39    DATA FOR SAMPLE SEVEN ONLY                           11/3/ 4

      * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Equation Number 1    Dependent Variable..   X

Multiple R           .99833
R Square             .99667
Adjusted R Square    .99417
Standard Error       .05000

Analysis of Variance
                   DF      Sum of Squares      Mean Square
Regression          3             2.99000           .99667
Residual            4              .01000           .00250

F =      398.66667       Signif F =  .0000
----------------------------------------------------------------------
Page  40    DATA FOR SAMPLE SEVEN ONLY                           11/3/ 4

      * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

uation Number 1    Dependent Variable..   X

------------------- Variables in the Equation -------------------

able                B         SE B        Beta          T   Sig T

             .525000      .017678     .857321     29.698   .0000
             .055000      .003536     .449073     15.556   .0001
             .060000      .007071     .244949      8.485   .0011
tant)     260.400000      .942735                276.217   .0000

ck Number  1    All requested variables entered.
----------------------------------------------------------------------
    DATA FOR SAMPLE EIGHT ONLY                                   11/3/ 4

      * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

Deletion of Missing Data

umber 1    Dependent Variable..   X

r  1.  Method:  Enter       P1        P2        P3
```

```
ion Number 1      Dependent Variable..    X


ple R               .99920
are                 .99840
ted R Square        .99720
ard Error           .03536

sis of Variance
                   DF       Sum of Squares       Mean Square
ession              3              3.12375           1.04125
lual                4               .00500            .00125

  833.00000        Signif F =  .0000
-----------------------------------------------------------------------------
 55   DATA FOR SAMPLE TEN ONLY                                         11/3/ 4

     * * * *   M U L T I P L E   R E G R E S S I O N   * * * *

tion Number 1    Dependent Variable..    X


--------------- Variables in the Equation -----------------

able                     B          SE B        Beta            T  Sig T

                   .537500       .012500     .859484       43.000  .0000
                   .057500       .002500     .459724       23.000  .0000
                   .055000       .005000     .219868       11.000  .0004
stant)          280.350000       .666615                  420.558  .0000

Block Number   1   All requested variables entered.
-----------------------------------------------------------------------------
SH.
```