Thermal Expansion Coefficient of Lubricant Oils.

A Thesis
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The Requirements for the Degree of Master
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in
Chemical Engineering.

by
Omar Mustafa Hussian
(B.Sc. in Chemical Engineering 2003)

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Certification

We certify that this thesis entitled "***Thermal expansion coefficient of lubricant oil***" was prepared by ***Omar Mustafa Hussein***, under my supervision at Nahrain University, College of Engineering, in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Signature:	Signature: D. M. KASSIM
Name: **Dr.Talib Kashmola**	Name: **Dr.Dhia Al-Deen M.Kaseem**
Date:	Date: 5/2/2007

Signature:

Name: Prof.Dr.Qasim.J.Slaiman

(Head of department)

Date: 5/2/2007

Certificate

We certify, as an examining committee, that we have read this thesis entitled" **Thermal expansion coefficient of lubricating oils)",** examined the student (**Omar Mustafa Hussian**) in its content and found it meets the standard of thesis for the degree of Master of Science in Chemical Engineering.

Signature: T. Kashmoula

Name: **Dr. Talib Kashmoula**
(Supervisor)

Date: 5 / 2 / 2007

Signature: D. M. KHSSIM

Name: **Dr.Dhia Al-Deen M.Kaseem**
(Supervisor)

Date: 5/ 2/ 2007

Signature:

Name: **Dr. Basim O.Hasan**
(Member)

Date: 5 / 2 / 2007

Signature: T.A. AL-Hadi

Name: **Dr.Talib Ahamd Al-Hadi**
(Member)

Date: 5/ 2 / 2007

Signature: Mahmoud Omar Abdullah

Name:**Prof.Dr. Mahmoud Omar Abduallah**
(Chairman)

Date: 5 / 2 / 2007

Approval of the College of Engineering

Signature: M - J. Jweeg

Name: **Prof.Dr.Muhsin J.Jweeg**
(Acting Dean)

Date(8/ 4 / 2007

Abstract

This investigation covers a study of the thermal expansion of basic lubricating oils. The three types of Iraqi base lube oil –Stocks, namely 40 Stock, 60 Stock, 150 Stock and also lubricating oil with additives from Al -Dura refinery. The investigation also covers the effect of additives on the thermal expansion coefficient of a lubricating oil. The additive that is used polymer poly-isoprene.

A study of the effect of the temperature changes and the effect of polyisoperne on the thermal expansion coefficient of lubricating oil has carried out.

Measurements were made on measuring the density variation with temperature of the base oil and then blending the basic oil with 4% of polyisoperen and measure the density variation with temperature.

Generally polyisoperne increases the thermal expansion coefficient of the base oils with keeping the density decreasing is rather constant during heating.

Also this study investigates the thermal expansion coefficient of base oil and additives currently used in Al -Dura refinery and compares that of the base oil +4%poly isoprene.

From the result obtaining in this study a good correlation for calculating the thermal expansion coefficient of three base oil at different temperatures are obtained.

List of contents

CHAPTER FIVE: Conclusions and Recommendation

Nomenclature

Variable Notations.

a , b = Constants in Eq. (4.1)

B_1,B_2,B_3 = Constants in Eq. (4.28) to (4.25).
$,B_4,B_5,B_6$

H = Viscosity of reference oil of 100 viscosity index at 37.8 °C.

L = Viscosity of reference oil of 0 viscosity index at 37.8 °C.

Mw = Molecular weight (g/g mole).

sp.gr. = Specific gravity 15 °C/15 °C.

EP = Extreme Pressure.

T_b = boiling point of blending Polyisoprene with base oil, (°C).

$C_{on.}$ = Weight percent of polyisoprene, (%).

wt_a = weight fraction of additive.

μ_o = the dynamic viscosity of blends in cP at T_o= 303.15 k

Greek Letters

μ = Dynamic viscosity (cP).

υ,η = Kinematic viscosity (cSt).

Subscriptions

V.I. = Viscosity Index.

n.d. = not determined.

CTE =Coefficient of thermal expansion.

CP =Paraffinics composition

CN =Naphthenic composition

CA =Aromatic composition

Abbreviation

ASTM = American society for Testing Materials.

ECN = Effective Carbon Number.

LOAS = Lubricating Oil Additives.

HDL = Hydrodynamic lubrication.

EHL = Elastohydrodynamic lubrication.

ISOVG = International Standard Organization viscosity.

OEM = Original Equipment Manufactures.

ppm = part per million.

PMMA = Poly methyl methacrylate.

PTFE = Poly tetra fluoro ethylene.

ALAN = Automatic laboratory analyzer network.

°API = American Petroleum Institute.

CHAPTER ONE

INTRODUCTION

- **GENRAL**

Lubricants were at one time almost exclusively animal or vegetable oils or fats, but modern requirements in both nature and volume have made petroleum the main source of supply. Fatty oils still have their uses although generally in ancillary role.

The main function of a lubricant is to reduce the friction between the moving surfaces and so facilitate motion. Its second most important function is to remove heat generated in the equipment being lubricated, such as piston engine, enclosed gears and machine tools. It has also to remove away debris from the contact area.

To understand how a lubricant function it is necessary to know something about the nature of the surfaces. Even the most carefully finished metallic surface is not truly flat but has a certain sub-microscopic roughness-something like sandpaper on a much smaller scale. When two dry surfaces are in contact, the asperities tend to inter lock and resist any effort to slide one surfaces over the other surfaces. This resistance is called the friction and before sliding takes place sufficient forces must be applied to overcome it.

The main project of lubrication is to replace this solid friction between the two inter locking surfaces by the much lower internal friction in a film of lubricant maintained between them and keeping them apart so that the asperities no longer touch. The viscosity is the measure of its internal friction.

Lubricant oil can be produced by modern methods of refining from crude .they may distillates or residues derived from vacuum distillation of primary distillate with a boiling range above that of gas oil. **[1]**

- **Origin of thermal expansion**

The energy displacement relation-ship from atoms in solid is shown schematically below:

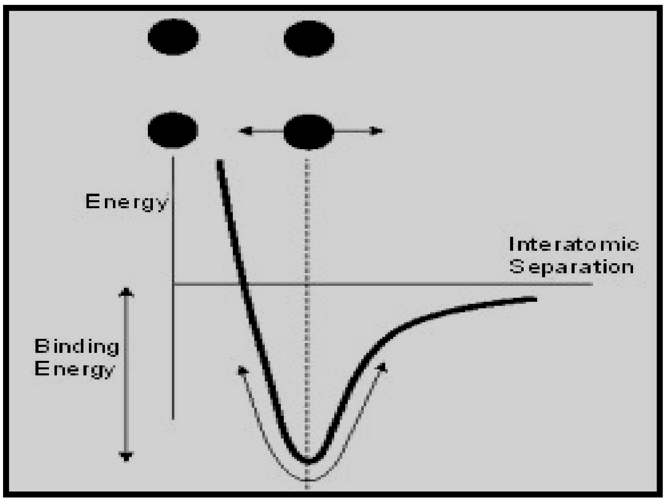


Figure 1.1 The Origin of Thermal Expansion.

As the temperature is raised the amplitude of vibration increase s. The asymmetrical nature of the potential well means that is accompanied by an increase in the average inter –atomic spacing for longitudinal vibrations. The coefficient of thermal expansion (CTE) or thermal expansibility, α, is the relative change in a linear dimensions per unit of temperature change. But the thermal expansion in liquid is due the the change in cubic dimension per the change in the temperature.[2]

The figure below shows the values of some selected material:

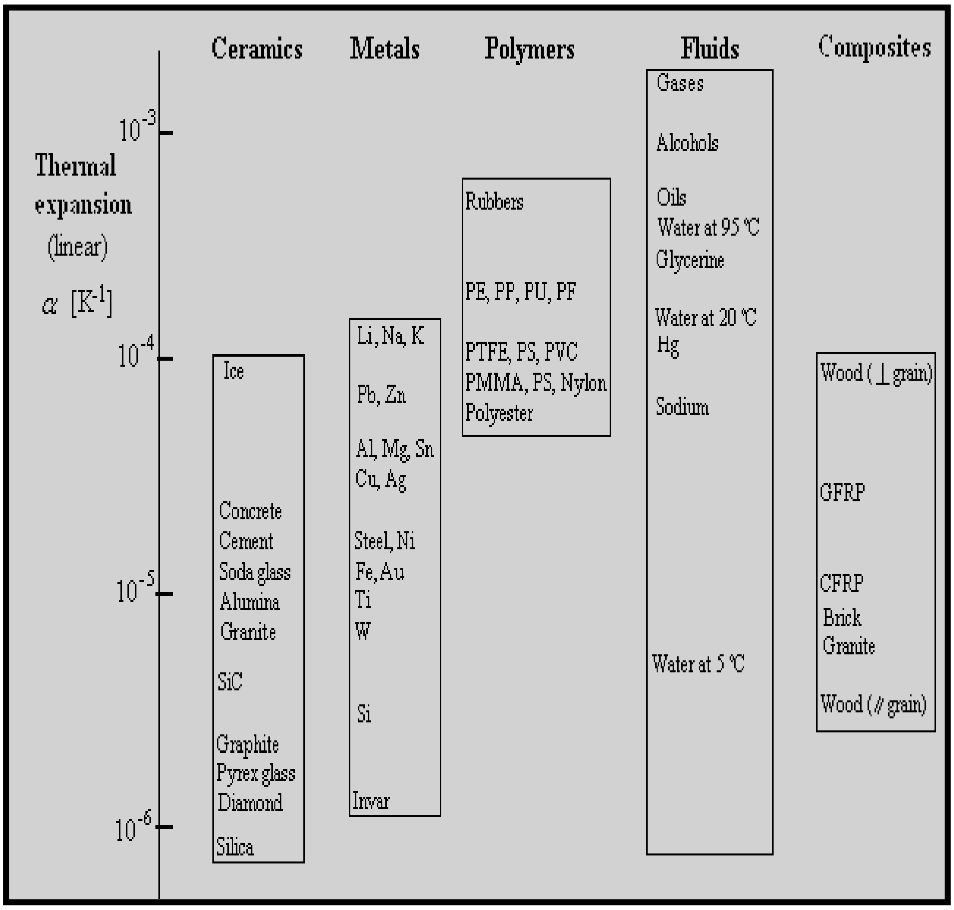


Figure 1.2 Shows the Thermal Expansion Coefficient of some Material.

- **Lubricant oil additives**

Lubricating oils additives (LOAs) are used to enhance the performance of the lubricants and functional fluids. Each additive is selected for its ability to perform one or more specific functions in combination with other additives.

Selected additives are formulated into package for use with a specific lubricant base stock and for a specified end-use application. The largest end use is in automotive engine crankcase lubricants. Other automotive applications include hydraulic fluids and gear oils. In addition, many industrial lubricants and metalworking oils also contain LOAs. The major functional additives types are dispersant, detergents, oxidation inhibitors, antiwear agents, extreme pressure (EP) additives, and viscosity index (VI) improves. Most oil additives are complex organic chemicals or mixtures evaluated by their performance rather than their composition or purity.

The selection of the right additive or of the most suitable combination of additives depends very much on the specific use of the oil, and in the respect there are certain notable differences between gasoline engine and diesel engine lubricants.[1]

The aim of this project is to find the thermal expansion coefficient's correlation of three base oils and to study the effect of polyisoperen as additive on the thermal expansion of base oil.

CHAPTER TWO
LITERATURE SURVEY

2.1.1 Thermal Expansion

The volume of given oil mass increases with temperature, therefore, its density decreases. The degree of expansion is expressed as the coefficient of thermal expansion. Thermal expansion is useful to determine the size of container needed when the oil will be heated. Inexperienced people often have an oil overflow of surprising amount of thermal expansion.

In HDL, the thermal expansion of the oil in the clearance of a bearing increases the hydraulic pressure. Some researches discuss the "thermal wedge" mechanism of film formation and apply it to parallel sliding surfaces, especially flat, non tilting, thrust bearings.

The coefficient of thermal expansion is the ratio of the relative change of a volume to a change in temperature. Thermal expansion is expressed as the ratio of volume change to the initial volume after heating 1 ^{o}C. Therefore, the unit is reciprocal ^{o}C, or degree C^{-1}. The values of the coefficient of thermal expansion for mineral oils are near 6.4×10^{-4} degree $^{o}C^{-1}$.

Thermal expansion (or contraction) determinations require the measurement of the volume of a given mass of oil at various temperatures. The sample is placed in a graduated cylinder and the volume observed as the temperature is either increased or decreased. [1]

2.1.2 Thermal expansion relation:

The instantaneous volumetric thermal expansion coefficient α is related to the density ρ by the thermodynamic relation[2]:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p + \beta_T\left(\frac{\partial P}{\partial T}\right)_P \qquad \textbf{...(2.1)}$$

Where **β**$\boldsymbol{\beta_T}$ is the isothermal compressibility and P is the vapor pressure. The subscripts on the partial derivatives indicate that they are along the saturation curve. Breitung and Reil state that the magnitude of the second term in Eq. (2.1) is much smaller than the first term and only contributes a few percent at 8000 K. This is because along the saturation curve, the volume change due to the pressure change is much smaller than the corresponding volume change due to thermal expansion. [3]

The linear instantaneous thermal expansion coefficient is one third of the instantaneous volumetric thermal expansion coefficient, given by Eq. (2.1). [7]

So the thermal expansion coefficient (α) is defined by:-

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right) \qquad \dots (2.2)$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) \qquad \dots (2.3)$$

$$\alpha = \frac{\gamma Cv}{K_T V} = \frac{\gamma Cp}{K_S V} \qquad \dots (2.4)$$

Where ρ is the density, T is the temperature, where $(\partial\rho/\partial T)$ indicates a derivative at constant pressure, V is the volume, γ is the heat capacity ratio Cv is the heat capacity at constant volume, K_T is the isothermal bulk modulus, Cp is the heat capacity at constant pressure and K_s is the adiabatic bulk modulus.

The volume of thermal expansion coefficient α is related to the coefficient of linear expansion β by

$$\alpha = 3\beta$$

Partial derivative are given by

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{K^2{}_T}\left(\frac{\partial K_T}{\partial T}\right)_P \qquad \textbf{...}\ (2.5)$$

$$\left(\frac{\partial \alpha}{\partial T}\right)_V = -\frac{\rho}{T}\left(\frac{\partial Cv}{\partial P}\right)_T \qquad \ldots(2.6)$$

Summarizing the relationships involving α,

$$\left[\frac{\partial(\alpha K_T)}{\partial V}\right] = -\frac{1}{V}\left(\frac{\partial K_T}{\partial T}\right)_T \qquad \ldots\ (2.7)$$

$$\left[\frac{\partial(\alpha K_T)}{\partial P}\right] = \frac{1}{K_T}\left(\frac{\partial K_T}{\partial T}\right)_T \qquad \ldots\ (2.8)$$

$$\left[\frac{\partial(\alpha K_T)}{\partial T}\right]_P = K_T\left(\frac{\partial \alpha}{\partial T}\right)_v \qquad \ldots\ (2.9)$$

2.1.3 Bulk Modulus or Compressibility

Bulk modulus expresses the resistance of a fluid to a decrease in volume due to compression. A decrease in volume would increase density. Compressibility is the reciprocal of bulk modulus or the tendency to be compressed. Bulk modulus varies with pressure, temperature, molecular structure and gas content. Generally, mineral oils are thought to be incompressible. In high pressure hydraulic systems a high bulk modulus or low compressibility is required to transmit power efficiently and dynamically. [13]

In EHL, bulk modulus is a factor used in some film thickness calculations. Bulk modulus is a consideration in some viscosity-pressure relationships. (Low viscosity polysiloxane fluids have a low bulk modulus or high compressibility compared to mineral oils). Dissolved gases decrease bulk modulus of mineral oils.

The unit for bulk modulus is pressure and the unit for compressibility is the reciprocal of pressure. The SI units are N m-2, and m2 N-1 respectively.

Bulk modulus is determined by measuring the volume of an oil at various pressures or derived from density measurements at various pressures. Bulk modulus can also be measured by the speed of sound in oils under various pressures. A discussion of bulk modulus and values are given in References 9 and 10. Since a graph of pressure versus volume gives a curve, the secant to the curve is used and is called Isothermal Secant Bulk Modulus. 2.1.4

2.1.4Density:

Density is the mass of a unit volume of a substance. Oil density is used to determine the mass of a given volume, or the volume of a given mass. Density is used in lubrication to identify an oil, or oil fractions, and in the measurement of kinematic viscosity (absolute viscosity divided by density). Also, density is in the equations for the calculation of temperature rise in an oil film, and the equation for Reynolds Number (which determines if flow of an oil film is laminar (smooth layers) or turbulent (tumbling)).[10]

2.1.5 Specific Gravity

volume to the mass of an equal volume of water. Therefore, specific gravity is dimensionless. The specific gravity of mineral oils also varies from 0.86 to 0.98

since the specific gravity of water is 1 at 15.6 degree C. Specific gravity decreases with increased temperature and decreases slightly as viscosity decreases for similar compositions. Reference 5 (pp. 482- 484) gives the specific gravity of 81 mineral oils at 15.6 degree C. [5]

Most lubricant supplier's typical data bulletins give A.P.I. (American Petroleum Institute) Gravity in degrees for lubricating oils instead of specific gravity. A.P.I. gravity is an expression of density measured with a hydrometer. A.P.I. gravity has an inverse relationship with specific gravity, as shown in the following Table 2.1

A. P. I. Gravity	Specific Gravity
15	0.97
34.9	0.85

Table2.1 API Vs. Specific Gravity Of Lubricant

mineral oil lubricants have an A.P.I. gravity value of around 27 ^{O}C. Reference 8 gives the equation for converting A.P.I. gravity to specific gravity.

Density, specific gravity, and A.P.I. gravity are measured by ASTM D-1298, using a calibrated, glass hydrometer and a glass cylinder. The cylinder is partially filled with the sample oil and the hydrometer is set into the oil and allowed to stabilize. A reading of the gravity is taken from the markings on the stem of the hydrometer at the surface of the oil. The temperature of the oil is measured and the final result is converted to 15.6 ^{o}C (60 ^{o}F) and reported as A. P. I. gravity at 60 ^{o}F. Two other oil properties related to density are thermal expansion and bulk modulus or compressibility.

2.2 Lubricating Oil Properties

2.2.1 General Properties of Lubricating Oils

The large number of natural lubricating and specially oils sold today are produced by blending a small number of lubricating oil base stocks and additives. The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications. The additives are chemicals used to give the base stocks desirable characteristics, which they lack, or to enhance and improve existing properties. The properties considered important are **[12]**: -

1. Viscosity.
2. Viscosity change with temperature (VI).
3. Pour point.
4. Oxidation resistance.
5. Flash point.
6. Boiling temperature.
7. Acidity (neutralization number)

2.2.1.1 Viscosity

Viscosity is the property of a fluid that causes it to resist flow, which mechanically is the ratio of shear stress to shear rate. Viscosity may be visualized as a result of physical interaction of molecules when subjected to flow. Lubricating oils have long chain hydrocarbon structures, and viscosity increases with chain length. Viscosity of an oil film, or a flowing column of oil, is dependent upon the strong absorption of the first layer adjacent to the solid surfaces, and the shear of adjacent layers. [1]

Viscosity is by far the most significant property for establishing the thickness, pressure, and temperature of an oil film in hydrodynamic lubrication (HDL) and in elastohydrodynamic lubrication (EHL). Viscosity is also a significant factor in predicting the performance and fatigue life of rolling element bearings and gears. Plastohydrodynamic lubrication accounts for the existence of hydrodynamic effects in metalworking. Calculations for oil film thickness require knowledge of the viscosity of the oil film at the temperature, pressure, and shear rate in the component. Viscosity is in the numerator of all equations predicting oil film thickness, fluid friction or hydraulic pressure. Oil film thickness increases with viscosity. Viscosity is also in equations for calculating the Sommerfeld Number, velocity in an oil film, shear stress, fluid friction force, and power loss for hydrodynamic bearings.[13]

2.2.1.2 Viscosity Index (VI)

VI is a commonly used expression of an oil's change of viscosity with temperature. VI is based on two hypothetical oils with arbitrarily assigned VI's of 0 and 100. The higher the viscosity index the smaller the relative change in viscosity with temperature. Most industrial mineral lubricating oils have a VI between 55 and 100, but VI varies from 0 to "high VI" oils with VI up to 175. . Viscosity-Temperature-VI relationship is shown in the following table:

Table2.2 Viscosity Index of Lubricant Oil.

Industrial Oil	Viscosity, cSt	Viscosity, cSt	Viscosity	Visc-Temp
ISOVG 32	40°C	100°C	Index	Coefficient
Machine Oil	30.4	4.8	58	0.842
Turbine Oil	32	5.4	102	0.831
Hydraulic Oil	30.4	6.1	154	0.799

A less arbitrary indication of the change in viscosity with temperature is the viscosity temperature coefficient.[12]

For 40 to 100^{O}C it is: Viscosity (cSt) at 40 ^{O}C minus Viscosity (cSt) at 100 ^{O}C = C^{-1}, divided by the Viscosity (cSt) at 40 ^{o} C. Calculated values of the viscosity-temperature coefficient are also shown in the table. The lower the value of the coefficient, the higher the VI. The coefficient for mineral oils can vary by a factor of 10 depending on the temperatures.

The most commonly used method for expressing the expressing the relationship between viscosity and temperature is the viscosity index of Dean and Davis, which is based on an empirical scale. The standards are two series of lubricating oil fractions; the one obtained from Pennsylvania crude which was arbitrarily assigned a viscosity index of 100 and the other from Gulf coast crude, which was assigned a viscosity index of zero.

The viscosity index is an arbitrary scale for comparing the rates of viscosity changes of lubricating oil with temperature. A high number (100 or more) indicates the oil is still fluid at low temperature and retains its viscosity at high temperature, an obviously desirable characteristic.[13]

2.2.1.3 Pour Point

Pour point is a viscosity temperature phenomenon. It is defined as the lowest temperature at which a lubricant will flow under specified conditions. Most lubricant suppliers give the pour point of their oils so that the user can determine if it can be pumped and would be fluid in low temperature applications. [12]

The pour point increases with viscosity. For example, an ISOVG 46 mineral oil might have a pour point of -39 ^{o} C, whereas an ISOVG 460 would have a pour point of -15 ^{o} C. For mineral oils, the increase in viscosity as temperature is reduced, is due to gelling of the oil by the precipitation of crystalline wax. The frgoing is a review of mineral oil properties, it should be noted that one advantage of many synthetic oils is their very low pour points because of the absence of wax. Pour point depressants for mineral oils are additives which lower the pour point by interfering with wax crystallization.

Pour point is measured by ASTM D 97, which describes the procedure for cooling an oil until it will not pour out of a vessel. Pour point, flash point, VI, and other properties of 81 mineral oils are given in Reference 7. Cloud point is defined as the temperature at which a wax cloud first appears on cooling mineral oil under specified conditions.

2.2.1.4 Oxidation Resistance

Lubricants are exposed to oxidation by atmospheric oxygen in practically all of their application. This results in formation of acids and sludge’s which interfere with the primary function of lubricant. Oxidation of lubricating oil leads to such difficulties as bearing corrosion, ring sticking, lacquer and sludge.

2.2.1.5 Flash Point

Flash point is an indication of the combustibility of the vapors of a mineral oil, and is defined as the lowest temperature at which the vapor of an oil can be ignited under specified conditions. Flash point is clearly related to safety. Flash point of lubricating oils is measured using ASTM D 92. An open cup of oil is heated at a specific rate while periodically passing a small flame over its surface. The flash point is considered to be the lowest temperature at which the oil vapors will ignite, but not sustain a flame. [14]

For example, the flash point of an ISOVG 32 turbine oil might be 222 ^{o}C. If one continues to heat the oil and continues to pass the small flame across the surface, the vapors will eventually sustain a flame and this is the fire point. The fire point of the same turbine oil would approach 252 ^{o} C.

2.2.1.6 Boiling temperature

The first step in the manufacture of petroleum products is the separation of crude oil into the main conventional fractions by distillation. A main distinguishing feature of the various products is their volatility or ability to vaporize. This is associated with the size of the molecule and volatility is related to the boiling point; the higher the boiling temperature rang of a fraction, the higher the molecular weights of the components; the lower the volatility, for given crude oil the greater the viscosity.[1]

2.2.1.7 Acidity

The acidity or alkalinity of petroleum products is determined by dissolving the product in a suitable neutral solvent and neutralizing the solution with either standard alkali or standard acid as the case may be. The neutral point may be indicated by a color indicator or electrometrically. Oxidation of petroleum products more often than not produces acid and the progress of deterioration can be used as a refinery control test or as a measure of change during use.[1]

2.2.2 Chemical properties

2.2.2.1 Oxidation

All petroleum products under normal condition of storage and use come into contact with air and hence with oxygen, often at high temperature, and sometimes when in a finely divided state, for example as a mist in an engine.

Such conditions are very favorable for oxidation to take place. Hydrocarbons vary in their susceptibility to oxidation, paraffin's or saturated chain compounds are generally more resistant than aromatic ring compounds, and unsaturated compounds are readily oxidized.[1]

Just as oxygen plays such an important part in controls the life of a lubricating oil. Oxygen may be regarded as the enemy ever eager to destroy it, but, of course, this is not wholly true. Blown are widely used in paints, and lubricating oils lubricating oils is very largely a scheme to render than resistant to oxidation. The study of oxidation is made difficult by the complexity of hydrocarbons in the oils, and the products of oxidation resulting there from. Analysis of compounds produced is tedious and difficult which makes progress slow. Oxidation of oils is of such fundamental interest and practical importance to lubrication that the introduction of antioxidants was a logical escape from a stubborn problem. The interaction of olefins with molecular oxygen is not only a subject of widespread importance, but is one of the most through understood chemical progresses.

The reaction of oxygen with a molecule that may or not may already contain oxygen, Oxidation may be partial, resulting incorporation of oxygen into the molecule or in the elimination of hydrogen from it, or it may be complete, forming carbon dioxide and water (combustion).

Oxidation is a markedly exothermic reaction and proceeds by a number of complex steps, the nature of the hydrocarbons in the lubricants having a considerable influence on the nature of the oxidation process.

Since oils are mixture of many hydrocarbons falling in different chemical classes, and covering a rather wide range of molecular weights of the main classes should be considered separately. This is possible for paraffins, naphthenes and aromatics, but not so well based for unsaturated compounds of the kinds likely to be produced by cracking of the other three types at engine temperature, reasoning by analogy is at least helpful. It has long been known that after some period of use lubricating oils show greater oiliness, and better protection against rusting than do the same oils when new. These effects are sometimes small, but have been amply confirmed. They are almost certainly produced by polar compounds resembling at least remotely some of the commercial additives used to improve many oils. This gives a hint as to the nature of the compound types produced during the early stages of the oxidation occurring in service, and a laboratory study confirms these surmises. A point of caution should be mentioned here; while the first changes caused by oxidation show beneficial effects, these are only stages of a deterioration, which quickly becomes harmful, at least motor oils.

With so many operative factors in the process of oxidation, it is not surprising to find that a vast range of materials has been proposed as oxidation inhibitors, functioning by various mechanisms. Some are (chain-breakers) in that they prevent propagation of the chain of reactions by interfering with an intermediate step. Others have a particular ability to react rapidly with hydroperoxides in a manner that does not produce free radicals, thus removing a source of initiation of the chain reaction. Some compounds can carry out both functions. A less important type acts as anti-oxidants by preventing or reducing the catalytic activity of metals by chelation, to form a non-reactive stable metal complex, or by forming stable metal complex, or by forming stable films on metal and thus preventing its dissolution into the oil. In practice, most inhibitors are themselves oxidizable and tend to be consumed in the process of inhibition.

The inhibitors most used can be divided into two main classes: the first class includes oil-soluble materials containing sulfur or phosphorus, and the second consists of amine or phenolic compounds.

2.2.2.2 Corrosion

Nearly all petroleum products are used under conditions that bring them into contact with metallic surface, and it is important that these surfaces should not be corroded thereby. Petroleum products must therefore be non-corrosive in them and should not become corrosive during use and, in same instances are also expected to provide positive protection against corrosive even though presents in only small quantities, and products are therefore tested to ensure either its absence or it limitation to relatively harmless amounts. Oxidation with formation of acids is another potential cause of corrosion and this is on reason why oxidation stability is of such great importance.[1]

Lubricants must be formulated so as to avoid the promotion of corrosion by any of the ingredients or by their degradation products. They must also be able to prevent corrosion in certain sets of adverse circumstances when potentially corrosive contaminants come in to the oil. Corrosion is too broad a subjected to be compressed in a limited number of words; suffice it to say that same aspects are within the orbit of the petroleum industries. All coating-fluids should have some ability to check corrosion according to circumstances. But when water is present greater corrosion activity is enticed.[1]

The corrosive effect may be minimized in two ways; either the production of harmful peroxides and carboxylic acids can be inhibited, or the reactive metal surfaces can be isolated from the reactive with an appropriate film. In practice the oxidation inhibitors, such as zinc dithiophosphate commonly used in internal combustion engine oils, will function in both ways. The inhibitors will also effective in preventing similar corrosion which might result with some combustion products their way past the piston into the crankcase.

Some sulfur compounds will prove very reactive towards certain metals, particularly cuprous and silver alloys, which can be applied as gearing or bearing metals. Objectionable black stains indicate that fatigue life of the metals can also be adversely affected. A copper strip corrosion test is commonly applied to lubricating oils. But although mineral oils contain naturally occurring sulfur compounds capable of producing stains in this type of test, these are largely removed by modern refining processes such as solvent refining, and base lubricating oils almost invariably give negative results. When additives incorporation active sulfur are used in gear and cutting oils, their general corrosive effect on non-ferrous metal can be minimized by metal deactivators, which do not influence the performance of the additives under boundary conditions; mercaptobenzothiazole has been used for this purpose. Rusting is a special kind of corrosion and both are belived to contribute to wear of moving parts, whereby corrosion products are removed mechanically. Wear caused by friction alone is quite slow where lubrication is adequate. In ordinary automobile use, the wear of cylinder bores and piston rings is usually of the mixed corrosion explains the fact that bore wear is always greater at the top of ring travel. The protection of metals against corrosion is important because corrosion, especially rusting, can cause very considerable losses to industry in both materials from coming into contact with the metal, and the application of an impervious coating is a convenient and effective means.

2.3Base oil

2.3.1 Base oil composition

Crude oil from which lubricating mineral oils are obtained, contain thousands of compounds, some of which remain after the refining processes. Most commercial lubricants are mixtures where the composition is chosen for the proposed use. The major mineral oil components are paraffinc, naphthenic,and smaller amount of aromatic compounds. The variations in composition directly affect lubricant performance.

Paraffinic oils are straight chain or branched aliphatic hydrocarbons belonging to the series with the general formula C_nH_{2n+2}. paraffin's are saturated with the respect to hydrogen. A typical oil molecule with 25 carbon and 52 hydrogen atoms has molecular weight of 352. Very high molecular weight paraffins are solid waxes, also dissolved in a small amounts of mineral oils.

Naphthenic or alicyclic oils have the characteristics of naphthenes, which are saturated hydrocarbons of which themolecules contain at least one closed ring of carbon atoms. Base oil may contain a small amount of aromatic hydrocarbons.

Aromatics are unsaturated molecules identified by one or more benzene rings or by chemical behavior similar to benzene. The concentration of the three major types compounds in a given base oil is determined by chemical analysis. The result are given as %CP for paraffinics, %CN for naphthenics, and %CA for aromatics. For example, a commercial base oil is 68%CP,32%CN,and less than 1%CA. the amount of each type of compound in mineral oil is calculated from equation given in (ASTM D3238-90)which require values of molecular weight, refractive index and density.

Mineral base oils contain many minor components, such as sulfur, nitrogen, oxygen, metal compounds, and water. The type and quantity of these compounds depends upon the degree of refining. For example, medicinal white oil contains at least amount of minor components, and a "bright stock" contains the most. The sulfur content of pure mineral oil, medicinal white oil, is less than 20 ppm, whereas the sulfur content of refined base oil depends on the type of refining processes, and may be 200 to 6000 ppm, while bright stock may range from 5000 to 10000ppm sulfur. These sulfur compounds are surfaces active and affect boundary lubrication. Medicinal white oil is an extremely poor boundary lubricant often used as a reference, primarily for research. However, medicinal whit oil is used in afood machinery lubricants where there may be a change of it being ingested. A bright stock is known to have better, but limited, boundary lubrication properties. Some of the minor components also provide natural oxidation inhibition or the base oils

2.3.2 Base oil lubricating properties:-

Paraffin are relatively un reactive and thus have better oxidation stability compared to naphthenes. Thus, they can be used longer at higher temperatures. For example, oil companies state that turbine oils are blended using the best paraffinic base stocks. However, because of the relative stability and another properties of paraffins, they have poor solvency for additives. For example, elemental sulfur has limited solubility in paraffinic base oils and higher solubility in naphthenic base oils. Conversely naphthenics have good solvency for many additives.

Aniline point is a measure of the solvent power of oil. It's an indication of the solvent effect of oil on the other organic compounds such as rubber, seals, gaskets, and electrical insulation. Aniline point is identified as the lowest temperature at which an oil is completely miscible, that is clear, with an equal volume of aniline. The lower the temperature, the greater he solvency and the more likely rubber and polymeric compounds will swell. A commercial "handy" oil has an aniline point of 90 C indicating it would cause more rubber swell than a paper machine oil with an aniline point of approximately 120 ^{o} C.

Aniline point is measured by (ASTM D611) where a sample of oil is introduced into vial containing an equal portion of aniline. The fluids are warmed and lightly mixed until they are completely soluble, then allowed to cool. The temperature at which a haze appears, indicating the two liquids are no longer soluble, is considered to be the aniline point. In addition, naphthenic oils dissolve greater quantities of gases than do paraffinics. Also, paraffinis have slightly higher flash points than naphthenics. Because of their wax content, paraffins have higher pour points naphtheneics. For example, for two oils of the same viscosity at 40°C, the paraffinic would have a pour point of -18°C, and the naphthenic a pour point of -43°C.

In general paraffins have higher viscosity index than naphthenics. For example, 100and 70VI respectively. The VI of turbine oils range from 96 for a low viscosity oil to 102 for high viscosity oil. In contrast, a general utility oil has a low VI of 29 to 60. Paraffins generally have a lighter color than naphthenics. Pure oil are not suitable lubrication for industrial use because of their poor lubricating and stability properties. With oxidation and corrosion inhibition they are suitable lubricants only under pure hydrodynamic lubrication. They are sold primarily to companies that blend their own additives into the base oil.

2.4 Lubricating Oil Additives (LOAS)

2.4.1 General

Straight mineral oils, together with compounded oils, were once able to meet normal lubrication requirements of automotive and industrial practice. As these requirements become more severe with the progressive development of engineers and general machinery it becomes necessary firstly to improve the quality of lubricating oils by new methods of refining and eventually to use (additives) either to reinforce existing qualities or to confer additional properties. In the early days of their use additives were regarded with suspicion-an oil that needed an additive was necessarily an inferior oil; today additives are an accepted feature of lubricants-as of other petroleum products-and most lubricants now contain one or more additives.[13]

Additives are substances that, in small quantities-from a few parts per million to a few percent-confer specific properties on the lubricant.

The progressive increase in the severity of engine operating conditions for motor oils have made necessary the use of chemical additives. These are employed for the following specific purposes.

- To improve flow properties by: -

Lowering solidification temperature;
Decreasing change of viscosity with change of temperature.

- To improve lubricating action by: -

Providing greater oiliness;
Decreasing meter wear;
Furnishing better film strength.

- To provide greater chemical stability by: -

Inhibiting oxidation;
Neutralizing oxidation promoters;
Inhibiting bearing metal corrosion;
Preventing sludge and varnish deposition.

- To preserve engine surfaces from rusting and corrosion.
- To prevent oil foaming during use.

Additives are usually called after their particular function, but many additives are multi-functional; it will give some idea of their multiplicity to name the chief functions they fulfill: to improve the viscosity index (VI improves); to increase oxidation stability (anti-oxidants); to keep contaminants in suspension (dispersants);to depress the pour point (pour point depressant); to prevent rusting (anti-rust);and to prevent foaming (anti-foam).

2.4.2 Types of Additives

A) Additives to Improve the Chemical Properties of Oils.

A.1) Oxidation Inhibitors

Oxidation Inhibitors Mineral oils readily react with oxygen at elevated temperatures to first form hydroperoxides, then organic acids. These compounds lead to viscosity increase, formation of sludge and varnish, discoloration, acidic odor, corrosion of metal parts, promote foaming, and tendency to emulsify. Resistance to oxidation is a critical property for all machines, but especially critical for machines requiring extended life at elevated temperatures, such as turbines, aircraft engines, and hydraulic systems. Also, good oxidation resistance prolongs storage life. Oxidation resistance may be due to natural inhibitors or commercial additives. Four types of oxidation inhibitor additives are: zinc dithiophosphates; aromatic amines; alkyl sulfides; and hindered phenols. Metal surfaces and soluble metal salts, especially copper, usually promote oxidation. Therefore, another approach to inhibiting oxidation is to reduce the catalysis by deactivating the metal surfaces. [13]

The effectiveness of the anti-oxidants in delaying oil oxidation can be measured by laboratory tests known generally as oxidation stability tests. Oxidation stability is measured in accelerated tests at high temperature, in the presence of excess oxygen, catalysts and possibly water. Results are expressed as the time required to reach a predetermined level of oxidation. Criteria can be a darkening color, the amount of sludge, gum, acids, and the amount of oxygen consumed, and in some cases by the depletion of the anti-oxidant chemical compound itself. The two most common test methods for oxidation resistance are ASTM D 943 "Oxidation Stability of Steam Turbine Oils" (TOST), and ASTM D 2272 "Oxidation of Steam Turbine Oils by the Rotary Bomb Method" (RBOT).

ASTM D 943 TOST is a widely used method for comparison of a lubricating oil's ability to resist oxidation. However, it is seldom the method of choice for used oil comparisons. In method ASTM D 943 a controlled flow of oxygen is bubbled through water, oil, and copper and iron catalysts mixture at 95 ^{o}C until the acid number reaches 2.0 mg KOH per gram (Reference 3). Results are given in hours. For example, a hydraulic oil with moderate oxidation resistance could be 1,000 hours, and a turbine oil could be greater than 4,000 hours(3).[13]

ASTM D 2272 RBOT is also used to compare new oils but has also proven effective in determining the remaining useful life of used oils. A sample of oil is introduced into a high pressure bomb, heated and rotated until the onset of oxidation takes place as evidenced by a pressure drop. The results are reported as the time in minutes it took for this reaction to occur. There are a variety of new developments in the measurement of the antioxidant concentration, such as Differential Scanning Calorimetry, and Cyclic Voltametry (References 11 & 12). Caution should be used when using any accelerated oxidation test to estimate the remaining useful life of an oil because it may not represent field experience.

A.2) Rust Inhibitors

Since water is a common contaminant in mineral oil lubricated systems used on earth, anti-rust additives are used. Rust inhibitors prevent the formation of rust (hydrated iron oxide) on iron surfaces by the formation of protective films, or by the neutralization of acids. Typical anti-rust compounds are highly basic compounds, sulfonates, phosphates, organic acids, esters or amines. The rusting of ferrous parts in a lubricated system is undesirable. The rust contributes to sludge, causes loss of metal, sticking of metal parts, and the formation of solid particles of rust that are abrasive. Rust indicates the presence of water in the system. The ability of a treated oil to prevent rusting may be measured by ASTM D 665, entitled Rust Prevention Characteristics. A 300 ml sample of lubricant is introduced into a beaker containing 30 ml of either salt or fresh water. A specially prepared bullet-shaped steel rod is placed in the beaker along with the oil/ water mixture. The mixture is heated and stirred for 24 to 48 hours to promote rust on the steel bullet. At the end of the test time the bullet is carefully inspected and rated for any sign of rust.

A.3) Dispersants and Detergents

These additives keep sludge, fine solid, and semi-solid contaminants dispersed in the oil rather than settling out as deposits. The compounds used are succinimides, neutral calcium and barium sulfonates, phenates, polymeric detergents and amine compounds. Detergent dispersants are also basic calcium sulfonates/phenates which neutralize sludge precursors. Ash content is the percent by weight of noncombustible residue of an oil. The metallic detergents and dispersants are the primary contributors to ash and may cause unwanted inorganic residue to form. The efficiency of some machines operating at high temperatures is reduced by a build-up of these undesirable deposits. For example, many compressor oils require very low ash, such as a trace.

Ash content using ASTM D 874 Sulfated Residue is the most commonly used technique. This method consists of slowly burning the oil in a crucible. The carbonaceous residue after burning is wetted with sulfuric acid and reheated. Once the sulfuric acid is completely volatilized more sulfuric acid is introduced and the crucible is heated in a muffle furnace at 875 degree C until a constant weight of inorganic residue is obtained. This residue is considered the sulfated ash in percent by weight.

B) Additives to Improve Boundary Lubrication Performance

B.1) Anti-friction

Anti-friction, sometimes called lubricity, is defined as the ability of a lubricant to reduce friction, other than by its purely viscous properties. Anti-friction additives reduce friction below that of the base oil alone under conditions of boundary lubrication. The additives are adsorbed on, or react with the metal surface or its oxide to form monolayers of low shear strength material. The compounds are long chain (greater than 12 carbon atoms), alcohols, amines, and fatty acids. A classic example is oleic acid reacting with iron oxide to form a film of the iron oleate soap. The low shear strength of the soap film causes the low friction.

B.2) Saponification Number

Saponification is a chemical test indicating the amount of fatty material in the oil and, therefore, one index of anti-friction. Saponification is a chemical process of converting fats to soap. Certain lubricants such as worm gear oils, steam cylinder oils, machine tool way lubricants, and pneumatic tool oils, contain fatty type additives to improve anti-friction properties. Saponification number is performed according to ASTM D 94. The saponification number indicates the amount of fatty substances in the oil. Saponification number is the number of milligrams of KOH that combines with the fat in 1 gram of oil to form the soap. Therefore, the higher the number, the greater the amount of fatty material.

Anti-friction is measured directly by laboratory bench tests, where a low coefficient of friction ("f"), measured under conditions of boundary lubrication indicates good anti-friction performance. Examples of bench tests are the four ball test machine and the pin-on-disk apparatus. A pin-on-disk apparatus with steel sliding on steel, with a base oil would give an f of 0.10 to 0.15, whereas the addition of 2% oleic acid to the oil, f would be reduced to 0.05 to 0.08. In an industrial machine, anti-friction reduces power requirements. No bench machine has been found to correlate satisfactorily with an industrial machine.

However, if materials and operating conditions in the bench machine simulates the industrial machine as closely as possible, the results are useful for screening lubricants, revealing wear mechanism, and warning of problems. The final lubricant test is in the industrial machine itself.

B.3) Anti-wear

Anti-wear additives are those which reduce or control wear. They form organic, metallo-organic, or metal salt films on the surface. Sliding or rolling occurs on top of, or within, the films thus reducing metal-to-metal contact. Anti-wear additives only reduce the rate of wear, which still occurs, but without a catastrophic failure. The films are sacrificed so that the wear fragments in the oil are primarily the film material.

Anti-wear performance is measured on numerous bench lubricant testers operating under moderate conditions, where the volume or weight of material removed is measured.

An example is the 4-ball wear test. Also, the pin-on-disk apparatus is used and run under conditions described in ASTM G 99-90. The types of anti-wear additives are zinc dialkyldithiophosphates (ZDDP), carbamates, organic phosphates such as tricresyl phosphates, organic phosphates and chlorine compounds. The most common anti-wear additive is ZDDP, which decomposes to deposit metallo-organic species, zinc sulfide or zinc phosphate, or reacts with the steel surface to form iron sulfide or iron phosphate. Operating conditions control the specific film material.

B.4) Anti-scuff

Anti-scuff additives are those that prevent scuffing. Scuffing is defined as damage caused by solid-phase welding between sliding surfaces. Anti-scuff additives reduce scuffing by forming thick films of high melting point metal salts on the surface which prevent metal to metal contact which, when extensive, may cause scuffing. The mechanical properties of the films, such as melting point, shear strength, ductility, and adhesion to the metal surface determine the effectiveness. Common anti-scuff additives are sulfur or phosphorous compounds more chemically active than anti-wear additives. A common gear oil anti-scuff additive is a mixture of an organic sulfur compound and an organic phosphorous compound usually identified as S/P. Excessive chemical activity of anti-scuff additives creates a danger of corrosive wear. For example, an active sulfur compound may reduce the risk of scuffing of steel gear teeth, but severely tarnish any corrodible metal.

Microscopically, the scuffed surface appears irregular, torn, with plastic deformation, and shows evidence of melting. The definitive test of scuffing is the evidence of metal transfer. Anti-scuffing properties of oils are also measured on lubricant testers run under severe conditions. Usually load, oil temperature, speed, or a combination are increased until scuffing occurs. Scuffing is usually accompanied by high f, such as between 0.2 and 0.5, and possible localized heat, oil smoking, and noise. Wear fragments in the oil are usually large metallic particles.

Note: There is some overlapping of anti-wear and anti-scuff performance. That is, some additives have good anti-wear properties and can prevent scuffing to a limited degree. Following are some components of oil or additives that affect lubrication under boundary lubrication conditions.

B.5) Oxygen

The oxygen in air dissolved in oil forms metal oxide films which have anti-wear and limited anti-scuff properties. Iron oxides, especially Fe_3O_4 on steel, is effective in reducing metal to metal contact. This oxide is frequently found as wear fragments in used oil when low wear occurs. Conversely, if an oil is deaerated so that the oxide film cannot be continuously repaired, high wear and scuffing occurs immediately.

B.6) Sulfur Compounds

Sulfur compounds in lubricating oils and their chemical activity are directly related to anti-wear and anti-scuff properties. Elemental sulfur was a historical additive used in a gear box to reduce oil temperature.

Sulfur content is useful in understanding boundary lubrication performance. The sulfur compounds may be naturally occurring in the base oil, or added as additives. A low sulfur content would explain poor boundary lubrication performance.

A very high sulfur content would explain corrosion problems where the corrosion product is found to be a metal sulfide, or where contamination by hydrogen sulfide was found. Iron sulfide films are frequently identified on undamaged ferrous surfaces in industrial equipment. The amount of sulfur in oil is reported as percent or ppm total sulfur. Therefore, one must consider the several sources of sulfur, such as in the base oil naturally, additives, ZDDP, and organo sulfur compounds such as sulfurized olefins. The source of sulfur can be narrowed down by analyzing for the stoichiometric amounts of associated elements. Examples are: analysis of zinc, sulfur and phosphorous for the ZDDP additive, sulfur and phosphorous for a S/P gear oil anti-scuff additive, or molybdenum and sulfur for a black oil possibly containing molybdenum disulfide. Usually, lubricating oil suppliers provide only physical properties and performance data, but little or no additive chemistry or elemental analysis. If the additive chemistry is of interest to a user, a laboratory might perform a series of tests for identification. For example, if analysis showed the presence of sulfur, and ES analysis showed zinc and phosphorous, and infrared analysis showed peak characteristic of ZDDP, then the presence of the ZDDP additive would be indicated.

B.7) Phosphorous Compounds

Various phosphorous containing compounds are added to lubrication oils to improve anti-wear properties. The most common is tricresyl phosphate (TCP). Other organo-phosphates and phosphites are used. These compounds are thought to adsorb on or react with the rubbing metal surface to form protective films of organometallic or iron phosphate. Some tribological parts, such as cam shafts, are pretreated to form thick iron manganese phosphate coatings to minimize metal-to-metal contact during break-in.

B.8) Chlorine Compounds

Chlorine compounds continue to be used in some oils and commercial additives based on their reputation for reducing friction and improving anti-scuff properties. However, considerable danger of corrosion is present because of the chloride ion. Therefore, if a problem of corrosion including rusting is found, a chlorine analysis is suggested. Further, any halogen compound in oil creates disposal or re-refining problems. Rowe, Reference 13, has collected from the tribology literature, the wear coefficients, K, for 55 phosphorous compounds, 23 sulfur compounds, 21 dialkyldithiophosphates, and some combinations. The lower the K, the better the lubricant.

The wear tests were conducted on a four ball lubricant tester under various conditions. K (dimensionless) is defined as:

K = V X H divide by d X L

where V is volume of metal worn off, m^3

H is metal hardness, kg m^{-2}

d is distance slid, m

and L is load, kg

For example, TCP reduced the K of a paraffinic base oil from 28.5 X 10-8

to 0.29 X 10-8, or 100 fold.

2.5 Lube oil processing

The first step in the processing in the lubricating oils is the separation on the crude oil distillation units in the individual fractions according to viscosity and boiling range specification. The heavier lube oil raw stocks are included in the vacuum-fractionating tower bottoms with the asphalts, resins, and author undesirable materials. The raw lube oil fractions from most crude oils contain components which have undesirable characteristics for finishing lubricating oils. These must be removed or reconstituted by processes such as liquid-liquid extraction, crystallization, selective hydro cracking, and/or hydrogenation. The undesirable characteristics include high pour points, large viscosity changes with temperature (low VI), poor oxygen stability, poor color, high cloud points, high organic acidity, and high carbon- and sludge- forming tendencies.

2.5.1Propane Deasphalting

The lighter feed stocks for producing lubricating oil base stocks can be sent directly to the solvent extraction units but the atmospheric and vacuum still bottoms require Deasphalting to remove the asphalts and resins before undergoing solvent extraction. In some cases the highest boiling distillate stream may also contain sufficient asphaltenes and resins to justify Deasphalting.

2.5.2 Dewaxing

All lube stocks, except those from a relatively few highly naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperatures. Dewaxing is one of the most important and most difficult processes in lubricating oil manufacturing. There are two type of processing in use today. One uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil. The other uses a selective hydro cracking processes to crack the wax molecules to light hydrocarbons.

2.5.3 Hydrofinishing

Hydrofinishing of Dewaxing of lube oil stocks is needed to remove chemically active compounds that affect the color and color stability of lube oil. Most hydrotreating operation use cobalt-molybdate catalyst and are operated at a severity set by the color improvement needed. Organic nitrogen compounds seriously affect the color and color stability of oils and their removal is a major requirement of the operation.

2.5.4 Blending

Blending is a physical process in which accurately measured or weighed quantities of two or more components is mixed together from a homogeneous blend. The components may all be petroleum fractions or may include other materials, for example fatty oils, dyes functional additives, referred to collectivity as (additives), in properties from a few parts per million to 10 or 20% W. the blends will be formulated to have required properties for particular applications and will usually be required to meet appropriate marketing specification.[12]

Blending is required for oil product of all kinds. Gasoline as marketed is usually a blend of several refinery grades derived from different processes, generally contains lead anti knock compounds, and may contain other additives, e.g. to prevent spark- plug fouling, carburetor icing, etc. Kerosene may be a blend of two or more refinery grades. Most lubricating oils are blends of two or more base oils with or without additives, ranging from the simplest two-oil blends to quite complex formulations containing several non-petroleum ingredients. Petroleum waxes are blended together and with natural waxes or polyolefin. Bitumens are blended together, or with volatile solvents to form cutbacks.[1]

In principle the process of blending is the same all these instance but the details will vary according to the nature of the components and the complexity of the mixture, for example gasoline components can be blended readily by very simple mixing, lubricating oils may require moderate heating (60-80 °C), waxes and bitumen require more heating and mixing of hot bitumen with cold volatile solvent obviously requires more care than the cold mixing of lubricating oils.

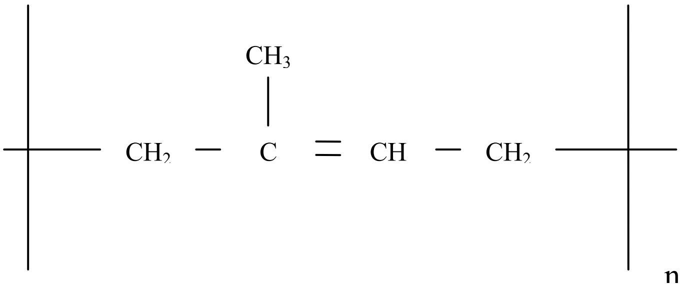
Blending can be carried out either intermittently by (batch blending) or continuously by (in-line blending).

2.5.5 Solvent extractions

There are three solvents used for the extraction of aromatics from lube oil feed stocks and the solvent recovery portions of the systems are different for each. The solvents are furfural, phenol, and N-methyl-2-pyrrplidone (NMP). The purpose of solvent extraction is to improve the viscosity index (VI) oxidation resistance, and color of the lube oil stock and to reduce the carbon-and sludge-formation tendencies of the lubrication by separating the aromatic portion from the naphthenic and paraffinic portion of the feedstock.

2.6 The elastic properties of rubber (polyisoprene)

Natural rubber is found in the latex of the tree Hevea brazilients; its principal constituent is polyisoprene:



$$\left[-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2- \right]_n$$

Fig. 2.1 Construction of Polymer Polyisoperne.

Polyisoprene occurs in other plants, some of which have commercial significance, such as the Russians dandelion and the Mexican guayule shrub. The well-known properties of natural rubber are displayed only at temperature above the glass transition temperature, which is -70°C; below that temperature it is a brittle glass. Every amorphous polymer, whether synthetic or natural, providing it cross-linked, displays comparable properties above its glass transition temperature. These properties are stated briefly:

Extremely high extensibility, frequently up to ×10, generated by low mechanical stress; complete recovery after mechanical deformation. To these must be added a third property, which is not so well known:

High extensibility and recovery are due to deformation induced changes in entropy.[9]

2.7 Criteria for Polymer Solubility:

The Solution process dissolving a polymer is a slow process that occurs in two stages. First, solvent molecules diffuse into the polymer to produce. A swollen gel. This may be all that happen-IF, for example, the polymer inter molecular forces are high because of cross linking, crystallinity, or strong hydrogen bonding. But if these forces can be over come by the introduction of strong polymer solvent interactions, the second stage of solution can take place. Here the gel gradually disintegrates into a true solution. Only this stage can be materially speed by agitation. Even so, the solution process can be quite slow (days or weeks) for material of very high molecular weight. The degree of swelling of a lightly cross linked polymer can be measured and related to the thermodynamic properties of the system, but this phenomenon is not widely utilized at the present time.

2..8 Solubility.

Can be see that (benzene) is an excellent solvent while cyclo hexane is a moderate solvent and decaline dioxin is a non-solvent for Polyisoprene, so that (benzene) solvent use in this investigating **[11].**

2..9Effect of polyisoprene on viscosity of base oil:

The dynamic viscosities of the three types of oil-stocks of 40stock 60stock, and

150 stock in the range of (20.65-34.97) API gravity, were mixed with different concentration in the range of 0-8wt. % of poly isoprene 1502 which has 0.789 and 0.853 and 0.9538 respectively .

The blending of the three types of oil-stocks with polyisoperne resulted in a noticeable increase in the viscosity when the weight percent of polyisoperne increased. Because polyisoperne (1502) has higher viscosity than the viscosities of each type of oil stocks. [35]

The increase in the viscosity for lighter oil stocks is greater than that of the medium and heavier one, i.e. the effect of polyisoperne on stock 40 higher than stock60 and stock 150 respectively.

The effect of poly isoprene (1502) on viscosities of three base oils shown in the figures 2.2 ,2.3 and 2.4:-

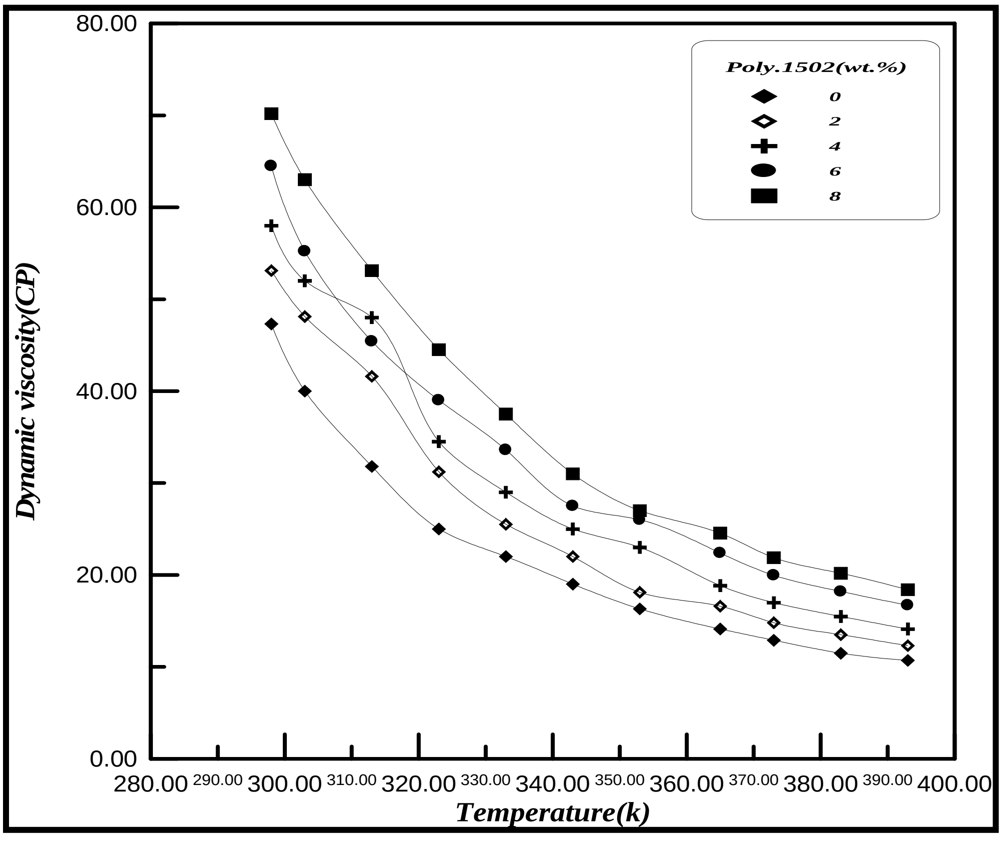


Figure2.2 Dynamic Viscosity of 40 Stock versus Temperature of Different wt.% of poly 1502.

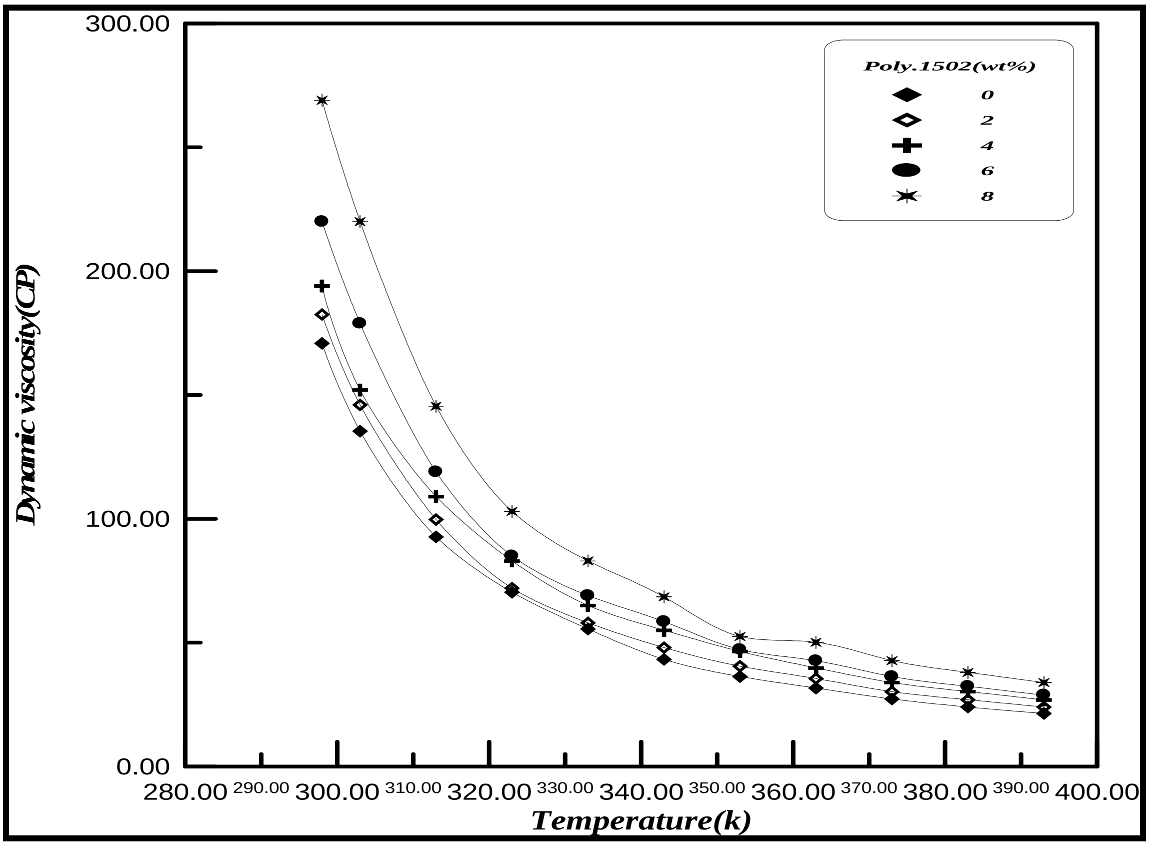


Figure 2.3 Dynamic Viscosity Of 60 Stock versus Temperature of Different wt.% of Poly 1502.

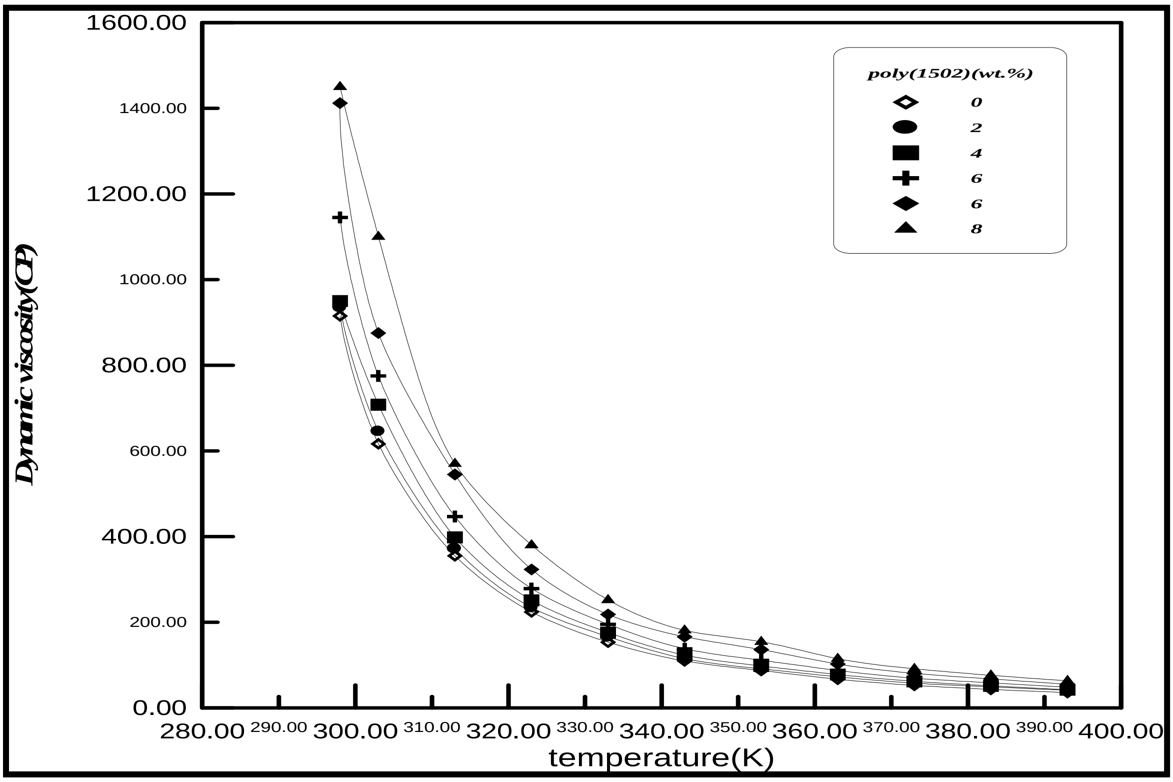


Figure 2.4 Dynamic Viscosity Of 150 Stock versus Temperature of Different wt.% of Poly 1502.

2.13 characterization scheme of hydrocarbon systems:

The gas –liquid equilibrium and thermodynamic properties calculations generally require critical properties, molecular weight, and acentric factor as input data. Over the years, the critical properties have been measured and complied for many hydrocarbons and other substances. For methane through decane and the impurities (nitrogen, carbon dioxide, and hydrogen sulfide), the critical pressure ,critical temperature and acentric factor are given in table 2.2

As it well-known that most laboratory analyses of produced fluid end with some residual or plus fraction. Typically this is C_{7+} so there is a need to obtain the physical properties of plus the fraction to perform equation of state calculation. In this study, Riazi and Daubert correlation has been used for estimate the physical properties of plus fraction with Peng-Robinson equation of state. Their equation has the form:

$$\theta = a(T_B)^b (\gamma_{c_{7+}})^c \qquad \text{...(2.10)}$$

Where (θ) is a physical property to be predict, $\gamma_{C_{7+}}$ specific gravity of plus fraction, and (a,b,c) are correlation constants as shown in Table 2.3

Table2.3 The Constant Physical Properties Of Pure Hydrocarbon Substances**[6]**

Compound	**Critical pressure(psia)**	**Critical temperature(^{o}R)**	**Acentric factor**
Nitrogen	493.1	227.6	0.0372
Carbon dioxide	1071	547.91	0.2667
Hydrogen sulfide	1300	672.45	0.0948
Methane	666.4	343.04	0.0104
Ethane	706.5	549.76	0.0986
Propane	616	665.68	0.1524
I-Butane	527.9	734.65	0.1848
N-Butane	550.6	765.3	0.1995
I-Pentane	490.4	828.7	0.2280
N-Pentane	488.6	845.4	0.2514
Hexane	436.9	913.4	0.2994
Heptane	396.8	972.4	0.3494
Octane	360.7	1024.5	0.3977
Nonane	331.8	1072.6	0.4445
Decane	305.2	1111.7	0.4898

Mahdi modification of Riazi and Daubert correlation has been used to predict the critical properties of the heavy fraction with Soave- Redlich - Kwong equation of state. The equation has the same form of equation above( ) but with different values for the constants (a,b,c). The values of these constants are shown in table (). With both equations of state, the value of the boiling point has been estimated from Whitson relationship which represented the following equation:-

$$T_B = \left[4.5579 \left(M_{c_7^+}\right)^{0.15178} \gamma_{c_7^+}^{0.15427}\right]^3 \qquad \textbf{...(2.11)}$$

Where T_B is the boiling point in degree Rankin.

Also the acentric factor has been estimated by Edmister approximation relationship, which has the following form:

$$\omega = \frac{3}{7}\left[\frac{\log Pc}{T_c / T_B - 1}\right] - 1 \qquad \textbf{...(2.12)}$$

Where P_c in atmosphere.

Table2.4 Constant For Riazi and Daubert correlation.

θ	a	b	c
M_w	4.5673×10^{-5}	2.1962	-1.0164
T_c	24.2787	0.58848	0.3596
P_c	3.12281×10^{9}	-2.3125	2.3201
V_c	7.5214×10^{-3}	0.2896	-0.7666

Table2.5 Constant For Mahdi modification of Riazi and Daubert Correlation.

θ	a	b	c
T_c	24.2787	0.58848	0.3596
P_c	3.12281×10^{9}	-2.3125	2.3201

CHAPTER THREE

EXPERIMENTAL WORK

3.1 Oil Stock

Three oil stocks from Al-Daura refinery stock (40), stock (60), and stock (150). Their properties are measured in Al-Daura refinery and given in Table 3.1. Where stock 40 is the lightest one with API gravity 34.97 while 60 stock is a middle type and 150stock is heavy one, with API gravity 29.29 and 20.65 respectively. The main properties of oil stocks were measured in Al-Daura refinery laboratories according to API and ASTM specification, as listed in Table 3.1

Table 3.1 Properties of Three Basic Stocks

Specification	40stock	60stock	150stock
Kin. Viscosity at40^{o}C, cSt	18.11	56.12	501.98
Kin. Viscosity at100^{o}C, cSt	3.14	7.69	33.38
Viscosity index(VI)	95	95	93
Specific gravity at(15.6)^{o}C	0.85	0.88	0.93
^{o}API gravity	34.97	29.29	20.65
COC flash.^{o}C	n.d.	200-300	290-300
P.M.flash,^{o}C	160	n.d.	n.d.
Pour point,^{o}C	-24	-6	-3
Sulfur content, wt.%	0.62	1.4	2.00
Ran.Res, wt.%	0.06	0.12	0.78

3.2 Additives

Lubricating oil additives (LOAS) impart desirable properties to base stocks to satisfy lubricant standards for high performance engines. Each additive is selected for ability to perform one or more specific functions, for example to restrict oxidation, to modify the viscosity –temperature characteristics, to act as detergents, to depress pour point, or to inhibit rust. Although (LOAS) are used in petroleum- based lubricants, they are not typical petroleum products; they are considered specially as chemicals.Whose property are tabulated in Table 3.2.

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Table 3.2 Physical Properties Of Poly isoprene

Properly	Value
Density	0.92 gm/c^{3}m
Heat composition	44770 J/gm
Thermal Conductivity	0.00134 J/sec/cm.^{o}C
Volumetric expansion factor	0.00062 ^{o}C

3.3.1 Set –Up and Procedure

From equation of thermal expansion (α):

$$\alpha = -\frac{1}{\rho} \times \left(\frac{\partial \rho}{\partial T} \right)_P \qquad \textbf{...(3.1)}$$

To calculate the density at reference temperature and find the density variation with temperature by using the following apparatuses are used:

1-Pyknometer.
2-Water bath (thermostat).
3-Electric balance.
4-Thermometer

3.3.2Definition

Density is defined as the mass of fluid per unit volume. In general, it varies with pressure and temperature. The dimension of density is kg/m^{3}in SI unit. And specific gravity (γ) is defined as the ratio of the weight of a volume of liquid to the weight of an equal volume of water at the same temperature.

3.3.3Procedure

1.The pycknometer and the stopper must be cleaned thoroughly using surfactant cleaning fluid, then rinsing well with distilled water and finally drying by using furnace.

2. measuring the weight of pycknometer, the stopper and the thermometer at room temperature.

3. Filling the pycknometer with basic oil at the same room temperature.

4.putting the stopper and making sure that there is no bubbles inside then drying the exterior surface of the pycknometer by wipping with lint -free clothe of paper.

5. The filled pycknometer is then weighted

Procedure used to measure the density for the base oil at room temperature.

For measuring the variation of density with temperature after the above steps, the pycknometer (filled)is placed in the thermostat (water bath) and setting the temperature above the room temperature with 5°C. The density at every set of temperature is measured. The interval of temperature between each point is taken to be 5°C. From the procedure above find the terms of equations can be found.

For preparing the base oil with poly-isoperne as additive of 4%composition, the mass of poly-isoperne must be found and then dissolved with benzene (solvent) and then blended with stock oil. Several days are required for complete mixing.

The above procedure is repeated for each sample

3.3.4 **Theory and evaluation**

A rise in temperature causes a greater thermal agitation of the molecules in the liquid and therefore an increase in its volume.

For the evaluation of thermal expansion coefficient (α) read the density at reference temperature is measured at room temperature which was (15^{o}C) and the term ($\partial\rho/\partial T$) is calculated from the plotting Temperature against density, and then the slope of the graph has been calculated.

Figure 3.1 Electric balance.

Figure 3.2 Water Bath (memert)

Figure3.3 Pycknometer.

CHAPTER FOUR
RESULT AND DISCUSSION

4.1 Effect of temperature on density, molar volume:-

The density and molar volume of the three oil- oil stocks at atmospheric pressure and Temperature range of 15-80^{o}C.Indicate that an increase in temperature leads to decrease in density and increasing in molar volume. The rate of decrease in the density of the heavy oil –stocks is less than the rate for the lighter one, i.e. the rate of 150 stock is less than the rate of 60 stock and 40 stock. While the molar volume variation with temperature show that the rate of volume change with temperature of 40 stock is greater than the 60and 150 stocks. Comparison between the result of base oil +additives from Al -Dura refinery shows different in the results. This is may be due to the nature additive used.

The use of poly –isoprene is to identify if the polymer will decrease or increase the thermal expansion value of base oil.

4.1.1.1 Effect of temperature on 40 stocks:

Tables (4.15) shows the experimental works and results and figures4.1 and 4.2 represent the results graphically. From the results one can obtain a good correlation which satisfies the results obtained for density and for molar volume by fitting the results.

A. Density correlation:

$$\rho = a + b \times T \qquad \ldots(4.1)$$

B. Molar volume correlation:

$$V = a + b \times T \qquad \ldots(4.2)$$

The coefficient of the above equations is shown in the table (4.1) and (4.2):

Table 4.1 The Coefficient Of Equations (4.1) and (4.2) For Stock 40.

property	Coefficient (a)	Coefficient (b)
density	0.8625	-0.000636
Molar volume	165.551	0.13368

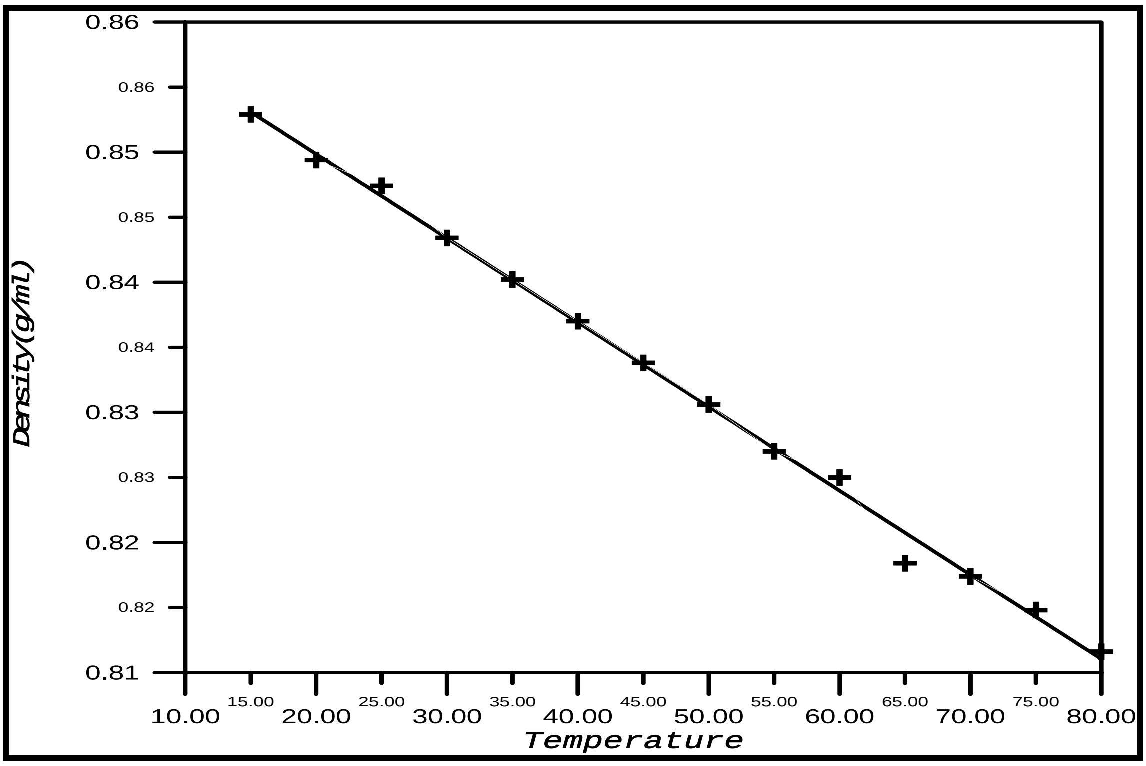

Figure 4.1 Density(gm/ml) Of 40 Stock Variations With Temperature °C.

The density of stock 40 at reference temperature (15 °C) is 0.8529 (g/cm^3) and molar volume is 167.645 (ml/mol.). When the density begins to decrease through heating, the molar volume increases. The rate of decrease is remains constant through heating. So the results appear to be linear variation as shown in figures 4.1and 4.2.

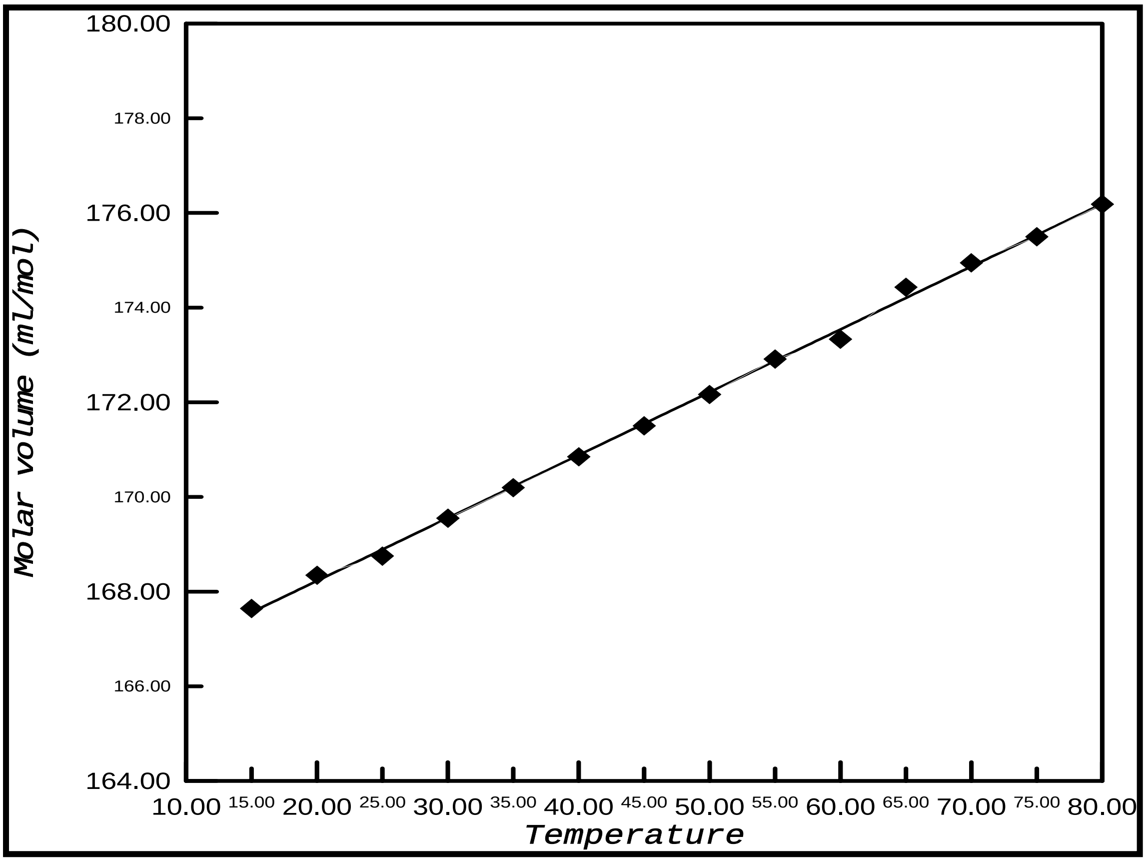

Figure 4.2 Molar Volume(ml/gm) Of 40 Stock Variations With Temperature °C

4.1.1.2 Effect of temperature on 60 stock:-

Table 4.16 shows the experimental results of the work and figures 4.3 and 4.4 represent the effect graphically. From the results a good correlation can be obtained which satisfies the variation for density and for molar volume by fitting .the coefficient of Eq.(4.1)and (4.2) are shown in Table (4.2). Figures 4.3and 4.4 shows the variation of density and molar volume with temperature.

Table 4.2 The coefficient of equation (4-1) and (4.2) for stock 60**.**

Property	Coefficient (a)	Coefficient (b)
Density	0.86407	-0.0005963
Molar volume	213.059	0.159629

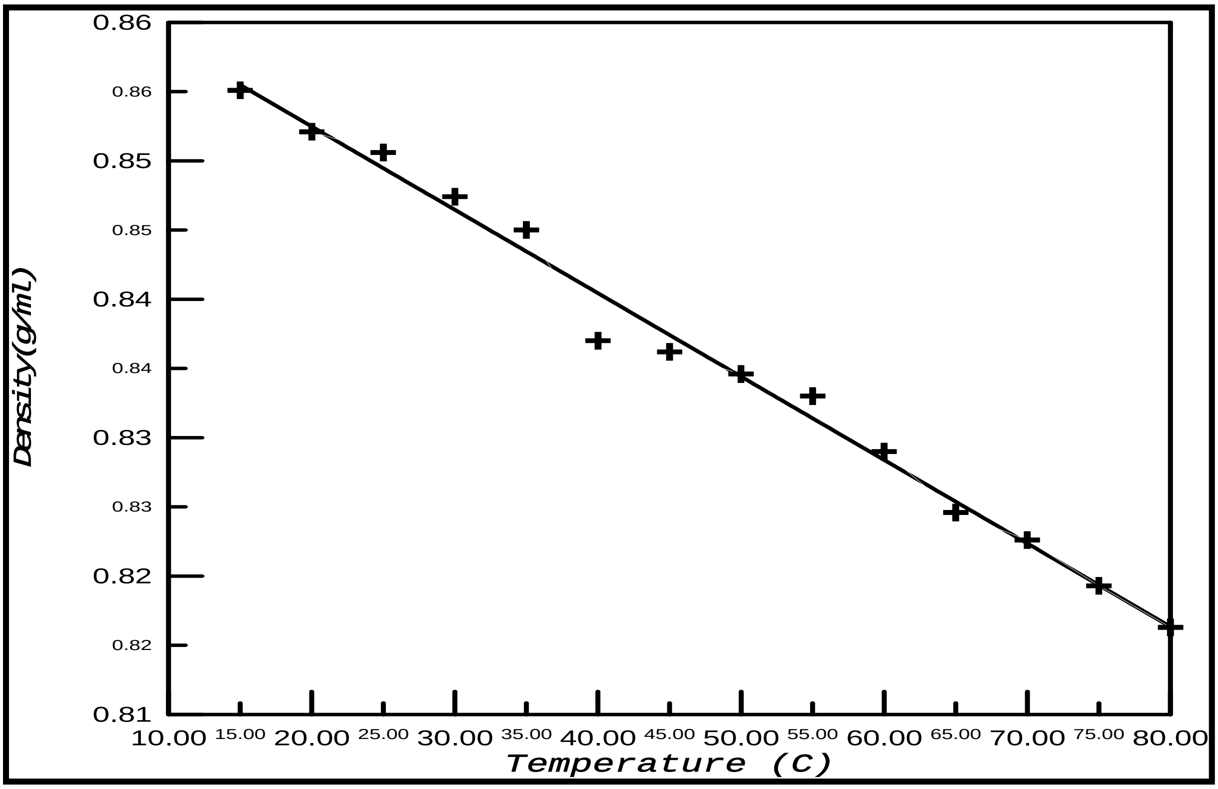

Figure 4.3 Density (g/ml) Of 60 Stock Variation With Temperature °C.

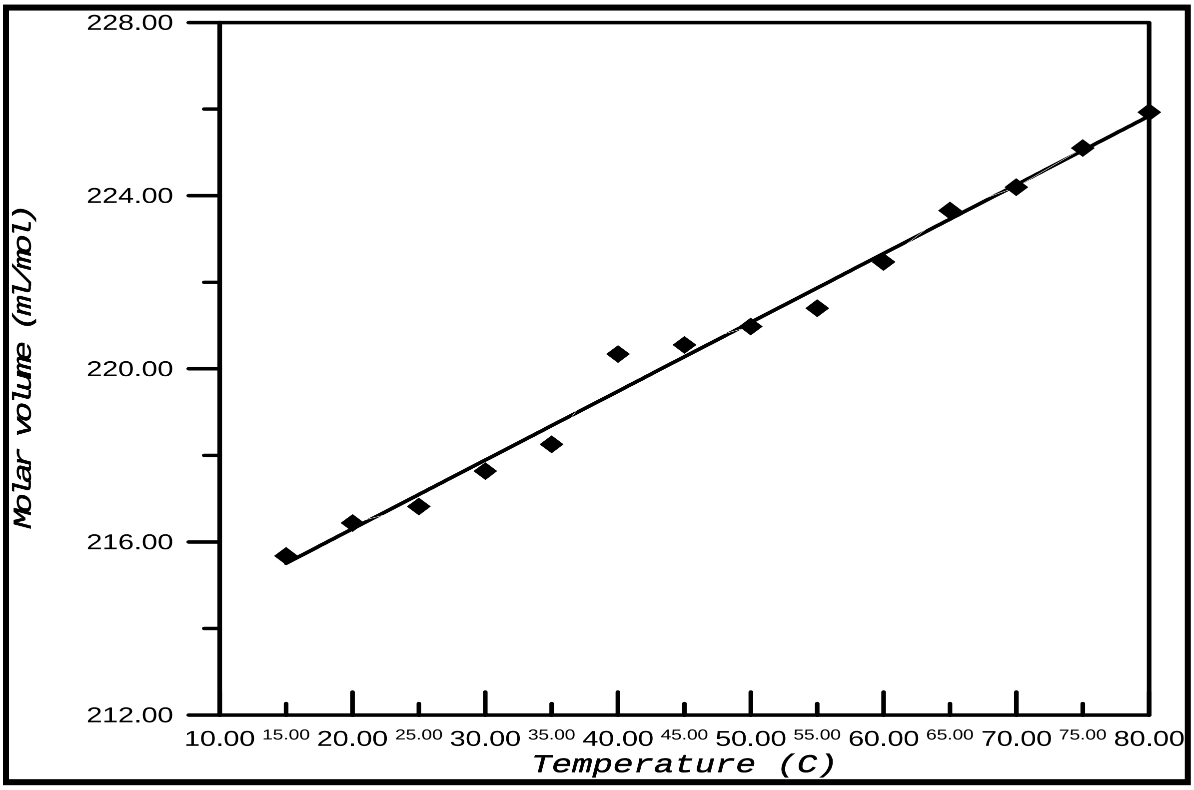

Figure4.4 Molar Volume (ml/gmol) Of 60 Stock Variation With Temperature °C.

The density of stock 60 at reference temperature (15 ^oC) is 0.8551 (g/cm^3) and molar volume 215.6765 (ml/mol.). When the density begins to decrease through heating, the molar volume increases. The rate of decrease remains constant through heating. Also the results show to be linear variation as shown in figures 4.3 and 4.4.

4.1.1.3 Effect of temperature on 150 stock :

Table 4.17 shows the experimental result of stock 150 and figures (4.5) and (4.6) illustrate the variation graphically. From the result one can find a good correlation for density and for molar volume by fitting our result as shown in figure (4.5) and (4.6).The coefficient of equations4.1 and 4.2 is shown in the table (4.3)

Table 4.3 The Coefficient Of Equation (4.1) And (4.2) For Stock 150.

property	**Coefficient (a)**	**Coefficient (b)**
density	0.9627	-0.00059066
Molar volume	196.697	0.1286

The density of stock 150 at reference temperature (15 ^oC) is 0.9538 (g/cm^3) and molar volume is 198.7135 (ml/mol.). When the density begins to decrease through heating, the molar volume increases.

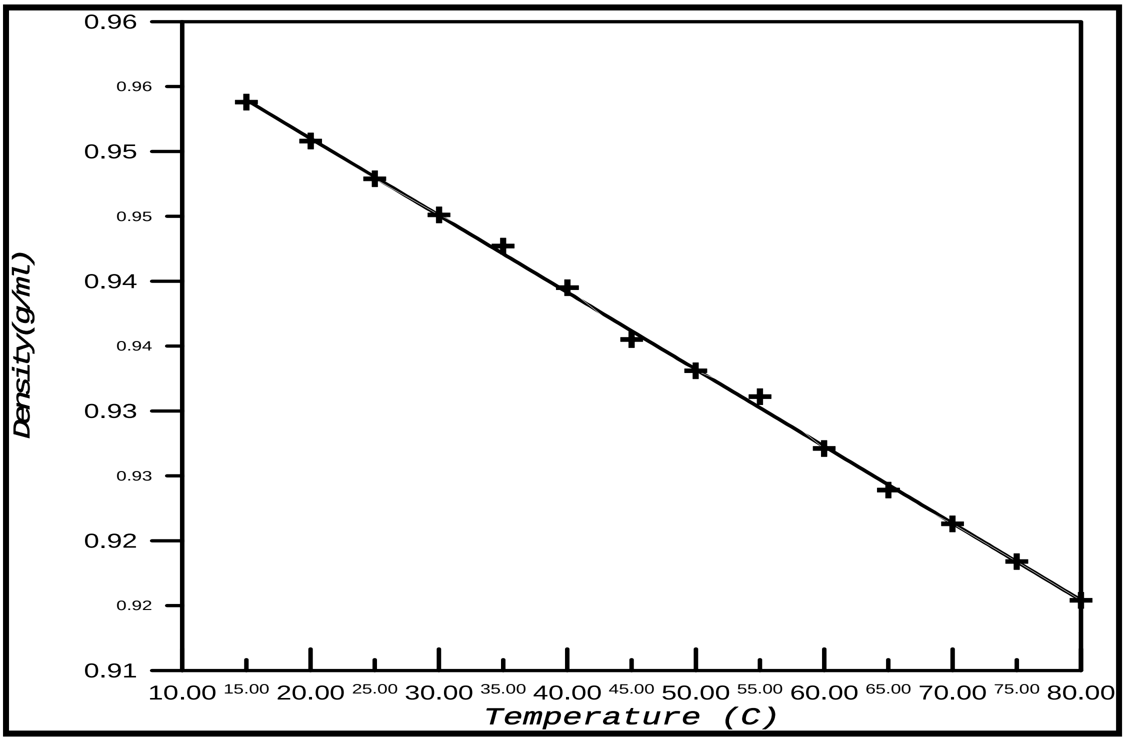

Figure 4.5 Density(g/ml) of 150 Sock Variation with Temperature °C.

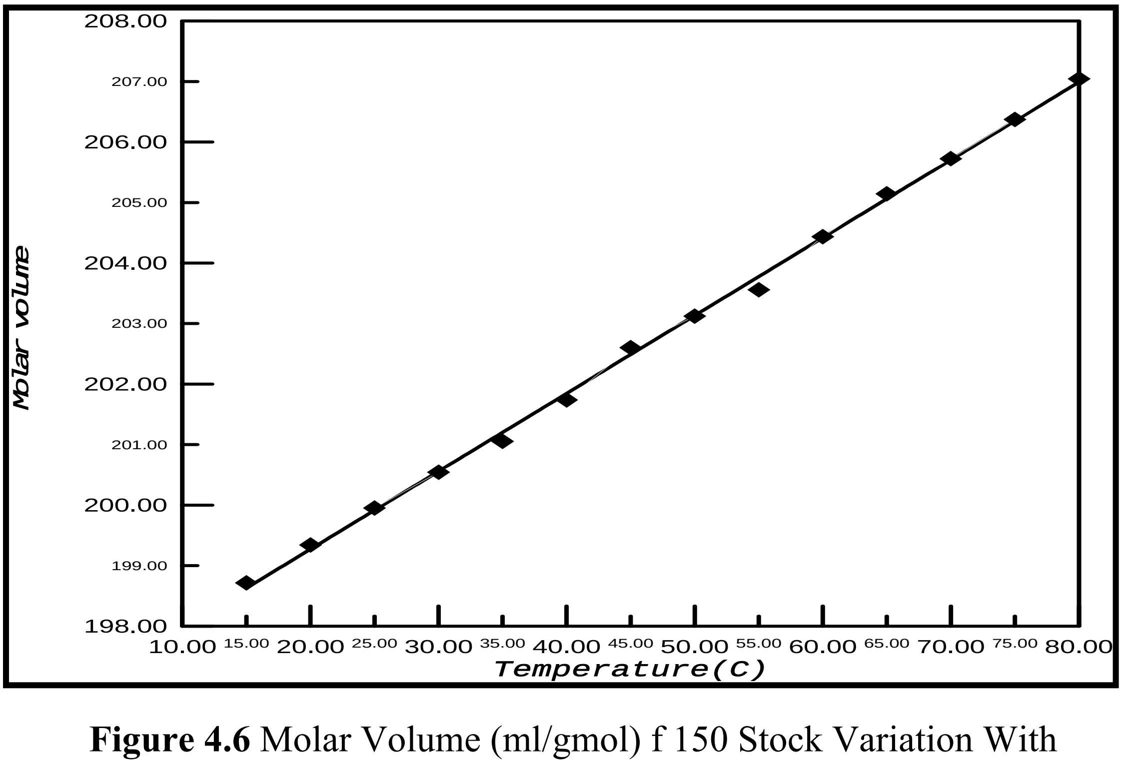

Figure 4.6 Molar Volume (ml/gmol) f 150 Stock Variation With Temperature °C.

4.2Thermal expansion of base oil:-

From the experimental results, after calculating the thermal expansion coefficient of the three basic oils it can be seen that the 40stock which is the lighter one has expansion coefficient higher than the heaviest one which is 150 stock, i.e.the thermal expansion of 40 stock is higher than 60 and 150 stocks respectivey.

4.2.1 Thermal expansion of 40 stock:

The thermal expansion coefficient for stock 40 are shown in the table 4.15 and graphically in the figure (4.7). A good correlation is obtained by fitting the data.

The correlation is of the form:-

$$\alpha = a + b \times T \quad \ldots(4.3)$$

Table 4.4 The Coefficient of Equation (4.3) for Stock 40.

cofficient	**a**	**b**
value	**0.000736288**	**5.94848×10^{-7}**

The theraml expansion of stock 40 is at ref. temperature which is 15^{o}C is 7.4561×10^{-4} k^{-1} , and the increasing of thermal expansion is postive so the increase in temperature increases in thermal expansion coefficient and also the increase is constant through the heating. So the result show a linear variation as shown in fig.(4-7).

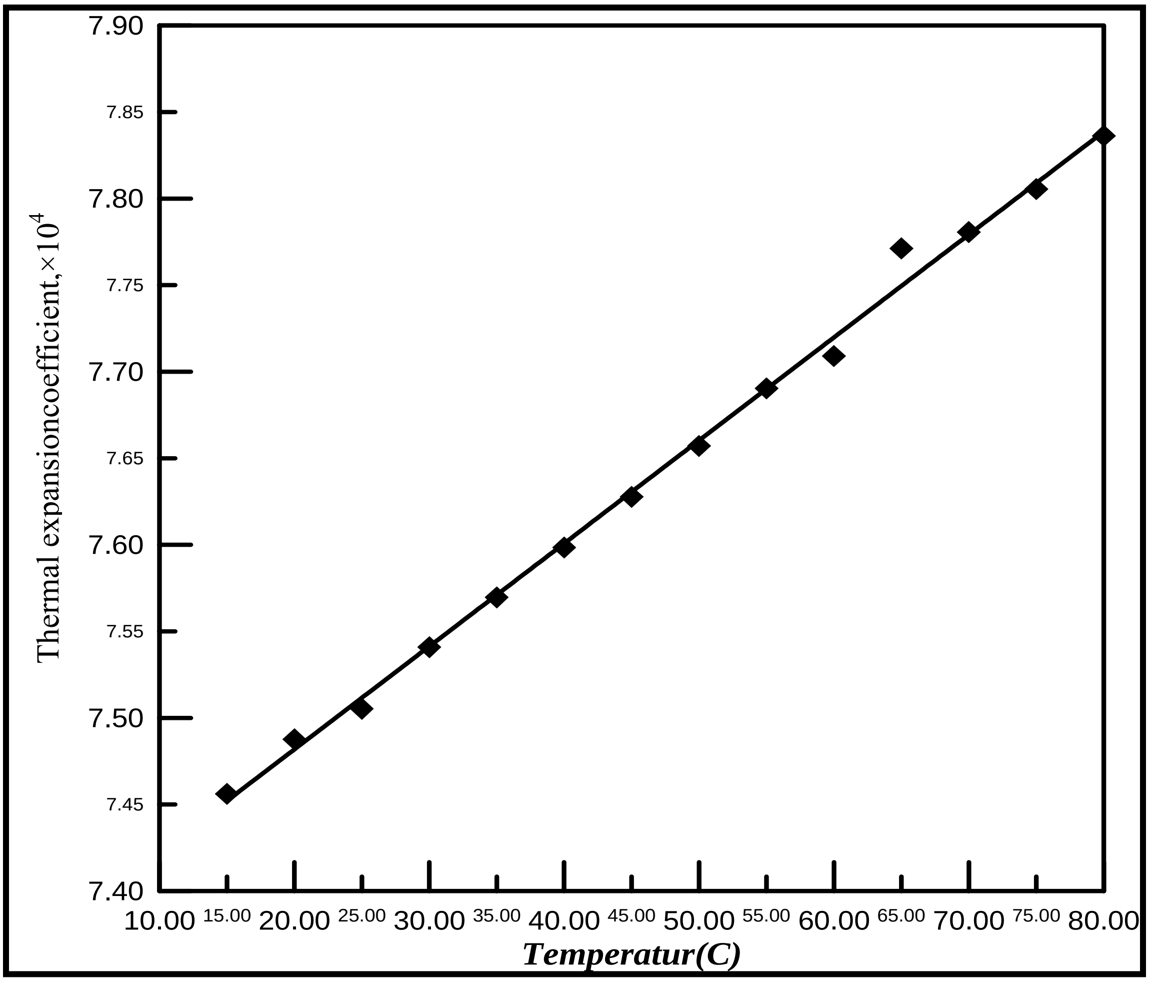

Figure 4.7 Thermal Expansion of stock 40 Variations with Temperature °C.

4.2.1 Thermal expansion of 60 stock:

The thermal expansion variation with temperature are shown in table (4.16) and graphically as shown in the figure 4.8. the correlation fitting the data is of form of Eq.(4.3). the coefficient of eq. (4.3) are in Table 4.5.

Table 4.5 The Coefficient Of Equation (4.3) For Stock 60.

cofficient	**a**	**b**
value	**0.000689481**	**5.09385×10^{-7}**

The theraml expansion of stock 40 at 15°C is 7.4561×10^{-4} K^{-1} , and the increase of thermal expansion is postive so the increasing temperature gives an increase in thermal expansion and the increasing is constant through heating. So the result shows a linear variation as shown in Fig.(4.7)

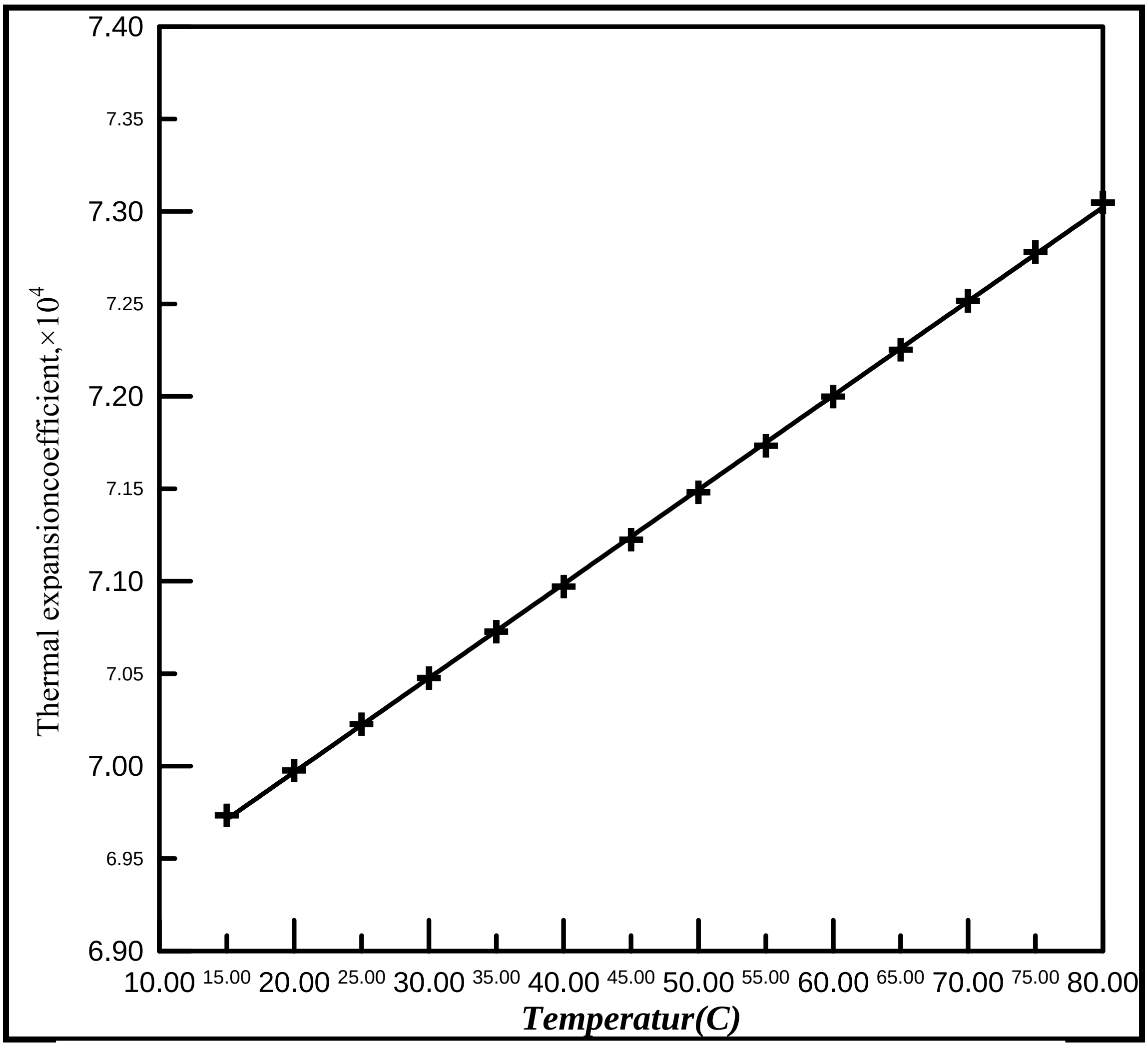

Figure 4.8 Thermal Expansion Variation of stock 60 with Temperature °C.

4.2.1 Thermal expansion of 150 stock:

The thermal expansion coefficient variation with temperature of stock 150is presented in table (4.17) and graphically in the figure (4.6). the coefficient of Eq.(4.3) for stock 150 are given in table 4.6.

Table 4.6 The Coefficient of Equation (4.3) for Stock 150.

Cofficient	**a**	**b**
Value	0.00061313	3.96088×10^{-7}

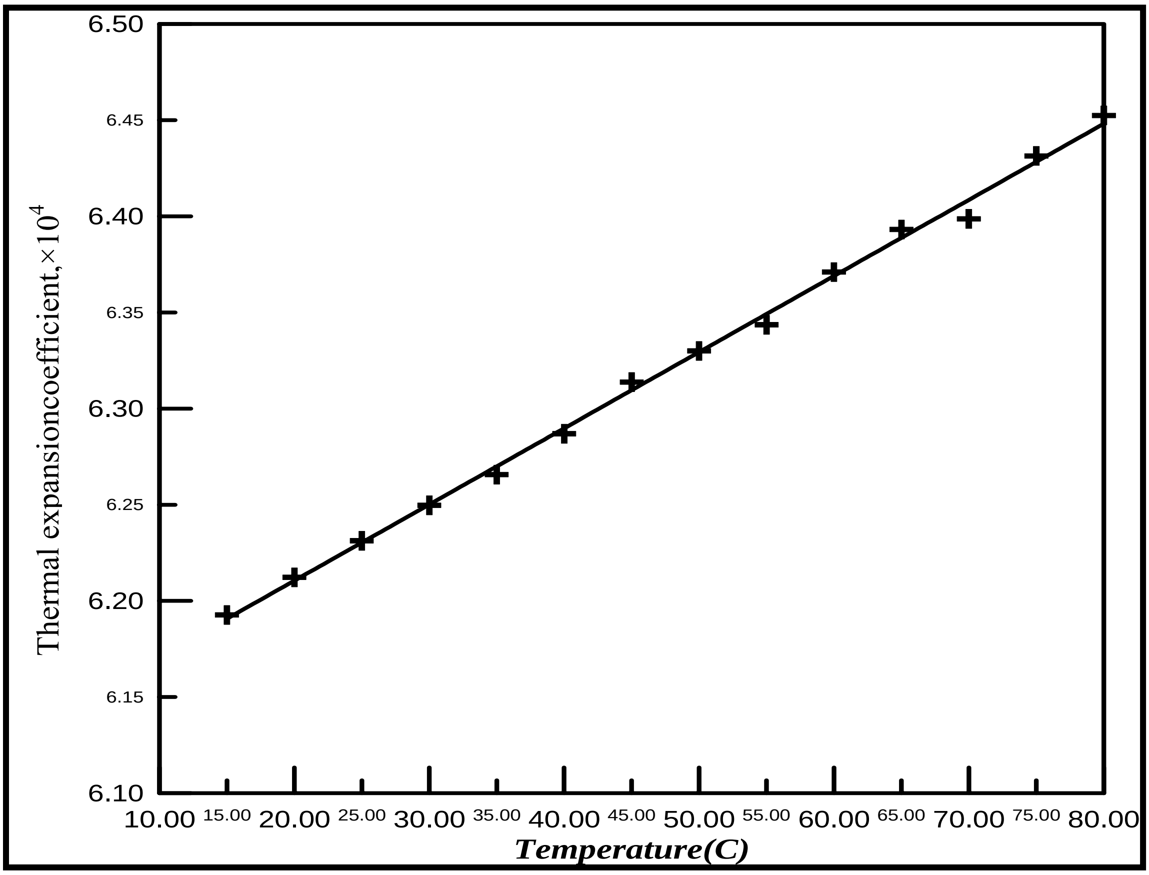

Figure 4.9 Thermal Expansion Variation of Stock 150 with Temperature °C.

The theraml expansion coefficient behaivor is as that of stock 40 and 60. The results show that the thermal exapnsion coefficent of base oil (pure) , i.e. the lighter one which is stock 40 has thermal exapnsion value more than that for the stock 60 and 150 respectively. This staisfis the equation used for calculation.

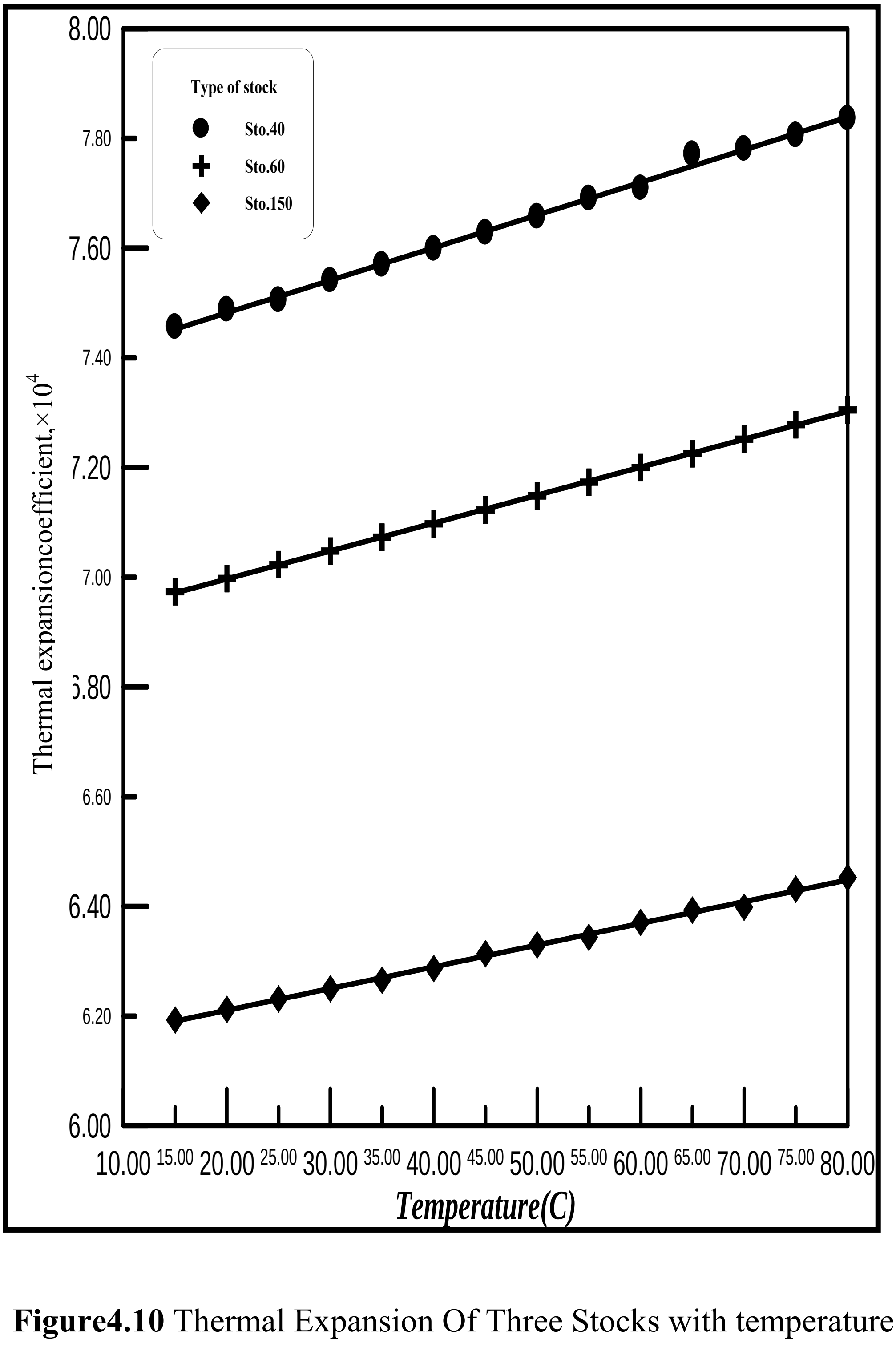

Figure4.10 Thermal Expansion Of Three Stocks with temperature ^{o}C.

4.3Effect of temperature on base oil and additives from Al-Dura Refinery:-

4.3.1 Effect on density:-

Table (4.21) shows the results of density variation with temperature. Figure (4.11) shows the result graphically. By fitting the results gives a good correlation for density as shown:

$$\rho = a + b \times T \qquad \ldots(4.1)$$

Table 4.7 The Coefficient Of equation (4.1)For Base Oil From Al Dura Refinery With Additive **.**

cofficient	**a**	**b**
value	**0.90491**	**0.00055309**

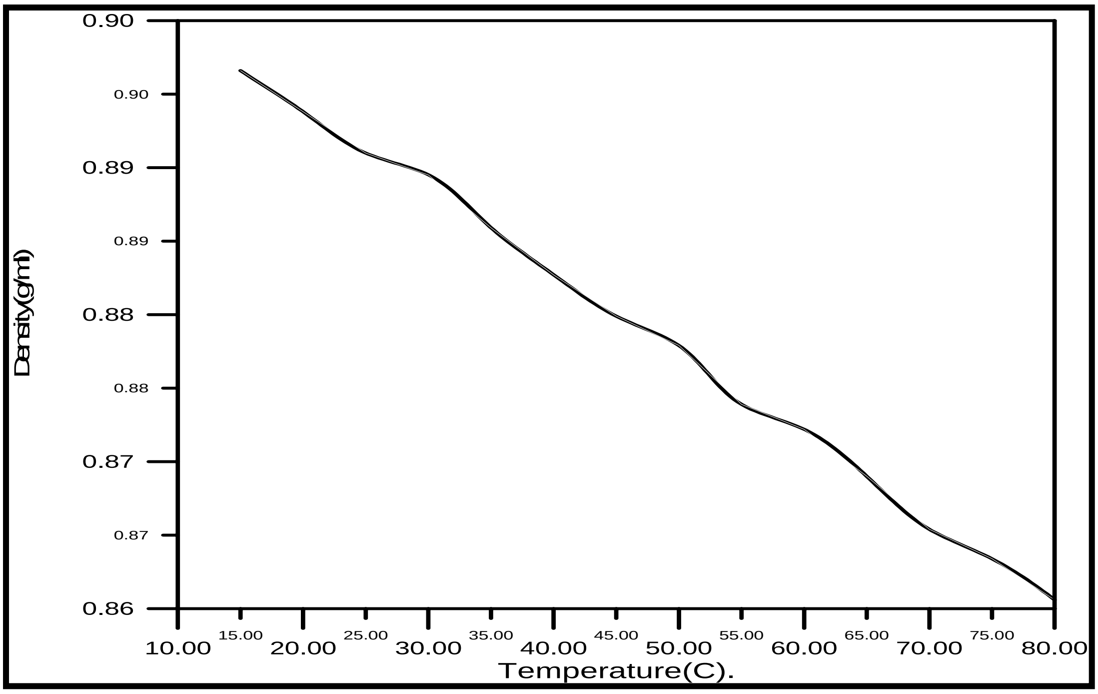

Figure 4.11 Density Variation with Temperatur of Base oil +additives from Al-Dura Refinery.

4.3.2 Thermal expansion coefficient:-

Table (4.21)shows the result of coefficient of thermal expansion coefficient. Figure 4.12 shows the results graphically.

$$\alpha = a + b \times T \qquad \ldots(4.3)$$

Table 4.8 The Coefficient Of Equation (4.3)For (Base oil+additives) From Al Dura Refinery.

cofficient	**a**	**b**
value	**0.0006107**	**3.96×10^{-7}**

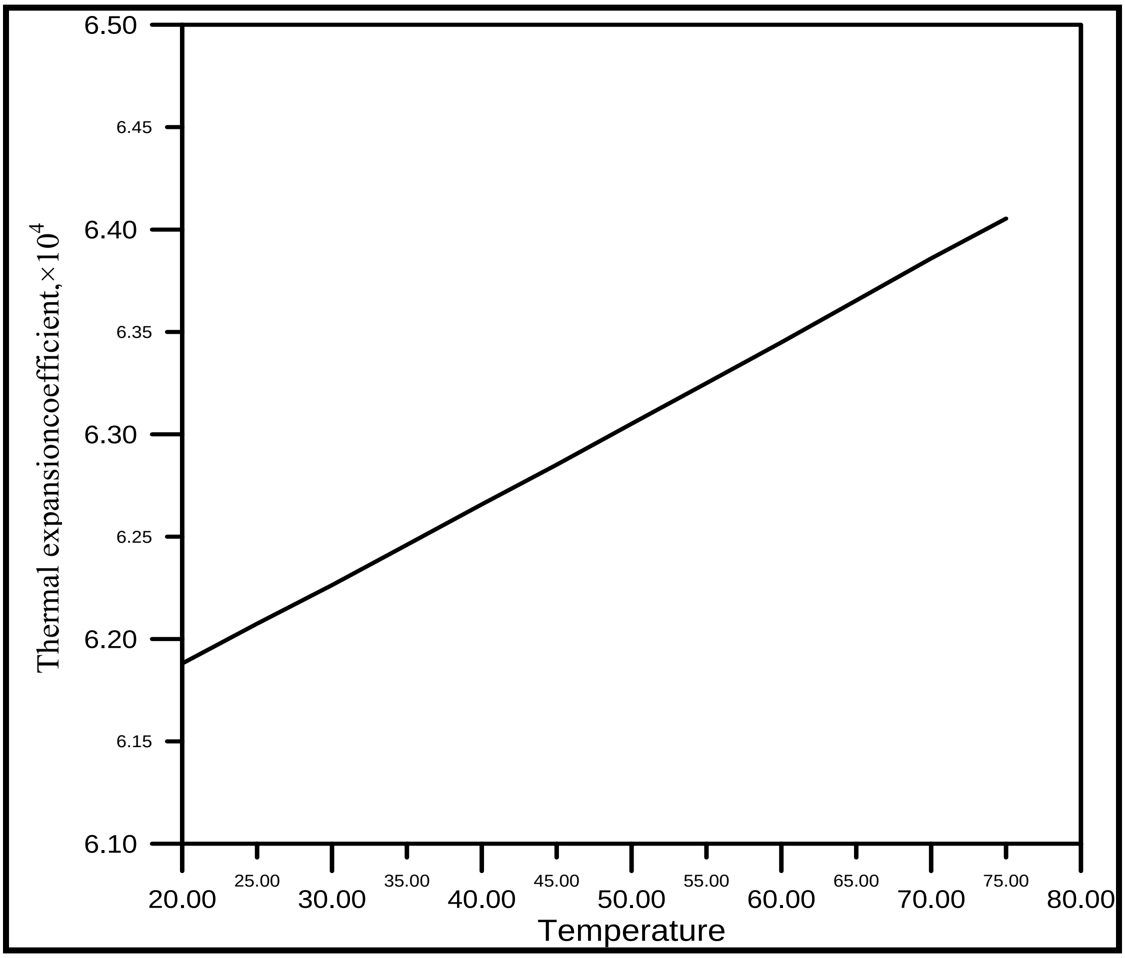

Figure 4.12 Variation of Thermal Expansion Variation with Temperatur Of (base oil +additives)From Al-Dura Refinery with Temperatue ^{o}C .

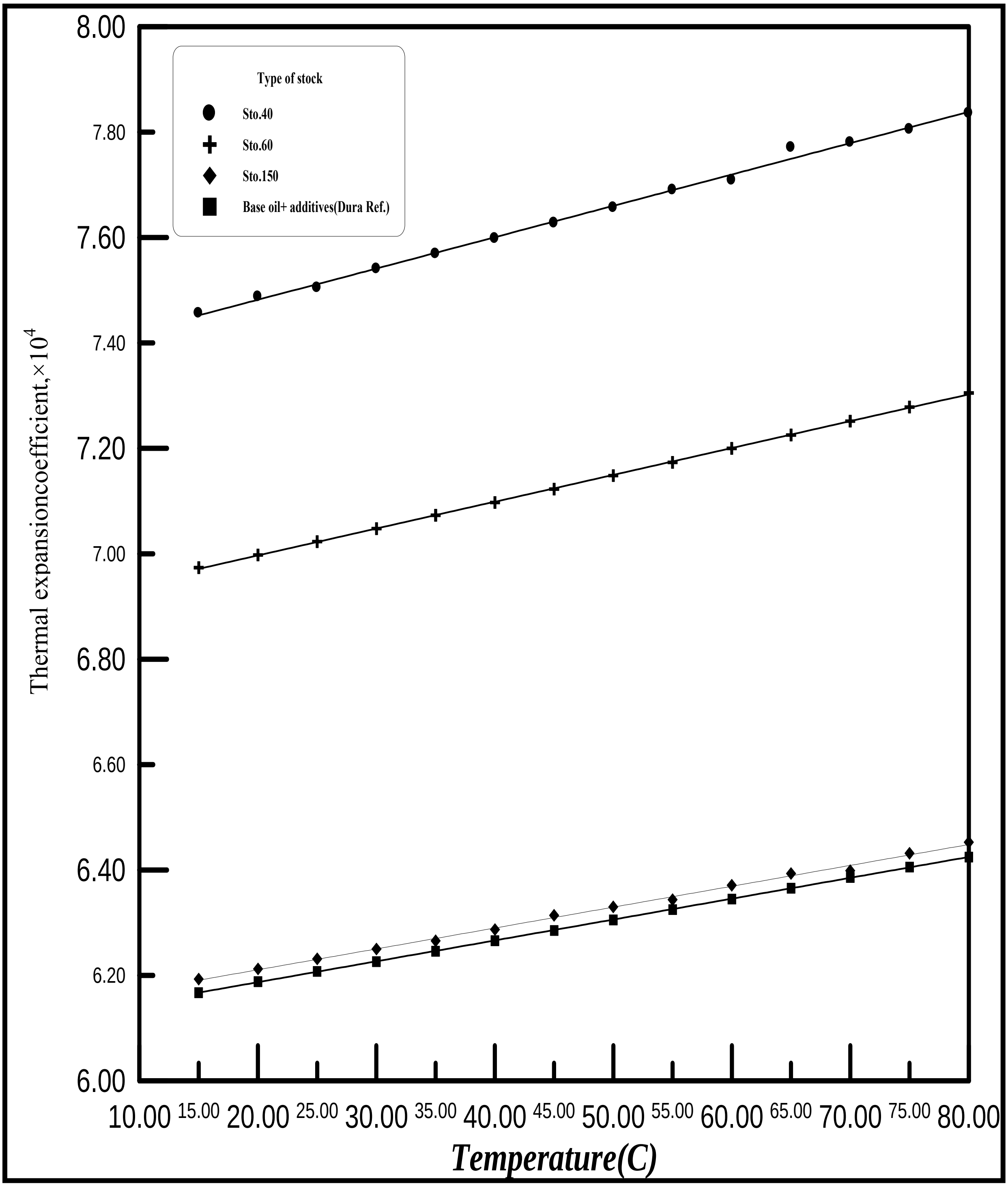

Figure4.13 Variation of Thermal Expansion with Temperatur of Base (oil +additives from Al-Dura Refinery And Three Types of Basic Stock.

The thermal expansion of base oil +additives is at ref. temp. 6.1671×10^{-4} .that means it is less than the theraml expansion coeefficient of pure basic stock as shown in figure (4.13).

4.4Properties of Oil Stocks after Blending :-

The density and molar volume of the basic oil stock afterblending the polymer with the polyisoperne are determined by the same procedure before blending.

4.4.1Density of stock 40 with 4% polyisoperne:

The density distribution with temperature is recorded in the table (4.4).The results are shown graphgially in figure (4.18). it is satisfies Eq.(4.1) .

Table 4.9 The Coefficient of Equation (4.1) for Stock 40 with 4% Poly isoprene After Blending.

cofficient	**a**	**b**
value	0.82227	-0.0006619

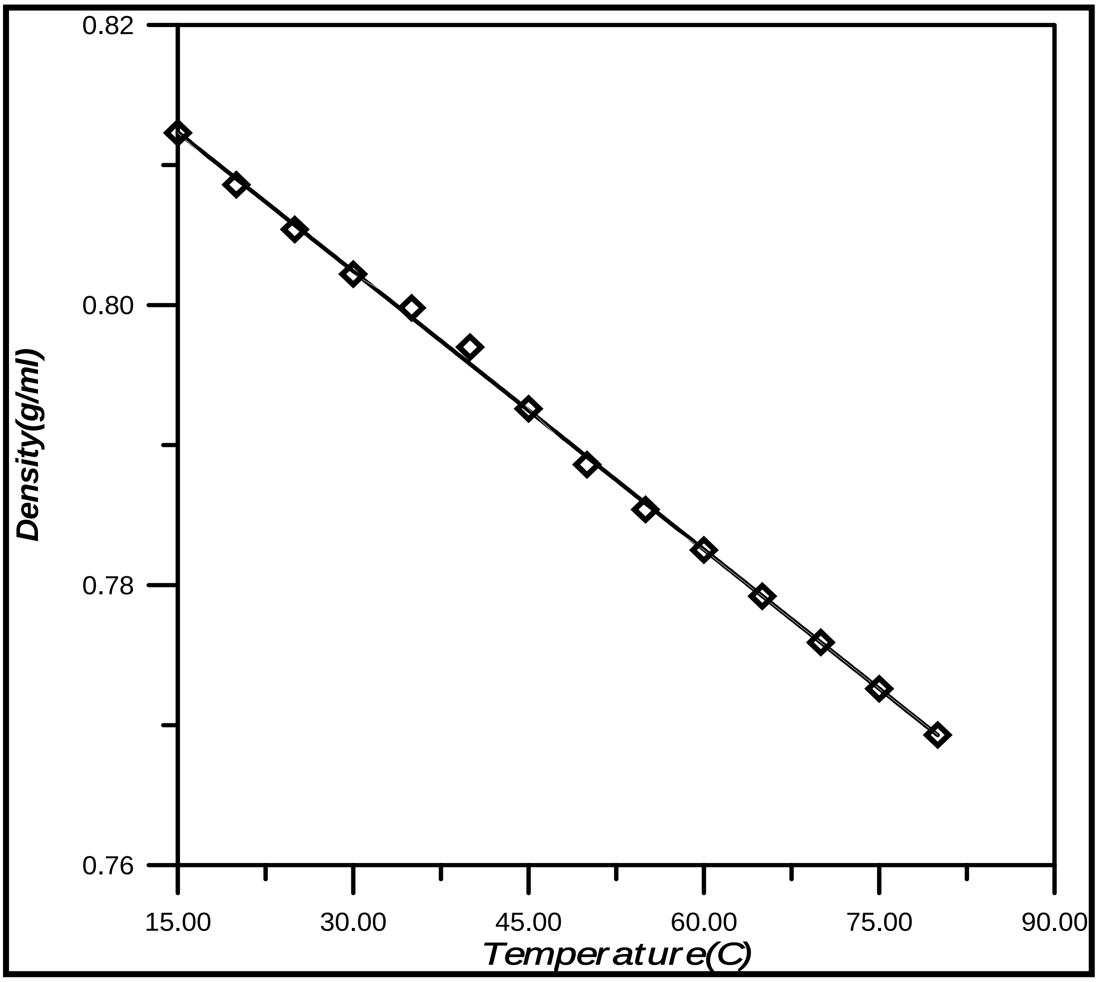

Figure 4.14 Density(g/ml) Of Stock 40 With 4% Poly-isoperne Variation With Temperature °C.

The density of stock 40 at ref. temp.0.8123g/cm^3 which less than the density before blending so the poly isoperne decrease the density of stock 40. and also the decresing rate is constant through the heating. So the result exhibt linear in variation.

4.4.2Density of stock 60 with 4% polyisoperne:

The density distribution with temperature is recorded in table (4.5)and shown graphgially in the figure (4.19).

Table (4.10) The Coefficient Of Equation (4-13)For Stock (60+4%Polyisopene).

cofficient	**a**	**b**
value	**0.828442**	**-0.000680505**

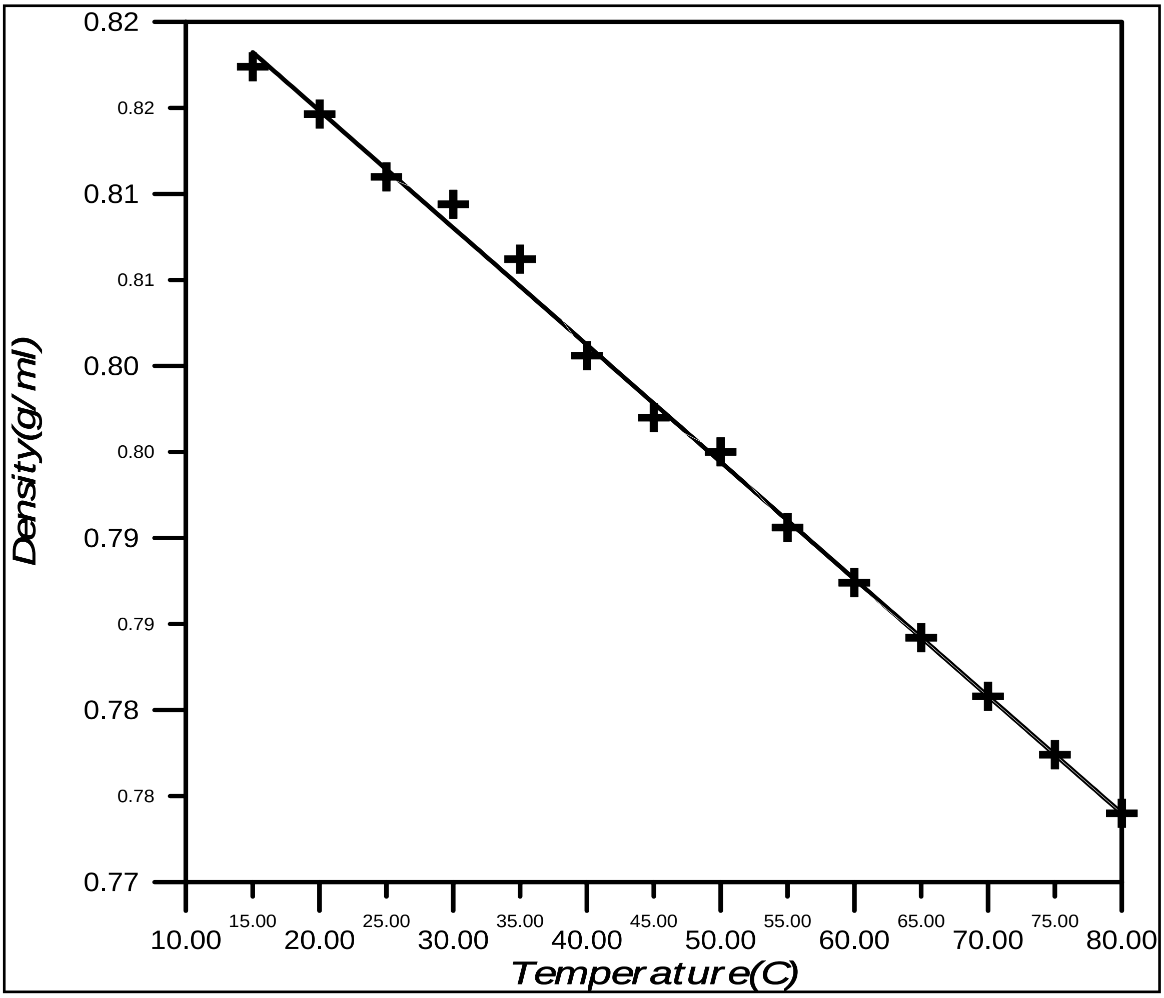

Figure 4.15 Density Variation With Temperature For Stock 60 With 4%Poly- isoprene.

4.4.3 Density Of stock 150 with 4%poly isopene :-

The density coefficients are listed in the table 4.11. The results is shown graphgially in figure 4.20. A good correlation is obtained .

Table 4.11 The Coefficient of Equation (4.1) For Stock 150 +4% Poly -isoprene .

cofficient	**a**	**b**
value	0.895947	-0.00060712

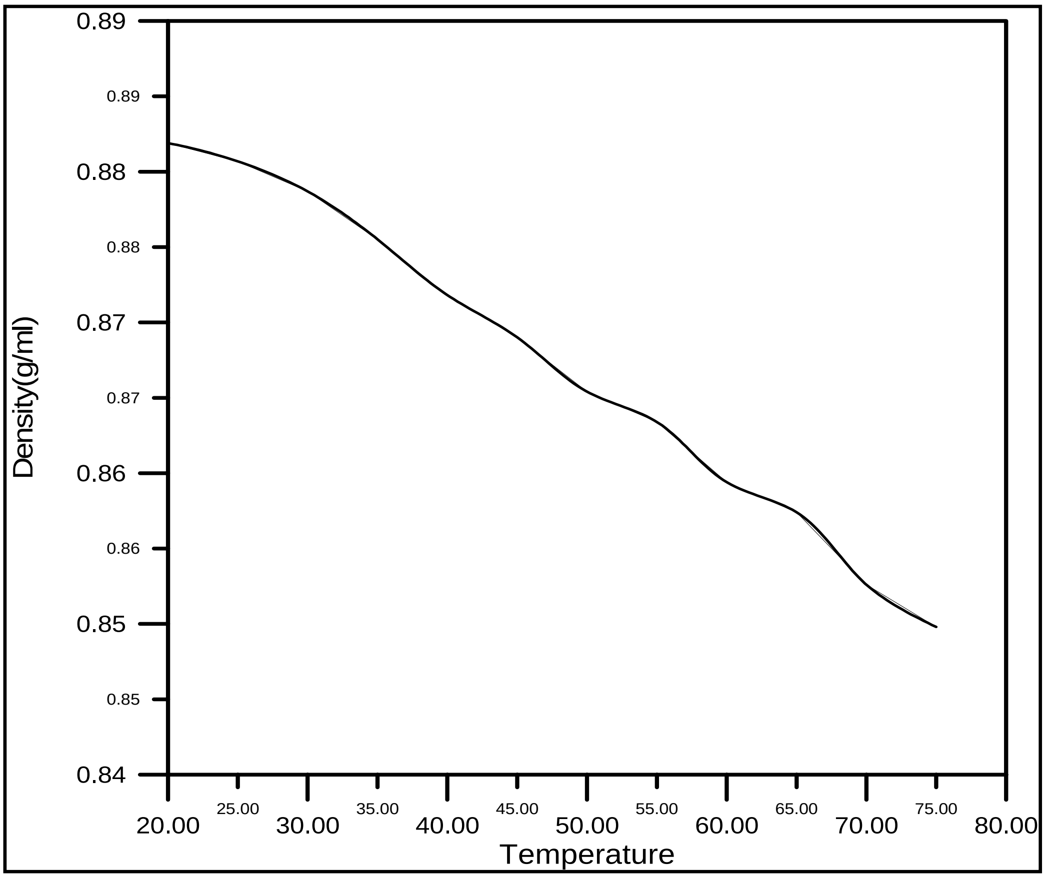

Figure 4.16 Variation of Density of Stock150+4%Polyisopene with Temperature ^{o}C.

4.5Thermal Expansion of Basic Stock After Blending :-

Thermal expansion of stock 40 and 60 after blendinding are calculated the experimental result are tabulated and represent the effect the of poly isoperne by plotting the result graphially and get a good agreement corrleation for the result obtained.

4.5.1 Thermal Expansion of Stock 40 with 4% Polyisoperne:

The results obtained are tabulated in table (4.18)and represented graphgially as shown in figure 4.12. Eq.(4.3) fits the data.

Table 4.12 The Coefficient Of Equation (4.3)For Stock 40 With 4%Poly- isoprene .

Cofficient	**a**	**b**
Value	0.000803784	7.00694×10^{-7}

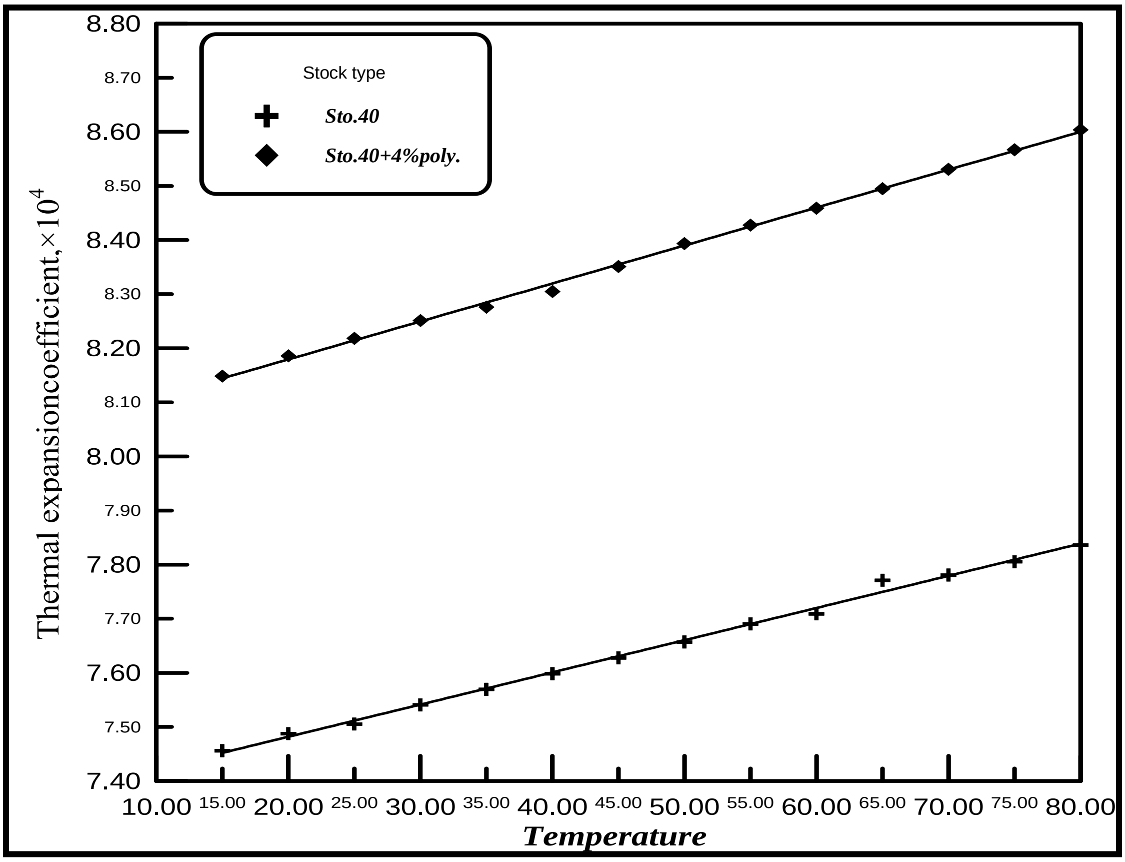

Figure 4.17 Variation of Thermal Expansion Of Stock 40 With4% Poly- isoprene With Temperature.

The thermal expansion coefficient of stock (40 +additves) is $(8.1484\times10^{-4})K^{-1}$. The theraml expansion of stock 40 with 4% poly isoperne is higher than the thermal expansion coefficient of stock 40

4.5.2Thermal expansion of 60 stock with 4% polyisoperne:-

The experimental work are tabulated in table 4.19 and represented graphically in fig. 4.13.

Table 4.13 The coefficient of equation (4.3)for stock 60 after blending**.**

cofficient	**a**	**b**
value	**0.0008199**	**7.3087×10^{-7}**

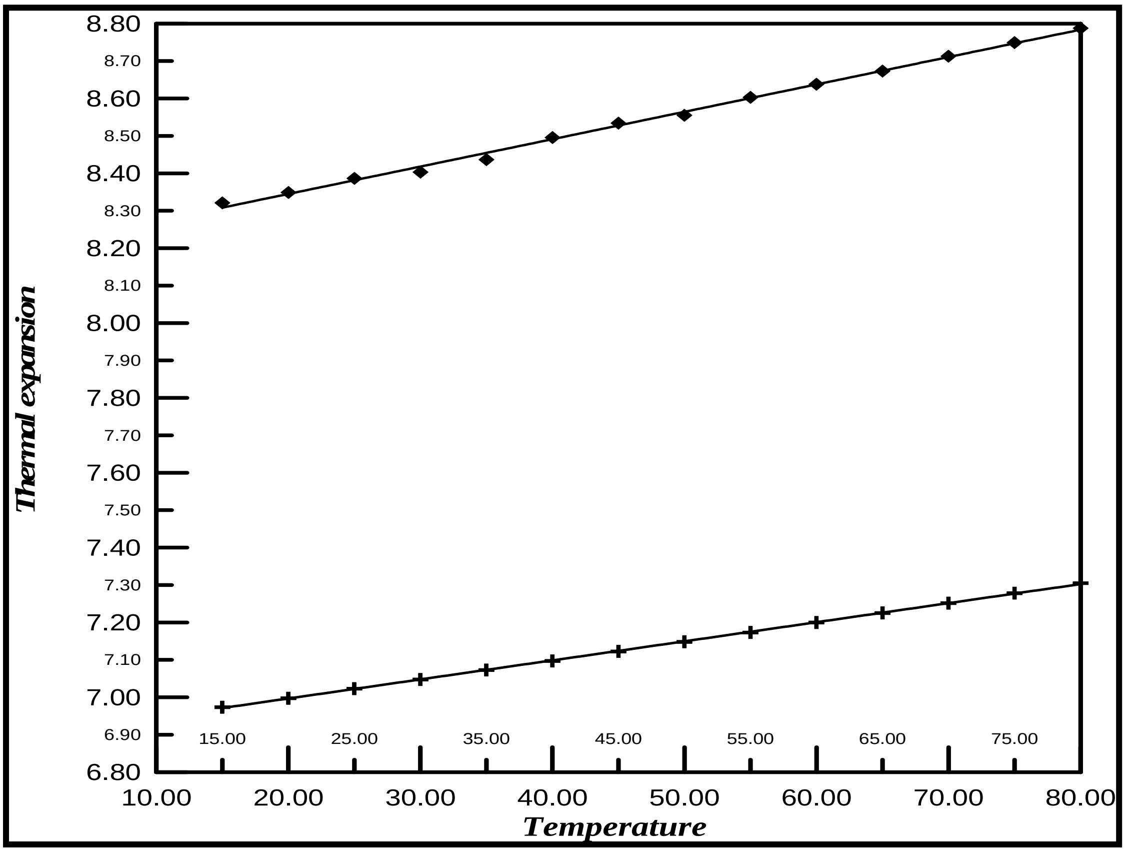

Figure 4.18 Variation Of Thermal Expansion Of Stock 60 With 4%Polyisoperne With Temperature ^{o}C**.**

The thermal expansion coefficient of stock (60 +additves) is $(8.3212\times10^{-4})k^{-1}$. The theraml expansion of stock 60with 4% poly isoperne is higher than the thermal expansion coefficient of stock 60

4.5.3 Thermal expansion of 150 stock and 4%poly isoperne :-

The experimental result are tabulated in table (4.20) and the result represented graphically in the figure (4.13).

.

Table4.14 The Coefficient Of Equation (4.3) For Stock 150 After Blending**.**

cofficient	**a**	**b**
value	0.000677136	4.8895×10^{-7}

The thermal expansion coefficient of stock (150 +additves) is $(6.8458.3212\times10^{-4})k^{-1}$. The theraml expansion of stock 150 with 4% poly isoperne is higher than the thermal expansion coefficient of stock 150

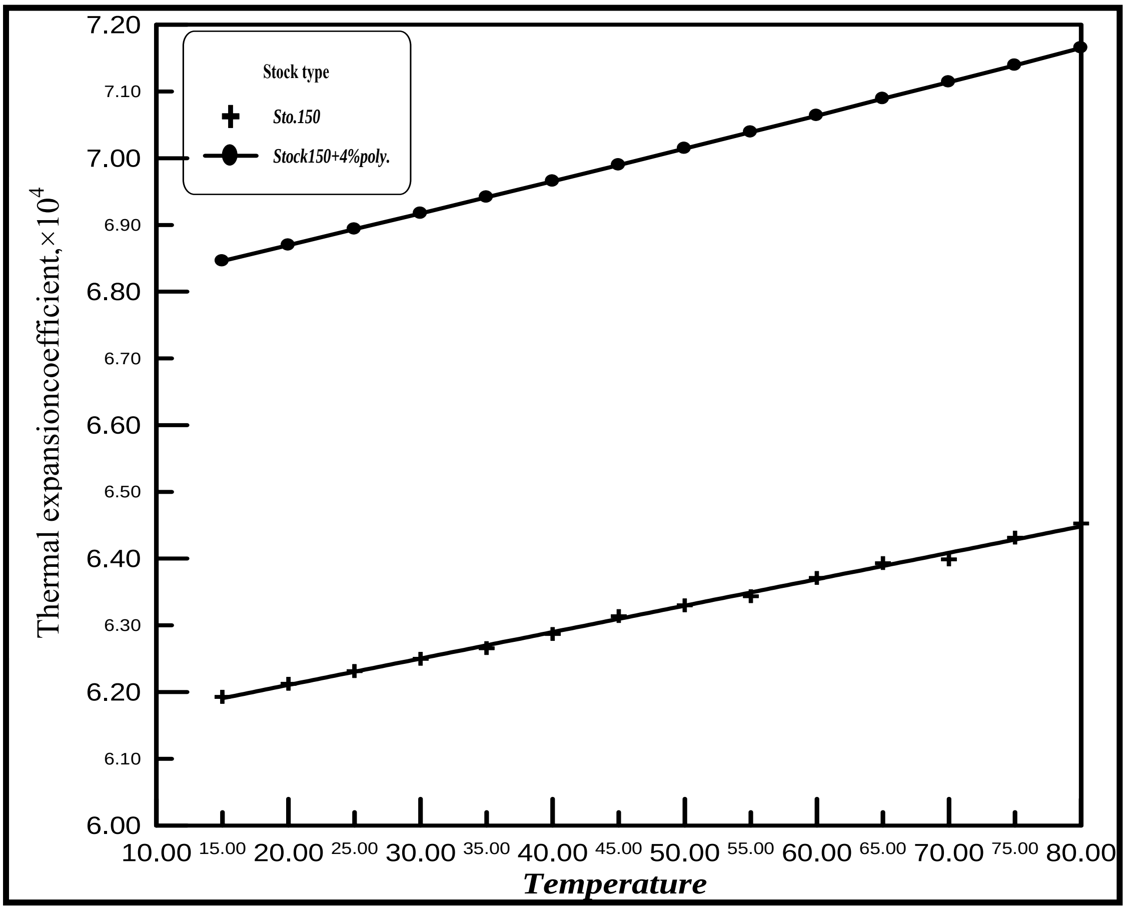

Figure 4.19 Variation Of Thermal Expansion Of Stock 150 With 4%Polyisoperne With Temperature.

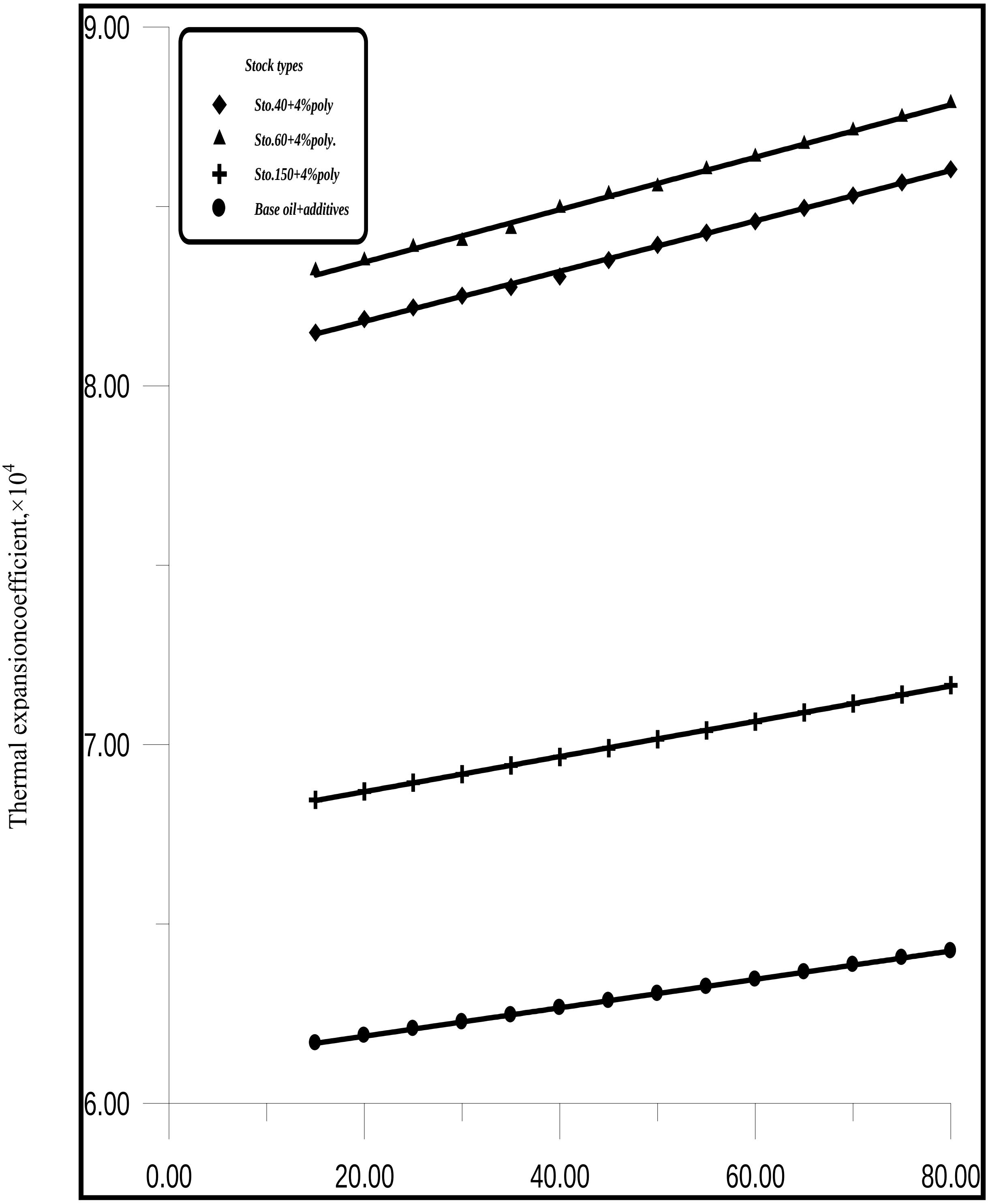

Figure4.21 The Effect Of Poly-isoperne On The Thermal Expansion Of Three Base Oil And Compared With Base Oil +Additives.

4.6Results of base oil

Tables 4.15 to 4.21 list the experimental results of base oil for the three stocks with and with out additives.

Table 4.15 Properties Of 40 Stock.

No.	Temperature(°C)	Density (g/cm^3)	Molar volume(cm^3)	Thermal expansion(α) ×10^4
1	15	0.8551	215.6765	6.9734
2	20	0.8521	216.4358	6.9976
3	25	0.8506	216.8175	7.0227
4	30	0.8474	217.6362	7.0476
5	35	0.8450	218.2544	7.0727
6	40	0.8370	220.3405	7.0971
7	45	0.8362	220.5513	7.1225
8	50	0.8346	220.9741	7.1481
9	55	0.8330	221.3985	7.1733
10	60	0.8290	222.4668	7.1999
11	65	0.8246	223.6538	7.2252
12	70	0.8226	224.1967	7.2516
13	75	0.8193	225.1006	7.2781
14	80	0.8163	225.9279	7.3049

Table 4.16 Properties of 60 Stock.

No.	Temperature (°C)	Density (g/cm^3)	Molar volume(cm^3)	Thermal expansion(α) ×10^4
1	15	0.8529	167.645	7.4561
2	20	0.8494	168.345	7.4876
3	25	0.8474	168.751	7.5053
4	30	0.8434	169.551	7.5409
5	35	0.8402	170.197	7.5696
6	40	0.8370	170.848	7.5985
7	45	0.8338	171.503	7.6277
8	50	0.8306	172.164	7.6571
9	55	0.8270	172.914	7.6904
10	60	0.8250	173.333	7.7090
11	65	0.8184	174.431	7.7712
12	70	0.8174	174.944	7.7807
13	75	0.8148	175.496	7.8055
14	80	0.8116	176.184	7.8363

Table 4.17 Properties of 150 Stock.

No.	Temperature (^oC)	Density (g/cm^3)	Molar volume(cm^3)	Thermal expansion(α) ×10^4
1	15	0.9538	198.7135	6.1927
2	20	0.9508	199.3405	6.2122
3	25	0.9479	199.9504	6.2312
4	30	0.9451	200.5427	6.2497
5	35	0.9427	201.0533	6.2656
6	40	0.9395	201.7381	6.2869
7	45	0.9355	202.6007	6.3138
8	50	0.9331	203.1218	6.3300
9	55	0.9311	203.5581	6.3436
10	60	0.9271	204.4360	6.3710
11	65	0.9239	205.1444	6.3931
12	70	0.9213	205.7234	6.3986
13	75	0.9184	206.3730	6.4314
14	80	0.9154	207.0443	6.4524

Table 4.18 Properties of 40 Stock With 4%Poly- isoperne.

No.	Temperature(^oC)	Density (g/cm^3)	Thermal expansion(α)
1	15	0.8123	8.1484
2	20	0.8086	8.1857
3	25	0.8054	8.2182
4	30	0.8022	8.2510
5	35	0.7998	8.2758
6	40	0.7970	8.3048
7	45	0.7926	8.3509
8	50	0.7886	8.3933
9	55	0.7854	8.4275
10	60	0.7825	8.4587
11	65	0.7792	8.4946
12	70	0.7759	8.5307
13	75	0.7726	8.5671
14	80	0.7693	8.6039

Table 4.19 Properties of 60 Stock With 4%Poly- isoperne.

No.	Temperature (^{o}C)	Density (g/cm^3)	Thermal expansion(α) ×10^4
1	15	0.8174	8.3212
2	20	0.8146	8.3493
3	25	0.8110	8.3869
4	30	0.8094	8.4035
5	35	0.8062	8.4368
6	40	0.8006	8.4958
7	45	0.7970	8.5342
8	50	0.7950	8.5550
9	55	0.7906	8.6033
10	60	0.7874	8.6383
11	65	0.7842	8.6735
12	70	0.7808	8.7113
13	75	0.7774	8.7494
14	80	0.7740	8.7878

Table 4.20 Properties of 150 Stock with 4%Poly- isoperne.

no	Temperature	Density (g/ml)	Thermal expansion (α) ×10^{-4}
1	15	0.8868	6.8458
2	20	0.8838	6.8694
3	25	0.8807	6.8936
4	30	0.8777	6.9171
5	35	0.8746	6.9416
6	40	0.8716	6.9655
7	45	0.8686	6.9896
8	50	0.8655	7.0146
9	55	0.8625	7.039
10	60	0.8595	7.0636
11	65	0.8564	7.0892
12	70	0.8534	7.1141
13	75	0.8504	7.1392
14	80	0.8473	7.1653

Table 4.21 Properties Of Base Oil +additives From Al -Dura Refinery.

no	**Temperature (^oC)**	**Density (g/ml)**	**Thermal expansion coefficient (α)×10^{-4}**
1	**15**	0.8966	6.1671
2	**20**	0.8938	6..1880
3	**25**	0.8910	6.2075
4	**30**	0.8895	6.2263
5	**35**	0.8859	6.2460
6	**40**	0.8827	6.2658
7	**45**	0.8799	6.2851
8	**50**	0.8779	6.3051
9	**55**	0.8738	6.3250
10	**60**	0.8722	6.3449
11	**65**	0.8690	6.3654
12	**70**	0.8654	6.3859
13	**75**	0.8634	6.4054
14	**80**	0.8606	6.4245

4.7 Thermal Expansion Correlation of Three Pure Base Oils:-

The general correlation obtained from the data can be applied for the three base oil namely 40, 60, and 150 stock oils by giving the temperature and the type of the base oil to obtain the thermal expansion value the valuesobtained from the correlation agree with experimental work figure 4.22 shows to the comparison.

The correlation is:-

$$\alpha = B1 + B2 \times T + B3 \times S^{B4} + B5 \times T^{B6} \qquad \text{...(4.4)}$$

Where (α) the thermal expansion coefficient and (T) the temperature in (^oC)and (S) is the type of stock and the (α)calculated from this equation in (K^{-1}). Where S takes the value of 40,60and 150 according to the type of stock.

Table 4.22 Coefficient Of Equation (4.4)

Coefficient	Value
B1	4.841907
B2	-0.477705
B3	19.25117
B4	-0.544311
B5	0.480288
B6	1.001061

The correlation is based on the experimental results which is measured in the laboratory. The correlation is very near to the experimental value with very small loss of (0.014060) and a variance of 0.99989. By denote the two parameters of temperature and the type of stock the thermal expansion coefficient of three stock can be calculated.

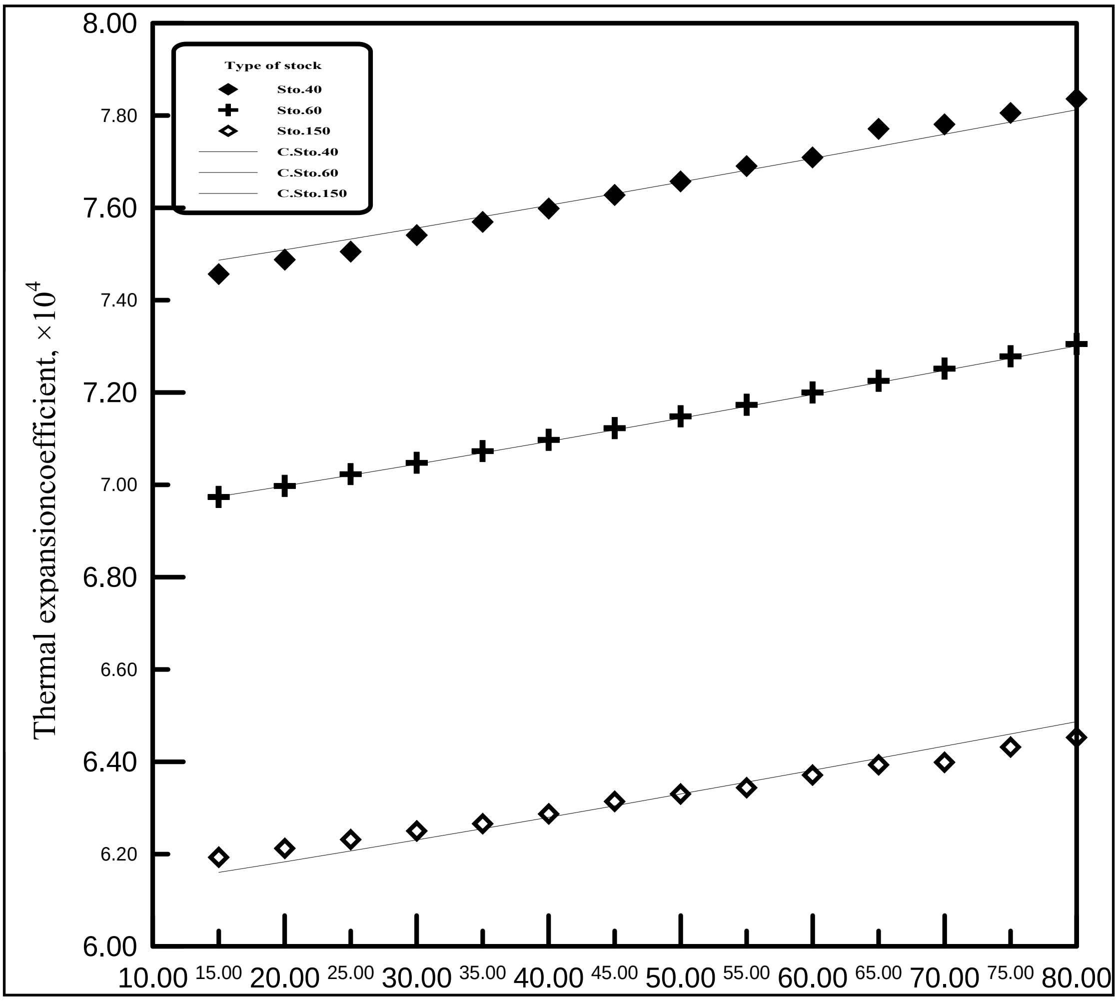

Figure 4.19 Show The Experimental Result Compared With Result Of The Correlation.

The correlation for three stock as compared with the experimental value is shown in figure 4.19.The thermal expansion of three stock from the experimental work is agree with to the correlation results obtained.

4.8 Discussion

The results show that the thermal expansion coefficients of pure base oil stock (40, 60,150) depends largely on their density. The results obtained indicate that the lighter base oil stock has thermal expansion value more than the heavy one. i.e., the thermal expansion of stock 40 is more than the stock 60, and 150 respectively.

The results of base oil that was blended with additives from Al – Dura refinery is less than the three base oil stocks. This is due to the addition of additives.

The decrease of density of three base oils during heating is constant. The variation of density with temperature to be linear. This is also noticed for base oil with additives.

The blending of polyisopenewith three stocks leads to increase the thermal expansion coefficient. The percent increasing of (α)due to the poly isoprene additives used is about 9% for stock 40,19%for stock 60, and 10%for stock 150.

The decrease of density during heating after blending was found to be constant. This leads to a linear variation in the density with temperature. The rate of decrease density is is the same with and without additives.

The selection of 4% poly isoprene as concentration of additives to the base oil was made , because the 4%poly isoprene is more efficient and the effect of additives cause noticeable change in experimental result.

The thermal expansion property of base oil is good for lubricant because it provides higher surface area and will coat the engines parts. The addition of poly-isoprene leads to increase viscosity index and made the decrease of density with temperature constant.

CHAPTER FIVE

Conclusions and Recommendations

5.1 Conclusions:-

An overall view of the results gives the following concluding points:

- The rate of changing density with temperature depends largely on the type of basic oil. This because this phenomenon can be demonstrated clearly for heavy, medium and light oil.
- Blending the three types of oil –stocks with additives results in noticeable increase in the thermal expansion coefficient of the mixture.
- The addition of poly-isoprene:

    1. Increase The thermal expansion coefficients of basic stocks.
    2. Make decrease of density with heating constant.

So the poly isoprene is good for improving the thermal expansion coefficient of the basic oil.

- The thermal expansion coefficient of lubricant from Al-Dura refinery with additives is smaller than that of base oil before and after blending of poly isoprene .
- Form comparison between imported lubricant oil, It can be seen that the thermal expansion coefficient has the same value.

5.2 Recommendations for future work:-

It is suggested that for future work the following points are recommanded:

- Further work can be carried out to study the effect of pressure on density and the thermal expansion coefficient of basic oil stocks.
- The use of another type of additives with different concentration to get new correlation for concentration thermal expansion coefficient of basic oil.
- The measurement of boiling point of the lubricant oil and basic stock oil measurement.
- Measurement of critical properties of the basic oil and lubricant oil

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شكـــر و تقــديـــر

اتوجه بالشكر لله على هنئ عطائه و محمود بلائه وتوالي سبوغ نعمائه والى استاذي الدكتور طالب بهجت كشموله والدكتور ضياء الدين محمد قاسم لمعاونتهما ومساندتهما ايا ي طوال فترة البحث.

اود ايضا ان اشكر جميع اساتذ ة وموظفي قسم الهندسة الكيمياوية في جامعة النهرين لابدائهم المساعدة اللازمة اثناء فترة البحث.

اود ايضا ان اشكر جميع منتسبي مصفى الدورة وبالاخص مختبر الزيوت والدهون الثقيلة لابدائهم المساعدة اللازمة لاجراء جميع الفحوصات اثناء فترة البحث.

لاانسى ان اتوجه بالشكر الى كل من ساندني خلال هذا البحث لاسيما اهلي واصحابي .

عمر مصطفى حسين
تشرين الثاني 2007

الخلاصة

يتضمن هذا البحث قياس معامل التمدد الحراري لزيوت التزييت الاساس وهي الانواع الثلاث التي تنتجها مصفاة الدورة والمسماة (stock(40,60,150.يتضمن البحث دراس تاثير اضافة البوليمرات على معامل التمدد الحراري على زيوت التزييت الاساسية والبوليمر الذي تم استخدامه يسمى ال(Polyisoperne).

البحث تضمن ايضا دراسة تاثير الزيادة في درجات الحرارة و الاضافة المستخدمة للزيوت من ناحية معامل التمدد الحراري .

لقد تم حساب معامل التمدد الحراري عمليا من خلال حساب الكثافة للزيوت المستخدمة الاساس وللزيوت مابعد المزج مع البوليمر المستخدم في درجات حراراة مختلفة.

وعموما البوليمر المستخدم قد زاد من معامل التمدد الحراري لزيوت التزييت الاساسية مع الحفاظ على مقدار التغير في الكثافة ثابت نسبيا .

البحث تضمن عمل مقارنة بين زيوت مع الاضافات من مصفى الدورة وبين زيوت التزييت الاساس بعد الاضافة ولقد اتضح ان الزيوت مع الاضافات المستخدمة من قبل مصفى الدورة يكون فيها معامل التمدد الحراري اقل من الزيوت مابعد اضافة البوليمر للزيوت الاساس.

تم التوصل من خلال البحث على معادلة يمكن تطبيقها على الزيوت الاساس الثلاث من خلال تثبيت النوع للزيت ودرجة الحرارة ون خلال هاتين المعلومتين يمكن قياس معامل التمدد الحراري للزيوت المستخدمة.

معامل التمدد الحراري لزيوت التزييت

رسالة
مقدمة الى كلية الهندسة في جامعة النهرين
وهي جزء من متطلبات نيل درجة ماجستير علوم
في الهندسة الكيمياوية.

من قبل
عمر مصطفى حسين
بكالوريوس في الهندسة الكيمياوية ٢٠٠٣

شوال	١٤٢٧
تشرين الثاني	٢٠٠٦