INFLUENCE OF POLYISOPRENE ADDITIVES ON THE VISCOSITY OF BASE LUBRICATING OILS

A Thesis
Submitted to the College of Engineering of
Al-Nahrain University in Partial Fulfillment of the
Requirements for the Degree of Master of Science
in Chemical Engineering.

by

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(B.Sc. in Chemical Engineering 2002)

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November 2004

Certification

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Abstract

The object of this research is to fined additives for oil base stocks which have the ability to raise its viscosity. Three polymers (polyisoprene 1502, 1320, Butile) where selected for that purpose. The three type of polyisoprene have been used and succeeded to raise the viscosity and the best of which was polyisoprene type 1320.

Measurement were made of the dynamic viscosities of three types of base lube oil stocks with a wide range of API gravities (20.65-34.97) with additives (polyisoprene (1502, 1320, Butile) at different temperatures in the range of 298 to 393 K.

A model was used to estimate the dynamic viscosity of oil-stocks with additives at different temperatures for binary mixtures. The method is based upon concentration (WT %) of the additive, as follows:

$$\left[\frac{\log(\mu)+k}{\log(\mu_\circ)+c}\right]=\left[\frac{T_\circ}{T}\right]^{s}$$

where,

$k = (E^* \, wt_a + B)$

$S = D * \log(\mu_\circ) + A^* \, wt_a$

Comparison between the measured and calculated viscosities of all the studied Iraqi-oil stock blends for different temperatures was found to be satisfactory, with an over all average absolute error of 8.2% for the 363 data points used. The result was compared with a previous research which used the same equation and found it's satisfactory.

CONTENTS

NOMENOCLATURE

A, B	Constants in eq.(2.5), (2-19), (2-20), (2-21)
b	Constants in eq.(2.8), (2-9), (2-10)
b, b_1, b_2	Constants in eq.(2.13)
C_1, C_2	Constants in eq.(2.14)
a_1,a_2, and a_3	Constants in eqs. (2.25)
A, B, C	Constants in Eq. (2.27)
b1, b2	Constants in Eq. (2.28)
^{o}API	American Petroleum Institute
H	Viscosity of reference oil of 100 viscosities Index at 37.8 ^{o}C
L	Viscosity of reference oil of 0 viscosity index At 37.8 ^{o}C
M	Molecular weight of each component In eq. (2-18)
Mw	Molecular weight (g/gmole)
P	Pressure (N/m^2)
P_c	Critical pressure (N/m^2)
Sp.gr	Specific gravity 15^{o}C/15^{o}C
T	Absolute temperature (K)
T_B	Mean average boiling point (^{o}R)
T_b	True boiling point (^{o}R)
T_c	Critical temperature (K)
T_F	Temperature (^{o}F)

T_p	Pure point (K)
W	Weight fraction
W_t	Walter function
X	Mole fraction

Greek Letters

μ	Dynamic viscosity (cp)
υ,η	Kinematic viscosity (cSt)
ω	Acentric factor

Subscriptions

Lab.	Laboratories
Cal.	Calculated value
exp.	Experimental value
i	Component i
m, mix	Mixture
VI	Viscosity Index

Abbreviations

ASTM	American Standard for Testing Materials
ECN	Effective Carbon Number
LOAs	Lubricating Oil Additives

CHAPTER ONE

INTRODUCTION

Lubricants include substances having a wide range of physical properties .they are usually in the liquid state (lubricating oil s), although solid (graphite) and gases (air) may be used in certain application [1].

Mineral oils, ranging from extremely fluid liquid to highly viscous products, are commonly used. They may serve many purposes such as conducting the heat of friction away from the bearings, serving as a seal to exclude undesirable substances from the area being lubricated, and acting as a carrier for rust preventives, anti-friction agents, extreme-pressure additives, and the like. However their primary purpose, is in general to lubricate, i.e., to reduce friction [2].

The internal flow resistance or viscosity is the most important property of lubricating oil, which is a measure of its internal friction or ability to flow, and largely determines its stability for any particular application. Viscosity depends on temperature increases and decreases as temperature increases [1].

For expressing the viscosity –temperature relationship, Dean and Davis introduce a scheme by which a single number, called viscosity index, classifies oil according to its viscosity-temperature characteristic. By this scheme oil which loses viscosity rapidly with temperature has a low viscosity index, and oil with a minimum change a high V.I. [3].

Mineral oils don’t have good antirust properties, although they do offer some protection, and the must be fortified with appropriate additives if any marked degree of rust prevention is to be achieved. Lubricating oil additives are normally used in low concentration from a fraction of a percent to five percent [2].

Their purpose may be one or more of the following [2]:

1. Improve lubricity under "boundary" condition.
2. Impart extreme pressure characteristics.
3. Reduce pour point.
4. Improve viscosity-temperature relationship (raise viscosity index).
5. Inhibit oxidation.
6. Combat catalytic effect of metals and contaminants.
7. Reduce bearing corrosion.
8. Disperse sludge particles, thus helping to maintain.
9. Cause emulsification (e.g soluble cutting oils).
10. Reduce or eliminate foaming.
11. Reduce or eliminate rusting.
12. Reduce ring and cylinder wear.

The aim of this research is to study the effect of defined additives on the dynamic viscosity behavior of lubricating oils, and fined a generalized dynamic viscosity-temperature correlation for this relation.

CHAPTER TWO

LITERATURE SURVEY

2.1 Lubricating oil properties

2.1.1Physical properties

- **Viscosity**

The viscosity of liquid is a measure of its resistance to flow and is a property of great importance for all petroleum products and of engine oil. It controls the speed of flow and the ease of getting to the points to be lubricated, and it influences the flow of the circulation of lubricating oils in an engine. it is therefore determined on many petroleum products both as routine control test and as a means of assessing suitability for or behavior in any given application [1].

- **Viscosity index**

The viscosity of an oil decreases with raise in temperature but to a varying degree depending on the type of crude from which it is derived and the refining treatment to which it has been subjected. The relationship between viscosity and temperature is of significance for lubricating oils since most oils have to operate over range of temperature [1].

The most commonly used method for 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 [2].

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 temperatures, an obviously desirable characteristic [4].

• Flash Point

The flash point is the lowest temperature at which a combustible material will give off enough vapor to form an inflammable mixture with air. In general, the relative volumes of liquid and vapor space, as well as the accessibility of air to the vapor space, will effect the flash point [1].

The flash point of a mixture of oils is not the flash point of the lowest flashing constituent, but the intermediate between the flash points of the highest and lowest component, in the case of straight run distillates the flash point raise with increase of viscosity [3].

• 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].

- **Pour point**

Pour point is the lowest temperature at which oil will flow when cooled under prescribed condition [3].

The pour point many mark the temperature at which crystallization of wax has proceeded to such flow to cease ("wax pour point") or it may, in the case of wax-free oils, represent the temperature at which the viscosity is so high that further cooling with the attendant further increase in viscosity causes flow to stop ("viscosity pour point").Oils which are free from wax or other components which precipitate on chilling behave like Newtonian liquids even at very low temperature. The viscosity at the pour point should be the same for all the liquids of this type. Most commercially used lubricating oils show a "wax pour point" rather than a "viscosity pour point" [2].

- **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 [5].

Oxidation of lubricating oil leads to such difficulties as bearing corrosion, ring sticking, lacquer and sludge [1].

- **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 followed by measuring acidity. Acidity determinations can therefore be used as a refinery control test or as a measure of change during use [1].

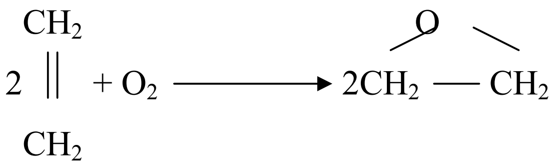
2.1.2 Chemical properties

- **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 would suffer in their function in the absence of oxygen. Refining of 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 thorough understood chemical progresses [3].

The reaction of oxygen with a molecule that may or may not 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) [1].



$$2\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + O_2 \longrightarrow 2\overset{O}{CH_2 - CH_2}$$

Partial oxidation (2-1)

Ethylene oxygen ethylene oxide

$2CH_3\,CH_2\,OH + O_2 \longrightarrow 2CH_3\text{-}CHO + 2H_2O$ Partial oxidation

Ethyl alcohol oxygen acetaldehyde water (2-2)

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ complete oxidation

Methane oxygen carbon dioxide water (combustion). (2-3)

- **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 attack by moisture or other agents. Sulpher is a common source of corrosion 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.

Protective properties are generally assessed by coating mild steel plates with the product in question in a manner simulating its normal usage and then exposing them to a corrosive atmosphere under specified conditions. The plates are inspected at intervals and the degree of protection assessed by the length of time before any, or a specified amount of corrosion occurs, or by the general state of the plates in comparison with others coated with different protective. Exposure may be outdoor, outdoor under cover, indoor or in a "humidity cabinet" in which the temperature and humidity are controlled, either to constant level or in cycle. The protection of metals against corrosion is important because corrosion, especially rusting, can cause very considerable losses to industry in both materials and time. Protection from corrosion depends on preventing moist air from coming into contact with the metal, and the application of an impervious coating is a convenient and effective means [1].

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. During use oil generates acids which may or may not set up corrosion according to circumstances. But when water is present greater corrosion activity is enticed [3].

The corrosive effect may be minimized in two; either the production of harmful peroxides and carboxylic acids can be inhibited, or the reactive metal surface can be isolated from the reactive materials with an appropriate film. In practice the oxidation inhibitor, such as zinc dithiophosphate commonly used in internal combustion engine oils, will function in both ways. The inhibitors will also be effective in preventing similar corrosion which might result with same combustion products finding their ways past the poison into he crank case [1].

2.2 Lubricating Oil Additives

2.2.1 Introduction

Basically, lubricating oil is composed of an infinite number of different hydrocarbon molecules, some of which are not suitable for lubricants and are removed by modern refining methods. This alone does not ensure satisfactory performance in many in instances, and its necessary to in corporate certain additives to improve the natural characteristics of the lubricant.

2.2.2Types of Additives:-

Table: 2-1Commonly used lubricant Additives [4].

Type of additive	*Type of compounds used*	*Reasons of use*	*Mechanism of action*
Viscosity Index	Polymerized olefins or iso-olefins. Butylenes polymers, methacrylic acid ester polymers, alkylated styrene polymers.	To lower rate of change of viscosity with temperature.	Improvers are less effected by temperature change than oil. They raise viscosity at 200 °F more in proportion than at 100 °F because of their change in solubilities.
Dispersants	Metallo-organic compounds such as naphthenates and sulfonates. Organic salts containing metals, like calcium, cobalt, and strontium.	To keep potential sludge-forming in-soluble in suspension to prevent their depositing on metal parts.	Agglomeration and deposition of fuel soot and insoluble –oil decomposition products is prevented by break down into finely divided state. In colloidal form contaminating particles remain suspended in oil.
Antioxidant or oxidation inhibitor	Organic compound containing sulfur, phosphorus, or nitrogen such as organic amines, sulfides, hydroxyl sulfide, phenols. Metals	To prevent varnish and sludge formation on metals parts. To prevent corrosion of alloy bearings.	Decreases amount of oxygen taken up by the oil, thereby reducing formationof acidic bodies. Terminates oil

	like tin zinc, or barium often incorporated.		oxidation reactions by formation of inactive soluble compound or by taking up oxygen. Additive may by oxidized in preference to oil.
Aanticorrosives, corrosion preventives or catalyst "poisons"	Organic compounds containing active sulfur, phosphorus, or nitrogen such as organic sulfides, phosphites, metals solts of thiophos-phoric acid, and sulfurized waxes.	To prevent failure of alloy bearings by corrosive action. To prevent corrosive attack on other metals surfaces.	Inhibits oxidation so that no acidic bodies are formed or enables a protective film to form on bearing or other metals surfaces. Chemical film formation on metal surfaces decreases catalytic oxidation of the oil.
Detergents	Metallo-organic compounds such as naphthenates, phenolates, sulfonates, alcoholates. High-molecular- weight soaps containing metals, like magnesium, barium, calcium, tin.	To keep metal surfaces clean and prevent deposit formation of all type.	By chemical reaction or oxidation direction, oil-soluble oxidation products are prevented from becoming insoluble and depositing on various engine parts.
Oiliness, film strength, extreme pressure (EP), and anti-wear	Organic compound containing chlorine, phosphoruse, and	To reduce friction, prevent galling, scoring, and seizure. To	By chemical reaction film is formed on metal contacting

agents.	sulpher such as chlorinated waxes, organic phosphates, and phosphitessuch as tricresyl phosphate and zinc dithiophosphate, and lead soaps such as lead naphthenate.	reduce wear.	surfaces which has lower shear strength than base meta, thereby reducing friction and preventing welding and seizure of contacting surfaces when oil film ruptured.	
Rust preventives	Solfonates, amines, fatty oils, and certain fatty acids, oxidized wax acids, phosphates, halogenated derivatives of certain fatty acids.	To prevent rust of metal parts during shout down periods, storage, or shipment of new or overhauled equipment.	Preferential adsorption of polar-type surface active materials on metal surface. This film repels attack of water. Neutralizing corrosive acids.	
Metal deactivators	Complex organic nitrogen and sulfer containing compounds such as certain complex amines and sulfides. Some soaps.	passify, prevent, or counteract catalytic effect of metals on oxidation.	Form inactive protective film by physical or chemical adsorption or absorption. Form catalytically inactive complex with soluble or insoluble metal ions.	
Stringiness and tackiness agents	Certain high-molecular-weight polymers and aluminum soaps of unsaturated fatty acids.	To increase adhiesiveness of lubricant on metal surfaces, form protective coating.	Increases viscosity of lubricating and imparts adhesive and tackiness	

			characteristics.
Water repellents	Organosilicon and other polymers, certain higher aliphatic amines, and hydroxyl fatty acids.	To provide water repellent or resistant properties to non-soap-thickened greases and other lubricants.	Surface active agents form protective film on grease thickeners or other components of lubricants to reduce their affinity for water.
Emulsifiers	Certain soaps of fats and fatty acids, sulfonic acids, or naphthenic acids.	To emulsify soluble oils with water to give coolant-lubricant-type fluid.	Surface-active chemical agents reduce interfacial tensions so oil can be finally dispersed in water.
Dyes	Oil-soluble organic compounds with high coloring power.	To provide distinctive or attractive color.	The organic compounds with high coloring power (dyes) dissolve to impart color.
Color stabilizers	Certain hydroquinones, dithiocarbamates, aliphatic amines, dicyclohexylamines.	To stabilize color and prevent formation of undesirable color.	Certain chemical can destroy color- forming bodies by stopping or changing chemical reaction forming them. Sometimes accomplished by oxidation inhibitors functioning as indicated above.

Odor-control agents	Certain oil-soluble synthetic perfumes, sometimesnitrobenzol.	To provide distinctive or pleasant odor or mask undesirable odors.	Small amounts of highly odoriferous substances impart fragrant or pleasant odor when mixed with lubricants.
Antiseptics (bactericide or disinfectant)	Certain alcohols, aldehydes, phenols, mercuric compounds, and chlorine-containing compounds.	To control odor, foaming, metal staining, emulsion breaking in emulsion-type lubricants.	Used insoluble oil to reduce or prevent growth of bacteria causing deleterious effect in emulsion lubricants.
Pour point	Wax alkylated naphthalene or phenol and their polymers. Methacrylate polymers.	To lower pour point of lubricating oils.	Wax crystals in oils coated to prevent growth and oil absorption at reduce temperature.
Foam inhibitors	Silicone polymers	To prevent formation of stable foam.	Reduces interfacial tension so small air bubblets can combine to form larger bubbles that separated faster.

2.3 Blending

Various subsidiary processes are employed to manufacture products meeting marketing specifications from the refinery grades produced by processes; the most important of these are blending [1].

The last step in the manufacture of lubricating oil is the blending of base stocks to meet viscosity requirements and the incorporation of specific additives [2].

Blending is required for oil products of all kinds; most lubricating oils are blends of two or more base oil with or without additives, ranging from the simplest two-oil blends to quite complex formulations containing several non-petroleum ingredients. In principle the process of blending is the same in all these instances but the details will vary according to the nature of the component and the complexity of the mixture. For example lubricating oils may require moderate heating (60-80 °C; 140-180 °F).blending can be carried out either intermittently by batch blending or continuously by "in-line blending" [1].

2.4 Effect of temperature on viscosity of oil-stocks

The viscosity-temperature coefficient of all liquids is high and the temperature must be carefully defined in any expression of viscosity. The dependence of viscosity upon temperature has received much study. For lubricating oils the following empirical equation, often referred to as the walther [2] equation, serves adequately, at least over a considerable range

$$\mathrm{Log\ Log}\ (V + k) = A + B\ \mathrm{Log}T \qquad (2\text{-}4)$$

Where

V is the kinematic viscosity in centistokes,

T is the absolute temperature,

A and B are constant for a given oil and

K except for very low values of V.

Singh, miadonge and puttagunta [6] developed a simple and generalized correlation for predicting temperature effect on the absolute viscosity of unrefined bitumens and heavy oil is as follows:

$$\left[\frac{\log(\mu)+c}{\log(\mu_\circ)+c}\right]=\left[\frac{T_\circ}{T}\right]^{s} \qquad (2\text{-}5)$$

Where:

T is the absolute temperature in K,

$S = 0.0066940 * \log(\mu_\circ) + 305565$, when $T_\circ$ is 303.15 K (30 °C).

The correlation allows for prediction of the viscosity of bitumen and heavy oils over a wide range of temperature by making only a single viscosity measurement, $\mu_\circ$ on the sample at any convenient temperature, $T_\circ$.

Mehrotra [7] suggested a correlation for the viscosity of pure hydrocarbons at different temperature, as follows:

$$\text{Log}(\mu + 0.8) = 100\,(0.01T)^{b} \qquad (2\text{-}6)$$

Where

μ is the absolute viscosity of pure liquid hydrocarbon in mpa.s and

$$b = -5.745 + 0.616\ \ln(ECN) - 40.468\ (ECN)^{-1.5} \qquad (2\text{-}7)$$

A modified mehrotra equation (2-7) has been considered for the development of a new generalized correlation for viscosity-temperature prediction [8].

The modification has been done by replacing μ by r; kinematics viscosity of petroleum fraction in cSt and changing the constant 0.8 by 0.7, so as to have equation of the following form:

$$\text{Log}(r + 0.7) = 100(0.01T)^{b} \qquad (2\text{-}8)$$

b Was calculated from equation (2-8), while ECN for Petroleum fractions was calculated by equation (2-10).

$$ECN\ (T_b\ ,API) = -1799.8195 - 0.0403386\ T_b + 8.19416 * 10^{-5}\ T_b^{2} - 352.5229(T_b / API)^{0.1} + 2158\ (T_b / API)^{0.02} \qquad (2\text{-}9)$$

where API at 15 °C and T_b is the pour point in K.

The most widely used approaches in calculating petroleum product blends are the ASTM-D341 method [9], which is based on the additives quantity. Log log $(r_t + 0.8)$, as follows:

$$\text{Log log } (r_b + 0.8) = \sum x_i /100 \text{ log log } (r_i + 0.8) \qquad (2\text{-}10)$$

Where r_b and r_i are the kinematic viscosities, at a given temperature, of the blend and of the blend component, in cst, respectively.

X_i is the percentage of the given component in the blend.

This function of viscosity appears in the walter equation [10, 11] as given below (walter function, w_t):

$$W_t = \text{log log } (r + 0.8) = A\text{-}B \text{ log } T \qquad (2\text{-}11)$$

The additives quantity function, which appears in eq (2-12), has a number of remarkable properties [12, 13] and it's additively is consistent.

Khan et al [14] developed two empirical double logarithmic models to predict the viscosity of gas-free athab as cabitumen. They proposed a non-linear viscosity model, as given below:

$$\ln \ln (\mu) = [1.0 + b_1T + b_2 (b_1T)^2]\, e^{b1\, t} \qquad (2\text{-}12)$$

And linear viscosity model:

$$\ln \ln (\mu) = c_1 \ln T + c_2 \qquad (2\text{-}13)$$

where μ is the viscosity in mpa.s and T is the temperature in K.

The two parameters for each model were determined by the least square technique. The non-linear viscosity model yielded slightly better results, with an average deviation of 7.1%compred with 8.23% with the linear model. The temperature range of the applicability of these correlations is from 20 °C to 130 °C.

Letsou [15] and stiel proposed a corresponding state approach that uses the centric facter ($\omega_\circ$).

$$\eta_3 = (\eta_3)^\circ + \omega_\circ (\eta_3)' \quad (2\text{-}14)$$

Where

$$(\eta_3)^\circ = 0.015174 - 0.012135\, T_r + 0.0075\, T_r^2 \quad (2\text{-}15)$$

$$(\eta_3)' = 0.042552 - 0.07674\, T_r + 0.034\, T_r^2 \quad (2\text{-}16)$$

$$\epsilon = T_c^{1/6} / (M^{1/2} * p_c^{2/3}) \quad (2\text{-}17)$$

Amin and Moddox carried out extensive research work on a correlative procedure of predicting the viscosity of petroleum fractions. The used several modifications of Eyring's equation and the one which the best correlated viscosity data was found to be of the following form [16, 17]:

$$\eta = A \exp (B/T) \quad (2\text{-}18)$$

where T is absolute temperature in K.

Begetal [18] formulated A and B to be functional to 50% boiling point and API gravity at 15 °C as following:

$$B = \exp(5.47) + 0.00342\ (T_b) \qquad (2\text{-}19)$$

$$A = -0.0339\ (API)^{0.188} + 0.241\ (T_b/B) \qquad (2\text{-}20)$$

Substitution of the expressions for parameters A and B Eyring's equation gives the following generalized kinematic viscosity correlation:

$$\eta = [\ -0.0339\ (API)^{0.188} + 0.241\ (T_b/b)]\ \exp[(\exp(5.47) + 0.00342\ T_b)/T] \qquad (2\text{-}21)$$

where T_b is the 50% boiling point temperature in K.

Amin et al [19] extended that work by introducing molecular weight as an additional parameter be side the other two parameters of API gravity and 50% boiling point.

The final form is:

$$\eta = -1.954*10^{-3} + 0.0906\ \exp(-7.773 + 10^{-3}\ MW)]\ \exp[(67.45 + \exp(5.329 + 0.00329\ T_b) + 44.263(MW/API)]/T] \qquad (2\text{-}22)$$

where

T_b is the 50% boiling point temperature in K and
T is the absolute temperature in K.

Orbey and sandler [20] proposed the following empirical method for calculating the viscosity of liquid hydrocarbon:

$$\ln(\eta/\eta_{ref}) = K\,[\,-1.6866 + 1.4010\,(T_b/T) + 0.2406\,(T_b/T_3)] \qquad (2\text{-}23)$$

where η_{ref} and K are adjustable parameters determined from experimental data.

Beggs and robbinson [21], presented an empirical viscosity-temperature correlation for dead or gas-free crude oils as function of API gravity and temperature, expressed by the following form:

$$\text{Log}\,\log\,(\mu_{\circ D} + 1) = a_1 + a_2\,\text{API} + a_3 \log T_f \qquad (2\text{-}24)$$

Emmanual [22] modified beggs and robinson equation by finding a significant deviation between measured and calculated viscosity values.

The modified beggs and robinson equation is given by:

$$\text{Log}\,\log\,(\mu_{\circ D} + 1) = 1.8653 - 0.025086\,\text{API} - 0.56441 \log T_f \qquad (2\text{-}25)$$

Allan and Teja [23] proposed viscosity-temperature correlation, which is based on the following 3-parameters, also known as the vogel equation as follows:

$$\ln(\mu) = A\left[\frac{-1}{B} + \frac{1}{T} + C\right] \qquad (2\text{-}26)$$

where T is the absolute temperature, K.

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 material. 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 hydrocracking, 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 [5].

2.6 Propane 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 asphaltenes and resins before undergoing solvent extraction. In some cases the highest boiling distillate stream may also contain sufficient asphaltenes and resins to justify Deasphalting [5].

2.7 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-pyrrolidone (NMP). The purpose of solvent extraction is to improve the viscosity index (VI) oxidation resistance, and color of the lube oil base stock and to reduce the carbon-and sludge-forming tendencies of the lubricants by separating the aromatic portion from the naphthenic and paraffinic portion of the feed stock [5].

2.8 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 hydrocracking processes to crack the wax molecules to light hydrocarbons [5].

2.9 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 [5].

CHAPTER THREE

Experimental work

3.1 oil-stocks

Three Base-stocks were used from Al-Dura refinery, namely 40 stocks, 60 stocks, 150 stocks. 40 stocks is the lightest one with API gravity 34.97 60 stocks is the middle type with API gravity 29.29 150 stocks is the heaviest type with API 20.65. The main properties of 40, 60, 150 stocks were measured in Al-Dura refinery laboratories according to API and ASTM specification, as listed in table 3-1.

Table 3-3: properties of oil stocks

specification	*40 stock*	*60 stock*	*150 stock*
Kin. Viscosity at 40 °C, cSt	**18.1**	**56.12**	**501.98**
Kin. Viscosity at 100 °C, cSt	**3.14**	**7.69**	**33.38**
Specific gravity at 15.6/15.6 °C	**0.85**	**0.88**	**0.93**
API gravity	**34.97**	**29.29**	**20.65**
COC Flash, °C	**n.d.**	**200-300**	**290-300**
P.M. Flash, °C	**160**	**n.d.**	**n.d.**
Pour point, °C	**-24**	**-6**	**-3**
Sulfur content, wt.%	**0.62**	**1.40**	**2.00**
Ram.res, wt.%	**0.06**	**0.12**	**0.78**

- n.d.: not determined

3.2 Additives

There are seven polymer (Polyalked resin, Polyester resin, Phenolic resin, PVA.emulsion, Polyisoprene (1502, 1320, Butile)) materials selected to be used as additives for lubrication oils with various weight ratios.

The group of polyisoprene and phenolic resin used as additives are originally hard materials used as liquid materials after solving it in its solvent in benzene and white spirit materials respectively when the amount of the solvent depends on its solving to the whole parts of the solved material.

The additives are tested before the use by discovering its ability to the blending with the lubrication oils and the formation of a homogenous solution without impurities or sediment and with various temperatures. The results of the test were at three groups.

1. The first group: - inability of blending with lubrication oils at any temperature, but it forms small balls near the walls of the container such material is PVA.emulsion.

2. The second group: - this material is blend with lubrication oils forming non-homogenous solution where a material like a dense and viscous liquid is sedimented the bottom and the walls of the container. From this group are polyester resin, phenolic resin, and polyalked resin.

3. The third group: - three materials are blended with the lubrication oils forming homogenous solution at different temperature degree and there is no sediments. These materials are the group of polyisoprene.

According to this results, it has been decided that the materials of group 1,2(PVA.emulsion, polyester resin, phenolic resin, and polyalked resin) should not used because they are not conceded with the conditions. and the material of group 3 will be used because it pass the test appositionally.

3.3 Procedure of mixing

The lubrication oils are prepared, the three types, with the material which decided to be used to discover the ability of improving viscosity, agents or as a disperse. The operation of addition and mixing by stirring accompanied by raising the temperature to (80-95) °C.

The following binary mixtures were prepared in this study:-

A. Binary mixtures of each oil-stock type (40 stocks, 60 stocks, and 150 stocks) with (0-8) wt% of polyisoprene 1502.
B. Binary mixtures of each oil-stock type (40 stocks, 60 stocks, and 150 stocks) with (0-8) wt% of polyisoprene 1320.
C. Binary mixtures of each oil-stock type (40 stocks, 60 stocks, and 150 stocks) with (0-8) wt% of polyisoprene Butile.

3.4 AAPARATUS

3.4.1 Viscometer

The Rheology international viscometer rotates a sensing element and a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed element, which is called a spindle, through a beryllium copper spring via the pivot point assembly. The percentage torque Wind- up of the spring due to the viscosity of the fluid is displayed as engineering units, ’’E‘‘. The electronic circuitry of the viscometer converts the measured torque into viscosity units, and displays it in cps, P or KP. The viscometer is able to measure over a number of ranges since the viscosity is proportional to the torque Wind-up of the spring; the torque Wind-up is proportional to the spindle speed, and is related to the spindle size and shape. For a material of a given viscosity the drag will be greater as the spindle size and/or rotational speed increase.

The minimum viscosity range is obtained by using the largest spindle at the highest speed and the maximum viscosity range by using the smallest spindle at the slowest speed. AUTOZERO is an important element of preparing the instrument for operation. It initiated by pressing the AUTOZERO switch on the front panel after power-up, after a spindle changes or when the user requires. It must be completed with a clean spindle attached, and the spindle runs in air. The AUTOZERO procedure rotates the spindle at 20 RPM, for 20 second, noting the mechanical and balance characteristics of the viscometer at that time. The value displayed during this process is not centipoises, etc., but a transducer reading value. The value achieved will be added or subtracted from all subsequent readings (until the next AUTOZERO or power down) to give a correct Centipoises reading. This ensures instrument accuracy over time. With the spindle immersed in the fluid under test, the instrument will continuously display (as selected) percentage torque wind-up in engineering unit (‘‘E’’) or viscosity in cps, p or KP. To freeze the display and hold a reading, press the ‘‘Hold’’ switch. The spindle continues to rotate but the display holds the last reading. The speed and spindle selected are displayed at the commencement of rotation, or after a speed/spindle change to allow the user check settings. It is essential that the correct spindle is selected otherwise Centipoises or the engineering unit conversions will be meaningless.

3.4.2 Choosing an Appropriate Spindle/Speed

The viscometer needs to know what spindle you have attached, and what speed you wish to rotate the spindle at communicate this information to the viscometer via the front panel speed and spindle selection switches. The mechanical model for calculating viscosity used by the viscometer very depending on the speed and spindle selected.

With the spindle/speeds available on the Rheology international viscometers it is possible to measure viscosity in the range 6cPs to 1000kP.

If the approximate viscosity of the fluid under test is known the appropriate speed/spindle combination can be located using the full-scale viscosity chart. For example, if the viscosity of the fluid is 980 cPs, choose a full-scale viscosity (from the chart corresponding to the viscometer model) such that 980 cPs is greater than 10%, and less than 90% of the full-scale value chosen. The viscosity of the fluid is then within the best accuracy range of the corresponding speed/spindle combination.

Taking 2000cPs full scale viscosity from the RI: 1: M chart at the end of this section 980cPs is 41% of this value. Hence the corresponding speed (20 RPM) and spindle (M2) would be suitable for testing this fluid.

However if 999.9cPs full-scale viscosity had been chosen, 980cPs would equal 98% of full-scale. The corresponding speed (10 RPM) and spindle (M1) will give a viscosity reading outside the best accuracy range of the instrument. This will be indicated on the right most digit of the display by "O".

If 333.3P full-scale viscosity had been chosen, 980cPs would be 2.9% of full-scale. Therefore the corresponding speed and spindle will give a reading under the best accuracy range of the instrument. This will be indicated on the right most digit of the display by "U".

To choose 333.3 cPs would give 980cPs equal to 117.6% of full scale. The viscosity of our fluid would then be outside the range of the corresponding speed and spindle. This will be indicated by four decimal point"….." on the display.

As stated in the introduction, when using Engineering units and with a display reading greater than 10 and less than 90, the viscometer is "In range".

3.5 Viscosity estimation

Viscosities of oil-stock and their mixtures were measured at eleven different temperatures, namely 298, 303, 313, 323, 333, 343, 353, 363, 373, 383, and 393 K with a Rheology international viscometer (Model RI: 1 :M, as shown in fig.3.1). And was placed in an oil bath, which was capable of maintaining the temperature within ± 0.1 °C of the selected temperature.

CHPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Effect of Temperature on Viscosity of Oil-Stocks

The viscosity was measured for different lubrication oils and for different temperatures ranges from 298 K to 393 K provided that 10 degrees are a separation between each measurement. The results were showed on the Fig.4-1 to enable the determination of the most important properties of these oils.

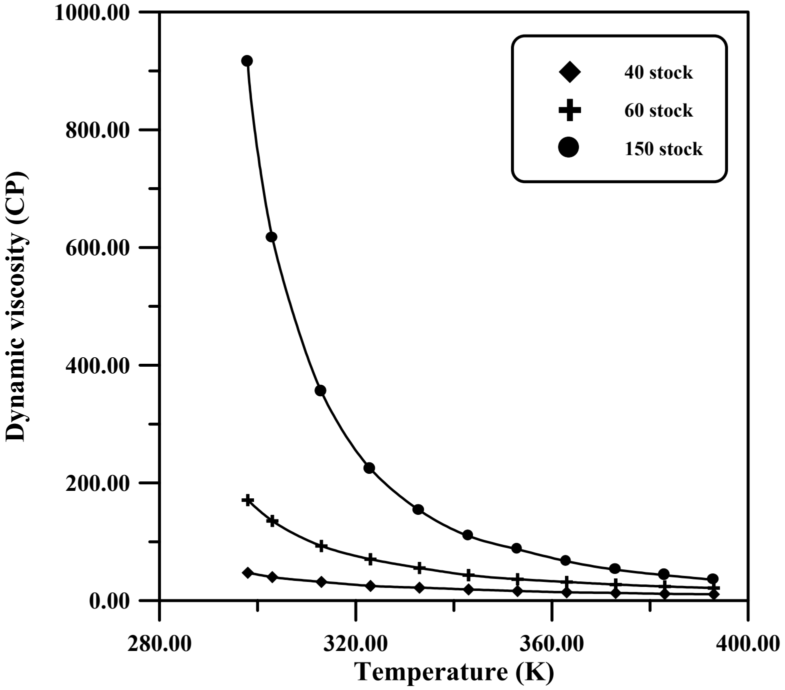


Fig. 4-1:-Effect of temperature on the dynamic viscosity of various oil stocks.

Fig. 4-1 indicates that an increase in the temperature of the oil-stocks results in a significant decrease in its viscosity. The rate of decrease in the viscosity of the heavy oil-stocks is greater than the rate for the lighter one, i.e. the rate of 150 stocks is greater than the rate of 60 stocks and 40 stocks.

Fig. 4-1 show the behavior of the lubrication oil is divided into two different regions and depends on temperature. The first region start at 298 K then, there is a transient area in which the behavior on the liquids changed from the first region to the second region between (343-363) where the behavior of the lubrication oil begin to behave according to the second region. The rate of viscosity change with temperature at the first region is greater than the rate for the second region.

4.2 Effect of Blending of Oil-Stocks with Polyisoprene on Viscosity

The dynamic viscosities of the three types of oil-stocks of 40 stock, 60 stock, 150 stock in the range of (20.65-34.97) °API gravity, were mixed with different concentrations in the range of 0-8 wt.% of polyisoprene 1502 and polyisoprene 1320 and polyisoprene Butile, which have 0.789 and 0.853 and 1.18 specific gravity respectively, at different temperatures, as follows:

- Each one of 40 stocks, 60 stocks, and 150 stocks was mixed with polyisoprene 1502 the effects are represented graphically in Figures 4-2 to 4-4.
- Each one of 40 stocks, 60 stocks, and 150 stocks was mixed with polyisoprene 1320 the effects are represented graphically in Figures 4-5 to 4-7.

- Each one of 40 stocks, 60 stocks, and 150 stocks was mixed with polyisoprene Butile the effects are represented graphically in Figures 4-8 to 4-9.

The blending of the three types of oil-stocks with polyisoprene resulted in a noticeable increase in the viscosity when the weight percent of polyisoprene increased, because each type of polyisoprene has higher viscosity than the viscosities of the three types of oil-stocks. The effect of polyisoprene 1320 on viscosity of oil-stocks is higher than the effect of 1502 and Butile.

The increase in the viscosity for lighter oil-stock is greater than that of the medium and heavier one, i.e. the effect of polyisoprene on 40 stock is higher than on 60 and 150 stock respectively, as shown in the Figures 4-2 to 4-9.

Figures 4-2 to 4-9 show the effects of increasing temperature on dynamic viscosities of oil-stocks with polyisoprene. It can be noted that the increase in temperature will decrease the value of the dynamic viscosity of the oil-stocks for all values of weight percentages of polyisoprene.

The reason of not using the ratios 6,8% wt of polyisoprene 1320 is ,due to, sedimentation of added material at the bottom of the container, and this refer that the oil can not stand more from this material, where it doesn't blend forming homogenous mixture, and the reason of not representing graphically the mixture of (150 stock and polyisoprene Butile), due to, uneffected the viscosity of the base stock (150 stock).

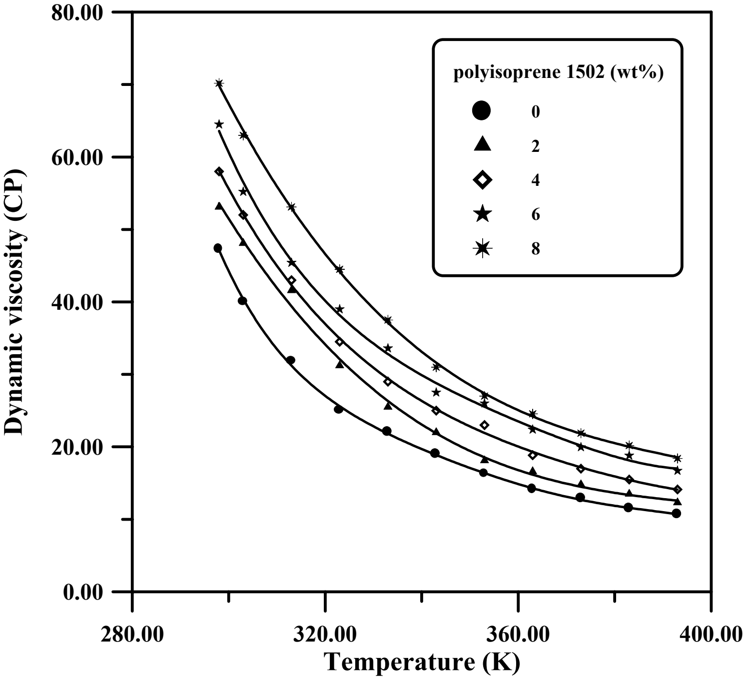


Fig. 4-2:-Dynamic viscosity of 40 stock versus temperature of different wt% of polyisoprene 1502.

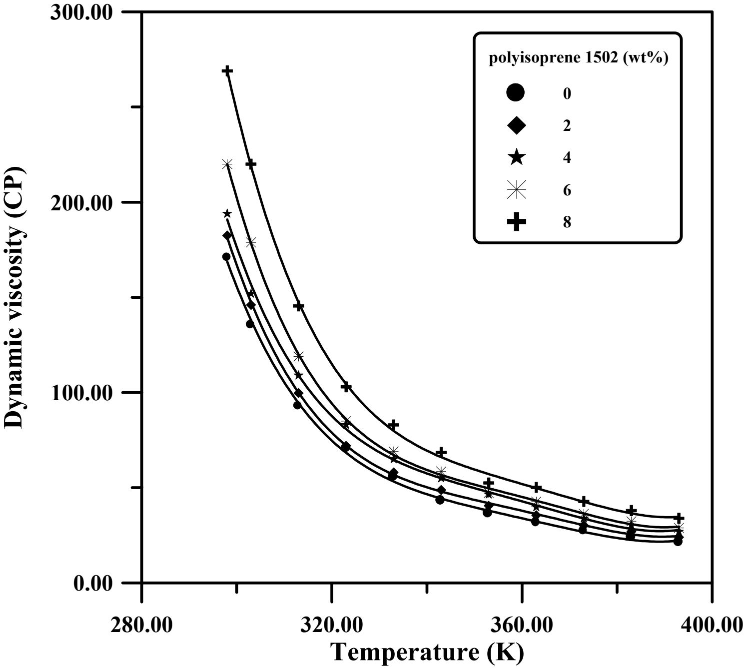


Fig.4-3:-Dynamic viscosity of 60 stock versus temperature of different wt% of polyisoprene 1502.

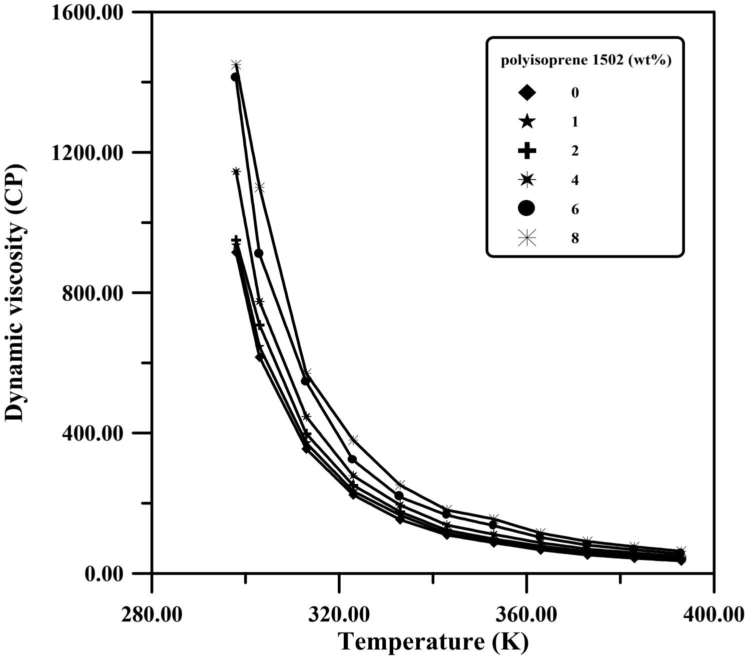


Fig.4-4:-Dynamic viscosity of 150 stock versus temperature of different wt% of polyisoprene 1502.

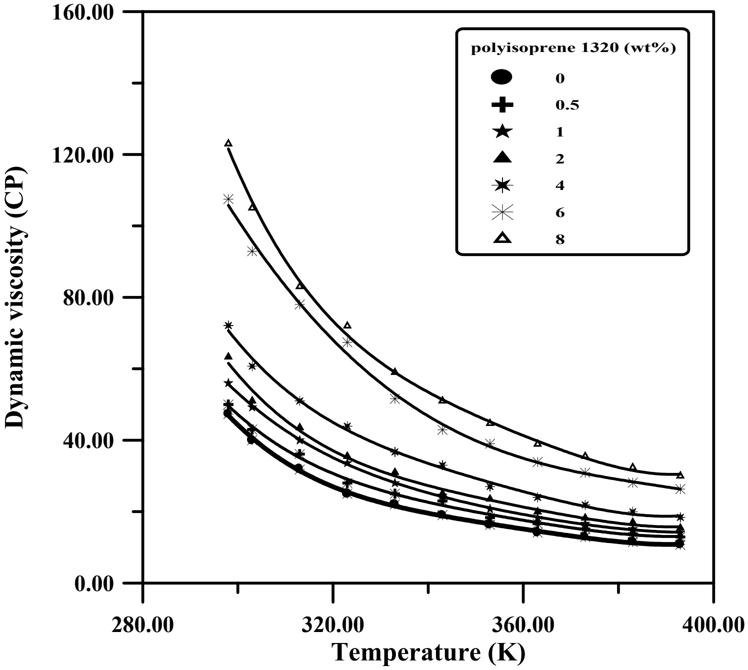


Fig.4-5:-Dynamic viscosity of 40 stock versus temperature of different wt% of polyisoprene 1320.

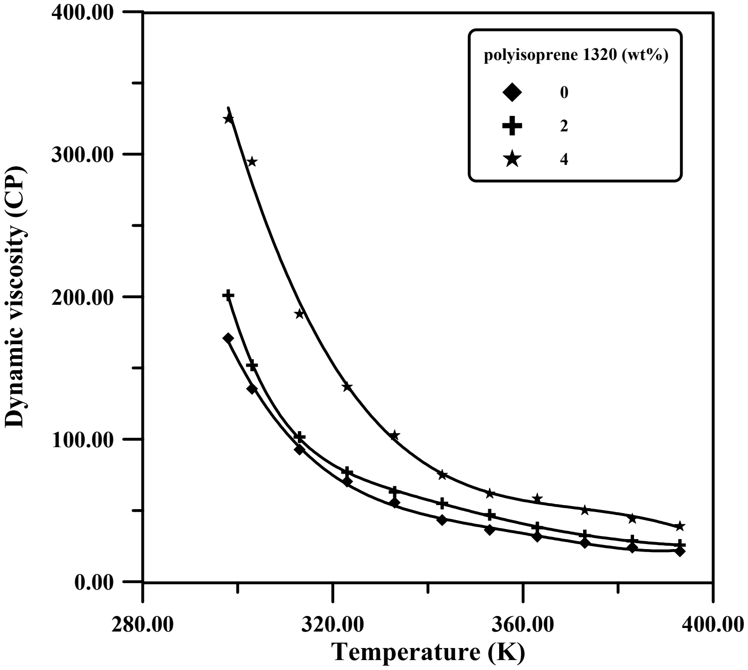


Fig.4-6:-Dynamic viscosity of 60 stock versus temperature of different wt% of polyisoprene 1320.

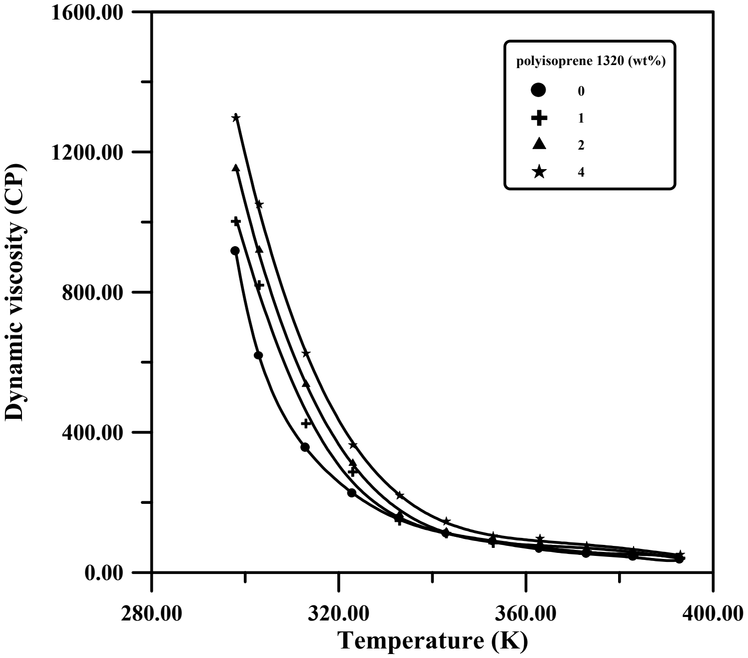


Fig.4-7:-Dynamic viscosity of 150 stock versus temperature of different wt% of polyisoprene 1320.

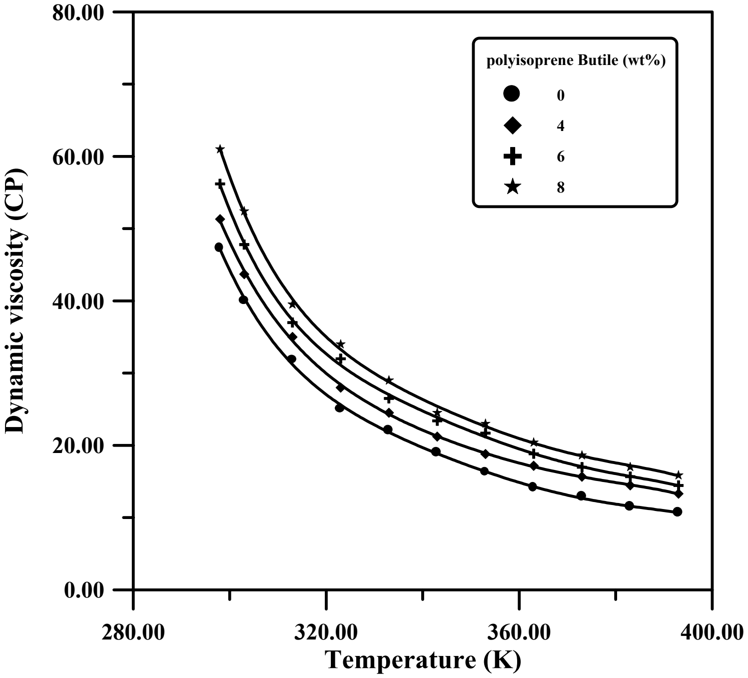


Fig.4-8:-Dynamic viscosity of 40 stock versus temperature of different wt% of polyisoprene Butile.

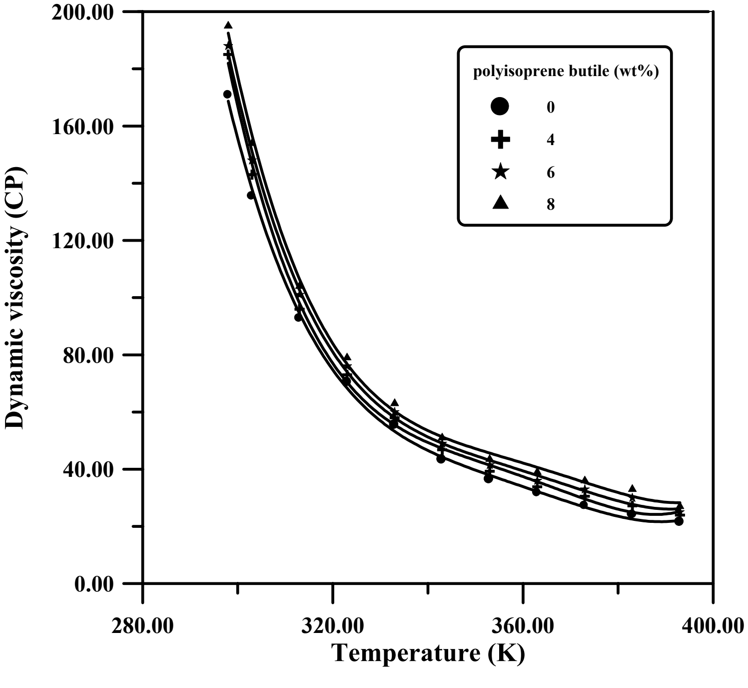


Fig.4-9:-Dynamic viscosity of 60 stock versus temperature of different wt% of polyisoprene Butile.

To know the activity of effect of these additive on the lubrication oil, logarithms of viscosity have been drawn against logarithms of temperature (K) where it appears of straight lines, and the point of intersection of these lines is the point of disappearance of the effect of these additives as shown in the Figures 4-10, 4-11, 4-12, 4-13, 4-14, 4-15, 4-16, and 4-17.

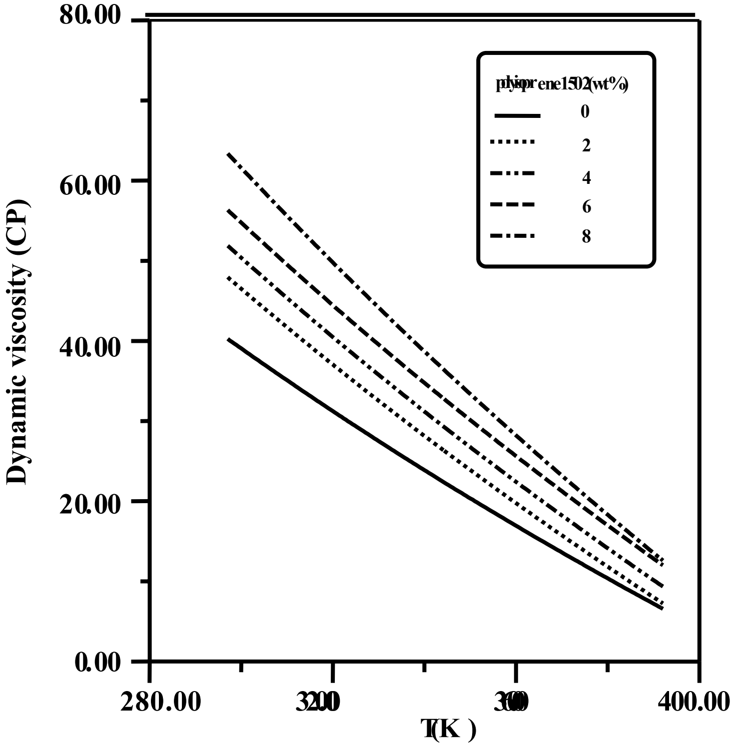


Fig.4-10:- logarithm of the dynamic viscosity of 40 stock versus logarithm of temperature of different wt% of polyisoprene 1502.

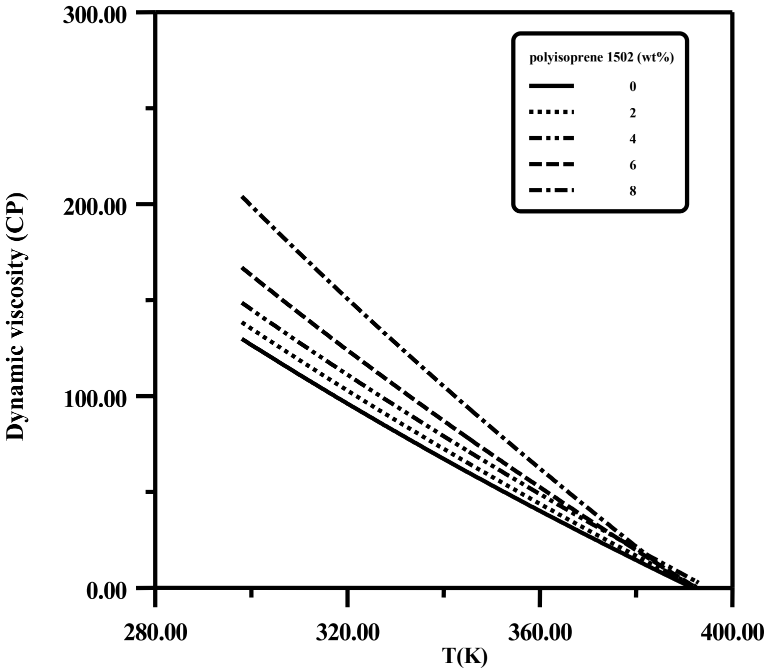


Fig.4-11:- logarithm of the dynamic viscosity of 60 stock versus logarithm of temperature of different wt% of polyisoprene 1502.

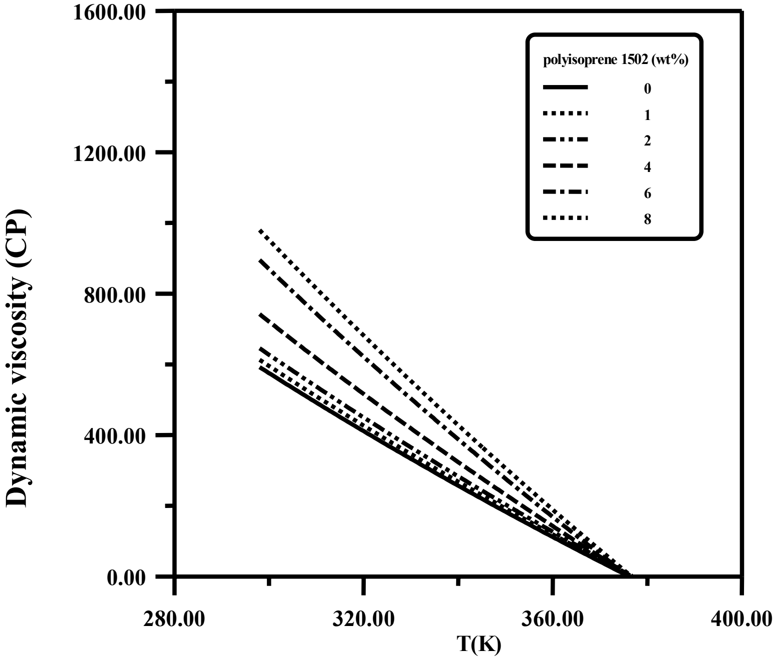


Fig.4-12:- logarithm of the dynamic viscosity of 150 stock versus logarithm of temperature of different wt% of polyisoprene 1502.

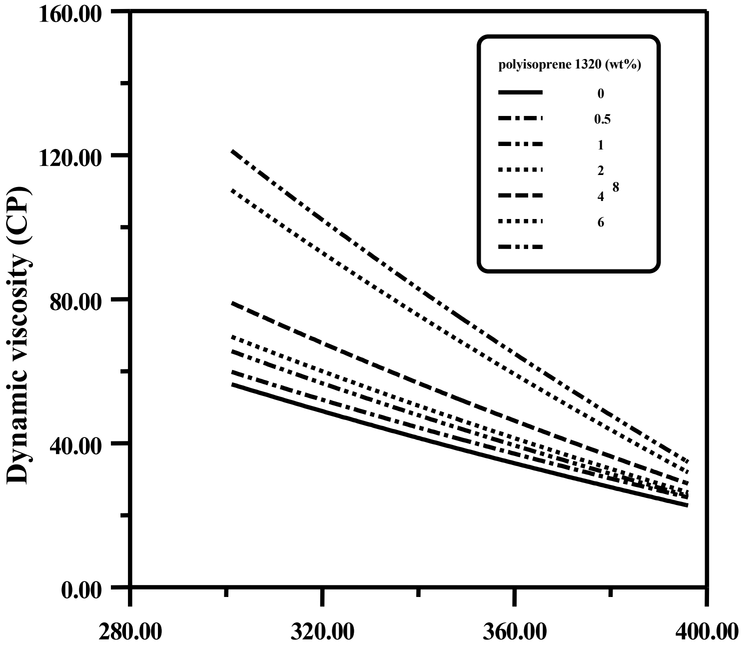


Fig.4-13:- logarithm of the dynamic viscosity of 40 stock versus logarithm of temperature of different wt% of polyisoprene 1320.

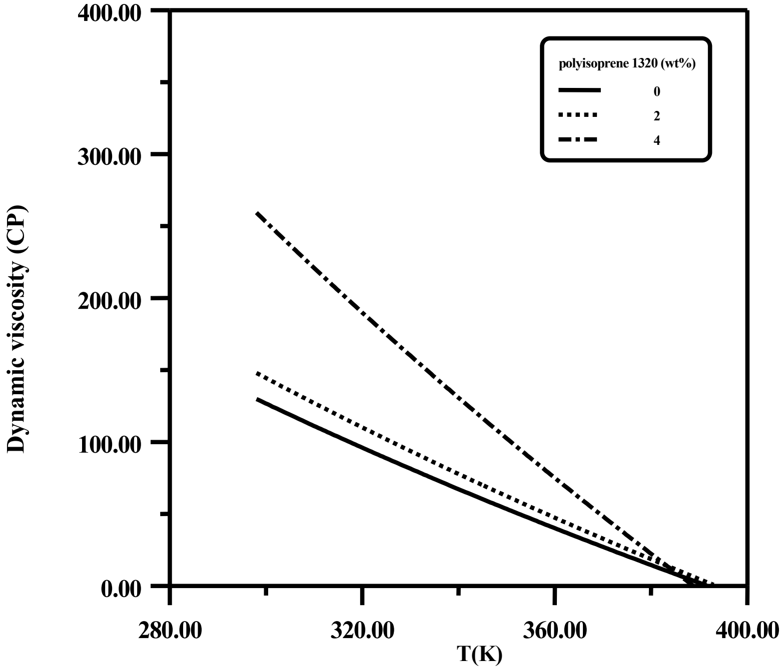


Fig.4-14:- logarithm of the dynamic viscosity of 60 stock versus logarithm of temperature of different wt% of polyisoprene 1320.

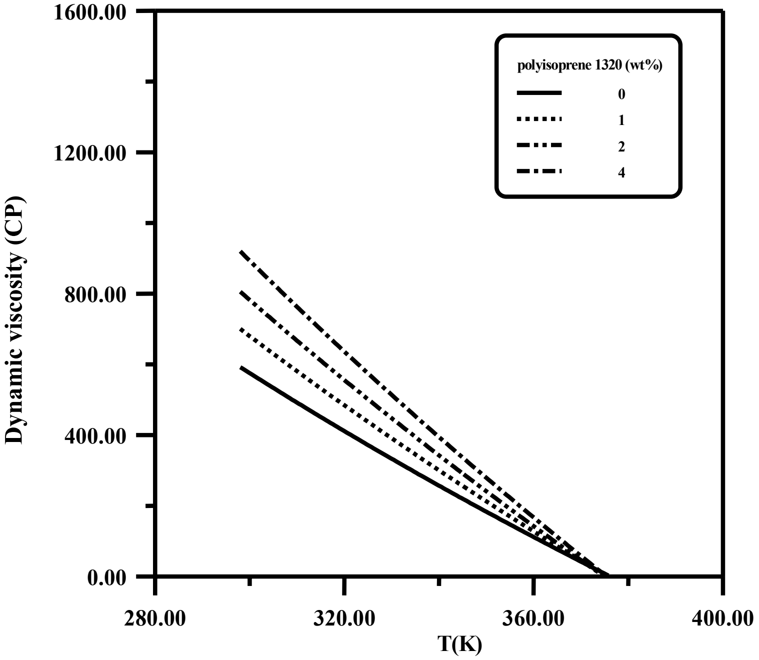


Fig.4-15:- logarithm of the dynamic viscosity of 150 stock versus logarithm of temperature of different wt% of polyisoprene 1320.

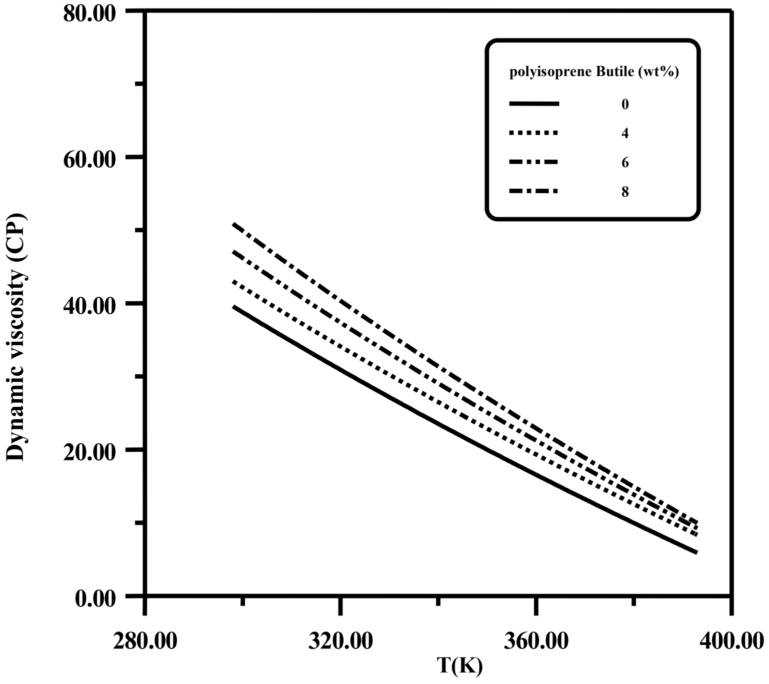


Fig.4-16:- logarithm of the dynamic viscosity of 40 stock versus logarithm of temperature of different wt% of polyisoprene Butile.

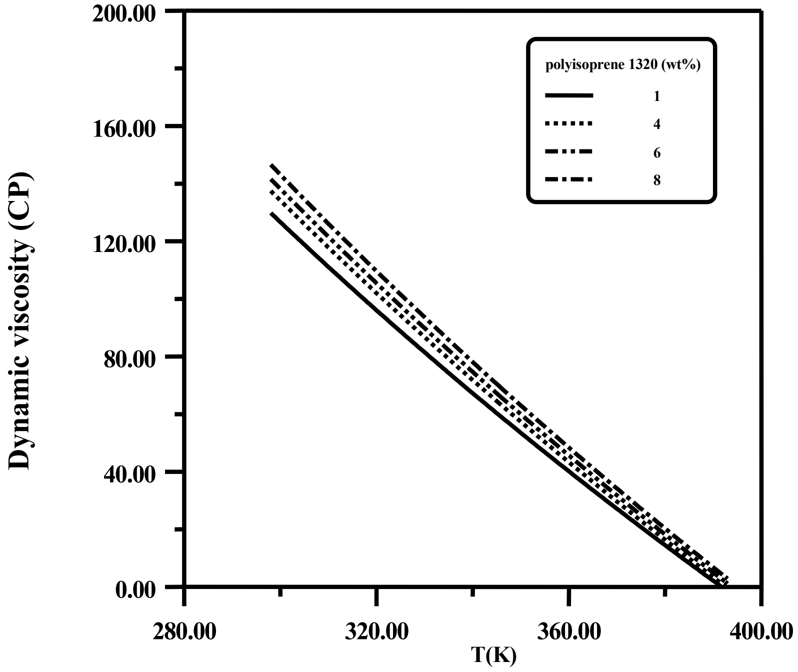


Fig.4-17:- logarithm of the dynamic viscosity of 60 stock versus logarithm of temperature of different wt% of polyisoprene Butile.

Figures 4-10 to 4-17 show the effects of adding additives on viscosities of oil-stocks are still at high temperature.

4.3 Effect of Blending of Oil-Stocks with Polyisoprene on Viscosity Index

Viscosity index improvers are less effected by temperature change than oil. They raise viscosity at the second region more in proportion than at the first region because of their change in solubilities. The reason of use viscosity index improver is to obtained lower rate of change of viscosity with temperature.The calculation of VI was done by using an empirical concept based on the behavior of mineral oil proposed by walther [2] equation:

$$\text{Log Log}(\mu + k) = A + B\ \text{LogT} \qquad (2\text{-}4)$$

Where

μ is the kinematic viscosity in centistokes,

T is the absolute temperature,

A and B are constant for a given oil and

K except for very low values of μ.

V.I α 1/B

It is noticeable from Figures 4-18, 4-19, and 4-20 that an increase of concentration of polyisoprene, which was blended with oil, decrease the viscosity index of it, i.e. VI at 2 wt.% higher than VI at 4 wt.%, because the additives are not raise the viscosity at the second region more than the first region.

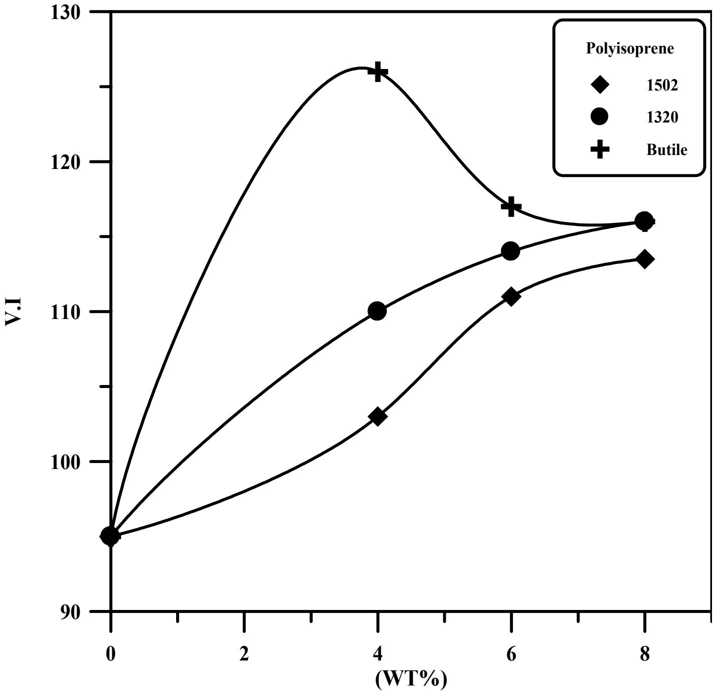


Fig.4-18:- V.I. versus wt% of 40 stock of different additives.

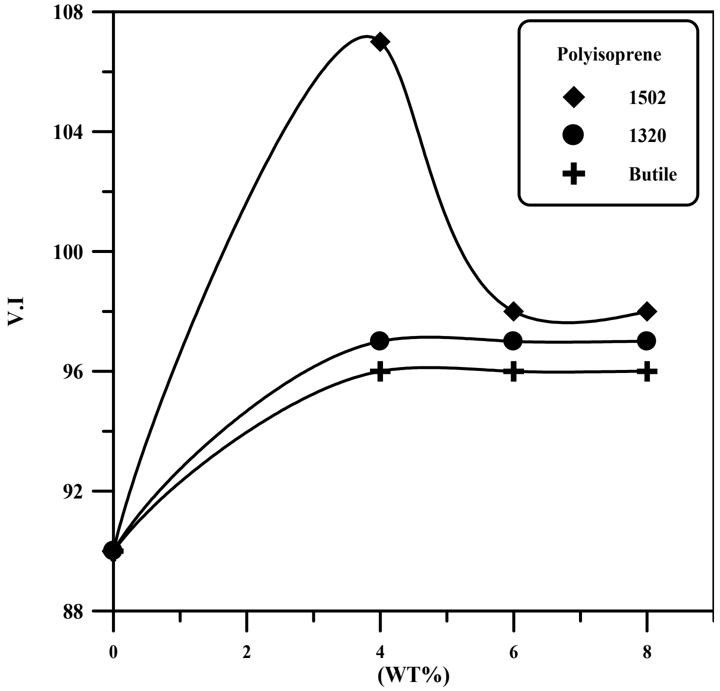


Fig.4-19:- V.I. versus wt% of 60 stock of different additives.

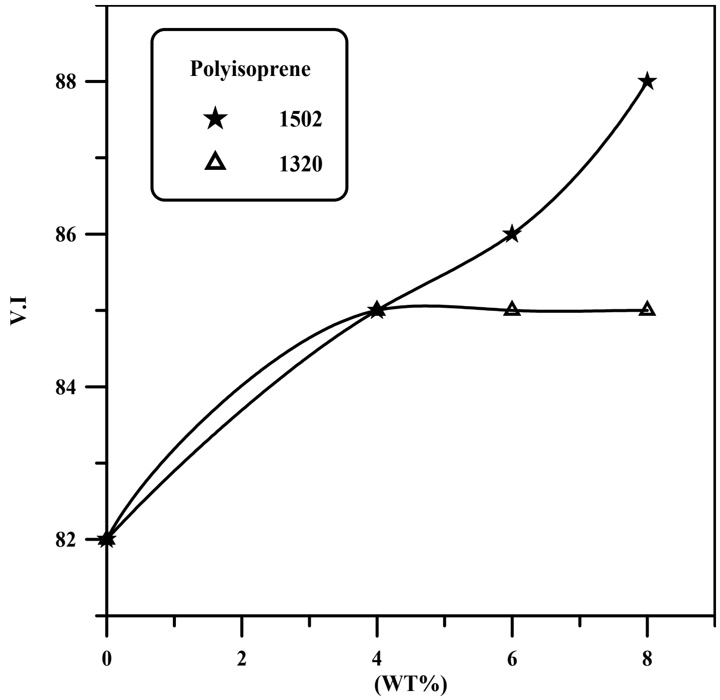


Fig.4-20:- V.I. versus wt% of 150 stock of different additives.

4.4 Viscosity-Temperature Relationship

The following viscosity correlation is particularly relevant to present study [6]:

$$\left[\frac{\log(\mu)+c}{\log(\mu_{\circ})+c}\right]=\left[\frac{T_{\circ}}{T}\right]^{s} \qquad (2\text{-}5)$$

where s = 0.066940*log ($\mu_{\circ}$) + 3.5565, when $T_{\circ}$ is K

Equation (2-5) was originally proposed as generalized dynamic viscosity-temperature correlation for unrefined bitumens and heavy oils [6].

In deriving the correlation shown in Eq (2-5), consideration was given to limiting the number of adjustable parameters.

The modified form is as shown in Eq (4-2) [6].

$$\text{Log }\mu = B^{*}\,[303.15/(t+273.15)]^{s} - C \qquad (4\text{-}2)$$

$$B = \log(\mu_{\circ}) + C \qquad (4\text{-}3)$$

where

$$S = 0.0066940 * B + 3.5565$$

The parameter B is indicative of the viscosity of the particular oil at 30 °C and one atmosphere pressure. The parameters were measured of the variation of viscosity with temperature.

Modification was done in Eq (2-5) for calculated the dynamic viscosity (μ), to get more accurate data on the effect of temperature on viscosity of oil stocks. Introducing a new parameter, namely the weight fraction of the additives for the base lubricating oil (40 stock, 60 stock, 150 stock), made the modification possible. The new formula of Eq (2-5) is proposed to predict the dynamic viscosity of oil-stock with additive at different concentration, and temperature range of 298-393 K with an average absolute error 8.2% applying it to 363 experimental data points (R= .9946).

The problem is to formulate the dynamic viscosity as a function of the main property of additive to base lubricating oil, as concentration (weight fraction).

Regression analysis has been used to give a functional relationship between the viscosity and concentration of each additive, as follows:

$$\left[\frac{\log(\mu)+k}{\log(\mu_\circ)+c}\right]=\left[\frac{T_\circ}{T}\right]^{s} \quad (4\text{-}4)$$

$$k = (E^{*}\, wt_a + B) \quad (4\text{-}5)$$

$$S = D * \log(\mu_\circ) + A^{*}\, wt_a \quad (4\text{-}6)$$

μ = the dynamic viscosity of blends in CP at different temperature (T)

wt_a = weight fraction of additive.

$\mu_\circ$ = the dynamic viscosity of blends in CP at $T_\circ$ = 303.15 K

A complete computer program performs a non linear least square fitting of proposed function of a given set of data the final constant of Eqs. (4-4), (4-5), and (4-6) are listed in 4-1.

Table 4-1: Constant of equation (4-4), (4-5), and (4-6).

A	B	C	D	E
-2.33319	-0.417146	-0.424021	1.064617	-0.063691

As can be seen from tables 4-2 to 4-9 the overall average absolute error between experimental and calculated values is not greater than 10.6%, which is obviously quite acceptable for engineering purposes.

The analyses of the proposed correlation fitted the experimental data consisting for viscosity measurements of the three types of additives (polyisoprene1502, polyisoprene 1320, polyisoprene Butile).

This result was very acceptable comparing with previous search [24], where it's used the same equation of this search at 231 measuring point. At absolute mean error was 7.6% and greater mean error between experimental and theoretical not exceeding 12.134% whiles in this search uses 363 measuring point at absolute mean error 8.2% and greater mean error between experimental and theoretical was not exceeding 10.6%, from this comparing this search is very acceptable.

Table 4-2: Comparison between measured and calculated dynamic viscosity value for the blends of 40 stocks with polyisoprene 1502.

polyisoprene 1502, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	µexp.	47.3	40	31.8	25	22	19	16.3	14.12	12.88	11.48	10.7	2.3
	µcal.	42.6	39.4	34	29.8	26.3	23.5	21.1	19.2	17.5	16.1	14.9	
	Error%	9.78	1.34	-1.05	-0.04	-0.17	-0.6	-0.22	-0.01	-0.13	-0.18	-8.8	
2	µexp.	53.1	48.1	41.6	31.2	25.5	22	18.1	16.59	14.79	13.49	12.3	20.5
	µcal.	51.7	47.5	40.5	34.9	30.6	27	24.1	21.7	19.7	17.9	16.5	
	Error%	2.57	1.24	2.64	-12.1	-20	-22.9	-33.3	-30.8	-33.1	-33.2	-34.2	
4	µexp.	58	52	48	34.5	29	25	23	18.83	16.98	15.48	14.12	12
	µcal.	56.3	51.6	43.8	37.7	32.9	29	25.8	23.1	20.9	19.1	17.5	
	Error%	2.9	0.73	8.63	-9.47	-13.5	-16	-12.2	-23	-23.4	-23.4	-24	
6	µexp.	64.5	55.2	45.4	39	33.6	27.5	26	22.38	19.95	18.19	6.7	6.4
	µcal.	60	54.9	46.6	40	34.9	30.7	27.2	24.2	22.1	20.1	18.4	
	Error%	6.9	0.44	-2.68	-2.8	-3.87	-5.55	-4.98	-9.33	-10.8	-10.5	-10.3	
8	µexp.	70.2	63	53.1	44.5	37.5	31	27	24.54	21.87	20.18	18.4	6
	µcal.	69	62.9	52.9	45.1	39	34.1	30.1	26.8	24.1	21.8	19.9	
	Error%	1.69	0.13	0.34	-1.47	-4.08	-10	-11.6	-9.52	-10.4	-8.46	-8.48	
Average absolute error %							9.4						

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Table 4-3: Comparison between measured and calculated dynamic viscosity value for the blends of 60 stocks with polyisoprene1502.

polyisoprene 1502, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	µexp.	170.8	135.4	92.7	70.3	55.5	43.2	36.3	31.62	27.22	23.98	21.37	1.5
	µcal.	155.7	133.8	101.2	78.6	62.6	50.9	42.2	35.6	30.4	26.3	23.1	
	Error%	8.8	1.13	-0.20	-0.79	-1.05	-0.93	-0.6	-1.07	-0.53	-1.53	-0.64	
2	µexp.	182.5	146	99.7	72	58	48	40.5	35.48	30.19	26.91	23.98	8.4
	µcal.	168.8	144.7	109	84.4	67	54.3	44.9	37.7	32.2	27.8	24.3	
	Error%	7.5	0.83	-9.35	-17.2	-15.5	-13.2	-10.9	-6.44	-6.73	-3.52	-1.64	
4	µexp.	194	152	109	83	65	55	46.4	39.8	33.88	30.2	26.9	3.9
	µcal.	176.1	151.1	113.9	88.2	70	56.8	46.9	39.4	33.6	29	25.4	
	Error%	9.18	0.54	-4.5	-6.32	-7.77	-3.28	-1.16	0.9	0.72	3.75	5.52	
6	µexp.	220	178.9	118.9	85	69	58.5	47.2	42.65	36.3	32.35	28.84	7.3
	µcal.	209.7	178.4	132.4	101.2	79.4	63.7	52.1	43.4	36.7	31.5	27.4	
	Error%	4.66	0.23	-11.4	-19.1	-15.1	-8.9	-10.5	-1.94	-1.37	2.37	4.8	
8	µexp.	269	220	145.5	103	83	68.5	52.5	50.11	42.7	38	33.88	7.9
	µcal.	261.8	220.9	160	120	92.6	73.2	59.2	48.7	40.8	34.7	29.9	
	Error%	2.67	-0.09	-9.98	-16.5	-11.6	-6.97	-12.7	2.67	4.33	8.5	11.63	
Average absolute error %							5.8						

Table 4-4: Comparison between measured and calculated dynamic viscosity value for the blends of 150 stocks with polyisoprene1502.

polyisoprene 1502, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	μexp.	915	616.5	354.8	223.8	153.3	109.6	87	66.8	52.48	43.15	35.48	5.7
	μcal.	806.5	611.7	370.4	238.1	161.1	113.9	83.6	63.4	49.5	39.6	32.4	
	Error%	11.8	0.77	-4.4	-6.4	-5.09	-3.9	3.86	4.99	5.57	8.05	8.49	
1	μexp.	935	645.6	371.5	234.4	165.9	114.8	91.2	72.4	57.5	48.97	40.73	7.7
	μcal.	847.7	641.6	387	247.9	167.2	117.8	86.3	65.3	50.9	40.7	33.25	
	Error%	9.335	0.54	-4.17	-5.77	-0.79	-2.69	5.31	9.7	11.4	16.86	18.34	
2	μexp.	950	708	398	251.1	175.7	123	97.72	77.62	61.65	51.28	42.17	7.8
	μcal.	937.3	704.7	420.1	266.4	178.1	124.6	90.6	68.3	52.98	42.16	34.31	
	Error%	1.340	0.46	-5.56	-6.12	-1.42	-1.38	7.13	11.97	14.05	17.78	18.62	
4	μexp.	1145	775	446.7	278.6	195	138	111	87.1	69.1	58.2	47.86	10.7
	μcal.	1033	773.7	457.8	288.4	191.7	133.4	96.6	72.4	55.9	44.37	35.99	
	Error%	9.75	0.153	-2.5	-3.53	1.67	3.29	12.9	16.8	19.01	23.7	24.7	
6	μexp.	1412	875	545	323	218	166	136	102.3	80.35	67.3	54.95	16.7
	μcal.	1178	876	511.9	318.9	209.9	144.8	104.1	77.55	59.55	46.97	37.93	
	Error%	16.55	-0.15	6.06	1.257	3.64	12.71	32.59	24.18	25.88	30.2	30.97	
8	μexp.	1450	1100	570	380	252	181	154.5	114.8	91.2	75.8	63	15.3
	μcal.	1513	1105	625.6	379.3	244	165.1	116.7	85.64	64.93	50.65	40.51	
	Error%	-4.04	-0.50	-9.75	-0.16	3.155	8.76	19.23	25.4	28.8	33.16	35.6	
Average absolute error %							10.6						

Table 4-5: Comparison between measured and calculated dynamic viscosity value for the blends of 40 stocks with polyisoprene 1320.

polyisoprene 1320, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	μexp.	47.3	40	31.8	25	22	19	16.3	14.12	12.88	11.48	10.7	1.25
	μcal.	42.6	39.4	34	29.8	26.3	23.5	21.1	19.2	17.5	16.1	14.9	
	Error%	9.7	1.34	-0.31	-1.05	-0.04	-0.17	-0.60	-0.22	-0.01	-0.14	-0.18	
0.5	μexp.	50	43	36.1	28	25	23	18.3	16.59	15.13	13.8	12.88	13.5
	μcal.	46	42.4	36.4	31.7	27.9	24.8	22.2	20.1	18.3	16.7	15.4	
	Error%	7.8	1.26	-1.02	-13.3	-11.6	-7.84	-21.5	-21.2	-21.0	-21.6	-21.2	
1	μexp.	56	49.2	40	33.6	28	24.2	20.7	18.19	17	15	14.1	11.6
	μcal.	53	48.6	41.2	35.5	30.5	27.2	24.2	21.7	19.7	17.9	16.4	
	Error%	5.2	1.17	-3.17	-5.72	-10.55	-11.31	-17.2	-19.7	-18.8	-18.7	-16.8	
2	μexp.	63.3	51	43.5	35.5	31	25	23.5	20	18.2	16	15.5	7.8
	μcal.	55.1	50.4	42.7	36.7	32	28.1	25	22.4	20.2	18.4	16.9	
	Error%	12.8	1.02	1.64	-3.59	-3.24	-12.6	-6.53	-12.5	11.5	-11.3	-9.97	
4	μexp.	72.1	60.7	51	43.9	36.7	33	27	24	22	19.95	18.4	2.9
	μcal.	66.3	60.2	50.4	42.8	36.8	32.1	28.3	25.2	22.6	20.4	18.6	
	Error%	8.03	0.71	1.13	2.42	-0.516	2.56	-4.92	-5.1	-3.42	-2.54	-1.27	
6	μexp.	107.5	92.9	78	67.4	51.6	42.9	39	33.88	30.9	28.1	26.3	5.8
	μcal.	104.1	92.5	74.3	60.9	50.8	43	36.9	32	28.2	25	22.4	
	Error%	3.13	0.35	4.65	9.58	1.53	-0.28	5.29	5.25	8.72	10.93	14.8	
8	μexp.	123	96	83	72	59	51	44.7	38.9	35.48	32.35	30	12.7
	μcal.	107.8	95.9	77.1	63.3	52.8	44.7	38.4	33.4	29.3	26	23.3	
	Error%	12.3	0.06	7	12	10.4	12.2	13.9	14.08	17.2	19.4	22.2	
Average absolute error %							9.25						

Table 4-6: Comparison between measured and calculated dynamic viscosity value for the blends of 60 stocks with polyisoprene 1320.

polyisoprene 1320, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	μexp.	170.8	135.4	92.73	70.3	55.5	43.2	36.3	31.62	27.22	23.98	21.37	1.5
	μcal.	155.7	133.8	101.2	78.6	62.6	50.9	42.25	35.6	30.4	26.4	23.1	
	Error%	8.8	1.13	-0.2	-0.79	-1.05	-0.93	-0.6	-1.07	-0.53	-1.53	-0.64	
2	μexp.	201	151.9	101.5	76.8	63	55	47	38	32.35	28.8	25.7	5.3
	μcal.	176.1	150.6	112.8	87	68.8	55.6	45.8	38.4	32.7	28.2	24.6	
	Error%	12.3	0.83	-11.2	-13.3	-9.23	-1.14	2.46	-1.14	-1.12	1.98	4.07	
4	μexp.	342.7	294.6	187.8	136.6	102.7	74.8	61.8	58.2	50.1	44.1	38.9	9.6
	μcal.	359.5	293.4	202.1	144.9	107.5	82.2	64.5	51.8	42.5	35.4	30.1	
	Error%	-4.9	0.4	-7.63	-6.08	-4.7	-9.93	-4.46	10.8	15.1	19.5	22.6	
Average absolute error %							5.4						

Table 4-7: Comparison between measured and calculated dynamic viscosity value for the blends of 150 stocks with polyisoprene 1320.

polyisoprene 1320, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	μexp.	915	616.5	354.8	223.8	153.3	109.6	87	66.8	52.48	43.15	35.48	5.7
	μcal.	806.4	611.7	370.4	238.1	161.1	113.9	83.6	63.4	49.5	39.6	32.4	
	Error%	11.8	0.77	-4.4	-6.4	-5	-3.9	3.86	4.99	5.57	8.05	8.49	
1	μexp.	1002	820	425	287	148	112	84.4	76.73	59.56	43	35	10.3
	μcal.	1102.	815.4	472.2	292.3	191.6	131.8	94.6	70.3	54.04	42.6	34.4	
	Error%	-10.0	0.56	-22.8	-1.86	-29.4	-17.7	-12	8.27	9.26	0.83	1.53	
2	μexp.	1152	920	537	311.2	164.8	115.5	92.9	83.1	64.55	53	43.45	11.5
	μcal.	1250	916.4	522.2	318.9	206	140.7	100.1	73.9	56.42	44.2	35.6	
	Error%	-8.5	0.38	2.74	-2.48	-25.3	-21.86	-7.79	11	12.58	16.45	18.02	
4	μexp.	1297	1050	612	363.9	219.7	145.6	103.8	96.6	75.58	61.65	51.28	12.4
	μcal.	1444	1049	588.8	354.9	227.3	153.3	108.1	79.2	60	46.8	37.5	
	Error%	-11.3	0.07	20.9	2.46	-3.47	-5.32	-4.2	17.9	20.7	23.9	26.8	
Average absolute error %							9.97						

Table 4-8: Comparison between measured and calculated dynamic viscosity value for the blends of 40 stocks with polyisoprene Butile.

polyisoprene Butile, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	μexp.	47.3	40	31.8	25	22	19	16.3	14.12	12.88	11.48	10.7	1.97
	μcal.	42.6	39.4	34	29.8	26.3	23.5	21.1	19.2	17.5	16.1	14.9	
	Error%	9.7	1.31	-1.05	-0.04	-0.17	-0.06	-0.22	-0.01	-0.14	-0.18	-8.8	
4	μexp.	47	43	37	32.4	28.4	25.2	22.6	20.4	18.5	17	15.6	2.1
	μcal.	46.8	43.3	37.4	32.7	28.9	25.7	23.1	21	19.1	17.6	16.2	
	Error%	0.22	-0.76	-0.4	-1.04	-1.83	-2.34	-2.64	-3.07	-3.73	-3.67	-4.35	
6	μexp.	56.2	47.8	40.5	35	30.44	27	24	21.5	19.5	17.8	16.3	4.05
	μcal.	51.5	47.5	40.9	35.6	31.3	27.8	24.9	22.5	20.5	18.8	17.3	
	Error%	8.2	0.46	-1.03	-1.78	-3.0	-3.2	-4.19	-5.04	-5.4	-5.79	-6.46	
8	μexp.	61	52.4	44	37.8	32.8	28.7	25.4	22.7	20.4	18.58	17	5.3
	μcal.	56.8	52.3	44.7	38.8	34	30.1	26.9	24.2	22	20.1	18.5	
	Error%	6.8	0.16	-1.8	-2.75	-3.84	-5.11	-6.14	-7.01	-8.08	-8.42	-8.92	
Average absolute error %							3.37						

Table 4-9: Comparison between measured and calculated dynamic viscosity value for the blends of 60 stocks with polyisoprene Butile.

polyisoprene Butile, wt%		Temperature, K											Error %
		298	303	313	323	333	343	353	363	373	383	393	
0	μexp.	170.8	135.4	92.7	70.3	55.5	43.2	36.3	31.62	27.22	23.98	21.37	1.57
	μcal.	155.7	133.8	101.2	78.6	62.6	50.9	42.2	35.6	30.4	26.4	23.1	
	Error%	8.8	1.13	-0.2	-0.79	-1.05	-0.93	-0.6	-1.07	-0.53	-1.53	-0.64	
4	μexp.	185	143	106.8	83	66	53	44.3	37	30.54	27.22	23.98	3.7
	μcal.	165	142	107.9	84.2	67.2	54.8	45.5	38.3	32.8	28.47	24.9	
	Error%	10.7	0.56	-1.10	-1.46	-1.88	-3.4	-2.7	-3.73	-7.55	-4.6	-4.07	
6	μexp.	188	148	111	85	67	55	45.4	36	33	30	25	4.17
	μcal.	171.4	147.6	112.2	87.6	70	57	47.4	39.9	34.2	29.6	26	
	Error%	8.96	0.27	-1.11	-3	-4.5	-3.8	-4.41	-11.0	-3.7	-1.13	-4	
8	μexp.	195	154	115	88	70	56.4	43.5	39	32	28	24	7.3
	μcal.	178.5	154.3	117.2	91.5	73.17	59.6	49.5	41.7	35.74	30.96	27.1	
	Error%	8.40	-0.02	-1.92	-4.04	-4.53	-5.8	-13.8	-7.14	-11.7	-10.5	-13.0	
Average absolute error %							4.2						

CHAPTER FIVE

CONCLUSIONS AND RECOMENDATIONS

5.1 Conclusions

1. Some polymers (polyisoprene 1502, polyisoprene 1320, and polyisoprene Butile) were studied as additives to the oil base stock in order to improve the viscosity at high temperature and viscosity index.
2. The rate of viscosity change of the heavy oil is greater than the rate for the medium and light oil.
3. Blending the three types of oil-stocks with additives (polyisoprene 1502, polyisoprene 1320, and polyisoprene Butile) results a noticeable increase in the viscosity of the mixture and the best one is polyisoprene 1320.
4. A method has been used to predict viscosity-temperature correlation of base oil-stocks with additives, based on temperature and concentration (wt. %). The overall average absolute error obtained by this correlation is 8.2%.

$$\left[\frac{\log(\mu)+k}{\log(\mu_\circ)+c}\right]=\left[\frac{T}{T_\circ}\right]^{s}$$

5.2 Recommendations

1. Study the effect of each polyisoprene type (polyisoprene 1502, polyisoprene 1320, and polyisoprene Butile) on corrosion and other properties.
2. Further work can be carried out to study the effect of the temperature and concentration on the viscosity change for types of multi-component mixtures of oil stock containing various concentrations of the oil-stocks blending with various concentrations of each polyisoprene type (polyisoprene 1502, polyisoprene 1320, and polyisoprene Butile).
3. Further work can be carried out to study the effect of Mixing each polyisoprene type (polyisoprene 1502, polyisoprene 1320, and polyisoprene Butile) with another type of additives has the ability to raise the viscosity index and test the mixtures by blending it's to the oil base-stocks to know if its have the ability to raise the viscosity and the viscosity index together.

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APPENDIX

Sample of Calculation

Example: Estimate the dynamic viscosity of a mixture which contains (6% of polyisoprene 1320 and 94% of 40stock) at 363.15 K and 1.01325 bar, given $\mu_o = 92.9$ Cp at $T_o = 303.15$ K.

Solution:

$K = (E * wt._a + B)$ (4-5)

$K = (-0.063691 * 0.06 + -0.417146) = -0.42096746$

$S = D * \log \mu_o + A * wt._a$ (4-6)

$S = 1.064617 * 1.968015 + -2.33319 * 0.06 = 1.9551915$

$$\left[\frac{\log(\mu) + K}{\log(\mu_o) + C}\right] = \left[\frac{T_o}{T}\right]^S \tag{4-4}$$

$$\left[\frac{\log(\mu - 0.42096746)}{\log(92.9) - 0.424021}\right] = \left[\frac{303.15}{363.15}\right]^{1.9551915}$$

$\mu = 32$ Cp

الخلاصه

يتضمن هذا البحث ايجاد أضافات لها القابليه على رفع لزوجة زيوت التزييت الاساس أو معامل لزوجتها ونجحت ثلاث مواد بوليمريه (polyisoprene(1502, 1320, Butile)) لاجل ذلك.

أستخدمت انواع ثلاثه من مادة (polyisoprene) و نجحت جميعها برفع اللزوجة و معامل اللزوجة عند درجات حرارة عالية. لقد أجريت قياسات اللزوجة الديناميكية على هذه ألانواع من زيوت ألاساس مع ألاضافات عند درجات حرارة تراوحت بين(298-393)مئوي.

لقد جرى استخدام معادلة لقياس اللزوجة الديناميكية لزيوت الاساس مع الاضافات عند درجات حرارة مختلفة للخلائط الثنائية استندت هذه المعادلة على التركيز للمضاف كما في المعادلة :

$$\left[\frac{\log(\mu)+k}{\log(\mu_\circ)+c}\right]=\left[\frac{T_\circ}{T}\right]^{s}$$

where,

$k = (E^{*}\ wt_a + B)$

$S = D * \log(\mu_\circ) + A^{*}\ wt_a$

قورنت نتائج اللزوجة التي تم الحصول عليها عمليا مع تلك التي جرى حسابها لزيوت ألاساس مع اضافاتها و لمختلف درجات الحرارة و كانت النتائج مرضيه بمعدل خطأ مطلق مقداره 8.2 باستخدام 363 نقطة قياس تجريبيه. كذلك تم مقارنة النتائج مع بحث سابق استخدم نفس المعادلة ووجد انها مقبولة جدا.

شكر و تقدير

اتوجه بالشكر لله على هنئ عطائه و محمود بلائه و توالي سبوغ نعمائه و الى أستاذي الدكتور طالب بهجت كشموله لمعاونته و مساندته اياي طوال فترة البحث.

اود ايضا ان اشكر جميع اساتذة وموظفي قسم الهندسه الكيمياويه في جامعه النهرين لأبدائهم المساعدة الازمه اثناء فترة البحث.

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

علي حميد محسن الطائي

تموز 2004

تأثير المطاط الصناعي على لزوجة زيوت التزييت

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

من قبل
علي حميد محسن الطائي
بكالوريوس في الهندسة الكيمياوية 2002

وذلك في

شهر شوال 1425 هـ

الموافق تشرين الثاني 2004 م