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EFFECT OF PRODUCTION PROCESSES OF MINERAL BASE OILS ON QUALITY AND SLUDGE FORMATION OF HYDRAULIC SYSTEM OILS

Gülsüm PULCU

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Gülsüm PULCU tarafından Yüksek Lisans tezi olarak sunulan "**Effect of Production Processes of Mineral Base Oils on Quality and Sludge Formation of Hydraulic System Oils**" başlıklı bu çalışma, E. Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E. Ü. Fen Bilimleri Enstitü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 18.09.2008 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET

MİNERAL BAZYAĞI ÜRETİM PROSESLERİNİN KALİTEYE VE HİDROLİK SİSTEM YAĞLARINDA ÇAMURLAŞMA OLUŞUMUNA ETKİSİ

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Hidrolik sistemlerin gelişen teknoloji ile birlikte ihtiyaçları artmıştır. Yeni sistemlerde daha fazla üretim yapabilmek amacıyla daha yüksek hızlarda ve sıcaklıkta ve ağır yük altında çalışma şartları oluşmuştur. Bu sebeple hidrolik system yağları bu şartlara karşılık verebilecek dayanıklılığa sahip olmalıdır. Yeni sistemlerde gelişen problemlerin başında vernikleşme oluşumu yer almaktadır. Yüksek sıcaklıklarda yağın termal bozulması ile çamurlaşma ve vernikleşme oluşur. Vernikleşmenin sisteme verdiği bazı olumsuz özellikler, filtrelerin tıkanması, aşınma miktarlarının çok yükselmesi, ısı aktarım özelliğinin yitirilmesi sonucu sistemin yeterince soğutulamaması, yağlama performans özelliklerinin kaybı şeklinde sıralanabilir.

Hidrolik yağ formüllerinin yaklaşık %99'unun bazyağlarından %1'inin katkıdan oluştuğu bilinmektedir. Bu nedenle bazyağların kimyasal ve ısıl özelliklerinin çok iyi bilinmesi gerekmektedir.

Bazyağları hidrokarbon yapıları rafineri süreçlerine ve onların derecelerine bağlıdır. Hidrojenle kırma ve hidrojenle tamamlama (reforming) gibi rafinasyon türleri bazyağlarının kimyasal yapılarını farklı yönlerde etkileyebilirler. Bu sebeple çeşitli rafinerilerden numuneler alınarak çalışmalar yapılmıştır. Termofiziksel ve kimyasal testler yapılarak rafineri proseslerinin bazyağı özelliklerine etkileri araştırılmıştır. Daha sonra hidrolik system yağları fromüle edilerek bu bazyağların son ürünlerde etkileri araştırılmıştır. Bu sebeple termogravimetrik analiz ve oksidasyon testleri yanında FT-IR analizleri ile değerlendirme yapılmıştır. Yapılan çalışmalar kimyasal ve termofiziksel özelliklerin çok iyi bilinmesi durumunda doğru bazyağı ve katığın seçilebileceğini göstermiştir.

Anahtar kelimeler: Bazyağlar, petrol rafinasyonu, yükseltgenme, vernikleşme

ABSTRACT

EFFECT OF PRODUCTION PROCESSES OF MINERAL BASE OILS ON QUALITY AND SLUDGE FORMATION OF HYDRAULIC SYSTEM OILS

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Hydraulic system oils requirements change due to technological developments. In the new systems higher temperatures, higher loads and high operation speeds which result in more production capacities are used. For this reason hydraulic oils need to be more resistant to severe working conditions. One of the growing problems in the new systems is varnish accumulation in the systems. Thermal and oxidative oil degradation result in varnish formation at high temperatures. Some negative effects of varnish in the system are filter plugging, excessive wear on the system, insufficient cooling due to the loss of heat transfer capability, and performance problems for lubrication.

Due to hydraulic oil formulation is obtained with almost 99% of base oil and 1% of additive it is necessary to investigate base oil structure and its thermal properties particularly.

Hydrocarbon chemistry of base oil depends on the refinery process and its severity. Type of hydroprocessing technologies, such as hydrocraking, hydrofinishing changes the properties of base oil. Base oil samples were taken from different refineries. Their thermophysical and chemical properties were determined at the laboratory. Their effects to finished hydraulic oil were also researched in the laboratory. The methods of the determination for the thermal properties of finished oil such as thermogravimetric analysis, oxidation test and FT-IR tests were conducted on the samples. The results indicate that extensive knowledge on chemical and thermophysical properties can help to choose right base oil and additive.

Key words: Base oils, petroleum refining, oxidation, varnish

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ABBREVIATIONS

ASTM : American Society for Testing and Materials

FT-IR : Fourier Transform Infrared

GTL : Gas to Liquid

OEM : Original Equipment Manufacturer

PAO : Polyalphaolefin

RCR : Ramsbottom Carbon Residue

SN : Solvent Neutral

TAN : Total Acid Number

TGA : Thermo gravimetric Analysis

VGO : Vacuum Gas Oil

1. INTRODUCTION

1.1. Hydraulic Fluids and Sludge Problem

Hydraulic fluids transfer the power to drive, control and move. Their operation is based on fluid compressibility which states that in a closed area compressed fluid transfers pressure throughout the system undiminished. Hydraulic systems are designed to transmit energy on the same basis. In everyday life we can encounter hydraulic systems in a wide variety of applications and formulations which show different performance qualities (Güven, 2001).

Typical conventional hydraulic oil is formulated with 99% (by wt) of base oil and 1% of additive. There are various types of base oils available today. Some of them have high quality and some of them have lower quality. Low quality base oils can cause significant performance problems, including emulsification of water which can increase pump wear, corrosion and poor filtration (Profilet, 2007). Hydraulic Oils formulated with low quality base oils may have shorter operating time, may cause oxidation in short period and filtration problems. Choosing wrong hydraulic oil can be another reason of the problems. Thus the performance of the hydraulic oils plays a significant role in the system.

In order to get good performance from Hydraulic System Oils it is important to use right fluid for the system. Besides getting informed about the main functions of hydraulic fluids, compressibility, power transmission, air release, foaming, viscosity, pour point are other important parameters for the selection. Finally the selected right fluid should finally meet all the requirements of the hydraulic systems.

Hydraulic Oils need to have long operation time and protect equipment by providing anti wear properties. They also should prevent rust and corrosion. Extended oxidation life is required for having high performance and long life in the operation. Having all these properties are depended on the hydraulic oil formulation.

Hydraulic fluids can be formulated by mineral oils, synthetic fluids and fire-resistant fluids. They can be used in all types of machinery and equipment such as machines or aircrafts. Hydraulic components are supplied nearly all industries such as agriculture and construction machinery sectors, conveyor technology, foodstuff and packaging industries, woodworking and machine tools, ship building, mining and steel industries, aviation and aerospace, medicine, environmental technology and chemicals. Simple schmetic illustration of a hydraulic circuit is also shown in Figure 1.1-1. Hydraulic system parts manufacturers are leading players in the global market. Hydraulic oil and base oil technology makes a significant contribution to the competitiveness. The innovative development of hydraulic components should also have high technology products. The consumption of hydraulic oils is high enough to evaluate its optimum formulation and its problems in the system. Sludge formation is one of the biggest problems for the users. In the following study the reasons of sludge are evaluated. Furthermore oxidation and oxidation reactions of mineral oils at high temperatures are investigated from the literature (Bock, 2001).

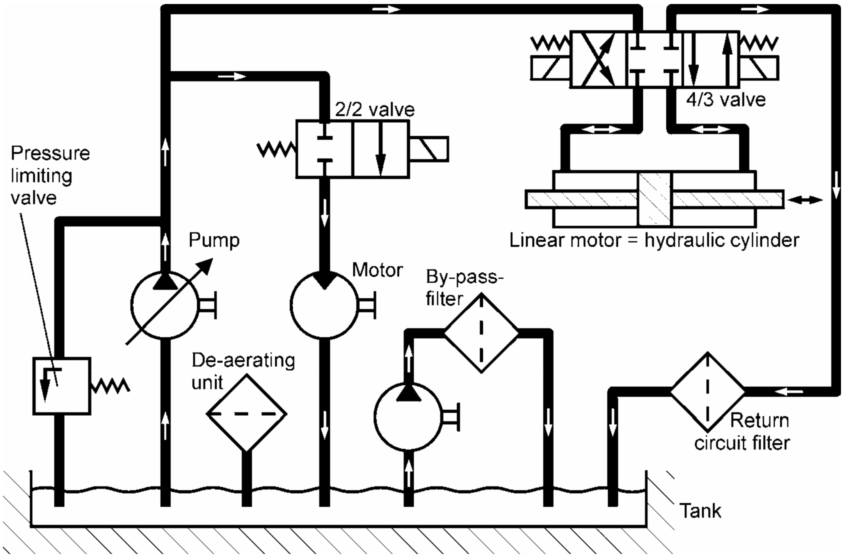


Figure 1.1-1 Schmetic illustration of a simple hydraulic circuit

Basic degradation reason of hydraulic oils is oxidation reactions. Oxidation is the most predominant reaction of lubricant in service, accounting for significant lubricant problems. It is the major source for viscosity increase, varnish formation, sludge and sediment formation, additive depletion, base oil breakdown, filter plugging, loss in foam properties, acid number increase, rust and corrosion. Therefore, understanding and controlling oxidation is a major concern for us. Since the majority of hydraulic oil formulation is based on the base oil and almost 99% by weight, base oil type and its production processes are important for this study. For this reason base oil production types and their properties are searched in the literature.

Base oils are categorized in five groups according to API (American Petroleum Institute) and they are Group I, II, III, IV and V. Group I, II and III are hydrocarbon based base oils, IV is polyalphaolefin one, V is the others (Mang and Dresel, .2007).

Group I base oils can also have different qualities because of their production process. The hydroprocessing technologies such as hydrocracking, hydrofinishing provide an opportunity to modify hydrocarbon bonds and improve quality. The effect of severity of hydrogenation is very important for base oil quality. In order to understand base oil quality in the finished hydraulic oil performance some of the experimental studies were done. In the first part of this study, the laboratory investigation results of Group I base oil from one refinery having same viscosity grade and different batches were explained. Sulphur content and refractive index were performed on the samples in order to understand their impurities. In the second part Group I base oils having four different viscosity grades were investigated. Carbon distribution, kinematic viscosity, flash point, sulphur content and refractive index were performed on the samples. In the third part Group I base oil from different refineries were investigated. Density at 15^{o}C, kinematic viscosities at 100 and 40^{o}C, viscosity index, evaporation loss by noack, sulphur content and ramsbottom carbon residue tests were performed on the samples. Base oils were compared to each other according to these physical and chemical properties. The same experiments were performed on the samples which were Group I, II, III and IV base oils having almost same viscosity grades. In this part also oxidation test according to IP 48 was performed on the samples. Viscosity as well as total acid number properties were compared to each other.

In the last part the laboratory study results of three different hydraulic oil formulations were illustrated. The base oils taken from different refineries show different qualities. Variation in oxidative stability of Group I base oils in the hydraulic oil formulation, was explained by using oxidation, FT-IR and TGA test methods in this part.

At the end of this study high quality hydraulic oil formulation can be chosen for the latest high performance hydraulic systems.

1.2. Historical Development

In 1795 British mechanic named Joseph Bramah developed the first hydraulic press according to the principle of Pascal’s law. He patented his hydraulic press, known as the Bramah press (Kopschinsky, 2002).

The principle of Pascal’s law describes that fluid is able to transmit energy from one point to another since hydraulic fluid is nearly incompressible. It is able to transmit power instantaneously. In the 1920’s use of water in the hydraulics decreased and use of oil increased. Since water volatility at high temperatures and pressures limits operation of hydraulic systems, refined mineral oils enabled the development of systems that could meet these requirements.

Synthetic hydraulic oil formulation based on ester first mentioned in the 1937 at Zurich Aviation Congress. During World War II synthetic hydraulic fluids development increased with military establishments.

Furthermore the U.S. military has a leading role on development of lubricants and hydraulic fluids. Additive and base oil quality is improving every day in order to meet the requirements of the new systems. The usage of group II and III base oils is increasing every day. The researchers are seeking to develop new products suitable for conventional mineral based base oil as well as for hydrocracked and synthetic based base oils (Gatto and Grina, 1999). Hydraulic oils can be formulated with Group I, II, III and ester based base oils. Since Group II, III base oils and esters are expensive it is required to choose Group I which has enough quality to meet new systems requirements. Sludge is the most popular problem for the new systems. In order to overcome to this problem high temperature properties should be investigated deeply. In the literature similar studies can be seen on this subject. For example in the “effect of hydroprocessing on structure and properties of base oils using NMR” study, paraffinic neutral base stock, oil sample after hydrogenation, naphthenic neutral, polyalphaolefin, first, second and third hydrogenation product of aromatic extract fraction samples were studied (Sharma et al., 2008). Distinctly in this study three types of Group I base oils obtained from different refineries, and Group II, III and IV type base oils and finished hydraulic oil formulations were studied. In addition FT-IR results of unoxidized and oxidized oils were compared. In the industrial developments the oils working at higher operating conditions are required. For this reason oxidation and high temperature properties are very important for hydraulic oil formulations to investigate.

2. LITERATURE REVIEW

2.1. Overview of Oxidation

Oxidation is generally defined as reaction with oxygen. However any reaction in which electrons transferred from molecule can be defined as oxidation. The first oxidation reaction was observed by, A.W. Hoffman more than 140 years ago. It was deterioration of rubber by oxygen, under atmospheric condition. Some examples of oxidation reactions are: Iron rusting, where the reaction is between oxygen and iron. Combustion is another rapid form of oxidation of a hydrocarbon producing water and carbon dioxide. In the case of slower reactions of a hydrocarbon, the typical final product of oxidation is an acid. Related to these reactions it is important to determine total acid number at the end of oxidation or after using hydraulic oils in the systems (Wooton, 2007).

Oxidation rate can double for hydraulic oils for every 10°C increase in operating temperature. Hydraulic oils can be used at 80°C operating temperatures efficiently but above this temperature oxidation rate will be accelerated and oil life will be shorter. As the oil becomes oxidized and degraded varnish particles may form. Varnish will deposit on valves and may then cause problems. Since varnish is sticky it attracts other wear particles resulting in excessive wear and restriction of moving parts. Loss of heat transfer, plugging of filters, increased maintenance costs are other potential problems caused by varnish (Atherton, 2007). Thus investigating oxidation reactions can help to minimize these problems.

The oxidation of a hydrocarbon involves three basic steps: initiation, propagation and termination as can be seen in Figure 2.1-1.

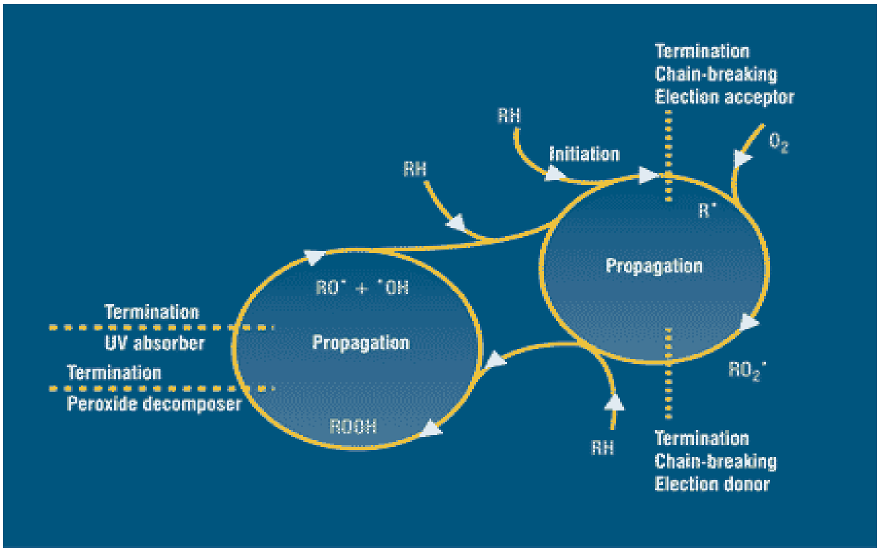


Figure 2.1-1 The Basic steps of oxidation reactions

2.1.1. Initiation

Speed of the initiation is very important. It affects the oxidation degree. The faster the initiation reactions occur, the higher degree of oxidation of lubricant we get. Free radicals are formed in this step and they are usually short lived and highly reactive. Free radicals are unpaired electrons which can easily react with other hydrocarbons *(RH)*.

Thermal degradation, oxygen, ultraviolet (UV)-light, nitro-oxides (nitrogen dioxide, nitric and nitrous oxide), electrostatic discharge can be reason for the formation of free radicals.

The types of initiation reactions include:

$$RH \quad + \quad O_2 \rightarrow \quad R\bullet \quad + \quad HOO\bullet \qquad (1)$$

Hydrocarbon Oxygen Alkyl Radical HydroperoxyRadical

$$R-R \quad + \quad UV-Light \rightarrow \quad R\bullet \quad + \quad R\bullet \qquad (2)$$

Hydrocarbon Alkyl Radical Alkyl Radical

$$R-R \quad + \quad Electrolytic \rightarrow \quad R\bullet \quad + \quad R\bullet \qquad (3)$$

Hydrocarbon Alkyl Radical Alkyl Radical

In these equations, RH and R-R represent hydrocarbons. They are part of the base oil or additives in the lubricant. $R\bullet$ and $HOO\bullet$ are the free radicals produced. As the temperature increases, the reaction rates increase.

In the first reaction oxidation occurs with oxygen. If the lubricants exposed to direct sunlight discoloration is observed as darker color. UV radiation of sunlight is the reason of this discoloration and it is another source of oxidation reaction in the second reaction. This reaction is slow because UV radiation intensity is low. Thermal cracking in the hot zones can also be the reason of initiation. In hydraulic or turbine oil applications there can be sparking in the filters and it can cause reaction as shown in third reaction.

During the initiation reactions peroxides (*ROOH* and *HOOH*) concentration will increase and in the fourth reaction free radicals will be formed:

$$ROOH \rightarrow RO\bullet + HO\bullet \qquad (4)$$

Alkyl Hydroperoxide Alkyloxy Radical Hydroxy Radical

This reaction usually will be occurred at elevated temperatures but if there is catalyst in the system free radicals of peroxide will be formed. Wear metal ion behave as catalyst in the system. Thus, wear metals often caused by oxidation reaction, will help formation of free radicals producing further oxidation:

$$ROOH + Fe^{3+} \rightarrow ROO\bullet + H^{+} + Fe^{2+} \qquad (5)$$

Alkyl Hydroperoxide Ferric Iron Alkylperoxy Radical Acid Ferrous Iron

In order to control oxidation at initiation step, the sources of reactions need to be blocked. For instance oxygen-nitrogen blanketing can be used, air entrainment can be restricted and also good antifoam control, or limiting thin film lubricants exposed to open air conditions, all can control this source. Other sources such as controlling UV-light exposure, preventing hot spots and controlling filter sparking can also help to slow down initiation reactions (Wooton, 2007).

2.1.2. Propagation and Branching

After a free radical formation propagation step will be occurred. In this step formation of additional alkyl- or peroxy- radicals and hydroperoxides (Reactions 6 and 7) will be observed, which will continue this cycle of radical formation.

$$R\bullet \quad + \quad O_2 \rightarrow \quad ROO\bullet \tag{6}$$

Alkyl Radical Oxygen AlkylperoxyRadical

$$ROO\bullet \quad + \quad RH \rightarrow \quad R\bullet + ROOH \tag{7}$$

Alkylperoxy Alkyl Radical Alkyl Hydroperoxide

In the sixth reaction peroxy-radical *(ROO•)* is produced rapidly. This peroxy-radical reacts with the base oil or additives in the lubricant to regenerate the alkyl-radical *(R•)* and restarts the cycle (Reaction 7). In this step, the hydroperoxide *(ROOH)* can also react with the lubricant (Reactions 4 and 8) to start the production of oxidation compounds-alcohol *(ROH)* and water *(H_2O)*.

$$RO\bullet \quad + \quad RH \rightarrow \quad ROH + R\bullet \tag{8}$$

Alkyloxy R. Hydrocarbon Alcohol Alkyl Radical

In the fourth decomposition reaction of the hydroperoxide it is usually required higher temperatures to occur rapidly (usually 120°C or greater). However, since iron or copper catalyze the reaction (Reaction 5), initiation temperature will be significantly lowered and reaction rate will be slower. Therefore lubricants operating temperature should be concerned at the system.

More oxidation-related products can often be caused by radical decomposition and radical transfer (radical from one molecule to another). The most common form of radical decomposition is the source of ketones and aldehydes (Reaction 9).

$$RR'R''C-O\bullet \rightarrow RR'C=O + R\bullet \qquad (9)$$

Alkyloxy Radical Ketone Alkyl Radical

$$2RR'C=O + 2O_2 \rightarrow 2RCOOH + 2R'COOH \qquad (10)$$

Ketone Oxygen Carboxylic Acid

2.1.3. Termination and Antioxidants

Oxidation cycle is stopped by the termination step. The more effective this step becomes, the less oxidation of the lubricant occur. That's why antioxidants are added into the lubricants formulation. Antioxidants influenced the propagation step and terminate the process by formation of stable radicals. There are several types of antioxidants:

- UV absorber
- peroxide decomposer
- chain breaking-electron donor
- chain breaking-electron acceptor

Each of them has a different duty to prevent propagation step (Figure 2.1-1).

In formulation of hydraulic system oils generally phenolic or aromatic amine type antioxidants are used and they are the most common type antioxidants (sometimes called primary antioxidants). Antioxidants absorb free radicals by binding hydrogen atom to them and form more stable molecules (Moehle et al., 2007).

In order to prevent sludge or varnish formation in the hydraulic system oils it is important to have free radicals under control. Some of the antioxidants make complex chemical reaction and then they regenerate themselves.

In the study of varnish formation in turbine oils it is observed that if phenolic and amine type antioxidants are used in the formulation turbine oil life will be longer. The mechanism of amine type antioxidants with free radicals and regeneration with phenolics are as follows;

$$ROO\bullet \quad + \quad AH \rightarrow \quad ROOH \quad + \quad A\bullet \tag{11}$$

Alkylperoxy Radical   Antioxidant   Alkyl Hydroperoxide   Antioxidant Radical

$$ROO\bullet \quad + \quad A\bullet \rightarrow \quad Inert\ Products \tag{12}$$

Alkyl Peroxy Radical   Antioxidant Radical

Primary antioxidants can stop more than one free radical. The reaction rates of antioxidants with free radicals are faster than that with a base oil molecule or other additive. Thus they can help to protect the lubricant.

There are other types of antioxidant which can also stop the oxidation propagation. The common type of it is the peroxide decomposer, or secondary antioxidant. Sulphur and phosphorous chemicals are typically included into this category. Phosphates and thiophosphates (such as ZDDP, alkyl phosphites and alkyl phosphates) or sulfides or polysulfides (such as phenothiazines, dithiocarbamates and sulphurized isobutylenes) are other typical examples. Peroxide decomposers destroy the peroxides or hydroperoxides into alcohols or water.

$$\underset{\text{Alkyl Hydroperoxide}}{ROOH} \quad + \quad \underset{\text{Alkyl Sulfide}}{RSR} \rightarrow \quad \underset{\text{Alcohol}}{ROH} \quad + \quad \underset{\text{Alkyl Sulfoxide}}{RRS = O} \tag{13}$$

The peroxide oxidation reaction doesn't occur above about 120°C (248^{o}F). They need this energy to cleave the peroxide molecule. Temperature has two effects on any reaction. First, the reaction occur when energy reach to the threshold point. If reaction has not enough energy to reach this point it will not occur. This reaction is the peroxide cleavage (*H*-abstraction of the propagation cycle). Second, if a reaction starts, in every 10°C (18°F) temperature, it will be faster, about double in rate.

Lubricant temperature in the system should be at 120°C (248^{o}F). The oxidation can be propagated in the hotter zones and after that deposits can be formed in the colder area. To control the oxidation propagation step, temperature of the system in hot or cold areas should be checked.

2.1.4. Ester Formation

Mostly esters are produced as a resultant of oxidation reaction. Sometimes esters height on FTIR peak can be read as oxidation level.

Esters are formed by primary free radical reaction mechanism (Baeyer-Villiger rearrangement 6 - Reaction 14) and also by esterification reaction which is secondary nonradical mechanism (esterification - Reaction 15).

$$ROOH \quad + \quad RRC = O \xrightarrow{Acid} ROH \quad + \quad RCOOR \quad (14)$$

Alkyl Hydroperoxide Ketone Alcohol Ester

$$ROH \quad + \quad RCOOH \rightarrow RCOOR \quad + \quad H_2O \quad (15)$$

Alcohol Carboxylic Acid Ester Water

In the Baeyer-Villiger reaction peroxide decompose to its free radicals easily in hot zone. Carboxylic acid which previously formed in the oxidation cycle treats as catalyst in this reaction. The esterification reaction can occur in both hot and cold zone.

2.1.5. Condensation/Polymerization

During the oxidation reactions various materials are produced and they start other reactions. If the materials produced with these side reactions are insoluble or have high molecular weight they increase viscosity. The more of these products are occurred the higher viscosity they reach.

The solubility of these materials decreases as the size and polarity of oxidation products increase. The reason of increasing in viscosity is the solubility of polar compounds is poor in nonpolar solutions and the polarity of an organic hydrocarbon increases as oxygen atoms are joined during the oxidation reaction. Insoluble oxidation components slow down the Newtonian flow properties of the liquid by adding thickening agents to the liquid.

During the reactions called Aldol and Claisen condensation, molecular-sizes of products increase (known as oligomers or low molecular polymers, Reactions 16-17).

$$3RCH_2C(O)CH_2R \xrightarrow{Acid} (RCH_2)_2C = C(R)C(O)C(R) = C(CH_2R)_2 + 2H_2O$$

Ketone Unsaturated Aldol condensation product Water (16)

$$2RCH_2C(O)OR \xrightarrow{\text{RO• AlkyloxyRadical}} RCH_2C(O)CH(R)C(O)R + ROH \quad (17)$$

Ester Condensation product Alcohol

The molecules are joined in the condensation reactions and grow in size. In Reaction 16 the unsaturated Aldol products can polymerize, initiated with the free radicals from the oxidation reactions. As the free radicals increases as a result of oxidation, the molecules grow in size (oligomerize) thus grow in molecular weight.

During oxidation reactions varnish, sludge, deposit formation and viscosity increase can be observed. Oxidation rate depends on the hydrocarbons of base oil and also additive. Additives used in the formulation can become a source of deposit formation when they loose their activation in the oil.

Oxidation of lubricants is a major source for viscosity increase, acid number increase or corrosion, additive depletions, dispersant failures, base oil deterioration, varnish and sludge formation, filter plugging, oil darkening and wear (Troyer, 2004). For this reason, it is very important for the laboratories to understand severity of oxidation. Some test methods help to evaluate oxidation state, some of them help to find out lifetime. None of these methods is able to provide a definite result about oxidation measurement.

In order to understand reason of sludge and varnish formation in hydraulic system additives and base oils should be investigated. Ninety nine percent of the formulation is base oil and 1% of it is additive. Since the majority of formulation is base oil it is important to understand effects of base oil type, its saturation amount and type of production process. Some production processes of base oils should be investigated at first.

2.2. Base Oil Production Processes

Base oils are major components of lubrication can be obtained from several sources as classified below;

Organic origin or man made

- Plants and animals
- Chemical synthesis

Mineral Origin

- Coal
- Oil shale
- Natural gas
- Crude Oil

Mineral base oils are refined from crude oil. Molecular structure of crude oils may be different depending on field. This variation effects severity degree of refinery process and also product quality.

Some crude oil appearances are shown in Figure 2.2-1 (Adamczewska, 2008).

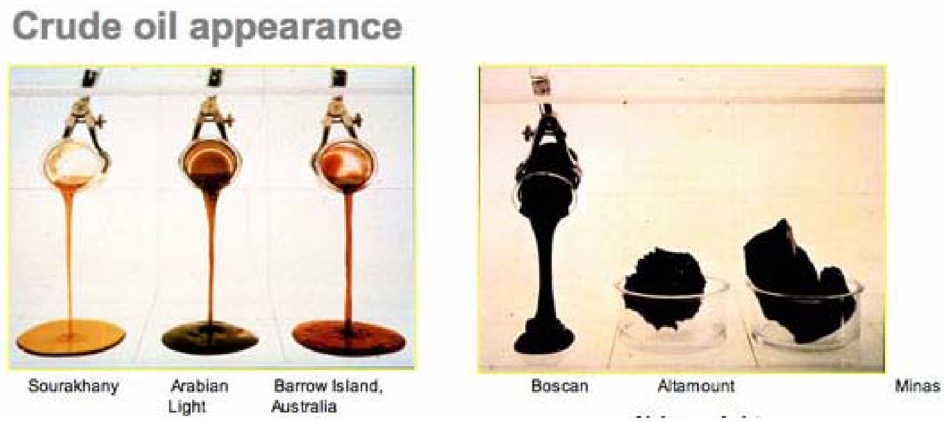


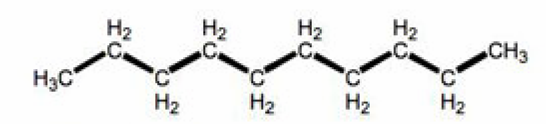
Figure 2.2-1 Appearances of crude oils from several resources

In the analysis of crude oil several components are found as shown in Table 2.2-1.

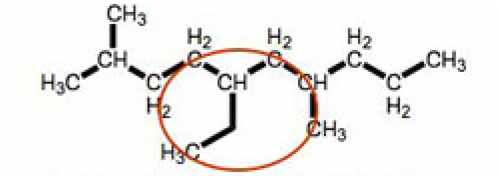
Table 2.2-1 List of typical elements represented in crude oil

Component	**% by weight**
Carbon	83-87
Hydrogen	11-14
Sulphur	0-8
Nitrogen	0-1
Oxygen	0.5
Metals	0.02

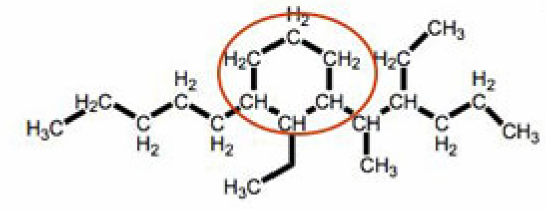
Furthermore typical hydrocarbon molecules can be found in crude oil such as straight chain, branched chain, cyclo chain and aromatic as below.



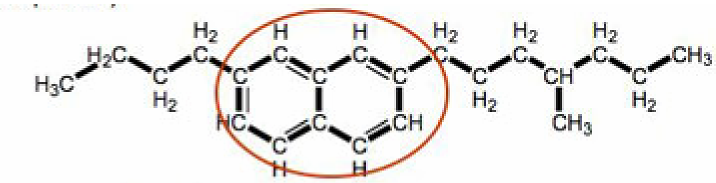
n-Paraffin (straight chain)



iso-Paraffin (branched chain)



Naphthene (cyclo paraffin)



Aromatic

Solvent extraction is used in order to separate impurities in refining of Group I base oils. Separation processes include distillation, solvent extraction, dewaxing and propane deasphalting. Conventional Group I base oils are being replaced by Group II and Group III base oils with the technological improvement in the world. Some of the production processes are reviewed as below.

2.2.1. Hydrotreating

In hydrotreating process hydrogen is added to the base oil at temperatures above 316^{o}C (600°F) and pressures above 34 atm in the presence of a catalyst. This method improves the quality and removes impurities. Thus base oil life prolongs in the applications.

2.2.2. Hydrocracking

In hydrocracking process, base oil passes through a high-activity catalyst bed at temperatures above 343^{o}C (650°F) and pressures above 68 atm. Molecules are reshaped and cracked into smaller molecules. Also in this process almost all of the sulphur and nitrogen are removed. Saturation of many aromatic compounds with hydrogen is done in this process. This process is more severe than hydrotreating.

2.2.3. Catalytic Dewaxing and Wax Hydroisomerization

In this process waxes in the base oil are cracked into light products, such as gas and naphtha at high temperature, high-pressure in which a catalyst used selectively. Since high-value wax is converted to lower value gas and light fuel, this process is wasteful. Difference between hydroisomerization process with this process is wax is selectively converted (isomerized) into high quality base oil (Kramer et al., 2003). In these processes since wax is removed lower pour point is obtained. Hydroisomerization product base oils have higher VI and better yields.

One of the lube oil plants in the USA can be seen in Figure 2.2.3-1.

Figure 2.2.3-1 Chevron Texaco's Richmond, Calif. Lube Oil Plant (RLOP)

By wax isomerization-dewaxing process the pour point of the base oil was lowered by isomerizing (reshaping) the n-paraffins (wax) and other molecules. Desirable branched compounds are obtained after this process and resultant high lubricating qualities.

2.2.4. Hydrofinishing

In this process sophisticated catalysts are used and pressures are above 68 atm. The base oil is polished at this final step. Remaining impurities are removed and stable base oil molecules are obtained.

2.2.5. Combination Process

Combination of hydrocracking, isodewaxing and hydrofinishing processes reshaped the molecules into higher-quality base oil molecules. In the catalytic processing steps Pour point, VI and oxidation stability are improved independently.

One of the benefits of combination of processes is to make high quality base oil it is not necessary to feed high quality crude oil all the time, it can be more flexible. Unlike solvent-refined base oil quality depends on the crude oil source.

Figure 2.2.5-1 shows a modern base oil plant in block flow diagram using vacuum gas oil as feed.

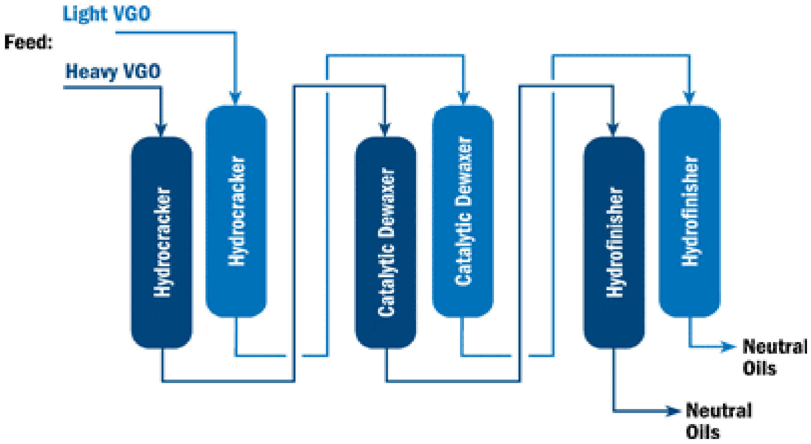


Figure 2.2.5-1 Hydroprocessing of Group II

2.2.6. Group II - Modern Conventional Base Oils

Base Oils are categorized into groups as shown in Table 2.2.6-1 by American Petroleum Institute (API) in 1993 (API Publication 1509).

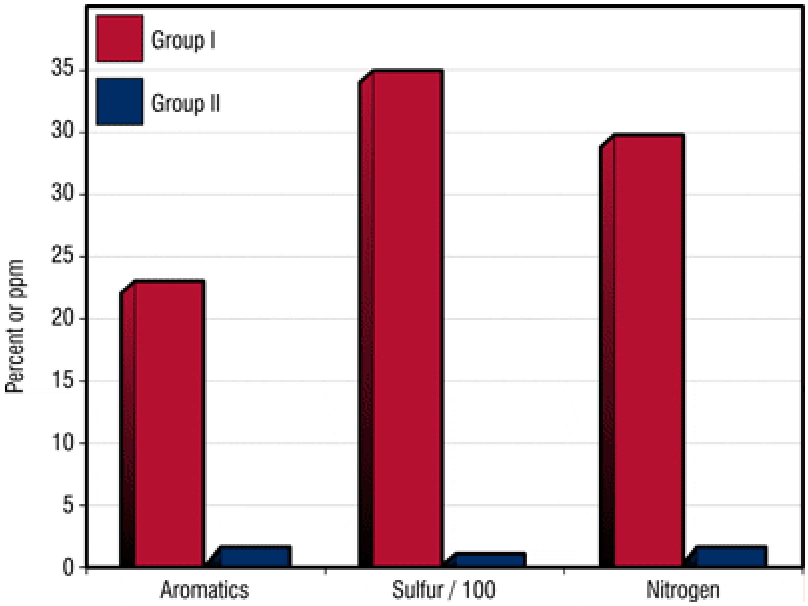
Table 2.2.6-1 API Base Stock Categories

GROUP	Sulphur wt %		SATURATES	VI
I	>0.03	And/Or	<90	80-119
II	≤0.03	And	≥90	80-119
III	≤0.03	And	≥90	≥120
IV	All Polyalphaolefins (PAOs)			
V	All Stocks Not Included in Groups I-IV (Pale Oils and Non-PAO Synthetics)			

Group I base oils are less improved and their lubricating properties may be weak in hydraulic oil formulations. According to Table 2.2.6-1 saturation level of Group III is higher than the others and polyalphaolefin is mostly estimated as fully saturated in the studies. Base oil impurities increase as the group number lowers. Viscosity Index of the base oils increase with higher group number. That is some of the high temperature properties are better with high viscosity index. Oxidation stability of base oils having high viscosity index is also better than the lower one. This table shows saturation level of the base oils. Since wide ranges of limits are given various refinery process products may influence finished oil performance test results. So they should be investigated deeply with respect to production processes.

Furthermore although using high quality base oils prolongs lubricating oil life the cost of the finished oil will be high. So it is always reasonable to use Group I and II which are able to give enough performance in the system.

In Figure 2.2.6-1 Group I and Group II base oils impurities are compared with respect to aromatic, sulphur and nitrogen content.



Type of impurity

Figure 2.2.6-1 Group II Stocks Have Lower Impurities

2.2.7. Group III - Unconventional Base Oils

Group III base oils are sometimes called unconventional base oils (UCBOs) or very high viscosity index (VHVI) base oils since their viscosity indexes are too high.

Solvent-dewaxed Group III base oils production is upgraded to Isodewaxed Group III oils. Although Group II and Group III base oils are produced essentially in the same way, to get higher VI hydrocracker severity may be increased, or higher VI feed is used. In some cases Group III base oils show the same performance as Group IV base oils.

In addition gas to liquid (GTL) technology has been developed recently. Liquefied natural gas facilities with advanced catalyst technology give highly saturated products. On the other hand high refinery costs make it unclear to decide production.

2.2.8. Group IV - Traditional “Synthetic” Base Oils (PAO)

Group IV base oils are polymerized base oils which are also called poly-alpha olefins (PAOs). They are made from small molecules.

Some lubricant producers improved Group III base oils to reach Group IV oil properties. Group IV oils have high costs to use them in the formulations. If very low temperature property is needed at the system unconventional base oils can not compete with PAO.

2.3. Effects of Hydroprocessing on Structure and Properties of Base Oils Using NMR

New hydraulic systems require high quality lubricating oils which have additional performances and longer operating time. In order to meet these requirements base oil must have some properties. These properties are investigated in this article according to hydoprocessing technologies of base oils.

Hydroprocessing Technologies such as hydrocracking, hydrofinishing as mentioned before modify the chemistry of hydrocarbons. Chemical structures and composition of base oils are controlled with the refining process and variable with respect to degree and severity of refining. Synthetic base stocks such as PAO have excellent lubricating properties but they are very expensive. Catalytic hydrocraking, isodewaxing and hydrofinishing processes provide to improve less expensive base oil properties to approach PAO.

During hydrocracking process most of the heteroatomic molecules are removed with many chemical reactions. The product of this process type base oil possesses excellent lubricating properties. On the other hand solubility of some additives in this kind of base oils decreases. For this reason variation in the performance properties with respect to base oil chemical structures is necessary to understand (Rudnick, 2006.)

Chemical structure of base oil plays significant role in oxidation stability and other performance qualities. Thus degree of refining process and and its effects on base oil properties are investigated in this article. Regarding thermo oxidative properties pressure differential scanning calorimetry (PDSC), thermogravimetric analysis (TGA), differential thermal analysis, derivative thermogravimetry and thin film micro oxidation (TFMO) tests are performed on the base oils. Nuclear magnetic resonance (NMR) spectroscopy is used for carbon, hydrogen distribution of base oils thus severity of refining process.

Naphthenic neutral, paraffinic neutral and polyalphaolefins are studied to understand chemical and physical characterization. Effect of hydrogenation on paraffinic neutral structure and properties is evaluated. Three aromatic extract fractions from different degree of hydrogenation of catalytic cycle stock are studied to evaluate performance properties. PAO sample is used as fully saturated reference sample. At the end of this study relation between base oil chemical structure and its physical properties and oxidation performance is discussed (Rudnick, 2006).

Paraffinic neutral, sample after hydrogenation, naphthenic neutral, polyalphaolefin, first, second and third hydrogenation product of aromatic extract fraction samples are used. Some of the results obtained at the end of the experiments are as follows;

1. Viscosity index of aromatic extracts is the lowest followed by naphthenic, paraffinic and PAO.

2. Refractive index of aromatic extract is the highest followed by paraffinic, naphthenic and PAO.

3. Viscosity index decreases with increasing refractive index.

4. Volatility of aromatics is higher than paraffinic where naphthenic has the highest volatility property. If base oils have high ring structure they have high volatility.

5. As a result of NMR test it is determined that PAO and naphthenic does not contain aromatic carbons.

6. If aromatic content of base oils decreases oxidation stability increases.

7. Viscosity, temperature properties is important for the formulations.

8. Oils having low viscosity tend to form less deposit during oxidation.

9. The average chain length of paraffinic base oils decreases with hydrogenation (Rudnick, 2006).

2.4. Evaluation of Kinetic Parameters of Thermal and Oxidative Decomposition of Base Oils by Conventional, Isothermal and Modulated TGA, and Pressure DSC

Gamlin et al. evaluated the degradation behavior of the base oils since ultimate performance of the finished lubricants depends on the quality of base oils. Different types and grades of base oils which are fully synthetic, semi synthetic, all natural are investigated by conventional and isothermal thermo gravimetric analyses (TGA) as well as modulated TGA (MTGA). In order to evaluate spontaneous ignition and oxidative degradation behavior of the base oils pressure differential scanning calorimeter (PDSC) is used. ALOR100 as all-natural, Yubase4 as semi synthetic, PAO4 as fully synthetic base oils are tested by a variety of thermo analytical techniques. The oils in the same grade having higher viscosities tend to degrade at higher temperatures. Despite this theory base oils have similar activation energies of degradation under an inert atmosphere. ALOR100 has naturally occurring antioxidants thus it is more resistant to oxidation than semi synthetic Yubase4 and fully synthetic PAO4. Lubricating oils are composed of long chain hydrocarbon structures and viscosity depends on the chain length. It increases with chain length. High viscosity base oils have higher thermal stability and lower volatility. Also it is determined that fully synthetic oils have higher thermal stability than semi synthetic and all natural oils when they are in same viscosity grades. It is due to lower molecular weight distribution of synthetic oils (Gamlin et al., 2002).

2.5. Practical Approaches Controlling Sludge and Varnish in Turbine Oils

Moehle et al. discussed turbine oils using Group I, II, III, and IV base oils and their field problems. Oxidation and spark discharge cause formation of free radicals in the system. Traditional methods of used oil analyses such as viscosity, acidity or carbonyl oxidation are inadequate for turbine oils formulated by Group II, III and IV base oils. The reason of different behavior of these formulations is evaluated in their study and performances are compared to each other (Moehle et al., 2007).

Performance of the turbine oils depends on the antioxidant used in the formulation. Since type of the antioxidant can be the reason of some problems such as short life in the system, insufficient performance, phenolic antioxidant and depletion of it are discussed. All data obtained from this study will help to understand deposit and varnish problems in turbine systems.

Varnish occurrences are more common today because of the new system operational conditions such as elevated temperatures, reduced dwell times, higher flow rates, tighter mechanical filters. Higher fluid operating temperatures results in oxidation and additive depletion.

Critical points for sludge and varnish formation are as follows;

1. Turbine oil formulation chemistry
2. Thermal degradation
3. Additive depletion
4. Fluid maintenance

Fluid oxidative stability is measured by RPVOT test ASTM D 2272, and TOST test ASTM D 943 in order to meet OEM’s specifications. Formulation with Group II and higher base stocks can easily meet these specifications. On the other hand good test results do not mean turbine oil has low sludge formation tendency. In order to create formulation that results in optimum sludge formation phenyl-alpha-naphtyl-amine (PANA) antioxidants should be used. The experimental studies are done with this antioxidant, results are discussed. According to end users sludge formation was not a problem 20 years ago. So they still prefer to use turbine oils formulated with Group I base oils. Although laboratory oxidation tests for Group II base oils shows very good results, sludge formation can be seen in the field. The reason for this is solubility decreases in Group II and higher base oils. Furthermore there is always difference between field applications and laboratory oxidation test results of turbine oils. This is because some of the additive components have a tendency to form deposits easily even they show very good oxidation test results. Another point is operating conditions in the field such as sparks from mechanical filters can not be simulated in the laboratory. The data show that using mixed antioxidant systems in formulation of turbine oils has minimum varnish formation problems.

During oxidation of lubricants free radicals are formed which are molecular fragments having one or more unpaired electrons. The duty of antioxidants in the formulation is to control free radicals by donating a hydrogen atom to them. Therefore more stable molecules are formed. Some of the antioxidants can go complex chemical reactions and regenerate themselves.

Amines and phenols are most commonly used additives. Amines give reactions with free radicals, phenols help them to regenerate. If there is no phenol additive in the system amines depletes more rapidly. Oxidation and FT-IR tests performed on aminic and aminic phenolic containing formulations. Additive depletion peaks are detected on FT-IR graph. When phenolic level drops to below critical point varnish formation becomes more. Thus turbine oils life depend on the phenolic content.

At high temperature, exceeding 300^{o}C, hydrocarbons breakdown due to hydrocarbon structure cracking. Spark events in turbine oil system cause thermal degradation and varnish problems.

It is concluded that although a lot of research has been performed on varnish formation there is still work to be done. One solution to prevent sludge formation is to control deposits. Amine and phenolic antioxidants are optimized for minimum varnish production. In their study formulators can find some solutions to get optimum formulations.

3. EXPERIMENTAL STUDY

3.1. Materials

Base oils and hydraulic system oil additive package were used in the study. Group I, II and III base oils are mineral based and typical characteristics are as shown in Table 2.2.6-1. Group IV is polyalphaolefin type and saturation level can be estimated as 100%. Zincalkyldithiophosphate type additive contains butylated phenol, calcium sulfonate, petroleum naphtha, substituted triazole, phenol and other unknown chemicals.

In the first part of the study, six samples of group I type base oil which are produced in different days were taken from the local refinery. Viscosity grade of the samples were the same and SN 500. Refractive index at 20°C (ASTM D 1218) and sulphur content (ASTM D 6481) were performed on the samples.

In the second part mineral base oil samples were taken from the same refinery having different viscosity grades. The sample which had a kinematic viscosity at 100°C is 3.46 cSt was designated as T1, following 5.56 cSt as T2, 11.32 cSt as T3, 33.9 cSt as T4.

In the third part mineral base oil samples were taken from different refineries but they had same viscosity grade of SN150.

In the fourth part of the study Group I, II, III and IV base oil samples were investigated. Also in order to compare test parameters of different type of refinery process products such as polyalphaolefin

(PAO), gas to liquid (GTL), hydrocracking, isodewaxing production samples were obtained. The physicochemical properties such as viscosity at 40°C, and at 100 °C, (ASTM D445), viscosity index (ASTM D 2270), refractive index at 20 °C (ASTM D 1218), density at 15 °C (ASTM D 4052), flash point (ASTM D 92) were measured. In addition sulphur content (ASTM D 6481), carbon distribution (ASTM D2140), evaporation by noack (ASTM D 5800), Ramsbottom Carbon Residue (ASTM D 524) tests were performed on the samples.

In the last part finished product samples were prepared in the laboratory. In these formulations Group I base oils T150, L150, M150 were used. Base oil samples were taken from various refineries. One type of antiwear and antioxidant Lubrizol additive package, LZ5703, was used in the formulations. In order to see antifoam effect on oxidation antifoam dditive which refers to AD2 was added to one type formulation and formulations were tabulated on table 4.2-1. Oxidation test (IP 48) at 200°C was performed on the samples and total acid number (ASTM D664), kinematic viscosity at 40°C, Ramsbottom Carbon Residue (ASTM D 524), thermo gravimetric analysis were used for testing the samples.

3.2. Methods

3.2.1. Oxidation Method

Oxidation Test was conducted by oxidizing 40 mL sample put in a glass tube. Model 16600-008 Seta high temperature bath was used which is aluminum alloy block heater thermostatically controlled to maintain oil at 200.0°C ± 0.5. The tubes were inserted into holes on the top of the bath. Insulation around the tubes using o-rings was provided to avoid any heat leakage. Dried air which was passed through cotton wool filter and pressure stabilizer was used. Air flow rate was 15.00 ± 0.25 L/h which was calibrated before the test. The flow rate was periodically checked during the test. Oxidation tubes were chemically cleaned and dried in a heater for 3 hours. Before the test oxidation tube with an oil sample in it was weighed. After 6 hours of oxidizing period, the tube was removed from the metallic bath and kept at room condition for 12 -18 hours. In the end of this cooling period, the test was repeated for 6 hours of oxidation, afterwards it was left to cool down to room temperature. Kinematic viscosity at 40°C and total acid number (TAN), and Ramsbottom carbon residue were determined on unoxidized oil sample. After oxidation same parameters were determined and deviation from the first sample was noted.

Viscosity ratio (Vr) of the samples was calculated as;

$$Vr = \frac{V_2}{V_1}$$

where V_2 refers to viscosity of oxidized oil and V_1 refers to viscosity of unoxidized oil.

Carbon residue (Cr) increase was calculated as;

$$Cr = C_2 - C_1$$

where C_2 is substituted Ramsbottom Carbon Residue of oxidized oil and C_1 is Ramsbottom Carbon Residue of unoxidized oil.

TAN increase was calculated as;

$$TAN\ Increase = TAN2 - TAN1$$

where *TAN2* refers to *TAN* of oxidized oil and *TAN1* refers to *TAN* of unoxidized oil.

After the tests increase in Ramsbottom Carbon Residue, viscosity and total acid number were evaluated.

3.2.2. TGA Method

For thermo gravimetric analysis TA instrument Q500 model was used. Dynamic Rate experiments performed with using very slow heating rates to improve resolution TGA scan.

In dynamic rate Hi-res mode, one or more Hi-Res ramp segments are used with positive resolution settings. In this mode, the furnace heating rate is varied between a fixed minimum and the maximum specified in the ramp segment, but is never reduced to zero (isothermal). A mathematical function is used to relate the rate of weight change (%/minute) to the sample heating rate (°C/minute). Dependent variables to this function are resolution setting, sensitivity setting and maximum heating rate.

Since dynamic rate Hi-Res mode reduces heating rate smoothly and only when necessary, it is the fastest and most reliable of the various techniques. This mode gives good results with most temperature separable transitions. It is preferred for fast survey scans of unknown materials over wide temperature ranges. If no other criteria exist to select a Hi-Res technique, then dynamic rate is the preferred choice.

In this experiment 20°C/minute heating rate and 100 ml/min pure nitrogen were used. Samples were heated until 600°C.

- **Heating Rate:** Dynamic rate high resolution TGA operates similarly to the conventional TGA constant heating rate experiment except that the actual heating rate varies dynamically during the experiment in response to the rate of weight change (%/minute). As the %/minute increases, heating rate decreases and vice versa. The range of heating rate variation is 0.001°C/minute (minimum) to the maximum specified. To shorten the total analysis time, the heating rate specified is 20–50°C/minute. That way, the TGA will heat rapidly through temperature regions where no weight changes are occurring and will heat slower where weight changes occur.

- **Final Temperature:** The final temperature is set above the last weight change of interest or 1000°C (600°C if using aluminum pans). The 1000°C is recommended when evaluating materials for the first time.

- **Resolution Number & Sensitivity Value:** The resolution number and sensitivity value are unitless numbers that help define the algorithm used to automatically adjust heating rate. The resolution number selects the range of percent/minute weight change values over which the heater control system will vary heating rate in response to rate of weight change. The sensitivity value controls the rate of system response to changes in the rate of weight change. Resolution values from -8 to +8 are acceptable. For dynamic rate experiments, values between

+3 and +5 are recommended. A sensitivity value of 1 is recommended for most dynamic rate experiments.

Short definitions of test methods used in this study are tabulated as in Table 3.2-1 below.

Table 3.2-1 Thermophysical and chemical properties

THERMOPHYSICAL PROPERTIES	**EXPLANATION**	**STANDARD**
Viscosity	This test method is determination of the kinematic viscosity of liquid petroleum products, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer.	ASTM D 445
Viscosity Index	Viscosity index of lubricating oils is calculated by using the parameters of their kinematic viscosities at 40 and 100°C.	ASTM D 2270
Refractive Index	This test method used for determination of refractive index of transparent and light-colored hydrocarbons in the range of 1.3300 to 1.5000 at temperatures from 20 to 30°C .	ASTM D 1218
Flash Point	Flash Point determination method is measuring the flash point and fire point of petroleum products by a manual Cleveland open cup apparatus or an automated Cleveland open cup apparatus.	ASTM D 92

Table 3.2-1 Thermophysical and chemical properties (continued)

THERMOPHYSICAL PROPERTIES	**EXPLANATION**	**STANDARD**
Density at 15^{o}C	This test method is determination of the density or relative density of petroleum distillates and viscous oils.	ASTM D 4052
Evaporation Loss by Noack	This metod covers the determination of the evaporation loss of lubricating oils. Noack evaporative tester equipment is used for the determination. In this study the test method is performed at 250°C set of operating temperature.	ASTM D 5800
CHEMICAL PROPERTIES	**EXPLANATION**	**STANDARD**
Carbon Distribution	This test method covers the calculation of the carbon distribution and ring content of olefin-free petroleum oils from measurements of refractive index, density and molecular weight (n-d-M).	ASTM D 3238
S Content	This test method covers the quantitative determination of additive elements in unused lubricating oils.	ASTM D 6481
Ramsbottom Carbon Residue(RCR)	This test method is the determination of the amount of carbon residue left after evaporation and pyrolysis of an oil. t is intended to provide some indication of relative coke-forming propensity.	ASTM D 524
Oxidation Test	Oxidation test indicates the tendency of a lubricating oil deterioration after oxidation conditions. Comparison is made by measuring the viscosity and carbon residue before and after oxidation. In this study total acid numbers were also compared.	IP 48

Table 3.2-1 Thermophysical and chemical properties (continued)

CHEMICAL PROPERTIES	**EXPLANATION**	**STANDARD**
Total Acid Number	This test method covers procedures for the determination of acidic constituents in petroleum products and lubricants soluble or nearly soluble in mixtures of toluene and propan-2-ol. The range of acid numbers included in the precision statement is 0.1 mg/g KOH to 150 mg/g KOH.	ASTM D 664
FT-IR	This metod covers the use of FT-IR in monitoring product picture as a graph. After reference oil data was input comparison can be made if there is additive depletion, contaminant buildup and base stock degradation in machinery lubricants, hydraulic fluids and other fluids used in normal machinery operation. Contaminants monitored include water, soot, ethylene glycol, fuels and incorrect oil. Oxidation, nitration and sulfonation of base stocks are monitored as evidence of degradation. Tests were performed on Perkin Elmer Spectrum 1 model and ATR was used for the samples.	ASTM E 2412
TGA	The metod covers the determination of the percent weight loss of a test sample. The sample is heated at a uniform rate in an appropriate environment. The metod provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability	ASTM E 1131

4. RESULTS AND DISCUSSION

4.1. Base Oils

First of all physicochemical tests were performed on the base oils in order to understand their effects on impurity. Since sulphur content is very important on finished lubricant performance, some relations were reviewed with other test results. One of them was between sulphur content (ASTM D 6481) and refractive index (ASTM D 1218). Group I base oil having viscosity grade of SN 500 was taken as an example. Six samples were taken from the same production process, in different times, having different sulphur contents. From various production batches sulphur contents and refractive indexes were noted. As shown in the Figure 4.1-1 refractive index increases as the sulphur contents increase. From these results it can be concluded that as refractive index decreases in the same viscosity grade, base oil impurities were observed less and oxidation stability was better.

In order to evaluate molecular structure of base oils impurities and their effects in the finished oil, first of all sulphur contents were determined by XRF. Higher aromatic carbons increase the refractive index of base oils (Sharma et al., 2008). For this reason to investigate relation between sulphur content and carbon distribution of base base oils refractive indexes were also determined.

Sulphur content of SN500 samples having various batches were determined and shown as in Figure 4.1-1.

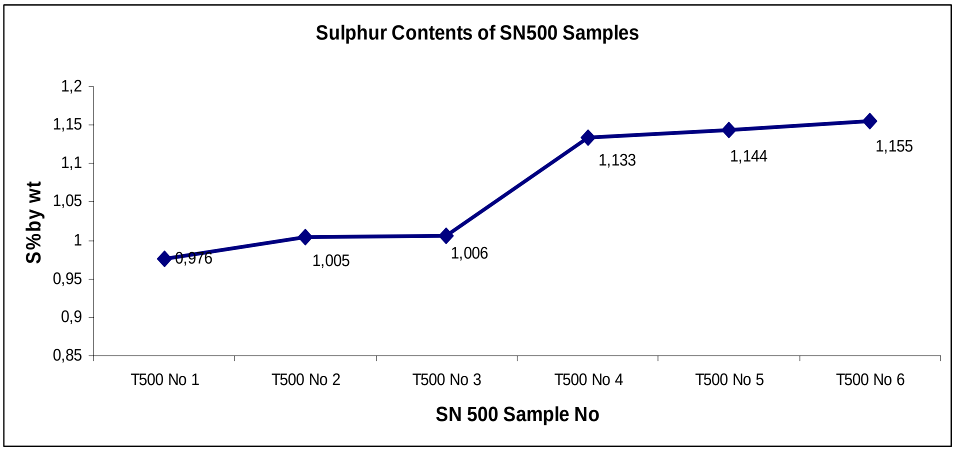


Figure 4.1-1 Chart illustrating sulphur content of SN500 samples having various batches.

Even SN500 samples were taken from the same refinery variation observed in sulphur contents. Refractive indexes of the same samples were determined and showed in 4.1-2.

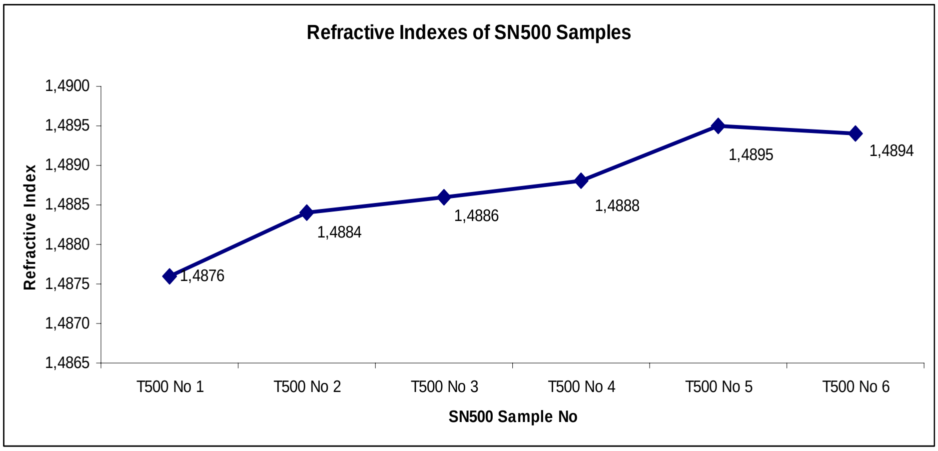


Figure 4.1-2 Chart illustrating Refractive Index of SN500 samples having various batches.

According to the comparison of two graphics, there is a positive correlation between sulphur content and refractive index. If the sulphur content increases, then the refractive index increases as well.

In the next part group I base oils having different viscosity grades were tested and compared to comment on their impurities. Further to thermophysical properties of kinematic viscosity, flash point, and refractive index, also carbon distribution, sulphur content tests were conducted to find out their qualities.

Table 4.1-1 shows the comparison of four types of base oils from the same refinery.

Table 4.1-1 Typical properties of Group I base oils from the same refinery

Tests		Methods	Unit	T1	T2	T3	T4
Carbon Distribution	Ca	ASTM D-2140	%	6	6	7	8
	Cn		%	30	30	28	29
	Cp		%	64	64	65	63
Kinematic Viscosity at 100°C		ASTM D-445	mm^2/s	3.46	5.56	11.32	33.9
Flash point COC		ASTM D-92	°C	200	228	242	316
Sulphur content		ASTM D-6481	%	0.75	0.77	0.98	1.42
Refractive index at 20°C		ASTM D-1218		1.476	1.482	1.489	1.500

The samples shown in this table were taken from the same refinery and they had various viscosity grades changing from 3.46 cSt to 33.9 cSt.

They were tested according to ASTM D 2140 method to determine aromatic, naphthenic and paraffinic contents. Among these compounds aromatic content influence the oxidation stability of finished lubricant drastically thus it is very important parameter to comment on sludge and varnish formation. In Table 4.1-1, as aromatic content rises sulphur content also rises with an increase in refractive index.

The relation between aromatic content and sulphur content can be seen both in the Figures 4.1-3 and 4.1-4 clearly below: Carbon distribution of each base oils were calculated as a ratio by taking naphthenic content as basis and shown in Figure 4.1-3.

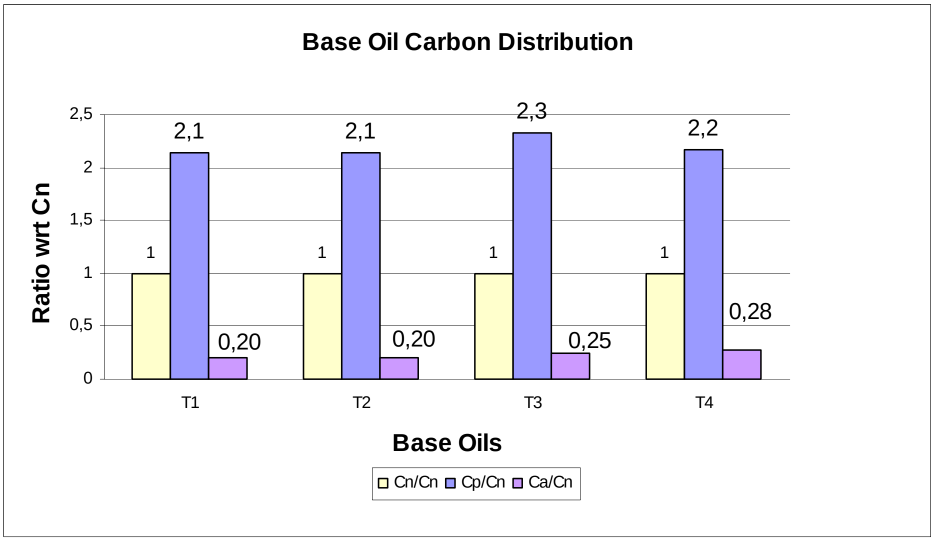


Figure 4.1-3 Chart illustrating carbon distribution of four type of Group I base oils.

In Figure 4.1-3 relative aromatic contents of base oils increase with respect to base oils type in parallel to viscosity grades. Relationships should be taken into consideration with the trend in Figure 4.1-4 which shows sulphur contents.

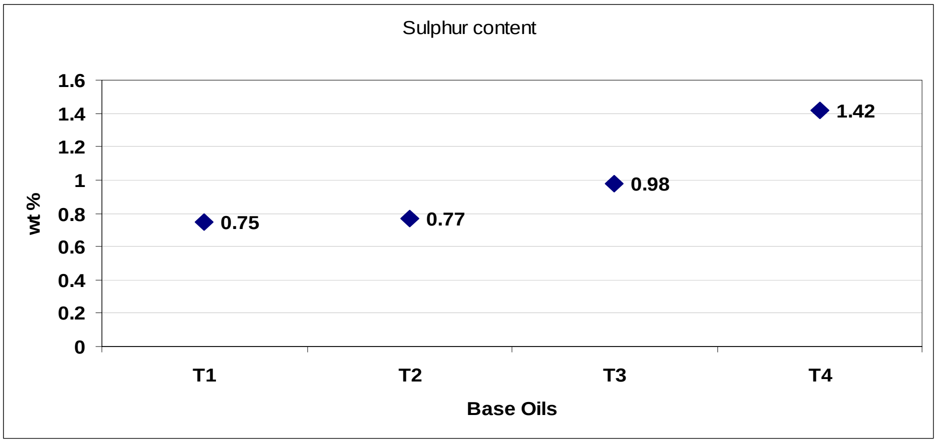


Figure 4.1-4 Chart illustrating wt% of sulphur content of four type base oils.

In Figure 4.1-4, four types of Group I base oils from the same refinery were compared to each other and it can be said that the higher sulphur content, the upper viscosity. In the next part, Group I base oils from different refineries were compared as shown in Table 4.1-2.

Table 4.1-2 Typical properties of Group I base oils from various sources.

Tests	**Methods**	**Unit**	**M150**	**T150**	**L150**
Density at 15°C	ASTM D 4052	kg/L	0.871	0.875	0.874
Viscosity @ 100°C	ASTM D 445	mm²/s	5.2	5.6	4.9
Viscosity @ 40°C	ASTM D 445	mm²/s	30.18	34.04	28.57
Viscosity Index	ASTM D 2270		101	100	94
Evaporation Loss by Noack	ASTM D 5800	%m/m	15.1	12.6	21.0
Sulphur Content	ASTM D 6481	wt %	0.335	0.796	0.237
Ramsbottom Carbon Residue	ASTM D 524	%m/m	0.485	0.500	0.555

In Table 4.1-2 base oils having same viscosity grades, SN150, were evaluated. It is known that the base oils with higher viscosity indexes have less impurity (Sharma et al., 2008). Thus if we compare qualities M150 has the highest quality level, T150 has the second and L150 has the third one.

In this part RCR can be discussed as effective parameter for sludge formation. Test was performed at 550°C and sample was burned 20 minutes at this temperature. Thus the residue of the sample could be impurities which can cause varnish or sludge in the finished oil application.

For this reason carbon residue and viscosity index of Group I base oils compared in Figure 4.1-5.

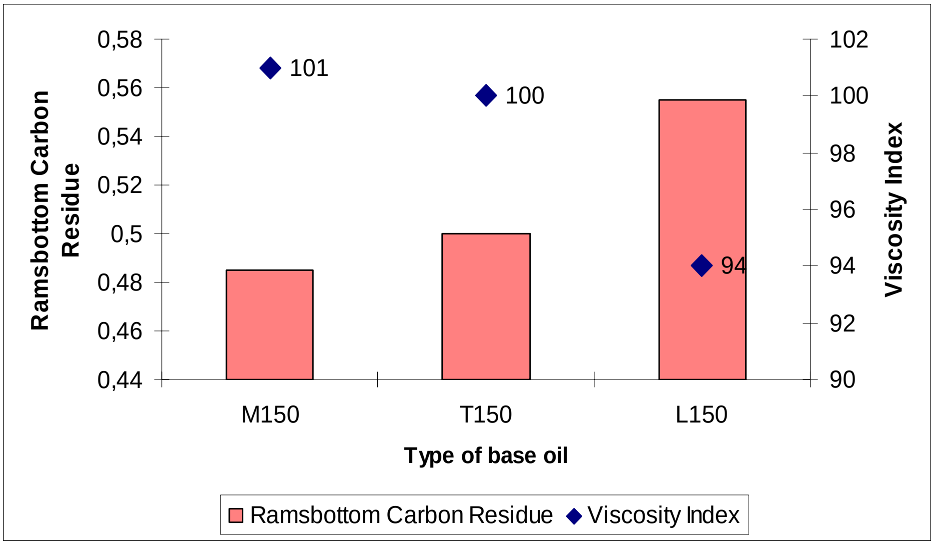


Figure 4.1-5 Chart illustrating ramsbottom carbon residue with respect to viscosity index. (Group I)

As shown in the Figure 4.1-5 carbon residue is increasing with decreasing viscosity index which means that increasing impurities. In the previous parts sulphur content was depend on refractive index and viscosity index. Thus it can be concluded that RCR also increases with increasing refractive index.

In this part Group I, II, III and IV base oils at the same viscosity grades were investigated. Thermophysical and chemical properties are given in Table 4.1-3.

Table 4.1-3 Typical properties of Group I, II, III and IV base oils.

Tests	**Methods**	**Unit**	**G I**	**G II**	**G III**	**G IV**
Density at 15°C	ASTM D 4052	kg/L	0.875	0.845	0.835	0.836
Viscosity @ 100°C	ASTM D 445	mm²/s	5.6	4.7	5.0	5.7
Viscosity @ 40°C	ASTM D 445	mm²/s	34.0	23.7	25.6	30.0
Viscosity Index	ASTM D 2270		100	119	125	135
Evaporation Loss by Noack	ASTM D 5800	%m/m	12.6	10.5	9.4	7.6
Sulphur Content	ASTM D 6481	wt %	0.796	0.002	0.002	0.002
Ramsbottom Carbon Residue	ASTM D 524	%m/m	0.50	0.50	0.27	0.01

Base oils having almost same viscosities were evaluated as shown in the table. Samples were supplied from different sources. Conventional Group I base oil was supplied from Turkey and designated as G I, Group II from the United States and designated as GII, Group III from Finland, Group IV from the United States. Sulphur contents in Group II, III and

IV base oils are almost zero. Their saturated levels are high thus the viscosity indexes are also high. As a result Group II, III and IV has higher oxidation stability than Group I base oil.

In Figure 4.1-6 carbon residue of Group I, II, III and IV base oils were evaluated with viscosity indexes.

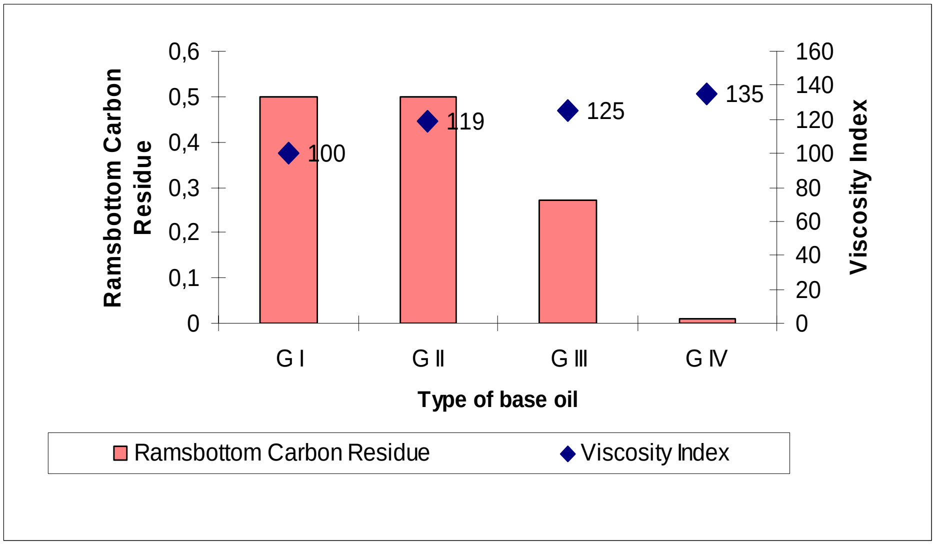


Figure 4.1-6 Chart illustrating ramsbottom carbon residue with respect to viscosity index (GI, GII, GIII, GIV).

As shown in the Figure 4.1-6 carbon residue of the base oils decrease with higher group numbers. Oxidation stability of base oils with higher group number is better and carbon residue is lower. If Group II and Group III base oils are used in hydraulic oil formulation, oxidation stability will be high but cost should also be taken into consideration for optimum formulation. On the other hand, since the solubility of the base oils decrease as the impurities decrease, they cause sludge because of the additives used in (Moehle et al., 2007).

Base oils properties change according to production processes. In this part aging properties of different refinery product base oils were investigated. In this experimental study, base oils of G I, G II, G III and G IV were used, which stand for PAO, GTL (Gas to Liquid), hydrocracked and isodewaxed respectively. According to IP 48 test method samples were aged at 170°C and 15 L/h air was passed through the sample. Kinematic viscosities at 40°C and total acid numbers were evaluated.

Total acid number differences with respect to time of oxidation for four types of high quality base oils are shown in Figure 4.1-7.

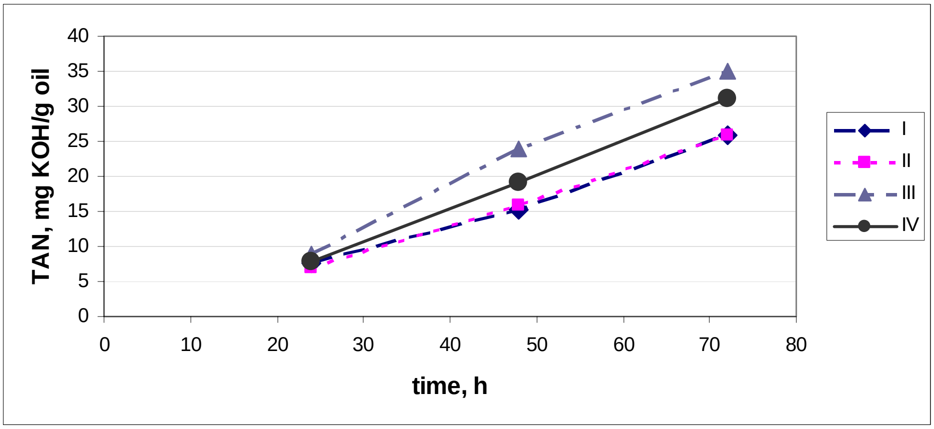


Figure 4.1-7 Chart illustrating total acid number with respect to time.

Total acid numbers of the samples after aging 24 h, 48 h and 72 h were determined. Changes of total acid number (TAN) during these periods were noted and shown on the graph. PAO and GTL product base oils have better oxidation stability results since changes are less. TAN results of hydrocracked base oil have the most deviation from the beginning. Isodewaxed base oil is better than hydrocracked base oil. In the next graph viscosities at 40^{o}C of same base oils were measured. After

48 hours hydrocracked base oil was pasty and viscosity could not be measured. TAN difference from the beginning was too high at this point. So it can be concluded that hydrocracked base oil has the less oxidation properties.

PAO and GTL oxidation properties are the best and followed by isodewaxed and hydrocracked base oils. According to production processes GTL base oil has enough quality as PAO has. In the future PAO can be replaced by GTL base oils.

In order to evaluate effect of additive into sludge formation three types of Group I base oil samples having different qualities were chosen and one type of antioxidant additive was used in them. First of all three different quantities of additive were used in each base oils and then one type was chosen to have tests in detail.

4.2. Finished Lubricants

In this part various hydraulic oil formulations were prepared in the laboratory. In the first trial T150, Group I, base oil and AD1 antioxidant additive which refers to LZ 5703, were used. First formulation which is designated as 1A contains 99.2%wt of Group I base oil T150, which can be estimated as medium quality, and 0.8%wt of additive. Formulation 1B contains 99.0%wt of same base oil and 1%wt of additive. Formulation 1C contains 98.5%wt of T150 base oil and 1.5%wt of additive. Finished lubricant formulations can be seen on the Table 4.2-1.

In the second trial low quality grade of Group I base oil was used. Since in the first trial higher additive content formulation had negative test results only two types of contents were evaluated. L150 base oil formulations are tabulated in Table 4.2-1.

In the third trial silicone free antifoamer additive was added to the 1A formulation in order to observe its effect on oxidation stability. Antifoamers help to prevent foaming when oil is used at the system. Since they capture air in the oil, the contact time of air with oil will be longer and oxidation rate will be higher. So they may influence the air release properties negatively which results in oxidation parameters can be worse.

In the last and the fourth trial Group I base oil, M150, having the highest quality was investigated. Formulations are tabulated in Table 4.2-1. In all formulations total acid number, carbon residue increase and kinematic viscosities at 40°C after and before oxidation were performed on the samples. At the end of the tests changes were noted.

Table 4.2-1 Finished hydraulic oil formulations

CODE NO	T150	L150	M150	AD1	AD2
1A	99.2			0.8	
1B	99.0			1.0	
1C	98.5			1.5	
2A		99.2		0.8	
2B		99.0		1.0	
3A	99.2			0.8	100 ppm
3B	99.2			0.8	150 ppm
4A			99.2	0.8	
4B			99.0	1.0	

In these trials effects of additives on the carbon residue increase and Total Acid Number were evaluated as shown in Figure 4.2-1.

Total Acid Numbers of the formulated hydraulic oils were measured before the oxidation. After oxidation which was conducted at 200^{o}C and 15 L/h of air passing through it during 6 hours, total acid number could not be read since the samples were pasty. Thus TAN results of formulations before oxidation were taken into consideration.

In Figure 4.2-1 total acid numbers with respect to carbon residue increase were evaluated for the formulations explained.

Total Acid Number increases with increasing additive content. In each group of formulations carbon residue increase also goes up with increasing additive content.

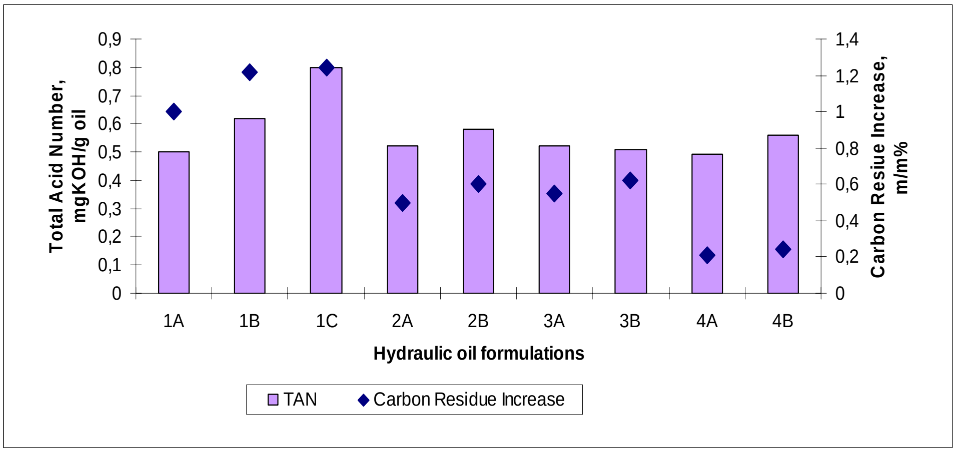


Figure 4.2-1 Chart illustrating total acid number with respect to carbon residue increase

Viscosities at 40^{o}C were determined before and after oxidation and then rates between them were recorded to observe viscosity increase. As it can be seen in the Figure 4.2-2 additive content affects the rates to up.

Furthermore to evaluate oxidized properties of the base oils and finished oils FT-IR analyses were performed on the samples. First of all original products were scanned on the FT-IR and then these same samples were oxidized according to IP 48 method. After oxidation FT-IR graphs were gained again and shown on the same graph as in the Figures 4.2-3-7 followed.

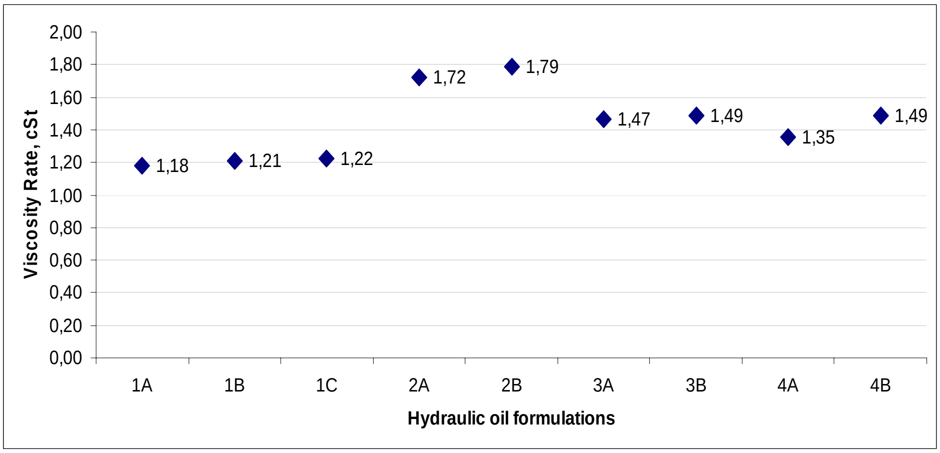


Figure 4.2-2 Chart illustrating viscosity rates of finished hydraulic oils.

In Figure 4.2-2 formulations 2A and 2B have higher viscosity rates. Thus it may be said that lower quality base oils affect viscosity rates negatively.

Three types of base oils were used in the formulations which were supplied from various sources. These base oils have different saturation levels. In order to observe their oxidation peak level their finished oil formulations were tested according to FT-IR test method. After oxidation of oil FT-IR test was conducted again. For this purpose base oil of low quality was used in the first trial as shown in Figure 4.2-3.

Base oil, L150, formulated with 0.8%wt of additive is shown on the FT-IR graph. As can be seen on the same graph the peak of 1719.2 cm^{-1} is different from the original. New product formation can be seen at the end of the oxidation. Other peak deviations may be estimated as negligible since peak shape is not so different. The same method was conducted to the other samples to compare oxidation peaks on the FT-IR graphs.

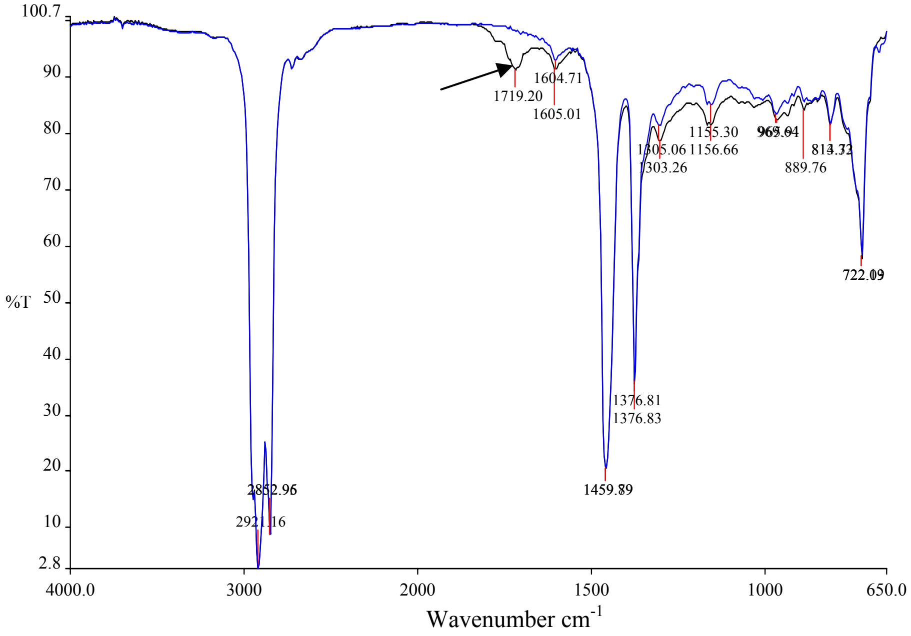


Figure 4.2-3 IR spectrum of hydraulic oil 2A before and after oxidation.

In the FT-IR graph below (Figure 4.2-4) oxidative behavior of oxidized oil can be compared with unoxidized oil. In this FT-IR graph T150 with 0.8%wt of additive is shown. Again oxidation product peak is similar with the previous one and it can be seen on 1715.81 cm^{-1} level.

In Figure 4.2-5 oxidation peak of hydraulic oil formulated with medium grade paraffinic base oil of T150 was evaluated.

Additive content was increased to 1% from 0.8%wt in this trial. T150 was used again as a Group I base oil. Oxidation product peak is 1718.35 cm^{-1} as in FT-IR graph.

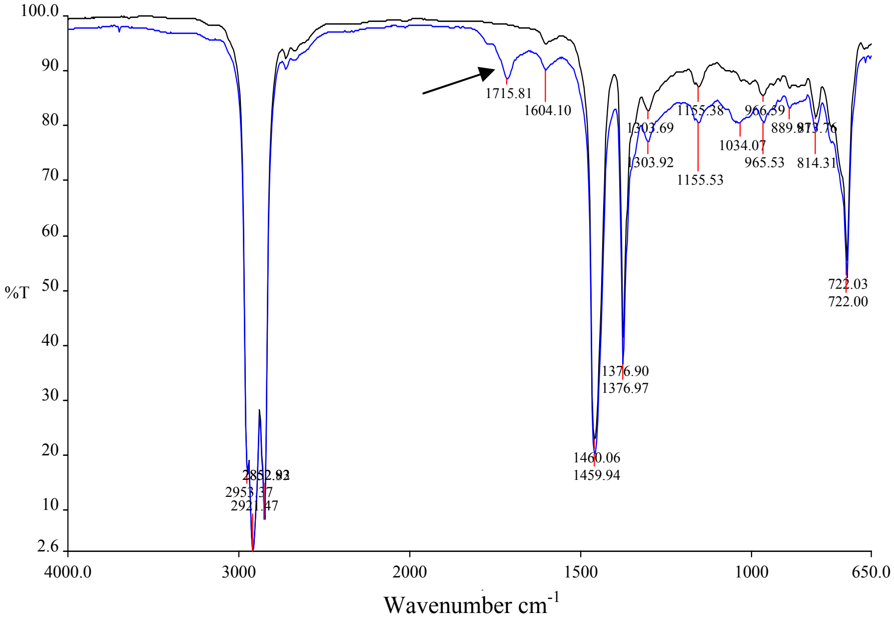


Figure 4.2-4 IR spectrum of hydraulic oil 1A before and after oxidation

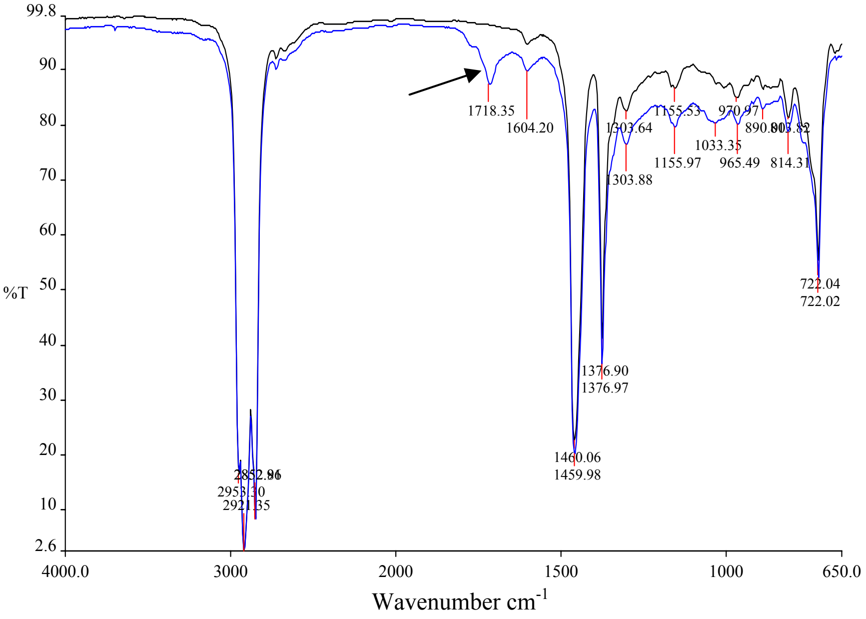


Figure 4.2-5 IR spectrum of hydraulic oil 1B before and after oxidation

In the next study 100 ppm of silicone free antifoamer was added to the formulation of T150 with 0.8%wt of hydraulic oil package. Formulation is shown as in the Figure 4.2-6.

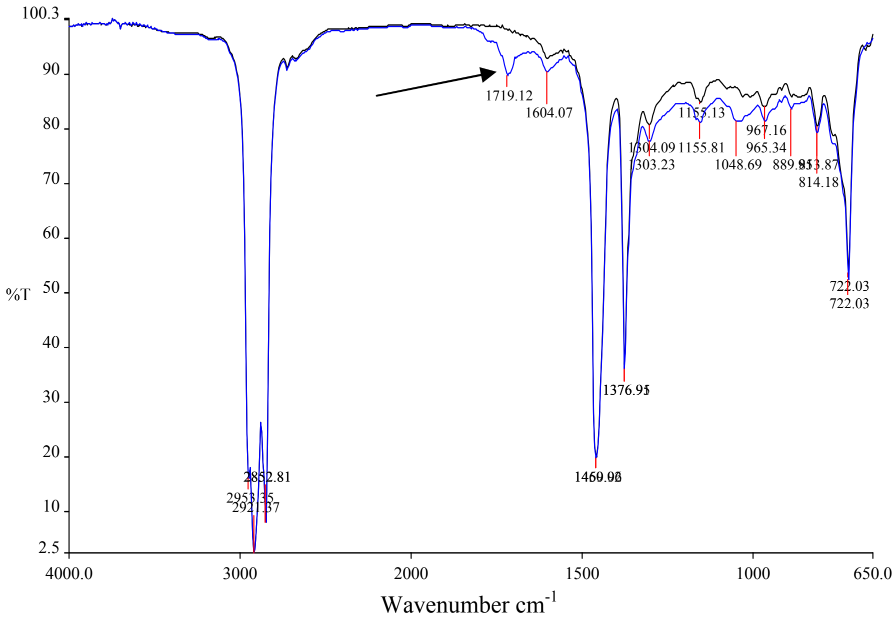


Figure 4.2-6 IR spectrum of hydraulic oil 3A before and after oxidation

After oxidation the product scanned in the FT-IR as in Figure 4.2-6. Small difference on oxidation peak was observed and it is 1719.12 cm^{-1}. It may be concluded that addition of small amount of antifoamer in the formulation can change oxidation by products of hydraulic oil.

In the next study M150 base oil formulated with 0.8%wt of additive was evaluated. Finished oil reference and oxidation of it can be seen in Figure 4.2-7.

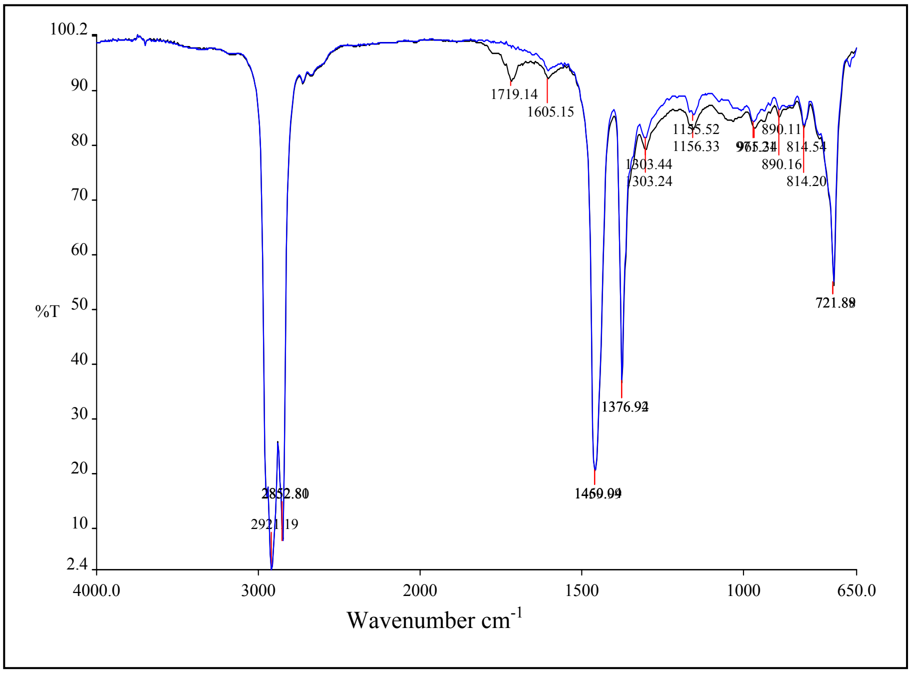


Figure 4.2-7 IR spectrum of hydraulic oil 4A before and after oxidation

Group I base oil which have higher purity than the others has the similar oxidation product peak of 1719.14cm^{-1}.

In all these studies oxidation peaks were similar and between 1715 and 1719.2 cm^{-1}. From the literature (Erdik, 2005) it can be found that peaks between 1710 and 1740 cm^{-1} can be estimated as ketonic type products which were also shown in oxidation reactions on previous pages (Adhvaryu et al., 1999). In the similar study elevated oxidation peaks were observed in the carbonyl region of 1714 cm^{-1} (Livingstone, 2003). FT-IR can also indicate oxidation by products such as, ketones, esters, carboxylic acids, carbonates, aldehydes, anhydrides and amines.

In order to evaluate propensity of sludge formation, carbonyl index of the samples were calculated as below;

$$CO\ Index = \frac{A_{1715}}{A_{1460}}$$

where A_{1715} represents the oxidation peak emerged after oxidation of the samples, and A_{1460} represents C-H bending peak.

Carbonyl indexes of 2A, 1A, 1B, 3A and 4A were calculated in the same way and minimum value was obtained for M150 (4Aformulation) which has the best quality. The highest value was obtained for 1B formulation which means that deposit formation can be seen more. Since the other formulations have almost similar values it may be concluded as lower quality base oils have higher carbonyl index.

Thermogravimetric analysis was conducted to base oils and finished formulation to evaluate evaporation loss. Three types of base oils L150, T150, M150 and finished hydraulic oil formulated with T150 and LZ5703 additive were used in this study. Their degradation behavior with respect to temperature is shown in the Figure 4.2-8.

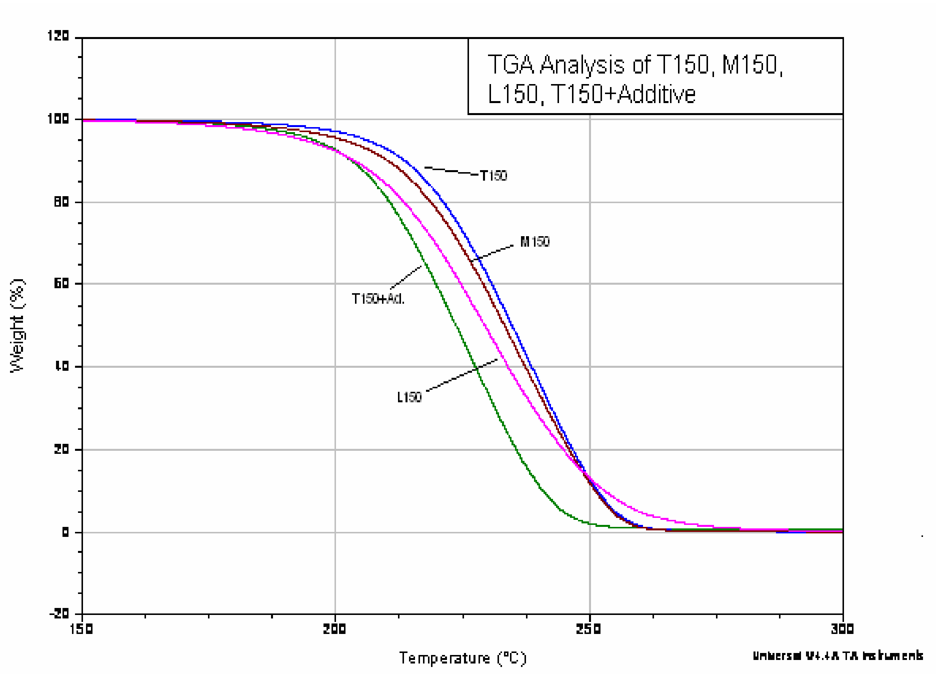


Figure 4.2-8 Graph illustrating TGA analysis of three base oils and one finished hydraulic oil.

According to this test, weight losses of base oils and finished hydraulic oils can be evaluated. Product containing additive left more residues than base oils after thermo gravimetric analysis. This may be because of the additive metals contents in the formulation. On the other hand although 100% of the T150 and M150 evaporated, L150 left some residue at the end of the test. This may be because of the impurities of this base oil which depends on the severity and type of refinery process.

4.3. Uncertainties

All samples were tested according to the ASTM standards as described before. Uncertainties of these test results should be taken into consideration while discussing formulations. ASTM test standards were used to find out uncertainties of methods and they were tabulated as shown in the Table 4.3-1.

Table 4.3-1 Table of uncertainties used in the test methods.

PROPERTY	UNCERTAINTY			STANDARD
Viscosity		Base oils (%)	Formulated oils (%)	ASTM D 445
	Repeatibility	0.21	0.26	
	Reproducibilty	0.65	0.76	
Refractive Index	Repeatibility	R (manual): 0,0002		ASTM D 1218
	Reproducibility	R (manual):0,0005		
Flash Point	Repeatibility	8°C (15°F)		ASTM D 92
	Reproducibility	8°C (32°F)		
Density at 15°C	Range, g/mL	Repeatability	Reproducibility	ASTM D 4052
	0.68-0.97	0.0005	0.0005	
Evaporation Loss by Noack	Repeatibility	5.8% x Average M/M Evaporation Loss		ASTM D 5800
	Reproducibility	18.3% x Average M/M Evaporation Loss		

Table 4.3-1 Table of uncertainties used in the test methods (continued).

Item	**UNCERTAINTY**				**STANDARD**
Carbon	Carbon Distribution	Range	Repeatability	Reproducibility	ASTM D 3238
	%Ca	2.7-34.6	0.6	1.7	
	%Cn	23.7-47.2	1.2	3.6	
	%Cp	32.3-68.6	1.0	3.4	
Sulphur	Mass% (X) Sulphur		Repeatability	Reproducibility	ASTM D 6481
	0.05		0.002	0.011	
	0.1		0.003	0.018	
	0.5		0.01	0.06	
	0.1		0.017	0.04	

5. CONCLUSION

Varnish formation problems on the application of hydraulic systems oils are most severe to give damage to the systems. High temperature operation conditions double the rate of oxidation which results in occurring of many reactions. Deposits which are formed during oxidation cause the formation of varnish. Since field applications can not be simulated in the laboratories it is difficult to comment on the results but high temperature properties may give opinion.

Thermophysical and chemical properties of mineral base oils are mostly depend on the refinery processes. Saturation level of hydrocarbon molecule influences the oxidation performance of hydraulic oils. On the finished oil formulations it is possible to regulate oxidation properties but very difficult to control varnish formation. Hydrocarbon molecule structure of base oils ultimately depend on the refinery process. During oxidation of hydraulic oils various oxidation reactions take place in the system. Additives help to slow down these reactions but after a period of time they start to lose their effectiveness. They may be source of deposit formation. Thus base oils and additives harmony is important for the life of finished hydraulic oils. Base oils and finished hydraulic oil formulations were studied to discover reason of sludge formation. TGA, Oxidation, Ramsbottom Carbon Residue and FT-IR tests were used for this purpose. Thermophysical and chemical properties of base oils according to refineries and group numbers may be concluded as below;

- As sulphur content of base oils increases, saturation level and oxidation properties decrease. It can also be said that refractive index rises with increasing sulphur content. This may be concluded as base oils having higher refractive index contain more impurities.

- As the group number of base oils increases higher viscosity indexes and lower carbon residues are obtained.

- Hydrocracked and isodewaxed base oil oxidation properties similar to each other but the base oil from gas to liquid process has better results which are close to PAO’s.

- Molecular structures and saturation level of base oils may change from source to source even they are all in same group number.

- Even in different production batches sulphur content may change.

In finished hydraulic oil formulations base oils having various molecular structures affected test results as below;

- An increase in total acid number increases the carbon residue which also depends on the additive content.

- More additive content leads to higher viscosity rates.

- Higher saturation level of base oils in the formulation decreases the viscosity rates.

- Oxidation peaks of three various Group I base oils, in same viscosity grades, were observed on FT-IR graph between 1715 and 1719.2 cm^{-1} which are possibly keton type products.

This study shows that both saturation level and sulphur content of the base oils affect the finished oil oxidation properties. Carbon residue increase mostly depends on the amount of additive content and impurities in the base oil. For the optimum formulations both of them should be taken into consideration.

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