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EVALUATION OF THE NATURAL AND SYNTHETIC FATTY ACID ESTERS IN HYDRAULIC OIL

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ÖZET

Petrol bazlı yağlayıcıların çevresel etkileri ve fosil yakıt rezervlerinin kısıtlı olması doğaya uygun yağlayıcı alternatiflerinin aranmasına sebep olm gelişimi mineral esaslı bazyağlarına dayanmaktadır. Bazyağlarının iyi teknik özellikleri ve düşük fiyatı mineral esaslı bazyağı teknolojisini desteklemiştir. Neyazıkki bazyağı sonlu bir kaynaktır. Mineral yağ sebebiyle oluşan kirlilikler üretimi kadar kolay doğaya karışamamaktadır. Bununla birlikte, mineral esaslı bazyağlarının sebebi genellikle politik nedenlere bağlıdır. Varolan stokları da her zaman aynı fiyatla fiyatla temin etmek mümkün olmamaktadır. Bir diğer olumsuz yanı ise mineral yağların doğaya karışma süresinin oldukça uzun sürmesidir. Zincir yağları, trafik ve inşaat sektörlerinde kullanılan yağlar açık yağlama sistemlerine ait olduğu için genellikle doğaya bırakılır. Ayrıca genel kapalı yağlama sistemlerinde de yanlışlıkla doğaya deşarj etme gibi riskli durumlarla karşılaşılmaktadır. Bu sebeple yağlayıcılar mümkün olan her alanda biyoparçalanabilir olmalıdır.

Batı Avrupa Bioyağlayıcılar Market araştırmasına göre (2004): toplam 4.750.000 ton/yıl'lık yağlayıcılar pazarında, bioyağlayıcıların yeri 172.000 ton/yıl'dır (Whitby, 2004). Aynı araştırmaya göre kompresör ve zincir yağlayıcılarının önemli bir kısmı bioparçalanabilir olarak üretilmektedir. Marketteki bioyağlayıcı ihtiyacı, motor yağı ve hidrolik yağlar olarak gözükmektedir. Günümüzde, otomativ üreticileri, kullanılan yağlayıcıların çevresel performansları ile ilgili bir talepte bulunmamaktadırlar, çünkü bu yağlayıcılar yüksek katkı maddesi içerdiklerinden çok karmaşık ürünlerdir. Bu sebeple, çevre dostu motor yağları formulasyon çalışması daha da zorlaşmaktadır. Hidrolik yağlar, Türkiye ve Batı Avrupa marketinde, çevre dostu yağlayıcı formulasyonları için üzerinde çalışılabilecek en uygun adaydır.

Yağ asidi esterleri, yağlayıcılarda ihtiyaç duyulan, yüksek viskozite indeksleri, yüksek parlama noktaları ve düşük uçuculukları ile etkin sınır yağlayıcılığı sağlarlar. Buna karşılık, bioparçalanabilir yağlayıcılar, mineral yağlayıcılar ile karşılaştırıldığında, oksidasyon stabilitesi ve düşük sıcaklık karakteristikleri göz önüne bulundurulduğunda daha düşük performans sergilemektedir. Bu çalışmada, farklı yağ asidi esterlerinin oksidasyon ve aşınma önleme üzerine etkileri ile hidrolik yağların fiziksel ve kimyasal özellikleri araştırılacaktır. Çalışmanın ilk basamağında, beş farklı yağ asidi esteri, termal oksidasyon stabilitesi ve akış özellikleri bakımından incelenecektir. Yağ asidi esterleri, Türkiye’deki yaygınlıkları, fiyatları ve viskozite sınıflarına göre seçilmiştir. Çalışmanın ikinci basamağında, en iyi sonucu veren; kanolo yağı ve trimetiloleat (TMP TO) hidrolik yağ formulasyonu karışımı çalışmasında kullanılmıştır. Hidrolik yağlarda, ISO VG 46 sınıfında DIN 51524 normlarına göre en iyi yağlayıcılık performansını elde edebilmek için farklı yağ karışımları hazırlanmıştır. Sonuçlar ortaya çıkarmıştır ki: hidrolik yağ formulasyonlarında esterler kullanıldığında, yağlayıcının yapısındaki polar grupların varlığından dolayı, formule edilen yağlayıcı, yüksek sıcaklık değişimlerine ve parçalanmadan kaynaklanan bozulmalara dayanmakta ve mükemmel yağ filmi oluşturmaktadır.

Çalışmanın sonunda, oksidasyon performansı incelenen esterlerin ana bileşen, katkı maddesi ve kalınlaştırıcı olarak hidrolik yağ formülündeki kullanım yerine karar verilmiştir. Yüksek sıcaklık ve ağır hidrolik uygulamalarında; sıcaklığın 150 C dereceden daha yüksek olduğu, TMP TO hidrolik yağ formülasyonunda yalnızca katkı maddesi olarak kullanılabileceği ortaya çıkmıştır. Orta zorluktaki uygulamalarda, özellikle orman ve inşaat alanında TMP TO hidrolik yağ formülünde baz yağı olarak kullanılabilinir.

Anahtar kelimeler: Triboloji, Ester, Yağlayıcı, Baz Yağı, Hidrolik Yağ, Oksidasyon, Aşınma, Sürtünme.

ABSTRACT

The concern over the potential impact of petroleum-based lubricants on the environment and the limited fossil fuel reserves has created an opportunity to promote environmentally acceptable alternatives. The development of lubricants like engine and hydraulic oil was mainly based on mineral oil as a base fluid. Good technical properties of base oil and reasonable price enhance technology with mineral base oil. Unfortunately mineral oil is a finite source. The deposits of mineral oil can not be replenished as fast as they are used up. In addition, the availability of mineral oil is highly dependent on political considerations. Even existing deposits do not guarantee that they will be available to us in the future, at least not at the current price. The second aspect is the pollution of environment associated with the use and discharge of chemicals. Nature can not easily tolerate the environmental problems associated with the production and use of mineral oils which are petroleum based. In open lubrication systems like power saw chain oils (forestry), switch lubricants (traffic), slab oils (construction) and hydraulic oil of harvesters are generally directly exposed to environment. Also in general closed lubrication systems, lubricants might be directly disposed to environment accidentally (primary/direct pollution). Lubricants are chemicals with high environmental relevance. Therefore, it is highly desirable to use environmentally friendly lubricants wherever possible.

According to Western European Biolubricants Market Survey in 2004; the total lubricant market is 4 750 000 tones/year where total Biolubricants are 172 000 tones/year (Whitby, 2004). According to the previous data market in the table, compressor and chainsaw oils are produced with biolubricants to a reasonable extent. The market need for biolubricants is mainly for automotive engine and hydraulic oils. Manufacturers do not make any claims about the environmental performance of automotive lubricants currently. And also they are complex products with high additivation. So a formulation study for environmentally friendly engine oil would be harder. Hydraulic oil is a good candidate either for Western Europe and Turkey market in order to work on environmentally friendly lubricants formulations.

Fatty acid esters provide good boundary lubrication, high viscosity index, high flash point and low volatility which are desirable properties in a lubricant. However, biodegradable lubricants have low performance compared to mineral oils, particularly from the standpoint of oxidation stability and low-temperature characteristics. In this study, the influence of different fatty acid esters on oxidation, antiwear, physical and chemical properties of hydraulic oil was investigated. In the first step of the study five different fatty acid esters were evaluated in terms of thermal oxidative stability and flow properties. The fatty acid esters were chosen according to its extensiveness in Turkey market, price and viscosity grade. In the second part of the study, best candidates; rapeseed oil and trimethylolpropantrioleate (TMP TO) were used in hydraulic oil formulation blend study. Different hydraulic oil blends were formulated in order to have the best lubricity performance in hydraulic oil according to DIN 51524 norm at viscosity of ISO VG 46. The results revealed that when esters were used in hydraulic oil formulations, because of the presence of the polar groups in structure the lubricant withstand extreme temperature variations, shear degradation and maintain excellent boundary lubricant film formation.

At the end of the study, after the investigation of the oxidative performance of the esters; it is determined that the esters can be used as base fluid, main component, additive or thickener in the formulation of hydraulic fluid. For high severity hydraulic applications; where operating temperatures are higher than 150ºC; TMP TO can only be used as an additive in hydraulic oil formulation. In medium severity applications; mainly in forestry and construction TMP TO can be used as a base fluid in hydraulic oil formulation

Keywords: Tribology, Ester, Lubricant, Base Oil, Hydraulic Oil, Oxidation, Wear, Friction

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1. INTRODUCTION

Fossil fuel reserves are decreasing and strict environmental regulations are set in most of the countries; there is an increasing demand for environmentally friendly hydraulic oils throughout the world. Not only because of the environmental regulations and future fossil fuel shortage; there is a big environmental hazard risk because of the spillage of lubricants directly to the nature. High amounts of hydraulic oils disappear by spillage or other reasons every year. As a result, ground water, soil are contaminated and animals or plants are poisoned by these accidents.

There is a trend to use biodegradable fluids. Especially in forestry, number of machine users prefers to use environmentally friendly hydraulic oils. Fatty acid esters are considered to be potential candidates as substitutes for conventional mineral-oil based lubricating oils and synthetic esters. Fatty acid esters have low volatility due to the high molecular weight of the triglyceride molecule and excellent temperature viscosity properties.

On the other hand, fatty acid esters have poor oxidative stability primary due to the presence of bis-allylic protons. These active sites are highly susceptible to radical attack subsequently the molecules undergo oxidative degradation. After this reaction, insoluble deposits are formed and oil acidity and viscosity increases. Insoluble deposits cause problems in hydraulic oil filtration and acid formation and viscosity increase cause problems in lubricating performance of the hydraulic oil.

This study presents an approach to evaluate five different fatty acid esters in hydraulic oil formulation in terms of oxidation and other hydraulic oil performance analysis. The oxidation properties of the ester containing hydraulic oil blends are tested according to IP 48 test method.

2. LITERATURE OVERVIEW

Tribology which is derived from the Greek tribos (meaning rubbing) is the science of friction, wear and lubrication. Although the use of lubricants is very old, the focus on lubricants and lubrication technology is relatively new. For example the term tribology was first introduced in 1966 and globally described as reach field activity since 1985. Although, lubrication technology is a new terminology; since saving energy and resources and cutting emission have become central environmental matters, lubricants are more attracting the public attention. It has been shown that 0,4 % of gross domestic product could be saved in terms of energy in Western industrialized countries if current tribological knowledge was applied to lubricated processes (Mang, 2007).

On metal surfaces under boundary lubrication a tribofilm is formed and this phenomenon is related with the combination of all sciences and technologies. The fundamentals of chemistry and physiscs are exploited in tribochemistry but also mechanics and material sciences are included. The development of lubricants has become an integral part of the development of machinery and its corresponding technologies. The annual consumption of lubricants (including automotive and industrial lubricants) is shown in Figure 2.1 according to year 2006.

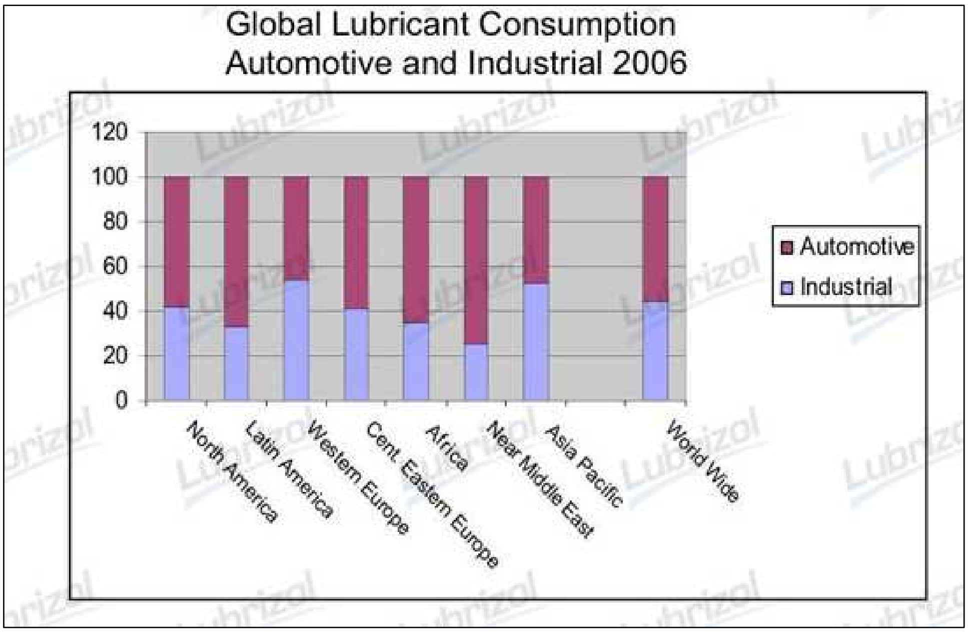


Figure 2.1. Global Lubricant Consumption in 2006

Lubricants are generally classified into two major groups: automotive lubricants and industrial lubricants. Industrial lubricants are also divided into two parts: industrial oils (hydraulic, compressor and turbine oils) and industrial specialities (greases, metal working fluids, solid lubricants etc.). The most important group of the lubricant is engine oils while the second important group is hydraulic oils.

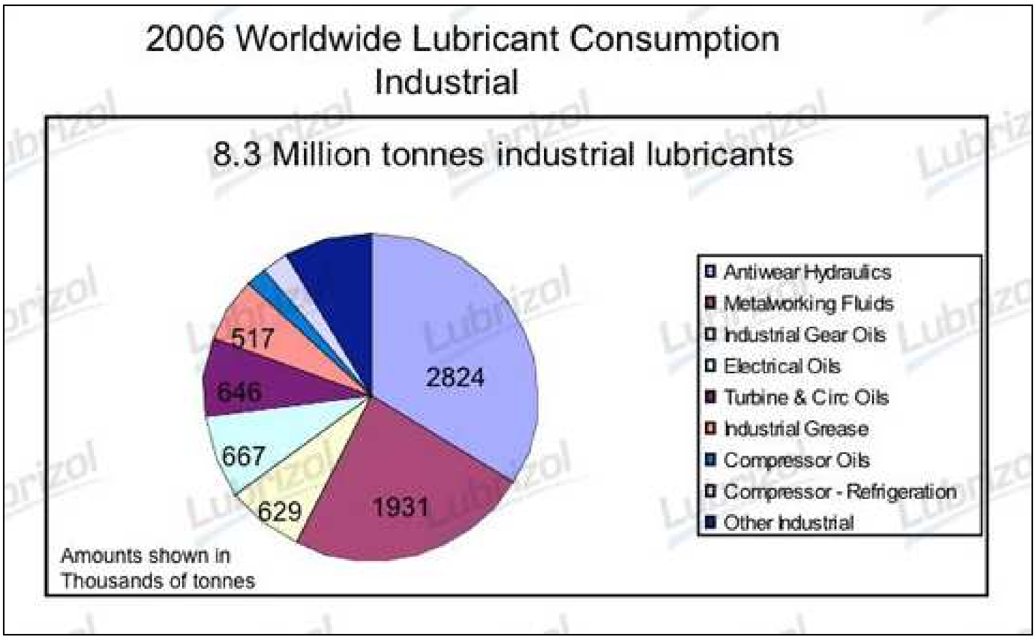


Figure 2.2 Global Industrial Lubricant Consumption in 2006.

Lubricants have an impact on health, safety and the environment at all stages of their production, use and disposal. They should be non-toxic to human health through contact or inhalation during production and use. Their accidental spill can have the potential to cause ecological diseasters (Rudnick, 2006).

Hydraulic Oils

Hydraulics is described as the transfer of energy and signal through the fluid to drive, control a device. Hydraulic fluids based on mineral oils, synthetic fluids and fire resistant fluids are used in all type of machinery and equipment. Hydraulic oils are used in a variety of machines, including automobiles, car transmissions, power steering systems, and power brakes. Hydraulic oils are also used in tractors, excavators, forklifts, bulldozers, trucks and other industrial machinery. Most aircraft flight control systems also require hydraulic fluid.

The use of hydraulic fluids relative to other industrial lubricants is shown in Figure 2.1-1 (Rudnick, 2006).

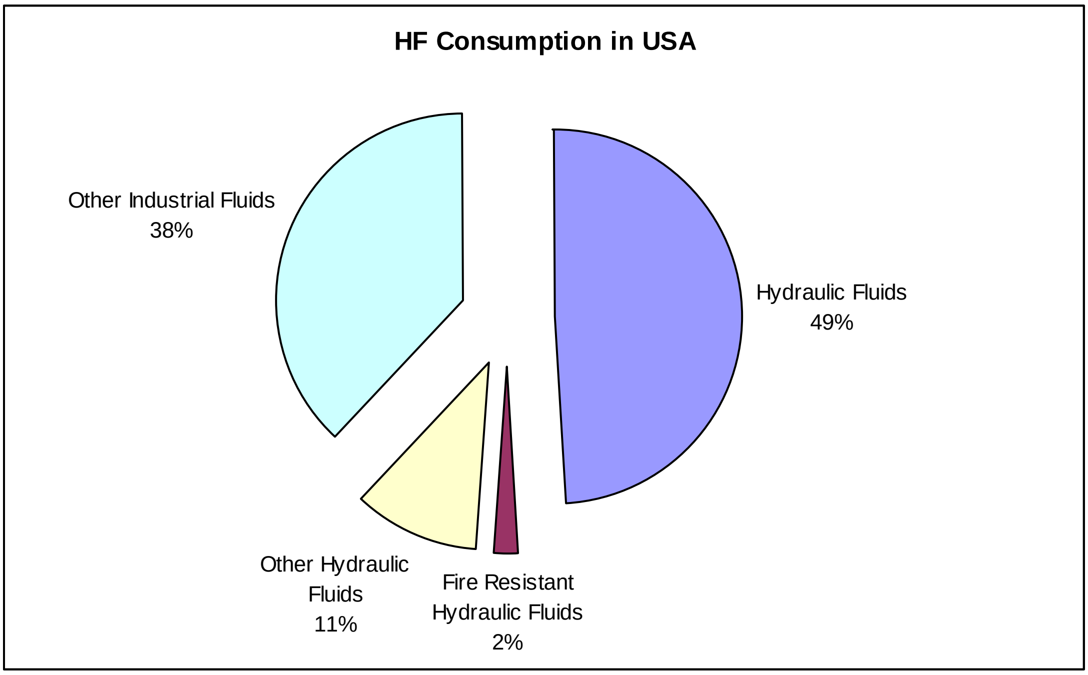


Figure 2.1-1 Hydraulic Fluid Consumption in United States.

After engine oils, hydraulic fluids account for approximately 15% of total lubricant consumption (Mang, 2007). In modern hydraulic systems, hydraulic fluids developments are mainly based on correct application, reducing maintenance intervals, reducing wear and increasing machine life.

2.1.1 Elements of a hydraulic system

In hydroulic sytems, the hydrostatic displacement is based on fluid power. According to Pascal's Law from the 17th century; "Pressure applied anywhere to a body of fluid causes a force to be transmitted equally in all directions. This force acts at right angles to any surface within, or in contact with the fuid" Pascal's hydrostatic principle.

In hydraulic systems, the flow of the liquid creates movement. Flow is created by the hydraulic pump and then flow is converted back to useful motion by activating motor/cyclinder. The most common elements of a hydraulic system are:

- Pumps and motors (eg, gear, rotory vane and piston pumps)
- Hydraulic cylinders (eg. Single - double – action)
- Valves (e.g pressure limiters and control valves)
- Circuit components (eg fluid tanks, filter systems, pressure tanks, pipework etc.)
- Seals, gasheds and elastomers

2.1.1.1 Pumps and Motors

Electricity or mechanical energy is converted into hydraulic energy by hydrostatic machines. Mostly electric motor or diesel engine are used to drive the hydraulic pump.The most important types of pumps are gear,rotory vane and axial and radial piston pumps.The type of pumps are generally dependent on the flow rates .The flow rates and approprite pump types are tabulated in Table 2.1. As a result, hydrauic fluids must protect (drive components and bearings) from wear and corrosion; also should reduce friction and the accumulation of the deposits.

Table 2.1 Hydraulic Pump Types

	Flow Rate (cm^3/rev)		Pressure (bar)	
	Minimum	**Maximum**	**Minimum**	**Maximum**
Gear Pump	**0,4**	**1200**	**160**	**250**
Rotary Vane Pump	**30**	**800**	**_**	**160**
Radial Piston Pump	**10**	**6000**	**480**	**700**
Axial Piston Pump	**5**	**3000**	**150**	**550**

2.1.1.2 Hydraulic Cyclinders

Hydraulic cyclinders transform hydraulic pressure into linear movement. The fluid flow is driven by this actuator so that work is performed. A hydraulic oil should lubricate the piston, avoid stick-slip and reduce wear in a cyclinder.

2.1.1.3 Valves

Valves are mechanisms that provide both control of pressure and direction of flow. Generally there are two types of valves; flow valves and proportional – servo valves. Flow valves have preset switching points (Mang, 2007). Proportional and servo valves are electrohydraulic so that their movement is proportional to the electrical input signal. In a valve, heat should be dissipated, wear should be reduced and friction should be minimized by the hydraulic fluid, also, high termal loads may lead to deposits and gumming in the valves, therefore the hydraulic oil should from no deposits

2.1.1.4 Seals, Gaskets and Elastomers

Every seal and elastomer is somehow exposed to the hydraulic fluid so the compatibility of hydraulic fluid and elastomeric seals are very important. A seal is mechanicaly stressed by the preasure and pulsation of the fluid. Also seals are chemically influenced by temperature, oxygen, water, additives and the oxidation by products of the hydroulic fluids. Ideally a seal not shrink when in contact with a hydraulic fluid because of the danger of leakage, although slight swelling is permissable. The duration of the usual hydraulic oil and elastomer media compatibility test is seven days at 100 ^{0}C (Mang, 2007). The hardness change, volume change, tensile streıght and elongation break point are tested in elastomer test.

The use of hydraulic oils is to transfer power in hydraulic machinery and equipment. Hydraulic fluids contain numerous chemical compounds, including oils, esters, silicones, butanol, polyalkylene glycols (PAG), corrosion inhibitors, and many others. The three most common types of chemicals used in hydraulic fluids, are polyalphaolefins (PAO), phosphate esters, and mineral oil.

Luckily, the current interest in protecting the environment has created a demand for biobased and biodegradable hydraulic fluids. A biodegradable hydraulic fluid has a base stock of vegetable oils such as soybean, canola, or sunflower. These biobased fluids help to minimize pollution in the case of an oil leak.

These biodegradable fluids are an important advance because the chemicals used in a conventional hydraulic fluid can be extremely harsh on the environment. When there is a leak or spill, some of the chemicals stay on top of the soil while others sink into the groundwater. If the fluid leaks into a body of water, some of the chemicals will sink to the bottom, where it can stay for over a year. Fish and other marine life that live in contaminated water can take hydraulic fluid. Unfortunately, a biodegradable hydraulic fluid is much more expensive than a conventional fluid, so these biobased fluids are not widely used.

People can become exposed to the chemicals in a hydraulic fluid by touching it, swallowing it, or breathing the air near a machine that uses it. Exposure can also occur by touching contaminated soil or water. Not much is currently known about how airborne exposure to a hydraulic fluid affects human health. Ingesting these fluids can cause intestinal bleeding, pneumonia, or death. Workers who handle hydraulic fluids on a regular basis have reported weakness of the hands. If one has prolonged contact with most hydraulics fluids, there is the possibility of skin irritation.

Hydraulic fluid becomes hazardous when heated to its flash point, sprayed, or is vaporized. Proper storage requires that hydraulic fluid be stored in sealed metal containers, and the storage of large quantities should be done properly. Rags and clothing soaked in hydraulic fluid should also be contained in closed metal containers to avoid a possible fire hazard, and disposed of in a proper manner.

2.2 Base Oils

The development of lubricants like, e.g. engine and hydraulic oils was traditionally based on mineral oil as a base fluid. This is mainly related to the good technical properties and reasonable price of mineral oils. According to the Report to the Club of Rome and depending on the two oil crises of 1979 and 1983; the mineral oil is a limited source. Additionally; environmental problems associated with the production and use of chemicals and the mineral oil spills to the environment made the market to search for alternative (Andreas, 2001).

The depletion of world petroleum reserves, the limited capacity of nature to tolerate the mineral oil pollution and the increased environmental concerns have stimulated the search for alternative sources for the lubricants, including hydraulic oils. Because of the closer properties, esters from vegetable oils are considered as the best candidate for hydraulic base oil substitute in lubricants.

Esters are investigated as a potential source of lubricants instead of mineral oils because of the strong environmental concerns and new regulations. In US market the overall lubricant market has an annual growth rate of 2 % whereas the annual growth rate of environmentally favorable lubricants is 7-10 % (Andreas, 2001).

2.2.1 Mineral oils

Mineral base oils are products of crude oil refining process which have long hydrocarbon chains with good lubrication properties. Base oils are not only a carrier medium for the performance additives within a lubricant, but also an integral part of the overall performance of modern lubricants. In a general lubricant formulation 75-95 % of a lubricant is base oil. Base oils have organic and man made sources; Mineral origin (coal from plants and animals) and Chemical Synthesis (oil shale, natural gas, crude oil). Mostly the major source is the crude oil, and crude oil differs according to the source. For example; in Figure 2.2.1-1 the difference in appearance is indicated.

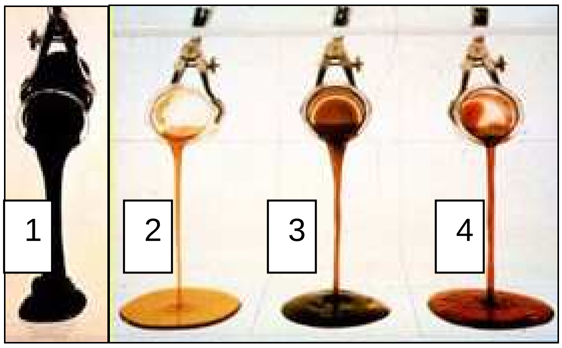


Figure 2.2.1-1. Boscan [1], Sourakhany [2], Arabian Light[3], Barrow Island[4] crude oil samples.

Not only the appearances, but also the chemical of the crude oils are based on the source.

Table 2.2 Physical differences in crude oil.

Field	**Brent**	**Boscan**	**Barrow Island**	**Arabian Light**
Location	North Sea	Venezuella	Australia	Middle East
Pour Point (°C)	-3	10	-30	-28
Sulphur (%w)	0,4	5,5	0,05	1,8
Viscosity@40°C	4	19000	3	
Density,15°C	0,833	0,993	0,841	0,878
% distillation<340°C	59	17	80	55
Vanadium (ppm)	6	1320		16

The original demands from the early refineries in the 1860s and 1870s were to maximize the production of kerosene as a cheaper and more efficient source of light than provided by whale oil (Rudnick,2006). The next important product was paraffin wax for the production of candles. Lubricating oils did not have a place in the early refineries and were often considered to be an un-welcome by product of the production of wax.

With the significant growth of industries in North America created by industrial expansion during the late 1900s, the interest in lubricating oils finally grew to such a level that it was able to displace animal and vegetable oils as the preferred option for machinery lubrication. And as refinery processing improved, the quality of lubricating oils also improved. The introduction of the internal combustion engine created a key demand for new products and refinery processing shifted toward the production of gasoline and diesel fluids. The evaluation of the aviation industry created a further need for higher quality aviation gasoline and later jet fuels. These advancements created a further and significant demand for lubricating oil.

Throughout the majority of the 20th century, the performance demand for lubricants has been fairly straight-forward. Prior to the 1930s, straight mineral oils (i.e., lubricant base stocks) were used for most applications, including high temperature conditions where the potential for oxidation would occur. As engines and equipment underwent design chances to operate higher speeds, loads and operating temperatures, the technical demands on the lubricants increased dramatically. Unfortunately, straight mineral oils or base stocks were not capable of meeting these new performance demands.

Base stocks did undergo a fundamental change beginning in the 1930s when a shift from napthenic to paraffinic base stocks occurred following the introduction of solvent dewaxing. Paraffinic base stock quality would range from 80 to 105 Viscosity Index (VI) with a typical VI of 95. Variations in base stock quality would be influenced by crude oil selection, process severity and application demands. Continued improvements in base stock manufacturing did occur over the next several decades. However, these advancements were more focused on improving unit efficiency, product yields, feed flexibility and unit safety.

Throughout the latter half of the 20th century, solvent refining or separation processing has been adequate to produce high volumes of quality base stocks for most applications. Special small volume products were formulated, when required to address severe operating conditions (e.g. high/low temperatures, high pressures, etc.) with high quality synthetic base stocks like polyalphaolefins (PAO) and esters that have outstanding VI, pour point, volatility and stability.

The benefits of hydrocracking included increased crude flexibility and the opportunity to produce higher VI base stocks. However, the higher cost to operate lube hydrocrackers combined with reduced unit reliability and lack of demand for premium products limited North American investment to only 10 % of capacity as late as 1995 with no significant capacity in other regions of the world (Rudnick,2006).

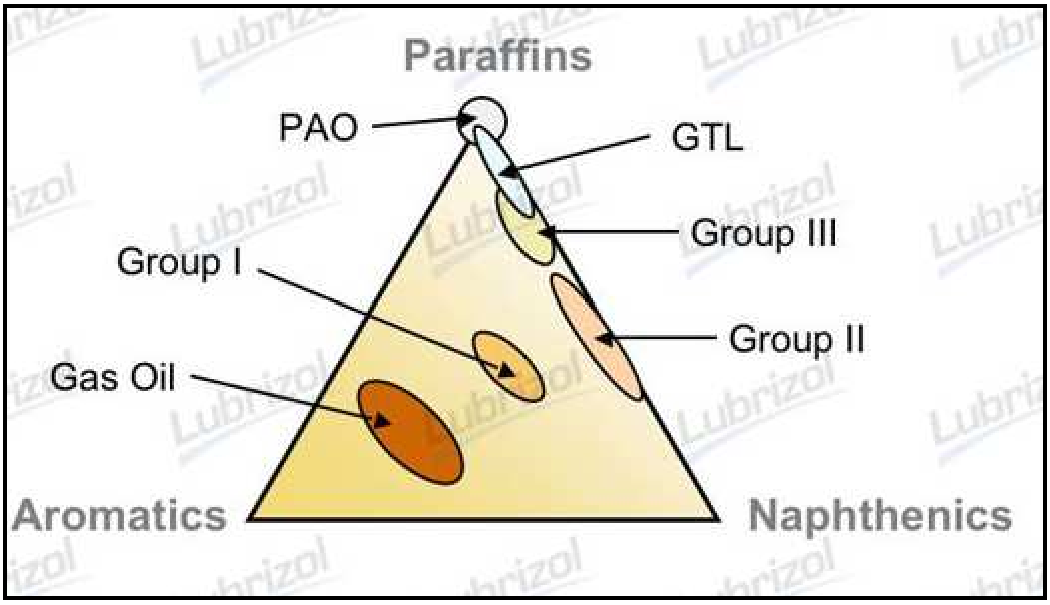


Figure 2.2.1-2 Typical paraffinic, napthenic and aromatic content of Base Oil types (Lubrizol Fluid Technology Seminar, 21-25 April 2008).

2.2.2 Classification of lubricant base stocks

The American Petroleum Institute (API) presently categorizes base stocks into five groups depending on physical and compositional properties. This is included in API 1509 that is the Engine Oil Licensing and Certification Systems (EOLCS). The original standard was introduced in the early 1980s in an effort to capture the differing qualities of lubricant base stocks that could be used in the formulation of engine oils.

API Groups I,II and III represent base stocks typically refined from crude oil and are differentiated by Viscosity Index (VI), saturated contents and sulphur content. API Group I is achieved through solvent refining or separation processing, whereas, API Group II and Group III are produced either directly from conversion or hydroprocessing technology or from an integration of solvent and hydroprocessing technologies.

Group 1 base oils are the least refined of all the groups. They are usually a mix of different hydrocarbon chains with little or no uniformity. While some automotive oils on the market use Group I stocks, they are generally used in less demanding applications.

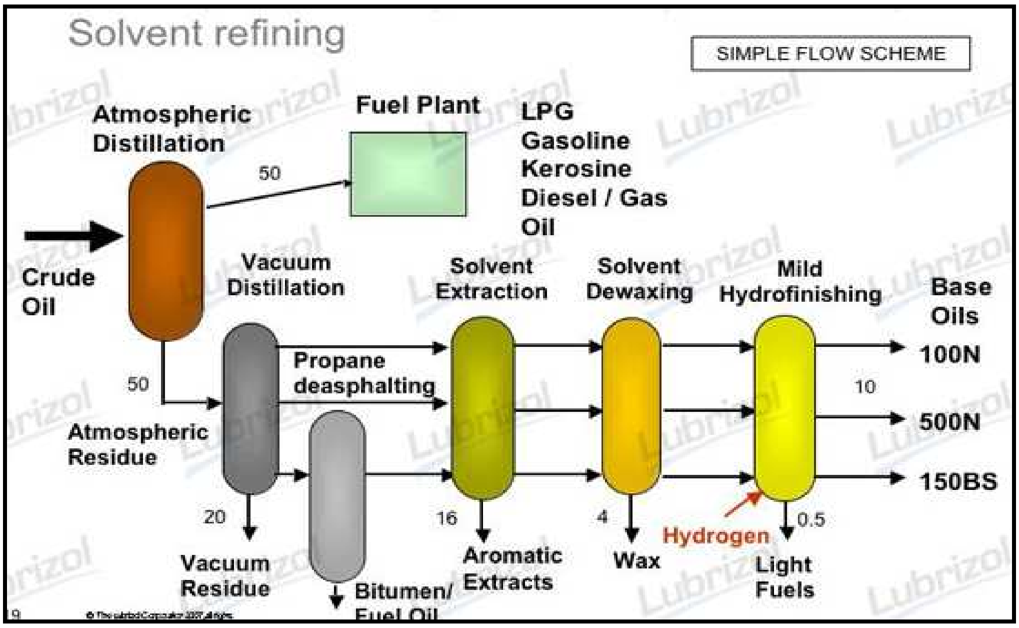


Figure 2.2.2-1. Scheme of Solvent Refining Process of Group I (Lubrizol Fluid Technology Seminar, 21-25 April 2008)

Solvent technology is commercially used since 1970s. Solvent extraction removes aromatic components and solvents generally used for extraction are furfural, n-methyl pirolidone (NMP), DUO-SOL^{TM} (propane and mixture of phenol and cresols) and phenol.

In Figure 2.2.2-1 solvent dewaxing is indicated. Solvent dewaxing is achieved by chilling and precipitation solvents for dewaxing are methyl-ethyl ketone and toluene or methyl-isobutyl ketone.

Table 2.3 American Petroleum Institute (API) Base Oil Categories

Base Oil Group	Sulphur (wt%)		Saturates (wt%)	Viscosity Index
Group I	> 0,03	And/or	< 90	80 – 119
Group II	≤ 0,03	And	≥ 90	80 – 119
Group III	≤ 0,03	And	≥ 90	≥ 120
Group IV	All Polyalphaolefins (PAO)			
Group V	All base stocks not included in Groups 1-4			

(Source: From American Petroleum Institute, Industry Services Department, Engine Oil Licensing and Certification System, API Publication 1509, 15th ed. April 2002)

Group II base oils are common in mineral based motor oils currently available on the market. They have fair to good performance in lubricating properties such as volatility, oxidative stability and flash/fire points. They have only fair performance in areas such as pour point, cold crank viscosity and extreme pressure wear.

Modern hydroprocessing makes products with exceptional purity and stability due to an extremely high degree of hydrogen saturation. The first major step is hydrotreating, adding hydrogen at temperatures above 300°C and pressures above 34 atm. and the next process is hydrocracking, which is performed at temperature above 350°C with a high pressure of 68 atm using catalyst.

During hydroisomerisation, assisting catalytic dewaxing the products is made a branched structure (Figure 2.2.2-2). The process is conducted under pressure and at elevated temperatures with the presence of catalyst-operation is easier than solvent dewaxing, provides additional benefit of cracking large molecules into smaller chains. Catalytic dewaxing produces much lower pour point base oils. Dewaxing with hydroisomerisation converts wax to high viscosity index isoparafins.

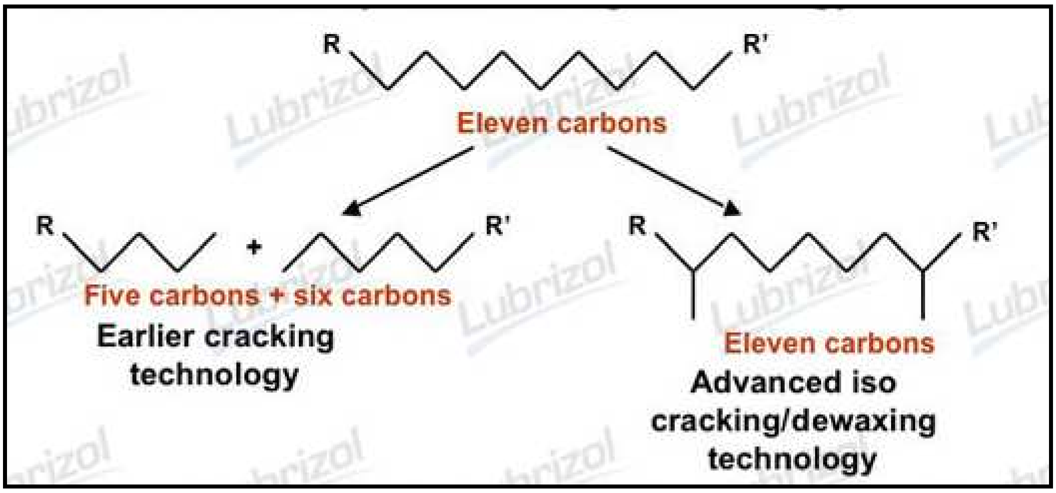


Figure2.2.2-2. Advanced catalytic dewaxing technology (Source: Lubrizol Fluid Technology Seminar, 21-25 April 2008)

Group III base oils are subjected to the highest level of mineral oil refining of the base oil groups. Although they are not chemically engineered, they offer good performance in a wide range of attributes as well as good molecular uniformity and stability. Group III base oils have become more common in America in the last decade.

API Category IV was also introduced for PAOs. This class of lubricant base stock has been recognized by the petroleum industry and by the consumer as the pinnacle in base stock quality where the best in lubrication performance can usually be achieved. It is not surprising, therefore, that PAOs are traditionally referred as synthetics. Because of the uniqueness of the PAO process and the consistency with its quality and compositional properties, all PAOs are considered equivalent and interchangeable provided they meet the same specifications regardless of the manufacturer.

API Group V, finally, is a collection name for all base stocks not covered by the Group I-IV guidelines, including but not limited to such materials as napthenic base stocks, esters, silicones, glycols, polyglycols, etc. A new category for polyinternalolefins (PIOs) was introduced in Europe by the Association Des Constructeurs Europeans D’Automobiles (ACEA) in 2003 (Rudnick, 2006) and designed as Group VI, although the base stocks themselves have been produced for several years. The ACEA organization has established some interchange guidelines with PAO; however, the category has yet to be considered by the API for the North American market place.

2. 3 Hydraulic Oil Additives

Base fluids-mineral oil and also synthetic products generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. Additives are synthetic chemical substances that can improve lots of different parameters of lubricants. They can boost existing properties, sup-press undesirable properties and introduce new properties in the base fluids.

Additives can be classified regarding different aspects. Important and helpful for the understanding of additives is the following differentiation that takes into consideration which part of the tribo system is influenced by the additives. According to these considerations additives can be classified into types that

i. influence the physical and chemical properties of the base fluids
    - physical effects : e.g. VT characteristics, demulsibility, low temperature properties, etc..

ii. affect primarily the metal surfaces modifying their physicochemical properties, e.g. reduction of friction, increase of EP behviour, wear protection, corrosion inhibition.

Additives are used at treat rates of a few ppm up to 20 or even more weight percentages. They can asist each other (synergism) or they can lead to antagonistic effects. Some additives are multifunctional produtcs that decrease the possibility of additives interfering with each other negatively. Although well balanced and optimized additive systems can improve the performance of lubricants enormously the formulation of high performance hydraulic oils may need excellent high quality base oils.

2.4 Biohydraulics

Hydraulic fluids represent a major growth area for biolubricants. The specific application is in mobile hydraulic equipment used in environmentally sensitive areas. Hydraulic fluids should therefore be biodegradable and there are also increasing demands for the lubricant to have a high renewability content (i.e.; to use natural based feedstocks). Table 2.4 compares the biodegradability vs. renewable content for a range of lubricants. It can be clearly seen that esters allow for the development of high performance hydraulic fluids.

Table 2.4 Comparison of Lubricant Biodegradability and Renewability according to OECD 301 B.

	Biodegradability %	Renewability %
Vegatable Oil	70 to 100	100
Mineral oil	20 to 40	0
PAO	20 to 60	0
Alkyl benzene	5 to 20	0
Diesters	40 to 80	0 to 80
Aromatic ester	5 to 70	0
Polyol ester	Polyol ester	0 to 85
Complex ester	20 to 90	0 to 100
Polyalkylene glycol	10 to 70	0

2.5 Natural Oils as Lubricants

The last decade has seen a slow but steady move toward the use of “environmentally friendly” or more readily biodegradable lubricant fluids. Biodegradability has become one of the most important design parameters both in the selection of the base fluid and in the overall formulation of the finished lubricants. By more readily biodegradable it is meant that the fluids, using standard methods and assays, are converted from the lubricating fluids to lower molecular weight components that have essentially no environmental impact. The rate at which lubricants, and other chemicals or additive components, biodegrade is related to their structure affects their properties, many of which affect performance in the various tests for biodegradability. For example, water solubility is critical in some tests for biodegradability, and toxicity is very important, because if the lubricant is toxic and reduces the organism population, then this directly and negatively the process of biodegradation (Rudnick, 2006).

The demand for biodegradable lubricants is due to a growing concern for the impact that our technology is making to our environment. This concern is occurring both as the result of a combination of local and national regulations, and as well as a result of consumer influence. European countries, specifically Germany and Austria, and the Scandinavian countries have led the efforts in this region.

The benefits of vegetable oils being both renewable and biodegradable have provided an incentive to find application for these fluids as chain-saw bar lubricants , outboard engine lubricants, drilling muds, and in partial loss applications such as hydraulic fluids and greases .

Vegetable oils cost approximately twice that of mineral oils, are biodegradable, and renewable. They are also able to provide biodegradable features, generally achievable by synthetic esters, but at substantial cost savings. Vegetable oils in general are deficient relative to mineral oils, chemically modified mineral oils (CMMOs), and most synthetic lubricants in terms of their thermal and oxidative stability. There are also, in some cases, serious limitations to the use of vegetable oils when used in applications requiring operation at low temperatures.

Fatty acids are primarily long chain unbranched aliphatic acids, with the carbon atoms attached to hydrogen and other groups and the chain terminating with a carboxylic acid. Most naturally occurring fatty acids contain an even number of carbon atoms in their backbone chains. These fatty acids have even-numbered chains with 14 to 22 carbon; those with either 16 or 18 carbons occur most frequently. The polar –COOH group is enough to make the shortest fatty acid chains water-soluble. As chain length increases, the fatty acid type becomes progressively less water-soluble and takes on oily or fatty characteristics. At points where hydrogen atoms are missing from adjacent carbon atoms, the carbons share a double instead of a single bond. If double bonds occur at multiple sites (up to a maximum of about six), the fatty acid is polyunsaturated. Unsaturated fatty acids have lower melting points than saturated fatty acids and are more abundant in living organisms. The carbon chain of a fully saturated fatty acid is more or less straight. An unsaturated fatty acid may take one or two forms at a double bond are positioned at a double bond. In the cis form, both the hydrogen atoms of the double bond are positioned on the same side of the C-C bond. In the trans form (hydrogen atoms on opposite sides of the double bonds), the chain is twice trans fatty acids are thermodynamically more stable than the cis form and therefore melt at a higher temperature.

If the three fatty acid bind to each of the three –OH sites of the alcohol (glycerol; propane-1,2,3-triol), the resulting compound is known as triacylglycerol. They are the fully acylated derivative of glycerol. Similarly, when one and two of the –OH groups are esterified with alcohol, monoacylglycerols and diacylglycerols are formed, respectively. Seed-based oils constitute mostly of triacylglycerols (98%), with minor amounts of diglycerols (0.5%), free fatty acids (0.1%), sterols (0.3%), and tocopherols (0.1%) (Rudnick,2006) .

The viscosity of lubricating oils is one of their most important properties when specifying oil for a particular application. The chemical structure of the vegetable oil affects the flow properties of the oil. For example, if fluid oil that contains a significant quantity of oleic, linoleic, or linolenic acids or other unsaturated components is hydrogenated to produce a saturated version, the new material would have the properties of grease. The effect of this hydrogenation is to convert molecular structures that are bent at the double bond to molecular structures that are essentially linear in nature. The effect of removing the double bonds improves the oxidative stability of the oil.

The key to the use of vegetable oil-based lubricants is that they cannot be used in every application. There is simply not enough vegetable oil produced globally on an annual basis. The entire production of vegetable oil does not go into lubricant application. Therefore, it is useful to consider application of vegetable oils in lubricant applications where the properties and performance are best matched. For vegetable oils, this is in applications where the maximum operating temperatures are on the order of less than 120 °C. At the other and of the spectrum are low-temperature properties of the vegetable oils relative to synthetic lubricants, mineral oils, and CMMOs. Many of these lubricants have excellent low-temperature properties and can be used under arctic conditions for extended periods of time. The limitations, described in the preceding section, show that vegetable oils should be employed in applications where the ambient temperatures remain above -40 °C.

Oxidative stability is dependent on the predominant fatty acids present in the vegetable oil. Oils containing mostly saturated fatty acids will have good oxidative stability compared to a vegetable oil containing oleic acid or other monounsaturated fatty acids. The vegetable oils that contain mostly polyunsaturated fatty acids exhibit poor oxidative stability.

Example of the naturally occurring oils and their respective applications are summarized in Table 2.5.

Table 2.5 Applications of various vegetable oils

Selected Applications for Various Vegetable Oils	
Canola Oil	Hydraulic oils, tractor transmission fluids, metal working fluids, food grade lubes, penetrating oils, chain bar lubes
Castor oil	Gear lubricants, greases
Coconut oil	Gas engine oils
Olive oil	Automotive lubricants
Palm oil	Rolling lubricant – steel industry, grease
Rapeseed oil	Chain saw bar lubricants Air compressor – farm equipment Biodegradable greases

	Hydraulic fluid, fuel, soap
Safflower oil	Light- colored paints, diesel fuel, resins, enamels
Linseed oil	Coatings, paints, lacquers, varnishes, stains
Soybean oil	Lubricants, biodiesel fuel, metal casting/working Printing inks, paints, coatings, Soap, shampoos, detergents, pesticides, disinfectants, plasticizers
Jojoba oil	Grease, cosmetic industry, lubricant applications
Crambe oil	Grease, intermediate chemicals, surfactants
Sunflower oil	Grease, diesel fuel substitute
Cuphea oil	Cosmetics and motor oil
Tallow oil	Used in steam cylinder oils, soap, cosmetics, lubricants, plastics

Rates of vegetable oxidation are directly related to the type and amount of unsaturation present in the fatty acids of the vegetable oil. The relative rates of oxidation of oleic acid, linoleic acid, and linolenic acids are 1,10 and 100, respectively.

Vegetable oils, in general, are less volatile than isoviscous mineral oils and synthetics. Using thermogravimetric analysis, Rudnick has measured volatility in the absence of oxygen so that no oxidation affects the physical volatilization of oils and has compared the volatility of hydrocarbon base fluids with vegetable oils and other esters (Rudnick, 2006).

The variety of chemical structures used to improve the properties and performance of lubricants is immense. The objective in designing fully formulated oils with biodegradable base fluids is to employ additive chemistries that are both compatible with the lubricants and are themselves nontoxic and biodegradable. Too often, the fate of additive components in the environment is ignored and additive choices are based on past performance with mineral oil or synthetic formulations. Formulations using vegetable oils should be composed to the extent possible with the least toxicity, ready biodegradability, and best performance for the application.

The tribological behavior of phosphate esters additives that contain the benzotriazole group in rapeseed oil blends has been investigated. The studies included the evaluation of friction and wear using four-ball testing. The result of these studies showed that the phosphate esters gave good load-carrying capacity. Wear scar diameters of blends containing the additives were smaller than when the additives were not used. Wear scars were shown to be dependent on the additive concentration, as expected.

Rapeseed oil was also investigated as a base fluid in the combination with a series of phosphate esters, similar to an earlier report on dialkyldithiophosphate esters, only without the sulfur functionality. These studies showed that phosphate esters also possess good load-carrying capacity and antiwear performance (Rudnick, 2006).

2.6 Neutral Phosphates Esters

Since the discovery of their excellent antiwear and fire-resistance properties in the 1940s, the use of phosphate esters by the lubricants industry has steadily increased. As a result of many years of research and practical experience, industry has learnt to manufacture and formulate these versatile chemicals to satisfy a wide variety of demanding applications. Although the basic composition of products currently in commercial use has remained unchanged for over 30 years, new applications continue to be found and the products are, today, regarded as cost-effective lubricant additives and safe, non-hazardous, hydraulic fluids and lubricants.

Phosphate esters are the most fire resistant of the non-aqueous synthetic basestocks in common use. Their high ignition temperatures, good oxidation stability, and very low vapor pressures make them difficult to burn while their low heats of combustion result in self-extinguishing fluids. Over 60 yr of use have shown them to be excellent lubricating additives and fluids with early shortcomings, for example, hydrolytic instability and neurotoxicity overcome by optimizing manufacturing techniques, raw materials, and stabilizer systems.

3. EXPERIMENTAL

3.1 Materials Studied

In the first part of the study, five different fatty acid esters were analysed:

- Methyl Oleate (MEO)
- 2 Ethyl Hexyl Oleate (EHO)
- Trimethylolpropantrioleate (TMP-TO)
- Rapeseed Oil (RS)
- Soybean Oil (SB)

The esters were chosen according to their application in lubricant area (by literature survey), availability easiness in local Turkey market and cost. The esters were obtained from commercial producers: MEO and TMP-TO were obtained from Sorel Kimya (İstanbul), EHO was from Cognis (Germany); RS and SB were obrained from Orkide Yağ (İzmir). All the esters were used as received without any further modification. A commercially available mineral oil (obtained from Tüpraş Refinery) was also used for comparison in the study.

After analyzing the fatty acid esters in terms of physical, chemical and lubricity properties, the best candidates for a hydraulic oil formulation were selected. In the second part; the esters were used in a hydraulic oil formulation. Hydraulic oil blends were prepared in the laboratory. The alternative hydraulic oil blends were evaluated according to rheological, chemical and tribological properties. The hydraulic oil samples were blended so that they were in ISO VG 32 viscosity grade band according to ASTM D 2422 (Table 3.1). With respect to ASTM D 2422; ISO VG 32, viscosity 40ºC of hydraulic oil may vary from 28,8 cSt to 35,2 cSt. To balance the viscosity Tüpraş Light Neutral and Tüpraş Spindle Oil were used in hydraulic oil blends. The viscosity and other parameters of the mineral base oils from Tüpraş Refinery are tabulated in Table 3.2. Again a hydraulic oil sample was blended with mineral oil in order to compare the performance of the ester containing blends.

In the second part of the study, for the hydraulic oil blend a commercial hydraulic oil additive package was used. Antiwear and Antioxidant Lubrizol additive package, LZ 5703 was used hydraulic oil blends for 0,85 % in the formulation. Also, in order to enhance the cold flow property of the hydrulic oils, pour point depressant was used as an additive. Pour Point Depressant was used for 0,1 % in the formulation and it was obtained from Rohmax/Degussa. Its commercial name is Viscoplex 1254. The additive is a viscous concentrate of polyalkyl methacrylate in a solvent refined neutral oil and helps to decrease the pour point of the industrial fluid.

Table 3.1 Viscosity system for industrial fluid lubricants

Viscosity System Grade Identification	**Mid-point viscosity cSt (mm^2/s) @40ºC**	**Kinematic Viscosity Limits cSt (mm^2/s) @40ºC**	
		min	**max**
ISO VG 10	10	9	11
ISO VG 15	15	13,5	16,5
ISO VG 22	22	19,8	24,2
ISO VG 32	32	28,8	35,2
ISO VG 46	46	41,4	50,6
ISO VG 68	68	61,2	74,8

Table 3.2 Tüpraş Refinery Light Neutral and Spindle Oil properties

Test	**Test Method**	**Light Neutral**	**Spindle Oil**
Colour	ASTM D 1500	1	0,5
Density, kg/L	ASTM D 4052	0,875	0,874
Viscosity,40 **ºC,cSt**	ASTM D 445	34,04	16,214
Viscosity,100 **ºC,cSt**	ASTM D 445	5,572	3,8
Viscosity Index	ASTM D 2270	100	100
Pour Point, **ºC**	ASTM D 97	-12	-12
Flash Point, **ºC**	ASTM D 92	228	180
TAN,mg KOH/gr	ASTM D 974	0,03	0,04

In the second part of the study, the hydraulic oil blends were studied in respect of physical properties suchs as; viscosity, pour point, flash point, foaming, demulsification, refractive index; chemical properties: oxidative stability, Total

Acid Number (TAN), Carbon Residue, and finally lubricity : Four Ball Antiwear Test.

3.2 Test Methods

3.2.1 Physical tests

3.2.1.1 Viscosity

The viscosity is the fluid resistance to flow and is a measure of the adhesive/cohesive or frictional fluid property. The resistance is caused by intermolecular friction exerted when layers of fluids attempt to slide by one another. The viscosity of a fluid is an important property in the analysis of liquid behavior and fluid motion near solid boundaries. Kinematic viscosity is determined by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The measurement is done according to ASTM D 445. Viscosity measurements were done with automatic viscometer Herzog HVM 472.

3.2.1.2 Viscosity index

Viscosity Index (VI) is a lubricating oil quality indicator; a measure for the change of kinematic viscosity with temperature. As temperature increases teh viscosity of the lubricant decreases. The VI is set up by Society of Automotive Engineers (SAE). The temperatures are chosen for reference as 40ºC and 100 ºC. The viscosity index is calculated according to ASTM D 2270. The higher viscosity index, the better lubricating oil is expected.

3.2.1.3 Refractive index

The test method is 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. The test method for refractive index measurement is ASTM D 2887.

3.2.1.4 Pour point

The pour point of lubricating oil is the lowest temperature at which it will flow. It gives an idea about the lowest pumpable temperature of the oil. The test is done according to ASTM 97. The test equipment is cooled inside a cooling bath to allow the formation of wax crystals. At about 9^oC above the expected pour point, and for every subsequent 3^oC, the test jar is tilted to check for movement. When the specimen does not flow when tilted, the jar is held horizontally for 5 seconds. If it does not flow, 3^oC is added to the corresponding temperature and the result is reported as pour point temperature.

3.2.1.5. Foaming tendency determination

The tendency of oils to foam can be a serious problem in systems such as high-speed gearing, high-volume pumping, and splash lubrication. Inadequate lubrication, cavitation, and overflow loss of lubricant can lead to mechanical failure if there is a foam problem in the system. This test method is used in the evaluation of oils for such operating conditions. The test method covers the determination of the foaming characteristics of lubricating oils at 24°C and 93.5°C. Foaming tendency is determined according to ASTM 892.

3.2.1.6. Demulsification (Water removal property)

Demulsification test of oils provides a guide for determining the water separation characteristics of oils subject to water contamination and turbulence. It is generaly used for specification of new oils and monitoring of in-service oils. This test method covers measurement of the ability of petroleum oils or synthetic fluids to separate from water. It is mainly developed specifically for steam-turbine oils having viscosities of 28.8–90 mm^2/s at 40°C, but there is a wide application range now. It is recommended that the test temperature should be raised to 82 ± 1°C when testing products more viscous than 90 mm^2/s at 40°C. The test method is ASTM D 1401.

3.2.2 Chemical tests

3.2.2.1 Total acid number (TAN)

TAN is the measure of acid concentration in a nonaqueous solution. It is determined by the amount of potassium hydroxide (KOH) base required to neutralize the acid in one gram of an oil sample. The standard unit of measure is mg KOH/g. The AN measurement detects both weak organic acids and strong inorganic acids. A change in the acid concentration of an oil can originate from multiple sources. Acidic contaminants, wrong oil, alkaline-reserve depletion and oxidation by-products can cause an increase in acid concentration. ASTM D974 is the measure of acidic constituents using a color change to indicate the inflection. The sample is dissolved into a solution of toluene, p-naphtholbenzne, and isopropyl alcohol containing water. The solution is titrated with KOH while the color is monitored. This test is used on new oils and oils that are not excessively dark.

3.2.2.2 Oxidation test

Oxidation test indicates the tendency of lubricating oil deterioration after oxidation conditions. The test is performed according to IP 48 test norms. 40 grams sample of oil is put under oxidation conditions for two times (each is 6 hours) and 15 liters/hour of air is fed into the sample and the sample is set on 200ºC oil bath. Finally the viscosity, TAN and carbon residue change are compared.

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 °C $\pm$ 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 $\pm$ 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 of the samples was calculated as;

$$Vr = \frac{V2}{V1}$$

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

Carbon residue increase was calculated as;

$Cr=C_2-C_1$

where C_2 is indicating ramsbottom carbon residue of oxidized oil and C_1 is ramsbottom carbon residue of unoxidized oil.

TAN increase was calculated as;

TAN Increase = TAN_2-TAN_1

where TAN_2 refers to TAN of oxidized oil and TAN_1 refers to TAN of unoxidized oil. After the tests; increase in ramsbottom carbon residue, viscosity and total acid number were evaluated.

3.2.2.3 Oxidation Stability comparison by rancimat test

The oxidation stability index is being used to determine the oxidation stability of fatty acid methyl esters (FAME), also known as rancimat test method, was published by CEN under the code EN 14112. The EN 14112 method expresses the oxidation stability of the tested material in terms of an induction period (OSI IP) for the production of volatile organic acids which are by products of fatty acid ester oxidative degradation with heat and oxygen. The CEN set a minimum limit of 6 hours for the OSI IP. OSI IP were obtained in accordance with the EN 14112 method “Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of oxidation stability (accelerated oxidation test)” using a Metrohm Rancimat Model 743. In the method, it is specified that the samples were heated to 110ºC with an air flow of 10 L/h. Different than the method, in the study Rancimat test is performed by heating up to 130, 140, 150 and 160 ºC. The induction time of the esters are reported.

3.2.2.4 Ramsbottom carbon residue

Ramsbottom Carbon residue test is the determination of the amount of carbon residue left after evaporation and pyrolysis of an oil. It is intended to provide some indication of relative coke-forming propensity. The test is performed according to ASTM D 524.

3.2.2.5 Fourier transform infrared (FTIR)

This method covers the use of FTIR in monitoring product organic structure. After reference oil data was input comparison can be made if there is additive depletion, contaminant build up and oxidation degradation in oils. Contaminants monitored generally include water, soot, ethylene glycol, fuels. Oxidation, nitration and sulfonation of base stocks are monitored as evidence of oxidation. The test method is ASTM E 2412.

4. RESULTS and DISCUSSION

The performance of hydraulic pumps and motors is a critical factor in overall hydraulic system reliability. There are two elements of hydraulic efficiency; volumetric efficiency and hydromechanical efficiency. Hydromechanical efficiency relates to the frictional losses within a hydraulic component and the amount of energy required generating fluid flow. Volumetric efficiency relates to the flow losses within a hydraulic component and the degree to which internal leakage occurs. Both of these properties are highly dependent on viscosity and wear protection of the hydraulic oil. In order to obtain the convenient hydraulic oil formulation for volumetric and hydromechanical efficiency; mentioned tests in experimental part have been done sequentially. The results are discussed in this part of the study.

4.1 Fatty Acid Ester Evaluation (Rancimat)

In the first part of the study 5 different fatty acid esters are analyzed both physically and oxidative aspect. Initially natural esters rapeseed oil and soybean oil fatty acid composition is tabulated in Table 4.1.

Oxidation stability of triglyceride-based vegetable oils is mainly limited by the degree of unsaturated double bonds. Unsaturated carbon-carbon bonds function as active sites for many reactions, including oxidation. Soybean oil linoleic acid content is approximately two times higher than rapeseed oil. The rapeseed oil oleic acid content is twice of the soybean oil. As a result, it is expected to observe more tendencies to oxide in soybean oil due to the high number of unsaturated bonds. In the rancimat OSI IP test, based on the molecular structure of soybean oil, it is expected to have poorer oxidation stability.

Table 4.1 Fatty acid composition of rapeseed oil and soybean oil

Fatty acid composition (%)	Rapeseed Oil	Soybean Oil
Lauric Acid $C_{12:0}$	0	0
Myristic acid $C_{14:0}$	0,06	0,08
Palmitic acid $C_{16:0}$	5,14	10,09
Palmitoleic acid $C_{16:1}$	0,25	0,11
Heptadecanoic acid $C_{17:0}$	0,05	0,08
Heptadecenoic acid $C_{17:1}$	0,06	0,06
Stearic acid $C_{18:0}$	2,03	4,38
Oleic acid $C_{18:1}$	58,07	25,86
Linoleic acid $C_{18:2}$	25,41	51,36
Linolenic acid $C_{18:3}$	6,55	6,59
Arachidic acid $C_{20:0}$	0,42	0,49
Gadoleic acid $C_{20:1}$	1,13	0,33
$C_{20:2}$	0	0
$C_{22:0}$	0,33	0,41
Erucic acid $C_{22:1}$	0,32	0
$C_{22:2}$	0	0
Lignoseric acid $C_{24:0}$	0,13	0,14
Nervonic acid $C_{24:1}$	0	0

Table 4.2 Rancimat test induction time results of fatty acid esters

	130°C induction time (hours)	**140°C induction time (hours)**	**150°C induction time (hours)**	**160°C induction time (hours)**
Rapeseed oil	10,06	4,58	2,09	1,02
Soybean oil	7,53	3,53	1,94	0,82
TMP TO	58,4	20,15	8,31	3,57
EHO	43,5	18,3	7,41	3,46
MEO	8,95	3,39	1,72	0,78

The OSI IP; rancimat test is applied for the esters to evaluate the oxidation stability. All esters have been tested with 0,5 % of a phenolic antioxidant. Results are reported in Table 4.2 comparatively including the increasing temperatures of test conditions.

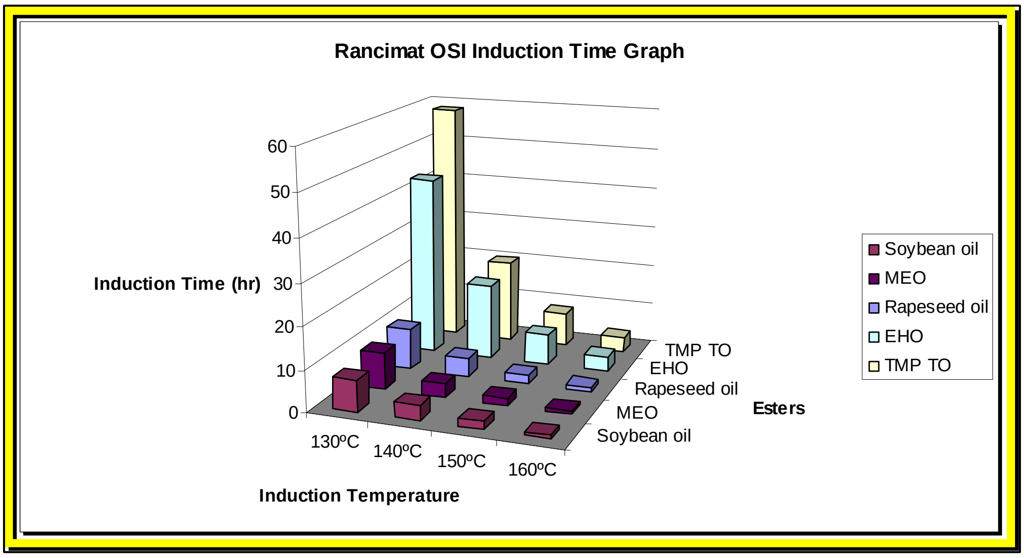


Figure 4.1 OSI Induction time of FA esters

Rancimat test method gives a realistic idea related with the oxidation life time of the fatty acid esters. Different than the EN 14112 method, the temperatures were increased in order to see the performance of the esters at high temperatures. It is really remarkable that TMP TO and EHO induction time were approximately four times higher than natural esters and methyl oleate. TMP TO and EHO are good candidates for hydraulic oil formulations.

4.2 Oxidation Stability Test (IP 48 Method)

Fatty acid esters were investigated according to IP 48 test method. IP 48 is a conventional widely used life time estimation test for hydraulic oils. In order to determine whether the ester could be used as a base medium in the formulation or only as an additive; IP 48 test method indicates reliable results. To compare the ester performance, Tüpraş Refinery mineral oil; light neutral was also analyzed. It would also will be helpful in order to evaluate that whether esters could be a candidate of base oil in hydraulic fluids. The oxidative stability of light neutral will be an indicative sample for the esters. The general features; visual appearance, viscosity, viscosity index and Total Acid Number (TAN) are tabulated in Table 4.3.

Table 4.3 Ester Viscosity and TAN comparison table

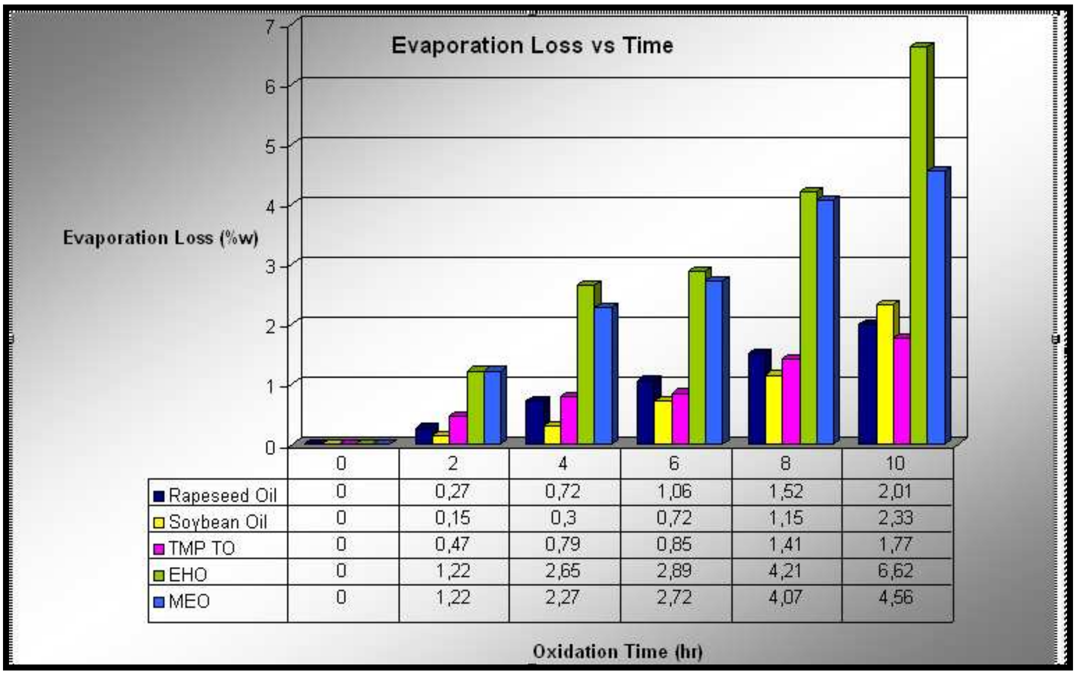
		Rapeseed Oil	**Soybean Oil**	**TMP TO**	**EHO**	**MEO**	**Light Neutral**
Visual Appearence		Clear	Clear	Clear	Clear	Clear	Clear
Viscosity 40ºC, cSt	cSt	36,54	32,04	44,99	8,23	4,96	34,04
Viscosity 100ºC, cSt	cSt	8,33	7,77	9,20	2,68	1,89	5,572
Viscosity Index		215	227	193	189	0	100
Total Acid Number	mg KOH/g	0,45	0,78	1,00	1,23	1,12	0,03
Demulsibility oil-water-emulsion	mL-mL-mL	15-0-65	38-30-12	42-38-0	40-40-0	40-40-0	40-40-0

Rapeseed oil, soybean oil and light neutral are approximately in the same viscosity level at 40ºC. The viscosity decreases while temperature increases and 100 ºC viscosity is important because viscosity index is calculated based on these values. A high viscosity index indicates small oil viscosity changes with temperature and will undergo very little change in viscosity with temperature extremes. Esters are outstanding in terms of viscosity index when compared with mineral oil, light neutral.

Hydraulic oil oxidation is analyzed with various methods like Turbine Oil Oxidation Test (TOST) , Rotary Bomb Oxidation Test (RBOT) and IP 48 Oxidation Test. In the study, oxidation stability of the esters was evaluated according to IP 48 Oxidation Test. IP 48 oxidation test is done under 200ºC for (6+6) 12 hours in two parts. In order to evaluate the esters between each other, IP 48 test method was modified and the esters were oxidized for 2,4,6,8, and 10 hours separately. The viscosity increase and TAN increase was observed for every two hours for each ester. The test results are tabulated in Table 4.4.

Table 4.4 Oxidation Stability Comparison of Esters

	Hours	Rapeseed Oil	Soybean Oil	TMP TO	EHO	MEO
Evaporation Loss (%w/w)	**2**	0,27	0,15	0,47	1,22	1,22
	4	0,72	0,30	0,79	2,65	2,27
	6	1,06	0,72	0,85	2,89	2,72
	8	1,52	1,15	1,41	4,21	4,07
	10	2,01	2,33	1,77	6,62	4,56
Viscosity Increase (cSt)	**0**	36,54	32,04	44,99	8,23	4,96
	2	47,60	53,30	52,10	10,43	6,23
	4	63,37	97,46	60,65	12,51	7,87
	6	94,20	172,14	73,35	14,01	10,51
	8	121,83	382,42	93,83	16,08	12,38
	10	144,13	677,43	104,67	21,70	13,87
Viscosity Change	**V_2/V_1**	3,9	21,1	2,3	2,6	2,8



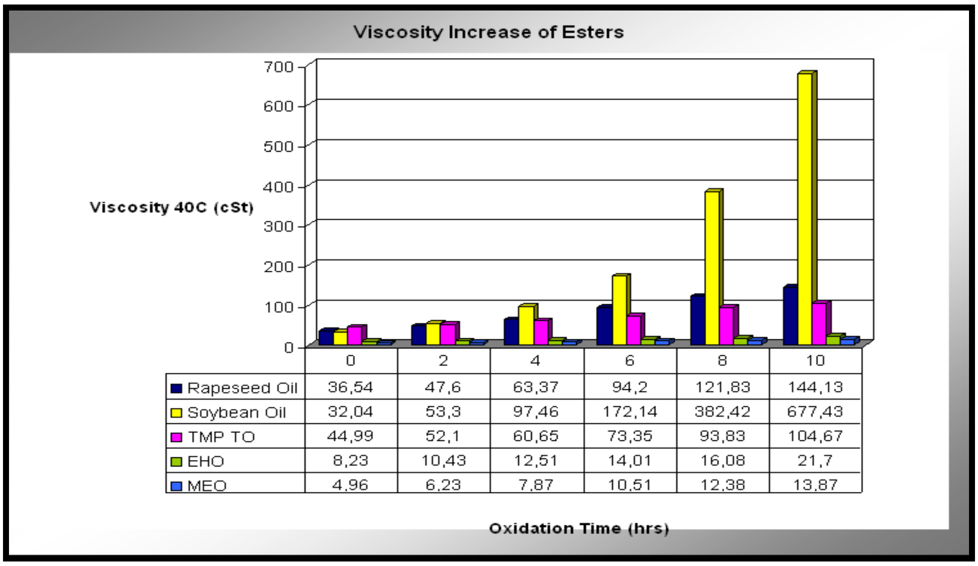
	0	2	4	6	8	10
■ Rapeseed Oil	0	0,27	0,72	1,06	1,52	2,01
■ Soybean Oil	0	0,15	0,3	0,72	1,15	2,33
■ TMP TO	0	0,47	0,79	0,85	1,41	1,77
■ EHO	0	1,22	2,65	2,89	4,21	6,62
■ MEO	0	1,22	2,27	2,72	4,07	4,56

Figure 4.2 Evaporation Loss of Esters in different time range

During the oxidation of vegetable oils polyunsaturated fatty acids in the triglyceride breakdown as a first step and produce the greatest amount of volatiles. Monounsaturated fatty acids in the triglyceride decompose at a much slower rate and release minimal levels of volatile compounds when compared to their polyunsaturated counterparts. As figured in Figure 4.2, TMP TO has the minimum evaporation loss. It is mainly based on the viscosity of the ester but also the higher unsaturated bonds the higher evaporation loss of the lubricant. High evaporation loss causes high lubricant loss in the tank, as a result the consumption would be high in the hydraulic tank which is an undesirable factor in a lubricant.

The ester autoxidation includes a complex series of reactions. The physical and chemical changes that occur within the oil during oxidation affect the lubricant performance. In the final stages of the oxidation process high molecular weight compounds are produced (cyclisation and polymerization reactions). High molecular weight compounds are insoluble and they increase the viscosity of the lubricant. During oxidation reactions also varnish, sludge and deposit formation can be observed.

The higher viscosity increase indicates the higher oxidation compounds. Soybean oil has the highest viscosity increase whereas TMP TO, EHO and MO have comparatively small viscosity increase (Figure 4.3) . Stachowiak mentioned that polymerization is generally classified as a drawback of lubricants during oxidation. Also higher operation temperatures and extended oxidation led to polymerization. Therefore the viscosity change after oxidation test should be as minimum as possible.



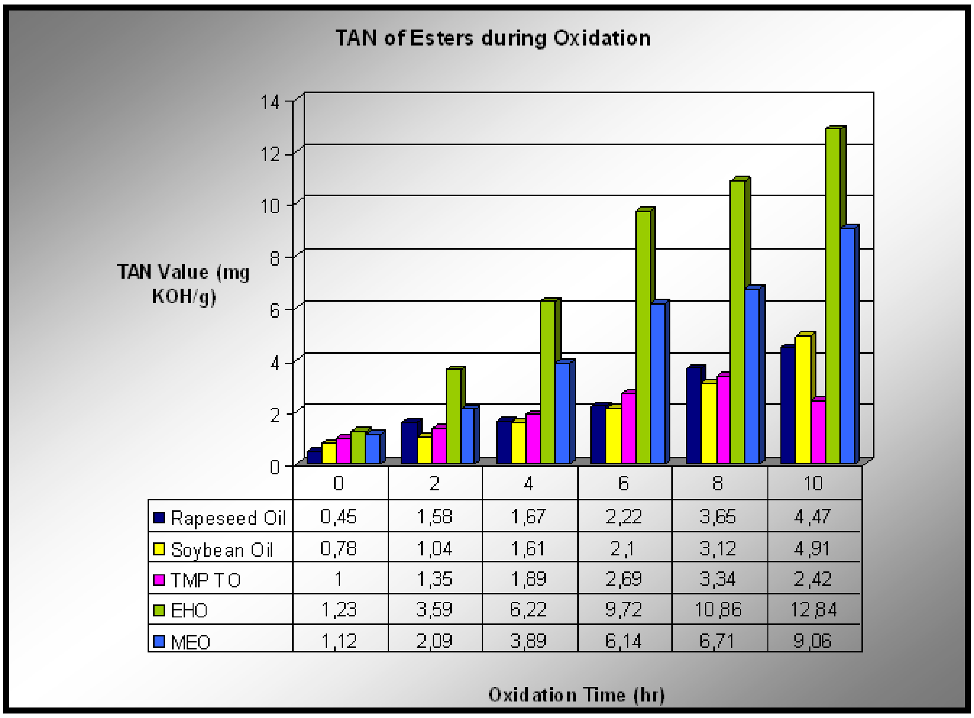
	0	2	4	6	8	10
■ Rapeseed Oil	36,54	47,6	63,37	94,2	121,83	144,13
■ Soybean Oil	32,04	53,3	97,46	172,14	382,42	677,43
■ TMP TO	44,99	52,1	60,65	73,35	93,83	104,67
■ EHO	8,23	10,43	12,51	14,01	16,08	21,7
■ MEO	4,96	6,23	7,87	10,51	12,38	13,87

Figure 4.3 Viscosity change of esters under 200°C (Viscosity 40°C vs time)

Free fatty acids appear during the degradation esters. Fatty acids are primarily coming out from the triglyceride by β hydrogen elimination and hydrolysis. In triglycerides, there is a lone hydrogen on the 2nd or β, carbon. If the β hydrogen removed, the middle carbon –oxygen bond becomes weak and a free fatty acid forms (Stachowiak, 2007). TAN also an indication of the free fatty acids in the system. TAN increase in the oxidation reaction is tabulated in Table 4.5 for every two hours. The data is also shown in Figure 4.4.

Table 4.5 TAN change of the esters during time

	Hours	**Rapeseed Oil**	**Soybean Oil**	**TMP TO**	**EHO**	**MEO**
TAN (mg KOH/g)	**0**	0,45	0,78	1,00	1,23	1,12
	2	1,58	1,04	1,35	3,59	2,09
	4	1,67	1,61	1,89	6,22	3,89
	6	2,22	2,10	2,69	9,72	6,14
	8	3,65	3,12	3,34	10,86	6,71
	10	4,47	4,91	2,42	12,84	9,06
TAN increase	**TAN_2-TAN_1**	4,02	4,13	1,42	10,44	8,09



	0	2	4	6	8	10
■ Rapeseed Oil	0,45	1,58	1,67	2,22	3,65	4,47
■ Soybean Oil	0,78	1,04	1,61	2,1	3,12	4,91
■ TMP TO	1	1,35	1,89	2,69	3,34	2,42
■ EHO	1,23	3,59	6,22	9,72	10,86	12,84
■ MEO	1,12	2,09	3,89	6,14	6,71	9,06

Figure 4.4 TAN increase of esters under 200°C

It is dedicated that higher free fatty acid and other relevant products are released after the oxidation of EHO and MEO than the other esters. TMP TO has the least increase in TAN. Rapeseed oil and Soybean oil have approximately the same number of TAN increase; around 4 mg KOH/g. Considering the rancimat and IP 48 modified oxidation test results; TMP to is the best fatty acid ester candidate in order to use in a hydraulic oil formulation. The comparative figures are shown in Figure 4.5.

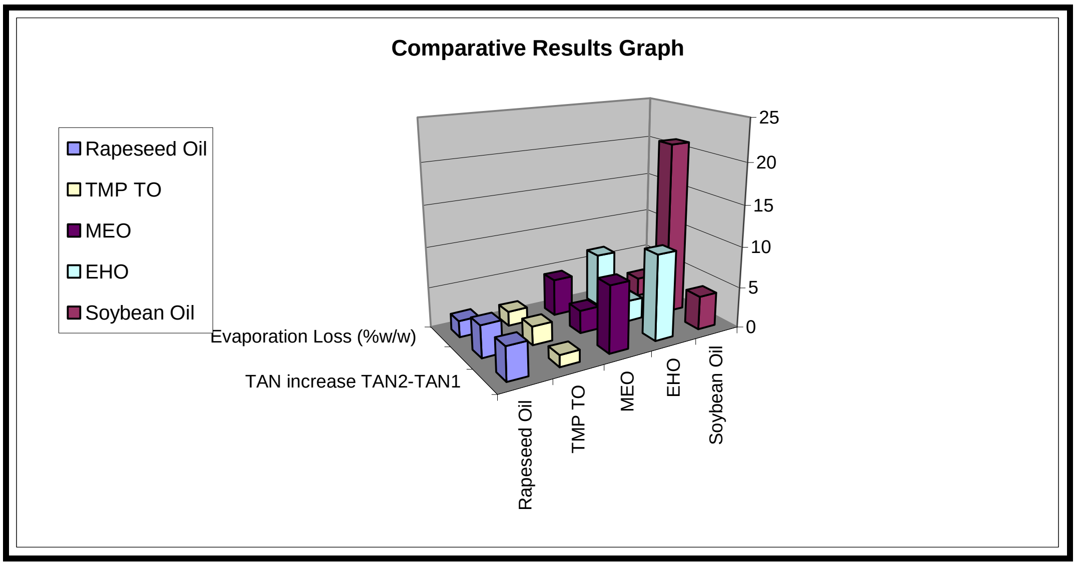


Figure 4.5 Comparative Results Graph of Esters

4.3 Ester Evaluation in Hydraulic Oil Formulation

In the previous part of the study five commercially available esters were evaluated in terms of oxidation and flow properties. The fatty acid esters were chosen so that they can be widely found in local Turkey market. The aim of the study is to formulate hydraulic oil including fatty acid ester inside.

A standard hydraulic oil should include antioxidant, rust inhibitor, metal deactivator, antiwear additive, demulsifiers and foam inhibitor additives in the formulation so that should serve properly in the hydraulic pumps. Without the above mentioned additives, hydraulic oil could not meet consistent performance, appropriate viscosity, hydrolytic stability, good filterability and compressibility. In the formulation blend of hydraulic oil, a hydraulic oil package is use. A global lubricant additive company Lubrizol has a hydraulic fluid package (LZ 5703) which has all the above indicated additives separately inside. The recommended treat rate of the additive is 0,85 %, so it was used in that percentage. Tüpraş light neutral pour point is -12ºC, therefore it was required to use pour point depressant additive to have a proper low temperature flow. Fatty acid esters have also poor low temperature flow property so it was also necessary for the formulations that are ester containing. Viscoplex 1254 of Rohmax Degussa was used with 0,1% treat rate.

In the previous study, it was concluded that TMP TO showed the most outstanding stability in terms of oxidation test. If we think among the natural fatty acid esters only, RO test results were better than SO. In the initial part of the ester containing hydraulic oil formulation study; rapeseed oil and TMP TO were used at different percentages in a standard hydraulic oil formulation. The final hydraulic oil blends were evaluated in terms of hydraulic performance tests, i.e.; viscosity, TAN, oxidation (IP 48), carbon residue, antiwear.

4.3.1 Hydraulic Oil Blend Study with RO and TMP TO

Proper hydraulic oil should meet the specifications of DIN 51524. The standard requirements are tabulated in Table 4.6. Standard hydraulic oil should include antioxidant, rust inhibitor, metal deactivator, antiwear, demulsifiers and foam inhibitor additives in the formulation.

In order to satisfy the requirements of the DIN 51524 standard, a hydraulic oil system package additive should be used. A global lubricant additive company Lubrizol hydraulic fluid package (LZ 5703) has all the above indicated additives separately inside. The recommended treat rate of the additive is 0,85 %.

It is also required to use pour point depressant additive to have a proper low temperature flow. Fatty acid esters have also poor low temperature flow property so it was also necessary for the formulations that are ester containing. Viscoplex 1254 of Rohmax Degussa was used with 0,1% treat rate.

Table 4.6 DIN 51524 Norm for ISO VG 32 Hydraulic Oil.

Hydraulic Oil Type		**Requirements**	**Test method**
Designation as in DIN 51502		**HL 32**	
ISO Viscosity Grade as in DIN 51519		**ISO VG 32**	
Kinematic Viscosity, in cSt at 40ºC	Max	35,2	ASTM D 445
	Min	28,8	ASTM D 445
Kinematic Viscosity, in cSt at 100ºC	Min	5	ASTM D 445
Pour point, equal to or lower than	ºC	-18	ASTM D 97
Flash point higher than	ºC	175	ASTM D 92
Demulsification capacity , in minutes at 54ºC	max	30	ASTM D 1401
Rust preventing characteristics on steel, Procedure A		Pass	ASTM D 665 A
Corrosiveness to copper 3h at 100ºC,corrosion class	max	2	ASTM D 150
Foaming characteristics, in mL at 24ºC	max	150/0	ASTM D 892

Rapeseed oil and TMP TO were used 2.5, 5 and 10 % in a standard hydraulic oil formulation respectively. Since TMP TO oxidation performance was the best, the concentration of the TMP TO was increased also to 20 and 30 % with additional blends. The blends are shown in Table 4.7 for each formulation study.

Table 4.7 Hydraulic oil blends composition

%	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
RO		2,50	5,00	10,00					
TMP TO					2,50	5,00	10,00	20,00	30,00
Light neutral	99,05	96,55	94,05	79,05	96,55	89,05	79,05	64,05	49,05
Spindle oil				10,00		5,00	10,00	15,00	20,00
LZ 5703	0,85	0,85	0,85	0,85	0,85	0,85	0,85	0,85	0,85
Visco. 1254	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10	0,10

The hydraulic oil viscosity grade was set to ISO VG 32, as a result to have the viscosity 32 cSt at 40ºC, Tüpras Light neutral and Tüpraş Spindle Oil were used to adjust the liscosity limit in the blend. Tüpraş light neutral viscosity at 40ºC as 32 cSt and spindle oil viscosity at 40ºC is 16 cSt.

Table 4.8 Chemical test results of Hydraulic oil blends

	1	2	3	4	5	6	7	8	9
Visual	C&B*	C&B	C&B	C&B	C&B	C&B	C&B	C&B	C&B
Viscosity 40ºC	31,37	31,22	32,13	31,12	32,69	31,58	30,85	32,29	30,50
Viscosity 100ºC	5,34	5,39	5,55	5,57	5,53	5,48	5,51	5,73	5,85
Viscosity Index	103	107	110	118	105	109	116	119	139
TAN	0,74	0,87	0,54	0,53	0,55	0,65	0,63	1,07	0,63
Pour Point(ºC)	-48	-32	-29	-32	-27	-27	-30	-32	-30

*C&B : Clear and Bright

In Table 4.8 the general chemical test results are tabulated for each hydraulic oil blend. First of all the viscosities are in the range of DIN 51524 standard for hydraulic oil.

The viscosity index (VI) of an oil is a number that indicates the effect of temperature changes on the viscosity. Low VI is a sign of a relatively large change of viscosity with changes of temperature. The oil becomes extremely thin at high temperatures and extremely thick at low temperatures. Contrary, a high VI signifies relatively little change in viscosity over a wide temperature range. In example, an oil having a high VI resists excessive thickening when the hydraulic pump is cold and, consequently, helps rapid starting and good circulation; it resists excessive thinning when the pump motor is hot and therefore provides full lubrication and prevents excessive oil consumption.

The initial Blend 1; is composed of only mineral base oil (Tüpraş Light Neutral).Viscosity Index of the blend with mineral oil is 103, but if ester is added into the blend, even the concentration of the ester is low (Blend 2 and Blend 5) the viscosity index increases. For 2,5 % ester addition into hydraulic oil formulation, viscosity index increases to 107 with RO and 109 with TMP TO respectively. When RO and TMP TO are compared, the contribution of TMP TO in order to increase the viscosity index is a little bit lower than RO.

Lubricating power varies with temperature changes; therefore, the climatic and working conditions are very important in determination of the lubricating qualities of a liquid. In order to have a good lubrication power, the viscosity index should be higher and esters help in higher viscosity index for the hydraulic oil blends.

Oil gets thickener when the temperature falls. At a certain temperature it does no longer flow by its own weight. That temperature is named as the pour point. The pour point depends on the viscosity and chemical structure of the oil. In paraffinic base oils, stiffening is caused by the wax in the oil, which is distinguished as crystal structure inside. The more the oil cools down the bigger the crystals grow, eventually forming a flow-preventing structure within the oil.

Naphthenic oils have less or no wax, and they remain fluid in lower temperatures than paraffinic oils. The oil eventually becomes so thick that it no longer flows with its own weight. Fully synthetic oils do not contain wax and their cold properties are excellent. Low temperature studies also show that most of the vegetable oil and esters undergo cloudiness, precipitation, poor flow and solidification at -10ºC upon long-term exposure to cold temperature (Erhan at. al, 2006).

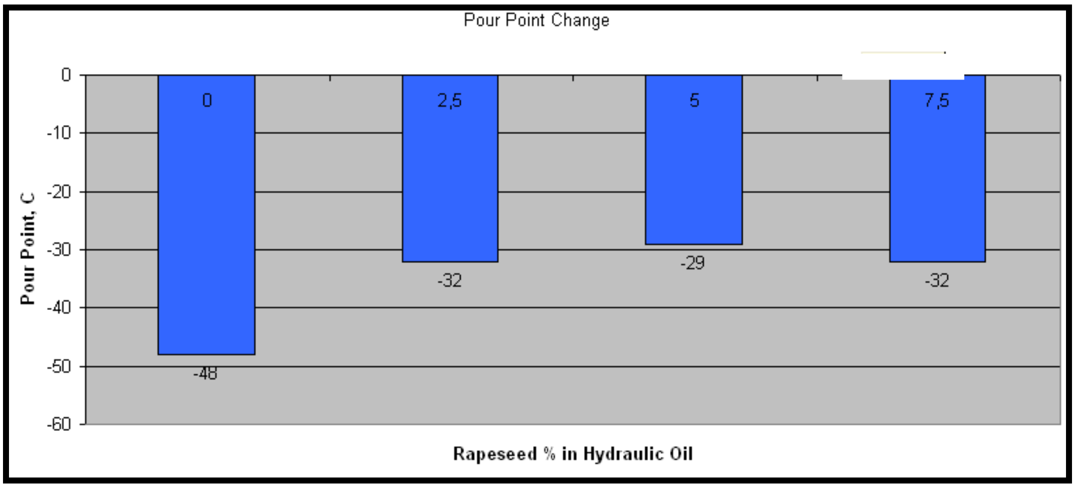


Figure 4.6 Pour Point values of the hydraulic oil blends with increasing RO

In the hydraulic oil blend study, the pour point is decreased by adding 0,1 % pour point depressant additive. The additive prevents the growth and interconnection of wax crystals. The pour point of the ester containing hydraulic oil blends are approximately 18 ºC higher than mineral oil blend. The pour point values for RO including blends are shown in Figure 4.6. As a result, if ester is included in the hydraulic oil blend, the pour point of the blend is higher when compared to a pure mineral oil blend. In order to reach the same degree of pour point, the pour point depressant additive ratio might be increased to 0,2 % or 0,3 %. The increase of the pour point depressant additive would make the cost of the blend a little bit higher.

Table 4.9 Demulsification, Foam Tendencies, Rust Preventing Characteristics and Copper Corrosion test results of Mineral Oil Ester Blends in Hydraulic Oil Formulation

	Demulsification capacity , in minutes at 54ºC*	***Foaming characteristics, in mL at 24ºC***	***Rust preventing characteristics on steel***	***Corrosiveness to copper 3h at 100ºC,corrosion***
DIN 51524 **requirement**	**30 minutes max**	**150/0**	**Pass**	**2**
1	41-39-0 (30)	10/0	Pass	1a
2	43-37-0 (30)	10/0	Pass	1a
3	40-40-0 (30)	10/0	Pass	1a
4	42-38-0 (30)	30/0	Pass	1a
5	41-39-0 (30)	20/0	Pass	1a
6	42-38-0 (30)	20/0	Pass	1a
7	41-39-0 (30)	50/0	Pass	1a
8	41-39-0 (30)	40/0	Pass	1a
9	41-39-0 (30)	10/0	Pass	1a

*oil-water-emulsion (mL)

Demulsification is defined as the property required for an oil to separate from water after it has been emulsified under specified conditions. As temperature increases in hydraulic oil tanks, the oil condenses and water droplets tend to form emulsion with the oil. A good lubricant should reject water inside, and the water should be collected from the bottom of the hydraulic tank.

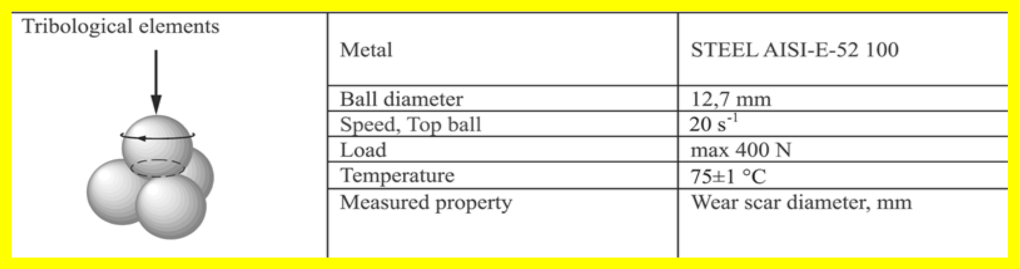
Demulsification property of a lubricant is detected by ASTM D 1401. The allowable limit of the test method is that the lubricant should separate the water inside in maximum 30 minutes and the maximum allowable emulsion volume is 3 mL. According to the ester blends, the ester containing blends have a tendency not to form emulsion, but they tend to get the water inside. So after the Demulsification test, some extend of water volume gets into oil. This is a disadvantage of ester containing blends. Also the mineral oil blend 1 is a not a good candidate for hydraulic oil demulsification. Mineral based hydraulic oil demulsification result shows that oil absorbs 1 mL water inside so that oil volume has been decreased from 40 to 39 mL. There is no emulsion phase formation after 30 minutes. Same as the mineral oil based hydraulic oil blend, RO and TMP TO including blends tend to absorb water to some extend. Although there is no emulsion phase observed. As a result, if ester used in the formulation, water resistivity of the hydraulic oil decreases to some extend. If water is absorbed by the ester, in the long run corrosion problems may occur in the hydraulic system.

In a hydraulic oil tank, excessive foam enhances the oxidation of the oil. Since the new hydraulic tanks are smaller designed, Hydraulic oils have less time to release air. As a result, new lubricants have to release air in a little time otherwise they will foam excessively. According to the results tabulated in Table 4.9**,** if fatty acid ester were added in the formulation the foaming tendency of the lubricant increase. With respect to ASTM D 892 foaming tendency test, the maximum allowable foaming limit is 50/0 mL, so the ester containing blends are still in allowable limits.

Rust and Corrosion Prevention Characteristics of the blends are in the DIN 51524:2006 limits so that there is no corrosion/rust risk.

One of the essential functions of a hydraulic fluid is to provide a lubricating film that reduces wear on moving pump parts. Film effectiveness depends upon a balance between viscosity, sliding speeds and loads, and fluid stability within a hydraulic pump. As temperatures increase and the film thins, the lubricant film ruptures, allowing metal-to-metal contact, wear within the pump and additional fluid heating. At the same time, high temperatures compromise volumetric efficiency as the result of low-viscosity fluid bypassing critical pump clearances. Thus, inadequate wear protection creates a destructive cycle of rising temperatures, accelerated wear and increased internal leakage.

Antiwear (AW) properties of the ester containing blends are tested according to ASTM D 4172. At 1200 rpm for 60 minutes the oil is set to 75ºC and 3 balls are left in stable position. The 4th ball is set on top moving at 1200 rpm for 60 minutes figured in Figure 4.7. In the end the average scar diameter on the three balls are reported.



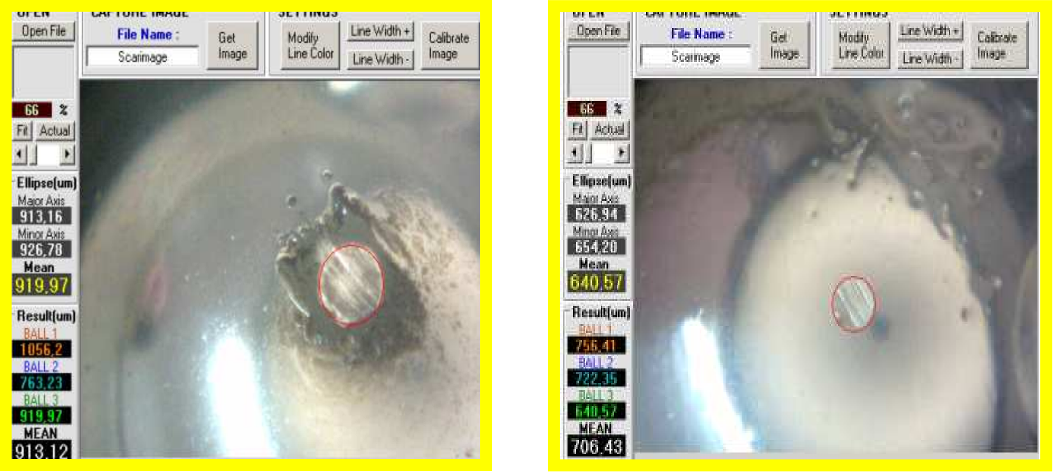
Tribological elements	Metal	STEEL AISI-E-52 100
	Ball diameter	12,7 mm
	Speed, Top ball	20 s^{-1}
	Load	max 400 N
	Temperature	75±1 °C
	Measured property	Wear scar diameter, mm

Figure 4.7 Four Ball ASTM D 4172 specifications

In Table 4.10 the results of the wear diameter are tabulated. It is obviously seen that RO helps to decrease scar diameter but as its concentration increases the AW property of the hydraulic oil decreases. So the best concentration for RO including hydraulic oil is 2,5 %. Whereas, TMP TO has very good results in terms of AW when compared with mineral oil blend 1. As the concentration of TMP TO increases the scar diameter decreases. A sample of the wear test is added in the Appendix part for Blend 2. It is very indicative that TMO TO is a very good AW additive in a hydraulic oil which enhances the useful life time of the hydraulic oil. Two samples for ASTM D 4172 wear scar diameter photos are shown in Figure 4.8.

Table 4.10 Wear Diameter of the ester containing hydraulic oil blends

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Scar Diameter (µm)	2012	913	967	1040	815	797	706	620	551



Scarimage
66 %
Ellipse(um)
Major Axis 913,16
Minor Axis 926,78
Mean 919,97
Result(um)
BALL 1 1056,2
BALL 2 763,23
BALL 3 919,97
MEAN 913,12

Scarimage
66 %
Ellipse(um)
Major Axis 626,94
Minor Axis 654,20
Mean 640,57
Result(um)
BALL 1 756,41
BALL 2 722,35
BALL 3 640,57
MEAN 706,43

Figure 4.8 ASTM D 4172 Wear Scar Diameter Photos a) Blend 2 Scar b) Blend 7 Scar

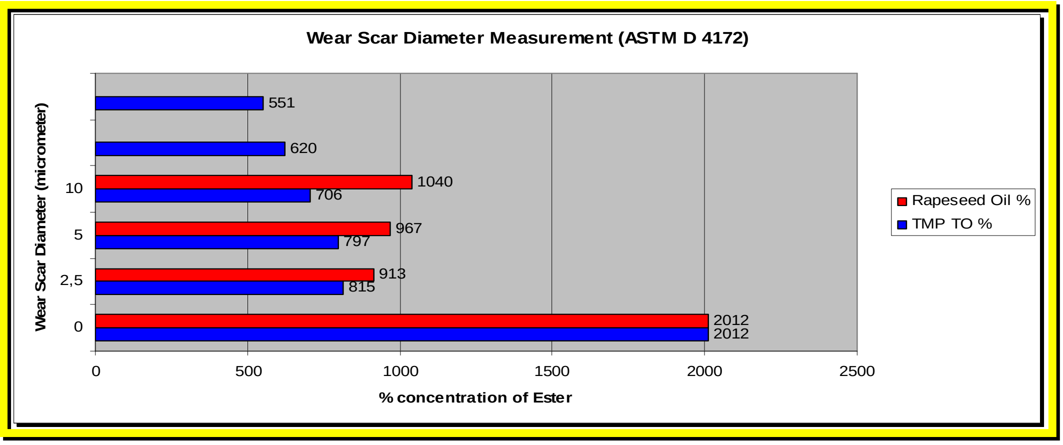


Figure 4.9 Wear Scar Diameter measurement for RO and TMP TO ester percentages in hydraulic oil blends

The four ball wear test is an indicative tribology test used in lubricants. The better wear property the less scar diameter is observed. It has a wide usage and acceptance in lubricating oil design and gives precise results. According to Figure 4.9 It is obviously dedicated taht in the same percentage, TMP TO antiwear performance is better than the contribution of Rapeseed Oil. 2,5% RO addition into the Mineral Base Hydraulic Oil Formulation decreases the scar diameter more than 50% when compared with a 100 % mineral oil based hydraulic oil formulation. 30 % TMP TO addition into the Mineral Base Hydraulic Oil Formulation decreases the scar diameter to ¼th of initial value.

Both RO and TMP TO are known to provide excellent lubricity due to their ester functionality. The ester ends of the fatty acid chain absorb to metal surfaces. Then they form a monolayer film. The fatty acid chain offers a sliding surface that prevents the direct metal-to-metal contact. Otherwise direct metal contact results in high temperatures at contact zone of moving parts and causes adhesion, scuffing or even metal-to-metal welding (B.K. Sharma et al, 2008)

5. CONCLUSION

There are three market segments for biohydraulics, defined by type of equipment and operating temperature. For low severity, high-loss equipment operating up to 60 °C, mainly farming equipment, vegetable oils may be used. For medium severity, medium-loss applications up to 100 °C, mainly in forestry operations, synthetic esters with a high content of renewable raw materials for example, TMP oleates are used. However, some applications, particularly in the construction industry, require fluids capable of extended lifetimes at operating temperatures in excess of 100 °C. Development of biodegradable fluids with the necessary high oxidative and thermal stability has been a major challenge for the industry. In the study all types of hydraulic fluids increase in viscosity and eventually solidify as temperature decreases. Only TMP TO is a candidate to be used in hydraulic oil formulation in terms of oxidation.

In the first part of the thesis study, two vegetable oils and three synthetic esters are evaluated in terms of chemical, physical and mainly oxidative properties. According to viscosity; EHO and MO have low viscosity values, therefore their application as lubricant is very limited. EHO and MO may only be used as lubricity additives in the lubricant formulations. TMP TO, RO and SO have wider application area due to the close viscosity value to ISO VG 32 and 46 (widest viscosity grade in hydraulics)

Rambsbottom Carbon Residue test indicates the soot formation when the lubricant is oxidized. At the end of the test, the residue of RO and SO are almost three times higher than MEO, EHO and TMP TO.

With respect to water separation property, RO and SO could not be an outstanding sample because they really form emulsion phase which is a poor quality indication. MEO and EHO are perfect samples, because they reject the water as soon as possible. TMP TO also forms no emulsion phase, but since it absorbs water in the oil phase, it is risky that in hydraulic oil it may cause corrosion problems.

In terms of oxidation, due to high TAN and viscosity increase in the other fatty acid esters; the besy candidate to be used in hydraulic oil formulation is TMP TO. It is the closest ester to be used as base oil in a hydraulic oil formulation. However since not only oxidation test results but also other chemical test results are important, TMP TO is better to be used as a main component in a hydraulic oil formulation, not as a base medium.

In the hydraulic oil blend study, because of the widespread usage in local market and convenient price, RO is also tried in the hydraulic oil blend studies.

It has been dedicated that for the optimum wear protection the best concentration of RO in the hydraulic oil formulation is 2,5 %. The rest is mineral oil and additives. As TMP TO concentration increases all the tribological properties of hydraulic oil gets better, but the demulsification gets worse. Therefore, 30 % TMP TO usage in a hydraulic oil formulation is the optimum percentage.

For the above recommended formulations of hydraulic oil, the biodegradability of the product is not 100 % but especially TMP TO including blend has decreased the environmental impact of a standard mineral based hydraulic oil to a considerable extend.

Some of the performance data discussed indicates that proper maintenance and control of the mechanical systems can ensure excellent performance and result in exceptionally long lubricant life.

Natural vegetable oils such as RO can be used in light duty operation hydraulic oil formulations as a base fluid. The operation temperature is generally smaller than 60ºC, and there is a low risk of sludge deposit formation due to oxidation. These equipments are small basic hydraulics used in forestry. They are also having the biggest attention because they are exposed directly to the environment.

For medium severity, medium-loss applications up to 100 °C, mainly in forestry and construction operations, TMP TO can be used as a base fluid. Its oxidative stability is rather higher than all the tester that had been analyzed. Also it has outstanding wear protection property, which makes the lubricant life longer. During operation, the low water and acid level should be traced by a fluid conditioning for the sae and long life of system.

For high severity applications where the hydraulic tanks are small, the operating temperatures are high, TMP TO can not be used as a base fluid. It should be mixed with mineral oil. (Blend 2,Blend 9)

This study reveals the comparative oxidative properties of widespread esters in Turkey market. It has been concluded that for severe operations TMP TO can be mixed with mineral based hydraulic oil for 30% and perform outstanding wear and temperature viscosity properties.

In the end of the thesis study a *hydraulic oil formulation* has been developed for severe application of hydraulic systems which is suitable to DIN 51524 standard. The formulation may be commercially sold in the market. In severe applications to obtain a 100 % biodegradable formulation with TMP TO, further formulation blends might be done by using antioxidants to increase the fluid life.

Although TMP TO is an ester, the alcohol part in the structure comes from petroleum products. In order to formulate a 100 % renewable product, used oil samples from food industry might be analyzed based on the type of fatty acids. And a combination of the fatty acid esters can be used in hydraulic oil or a chain saw oil formulation.

The alternative route is to redesign the molecular structure more fundamentally, using saturated acids or chemically modified vegetable oils to optimize thermo-oxidative stability and biodegradability. Also some antioxidants may be used in the formulation. This approach significantly reduces the renewable raw material content but has lead to development products, which combine ready biodegradability with thermo-oxidative stability.

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