

Sudan University of Science & Technology
College of Graduate Studies

**Effect of Engine oil (CF50) on Water Separability of
Industrial oil (Gear 320) and Hydraulic oil (Ep150)**

**تأثير زيت المحرك (CF50) على فصل الماء للزيت الصناعي
(Gear 320) والزيوت الهيدروليكية (EP150)**

**A Thesis Submitted to the Graduate College Sudan University of
Science and Technology in Partial Fulfillment of the Requirements
for the Degree of Master of Science**

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Dedication

To my family

To my teachers

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First of all thanks and praise to Allah for giving me the strength to complete this study.

I would like to express my sincere gratitude to my supervisor Dr. Elfatih Ahmed Hassan for his patience, understanding and cooperation which were of great value for me.

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Abstract

This study was designed to quantify the effect of engine oil on water separability of Industrial oil (Gear 320) and Hydraulic oil (EP 150). An engine oil (CF50) was added as a contaminant for the two blends samples. Water separability was determined for contaminated lubricating oils. Industrial oil (Gear 320) showed a significant drop on the water separability at low concentration of calcium (0.0004%), but the hydraulic oil (EP 150) showed the same effect in high concentration of calcium (0.014%) compared to industrial oil (Gear 320). The study concluded that contamination with engine oil has a negative impact on the water separability of Industrial oil (Gear 320) and a Hydraulic oil (EP150), also an Industrial oil is extremely sensitive to contamination with engine oil than the hydraulic oil.

المستخلص

صممت هذه الدراسة لتحديد تأثير زيت المحرك على فصل الماء لعينات مخبرية من الزيت الصناعي (Gear 320) والزيت الهيدروليكي (EP 150) . تمت اضافة زيت المحرك (CF50) إلى الزيت الصناعي (Gear 320) والزيت الهيدروليكي (EP 150) كمادة ملوثة. تم تحديد الماء المفصول من زيت التشحيم الملوث. اظهر الزيت الصناعي (Gear 320) انخفاضاً كبيراً في فصل الماء عند تركيز منخفض من الكالسيوم بينما اظهر الزيت الهيدروليكي (EP 150) نفس التأثير عند تركيز عالي من الكالسيوم مقارنة بالزيت الصناعي. خلصت الدراسة الى ان زيت المحرك له تأثير سلبي على فصل الماء في كل من الزيت الصناعي والزيت الهيدروليكي. ايضاً الزيت الصناعي شديد الحساسية تجاه التلوث بزيت المحرك مقارنة بالزيت الهيدروليكي.

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LIST OF ABBREVIATIONS

SAE	Society of Automotive Engineering
API	American Petroleum Institute
CF	Commercial for off road indirect –injected and other Diesel engines
EP	Extreme Pressure
DIN	German Institute for Standardization
ASTM	American Society For Testing and Materials
ISO	International Standard Organization

CHAPTER ONE

Introduction and Literature Review

1.1 Introduction:

The use of lubricants is as old as the history of mankind but the scientific analysis of lubrication, friction and wear as an aspect of tribology is relatively new. The reduction of friction along with the reduction or even avoidance of wear by the use of lubricants and lubrication technologies results in energy savings, the protection of resources and also fewer emissions. These benefits describe the economic and ecological importance of this field of work.

The most important function of lubricants is the reduction of friction and wear and in some cases; the relative movement of two bearing surfaces is only possible if a lubricant is present. In times when saving energy and resources and cutting emission have become central environmental matters, lubricants are increasingly attracting public awareness.

Apart from important applications in internal combustion engines, vehicle and industrial gearboxes, compressors, turbines or hydraulic systems, there are a vast number of other applications which mostly require specifically tailored lubricants. This is illustrated by the numerous types of greases or the different lubricants for chip-forming and chip-free metalworking operations which are available. Between 5000 and 10 000 different lubricant formulations are necessary to satisfy more than 90 % of all lubricant applications. If one thinks of lubricants today, the first type to come to mind are mineral oil based. Mineral oil components continue to form the quantitatively most important foundation of lubricants.

Petrochemical components and increasingly derivatives of natural, harvestable raw materials from the oleo-chemical industry are finding increasing acceptance because of their environmental compatibility and some technical advantages. On average, lubricating oils, which quantitatively account for about 90 % of lubricant

consumption, consist of about 93 % base oils and 7 % chemical additives and other components (between 0.5 and 40 %). The development of lubricants is closely linked to the specific applications and application methods.

In addition to this lubricants serve as coolants or heat transfer mediums, they also help seal at compression rings and suspend materials which help to keep engines clean. Lubricants are commonly divided into two groups; automotive lubricants, which consist of engine and gear oils, and industrial lubricants, were the major classes are working fluids, hydraulic oils, and turbine oils (**Sethuramiah A.; 2003**).

Engine oils:

Engine oils are complex mixtures which are best described as formulations containing base oils and additives. Compared to other groups of lubricants, the base oils play an important role (**Prince R.J, 1992**). Without going into the characteristics and manufacturing in detail, mixtures of base oils are selected which have the necessary viscosity and performance to correspond to a rough classification.

Hydraulic Fluids:

In general, a hydraulic fluid consists of a base fluid, usually called base oil, and chemical substances, usually called additives. The quality and performance of a hydraulic fluid depends on the quality of the base fluid and the combination of the additives or additive systems used.

Gear Lubrication Oils:

The gear lubrication oil is a machine component of particular significance for gear and transmission.

1.1.1 Demulsibility and Water Separation:

Water is a poor lubricant and facilitates corrosion and should, therefore, be kept away from the lubricant. Often, however, the water cannot be prevented from penetrating the lubricant. Once the water proportions in the oil have exceeded a certain limit, the only possibility left is to drain the oil or to separate oil and water. In large lubrication systems, the water will sink to the bottom of the oil tank due to the

higher specific weight and can be released through a drain cock. This, however, requires a good water separation behavior of the lubricant.

1.1.2 Oil Cleanliness Grades:

Several methods can be used to classify oil cleanliness. The best known are ISO 4406 and NAS 1638. Determining oil cleanliness according to ISO 4406 involves examining the number and size of particles in a 100-mL sample of fluid. The particles can be counted with a microscope or by suitable automatic particle counters. ISO 4406 or NAS 1638 defines the maximum permissible contamination according to the type of hydraulic system, how sensitive it is, and which critical components form part of the system depending on the operating conditions.

1.1.3 Contaminants in Hydraulic Fluids:

There are several types and causes of hydraulic fluid contamination. The first major differentiation is between primary and secondary contamination. Primary contamination is that which existed in the hydraulic circuit before it was commissioned. This can include machining residues, assembly residues, and fresh-oil contaminants. The secondary variety is that formed after the system began to operate.

1.1.4 Contaminants in Gear Fluids:

Contamination is most common in gearboxes in cement plants and plants that handle coal, such as coal mines and coal-fired power plants. Water contamination can corrode gear surfaces and, in the extreme, destroy a gear completely. Consider that industrial gear oil with just *one-percent* water content can reduce bearing life by up to 90 percent (**Dennis W., 2006**) and the damage and contamination can quickly escalate. The effectiveness of gear oil is compromised when the oil and water do not separate and the oil becomes diluted. Experts agree that using gear oil that quickly separates from water is the most effective way of reducing the risk and consequences of water contamination. Gear oil with improved water separation properties not only allows faster and easier water draining; it also reduces the frequency of oil changes. Contaminations between the lubricants represent one of the most importance issues in the lubricant industries because effect in production quality therefore, is rich field

for study. *Engine oils* will be expected to affect negative in water separability of fresh hydraulic and industrial gear oils but, study concern to investigate the amount of effect.

Objectives of the study:

The objectives of this project are to investigate:-

- 1- The effect of engine oils as contaminant in water separability of hydraulic and Gear industrial oils.
- 2- Quantify the amount of effect and its negative impact in the quality and the production processes.

1.2 Literature Review

1.2.1 Lubricants industry:

Lubrication oils are used for many applications in today's modern society. Their most obvious use is to reduce friction and wear by interposing a fluid film between rubbing surfaces in motion.

Worldwide, there are 1380 lubricant manufacturers ranging from large to small. On one hand there are vertically-integrated petroleum companies whose main business objective is the discovery, extraction and refining of crude oil. Lubricants account for only a very small part of their oil business. At present, there are about 180 such national and multinational oil companies engaged in manufacturing lubricants. The 1200 independent lubricant companies mainly concentrate on the manufacturing and marketing of lubricants and view lubricants as their core business. While the large, integrated companies focus on high-volume lubricants such as engine, gear and hydraulic oils, many independent lube companies concentrate on specialties and niche business, where apart from some tailor-made lubricants, comprehensive and expert customer service is part of the package. The top 1 % of the world's manufacturers of finished lubricants (of which there are more than 1380) account for more than 60 % of global sales; the other 99 % share less than 40 %. The independent lubricant manufacturers also generally purchase raw materials on the open market and they rarely operate base oil refineries. They buy their raw materials from the chemical and oleo-chemical industry and their mineral base oils from the large petroleum companies. The production of simple lubricants normally involves blending processes but specialties often require the use of chemical processes such as saponification (in the case of greases), esterification (when manufacturing ester base oils or additives) or amidation (when manufacturing components for metalworking lubricants). Further manufacturing processes include drying, filtration, homogenizing, dispersion or distillation. Depending on their field of activity, lubricant manufacturers invest between 1 and 5 % of their sales in research and development. Towards the end of the nineties, the petroleum industry was affected by a wave of mergers which will continue. These created new and larger lubricant

structures at the merged companies. The principal reasons for these mergers were economic factors in crude oil extraction and refining which resulted in lower refining margins. Independent lube companies also experienced a continuing concentration with technological, safety-at-work and ecological considerations along with the globalization of lubricant consumers playing an important role. Critical mass is becoming increasingly important in company strategies.

1.2.2 Lubricant Systems:

Apart from the most common lube oils, the many thousands of lubricant applications necessitate a diverse number of systems which is seldom equaled in other product groups. The groups next to oils are emulsions, which as oil-in-water emulsions are central to water-miscible cutting fluids, rolling emulsions and fire-resistant HFA hydraulic fluids. In these cases, the lubricant manufacturer normally supplies a concentrate which is mixed with water locally to form an emulsion. The concentrations of these emulsions with water are generally between 1 and 10 %. The annual consumption of such emulsions in industrialized countries is about the same as all other lubricants together. From this point of view, the volumetric proportion of these products (as concentrates) is significantly under-rated in lubricant statistics with regard to the application engineering problems they create and their economic significance. The next groups of lubricant systems are water-in-oil emulsions. Their most important application is in metal forming. These products are supplied ready-to-use or as diluted concentrates. Fire resistant HFB fluids are designed as water-in-oil emulsions too (invert emulsions). In some special cases, oil-in-oil emulsions are developed as lubricants and these are primarily used in the field of metalworking. Water-based solutions in the form of non-dispersed systems are sometimes used in chip-forming metalworking operations. Greases are complex systems consisting of base oils and thickeners based on soaps or other organic or inorganic substances. They are available in semiliquid form (semifluid greases) through to solid blocks (block greases). Special equipment is required for their production (grease-making plants). A group of products closely related to grease are pastes. Solid lubricant suspensions normally contain solid lubricants in stable suspension in a fluid such as water or oil. These products are often used in forging and extrusion as well as other

metalworking processes. Solid lubricant films can also be applied as suspensions in a carrier fluid which evaporates before the lubricant has to function. Solid lubricant powders can be applied directly to specially-prepared surfaces. In the case of dry-film lubricants, solid lubricants are dispersed in resin matrices. Dry-film lubricants are formed when the solvent (principally water or hydrocarbons) evaporates. Molten salts or glass powder are used for hot forming processes such as extrusion. These are normally supplied as dry powders and develop lubricity when they melt on the hot surface of the metal. Polymer films are used when special surface protection is required in addition to lubricity (e.g. the pressing of stainless steel panels). Together with greases, these products are also used to some extent in the construction industry. An intermediary field between materials and lubrication technology is the wide area of surface treatment to reduce friction and wear. While the previously mentioned dry-film lubricants are an accepted activity of the lubricants industry, chemical coatings are somewhat controversial. These coatings are chemically bonded to the surface of the metal. They include oxalation and phosphating (zinc, iron and manganese). In cases when such coatings adopt the carrier function of an organic lubricant, the entire system could be supplied by the lubricant manufacturer, if the chemical coating is not designed to be supplemented with an additional lubricant coating (e.g. dry film on phosphatized gear), it will probably be supplied by a company which specializes in surface degreasing and cleaning. Even more different from traditional lubricants are metallic or ceramic coatings which are applied with chemical vapor deposition (CVD) or physical vapor deposition (PVD) processes. They also sometimes replace the EP functions of the lubricants. Such coatings are increasingly being used together with lubricants to guarantee improved wear protection in extreme conditions and over long periods of time.

1.2.3 Rheology of Lubricants:

Consistency, flow properties, or viscosity in the case of oils, are key parameters to create lubrication efficiency and the application of lubricants. These are terms which appear in nearly all lubricant specifications. Viscosity is also the only lubricant value which is adopted into the design process for hydrodynamic and elastohydrodynamic lubrication.

Viscosity:

Friction generated by fluid surrounding contacting partners. The measure of internal friction in a fluid is viscosity. If this packet of fluid layers is sheared ($\dot{\gamma}$), the individual fluid layers are displaced in the direction of the shearing force. The upper layers move more rapidly than the lower layers because molecular forces act to resist movement between the layers. These forces create resistance to shearing and this resistance is given the term dynamic viscosity. The difference in velocity between two given fluid layers, related to their linear displacement, is referred to as shear rate. This velocity gradient is proportional to the shear stress. The proportionality constant η is called dynamic viscosity and has the units $\text{Pa} \cdot \text{s}$. The laboratory determination of viscosity in run-out or capillary tubes is influenced by the weight of the fluid. The relationship between dynamic viscosity and specific gravity is referred to as kinematic viscosity.

Newtonian fluids:

Fluids which display the proportionality constant between shear stress and shear rate are referred to as Newtonian fluids, i.e. the viscosity of Newtonian fluids is independent of shear rate. Deviations from this Newtonian behavior are sometimes referred to as structural viscosity. Those viscosities are named as apparent viscosities.

Influence of Temperature on Viscosity (V–T Behavior):

The viscosity of all oils used for lubrication purposes drops significantly when their temperature increases. In linear systems, this V–T behavior is hyperbolic and the practical differentiation necessary in practice is difficult to replicate and the interpolation between two measured viscosities is also problematic. For these reasons, V–T behavior has been allocated to a function which results in a straight-line graph if suitable co-ordinates are selected.

Viscosity Index

This value was first introduced in the USA in 1928. It was based on the then greatest ($\text{VI} = 100$) and the smallest ($\text{VI} = 0$) temperature dependence of US base

oils. Viscosity index is also defined in the most international standards. The evaluation of V-T behavior at low temperatures according to Ubbelohde-Walter lines or other straight-line V-T graphs often leads to inaccuracies. The previously described dependency effects do not apply to base oils which can suffer thickening caused by crystallization of some components (e.g. paraffins) at low temperatures or those whose polymer molecules simulate viscosity effects at low temperatures.

Viscosity-Pressure Dependency

The significance of viscosity-pressure dependency (V-p behavior) was, and still is, underestimated for numerous lubrication applications. V-p behavior has become a part of the calculation of elasto-hydrodynamic lubricant films. The exponential dependence of viscosity on pressure means that viscosity increases very rapidly with pressure. Metal-forming lubricants can be subject to such pressures that the viscosity of such oils can increase by a number power of 10.

V-p dependence is defined by the chemical structure of the substances with the steric geometry of the molecules being of particular significance. Pressure coefficient can increase significantly with falling temperature which has an exponential effect on viscosity. Practical lubrication technology therefore necessitates consideration of pressure and temperature to make a reasonable evaluation of viscosity. It has recently been shown that VI Improvers have an important effect on pressure-viscosity behavior. This affects the lubricant film thickness between lubricated highly stressed contacts under elasto-hydrodynamic (EHD) conditions. Depending on the molecular weight and concentration of the VI improvers, lubricants behave differently when such films are formed. At low temperatures a thin lubricant film is formed. At higher temperatures, VI-improved lubricants form a thicker film as a consequence of a higher viscosity pressure coefficient.

The Effect of Shear Rate on Viscosity:

The definition of the viscosity of Newtonian fluids is a constant (proportionality factor) between shear force and the shear rate. This means that viscosity does not change (with the exception of temperature and pressure

dependence) even when subject to greater shear forces in a friction contact zone or in other words, in isothermal and isobaric conditions. Lubricants which display dependence on shear rate are known as non-Newtonian or fluids with structural viscosity. Oils containing polymers with specific additives or thickeners and mineral oils at low temperatures (long-chain paraffin effects) display such structure-viscous behavior. At normal application temperatures, most major lubricant base oils such as hydrocarbon oils (mineral oil raffinates or synthetic hydrocarbons), synthetic esters and natural fatty oils can withstand very high shearing forces (e.g. 10^9 s^{-1}) as found in highly loaded machine elements (e.g. gearboxes) and are independent of shear rate. Engine oils containing polymer VI improver or polymer ash-free dispersant display structural-viscosity effects at low and high temperatures. As a rule, the dependence of viscosity on shear rate is undesirable. However, one can use this effect in fuel-efficiency oils. At high sliding speeds when hydrodynamic lubrications are given, lower viscosity generates lower friction and lower energy consumption. To keep this process under control, high temperature high shear (HTHS) viscosity was introduced. This measures viscosity at higher temperatures (corresponding to the oil temperature at friction points) and at high shear rates, while the reduction in viscosity caused by the shearing of structure-viscous fluids is reversible, i.e. after the shearing stops, the original viscosity returns, polymer-based oils can suffer a permanent reduction in viscosity. In these cases, the shearing forces lead to a mechanical change or reduction in the size of the polymer molecules so that their desired effects are minimized. These effects have been observed, in particular, with multigrade engine oils and high-VI hydraulic oils. The shear stability of these polymers is therefore an important quality parameter.

1.2.4 Viscosity Grades:

To simplify the classification of lubricants according to their application, viscosity grades were introduced which are now internationally accepted. ISO viscosity grades apply to industrial lubricants while SAE classifications apply to automotive engine and gear oils.

ISO Viscosity Grades:

Eighteen viscosity grades are laid down in the ISO standard 3448. Over the range from 2 to 2,500 mm² s⁻¹, these are the international standard number series E6 rounded to whole numbers when the 6 numerals correspond to one power of ten (the first and fourth power of 10 are reduced). The viscosity grades were also adopted into or added to national standards such as American Standard for Testing Material (ASTM) or DIN. Viscosity grades are not used for all industrial lubricants. Particularly oils for chip-forming and chip-less metalworking processes are not classified in this way. Apart from the viscosity grades, ISO 3448 defines tolerances as well as median viscosities.

1.2.5 Engine Oils:

The viscosity of engine oil is an indicator of how readily a load-carrying film can be formed at all lubrication points in an engine. As viscosity is a function of temperature, this applies to all potential ambient and operating temperatures. The adequate and rapid circulation of the oil at low temperatures which is given by low viscosity must be achieved at cold start cranking speeds (**Kenderson K.O, Sticking J.M, 1990**). On the other hand, viscosity must not fall too much at high temperatures so that adequate lubricating film stability is given at high thermal loads. All viscosity grades can be described by their minimum kinematic viscosity at 100 °C. Additional dynamic viscosity thresholds apply to winter grades, which display the letter W. These values are determined in cold cranking simulators (CCS) or in mini-rotary viscometers (MRV). The dynamic viscosity value given by the CCS is a measure of flow properties at low temperatures where by the high shearing rate can mask paraffin crystallization, in the MRV, a so-called threshold viscosity of max. 60 000 cP has been determined for 10 °C lower temperatures to ensure that the oil pump does not draw air. The high-temperature high-shear viscosity is an additional criterion for evaluating lube film stability at high shear rates and high temperatures in summer grades. In principle, mono or multigrade oils could be used, depending on the climate. As already stated, modern engine oils are multigrade oils whose low temperature characteristics are indicated by the W and the high temperature viscosity

by the number following the W. In central Europe, 90 % of the engine oil market is accounted-for by multigrade oils. Manufacturers ensure that the correct viscosity grade for the climate considered is used in their engines by general descriptions and/or by specific product approvals. To define the viscosity of engine oils, two or three viscosity thresholds were selected to define flow properties at low temperatures and to define a minimum viscosity at high temperatures. Maximum viscosity at low temperature should ensure the rapid oil circulation to all lubrication points and permit a sufficiently higher cranking speed for starting and the minimum viscosity at 100 °C should ensure that adequate lubrication of the bearings occurs at high temperatures. Although the classification system was introduced by the Society of Automotive Engineers (SAE) together with the American Society for Testing and Materials (ASTM), it is used throughout the world and has been adopted into all national standards. Low temperature viscosity is measured as dynamic viscosity with a specially constructed rotational viscosimeter (cold cranking simulator) at low shear rates. Oils which only fit into one viscosity grade are known as monograde oils. The V–T behavior of such oils corresponds to that of conventional mineral oils without VI improvers. Oils which cover two or more viscosity grades are multigrade oils and are based on oils containing VI improvers or base oils with high natural VI.

Formulation of Engine Oils:

Engine oils are complex mixtures which are best described as formulations containing base oils and additives. Compared to other groups of lubricants, the base oils play an important role (**Prince R.J, 1992**). Without going into the characteristics and manufacturing in detail, mixtures of base oils are selected which have the necessary viscosity and performance to correspond to a rough classification. The final products are then marketed as conventional mineral oil-based, unconventional semi-synthetic (hydrocracked) and synthetic engine oils. Precise international nomenclature divides base oils into six groups:

API group I, II, and III are categorized based on viscosity index (VI), amount of saturated molecules, and sulphur content. Group IV base oil contains polyalphaolefins, while group V includes base oils not comprised in the other groups such as esters, glycols, and silicones (**Anwar M, et al, 2002**). Group I base oils are

least processed. They are manufactured by a solvent extraction refining technique which separates oil molecule by size and removes some harmful constituents such as heavy metals, wax, and aromatics. Group I base oils consist of three molecule types, paraffinic, naphthenic, and aromatic, as well as a variety of sulphur- and nitrogen-based compounds. They have <90% saturated molecules, consequently 10% aromatics, and more than 0.03% sulphur. Sulphur compounds and aromatic molecules are highly reactive and tend to react rapidly with oxygen to form various soluble and insoluble degradation by-products. This means a higher risk of oxidation and shorter lubricant lifecycles. Some automotive oils on the market use group I base oils, especially in heavy-duty application and high-viscosity single-grade oil (**Anwar M, et al, 2002**).

Group II oils follow a processing path similar to group I oils, but instead of using solvent extraction they are hydrocracked. This is a process that uses extremely high temperatures and pressures to catalytically react hydrogen with the base stock, this result in a series of molecular rearrangements; including formation of paraffin isomers, breaking of long-chain, and naphthenic molecules and opening and reshaping of aromatic ring formations. In the end of the process aromatic molecules, sulphur, and nitrogen components are nearly eliminated from the stock. Group III oils are more severely treated with higher pressure, higher temperature, and longer process times than group II which give even better properties (**Gresham B, 2007**). Group II and III oils are more stable, more resistant to oxidation, experience less temperature- induces viscosity change, and produce less sludge than group I oils. One drawback with group II and III oils is their reduced ability to dissolve or suspend polar additives and polar by-products from lubricant degradation. Hydroprocessing and hydrocracking reduces the natural solubility of the base stock by reducing the concentration of aromatic and naphthenic hydrocarbon. Lubricant stocks with high solvency are able to soak up polar additive compounds and “lock them in place”. Stocks with low solvency are unable or less able to soak up these additive compounds or the polar by-products of the oxidation process (**Johnson M, Spurlock M, 2010**).

Automotive Gear Oils:

Specific Society of Automotive Engineers (SAE) viscosity grades have been created for automotive gearbox, axle and differential oils. Compared with engine oils, the low temperature behavior of these oils is more heavily weighed in that a single maximum dynamic viscosity figure and the corresponding maximum temperatures are determined for a number of viscosity grades.

1.2.6 Base Oils:

In terms of volume, base oils are the most important components of lubricants. As weighed average of all lubricants, they account for more than 95 % of lubricant formulations. There are lubricant families (e.g. some hydraulic and compressor oils) in which chemical additives only account for 1 % while the remaining 99 % are base oils. On the other hand, other lubricants (e.g. some metalworking fluids, greases, or gear lubricants) can contain up to 30 % additives. The origin of the overwhelming quantity of mineral lubricant base oils has led to lubricants being viewed as a part of the petroleum industry and this is underlined by their inclusion in petroleum statistics. Over the last few years, lubricants have increasingly become a separate discipline with clear differences from petroleum mass products. This was caused by the high added value which is generated in this product segment along with the fact that many high-performance lubricants no longer contain petroleum base oils

Chemical Characterization of Mineral Base Oils:

The characterization of mineral oil fractions, whether crude oil or lubricant base oil fractions, by use of normal chemical practices to determine their exact structure is not possible without great expense. Crude oil generally consists of many thousands of single components and these are reflected in the processing of each fraction. It was, therefore, always an objective to describe mineral oil fractions by the comparatively simple expedient of defining their technical properties or to identify and quantitatively determine groups of components with similar chemical character. Advanced physicochemical methods are, however, increasingly being used in routine testing.

Viscosity–Gravity Constant (VGC):

This value enables only rough chemical characterization of oils. Values near 0.800 indicate paraffinic character whereas values near to 1.000 point to a majority of aromatic structure (ASTM D 2501-91).

Aniline Point:

The aniline point is also a help when characterizing the hydrocarbon structure of mineral oils. When, aniline and oil are mixed and then cooled to a certain temperature (aniline point), two phases form. Because of their good solubility, aromatic structures give the lowest values.

Carbon Distribution:

The most important means of analysis for characterization of mineral oil hydrocarbons was, and remains, the determination of carbon in terms of its three categories of chemical bond aromatic (C A), naphthenic (C N), and paraffinic (C P). N–D–M analysis uses physicochemical data which are easy to obtain. These include refractive index, density, and molecular weight. Molecular weight can be determined by measuring the viscosity at different temperatures (e.g. ASTM D 2502-92). Carbon distribution is given in % C A, % C N and % C P (100 % in total). N–D–M analysis also determines the average total number of rings per molecule (R_T) and the breakdown into aromatic and naphthenic rings (R_N) per molecule ($R_N = R_T - R_A$). Brandes created a method of determining carbon distribution according to specific bands in the infrared spectrum. The method has proven itself for lube base oils and can be performed at acceptable expense. Exact determination of aromatic carbon content can be performed by high-resolution nuclear magnetic resonance (NMR) (ASTM D 5292-91).

Hydrocarbon Composition:

A further refinement in the characterization of lubricant base oils is the determination of molecular families. Chromatography is used first to separate components and the fractions are then subjected to advanced analytical procedures. To differentiate mineral oils including lube base oils in the boiling range from 200 to

550°C, high ionizing voltage mass spectrometry (ASTM D 2786-91) is used for saturated fractions and ASTM D 3239-91 for aromatic fractions. Saturated fractions are separated into alkanes (0-ring), 1-ring, 2-ring, 3-ring, 4-ring and 5-ring naphthenes. The aromatic fractions are subdivided into seven classes: monaromatics, diaromatics, triaromatics, tetraaromatics, pentaaromatics, thiopheno aromatics, and unidentified aromatics.

Polycyclic Aromatics in Base Oils:

Polycyclic aromatics, polycyclic aromatic hydrocarbons (PAH), or, in general, polycyclic aromatics (PCA) are carcinogenic, environmentally harmful substances which are found in crude oils. In general they are not created when a lubricant is used. PAH formed by the combustion of gasoline can gather in engine oils. They can also gather in quenching oils after long periods of heavy-duty use. In traditional solvent refining processes, PAH largely remain in the extract. Non-solvent extracted distillates contain PAH in line with their boiling point. The carcinogenic characteristics of non-severely treated distillates in the petroleum industry were established by the International Agency for Research on Cancer (IARC) in 1983 (IARC, 1984).

Vegetable oil-based lubricants:

Lubricants used today originate mainly from petroleum-based products and are therefore toxic to the environment. Through accidental spillage, volatility, and industrial waste (among others) 50-60% of all lubricants end up in the environment. For hydraulic fluids the loss is estimated to be as high as 70-80% (Adhvaryu A, *et al* 2008). Lubricants based on vegetable oil are biodegradable and non-toxic, therefore highly preferable in industries such as the wood-processing industry. Public demand, industry concerns, and governmental agency policies will increase the need for renewable and biodegradable lubricants (Castro W, *et al*, 2006). Today the most important sources for vegetable oil are rapeseed (canola), sunflower, and soybean (Schneider P. M, 2006).

Vegetable oils consist primarily of triacylglycerides. Triacylglycerides are glycerol molecules with three long chain fatty acids attached at the hydroxyl groups

via ester linkage. Due to high molecule weight triacylglycerides have low volatility and high viscosity index. Vegetable oils also have a higher solubilising capacity for additives and contaminants than mineral oils. Long and polar fatty acid chain gives high strength lubricant films which reduce both friction and wear and interact strongly with metal. However vegetable oils have poor oxidation stability, primarily due to unsaturated double bonds. When the molecules undergoes oxidative degradation polar oxycompounds are formed which eventually results in insoluble deposits and increase in acidity and viscosity. Presence of esters also makes the oil more susceptible to hydrolytic breakdown and gives a poor corrosion protection (**Adhvaryu A, *et al*, 2008**).

Reducing or eliminating unsaturation by genetic or chemical modifications can overcome these shortcomings. Structural modifications of vegetable oil are accompanied by economic implications and genetically modified lubricant base oils might in the future meet the same public resistance as have food products. Improvements can obviously also be made by adding additives (**Adams R. J, *et al*, 1997**).

Synthetic base oils:

Synthetic lubricants are those fluids which are chemically synthesized, unlike mineral oils that originate from crude oil. There are many different types of synthetic base fluids, but the most commonly used in lubricant formulation are polyalpha olefin (PAO) and different types of synthetic esters (SE). Desired characteristics of the synthetic base oil can be customized for each use of application and it is therefore often the cost that limits the use of these lubricants. The price of a synthetic lubricant is often 2-3 times more than for a mineral oil based lubricant (**Anwar M, *et al*, 2002**). Synthetic esters are an interesting alternative to traditional base fluids when switching to environmentally adapted fluids. Their properties can be altered to match different demands, they are nontoxic, and have good biodegradability. Vegetable oil, i.e. triglycerides, contains glycerol as the alcohol component. This makes them prone to hydrolysis and thermal degradation. If the glycerol is replaced by other polyols, e.g. trimethylolprone (TMP), their performance is improved (**Petterson A, 2007**).

Refining:

Since the beginning of the petroleum industry, mineral oils have been used for lubricant base oils. The process of converting crude oil into finished base oil is referred to as refining. As far as base oil manufacturing is concerned, the actual refining process begins only after the distillation stages. Refining is thus the term often used to describe all the manufacturing stages after vacuum distillation. Lubricant refineries are divided into integrated and non-integrated plants. Integrated refineries are linked to primary crude oil refineries and are fed with vacuum distillate by pipeline. Non-integrated refineries purchase vacuum distillate on the open market or buy atmospheric residues and perform their own vacuum distillation.

Distillation:

By way of fractional distillation, products are removed from crude oil which approximately meets the viscosity grades ultimately required. Often only four or five cuts suffice to fulfill lubricant requirements. As described later, the viscosity of the primary vacuum distillate is independent of the finished base oils in hydrocracking processes because the hydrocracking process creates new molecule dimensions. After the corresponding separation of the lighter components from the crude oil by atmospheric distillation, the lubricant components are in the atmospheric residue. The atmospheric residue is subjected to vacuum distillation to remove the components required for lubricants. In a vacuum, the boiling points of the heavier cuts fall so that distillation without thermal destruction (cracking) is possible.

De-asphalting:

Although the vacuum residue still contains highly viscous hydrocarbons which can supply valuable components for lube base oils, distillation cannot separate these from the asphalt which is also present and extraction processes must be used to separate these highly viscous base oils, commonly known as bright stocks. Bright stocks are produced in lube oil refineries when the use of the asphaltene by-product (hard asphalt) is worthwhile. The quality of the hard asphalt for the manufacture of high quality bitumen depends on the crude oil. Extractive separation uses light hydrocarbons (propane to heptane), of which propane is the leading product for de-

asphalting. Bright stocks can be manufactured with viscosities of more than $45 \text{ mm}^2 \text{ s}^{-1}$ at 100°C .

Acid Refining:

Acid refining has become less popular because the acid sludge waste produced is difficult to dispose of and this method has been replaced by solvent extraction. Acid refining is still used to some extent for the re-refining of used lubricating oils and for the production of very light-colored technical or pharmaceutical white oils and petroleum sulfonates as by-products.

Solvent Extraction:

Whereas acid refining uses chemical reaction to reduce aromatic content and to eliminate reactive, oil-aging accelerators, solvent extraction is based on physicochemical separation. Solvent extraction creates base oils which are known as solvent raffinates or solvent neutrals (SN). Extraction processes using solvents create both base oil and, after evaporation of the solvent, an aromatic-rich extract.

Solvent Dewaxing:

In traditional refining processes, solvent extraction is followed by solvent dewaxing. Long-chain, high melting point paraffins negatively affect the cold flow properties of lube oil distillates and lead to a high pour point. This is caused by the crystallization of waxy substances at low temperatures which results in turbidity and an increase in viscosity. Their removal has, therefore, been an important consideration since the beginning of crude oil refining. Dewaxing by crystallization of paraffins at low temperatures and separation by filtration are the principal processes in traditional refining. Compared with catalytic dewaxing with hydrogen, urea-dewaxing to separate n-paraffins is of relatively minor importance in lube oil refining. Crystallization methods involve mixing the solvent with the oil; this improves filtration, as a result of dilution, and promotes the growth of large crystal formations.

Finishing:

A finishing stage often follows the two refining stages of extraction and dewaxing. In the past, methods which employed absorbents were often used but these days the processes almost all use hydrogen (hydrofinishing). Finishing should improve the color of the product and remove surface-active substances which can negatively affect the air-release or demulsifying properties of lubricating oil. Depending on the temperature, pressure, catalyst, and space velocity of the hydrofinishing, a more or less severe hydrogenating process can be initiated. In general, the hydrofinishing process is referred to as mild hydrotreating and focuses on improving color, odor, and ultra-violet stability. Ferrofining (BP) has achieved major economic importance as a finishing process.

Lube Crudes:

Crude oils which yield high-grade base oils are preferred for the production of lube base oils. Of importance to the vacuum gas oils (VGO) which are derived from the crude oil and which are the direct feeds for lube refining are, particularly, VI, wax content and sulfur content. A high VGO VI leads to low extraction losses in solvent extraction processes and low hydrogen consumption during hydrogenating processes. High wax contents increase production costs, as a result of the high operating costs of the dewaxing plant, as well as reducing base oil yield. In a base oil production unit using a wax isomerization process, high wax content can also contribute to a higher VI. The finished base oils have high sulfur content, especially after conventional solvent refining. Hydrogenating processes almost fully eliminate sulfur but desulfurization consumes hydrogen.

Base Oil Manufacturing by Hydrogenation and Hydrocracking:

Hydrogenation and hydrocracking in the manufacture of lubricant base oils significantly influence the chemical structures of mineral oil molecules. On one hand, unstable molecules are chemically stabilized by the removal of the heteroatoms (sulfur, oxygen, nitrogen) and on the other, severe hydrogenation can convert aromatics into saturated naphthenic or paraffinic structures. In addition to the hydrogenation process, hydrocracking breaks-down or cracks larger molecules into

smaller ones. Larger molecular structures can re-form from small fragments. The principal process criteria are temperature, pressure, the catalyst and space velocity. Besides the saturation of aromatics, opening of the naphthenes rings can occur. The future of lube base oil production thus lies with hydrogenation and hydrocracking. An additional advantage of advanced hydrocracking is the lower dependence on the quality of the crude oil.

Manufacturing Naphthenic Base Oils by Hydrogenation:

Naphthenic oil, which normally has good natural low-temperature properties, did not need to be dewaxed and it was possible to convert the vacuum distillates into low viscosity index (LVI) and moderately good aging behavior lubricant base oils by simple refining (acid refining or hydrofinishing). In the past these base oils were much cheaper than paraffinic solvates and this also explained their popularity. Although the IARC publication and subsequent legislation and classification requirements led to the disappearance of this type of oil from important markets, naphthenic base oils were still required for some lubricant applications (greases, metalworking oils, and refrigerator oils) because of their outstanding solubility and these are now manufactured with severe hydrogenation which produces non-carcinogenic base oils. Severely hydrotreated Group C distillates are the most accepted naphthenic base oils in western markets (**Okamoto T, 1996**).

1.2.7 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, suppress 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:

1- Influence the physical and chemical properties of the base fluids in the volume -

temperature characteristics, demulsibility, low temperature properties, etc., chemical effects: e.g. oxidation stability.

2- Affect primarily the metal surfaces modifying their physicochemical properties, e.g. reduction of friction, increase of EP behavior, wear protection and corrosion inhibition.

Additives are used at treat rates of a few ppm (antifoam agents) up to 20 or even more weight percentages. They can assist each other (synergism) or they can lead to antagonistic effects. Some additives are multifunctional products that decrease the possibility of additives interfering with each other negatively. Also additives have a very big influence on the performance of lubricants that make it possible to fulfil new performance levels, of course there are some properties that cannot be influenced by additives, e.g. volatility, air release properties, thermal stability, thermal conductivity, compressibility, boiling point etc. Also well balanced and optimized additive systems can improve the performance of lubricants enormously the formulation of high performance lubricants requires also excellent high quality base fluids. The present trend to use more and more hydrocracked and severely hydrotreated highly refined mineral oils as well as to synthetic esters and PAOs underlines this statement.

Antioxidants:

Industrial lubricants must fulfill many different functions, e.g. power transmission and wear protection just to name two of them. Mostly the function of a lubricant is limited by the aging of the lubricant base stock. Typical characteristics of aged lubricants are discoloration and a characteristic burnt odor. In advanced stages the viscosity will begin to rise significantly, acidic oxidation products are build, which in turn may induce corrosion and lubricant problems. This aging process can be delayed tremendously by the use of antioxidants. The aging of lubricants can be differentiated into two processes: the oxidation process by reaction of the lubricant molecules with oxygen and the thermal decomposition (cracking) at high temperatures. In practice the oxidative aging of the lubricant is the dominating process which influences significantly the lifetime of the lubricant. Caused by

steadily increased power density and reduced lubricant volumes (higher load-to-oil ratio) as well as extended service life in the last years, the thermal stress on the lubricant molecules grows constantly.

Physical Description of Viscosity Index:

A fundamental characteristic of every fluid is its viscosity. The kinematic viscosity of a fluid is dependent on the external parameters of pressure and temperature. A great number of applications specify viscosity at a defined temperature, in the case of hydraulic equipment at 40 °C and 100 °C, to achieve optimum pump efficiency. The viscosity index is defined exactly by the gradient between 40 and 100 °C. This simple-to-calculate characteristic has a significant impact on lubrication technology and is practically a standard feature of every specification. The viscosity index defines molecular structure and has been exactly described for defined molecules. Depending on their source, conventionally refined base oils display between 80 and 120 VI points and the most common, central European paraffinic solvent cuts have VI s of around 100 points. In the simplest of cases, a desired viscosity index can be achieved by mixing fluids with corresponding VIs. Usually, however, the viscosity requirements of modern lubricant specifications can be met only by addition of viscosity modifiers (Vms) also known as viscosity index improvers (VIIs). As opposed to those present in low-molecular base fluids, viscosity modifiers have a polymer nature. These molecules are described as being chain-like molecules whose solubility depends on chain length, structure and chemical composition. As a rule, the base oil solubility of these polymer chains deteriorates as the temperature falls and improves with increasing temperature so that an increase in viscosity induced by viscosity modifiers also increases the viscosity index. In 1958 T. W. Selby published a descriptive explanation of the mechanism of Vms. Because of poor solubility at low temperatures the chain-like VM molecules form coils of small volume and as the temperature is increased these molecules expand and unravel, resulting in an increasing beneficial effect on high-temperature viscosity. The absolute increase in viscosity and the VI depends on the type, the molecular weight and the concentration of viscosity modifiers in the formulation.

Pour point Depressants (PPD):

With the exception of polyalkylated naphthalenes, pour-point depressants (PPD) are closely linked to a series of viscosity modifiers. The major difference of these polymers is their application concentration and the selection of monomer building blocks. Molecular weight and thickening efficiency only play a subordinate role in a band from 0.1 to max. 2 %. An additional thickening effect is always welcome but is usually limited by solubility thresholds. As is generally the case with flow improvers, although paraffin crystallization cannot be suppressed, the crystalline lattice and thus the morphology of the paraffin crystals can be significantly altered. While polyacrylates and ethylene vinyl acetate copolymers are used for crude oils and petroleum, special polyalkyl methylacrylates are normally used for mineral oil-based formulations. The fundamental background for this is co-crystallization of paraffinic components in the base oil and the polymer chain. This interaction results in an alteration of the crystal morphology. Instead of the needle-like paraffin crystals which rapidly cause paraffin gelation, densely packed, round crystals are formed which hardly affect flowing properties even at temperatures below the pour point. The corresponding PAMA-PPDs are in principle, comb-like and contain C12 –C24 paraffinic side chains by determining the polymer solubility and crystallization of paraffinic components in the base oil, the optimum PPD-mix and concentration can be determined for every base oil mixture. However, as a wide range of base oils are used in practice, standard products are often used which cover almost the entire spectrum. In such cases, efficiency is controlled via PPD concentration.

Detergents and Dispersants:

Detergents and dispersants often called DD or heavy-duty (HD) additives have been indispensable for the development of modern engine oils for gasoline and diesel combustion motors. These lubricants are especially severely stressed due to the high temperatures that they are exposed to and the additional influence of aggressive blow-by gases of the combustion process. DD additives keep oil-insoluble combustion products in suspension and also prevent resinous and asphalt-like oxidation products from agglomerating into solid particles. The over based metal-

containing compounds additionally are able to neutralize acidic combustion products as well as oxidation products by their alkaline reserve. Thus, DD additives prevent oil thickening, sludge and varnish deposition on metal surfaces and corrosive wear. The original definition of detergents refers to their cleaning properties similar to the detergents in washing agents although their function appears to be more the dispersing of particulate matter like abrasive wear and soot particles rather than cleaning up existing dirt. Historically these kinds of additives have been metal-containing compounds, often with high alkaline reserve. To meet the dramatically increased requirements of modern high-performance engine oils new ashless dispersants with improved dispersing properties have been developed. As these ashless compounds possess also cleansing properties in fact there is no real difference between detergents and dispersants and it is more an arbitrary definition to call the metal-containing compounds as detergents and the ashless types as dispersants. Thus it seems to be more appropriate to speak of metal-containing and ashless DD or HD additives (**Raddatz, J. H., 1994, Small N. J. H., 1978**).

Detergents and dispersants are generally molecules having a large oleophilic hydrocarbon 'tail' and a polar hydrophilic head group. The tail section serves as a solubilizer in the base fluid, while the polar group is attracted to contaminants in the lubricant. A multitude of dispersant molecules are able to envelope solid contaminants forming micelles whereby the non-polar tails prevent the adhesion of polar soot particles on metal surfaces as well as the agglomeration into larger particles.

Phenates represent an important class of detergents which are synthesized by reaction of alkylated phenols with elemental sulfur or sulfur chloride followed by the neutralization with metal (calcium, magnesium, barium) oxides or hydroxides. Calcium phenates are currently the most widely used types. Basic calcium phenates can be produced by using an excess of the metal base. Beside their good dispersant properties they also possess greater acid neutralization potential.

Salicylates are generally prepared by carboxylation of alkylated phenols with subsequent metathesis into divalent metal salts. Typically also these products are over based by an excess of metal carbonate (calcium and magnesium) to form highly

basic detergents that are stabilized by micelle formation. Salicylates exhibit additional antioxidant properties and have proven effective in diesel engine oil formulations.

These representatives of the detergents are produced by the reaction of polybutene (molecular weight from 500 to 1000) with phosphoruspentasulfide followed by hydrolysis and formation of metal (calcium, formerly also barium) salts. The reaction products consist mainly in thiopyrophosphonates combined with thiophosphonates and phosphonates. Overbased products have almost vanished from use.

As opposed to detergents containing metals, Ashless Dispersants (ADs) are by definition free of metals. They are generally derived from hydrocarbon polymers. The best known and economically most interesting raw material group are polybutenes with molecular weights of 500 to 3000 g mol⁻¹ (**Omeis J, Pennewiss H**).

Antifoam Agents:

The foaming of lubricants is a very undesirable effect that can cause enhanced oxidation by the intensive mixture with air, cavitation damage as well as insufficient oil transport in circulation systems that can even lead to lack of lubrication. Beside negative mechanical influences the foaming tendency depends very much on the lubricant itself and is influenced by the surface tension of the base oil and especially by the presence of surface-active substances such as detergents, corrosion inhibitors and other ionic compounds. Very important for the understanding of foaming effects is the difference between the so-called surface foam and the inner foam. Surface foam can be controlled by antifoam agents. Effective defoamers possess a lower surface tension compared to the lubricant base oil, are usually not soluble in the base oil and therefore have to be finely dispersed in order to be sufficiently stable even after long-term storage or use. The particle size of the dispersed defoamers should be smaller than 100 nm or even smaller than 10 nm (**Hellberg H., 1978**). The inner foam refers to finely dispersed air bubbles in the lubricant that can form very stable dispersions. Unfortunately the common defoamers dedicated to control the surface foam tend to stabilize the inner foam. Generally the

air release properties of lubricants cannot be improved by additives. In the contrary lots of additives have a negative influence. Lubricants which need excellent air release properties e.g. turbine oils have to be formulated using specially selected base oils and additives. Air is not only present in the lubricants in form of dispersed air bubbles (surface and inner foam) but can also be truly physically dissolved up to 9 % (v/v) in mineral oil. Also this air can cause severe problems like cavitation (diesel effect') but this m effect cannot be controlled by additives.

Liquid silicones, especially linear and cyclic polydimethylsiloxanes, are the most efficient antifoam agents at very low concentrations of 1 to max. 100 mg kg⁻¹ to guarantee a stable dispersion silicones usually are predissolved in aromatic solvents. Compared to other additives silicone defoamers have the disadvantage of being particularly easily carried out of the lubricant due to their insolubility and their strong affinity to polar metal surfaces.

Nowadays silicone-free defoamers are used more and more in many applications. Especially in metalworking processes cutting fluids as well as hydraulic fluids used close by have to be silicone-free to guarantee the subsequent application of paints or lacquers on the workpieces. Silicones have caused lots of problems in this application. The main representatives of silicone-free defoamers are special poly(ethylene glycols) (polyethers), polymethacrylates, and miscellaneous organic copolymers. Also tributylphosphate has been proposed as antifoam agent.

Demulsifiers:

Most of the industrial oils in circulation systems (hydraulic, gear, turbine and compressor oils) require good or excellent demulsification properties to separate water contamination from the lubricating system. Without demulsifiers lubricating oils can form relatively stable water-in-oil emulsions. In principle, all surface-active substances are suitable demulsifiers. One of the first known types have been alkaline-earth metal salts of organic sulfonic acids particularly barium and calcium dinonylnaphthenesulfonates. Nowadays special polyethylene glycols and other ethoxylated substances have proved to be highly efficient demulsifiers which are often part of many additive packages. Surprisingly the same class of chemical

substances is used as emulsifiers. Here the molecular weight, the degree of ethoxylation and the treat rate are very important to guarantee the demulsifying properties.

Emulsifiers:

It's importance for the formulation of water-based metal working fluids.

Dyes:

For marketing, identification or leak detection purposes some lubricants contain dyes which are classified according to the International Color Index (**The Society of Dyers and Colourists, 1997**). Most of these substances are solids which often are suspended in mineral oil or dissolved in aromatic solvents to make their handling easier. Generally oil-soluble azo dyes are used. Some of these products may be removed in the near future because they have to be labeled as potentially carcinogenic. Fluorescent dyes are typically used to detect leaks under UV light when the coloration of lubricants is not appreciated.

Antiwear (AW) and Extreme Pressure (EP) Additives:

When two contacting parts of a machinery start to move and the hydrodynamic lubrication has not yet build up or in the case of severe stress and strong forces the lubricating system runs in the area of mixed friction. In this case antiwear (AW) and extreme pressure (EP) additives are necessary in any metalworking fluid, engine oil, hydraulic fluid or lubricating grease to prevent welding of the moving parts respectively to reduce wear.

Function of AW/EP Additives, because of their polar structure these additives form layers on the metal surface by adsorption or chemisorption that guarantees their immediate availability in the case of mixed friction conditions. When the hydrodynamic lubricating film is not yet or no longer present, temperature will increase and the AW and EP additives can react with the metal surface forming tribochemical reaction layers (iron phosphides, sulfides, sulfates, oxides and carbides – depending on the chemistry of the additive) that will prevent direct contact between the sliding metals. These friction reducing, slideable reaction layers can smooth the

asperity of the metal surface by plastic deformation and reduce wear that would occur due to microwelding processes respectively. Avoid real welding of the moving parts under extreme pressure conditions. Layers formed by only physically adsorbed polar substances like fatty oils, fatty acids and others exhibit only poor or moderate high pressure properties. These kinds of additives are called friction modifiers. More effective and more stable are chemically reactive products (AW and EP additives) that can form tribo-chemical reaction layers. AW additives are mainly designed to reduce wear when the running system is exposed to moderate stress whereas EP additives are much more reactive and are used when the stress of the system is very high in order to prevent the welding of the moving parts that otherwise would lead to severe damage. Typically EP additives increase wear effects due to their high reactivity. This differentiation cannot be precise and there are many additives that can be related to both groups.

Under condition of medium stress organic phosphorus compounds work excellent as antiwear additives. Most of these additives are neutral and acidic phosphoric acid ester derivatives, their metal or amine salts or amides. As the acidic form of these compounds is the most reactive one, the reactivity decreases with the degree of neutralization.

The most important and well known additive groups of the sulfur–phosphorus compounds are the zinc dialkyldithiophosphates (ZnDTP) (**Von Eberan-Eberhorst C. G. A, *et al.*, 1994**). They are synthesized by reaction of primary and secondary alcohols (C3 –C12) as well as alkylated phenols with phosphorus (V) sulfide followed by neutralization of the resulting dialkyldithiophosphoric acids with zinc oxide. Usually this last reaction step is done in mineral oil solution but it is also possible to make mineral oil free compounds by using solvents that can be removed afterwards by distillation. Beside the neutral species also basic ZnDTPs can be obtained when the neutralization is done with an excess of zinc oxide. ZnDTPs based on isopropanol or n-butanol is solids, whereas mixtures of short and long chain alcohols are liquid. The thermal and hydrolytic stability of ZnDTPs and thus their reactivity (AW/EP-performance) can be influenced by the structure of the alkyl groups. So the thermal stability increases with the chain length of the alkyl groups

and their structure in the sequence secondary, primary and aromatic. By carefully directed alcohol composition the specific requirements of different applications can selectively be adjusted. Beside excellent antiwear and extreme pressure properties ZnDTPs are also efficient antioxidants and even metal passivators. These multifunctional properties make them the widest spread cost effective additive group that is used nowadays in huge quantities in engine oils, shock absorber oils and hydraulic fluids. Beyond ZnDTPs also ammonium, antimony, molybdenum and lead dialkyldithio-phosphates are known, which the latter no longer has real significance because of toxicological and ecotoxicological concerns. MoDTPs are effective antiwear additives with remarkable friction reducing properties and excellent antioxidant behavior. Ashless dialkyldithiophosphoric acid-O,O,S-triesters distinguish by improved hydrolytic stability in comparison to metal salts of the dithiophosphoric acid. On the other side their antioxidant properties are reduced. Similar to the ZnDTPs the reactivity can be influenced by variation of the organic substituents.

Zinc-bis (diamyldithiocarbamate) and the ashless methylene-bis (di-n-butylthiocarbamate) are highly effective EP additives and excellent antioxidants. Beside these main species also antimony and tungsten derivatives are known. Dithiocarbamates are predominantly used in lubricating greases and to some extent in gear oil formulations.

From the early days of lubrication until now elemental sulfur has been added directly to mineral oil (up to 1.5 %) to improve the EP properties of metal working fluids. Oil-soluble organic sulfur compounds, the so-called sulfur carriers, of the general formula $R-S_x-R$ offer improved solubility and better control over the reactivity of the sulfur. Fundamentally, it can be differentiated between inactive and active sulfur carriers. The inactive types with predominantly disulfide bridges ($x = 2$) possess relatively stable C-S bonds which will react at elevated temperatures only. The active forms with x between 3 and 5 (so-called pentasulfides) are much more reactive as the sulfur of the relatively labile polysulfide bridges can easily be made available even at low temperatures. Moreover numerous sulfur carriers with specific

distribution of the different polysulfide bridges ($x = 1-5$) are used to cover the whole field of application with its varying stress requirements.

PEP Additives:

Over based sulfonates, especially calcium and sodium salts can be used as highly efficient boosters in combination with active sulfur carriers to formulate metal working fluids with extremely high load carrying behavior. These overbased products are called PEPs (passive EP).

The excellent AW/EP properties of chlorine compounds have been conventionally explained by their ability to coat the metal surface with a slideable metal chloride film under the influence of high pressure and in the presence of traces of moisture. Because of the formation of hydrogen chloride alkaline buffers have to be added to avoid severe corrosion. Another approach refers to the formation of high pressure stable adsorption layers due to the affinity of the additive's heteroatom (Cl) showing outstanding lubricity at low machining speed and moderate temperature but reduced efficiency with increasing temperature (speed) (**Rossrucker T, Fessenbecker A., 1999**). For environmental and toxicological reasons concerning the disposal of the chlorinated used fluids chlorine compounds are increasingly replaced although this additive technology has been extremely successful in metalworking fluids. Beside the corrosivity of their decomposition products, primarily hydrogen chloride, the biggest problem is the possible formation of highly toxic dioxins at the incineration of used oil especially when the incineration temperatures are not high enough. Typical additives have been chlorinated paraffins with a chlorine content of 35 to 70 % and a hydrocarbon base of 10 to 20 carbon atoms as well as chlorinated sulfur carriers.

Mainly finely ground powders of graphite and molybdenum disulfide respectively their dispersions are used as solid additives. They are distinguished by excellent emergency running properties when the oil supply is breaking down. Also for extreme high temperature applications solid lubricating compounds are used due to their high thermal stability. Other compounds that are used especially in lubricating greases are polytetrafluoroethene, calcium hydroxide and zinc sulfide.

Friction Modifiers (FM):

In the case of liquid (hydrodynamic) lubrication friction can be reduced only by the use of base oils with lower friction coefficients and lower viscosity respectively high viscosity indices. In the area of low slide velocities, moderately increased loads and low viscosities at higher temperatures the liquid lubrication can easily precede to mixed friction conditions. In this case so-called friction modifiers have to be used to prevent stick–slip oscillations and noises by reducing frictional forces. They work at temperatures where AW and EP additives are not yet reactive by forming thin mono- molecular layers of physically adsorbed polar oil-soluble products or tribochemical friction reducing reaction layers that exhibit a significantly lower friction behavior compared to typical AW and EP additives (**Völtz M and Rulfs H., 1982, Papay A.G., 1983**). Therefore friction modifiers can be regarded as mild AW or EP additives working at moderate temperatures and loads in the area of beginning mixed friction. Friction modifiers can be classified into different groups regarding their function (**Christakudis D., 1994**).

Corrosion Inhibitors:

Corrosion inhibitors are used in nearly every lubricant to protect the metal surface of any machinery, metalworking tool or work piece from the attack of oxygen, moisture and aggressive products. These mostly acidic products may be formed by the thermal and oxidative decomposition of the lubricant (base oil and additives), brought in directly from the environment (acid atmosphere) or caused by the specific application (aggressive blow-by gases in internal combustion engines). The base oil itself forms a kind of protective layer on the metal surface. But in general this will not be sufficient especially when highly refined oils without natural inhibitors are used. Then highly efficient anticorrosion additives are necessary.

The mechanism of anticorrosion additives is relatively simple. Anticorrosion additives are molecules with long alkyl chains and polar groups that can be adsorbed on the metal surface forming densely packed. The adsorption mechanism can base on a physical or chemical interaction of the polar anticorrosion additive with the metal surface (**Ford J. F, 1968**). Because of this high surface activity, anticorrosion

additives compete with other polar additives like antiwear and extreme pressure additives for the metal surface and can therefore reduce their efficiency. Corrosion inhibitors can be divided into 2 main groups: antirust additives for the protection of ferrous metals and metal passivators for non-ferrous metals.

Antirust Additives (Ferrous Metals):

Petroleum sulfonates (mahogany sulfonates) are by-products at the production of white oils by treatment with oleum. The resulting acid tar contains long chain alkylarylsulfonic acids that can be neutralized with lyes. Sodium sulfonates with low molecular weights (below approx. 450) are typically used as low-priced emulsifiers and detergents with additional anticorrosion properties in water based metal working fluids, engine oils and rust preventatives. Sulfonates with higher molecular weights distinguish as highly efficient corrosion inhibitors especially when based on divalent cations like calcium, magnesium and barium. The importance of the barium compounds is going to decrease constantly due to toxicological and ecotoxicological concerns. Nowadays synthetic alkylbenzene sulfonates are used preferably in spite of a higher price level due to their higher and more constant quality. A special group of synthetic sulfonates are the dinonylnaphthenesulfonates of which the neutral calcium and barium salts distinguish by additional demulsifying properties and a good compatibility with EP additives. Beside the neutral or only slightly basic sulfonates overbased sulfonates with high alkaline reserve (TBN 100 to 400 mg KOH g⁻¹) play an important role especially in the formulation of engine oils. There they exhibit detergent properties and can neutralize acidic oxidation products. Moreover in metal working fluids they act as so called passive EP additives to prevent welding under high pressure conditions.

Many different long-chain carboxylic acid derivatives have been proposed as corrosion inhibitors at which the carboxylic group acts as polar part that can easily be adsorbed on the metal surface.

Some special amine salts of mono- or dialkylphosphoric acid partial esters exhibit excellent anticorrosion properties in addition to their highly efficient antiwear properties (Olszewski W.F., Neiswender D.D., 1976). Because of the well-known

antagonism of anticorrosion and antiwear additives this behavior makes them one of the mostly used components in ashless industrial oils.

Vapor phase corrosion inhibitors (VCIs) for closed systems are substances with high affinity to metal surfaces and relatively high vapor pressure to guarantee their availability on parts that are not steadily in direct contact with the corrosion inhibited lubricant. The mostly used product groups for this application are amines. Morpholine, dicyclohexylamine and diethanolamine have proved to be highly efficient for that purpose, because of toxicological concerns that refer mainly to the nitrosamine forming potential of secondary amines, these products are going to be partly substituted by tertiary amines like diethanolmethylamine and similar products. Another group of oil soluble VCIs are low molecular weight carbonic acids (n-C 8 to n-C 10).

The metal passivators can be classified into three groups: film forming compounds, complex forming chelating agents and sulfur scavengers. The fundamental function of the film forming types consists in the building of passivating protective layers on the non-ferrous metal surface thus preventing the solubilization of metal ions that would work as pro-oxidants. The complex forming agents are able to build oil-soluble complexes with significantly reduced catalytic activity regarding the influence of non-ferrous metal ions on the oxidative aging process of lubricants. Sulfur scavengers are even able to catch corrosive sulfur by integrating sulfur into their molecular structure.

Metal passivators in combination with antioxidants show strong synergistic effects as they prevent the formation of copper ions respectively suppress their behavior as pro-oxidants. Thus these additives are used in nearly every formulation of modern lubricants.

1.2.8 Hydraulic Fluids:

Hydraulics describes the transfer of energy and signals through fluids. Hydraulic fluids are used in nearly all industries such as agriculture, construction, woodworking, and steel with the main purpose to transmit power. After engine oils, hydraulic fluids are the second most important group of lubricants. The most

important elements of a hydraulic system are pumps, motors, cylinders, valves, and circuit components which mean that the hydraulic fluid must be resistant to both high pressure and relative high temperatures up to 90°C. The operating temperature for a hydraulic system is generally 40-50°C and for systems working at high pressures 60-70°C. In contrast to engine oil the amount of additives in hydraulic oil is often small and in general only 1-2% (**Schneider P. M., 2006**).

Hydraulic oils are classified according to International Standard Organization (ISO) viscosity grades (VG). According to this system a hydraulic oil is named by ISO followed by a number equal to the oil viscosity measured in centistokes at 40°C, ISO VG 46 etc.

In general, a hydraulic fluid consists of a base fluid, usually called a base oil, and chemical substances, usually called additives. The quality and performance of a hydraulic fluid depends on the quality of the base fluid and the combination of the additives or additive systems used. Additives improve certain characteristics which the base fluid cannot provide, or cannot provide not to a sufficient extent. Bearing in mind technical and ecological aspects, the type of base fluid and the types of additive ultimately decide the classification of a hydraulic oil (**Mang T.,1998**).

Mineral oil-based fluids (paraffinic oils, naphthenic oils and white oils) and/or mixtures thereof are used as base fluids or base oils. Synthetic fluids based on hydrocracked oils (HC oils or so-called group III oils), polyalphaolefins (PAO), ester oils (POE) and polyglycols (PAG) are mainly used in fire-resistant, rapidly biodegradable fluids or special hydraulic fluids. Natural vegetable oils such as rapeseed oil are often found in rapidly biodegradable fluids. Food-grade hydraulic oils are generally based on special white oils, polyalphaolefins and polyglycols (Base Oils and Synthetic Base Oils), (**Murrenhoff H., 1997, Mang T., 1998, Bartz W.J., 1995**).

Mineral oils account for ~ 88 % (mainly paraffinic Group I Oils); synthetic oils account for 12 % (80 % Ester, 15 % Polyglycols, etc.).

Hydraulic Fluid Additives:

The required lubricity of hydraulic fluids is normally provided by special additives. The additives are usually included in the form of additive packages (mixtures) to Hydraulic Oils achieve the desired results. The additive components can either complement each other or counter each other. The characteristics which can be improved by the use of additives include aging stability, corrosion protection, wear protection, EP behavior, viscosity–temperature behavior, foaming, detergency, water separation, friction coefficient and many more.

H Hydraulic Oils:

Type H, mineral-based hydraulic oils are generally base oils without additives. Accordingly, they are hardly used in Western Europe. Classification: ISO 6743/4–HH (ISO., 1997).

HL Hydraulic Oils:

Hydraulic fluids with additives to improve aging stability and corrosion protection, these oils are used in hydraulic systems which need not be protected from wear such as in steel and rolling mills where the prevailing conditions cause the fluids to be contaminated with water. Thus these types of fluid can separate water well, usually also release air rapidly, and are compatible with special – white metal and Morgan – bearings.

HL hydraulic oils according to DIN 51 524-1 (DIN., 2006). HL hydraulic oils according to ISO 6743/4 (ISO., 1997).

HLP Hydraulic Oils:

Compared with HL fluids, these oils contain additional agents to reduce wear and/ or improve EP behavior. This is the dominant group of hydraulic oils in Europe and the rest of the world. They are universal hydraulic oils for a wide range of applications and highly loaded components and are used for applications which require good aging stability, corrosion protection, and wear protection. At the same time, these lubricants offer good demulsifying properties. These fluids are used as

universal products in hydraulic presses, die-casting machines and in steel mills when a fluid with wear protection is specified. HLP according to DIN 51 524-2 (**DIN ., 2006**). HM according to ISO 6743/4 (**ISO ., 1997**).

HVLP Hydraulic Oils:

Compared with HLP grades, these fluids have a high viscosity index ($VI > 140$, HLP oils: $VI \approx 100$). They therefore have good viscosity–temperature behavior. The high VI is achieved by use of additives and/or by use of appropriate base oil. The natural high VI of the base oil is preferred because shear losses do not happen. According to DIN 51 524-3 in conjunction with DIN 51 350-6 (VRA – Determination of shear stability of Lubricating oils containing polymers) the shear loss has to be reported (recommended max 15–20 %, OEMS < 15 %). A low start-up viscosity at low temperatures and a high operating viscosity at higher temperatures is a significant technical advantage over equi-viscous HLP oils. The absorption of energy is low, pre-heating the system is usually not necessary, and operating temperature is achieved rapidly. The use of HVLP oils affords significant rationalization potential. Generally speaking, HVLP oils have a multigrade character (**Murrenhoff H., 1997**), **Jaroslav und Monika Ivantysyn., 1993**, **Mang T., 1998**). The use of these oils has grown rapidly over the last few years. They are perfect for fluctuating operating temperatures such as those found in mobile hydraulic systems, canal locks and cable-car hydraulics. HVLP according to DIN 51 524-3 (**DIN ., 2006**)

HLPD Hydraulic Oils:

Compared with HLP products, these hydraulic oils contain DD additives which finely disperse, suspend, and emulsify water, dirt, aging products and contaminants and thus hinder the accumulation of deposits on hydraulic components. The mostly polar DD additives also reduce friction and wear. Their polarity also affords good wetting, reduces stick–slip and leads to a lower coefficient of friction. These oils are often used in machine tools and other systems with sensitive control valves because they combat deposits. For machine tools, where cutting fluids can contaminate the hydraulic system, HLPD oils combat valve and cylinder gumming

by emulsifying ingressed cutting fluid. HLPD oils hinder the precipitation of solid and fluid impurities. These are kept in suspension and are removed at the filtering stage. This is why filter capacities must often be increased if HLPD oils are used (Murrenhoff H., 1997, Jaroslav und Monika Ivantysyn., 1993, Bartz W.J., 1995).

Fire-Resistant Hydraulic Fluids:

Fire-resistant fluids have been developed for mining, die-casting, steel mill, and aviation applications. These fluids have significantly higher ignition temperatures or fire-resistant properties and thus afford better fire protection than mineral oils. Use of these fluids is compulsory for some applications, for example underground coal mining.

1.2.9 Gear Lubrication Oils:

The gear lubrication oil is a machine component of particular significance for gear and transmission. During operation, the lubricant comes into contact with most of the other in build machinery components. Apart from the important function of lubricating the sliding rolling contacts, the oil also fulfills the task of cooling and removing the friction heat generated in the sliding rolling contacts. Various types of lubricant are used in the lubrication of gear and transmissions, whereby lubrication oil mainly consists of a base-oil and an additive adjusted to the base-oil and the application. The following base-oils are not only used for the lubrication of transmissions but also many other applications:

- 1- Mineral oils and Synthetic hydrocarbons (polyalphaolefins)
- 2- Poly (alkylene glycols) (homopolymers)
- 3- Esters (environmental-friendly oils, mainly on synthetic basis)
- 4- Naphthenic oils (rapeseed oil, castor oil)

Apart from the various base-oils, the type and quantity of the additive, which depends heavily on the base-oil, has a significant influence on the function and service life of gear and transmission.

Requirements of Gear Lubrication Oils:

The heavily loaded lubricants in hypoid gears require high oxidation stability, together with a very good scuffing and scoring and wear load capacity, due to the high load of the tooth contacts. At the same time, the formation of a load-capable and separating film thickness for sufficient lubrication and cooling of the sliding rolling contacts in hypoid gears requires a lubricant with an adequately high viscosity at operating temperature.

On the other hand, lubricants used in hydrodynamic gears, such as torque converters, hydrodynamic wet clutches or retarders, don't need to have a good scuffing and scoring load capacity. However, they must have high oxidation stability. Due to the viscosity-dependent losses, lubricants which are used in hydrodynamic gears therefore have a clearly lower viscosity at operating temperature in comparison to lubricants used in hypoid gears. The heat development in a gear generates heat and raises the temperature of the oil sump and the temperature in the oil tank. This is of a major significance for the lubricant's service life since it accelerates the oil's aging process and, therefore, can cause a reduction of the oil's service life. The heat development and, thus, the oil temperature, is determined by the type of gear, the transferred torque, the specific load, as well as from the switching periods – permanent or intermittent operation and from the environmental conditions – use of the gear in warm or cold climates or in a mobile or stationary application.

Gears that require extended service lives, such as paper machines or presses, the lubricant has to be exchanged according to the mechanical and thermal claim, in compliance with the oil producers' recommendations. Assuming that the average oil sump temperature in such transmissions is approx. 90 °C, the oil should be exchanged in intervals of 2500 hours of operation. An increase of the oil sump temperature of 10 K leads to a 50 % reduction of the service life, reducing the temperature by the same value doubles the oil's service life in general.

Gear Lubricants for Industrial Gears:

The industrial gear applications differ from vehicle transmissions mainly due to their larger variety and higher number of combinations of toothing types and sizes

used. Gears for industrial application are also different due to a larger variety of possible operating and ambient conditions. They stand out due to much higher torque and performances, connected with clearly larger housing dimensions. At the same time, the gears size also requires larger volumes of lubricant. According to the conditions of the industrial gears use, the service life requirements are clearly higher than those made on vehicle transmissions.

Viscosity-Temperature Characteristics:

According to the ambient and operating conditions, the required viscosity-temperature behavior of gear lubrication oils constitutes a very important requirement during the application. Here, the base oil's properties according to the viscosity range are of great importance. Worldwide, the lubrication oils for industrial gears are subject to the ISO viscosity grade conversions.

CHAPTER TWO

Materials and methods

2.1 Experimental summary:

The lubricant oils in this study are lab blend (the engine oil CF50, Hydraulic EP150 and Industrial Gear oil 320). Engine oil was added to Hydraulic EP150 with concentration range from 0.99% to 10% and to the Industrial Gear oil 320 from 0.196% to 0.8%, to evaluate how engine oil contamination impacts the water separability of the lubricant. The metals (ASTM D7751-12), water separability (ASTM D1401), Density (ASTM D4052-11) and kinematic viscosity (ASTM D445-12) was measured for the investigated samples.

Table: 2.1 blended oils used in the study specifications

Lubricant oils	Viscosity@ 40°C cSt	Viscosity@ 100 °C cSt	V.I	Density @ 15°C (g/cm ³)	Metals (W/W)%		
					Ca	Zn	P
CF50	217.4	18.99	98	0.9006	0.286	0.110	0.105
Hydraulic EP150	151.2	14.71	96	0.8914	0.004	0.032	0.023
Industrial Gear 320	306.3	23.67	97	0.8980	0.00	0.00	0.021

2.2 Apparatus and chemicals:

- 1- XRF (X-supreme 8000 SN: X13021) and Filling cup and poly film
- 2- Calibrated viscometer, Calibrated thermometer and 3ml Syringe
- 3- Calibrated NVB Classic @ 40°C SN: 13T107 and Calibrated NVB Classic @100°C SN: 13T106
- 4- Cylinder, 100-mL, graduated from 5 to 100 mL in 1.0-mL divisions, made of glass, heat-resistant glass, like borosilicate glass, or a chemical equivalent.
- 5 - DEM CLASSIC SN: 88791 and Calibrated Stop watch
- 6- Anton Par Density Meter SN: 81242597 and syringe
- 7 - Toluene AR Grade, Acetone AR Grade and Dry air

2.3 Metals measurement Procedure:

Metal content was determined using X-supreme 8000 ASTM D7751. The sample cup was filled to the mark. The sample was placed in the instrument and the measurement was performed according to instrument manufacturer's instructions. The concentration for all elements of interest was determined (ASTM D7751, 2012).

2.4 Kinematic Viscosity measurement Procedure:

The time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity (determined value) is the product of the measured flow time and the calibration constant of the viscometer. Two such determinations are needed from which to calculate a kinematic viscosity result that is the average of two acceptable determined values (ASTM D445, 2012).

2.5 Water separability Procedure:

Graduated Cylinder, 100-mL, consisting of a 40-mL sample and a 40-mL quantity of distilled water, are stirred for 5 min in a graduated cylinder at 82°C. The

time required for the separation of the emulsion is recorded after every 5 min. the separation standing for 30 min, the volumes of oil and water is recorded (ASTM D1401, 2012).

2.6 Density measurement Procedure:

A small amount (about 1 to 2 mL) of sample is introduced into the clean, dry sample tube of the instrument by a suitable syringe. The sample tube is properly filled and no gas bubbles are present. The instrument is displayed a steady reading to four significant figures, indicating that temperature equilibrium has been reached, the density is recorded (ASTM D4052, 2011).

CHAPTER THREE

The results

3.1 Elements (%) and water separability of Industrial oil (Gear 320)

Table 3.1 shows seven samples of fresh industrial oil (Gear 320) contaminated with engine oil (CF50) in addition to reference sample (0.00%) contaminant. The following concentrations of engine oil (CF50) were added (0.196, 0.200%, 0.385% 0.400%, 0.566%, 0.600 and 0.77%) also the results of elements (Phosphorus, Calcium and Zinc) were shown in the same table.

Table 3.2 shows water separability of contaminated industrial oil (Gear 320) at interval of time (5min, 10min, 15min, 20min, 25min and 30min) for concentrations mentioned in table 3.1.

The effect of calcium concentration on water separability of industrial oil (Gear 320) at interval of time has been shown in figure 3.1 in addition to that, the effect of contaminant in the viscosity and viscosity index was showed in table 3.5 and figure 3.3.

3.2 Elements (%) and water separability of oil (EP150)

Table 3.3 shows twelve samples of fresh hydraulic oil (EP150) contaminated with engine oil (CF50) in addition to reference sample (0.00%) contaminant. The following concentrations of engine oil (CF50) were added (0.99%, 1.96%, 2.00%, 2.91% 3.00%, 3.85% 4%, 4.76 %, 5.00% 5.66%, 6.00% and 9.09%) also the results of elements (Phosphorus, Calcium and Zinc) were shown in the same table.

Table 3.4 shows water separability of contaminated hydraulic oil (EP150) at interval of time (5min, 10min, 15min, 20min, 25min and 30min) for concentrations mentioned in table 3.3.

Figure 3.2 shows the effect of calcium concentration on water separability of hydraulic oil (EP150) at interval of time and the effect of contaminant in the viscosity and viscosity index were showed in table 3.6 and figure 3.4.

Table: 3.1 Phosphorus, Calcium and Zinc concentrations of contaminated industrial oil (Gear 320)

Elements	Percentage of contaminant CF50							
	0.00%	0.196%	0.200%	0.385%	0.400%	0.566%	0.600%	0.770%
Phosphorus (%)	0.0021	0.0023	0.0023	0.0025	0.0027	0.0027	0.0027	0.0050
Calcium (%)	0.0000	0.00039	0.0004	0.00096	0.0010	0.00151	0.00160	0.00193
Zinc (%)	0.0000	0.0002	0.0002	0.0005	0.0005	0.0008	0.0008	0.0010

Table: 3.2 Water separability / min for contaminated industrial oil (Gear 320)

Water Separability/min	Percentage of contaminant CF50							
	0.00%	0.196%	0.200%	0.385%	0.400%	0.566%	0.600%	0.770%
5	27	0	0	0	0	0	0	0
10	32	6	6	5	0	0	0	0
15	38	20	22	19	7	5	0	0
20	39	33	35	30	20	11	4	0
25	40	40	40	39	27	20	10	2
30	40	40	40	39	35	26	14	9

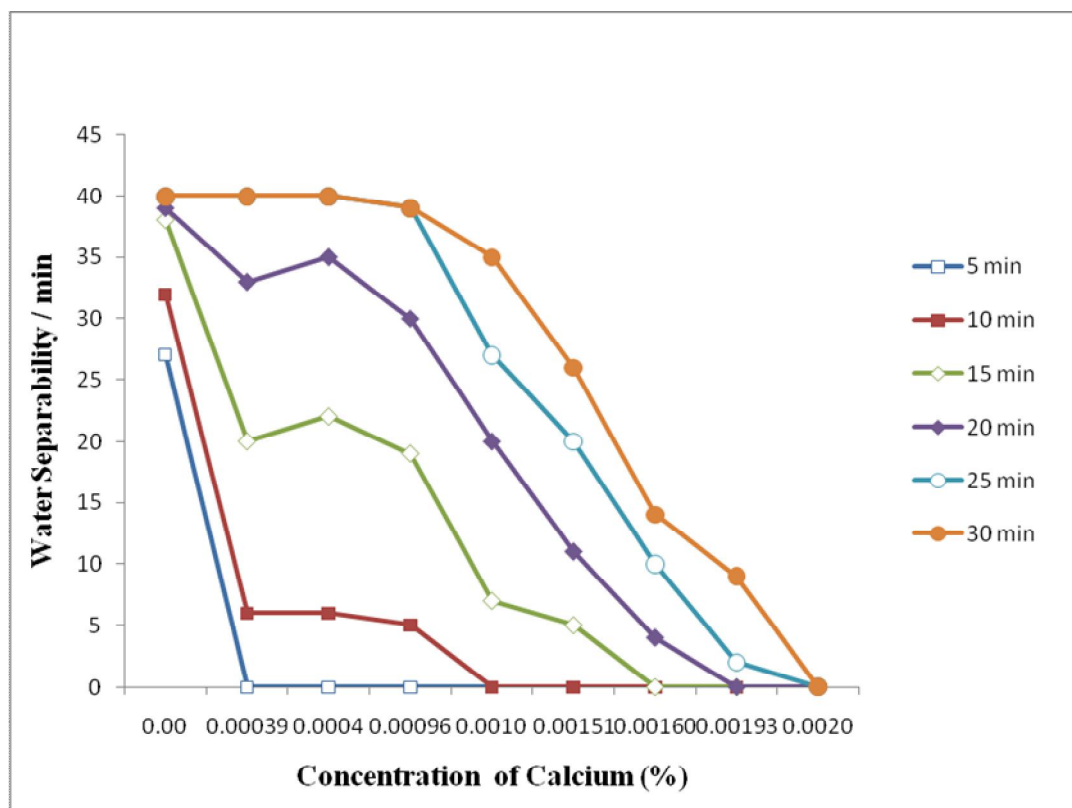


Figure:3.1 Effect of Calcium concentration (W/W%) in water separability of Industrial oil (Gear 320).

Table: 3.3 Phosphorus, Calcium and Zinc concentrations of contaminated hydraulic oil (EP150)

Elements	Percentage of contaminant CF50												
	0.00%	0.99%	1.96%	2%	2.91%	3%	3.85%	4%	4.76%	5%	5.66%	6%	9.09
Phosphorus (%)	0.023	0.024	0.025	0.025	0.026	0.026	0.027	0.026	0.028	0.030	0.028	0.028	0.033
Calcium (%)	0.004	0.007	0.010	0.010	0.014	0.014	0.016	0.016	0.019	0.019	0.022	0.022	0.031
Zinc (%)	0.032	0.033	0.033	0.033	0.035	0.035	0.036	0.035	0.035	0.035	0.038	0.037	0.042

Table: 3.4 Water separability / min for contaminated hydraulic oil (EP150)

Water Separability/min	Percentage of contaminant CF50												
	0.00%	0.99%	1.96%	2%	2.91%	3%	3.85%	4%	4.76%	5%	5.66%	6%	9.09
5	38	37	32	30	0	0	0	0	0	0	0	0	0
10	40	39	39	39	20	18	13	10	9	8	7	0	0
15	40	40	40	40	40	40	40	37	30	26	20	14	5
20	40	40	40	40	40	40	40	37	37	35	32	29	14
25	40	40	40	40	40	40	40	38	37	36	34	30	25
30	40	40	40	40	40	40	40	38	37	36	36	30	25

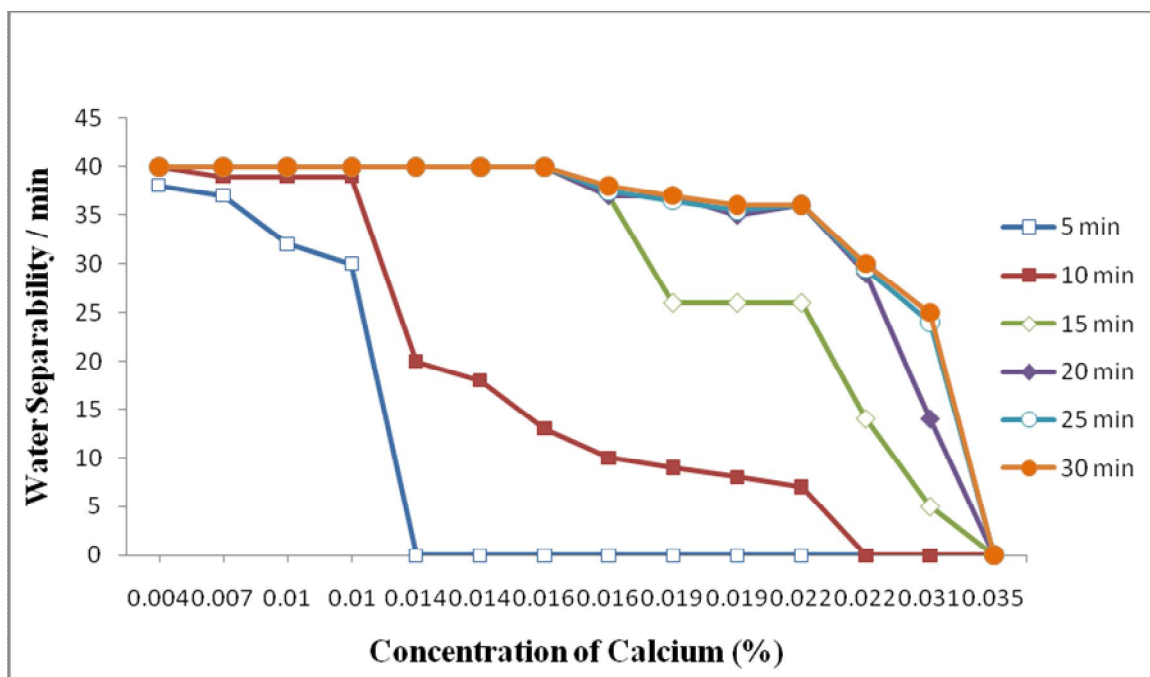


Figure:3.2 Effect of Calcium concentration (W/W%) in water separability of Hydraulic oil (EP150).

Table 3.5 Viscosity and viscosity index of Gear Industrial 320 at various concentrations of contaminant (CF50)

Viscosity & Viscosity Index	Contaminant (CF50)							
	0.00%	0.196%	0.200%	0.385%	0.400%	0.566%	0.600%	0.770%
V@40 ⁰ C	306.3	306.1	306.1	305.9	305.9	305.8	305.7	305.5
V@100 ⁰ C	23.67	23.66	23.66	23.65	23.65	23.64	23.63	23.63
V.I	97	97	97	97	97	97	97	97

Table 3.6 Viscosity and viscosity index of Hydraulic oil (EP150) at various concentrations of contaminant (CF50)

Viscosity & Viscosity Index	Contaminant (CF50)												
	0.00%	0.99%	1.96%	2%	2.91%	3%	3.85%	4%	4.76%	5%	5.66%	6%	9.09
V@40 ⁰ C	151.2	151.7	152.3	152.3	152.8	152.9	153.3	153.4	153.8	153.9	154.3	154.5	156.1
V@100 ⁰ C	14.71	14.74	14.78	14.78	14.82	14.82	14.85	14.86	14.88	14.89	14.92	14.93	15.04
V.I	96	96	96	96	96	96	96	96	96	96	96	96	96

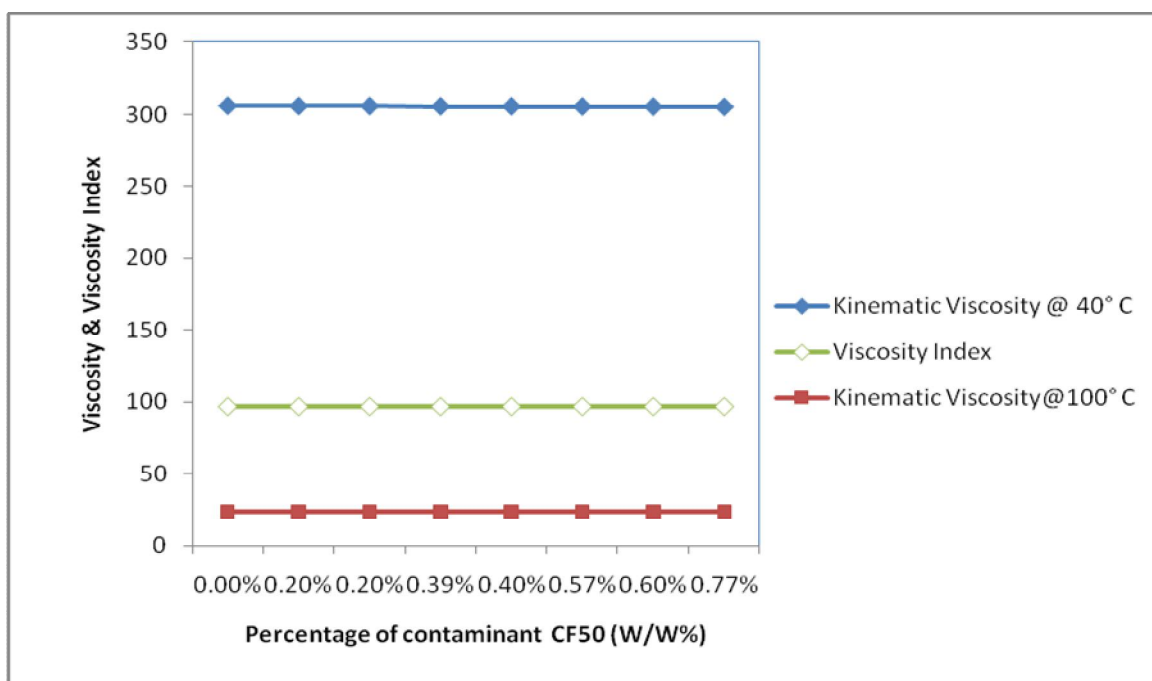


Figure:3.3 Viscosity and viscosity index of Industrial oil (Gear 320) at various concentrations of contaminant (CF50)

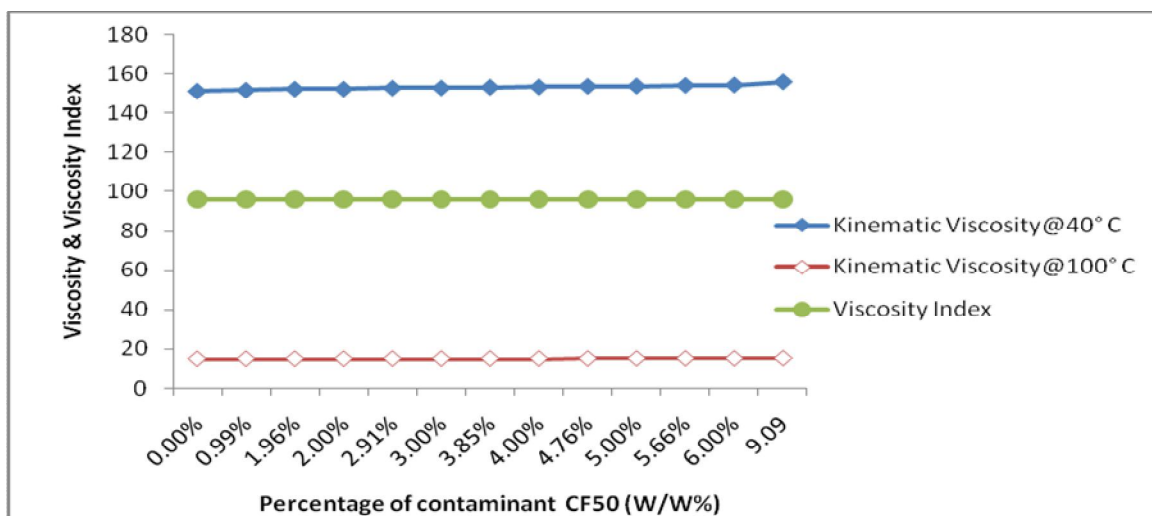


Figure:3.4 Viscosity and viscosity index of Hydraulic oil (EP150) at various concentrations of contaminant (CF50)

CHAPTER FOUR

Discussion and Recommendations

4.1 Discussion

4.1.1 Water separability:

Water separability could be considered as an important method to explain the effect of engine oil in efficiency and quality of separated water volume. Data of the present study revealed that various percentages of engine oil (CF50) added to Industrial oil (Gear 320) and Hydraulic oil (EP150) resulted in considerable effect on the quality of the oil and there is a critical concentration beyond which any increase in the engine oil lubricant will result in oil deviation from specification.

4.1.2 Contaminated Industrial oil (Gear 320):

Contamination is most common in gearboxes in cement plants and plants that handle coal, such as coal mines and coal-fired power plants. Water contamination can corrode gear surfaces and, in the extreme, destroy a gear completely. Consider that industrial gear oil with just one-percent water content can reduce bearing life by up to 90 percent (**Dennis W., 2006**) and the damage and contamination can quickly escalate.

The effectiveness of gear oil is compromised when the oil and water do not separate and the oil becomes diluted. Experts agree that using gear oil that quickly separates from water is the most effective way of reducing the risk and consequences of water contamination. Gear oil with improved water separation properties not only allows faster and easier water draining; it also reduces the frequency of oil changes.

From the table 3.1 and 3.2 it's clearly seen that separated water is affected negatively by increasing of engine oil metals concentration. The calcium in the contaminant is mainly responsible for decreasing the water separability because,

detergent and dispersant are in engine additives, which have polar side that enhance the formation of emulsion.

The figure 3.1: shows the effect of calcium concentration on the volume and rate of water separability. It explain the sensitivity of industrial oil (Gear 320) to engine oil, (0.0004%) from calcium, it's effect appeared in the first 5 minutes and (0.0010%) completely put the lubricant out of specification because, the standard limit is 37ml/30min in American Standard for Testing Materials (ASTM).

4.1.3 Contaminated Hydraulic oil (EP150):

In agricultural machinery and construction machinery, it is both possible and practical to use the same oil for both engine and hydraulic system. It is important to know that hydraulic and engine oils have different structures. For example, engine oils contain detergent (cleaning) and emulsifying (hold particles in suspension) additives. Engine oils are comprised in such a way that they should bind a relatively large amount of water, while hydraulic oils are comprised so that they separate out water. The water can create an emulsion with the detergent and the emulsifying additives (“self-cleaning”), and this can lead to filtration problems.

Table 3.3, 3.4 and figure 3.2 shows the results of various samples of hydraulic oil (EP150) subjected to engine oil contamination. Twelve samples were held at different concentration of contaminant. The reference sample (zero contaminant), separated water completely in 10 minutes. For the other, there is a decrease in separated water volume with increase of contaminant percentage. The sensitivity of Hydraulic oil (EP150) to engine oil contamination is less comparing to Industrial oil (Gear 320) which 35 time sensitive than hydraulic oil (EP150). Calcium concentration (0.014%), effect appeared in the first 5 minutes. At calcium concentration of (0.019%) the lubricant is completely out of (ASTM) specification limits. This proves that engine oil had negative effect in water separability of Hydraulic oil (EP150).

From figure: 3.3 and figure: 3.4 it is clear no significant change in viscosity and viscosity index of both lubricants under study due to contamination with engine oil (CF50).

Conclusion:

Contamination of Hydraulic oil (EP150) and Industrial oil (Gear320) with engine oil (CF50) affects negatively the water separability of these lubricants. The Industrial oil (Gear 320) is very sensitive to such contamination which 35 time greater compared to that of Hydraulic oil (EP150).

Recommendations:

Further studies are needed to examine the effect of contaminations with engine oil in case of multi additive.

References:

- A.von Eberan-Eberhorst, C. G., Hexter, R. S., Clark, A. C. Connor, B. O, and Walsh, R. H, (1994);** Ash giving extreme pressure and anti-wear additives, in: additives for lubricants (Ed W. J.Bartz.), Expert Verlag, p.53-83.
- Adams R. J, and Petlyuk A. M, (1997);** Oxidation Stability and Tribological Behavior of Vegetable Oil Hydraulic Fluids, *Tribology International*, **30**: p. 677-683.
- Adhvaryu, A., Erhan, S.Z., Sharma, B. K, and Liu, Z., (2008);** Lubricant Base Stock Potential of Chemically Modified Vegetable Oils. *Journal of Agricultural and Food Chemistry*, **56**(19),p. 8919-8925.
- Anon., (1968).** Petroleum Additives – Pour Point Depressants” *Encycl. Polym. Sci. and Tech.*, **9**, p.843–844.
- Anwar M, Kaushik R. S, Srivastava M, (2002);** Basics: Current Base Oil Quality and Technological Options for its Improvement –an Overview, *Lubrication Science*, **14**: p. 425-434.
- ASTM D1401., (2012);** Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids 1. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959,USA.
- ASTM D445., (2012);** Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity). ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States.
- ASTM D7751., (2012);** ASTM, Standard Test Method for Determination of Additive Elements in Lubricating Oils by EDXRF Analysis1. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959,USA.
- ASTM., (2012);** ASTM D7751, Standard Test Method for Determination of Additive Elements in Lubricating Oils by EDXRF Analysis1. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959,USA.

- ASTM4052., (2011);** Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter 1. ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, USA.
- Bartz, W. J, and 18 co-authors, (1995);** hydraulic fluids, Volume 475, Expert Verlag, 71272 Renningen.
- Castro W, Perez J. M, Erhan S. Z Caputo F, (2006);** A Study of the Oxidation and Wear Properties of Vegetable Oils: Soybean Oil Without additives, *JAACS* **83** (1); p. 4-52.
- Cherry, W and Man W.H, (1998);** Hydac Technology, Sulzbach: Fluid Controlling Fluid Power to Erhöhungder operating security systems, IFK, 1st International Fluid Power Conference, Aachen.
- Christakudis D, (1994);** Friction modifiers and their examination, in: additives for lubricants (Ed Bartz W. J. Am.), *Expert Verlag*, p.134-162.
- Corsico, G., Pacor, P., Ciali, M., Zatta, A, and Gatti, N., (no yr);** PIO: A New Synthetic Base stock, Presentation of Mixoil.
- DIN, (2006);** DIN 51 524, Part 1-3, hydraulic fluids, hydraulic oils HL, HLP, HVLP, Minimum requirements.
- Ford J. F, (1968);** lubricates oil additives – a chemist’s eye view, *J. Inst. Petrol*, **54**, p.198.
- Gresham B, (2007);** Lubricant base oils, *Tribology & Lubrication Technology*, **63** (8): p.33-34.
- Hellberg H., (1978);** Foam inhibitors, dyes and odor masking agents, in: catalysts, surfactants and petroleum additives (Eds J. Falbe, U. Hasserodt), Georg Thieme Verlag, Stuttgart, 257th
- IARC, (1984);** Classification of Mineral oils according to their Carcinogenicity, Vol.33.

ISO ., (1997); ISO 6743/4 Lubricants, Industrial Oils and Related Products (Class L) Classification—Part 4: Family H (Hydraulic systems).

Jaroslav and Ivantysyn. I., (1993), Hydrostatic pumps and motors, Construction and calculation, bird book publishing and printing KG, Würzburg.

Johnson M, Spurlock M, (2010); Strategic oil analysis, estimating remaining lubricant life, *Tribology & Lubrication Technology*, **66** (1): p. 22-24+26-30.

Kenderson K.O, Sticking J.M, (1990); The Effect of Shear Rate and Shear Stress on Viscosity Determinations at Low Temperature for Engine Oils, SAE Paper No. 902091.

Mang. T, (1998). Hydraulic oil, transfer printing to lecture, RWTH Aachen, Institut für Fluid Power Drives and Controls.

Mang.T., Dresel.W., (2007); Lubricants and Lubrication. 2Nd edition, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 978-3-527-31497-3

Murrenhoff H., (1997); Fundamentals of Fluid Power, Part 1: Hydraulic transfer printing to the lecture. 1st edition, Institute for Fluid Power Drives and Controls, Aachen, Steinbachs st. **53**, p.52074.

Nütscher, J, Eisenbach, E, and Rexroth GmbH, M, (1995); Contamination in hydraulic fluids and their influence on the design, in: W. J. Bartz, hydraulic fluids, Jahnstr. 3-5, 97816 Lohr, 71272 Renningen, *Expert Verlag Volume* 475.

Okamoto T, (1996); Naphthenic Base oil, UEIL General Assembly, Lyon.

Olszewski W.F and Neiswender D.D, (1976); Development of a Rear Axle Lubricant, SAE Paper 760, 326.

Omeis J, Pennewiss H, European Patent 699694.

Pall Ltd., (1997); Oil care system, technical information, industrial hydraulics, Philip Reis-Str. 6, 63303 Dreieich.

Papay A.G, (1983); Oil-soluble friction reducer, *Lubrication Engineering*, 39(7), 419–426.

- Petterson A, (2007);** High-performance base fluid for environmentally adapted lubricant, *Tribology International*, 40: p. 638-645.
- Prince R.J, (1992);** Base oils from petroleum, in: *Chemistry and Technology Of Lubricants* (Eds R. M. Mortier, S. T. Orszulik), Blackie, London.
- Raddatz, J. H, (1994);** Detergent-dispersant additives, their manufacture, use and mode of action, in: additives for lubricants (Ed W. J. Bartz.), Expert Verlag, 163-196.
- Rossrucker T, Fessenbecker A, (1999);** Performance and Mechanism of Metal working Additives: New Results from Practical Focused Studies, STLE Annual Meeting, Las Vegas.
- Schneider P. M, (2006);** Plant-oil-based lubricants and hydraulic fluids, *Journal of the Science of Food and Agriculture*, **86**: p. 1769-1780.
- Sethuramiah A, (2003);** Lubricated Wear Science and Technology, Amsterdam, the Netherlands, *Elsevier Science*.
- Small N. J. H., (1978);** Dispersants, in: catalysts, surfactants and petroleum additive (Ed Falbe J, U. Hasserodt.), Georg Thieme Verlag, Stuttgart, p.235-239.
- The Society of Dyes and Colourists, (1997);** Colour Index International, Pigments and Solvent Dyes, Bradford, West Yorkshire, UK.
- Völtz M and Rulfs H, (1982);** Smooth running due to lube oils - causes and effects, petroleum engineering, **27** (6), 1-23.

