2.1 INTRODUCTION

Liquid lubricants are low-viscosity, low shear strength natural or artificial substances introduced between two moving surfaces to reduce the friction between them as well as reducing wear, thereby improving efficiency and service life. They also may dissolve or transport foreign particles and distribute heat. Internal combustion engines of motor vehicles and similar such powered equipments are the single largest user of such lubricants, in the form of motor oil. Lubricants generally contain 90% base oil and less than 10% additives. Vegetable oils or synthetic liquids such as hydrogenated polyolefins, silicone, esters, fluorocarbons and many others are used as base oils. In view of this, there is a need to understand the different performance characteristics of lubricants which plays important role in wear and friction problems.

2.2 HYDRODYNAMIC OR FLUID FILM LUBRICATION

In heavily loaded bearings such as thrust bearings and horizontal journal bearings, the fluid's viscosity alone is not sufficient to maintain a film between the moving surfaces. In these bearings higher fluid pressures are
required to support the load until the fluid film is established. If this pressure is supplied by an outside source, it is called hydrostatic lubrication. If the pressure is generated internally, that is, within the bearing by dynamic action, it is referred to as hydrodynamic lubrication. In hydrodynamic lubrication, a fluid wedge is formed by the relative surface motion of the journals or the thrust runners over their respective bearing surfaces. The guide bearings of a vertical hydroelectric generator, if properly aligned, have little or no loading and will tend to operate in the center of the bearing because of the viscosity of the oil.

### 2.2.1 THRUST BEARINGS

In hydrodynamic lubrication, sometimes referred to as fluid film lubrication, the wearing surfaces are completely separated by a film of oil. This type of lubricating action is similar to a speedboat operating on water. When the boat is not moving, it rests on the supporting water surface. As the boat begins to move, it meets a certain amount of resistance or opposing force due to viscosity of the water. This causes the leading edge of the boat to lift slightly and allows a small amount of water to come between it and supporting water surface. As the boat’s velocity increases, the wedge-shaped water film increases in thickness until a constant velocity is attained. When the velocity is constant, water entering under the leading edge equals the amount passing outward from the trailing edge. For the boat to remain above the supporting surface there must be an upward pressure that equals the load. The same principle can be applied to a sliding surface.
Fluid film lubrication reduces friction between moving surfaces by substituting fluid friction for mechanical friction. To visualize the shearing effect taking place in the fluid film, imagine the film is composed of many layers similar to a deck of cards. The fluid layer in contact with the moving surface clings to that surface and both move at the same velocity. Similarly, the fluid layer in contact with the other surface is stationary. The layers in between move at velocities directly proportional to their distance from the moving surface.

The principle of hydrodynamic lubrication can also be applied to a more practical example related to thrust bearings used in the hydropower industry. Thrust bearing assembly is also known as tilting pad bearings. These bearings are designed to allow the pads to lift and tilt properly and provide sufficient area to lift the load of the generator. As the thrust runner moves over the thrust shoe, fluid adhering to the runner is drawn between the runner and the shoe causing the shoe to pivot, and forming a wedge of oil. As the speed of the runner increases, the pressure of the oil wedge increases and the runner is lifted as full fluid film lubrication takes place. In applications where the loads are very high, some thrust bearings have high pressure-pumps to provide the initial oil film.

2.2.2 JOURNAL BEARINGS

Although not as obvious as the plate or thrust bearing examples above, the operation of journal or sleeve bearings is also an example of hydrodynamic lubrication. When the journal is at rest, the weight of the journal squeezes out
the oil film so that the journal rests on the bearing surface. As rotation starts, the journal has a tendency to roll up the side of the bearing. At the same time fluid adhering to the journal is drawn into the contact area. As the journal speed increases an oil wedge is formed. The pressure of the oil wedge increases until the journal is lifted off the bearing. The journal is not only lifted vertically, but is also pushed to the side by the pressure of the oil wedge.

The minimum fluid film thickness at full speed will occur at a point just to the left of center and not at the bottom of the bearing. In both the pivoting shoe thrust bearing and the horizontal journal bearing, the minimum thickness of the fluid film increases with an increase in fluid viscosity and surface speed and decreases with an increase in load.

2.2.3 FILM THICKNESS

As viscosity or velocity increases, the film thickness increases. When these two variables decrease, the film thickness also decreases. Film thickness varies inversely with the load, as the load increases, film thickness decreases. Viscosity, velocity, and operating temperature are also interrelated. If the oil viscosity is increased the operating temperature will increase, and this in turn has a tendency to reduce viscosity.

2.2.4 FACTORS INFLUENCING FILM FORMATION

The following factors are essential to achieve and maintain the fluid film required for hydrodynamic lubrication:
• The contact surfaces must meet at a slight angle to allow formation of the lubricant wedge.

• The fluid viscosity must be high enough to support the load and maintain adequate film thickness to separate the contacting surfaces at operating speeds.

• The fluid must adhere to the contact surfaces for conveyance into the pressure area to support the load.

• The fluid must distribute itself completely within the bearing clearance area.

• The operating speed must be sufficient to allow formation and maintenance of the fluid film.

• The contact surfaces of bearings and journals must be smooth and free of sharp surfaces that will disrupt the fluid film.

Theoretically, hydrodynamic lubrication reduces wear to zero. In reality, the journal tends to move vertically and horizontally due to load changes or other disturbances and some wear does occur.

2.3 BOUNDARY LUBRICATION

When a complete fluid film does not develop between potentially rubbing surfaces, the film thickness may be reduced to permit momentary dry contact between wear surface high points or asperities. This condition is characteristic of boundary lubrication. Boundary lubrication occurs whenever any of the essential factors that influence formation of a full fluid film are missing. The most common example of boundary lubrication includes
bearings, which normally operate with fluid film lubrication but experience boundary lubricating conditions during routine starting and stopping of equipment. Other examples include gear tooth contacts and reciprocating equipment.

2.3.1 OILINESS

Lubricants required to operate under boundary lubrication conditions must possess an added quality referred to as oiliness or lubricity to lower the coefficient of friction of the oil between the rubbing surfaces. Oiliness is an oil enhancement property provided through the use of chemical additives known as antiwear (AW) agents. AW agents have a polarizing property that enables them to behave in a manner similar to a magnet. Like a magnet, the opposite sides of the oil film have different polarities. When an AW oil adheres to the metal wear surfaces, the sides of the oil film not in contact with the metal surface have identical polarities and tend to repel each other and form a plane of slippage. Most oils intended for use in heavier machine applications contain AW agents.

Examples of equipment that rely exclusively on boundary lubrication include reciprocating equipment such as engine and compressor pistons, and slow-moving equipment such as turbine wicket gates. Gear teeth also rely on boundary lubrication to a great extent.
2.4 EXTREME PRESSURE (EP) LUBRICATION

Anti wear (AW) agents are effective only up to a maximum temperature of about 250 °C (480 °F). Unusually heavy loading will cause the oil temperature to increase beyond the effective range of the antiwear protection. When the load limit is exceeded, the pressure becomes too great and asperities make contact with greater force. Instead of sliding, asperities along the wear surfaces experience shearing, removing the lubricant and the oxide coating. Under these conditions the coefficient of friction is greatly increased and the temperature rises to a damaging level.

Applications under extreme pressure conditions rely on additives. Lubricants containing additives that protect against extreme pressure are called EP lubricants, and oils containing additives to protect against extreme pressure are classified as EP oils. EP lubrication is provided by a number of chemical compounds. The most common are compounds of boron, phosphorus, sulfur, chlorine, or combinations of these. The compounds are activated by the higher temperature resulting from extreme pressure, not by the pressure itself. As the temperature rises, EP molecules become reactive and release derivatives of phosphorus, chlorine, or sulfur (depending on which compound is used) to react with only the exposed metal surfaces to form a new compound such as iron chloride or iron sulfide. The new compound forms a solid protective coating that fills the asperities on the exposed metal. Thus, the protection is deposited at exactly the sites where it is needed. AW agents in the EP oil continue to provide antiwear protection at sites where wear and temperature are not high enough to activate the EP agents.
2.5 ELASTOHYDRODYNAMIC (EHD) LUBRICATION

The lubrication principles applied to rolling bodies, such as ball or roller bearings, is known as elasto-hydrodynamic (EHD) lubrication.

2.5.1 ROLLING BODY LUBRICATION

Although lubrication of rolling objects operates on a considerably different principle than sliding objects, the principles of hydrodynamic lubrication can be applied, within limits, to explain lubrication of rolling elements. An oil wedge, similar to that which occurs in hydrodynamic lubrication, exists at the lower leading edge of the bearing. Adhesion of oil to the sliding element and the supporting surface increases pressure and creates a film between the two bodies. Because the area of contact is extremely small in a roller and ball bearing, the force per unit area, or load pressure, is extremely high. Roller bearing load pressures may reach 34,450 kPa (5000 lb/sq in) and ball bearing load pressures may reach 689,000 kPa (1,000,000 lb/sq in). Under these pressures, it would appear that the oil would be entirely squeezed from between the wearing surfaces. However, viscosity increases that occur under extremely high pressure prevent the oil from being entirely squeezed out. Consequently, a thin film of oil is maintained.

2.5.2 EFFECT OF FILM THICKNESS AND ROUGHNESS

The roughness of the wearing surfaces is an important consideration in EHD lubrication. Roughness is defined as the arithmetic average of the
distance between the high and low points of a surface, and is sometimes called the centerline average (CLA).

As film thickness increases in relation to roughness fewer asperities make contact. Engineers use the ratio of film thickness to surface roughness to estimate the life expectancy of a bearing system. The relation of bearing life to this ratio is very complex and not always predictable. In general, life expectancy is extended as the ratio increases. Full film thickness is considered to exist when the value of this ratio is between 2 and 4. When this condition prevails, fatigue failure is due entirely to subsurface stress. However, in most industrial applications, a ratio between 1 and 2 is achieved. At these values surface stresses occur, and asperities undergo stress and contribute to fatigue as a major source of failure in antifriction bearings.

2.6 FUNCTIONS OF LUBRICANTS

Lubricants perform the following functions:

- Keep moving parts apart
- Reduce friction
- Transmit power
- Transfer heat
- Protect against wear
- Prevent corrosion
- Carry away contaminants & debris
- Seal for gasses
- Stop the risk of smoke and fire of objects.
2.7 BASE OIL

Oils are generally classified as refined and synthetic. Examples of refined are Paraffinic and naphthenic oils. They are refined from crude oil while synthetic oils are manufactured. Literature on lubrication frequently makes references to long chain molecules and ring structures in connection with paraffinic and naphthenic oils, respectively [7]. Table-2.1 shows that each category of oil analysis is well suited to provide important information, but no single test can provide complete information about the causes of lubricant deterioration.

2.7.1 PARAFFINIC OILS

Paraffinic oils are distinguished by a molecular structure composed of long chains of hydrocarbons, i.e., the hydrogen and carbon atoms are linked in a long linear series similar to a chain. Paraffinic oils contain paraffin wax and are the most widely used base stock for lubricating oils. In comparison with naphthenic oils, paraffinic oils have:

- Excellent stability
- Higher resistance to oxidation
- Higher viscosity index.
- Higher pour point.
- Low specific gravities.
- Low volatility and, consequently, high flash points.
Table 2.1: Categories of Oil Analysis

<table>
<thead>
<tr>
<th>What is being analyzed</th>
<th>Fluid Properties (Physical Chemical Properties of used oil) (aging process)</th>
<th>Contamination (Fluid and machine destructive contaminants)</th>
<th>Wear Debris (Presence and identification of particles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle counting</td>
<td>No benefit</td>
<td>Primary benefit</td>
<td>Minor benefit</td>
</tr>
<tr>
<td>Moisture analysis</td>
<td>No benefit</td>
<td>Primary benefit</td>
<td>No benefit</td>
</tr>
<tr>
<td>Viscosity analysis</td>
<td>Primary benefit</td>
<td>Minor benefit</td>
<td>No benefit</td>
</tr>
<tr>
<td>Wear debris analysis</td>
<td>No benefit</td>
<td>No benefit</td>
<td>Primary benefit</td>
</tr>
<tr>
<td>Analytical ferrography</td>
<td>No benefit</td>
<td>Minor benefit</td>
<td>Primary benefit</td>
</tr>
<tr>
<td>TAN/TBN</td>
<td>Primary benefit</td>
<td>Minor benefit</td>
<td>Minor benefit</td>
</tr>
<tr>
<td>FTIR</td>
<td>Primary benefit</td>
<td>Minor benefit</td>
<td>No benefit</td>
</tr>
<tr>
<td>Patch test</td>
<td>No benefit</td>
<td>Primary benefit</td>
<td>Minor benefit</td>
</tr>
<tr>
<td>Flash point test</td>
<td>Minor benefit</td>
<td>Primary benefit</td>
<td>No benefit</td>
</tr>
<tr>
<td>Elemental analysis</td>
<td>Primary benefit</td>
<td>Minor benefit</td>
<td>Primary benefit</td>
</tr>
</tbody>
</table>
2.7.2 NAPHTHENIC OILS

In comparison to paraffinic oils, naphthenic oils are distinguished by a molecular structure composed of “rings” of hydrocarbons, i.e., the hydrogen and carbon atoms are linked in a circular pattern. These oils behave differently than paraffinic oils and do not contain wax. These oils have:

- Good stability.
- Lower viscosity indexes.
- Lower pour point due to absence of wax.
- Higher specific gravities.
- Higher volatility (lower flash point).
- Naphthenic oils are reserved for applications with narrow temperature ranges and where a low pour point is required.

2.7.3 SYNTHETIC OILS

Synthetic lubricants are produced from chemical synthesis rather than from the refinement of existing vegetable or petroleum oils. These oils are generally superior to petroleum (mineral) lubricants in most circumstances. These oils perform better than mineral oils in the following ways:

- Better viscosity index.
- Better oxidation stability or resistance.
- Lower coefficient of friction.
- Much lower pour point, as low as -46 °C (-50 °F).
The advantages offered by synthetic oils are most notable at either very low or very high temperatures. Good oxidation stability and a lower coefficient of friction permits operation at higher temperatures. The better viscosity index and lower pour points permit operation at lower temperatures.

The major disadvantage to synthetic oils is the initial cost, which is approximately three times higher than mineral-based oils. However, the initial premium is usually recovered over the life of the product, which is about three times longer than conventional lubricants. The higher cost makes it inadvisable to use synthetics in oil systems experiencing leakage.

Plant Engineering magazine’s “Exclusive Guide to Synthetic Lubricants,” which is revised every three years, provides information on selecting and applying these lubricants. Factors to be considered when selecting synthetic oils include pour and flash points, demulsibility, lubricity, rust and corrosion protection, thermal and oxidation stability, antiwear properties; compatibility with seals, paints, and other oils and compliance with testing and standard requirements. Unlike Plant Engineering magazine’s “Chart of Interchangeable Lubricants,” it is important to note that synthetic oils are as different from each other as they are from mineral oils. Their performance and applicability to any specific situation depends on the quality of the synthetic base-oil and additive package, and the synthetic oils listed in Plant Engineering are not necessarily interchangeable.

Table-2.2 outlines the procedures for conducting a visual test of oil samples. The sample to be inspected should be stored at room temperature away from direct sunlight for at least 24 hours before the inspection. Table-2.3 are used to determine contamination and degradation of the oil.
### Table-2.2: Visual Examination of Used Lubricating Oil

<table>
<thead>
<tr>
<th>Appearance of Sample</th>
<th>Action To Be Taken</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>When Taken</strong></td>
<td><strong>Reason</strong></td>
</tr>
<tr>
<td>Clear</td>
<td>------</td>
</tr>
<tr>
<td>Opaque</td>
<td>Clear</td>
</tr>
<tr>
<td></td>
<td>Clear oil with separated water layer</td>
</tr>
<tr>
<td></td>
<td>No Change</td>
</tr>
<tr>
<td>Dirty</td>
<td>Solids separated</td>
</tr>
<tr>
<td>Black (acrid smell)</td>
<td>No Change</td>
</tr>
</tbody>
</table>

### 2.7.4 BASE OIL CLASSIFICATION SYSTEM

The American Petroleum Institute (API) has developed a classification system for base oils in order to smooth the progress of engine oil interchange guidelines. The base oils are divided in to five groups as follows [8]:

**Group I** base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have viscosity index greater than or equal to 80 and less than 120.

**Group II** base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have viscosity index greater than or equal to 80 and less than 120.

**Group III** base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have viscosity index greater than or equal to 120.

**Group IV** base stocks are polyalphaolefins (PAO).

**Group V** base stocks include all other base stocks not included in groups I, II, III or IV. Naphthenic oils are considered Group V.

### 2.8 LUBRICANT CLASSIFICATION SYSTEMS

Professional societies and organizations have established classifications for oil and grease. The most widely encountered systems are those of the following organizations:

- SAE (Society of Automotive Engineers)
- API (American Petroleum Institute)
- AGMA (American Gear Manufacturers Association)
- ISO (International Standards Organization)
- NLGI (National Lubricating Grease Institute).
Table-2.3: Key Tests for Oil Quality Control Monitoring

<table>
<thead>
<tr>
<th>Property Test</th>
<th>ASTM Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total acid number (TAN)</td>
<td>D 664, D 974</td>
</tr>
<tr>
<td>Color</td>
<td>D 1500</td>
</tr>
<tr>
<td>Appearance</td>
<td>Visual</td>
</tr>
<tr>
<td>Viscosity</td>
<td>D 445</td>
</tr>
<tr>
<td>Rotating Bomb Oxidation Test</td>
<td>D 2272</td>
</tr>
<tr>
<td>Water content</td>
<td>D 95, D 1744</td>
</tr>
<tr>
<td>Rust test</td>
<td>D 665A</td>
</tr>
<tr>
<td>Cleanliness</td>
<td>Particle counter, F 311 and F 312</td>
</tr>
</tbody>
</table>

2.8.1 CHARACTERISTICS OF LUBRICATING OILS

The following are the important characteristics of lubricating oils:

2.8.1.1 VISCOSITY

The viscosity of oil is a measure of the oil’s resistance to shear. Viscosity is also known as resistance to flow. A high viscosity indicates high resistances to flow while a low viscosity implies a low resistance to flow.
Viscosity varies inversely with temperature. Viscosity is also affected by pressure. A higher pressure causes the viscosity to increase and later also increases the load carrying capacity of the oil. This property enables the thin oils to lubricate heavy machinery. The load carrying capacity also increases when operating speed of the lubricated machinery is increased. For measuring Viscosity, two methods are commonly used: shear and time.

2.8.1.1 SHEAR

When viscosity is determined by directly measuring shear stress and shear rate, it is expressed in centipoise (cP) and is referred to as the absolute or dynamic viscosity. In the oil industry, it is more common to use kinematic viscosity, which is the absolute viscosity divided by the density of the oil being tested. Kinematic viscosity is expressed in centistokes (cSt). Viscosity in centistokes is conventionally given at two standard temperatures: 40 °C and 100 °C (104 °F and 212 °F).

2.8.1.2 TIME

Another method used to determine oil viscosity measures the time required for an oil sample to flow through a standard orifice at a standard temperature. Viscosity is then expressed in SUS (Saybolt Universal Seconds). SUS viscosities are also conventionally given at two standard temperatures: 37 °C and 98 °C (100 °F and 210 °F). As previously noted, the units of viscosity can be expressed as centipoises (cP), centistokes (cST), or Saybolt Universal
Seconds (SUS), depending on the actual test method used to measure the viscosity.

2.8.1.2 VISCOSITY INDEX

The viscosity index also designated as (VI) is an arbitrary numbering scale that indicates the changes in oil viscosity with changes in temperature. Viscosity index are classified as: Low VI - below 35; Medium VI - 35 to 80; High VI - 80 to 110; Very high VI - above 110. A high viscosity index indicates small oil viscosity changes with temperature. A low viscosity index indicates high viscosity changes with temperature. Therefore, a fluid that has a high viscosity index can be expected to undergo very little change in viscosity with temperature and is suppose to have a stable viscosity. A fluid with a low viscosity index can be expected to undergo a significant change in viscosity as the temperature changes.

2.8.1.3 POUR POINT

The pour point is the lowest temperature at which oil will flow. This property is important for oils that have to flow at low temperatures. A thumb rule is used for selecting oils to ensure that the pour point is at least 10 °C (20 °F) lower than the lowest anticipated ambient temperature. Table 12.4 shows pour point temperatures for mineral and synthetic lubricants.
2.8.1.4 CLOUD POINT

The cloud point is the temperature at which dissolved solids such as paraffin wax, in the oil begin to form and separate from the oil. As the temperature drops, wax crystallizes and becomes visible. Certain oils are maintained at temperatures above the cloud point to prevent clogging of filters depending upon the environmental conditions.

2.8.1.5 FLASH POINT AND FIRE POINT

The flash point is the lowest temperature, to which a lubricant must be heated before its vapor, when mixed with air, will ignite but not continue to burn. The fire point is the temperature at which lubricant combustion sustained. The flash and fire points are useful in determining a lubricant’s fire resistance and volatility.

2.8.1.6 ACID NUMBER OR NEUTRALIZATION NUMBER

The acid or neutralization number is a measure of the amount of potassium hydroxide required to neutralize the acid contained in a lubricant. The acid number of an oil sample indicates the age of oil and can be used to find out when the oil must be changed.
2.8.1.7 TOTAL BASE NUMBER

Total base number is a measure of reserve alkaline additives added into lubricants to neutralize acids, to retard corrosion and oxidation, enhance lubricity, improve viscosity characteristic and reduce the tendency of sludge buildup. It is a test to measure the ability to neutralize corrosive acids that may be formed during normal operation.
2.9 ADDITIVES

Additives are used to impart performance characteristics to the lubricants. The functions of additives are [7]:

- Protecting lubricated surfaces. Examples are Extreme pressure (EP) additives and rust inhibitors. These additives prevent surfaces from wear or rust.
- Improving performance. Examples are Viscosity index improvers and antifoaming agents. They make the oil to perform in a desired manner for specific applications.
- Protecting the lubricant itself. Example is Antioxidants. They reduce the tendency of oil to oxidize and form acids and sludge.

The most common additives are listed in Table-2.5. The families of additives are:

- Antioxidants
- Anti-wear
- Friction modifiers
- Metal deactivators
- Corrosion inhibitors, Rust inhibitors
- Extreme Pressure
- Detergents
- Anti-foaming agents
2.9.1 **FRICTION MODIFIERS**

Friction modifiers reduce coefficient of friction, resulting in less fuel consumption. Crystal structure of friction modifiers consists of molecular platelets (layers), which may easily slide over each other.

The following materials are used as friction modifiers:

- Graphite
- Molybdenum disulfide (MoS$_2$)
- Tungsten disulfide (WS$_2$)
- Boron nitride (BN)
- Polytetrafluoroethylene (PTFE)

2.9.2 **ANTI-WEAR ADDITIVES**

Anti-wear additives prevent direct metal-to-metal contact between the machine parts when the oil film is broken down. These additives results in longer machine life due to higher wear and score resistance of the components. The materials which are used as anti-wear additives are:

- Zinc dithiophosphate (ZDP)
- Zinc dialkyldithiophosphate (ZDDP)
- Tricresylphosphate (TCP)
2.9.3 EXTREME PRESSURE (EP) ADDITIVES

Extreme pressure (EP) additives prevent seizure conditions caused by direct metal-to-metal contact between the parts under high loads. These additives in similar way as that of anti wear. The coating protects the part surface from a direct contact with other part, decreasing wear and scoring.

The materials which are used as extreme pressure (EP) additives are:

- Chlorinated paraffins
- Esters
- Sulphurized fats
- Zinc dialkyldithiophosphate (ZDDP)
- Molybdenum disulfide (MoS$_2$)

2.9.4 RUST AND CORROSION INHIBITORS

Rust and Corrosion inhibitors forms a barrier film on the substrate surface reducing the corrosion rate. These also absorb on the metal surface forming a film protecting the part from the attack of oxygen, water and other chemically active substances.

The materials which are used as rust and corrosion inhibitors are:

- Alkaline compounds
- Esters
- Organic acid derivatives
- Amino-acid derivatives
2.9.5 ANTI-OXIDANTS

These additives are used to protect the oxidation reaction products such as increase of the oil viscosity, formation of sludge and varnish, corrosion of metallic parts and foaming.

The materials which are used as anti-oxidants are:

- Zincdithiophosphate (ZDP)
- Aromatic sulfides
- Alkyl sulfides
- Aromatic amines

2.9.6 DETERGENTS

Detergents neutralize strong acids present in the lubricant and remove the neutralization products from the metal surface. They also form a film on the part surface preventing high temperature deposition of sludge and varnish.

Some of the examples of this category are:

- Phenolates, sulphonates and phosphonates of alkaline earth elements, such as calcium (Ca), magnesium (Mg), sodium (Na) or Ba (barium).

2.9.7 DISPERSANTS

Dispersants keep the foreign particles present in a lubricant in a dispersed form. The foreign particles are in the form of sludge, varnish, dirt, water, products of oxidation, etc. Dispersing agents are added to lubricating oils used in automotive
engines to prevent the accumulation of varnish like deposits on the cylinder walls and to gasoline to prevent the buildup of gummyish residues. Examples of this category are Long chain hydrocarbons succinimides, such as polyisobutylene succinimides.

2.9.8 POUR POINT DEPRESSANTS

Pour point is the lowest temperature, at which the oil may flow. Pour point depressant inhibits formation and agglomeration of wax particles keeping the lubricant fluid at low temperatures. Example of this category are Co-polymers of polyalkylmethacrylates.

2.9.9 VISCOSITY INDEX IMPROVERS

Viscosity index improvers keep the viscosity at acceptable levels, which provide stable oil film even at increased temperatures. Viscosity improvers are widely used in multigrade oils, viscosity of which is specified at both low and high temperature. Example of this category: Acrylate polymers.

2.9.10 ANTI-FOAMING AGENTS

Anti foaming agents removes formation of air bubbles in the oil foaming caused due to Agitation and aeration of lubricating oil occurring at certain applications. Foaming also enhances oil oxidation and decreases lubrication effect causing oil starvation. Dimethylsilicones (dimethylsiloxanes) is common example of anti-foaming agent.
### Table-2.5: Types of Additives

<table>
<thead>
<tr>
<th>Main type</th>
<th>Functions &amp; Subtypes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid neutralizers</td>
<td>Neutralize contaminating strong acids formed, e.g., by combustion of high sulfur fuels or by decomposition of active EP additives</td>
</tr>
<tr>
<td>Antifoam</td>
<td>Reduce surface foam.</td>
</tr>
<tr>
<td>Antioxidants</td>
<td>Reduce oxidation. Various types are: oxidation inhibitors, retarders, anticatalyst metal deactivators, metal passvators.</td>
</tr>
<tr>
<td>Antirust</td>
<td>Reduce rusting of ferrous surfaces swept by oil.</td>
</tr>
<tr>
<td>Antiwear agents</td>
<td>Reduce wear and prevent suffing of rubbing surfaces under steady load operating conditions.</td>
</tr>
<tr>
<td>Corrosion inhibitors</td>
<td>Type (a) reduces corrosion of lead, type (b) reduces corrosion of cuprous metals.</td>
</tr>
<tr>
<td>Detergents</td>
<td>Reduce or prevent deposits formed at high temperatures, e.g., in internal combustion engines.</td>
</tr>
<tr>
<td>Dispersant</td>
<td>Prevent deposition of sludge by dispersing a finely divide suspension of the insoluble material formed at low temperature.</td>
</tr>
<tr>
<td>Emulsifiers</td>
<td>Form emulsions, either water in oil or oil in water, according to type.</td>
</tr>
<tr>
<td>Extreme pressure</td>
<td>Prevent scuffing of rubbing surfaces under severe operating conditions, e.g., heavy shock load, by formation of a mainly inorganic surface film.</td>
</tr>
<tr>
<td>Oiliness enhancers</td>
<td>Reduce friction under boundary lubrication conditions; increase load-carrying capacity where limited by temperature rise by formation of mainly organic surface films.</td>
</tr>
<tr>
<td>Pour-point depressants</td>
<td>Reduce pour point of paraffinic oils.</td>
</tr>
<tr>
<td>Tackiness agents</td>
<td>Reduce loss of oil by gravity, e.g., from vertical sliding surfaces, or by centrifugal force.</td>
</tr>
<tr>
<td>Viscosity index improvers</td>
<td>Reduce the decrease in viscosity due to increase of temperature</td>
</tr>
</tbody>
</table>
2.10 ROLE OF ‘ADDITIVES OR ADDITIVE PACKAGE’ IN LUBRICANT

Oil serves the basic vital function of lubrication. The major causes of engine malfunction due to lubricant quality are deposit formation, contamination, oil thickening, oil consumption, ring sticking, corrosion, and wear. The performance of engine lubricants is judged on their ability to reduce friction, resist oxidation, minimize deposit formation, and prevent corrosion and wear. To meet these functional requirements, engine lubricants must be supplemented with additives. Diverse important functions required in engine are provided by incorporating different types of additives. So additives can be classified as materials that impart new properties to or enhance existing properties of the lubricant or fuel into which they are incorporated [4].

2.11 WEAR

Wear is defined as the progressive damage resulting in material loss due to relative motion and contact between adjacent working parts. Some wear is to be expected during normal operation of equipment and some premature wear due to excessive friction and this creates significant economic costs due to following reasons as: cost for replacement parts, equipment failure, and downtime. Friction and wear also generate heat, which represents wasted energy that is not recoverable. Wear is also responsible for overall loss in system efficiency [7].

The wear rate of a sliding or rolling contact is defined as the volume of material lost from the wearing surface per unit of sliding length, and is expressed in units of \([\text{length}]^2\). For any specific sliding application, the wear rate depends on the...
normal load, the relative sliding speed, the initial temperature, and the mechanical, thermal, and chemical properties of the materials in contact.

The effects of wear are commonly detected by visual inspection of surfaces. Surface damage can be classified as follows:

(a) Surface damage without exchange of material
- Structural changes: aging, tempering, phase transformations, and recrystallization.
- Plastic deformation: residual deformation of the surface layer.
- Surface cracking: fractures caused by excessive contact strains or cyclic variations of thermally or mechanically induced strains.

(b) Surface damage with loss of material (wear)
- Characterized by wear scars of various shapes and sizes.
- Can be shear fracture, extrusion, chip formation, tearing, brittle fracture, fatigue fracture, chemical dissolution, and diffusion.

(c) Surface damage with gain of material
- Can include pickup of loose particles and transfer of material from the opposing surface.
- Corrosion: Material degradation by chemical reactions with ambient elements or elements from the opposing surface.

Wear may also be classified as mild or severe. The distinguishing characteristics between mild and severe wear are as follows:

(a) Mild
- Produces extremely smooth surfaces - sometimes smoother than the original.
• Debris is extremely small, typically in the range of 100 nanometers (nm) \((3.28 \times 10^{-13} \text{ ft})\) in diameter.

• High electrical contact resistance, but little true metallic contact.

(b) Severe

• Rough, deeply torn surfaces - much rougher than the original.

• Large metallic wear debris, typically up to \(0.01 \text{ mm} \ (3.28 \times 10^{-5} \text{ ft})\) in diameter.

• Low contact resistance, but true metallic junctions are formed.

2.11.1 TYPES OF WEAR

2.11.1.1 ABRASIVE WEAR

Abrasive wear occurs when a hard surface slides against each other and cuts grooves from a softer surface. This situation is referred to as two-body abrasion. Particles cut from the softer surface or dust and dirt introduced between wearing surfaces also contribute to abrasive wear. This condition is referred to as three-body abrasion.

2.11.1.2 ADHESIVE WEAR

Adhesive wear occurs due to shearing at points of contact or asperities that undergo adhesion or cold welding. Shearing occurs through the weakest section. In
many cases, shearing occurs in the softer material, but such a comparison is based on shear tests of relatively large pure samples.

2.11.1.3 PITTING WEAR

Pitting wear occurs due to surface failure of a material as a result of stresses that exceed the endurance (fatigue) limit of the material. Metal fatigue is demonstrated by bending a piece of metal wire, such as a paper clip, back and forth until it breaks. Whenever a metal shape is deformed repeatedly, it eventually fails.

2.11.1.4 CORROSIVE WEAR

Corrosive wear occurs as a result of a chemical reaction on a wearing surface. The most common form of corrosion is due to a reaction between the metal and oxygen i.e. oxidation. Corrosion products, usually oxides, have shear strengths different from those of the wearing surface metals from which they were formed [7].

2.11.2 WEAR MECHANISM

The mechanism of wear is very complex and the theoretical treatment without the use of rather sweeping simplifications (as below) is not possible. It should be understood that the real area of contact between two solid surfaces compared with the apparent area of contact is invariably very small, being limited to points of contact between surface asperities.

The load applied to the surfaces will be transferred through these points of contact and the localised forces can be very large. The material intrinsic surface
properties such as hardness, strength, ductility, work hardening etc. are very important factors for wear resistance, but other factors like surface finish, lubrication, load, speed, corrosion, temperature and properties of the opposing surface etc. are equally important.

2.11.2.1 THE DELAMINATION THEORY OF WEAR BY SUH N P

The theory is based on the behavior of dislocations at the surface, subsurface crack and void formation due to plastic deformation of the surface layer, and subsequent joining of cracks by shear deformation of the surface and by crack propagation. The proposed theory predicts qualitatively that the wear particle shape is likely to be thin flake like sheets and that the surface layer can undergo large plastic deformation.

2.12 WEAR DEBRIS

Debris particles exist in most lubrication systems. They are responsible for the early failure of tribological machine elements. Particles come from the surrounding environment or may be generated within the machine components. As the lubricant circulates, these particles get flushed into the machine elements. Contact pressures are high and oil films are small, so that the relatively large particles damage even the hardest gear, bearing, or cam surface. This damage can lead to contact fatigue or wear, and thus premature failure of the whole machine. Further, one failure can result in the generation of further wear debris, often in very great quantities, that then can
have a knock-on effect in other parts of the lubricated system. Depending on the nature of the oil supply, contamination levels vary from around $10^{-1}$ to $10^{1}$ g/l.

A motor car oil system contains something like one teaspoon of debris particles in the sump. This may not sound much, but particle sizes are small, so this corresponds to millions of individual particles, each of which has the possibility of causing damage to lubricated machine elements. Figure-2.1 shows the some pictures of some typical entrained and self-generated debris particles [9].

As mentioned above that they may be entered into an oil system from the environment or generated from with the machine. The former category is most likely to be minerals or handled products such as coal, sand or earth. The sizes of these sorts of particles vary from sub-micron to millimeter whilst the shapes tend to be blocky and angular. The nature of circulating lubricant system is such that only those less than around 100 µm will find their way to machine components. However, grease lubricated bearings on a mining conveyor belt may see much larger particles. Particles may also be generated from within a machine or engine [10].

Components where there is not full lubricant separation will produce wear particles, either by abrasion (where the asperities of one surface plough material out of another) or by adhesion (where particles from one surface are plucked out by adhesion to the other).

The Table 2.6 shows the classification of debris particle and its source from where they generates.
2.13 CONTRIBUTIONS OF RESEARCHERS

In view of arrival of efficient engines with advanced designs, such as overhead valves and V 6 or V 8 engines with increased compression ratio, lubricating oils with no or ordinary additives were rendered useless because the stresses on engine com-

Table-2.6: Classification of Debris Particles found in Lubrication Systems [9].

<table>
<thead>
<tr>
<th>Classification</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>External contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>environmental</td>
<td>dust, airborne particles</td>
</tr>
<tr>
<td>handled materials</td>
<td>coal dust, sand, railway track ballast</td>
</tr>
<tr>
<td>pre-installed</td>
<td>grinding grits, weld spatter, oil can rust, swarf</td>
</tr>
<tr>
<td><strong>Internal contaminants</strong></td>
<td></td>
</tr>
<tr>
<td>process generated</td>
<td>combustion products - soot</td>
</tr>
<tr>
<td>fatigue debris</td>
<td>bearing spalls, gear tooth pits</td>
</tr>
<tr>
<td>wear debris</td>
<td>cutting slithers, filmy particles,</td>
</tr>
<tr>
<td>scuffing debris</td>
<td>White metal from a seized journal</td>
</tr>
<tr>
<td>component breakdown debris</td>
<td>fracture fragment, broken strainer, hose flexing</td>
</tr>
</tbody>
</table>
-ments such as the cam mechanisms commonly working at 1m/s speed increased to as high as 1 GPa [11]. Also, the demand for lightweight and high-speed automobiles resulted in shift to material selection for engine components from Steels to Aluminum alloys, again increasing demand for better lubricants in view of poor wear resistance of Al alloys. Similarly, poorer load bearing capability of Babbit, when used in high horse power engines resulted in use of cadmium/silver, cadmium/nickel and copper/lead as stronger bearing material but with inferior wear and corrosion resistance. These factors led to discovery and usage of Zinc DialkylDithio Phosphate (ZDDP) as an anti-wear additive for motor vehicle lubricants as early as 1941.

ZDDP is used as a bearing passivator to coat a metal in order to reduce the chemical reactivity of its surface. ZDDP concentration in such cases is low-less than 0.3%. It also has anti-oxidant when added in oils. Moreover, it is also effective anti-wear agent, an EP additive for heavily loaded steel-on-steel sliding mechanisms such as camshafts and valve lifters or tappets [12]. It reduces the risk of metal-to-metal contact, which can lead to increased heat, result in oxidation and negatively affect the film strength.

In order to improve the understanding as to how wear and friction are affected by simultaneous interaction of variables such as loading, oil contamination due to wear debris, ZDDP presence in oil and the tribological system configuration, it is imperative to review the work, which has been carried out for each of these factors. Such understanding should help in setting up dedicated experiments to understand the synergic effect of these factors. Also, it should elucidate in establishing a clear condition monitoring parameter for such tribo-systems.
Fig-2.1: Micrographs of typical debris particles (top left to bottom right: 150 \( \mu \)m iron platelet, 2mm fatigue chunk, 1mm sand, spall fragment, 60 \( \mu \)m silicon carbide grinding grit, 50 nm soot) [9].
Lubricating oils contain different types and amounts of additives, blended with the base stock of the oil, to enhance its desirable qualities. It is well established now that using additives in lubricants reduces wear. However, these additives get degraded or depleted gradually with operating time. The degradation rate increases dramatically once one or more of these additives and their decomposition products are depleted to roughly 10-20% of their original concentration [13].

It is of paramount importance to understand that using more oil additives is not always better. Sometimes when more additive is added into the oil, there is not much benefit gained, and to the contrary, the performance actually deteriorates. Moreover, in some cases, increasing the percentage of a particular additive may improve one property of lubricating oil and degrade another property. In addition, if the concentrations of additives in lubrication oils become more than desired and unbalanced, overall oil quality may also get affected. Most importantly, some additives may compete with each other in the same volume of oil thus affecting their surface chemistry. It is seen in cases such as when higher concentration of an anti-wear additive is blended with the lubrication oil, it may suppress a corrosion inhibitor present in the oil, resulting in an increase in corrosion-related problems [14].

In the past two decades, the role of lubricant additives in wear reduction has been extensively investigated in various research studies all across the world. These studies have different study parameters and have established different facts about effectiveness of different types of additives in different conditions. Due to such a vast area of application, no study could clearly identify or zero in to a very limited range of additives which can be recommended for most applications and conditions. It has been established through such studies that wear reduction is achieved in particular
conditions when lubricant additives are added in oils. But studies have also shown that additives (ZDDP) reduces wear in lubricated sliding only under low loads and when loads are high, wear increases at high loads indicating change in surface due to chemical action of additive in oil[15-17].

Presence of contaminant is another significant factor to be considered in lubricated systems, particularly when they are hard and abrasive. Presence of any such contaminants in the lubricating oils or greases are found to be one of the major causes of tribo-elements failure [18]. Investigations into such test conditions have proved that such contaminants increase wear of the sliding contacting surfaces and also the friction coefficient. It is also found that the nature of contacting materials determine the severity of such behavior [19-20]. Solid contaminants are generally grouped into three categories. The external contaminants, which enter the lubricating oils through air, fuel and fresh oil, are put in first categories. The second category of contaminants is that which are generated due to friction and wear of the rubbing surfaces, which are generally known as wear debris and which this work is focusing on. The contaminants, which get introduced into the tribo-system initially during manufacturing and assembly of such tribo-systems, are the third category of contaminants [21].

Considering wear debris, which as stated above, circulates during operation of machine, getting flushed into the system and if the operating contact pressures are high and oil films are small, then damage even the hardest gear, bearing or cam surfaces. This damage can lead to contact fatigue or wear, and thus premature failure of the whole machine. Further, one failure can result in the generation of further wear
debris, often in very great quantities, that then can have effect on other parts of the tribological system.

These wear debris particles vary from sub-micron to millimeter in size whereas the shapes tend to be blocky and angular. Generally, the nature of circulating lubricant system is such that only the particles less than around 100µm find their way into machine components (larger particles settle quicker in a lubrication sump). However, in case of grease lubricated bearings, such as on a mining conveyor belt may see much larger particles. Table-2.7 gives conditions under which some prominent tribo-elements will give rise to a particular nature of wear debris under specific tribological condition.

2.13.1 ZINC DIALKYL DITHIO PHOSPHATES (ZDDPS) AND THEIR EFFECT ON WEAR DEBRIS

Zinc DialkylDithio Phosphates (ZDDPs are, till now, the most important and widely used anti-wear and anti-oxidant additive, which is added to engine oils. Generally, ZDDP is a mixture of neutral ZDDP and basic ZDDP.

\[
(RO)_{2}PS_{2}Zn
\]

Figure 2.2: Structure of Neutral ZDDP

Figure 2.2 shows the structure of the neutral ZDDP (monomer) having chemical formula \([(RO)_{2}PS_{2}]_{2}Zn\). ZDDP are oil soluble chemicals which are used as additives in lubricating oils for internal combustion engines and transmissions. Also, the neutral ZDDP can exist as a dimer, or an infinite linear polymer in the solid state.
<table>
<thead>
<tr>
<th>Nature of Wear Debris</th>
<th>Type of Component</th>
<th>Example of Tribo-Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrous particles of various size and shapes</td>
<td>Loaded, moving components in which load is concentrated in a non-confirmed contact</td>
<td>Rolling bearings, gear teeth, cams and tappets</td>
</tr>
<tr>
<td>Ferrous flakes less than 150 µm across, and fine iron or iron oxide particles</td>
<td>Loaded, moving components in which load is concentrated in a small area</td>
<td>Piston rings and cylinders splines, gear couplings</td>
</tr>
<tr>
<td>Usually very small and ferrous and non-ferrous flakes and particles, bearing fatigue can give rise to larger flakes</td>
<td>Loaded, moving components with the load spread over a large area</td>
<td>Plain bearings, pistons and cylinders</td>
</tr>
</tbody>
</table>
depending upon nature of the alkyl group. It is known from the literature, that ZDDP acts as an anti-wear additive in lubricants in three main ways (i) by forming a mechanically protective film, (ii) by removing corrosive peroxides or peroxy-radicals, (iii) by ‘‘digesting’’ hard and thus abrasive iron oxide [22-23].

Rubbing surfaces of engines are protected against wear by anti-wear ZDDPs’ films, generated in situ, which act as sacrificial films when being rubbed. These films are dynamic as they are constantly regenerated in a rubbing environment [24-25].

It has been found that the products produced as a result breakdown of ZDDPs during sliding, (not the ZDDPs itself) provides the anti wear protection to sliding steel surfaces. ZDDPs form tribo-films by two mechanisms, one when it decomposes upon rubbing as well as second due to thermal decomposition. These films have an amorphous polyphosphate glass structure [26].

Studies on such anti-wear films generated from neutral and basic ZDDP salts do have any substantial difference. The wear scar diameter and the P and S chemical environment in the tribo-film has been found to be similar, however, the chemical composition has differences. Basic ZDDP mostly produce wear debris either of unreacted ZDDP or of a linkage isomer of ZDDP (LI-ZDDP), and zinc polyphosphate. On the other hand, the wear debris of neutral ZDDP is exclusively composed of zinc polyphosphate and sulphur species [27].

Also, more iron is reported in the wear debris with basic ZDDP, a possible indication of the iron content of the tribofilm. Differences in chemical structure are also reported in case of thermal films. Neutral ZDDP forms polyphosphates at 150°C, whereas basic ZDDP forms the same product at higher temperature of 175°C.
Anti-wear chemistry of ZDDPs has also been studied by different workers. The zinc polyphosphate glass, formed as breakdown product, is attributed to digestion of abrasive particles during sliding. The driving force for this tribo-chemical reaction is not temperature but entropy due to mechanical mixing at the atomic scale [28].

In another substantial work, it is reported that the reaction products of ZDDP, which are phosphates, are present as short chain phosphates, which is a mix of iron and zinc phosphates. It has greater proportion of phosphates compared to sulfur species [29].

In one of the most important and recent study to compare the anti-wear properties of ZDDP and fluorinated ZDDP, it is established that the wear debris produced in presence of both types of additives, is essentially amorphous but contains nanocrystalline particles of Fe3O4. Also, F-ZDDP results in lower wear in comparison to ZDDP under identical tribological conditions [30].

2.14 GAP IN RESEARCH ON CONTAMINATED TRIBOLOGICAL ENVIRONMENTS

In spite of substantial research efforts, complete tribo-mechanism of ZDDP and its reaction mechanism by which anti-wear tribo-films are formed on the tribo-surfaces is not totally understood. Problems associated with lack of understanding gets magnified due to the fact that ZDDP goes through complex reactions which are dependent on many variables and anti-wear process being multidisciplinary, involving metallurgy, chemistry, metrology and mechanical areas.
In this study, therefore, ductile metallic wear particles are artificially introduced into the testing system, starting with base oils and going up to oils containing some synergetic anti-corrosion, and load carrying additives, in addition to ZDDP, to investigate their anti-wear and anti-scuffing behavior properties during metal to metal sliding, which is then compared with a similar commercially selected automotive lubricant.

2.15 OBJECTIVE

The objective of the proposed work is:

- To prepare an artificial liquid lubricant from liquid paraffin based oil, similar in nature to a commercially available lubricant.
- Incorporating anti-wear and anti-friction properties to this artificial lubricant.
- Investigate their role during sliding of steel-on-steel couples with and without the presence of wear debris of various sizes and quantity.
- To Compare the anti-wear and anti-scuffing properties of prepared lubricant and selected commercial lubricant.