

1.1. Tribology

Energy and material losses due to friction and wear lead to negative impacts such as high energy consumption, frequent failure of engineering parts and increased greenhouse gas emission etc. The efficient lubricant system can reduce such undesirable events. Friction, wear and lubrication are collectively represented by Tribology. The word "Tribology", coined by Peter Jost (1964) was taken from Greek word "*tribos*" meaning "rubbing" and later on it has been popularized as the science and engineering of rubbing/interacting surfaces in the relative motion [Bhushan (2001a)]. Tribology is defined as "Science and technology of the surfaces in relative motion and it encompasses the aspects of friction, wear and lubrication" [Sethuramiah, (2003)]. Surface interactions in tribology are highly complex and require understanding of diversified subjects like physics, chemistry, material science, mechanical engineering, machine design, heat transfer, thermodynamics etc. and their applications are ranging from spacecraft, automotive to household appliances [Bhushan (1999)]. Tribology is not only for materials and machineries world but also equally important for several activities in the human-body [Zhou *et al.* (2015)].

1.1.1. Friction

Friction is defined as the force that opposes the relative motion of one body over another body under the applied load. Friction is related to the energy loss of system; high friction leads to high energy loss and vice versa. We too experience the friction in our daily life e.g. during walking (between the floor and shoes), shaving (between skin and blade), driving a car, playing any instrument etc. The pioneer researchers in the field tribology are Amontons (1699), Coulomb (1785), Towers (1884), Reynolds [(1986), (1988)], Block (1937), Bowden and Tabor [(1954), (1964a,b)].

Amontons postulated the well-known laws of friction:

- **First Law:** Frictional force is directly proportional to the applied normal load.

$$F_f \propto F_N \dots \dots \dots \text{(Equation 1.1)}$$

$$F_f = \mu \cdot F_N \dots\dots\dots \text{(Equation 1.2)}$$

Where μ stands for coefficient of friction; F_f is frictional force and F_N is applied normal load. The coefficient of friction is unit less parameter and depends only on material used, working conditions, quality of surfaces etc. and widely used to measure the frictional force. Its value ranges from 0 to sometimes greater than 1.

- **Second Law:** Frictional force is independent of the geometrical contact area.
- **Third Law:** Kinetic friction is independent of the sliding velocity.

These laws have been proved experimentally over a wide range of conditions. A deviation from the first law is shown by very hard material like, diamond and very soft material like, teflon. Very smooth surface or polished surface shows deviations from the second law. Deviations from the third law or Coulomb's law are quite common. Over speed range of a million times, the friction coefficient is almost double.

1.1.2. Wear

Wear is the progressive loss of material from the contacting surfaces under the applied normal load and leads to dimensional changes eventually causing poor performance. Sometimes, replacement of worn component is highly needed [Bhushan (2001b)]. It is controlled by the properties of material like surface roughness, environment, operating conditions, mechanical strength, hardness and geometry of contacting bodies. Wear can occur due to mechanical or chemical processes. Like friction, wear is also a complex process and the most common types of wear are explained on the basis of engineering practices.

1.1.2.1. Adhesive wear

Adhesive wear is a result of micro-junctions caused by welding between the opposing asperities on the rubbing surfaces of the counter bodies. The strength of these junctions depends on the physicochemical nature of contacting surfaces which leads to plastic deformation and shearing by dislocation of the material. The load applied to the contacting asperities is so high that they deform and adhere to each

other forming micro-joints. The motion of the rubbing counter bodies results in rupture of the micro-joints. Thus some of the material is transferred by its counter body. This effect is called scuffing or galling.

1.1.2.2. Abrasive wear

Abrasive wear is normally associated with material removal when a hard sharp particle slides against a comparatively softer material. Grinding of material is a good example of the process in which abrasive grains remove material from the softer surface by cutting action. In this mode the grain penetrates the surface and grooved volume is removed during sliding. Abrasive action depends on relative hardness of sliding materials resulting into formation of an abrasive groove on the weaker surface. It may be classified as two-body or three-body depending upon the role of worn out or dust particles in affecting phenomenon of wear [Dorinson (1985)].

1.1.2.3. Chemical Wear

The chemical reactivity on the metal surfaces combined with rubbing action that scuffs off metal results in chemical wear. Various chemical agents like CO₂, H₂O and acidic compounds formed in the oil can cause corrosive wear. Corrosive wear can be reduced by adding anticorrosive agent in the lubricant. The most common example of corrosive wear is rusting of moving steel parts. The extreme pressure lubrication can be considered as an example of controlled corrosive wear.

1.1.2.4. Surface Fatigue Wear

The above three types of wear are associated with sliding friction. Rolling and sliding conditions produce surface fatigue type wear which is characterized by pitting or cyclic crack growth and appears suddenly after a large number of revolutions. Fatigue wear can occur between surfaces due to cyclic stresses at the asperity and sub-surface level. Such stresses when repeatedly applied on the surface result into detachment of wear particle that may be termed as micro-fracture event. Fatigue cracks start at the material surface and spread to the subsurface regions. The cracks may connect to each other resulting in separation and delamination of the material pieces. This occurs in rolling element bearings and gears where there is high degree of rolling and adhesive wear associated with sliding is negligible.

1.1.3. Lubrication

The technological revolution, changes in machine designs, replacement of heavy-weight metal tools by low-weight metals, stringent regulation towards protection of environment by reducing the emissions etc. are key challenges for design and development of energy efficient lubricants. The word "lubrication" stands for the introduction of foreign substance i.e. lubricant between two or more moving bodies which reduce the friction and wear by avoiding direct contact between the interacting surfaces. Poor lubrication is responsible for energy and material losses. The lubrication is also required to accomplish other purposes such as dissipation of heat from the contact surfaces, inhibit the corrosion, removal of wear particles from the contact zone etc. [Dorinson (1985), Jones (1983)]. The lubrication not only plays important roles in manufacturing processes and machine components but also in human body e.g. artificial joints, hip replacements etc. [Grupp *et al.*(2010), Davim *et al.*(2010)]. A good lubricant should exhibit low volatility, excellent thermal and oxidative stability, good fluidity at low temperature, non-corrosiveness and high viscosity index [Kuratomi *et al.*(2009)].

Viscosity of lubricant, applied normal load and speed are critical parameters that control different lubrication regimes. These regimes are better understood by Stribeck curve, based on the thickness of lubricant film between the interacting tribo-surfaces. The thickness of lubricant film is mainly determined by bearing parameter which is given by [(speed x viscosity)/load]. The changes in coefficient of friction as a function of bearing parameter is demonstrated in the Figure 1.1, Stribeck curve [Husban (1955), Wang *et al.*(2006)]. On the basis of lambda ratio which is the ratio of minimum film thickness (h) to composite roughness (σ^*) i.e., average roughness of interacting surfaces, Stribeck curve may be divided into boundary, mixed and hydrodynamic lubrication regimes.

$$\text{Lambda ratio, } \lambda = \frac{h}{\sigma^*}$$

where, h = Minimum film thickness

σ^* = Composite roughness

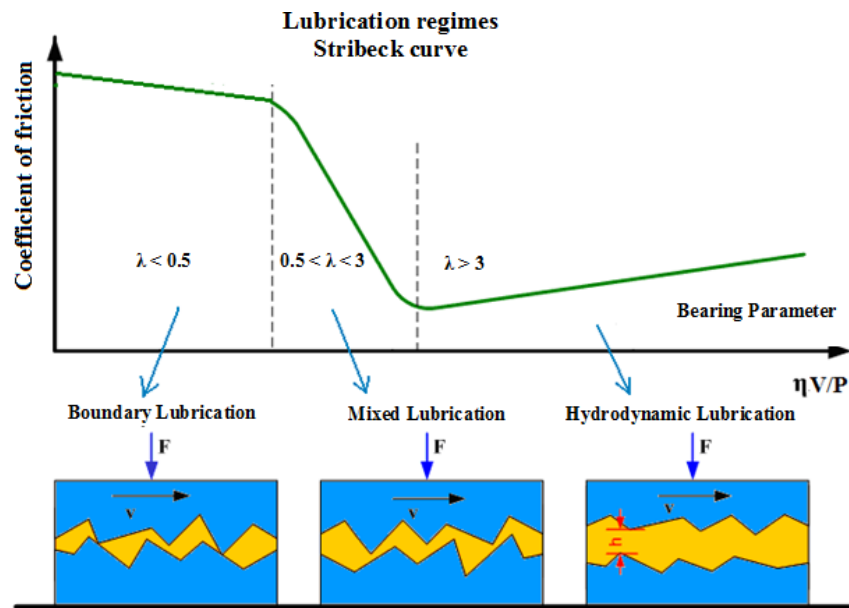


Figure 1.1. Stribeck curve: Dependence of the friction coefficient on viscosity, speed and load for a lubricated sliding system.

1.1.3.1. Boundary Lubrication

The term boundary lubrication firstly used by Hardy and Doubleday (1922) to describe friction and wear reduction in sliding of two solid bodies. Boundary lubrication is a result of a combination of low viscosity, low velocity and high load. The fluid film thickness is negligible under boundary lubrication regime therefore; considerable contacts are developed between the tribo-surfaces and all the load is supported by asperity-asperity contact. This leads to a high coefficient of friction and for this lubrication regime the value of lambda ratio is less than 0.5. The regime is therefore, the most unfavourable since it provides high coefficient of friction causing huge loss of energy along with wear of material from the surface [Myshinn *et al.*(1997)].

1.1.3.2. Mixed Lubrication

The lubricant film is able to separate two contact surfaces at few points only while some asperities are in contact to each other. This lubrication regime is an intermediate of hydrodynamic lubrication and boundary lubrication. Due to the contact of asperities of tribo-surfaces, friction is relatively much more than

hydrodynamic lubrication [Myshinn *et al.*(1997)]. For this lubrication regime the value of lambda ratio lies in between 0.5-3.0.

1.1.3.3. Hydrodynamic Lubrication

In the mixed lubrication regime, there is a lubricant film between the moving surfaces but some asperities are present in the contact. Both asperities and the lubricant film therefore, carry the load. In hydrodynamic lubrication, lubricant film is thick enough to prevent any direct contact between lubricated surfaces and load is carried completely by the lubricant film. Hence, this regime is characterized by a low friction and negligible wear. The load carrying surfaces are separated by a relatively thick film of lubricant, so that there is no contact between the tribo-surfaces [Myshinn *et al.*(1997)]. Moderate viscosity of lubricant and moderate speed at relatively low load provides hydrodynamic friction and the value of lambda ratio is greater than 3.0.

Chemical Aspects of Tribofilm Formation

The chemical interactions between two or more interacting surfaces are studied under tribochemistry which is gaining attention for understanding the role of lubricant additives, particularly, under the boundary or mixed lubrication regimes [Hutchings (1992)]. Tribochemistry is the chemistry that occurs between the lubricant/environment with the rubbing surfaces under tribo-conditions [Hsu *et al.* (2002)]. The nature of tribochemical reactions and their mechanism are gaining large interest in understanding the role of lubricant in reduction of friction and wear. In boundary or mixed lubrication regimes, lubricant additives get adsorbed on the interacting surfaces. This adsorbed layer of the additive molecules reduces the contact between moving surfaces. At higher load and elevated temperature, these additives undergo decomposition forming a protective tribofilm. This tribofilm prevents direct metal to metal contacts thereby protecting the interacting surfaces. The reactivity of the additive with surfaces is crucial and must be optimized for the best performance. If an additive is not sufficiently reactive, then no adequate tribofilm can be formed before the parts become severely damaged. If the additive is too reactive, then the additive may lead to a corrosive attack on the surface resulting in tribochemical wear. The reactivity of AW/AF/EP additives in real applications depends on the base oil, presence of other additives and the nature of surfaces. A tribochemical reaction of an

additive with a surface is generally catalysed by the contact asperity temperature and the nascent metal surface. The contact temperature also called “flash temperature” is usually very high (>400 °C) but short lived. A raise in contact temperature is caused by the frictional heat between the sliding asperities [Hsu *et al.* (2005)]. The nascent surface possesses very high surface energy and active sites. A variety of chemical reactions may occur due to the combined effect of heat and the active surface. These reactions mainly include oxidation of surfaces, oxidation and degradation of the lubricant, surface catalysis, polymerization and the formation of inorganic and organometallic products on the sliding surfaces [Hsu (1996)]. The nature of these products formed on the tribo-surfaces depends on the reactivity, structure and composition of the additive.

1.2. Lubricants

Any material which reduces friction and wear when it interposed between two moving surfaces is called lubricant. The main function of a lubricant is to abstract heat and thus to increase mechanical efficiency. Besides this, it acts as a sealing agent and prevents entry of dirt and moistures between the moving parts. The ever progressing development of engines and general machinery resulting in very arduous operating conditions calls for improvement of the lubricants to withstand high temperatures and pressures. Based on the physical state the lubricants may be classified as follows:

1.2.1. Liquid Lubricants

The base oil which may have different origins either mineral or synthetic should have low viscosity and high viscosity index, in general but it must be viscous enough to maintain a lubricant film under the required operating conditions. The oil should be as fluid as possible to remove heat and to avoid power loss due to viscous drag. It should also be stable under thermal and oxidative stresses, have low volatility and possess some ability to control friction and wear by itself. The advantages of using liquid lubricant are that they can be used over wide range of temperatures, dissipate heat from contact points and also act as cleaning agents. The liquid lubricants are of the following types-

1.2.1.1. Vegetable oil

Vegetable-based oils are triglycerides or natural esters that come from agricultural crops. They have some undesirable characteristics. Their cold temperature properties and oxidation instability are their main disadvantages compared to petroleum-based oil. Vegetable oils have many good natural properties including good lubricity, good resistance to shear, a high flash point, and a high viscosity index. Vegetable oils and fats have a property called “oiliness” by virtue of which they are adsorbed on metallic surfaces tenaciously and offer lower friction coefficient and higher load carrying capacity. Some of the important vegetable oils having potential use as lubricants are castor oil, olive oil, rapeseed oil, palm oil, cotton seed oil etc.

1.2.1.2. Animal oils and fats

Different types of animal oils are used as lubricants *viz* lard oil, tallow oil, neat foot oil, sperms oil, whale oil, seal oil etc. The use of these oils is also limited due to their decomposition at higher temperature.

1.2.1.3. Mineral oil

Mineral oils have largely replaced animal and vegetable oils as lubricants in view of their cheaper cost, easy availability in bulk quantities, stability under severe conditions and reusability. Mineral oils are the most commonly used base stocks in the lubrication. They are composed of either straight or branched carbon chains with 20-40 carbon atoms in each molecule, sometimes containing aromatic or aliphatic rings. The examples are paraffin and naphthenic base oils which can be refined to remove wax and gum impurities.

1.2.1.4. Synthetic lubricants

Synthetic oil made from more advanced refining process of crude oil and hence it is more pure than mineral oil. The structure of synthetic oils such as carbon chain and functional groups can be designed to have specific properties and applications. Synthetic oils are used for more demanding applications where insulating, thermally or chemically resistant lubricants are required [Huang *et al.*

(2004a)], and therefore they are more expensive. These oils possess high viscosity index (120-170), low volatility and good oxidation stability. These can be generally characterized as oily, neutral liquid materials having at least some properties similar to the petroleum lubricants. However, requirement of lubricants functioning over increasing temperature range has stimulated the continuous development of synthetic lubricants. The important examples are: polyalphaolefins (PAOs), alkylated aromatics, polybutenes, aliphatic diesters, polyesters and polyalkyleneglycols. Other materials such as silicone, perfluoroethers and polyphenylene ethers are also of importance but their applications are restricted due either to high cost or performance limitations.

1.2.2. Semi-solid Lubricants

Greases are the most common example of semi-solid lubricants. These are produced by emulsifying oils or fats with metallic soap and water. Advantages of using semi-solid lubricant is that it adheres at contact surfaces and remains at application point to provide better mechanical lubrication cushion under the extreme conditions. However, again poor heat dissipation is a major drawback of using semi-solid lubricants. Additionally, if once contaminants like dust, dirt and wear debris enter into grease, it is very tough to separate it out.

1.2.3. Solid Lubricants

A solid lubricant is basically a solid material/solid thin film which can be placed between two contact surfaces and provides low shearing under a given load. Bearing used under vacuum at very high temperature cannot be lubricated by liquid lubricants or greases. In such cases, solid lubricants are used. These materials have layered crystalline structure which ensures low shear strength and thereby minimizes friction. The most common solid lubricants are graphite, MoS₂, WS₂, ZnO, ceramic coatings etc. In general, solid lubricants must have high mechanical strength, low shear strength, high thermal and chemical stability and lamellar structure. The poor

self-healing and high coefficient of friction in comparison to liquid lubrication are main drawbacks associated with solid lubricants.

1.2.4. Gaseous Lubricants

Gaseous lubricants include air, nitrogen, oxygen, helium etc. and are used in aerodynamic and aerostatic lubrication. It can be used over a wide range of temperature. The viscosity of gaseous lubricants increases with increasing the temperature. This is main advantage of gaseous lubricants over liquid lubricants. On the other hand, storage of gaseous lubricants is the main problem.

1.3. Lubricant Additives

Lubricant additives are chemical compounds/materials, especially organic or organometallic, added to the lubricant in small amount for enhancing the specific properties of lubricants [Ludema (1996)]. The additives are added to the lubricants for different purposes, some impart new and useful properties to the lubricant; some improve their inherent properties while some reduce the rate at which undesirable changes take place during its service life. In today's market, different types of lubricant additives are commercially available like viscosity improver, corrosion inhibitor, antioxidant, pour point depressant, friction modifier, antiwear and extreme pressure etc. and a fully formulated lubricant contains few of them, depending on targeted application. Modern lubricating oil additives based on years of scientific research desired to meet the extreme demands of modern machines and for high performance rating under real working conditions, have become indispensable in many applications. During the past 70 years, various types of lubricants and oil additives have been developed to improve the service life of machines. Organic or organometallic compounds containing tribologically active elements (P, S, N, Cl, Zn, Mo and B) or combinations of compounds with these elements are added to base oils at low concentrations. Lubricant additives can be classified into two categories on the basis of their chemical behaviour: chemically-inert and chemically-active. Chemically-inert additives such as viscosity modifiers, foam inhibitors, and pour point depressants modify the physical properties of the base oil whereas the chemically-active additives such as antiwear, extreme pressure and corrosion

inhibitors enhance the tribological properties of base lube. In general, AW/AF/EP lubricant additives are further classified into the following types based on their chemical compositions: sulfur compounds, ashless phosphorus compounds, dialkyldithiophosphate complexes of metals (MDTPs), dialkyldithiocarbamate complexes of metals (MDTCs), heterocyclic compounds, halogens, boron compounds, ionic liquids (ILs), ceramic nanoparticles and carbon based nanomaterials. A short description of these classes of compounds is given below:

1.3.1. Sulfur Compounds

Sulfur alone or together with other metals in different chemical compositions is one of the most important elements in lubrication field [Stewart *et al.*(1963)]. The main functions of sulfur-based additives are to improve the antiwear, extreme pressure and frictional properties of lubricants used under severe conditions. Sulfur containing EP/AW additives namely sulfurized hydrocarbons, sulfurized fatty oils, sulfurized synthetic esters of short chain alcohol, animal or vegetable fatty acids, sulfurized ester of glycol, thioglycolic acid ester, sulfurized terpenes, alkyl or benzyl monosulfide and disulfide have been used to understand the action mechanism of this category of additives since they have simple chemical structures [Shao *et al.*(2005), Otto (1993), Cao *et al.*(2000)]. The action mechanism of the sulfur compound type EP/AW additives was originally proposed by Davey *et al.*(1957) and then refined by Forbes *et al.*(1973). In the proposed mechanism, sulfur compound (disulfide or monosulfide) physically adsorbs on an iron surface first, and then reacts to form an iron sulfide film which can reduce friction and wear thereby preventing from seizure. The monosulfide directly forms the iron sulfide film after physisorption whereas the disulfide forms the iron sulfide film through formation of an iron mercaptide. Antiwear property under a mixed lubrication condition depends on the ease of physisorption and decomposition of the S-S bond i.e., the ease of formation of the iron mercaptide while anti-seizure property under a boundary lubrication condition depends on the ease of forming the iron sulfide film (Figure 1.2). Allum *et al.* (1965, 1967) said that the wear and seizure mechanism of sulfur compound type EP/AW additives such as monosulfide, disulfide, sulfoxide and sulfone can be explained by this theory. In other words, tribological performance of the sulfur containing EP/AW

additives depends on their chemical structure, stability of the S-S and C-S bonds. As Forbes *et al.*(1973) himself pointed out, it should be emphasized that there was no evidence that pure iron sulfides were the load-carrying layers and these layers were more likely to be complex mixtures of iron-sulfur, and possibly carbon-oxygen compounds. In fact, Dacre *et al.*(1982) mentioned that antiwear property should be dependent on the physisorption from the viewpoint of iron mercaptide. Hiley *et al.*(1981) using polysulfide showed that antiwear and antiseizure performance increases with higher multi-sulfide.

The polar interaction and chemical reactivity between the surfactant and iron sulfide film are important. It has been shown that activity of sulfur EP additives depends both on formation of the sulfide film and on subsequent strong chemisorption of surfactant or EP additive molecules on top of the film [Spikes *et al.*(1973)]. The tribological reaction between solid surfaces and lubricant with suitable additives leads to the formation of effective films for EP lubrication. Both iron sulfide and ferric oxide produced on the rubbing surface are effective in EP lubrication [Godfrey (1962)]. Nakamaya *et al.*(1981) suggested that optimum sulfur concentration is needed for effective wear prevention. Adhesive wear takes place below optimum concentration. Rowson *et al.*(1981) have found that at 30 °C sulfur as an additive is detrimental to the pitting performance but at 100 °C, it is beneficial. Najman *et al.*(2003) using XPS and XANES spectroscopy have found that the film composition in the presence of several organosulfurs depends on the applied load. They have provided detailed insight into the chemistry of both thermo-oxidative and tribochemical films generated from organosulfur additives. They found sulfate in the non-contact areas, iron disulphide and sulfate in tribofilms formed under moderate conditions and iron sulfide under extreme pressure environment.

The various types of organic sulfur compounds e.g. xanthates [Agrawal *et al.*(1980), (1981)], dithiocarbamates [Mamman *et al.*(1981), (1983), (1984)], isothiobiurets [Trofimov *et al.*(1999), (1988)], isothioamides [Kuliyev *et al.*(1983), (1988)], phenylacetothioamides [Kuliyev *et al.*(1983)], thioamide [Kuliyev *et al.*(1989a)], thioacetamide [Kuliyev *et al.*(1989b)], dialkanoylacetamide [Croudace

(1990)], alkano-amidosulfides [Bhattacharya et al.(1995)], etc. have been reportedly evaluated as potential AW/EP additives.

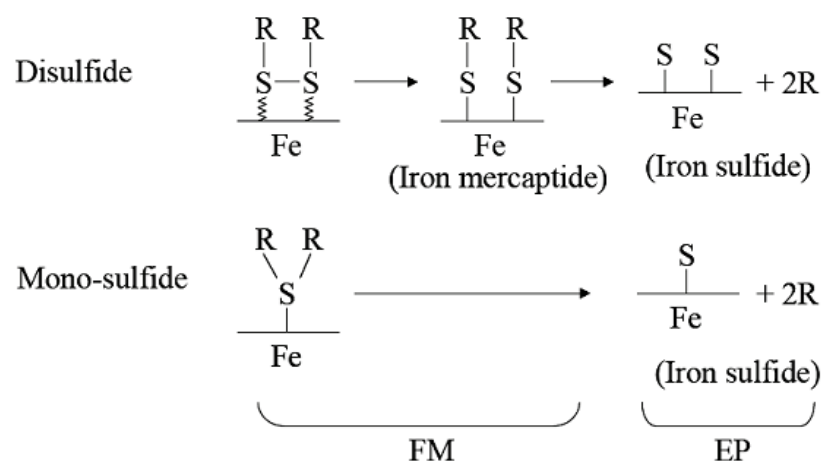


Figure 1.2. Mechanisms of formation of iron sulfide tribofilms from sulfur compounds adsorbed at iron surface. Adapted from Shah *et al.*(2011).

1.3.2. Ashless Phosphorus Compounds

More than a hundred of different phosphorus compounds have been investigated for possible application in tribology but only a small fraction of them are commonly used in industry [Saba *et al.*(2002)]. These include phosphates [Najman *et al.*(2002), Rossi *et al.*(2006)] and dithiophosphates etc. [Najman *et al.*(2004a,b), Sharma *et al.*(2003)]. Schumacher and Zinke *et al.*(1997) studied the antiwear behavior of several compounds based on the structure of dithiophosphates, replacing sulfur by oxygen atoms and varying the length and branching of alkyl groups. It was established that an increased thermal stability of phosphorus-containing compounds maintained good performance at high temperatures but some thermal instability is required to allow the compound to react and form protective antiwear tribofilms. Sarin *et al.*(1993) studied antiwear, extreme pressure and antioxidative performance of a series of *O,O'*-dialkylphosphorodithionic disulfides $(\text{RO})_2\text{P}(\text{S})\text{S}-\text{SP}(\text{S})(\text{RO})_2$ as potential replacements of zinc dialkyldithiophosphate. They found that these additives provide antiwear properties comparable to a commercial zinc dialkyldithiophosphates. The antiwear performance of other dithiophosphate disulfide compounds was also investigated. It was shown that the disulfide group can provide superior EP properties

as compared to normal dithiophosphates. Heuberger *et al.*(2008) have investigated the reactivity of alkylated phosphorothionates, such as triphenyl phosphorothionate with steel surfaces. They found that the cleavage of P=S double bonds in adsorbed molecules takes place under impact of a high contact pressure and under the frictional heat sulfur reacts with iron forming iron sulfide [Zeng *et al.*(2004)].

An investigation by Filippo Mangolini *et al.*(2009) on the thermo-oxidative behaviour of antiwear additives triphenyl phosphorothionate (TPPT) in lubricant oil solution at high temperature significantly contributes to an understanding of the mechanism of thermal film and tribofilm formation on metal surfaces. They have proposed that thermo-oxidative reaction of TPPT in lubricant oil solution starts with the scission of the P=S bond, leading to the formation of triphenyl phosphate. Further, a group of researchers have investigated thermal and oxidation stability of organo-phosphorous AW/EP additives such as tributyl thiophosphate - *O,O,O*-tributyl phosphorothioate [Rossi *et al.*(2006)], phenylphosphate [Najman *et al.*(2002)], dibutyl-3,5-di-*t*-butyl-4-hydroxy benzylphosphonate (DBP) [Choi *et al.*(1997)], *S*-alkyl-*O,O*-dialkyl phosphorodithioate, alkylamine salt of dialkyldithiophosphoric acid, dialkyl hydrogenphosphate [Bansal *et al.*(2002)]. The results show that at temperatures lower than 373K the molecule forms a physisorbed layer on the iron substrate. At 373K a reaction takes place with the formation of an organic layer, together with iron polyphosphate and sulfate. At higher temperatures, temperature-programmed desorption results suggest that the mechanism involves P–O bond scission to yield alkoxy groups. This could be preceded by P=S bond scission to give trialkyl phosphite, which then, in turn, undergoes P–O bond scission to produce alkoxy groups. The results obtained following tribological testing are in agreement with those of thermal tests.

1.3.3. Heterocyclic Compounds

In the last few decades, the tribological performance of N, S and O heterocyclic compounds as lubricant additives was in focus because of their promising friction and antiwear properties [Heuberger *et al.*(2008), Zhang *et al.*(1998),(1999a-d), Xue *et al.*(1999), George *et al.*(1987), Wan *et al.*(1997), Zeng *et*

al.(2007a,b), He *et al.*(2002)]. N-heterocyclic compounds have a high affinity to nascent iron surfaces and they readily adsorb on steel surfaces forming antiwear tribofilms. Ren *et al.*(1993) studied antiwear properties of a series of N-heterocyclic compounds with one, two and three nitrogen atoms. They found that antiwear properties of these compounds increase with the number of nitrogen atoms in heterocycles. The benzotriazole and its derivatives are the most effective antiwear additives in this class of compounds because of an increase in coordinating ability to Fe atoms with a number of basic nitrogen atoms in the molecule. XPS analysis of these N-heterocyclic compounds showed the same spectra for surfaces rubbed in solution and immersed in solution without rubbing. Therefore, these N-compounds were not chemically changed during rubbing. Dialkyldithiocarbamate derivatives of heterocyclic compounds have also been used as multifunctional additives in both mineral and vegetable base oils [Ren *et al.*(1993), (1994), Huang *et al.*(2004,a,b,c)]. It was found that when the above mentioned N-heterocyclic compounds are bound in a single molecule with dithiocarbamates, their antiwear ability is further improved. However, this is not the case for all types of base oils. For example, triazine derivatives of dithiocarbamates added in small concentrations to mineral oils decrease wear of steel-steel contacts [Huang *et al.*(2004a)] while the same additives may increase wear in vegetable (rapeseed) oils [Xu *et al.*(2000), Zhan *et al.*(2004)]. Organic compounds are thought to adsorb on metal surfaces via either negatively charged centers or by π electrons in double-bond or aromatic systems. A partial transfer of electrons occurs from polar (donor) groups to atoms on the metal surfaces. In the case of compounds with nitrogen heterocycles, coordinatively saturated or unsaturated covalent bonds can be formed in the process of such chemisorption, thus, providing antiwear and corrosion suppressing properties [Zeng *et al.*(2007b)]. This is one of the plausible reasons for tremendous use of nitrogen-carbon heterocyclic compounds in lubricant industries as both metal passivators and effective corrosion inhibitors [Wu *et al.*(2009a)]. The latter is due to their chelating action and their ability to form insoluble diffusion barriers on oxidized surfaces of metals, thus, preventing metal reaction and dissolution. Benzotriazole, benzimidazole, benzthiazole, pyridazole, tetrazole, other nitrogen containing heterocycles and their derivatives were found to be highly effective in inhibiting corrosion for copper, nickel, iron and other metals [Babic *et al.*(2005), Wu *et al.*(2009b), Waynick *et*

al.(2001)]. Schiff bases are used immensely because they have been proved to possess excellent antioxidant [Tang *et al.*(2007), Chen *et al.*(2003), antiwear [Agarwal *et al.*(1992), McHuge *et al.*(1965), Ishchuk *et al.*(1994)], anticorrosion properties [Ju *et al.*(2008), Asan *et al.*(2006)] and high thermal stabilities [Mohamed *et al.*(2003)]. With the development of modern machines and to meet the requirement of environment protection, nitrogen-containing heterocyclic derivatives are also regarded as potentially excellent ashless multifunctional lubricating oil additives.

1.3.4. Dialkyldithiocarbamate Complexes of Metals (MDTCs)

Dialkyldithiocarbamate complexes of several metals have been widely investigated as multifunctional lubricant additives. Dithiocarbamates of several different metals and metalloids including zinc [Verma *et al.*(2004)], molybdenum [Braithwaite *et al.*(1978)], cerium [Chen *et al.*(1997)], copper [Chen *et al.*(1997)], lead [Beatty *et al.*(1968)], antimony and bismuth [Palacios (1987), Grossiord *et al.*(1998a)] have already been thoroughly studied. Molybdenum dialkyldithiocarbamates (MoDTC) were initially known as antioxidants and extreme pressure additives. They have also been widely used as friction modifiers. Formation of low friction tribofilms from MoDTC-containing lubricants was the main subject of several studies [Grossiord *et al.*(1998b), Morina *et al.*(2006a,b)]. It is known that MoDTCs are decomposed in a sliding contact forming MoS₂ nanocrystals [Grossiord *et al.*(1998a)]. Further investigations by Barros *et al.*(2005) on the tribochemistry of these additives on steel surfaces have shown that ZnDTP additives, also present in the lubricating oil, may stimulate formation of MoS₂. The following mechanism of MoS₂ formation in the presence of ZnDTP has been proposed. Electrons are transferred via Mo–S bonds in the MoDTC molecule leading to formation of free radicals during the rubbing process. The chain-end radicals are recombined to form thiuram disulfide. The oxysulfide decomposes into MoS₂, which crystallizes into MoS₂ sheets and MoO₂ (Figure 1.3). The role of ZnDTP in these processes is to provide the sulfur atoms to complete the sulfuration of the oxysulfide. The amount of MoS₂ formed depends on the concentration of ZnDTP present in the lubricant. Therefore, the majority of research has been focused on the mixture of MoDTC and ZDDP as additives in lubricants [Morina *et al.*(2007)]. These MoS₂ units meet together forming a lamellar sheet, which covers asperity tips and efficiently reduces friction. There is a strong

covalent bonding between atomic species but only a very weak van der Waals interaction between lattice layers. These weak van der Waals forces between MoS₂ layers are easy to overcome by shearing within the molecule. They are responsible for low friction properties of lubricants.

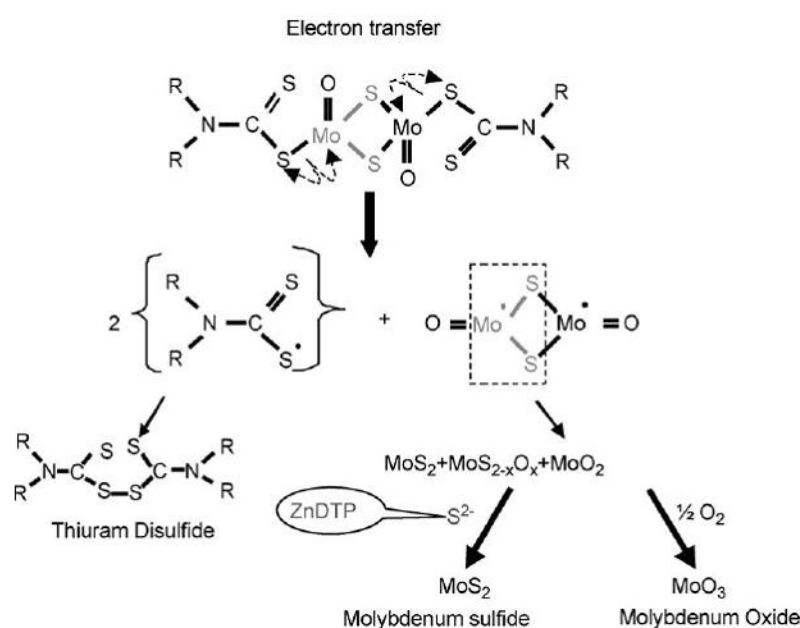


Figure 1.3. Chemical processes leading to MoS₂ formation from MoDTC. Adapted from Barros *et al.*(2005)

1.3.5. Dialkyldithiophosphate Complexes of Metals (MDDPs)

Dialkyldithiophosphate complexes of metals, MDDPs are being used in lubricating oil formulations for several decades due to their excellent antiwear, extreme pressure, friction modifier, antioxidant and corrosion resistance properties. Dialkyldithiophosphates of different metals such as zinc, molybdenum [Furey (1973)], cadmium [Sarin *et al.*(1994)], copper [Jianqiang *et al.*(2005)], titanium [Zhang *et al.*(1998)], gadolinium [Sarin *et al.*(1995)], iron, antimony and other metals [Boshui *et al.*(1996), Margielewski *et al.*(2002), Rowe *et al.*(1967a,b)] have been used as multifunctional lubricant additives. Among MDDPs, zinc dialkyldithiophosphates (ZDDPs) are the most widely used for several decades [Born *et al.*(1992), Martin *et al.*(1984), Sheasby *et al.*(1992), Wu *et al.*(1997), George *et al.*(1979), Spedding *et al.*(1982), Watkins (1982)].

Zinc dialkyldithiophosphate (Figure 1.4) is the most famous EP/AW additive for engine oil [Lin *et al.*(2004), Hu *et al.*(2003), Hartley *et al.*(2002)]. A lot of research has been reported concerning the action mechanism of ZDDP, including the thermal decomposition [David (2002), Moerina *et al.*(2006), Willermet *et al.*(1995), Spikes (2004), Fuller *et al.*(1998), Rowe *et al.*(1967b)], hydrolytic [Spedding (1982)], and oxidative [Mitchell (1984)] mechanism. Dorinson (1979) and Rounds (1981) advocated a theory that sulfur and phosphorus in ZDDP directly react with a steel surface, resulting in the formation of a boundary lubrication film. Recently many discussions have centred on the “frictional polymer theory”, derived originally from the thermal decomposition investigation of Feng *et al.*(1960) where the boundary lubrication film is formed through the formation of frictional polymer on a steel surface. Brazier *et al.*(1967) also estimated the polymer. Then, Coy *et al.*(1975) and Bird *et al.*(1980) supported the formation of the polymer but did not discuss its chemical structure. Later on, Barcraft *et al.*(1982) brought the “double function theory” into the aforementioned frictional polymer theory by investigating the thermal decomposition mechanism by means of a “hot wire method” using three different types of ZDDPs. Their work revealed that ZDDP gradually forms the polymer film by the thermal decomposition as temperature rises not only on steel surface but also on surfaces of other materials [Martin *et al.*(1996)]. The work also revealed that the composition of the generated polymer film differs depending on the temperature. Moreover, when a lubrication condition becomes severe, it decomposes further by frictional heat resulting into formation of iron sulfide and iron phosphate films [Martin (1999)]. Therefore, one of the most promising mechanisms of the ZDDP action is the “frictional polymer theory” where ZDDP decomposes and forms polymer film on the interacting surfaces. The prime function of this polymer film is to prevent wear and then decompose under more severe conditions to form the iron sulfide or iron phosphate, which work to prevent seizure. It is considered that antiseizure or antiwear performance of ZDDP depends on its chemical structure and length of alkyl chains. Basically, ZDDP reduces the wear under boundary or mixed lubrication conditions due to tribofilm generation (50-100 nm thick) on rubbing surfaces [Barnes *et al.*(2001), Sheasby *et al.*(1991), Minfray *et al.*(2008)]. Surface analysis such as the

X-ray Photoelectron Spectroscopy (XPS) showed that the bulk ZDDP tribofilms are mainly composed of a mixed zinc and iron short chain (ortho or pyro) phosphate glass with iron sulfides precipitates [Barros *et al.*(2003), Minfray *et al.*(2004)]. The phosphate chains are longer [Rossi *et al.*(2004), Minfray *et al.*(2006)] on the top of the tribofilm than in its bulk [Yin *et al.*(1997)]. Recently, Zhou *et al.*(2010) assumed the presence of ultra-polyphosphate in the outer layer. The structural evolution of tribofilm material (i.e. zinc polyphosphate) during tribological sollicitation is important to provide a better understanding of ZDDP antiwear mechanism.

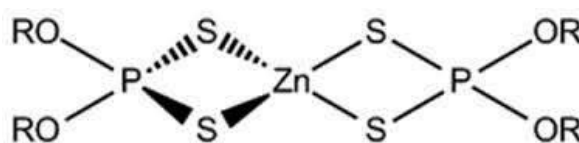


Figure 1.4. Structure of zinc dialkyldithiophosphate

As mentioned above, the most frequently used additives ZDDPs form ash which consists of tiny solid, metallic salt particles. Since, it contains large amounts of phosphorus, sulfur and zinc which impair the environment directly and also indirectly by poisoning exhaust catalysts and reducing the life of the emission system, international regulations are limiting the concentration of phosphorus and sulfur in engine oils and thus the excessive use of ZDDPs has to be limited [Lin *et al.*(2004), Morina *et al.*(2006b)].

1.3.6. Halogens

Among halogen compounds, chlorine has been one of the earliest AW and EP elements used by the lubricant industry. Chlorine compounds possess extreme pressure and antiwear properties [Furey *et al.*(1973), Gong *et al.*(1990)]. Kotvis *et al.*(1991) and Crumer *et al.*(1994) showed that some chlorine-containing compounds react with iron surface producing iron chloride. The main drawback of chlorine containing additives is due to the health and environment hazards caused by them. Therefore, chlorine-containing additives are not considered as a viable option for modern lubricants.

1.3.7. Boron Compounds

Boron compounds have unique combination of tribological properties. In addition, they are generally believed to have little, if any, detrimental effect on either the machine components or the environment [Baldwin (1977)]. Therefore, research on boron based additives has considerably increased within the last decade. Specifically, boron compounds have been extensively studied as boundary lubricating oil soluble additives, solid lubricants and surface coatings [Kimura *et al.*(1999), Li *et al.*(2010), Klepper *et al.*(2010), Wu *et al.*(2006)]. Oil soluble organoboron compounds are promising friction modifiers, corrosion inhibitors, antioxidants and effective antiwear additives [Hu *et al.*(2000a), Liu *et al.*(1994), Herdan (2000), Zhang *et al.*(1999a), Shen *et al.*(2000)]. Boron compounds are capable of forming glassy structures in a manner similar to ZDDP but with different glass transition temperatures [Feng *et al.*(1963)]. It is known that crystalline or amorphous boron, boron nitride and metal boride are very hard materials.

Borates have been frequently used as lubricant additives because these possess wear resistance and friction-reducing properties [Adams (1977), (1978), Baldwin (1977), Dong *et al.*(1994), Kreuz *et al.*(1967)]. Their low toxicity and a pleasant odour make them important in providing possible solution for partial replacement of sulfur and phosphorus-based additives [Kreuz *et al.*(1967)]. Several kinds of borate additives have been investigated for their tribological properties. Inorganic-dispersed potassium borates have been reported to possess the extreme pressure properties [Adams (1977), (1978)]. More recently, the micellar calcium borates have been largely investigated in interaction with other common additives [Grossiord *et al.*(2000), Martin *et al.*(2000), Varlot *et al.*(1999), Normand *et al.*(1998)]. Such additives under boundary lubrication lead to the formation of a thin amorphous film of borate glass. This tribofilm preserves the contact surface from wear due to its particular rheological properties. The main drawback of inorganic borates is their low solubility in the base oil. Borate esters have been proposed as tackling the solubility problem of inorganic borates. Kreuz *et al.*(1967) have studied the extreme pressure behaviour of tribenzylborate ester and it has been found that the borate additives in

both ester and mineral oils improved the load carrying capability. Borate esters were found to form a non-sacrificial film [Feng *et al.*(1963)]. Indeed, unlike the S-containing additives leading to iron sulfides FeS_x formation, boron did not attack the iron surface. It was found that the tribofilm was composed of a heterogeneous structure containing ferrous oxide and boric acid as well as an organic phase. One of the drawbacks of borate esters is their low stability in air. They rapidly hydrolyze to produce boric acid. Some studies have reported higher stability of borate esters containing nitrogen [Yao (1997), Zheng *et al.*(1998)]. These additives were also found to produce tribofilm containing boron nitride thereby enhancing antiwear performances at a higher load. Excellent antiwear, load-carrying and friction reducing properties of ferrous octoxyborates were found to be due to presence of iron borides (FeB) in the tribofilms [Hu *et al.*(2000b)]. Finally, Erdemir *et al.*(1991a,b) reported the lubricious effect of self-formed boric acid on surfaces containing boron (boron, boron oxide). For engine and gearbox lubrication, organic borates are especially interesting candidates since they have good solubility in base oils. However, their mechanism of action is still not clear and the product responsible for their tribological properties is not known. As presented above, some authors attribute the tribological properties to the particular rheological properties of borate glass. Others explain the friction-reducing properties as due to the formation of boric acid, meanwhile others say that boric acid is abrasive. Choudhary and Pande (2002) have written an extended review on boron-based additives. Analyses of the formed tribofilm have shown that the film was very hard, amorphous, 100-200 nm thick, and it contained boric and ferrous oxide components [Spikes (2008)]. Papay *et al.*(1998) have investigated both wear and friction properties of different triborate esters with the molecular structure $(\text{R}_1\text{O})(\text{R}_2\text{O})(\text{R}_3\text{O})\text{B}$. It has been found that all the tested additives were able to reduce wear and friction whereas the compounds with longer chains gave superior tribological performances. It has been also observed that an increase in the alkyl chain length at the nitrogen atom side leads to improved hydrolytic stability of the additive. Many borate esters are liable to hydrolysis as shown in Figure 1.5.

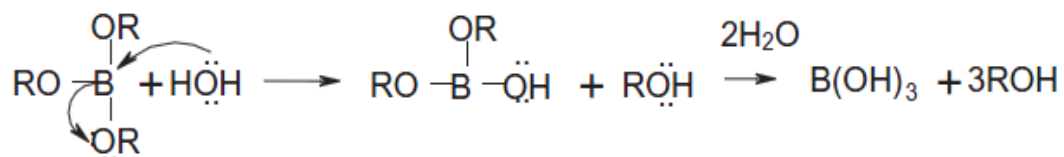


Figure 1.5. Hydrolysis of borate esters, adapted from Kreuz *et al.*(1967)

Significant attempts have been made to improve stability of alkylborates to hydrolysis: (i) the use of phenols, which hinder the hydrolytic attack at the B—O bond, (ii) amines, which may coordinate to boron atoms and prevent the B—O bond from hydrolysis [Kreuz *et al.*(1967)]. Antiwear properties of several compounds containing boron and sulfur, such as borate esters with mercaptobenzothiazole and dithiocarbamate, have been investigated. Both types of these compounds especially borated dithiocarbamates have shown good antiwear performances [Zhang *et al.*(1999a,c)]. Kapadia *et al.*(2007) have used optical interferometry to compare the tribofilm properties of ZDDP and boron based additives in rolling-sliding contact at 100 °C and have found that boron compounds form a thick tribofilm (~180 nm) similar to ZDDP. Significant levels of diffusion of boron into the surface have been detected using SIMS. In a moist atmosphere, surface oxide of boron (B₂O₃) reacts with water to form boric acid (H₃BO₃) which performs as a solid lubricant.

Lubrication performance of boric acid is related to its tendency to form a triclinic crystal structure, which consists of several atomic layers parallel to the basal plane. Boron, hydrogen and oxygen in each layer are closely packed and bonded to each other with covalent bonds. Weak Van der Waals forces keep layers together in one structure. These weak interactions promote layers to slide easily against each other that provide good lubricity in the system Lovell *et al.*(2006)]. D. Philippon and his co-workers (2011) have studied the tribochemical reactions of borate esters on steel surfaces simulated experimentally in order to better understand the mechanism of decomposition of such additives and the nature of the formed tribofilm. This study reports on the first research carried out with trimethylborate (TMB) under gas phase lubrication as an experimental model to understand the action mechanisms of organic borate additives. Friction tests under gaseous TMB were conducted with a new tribometer dedicated to the study of gaseous lubrication. The generated tribofilms

were analysed by X-ray photoelectron spectroscopy (XPS) as well as Auger electron spectroscopy. XPS data have confirmed that reactions between decomposition products of TMB and iron oxide on steel surfaces followed the hard and soft acid base (HSAB) principle. Friction processes cause mechanical degradation of TMB through the C–O bond producing CH_3^+ and BO_3^{3-} ions as shown in Figure 1.6. BO_3^{3-} is considered as a “borderline” base and it may possibly react with acid groups e.g. iron oxides, Fe^{2+} or Fe^{3+} which are hard and “borderline” acids, respectively. As the reaction between BO_3^{3-} and Fe^{3+} includes a “borderline” base and a hard acid, respectively, BO_3^{3-} may partially react with iron oxides. As a consequence, tribofilms of borate glasses can be formed on the substrate surface by digestion of the abrasive iron oxide [Philippon *et al.*(2011), Varlot *et al.*(1999)]. It is believed that boron based additives can be used as an environment friendly replacement of different conventional additives. Some boron compounds have already shown excellent tribological performances as additives dissolved in base oil, dispersed nanoparticles and as solid lubricants. Boron compounds are known to form stable tribofilms on ferrous and non-ferrous materials [Shah *et al.*(2011)].

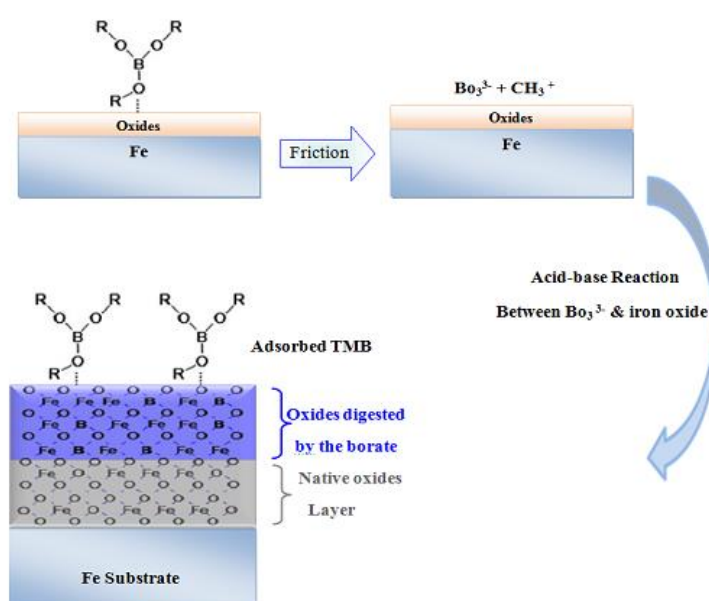


Figure 1.6. A schematic representation of the tribochemical reactions between borate esters and stainless steel surfaces, adapted from Philippon *et al.*(2011)

1.3.8. Ionic liquids

The use of ionic liquids as lubricants came in light by the efforts of Ye *et al.*(2001). They used dialkylimidazolium tetrafluoroborate ionic liquids as lubricants for various tribo-surfaces such as steel/steel, steel/aluminium, steel/copper, steel/SiO₂, Si₃N₄/SiO₂, steel/Si(100), steel/sialon and Si₃N₄/sialon and found excellent friction reducing, antiwear and load bearing properties. Several studies have been made demonstrating superior lubrication properties of ionic liquids than the conventional lubricants for a number of systems [Zhou *et al.*(2009), Somers *et al.*(2013), Chen *et al.*(2003), Liu *et al.*(2002)]. The inherent polarity, conductivity, thermal and chemical stability of ILs are important parameters for determining the lubricious properties. The interaction of ionic liquids with tribo-surfaces and formation of tribochemical thin film which reduces the friction and avoids the direct contact between the interacting engineering surfaces are mainly controlled by the molecular structure of cation and anion [Atkin *et al.*(2009), Perkin *et al.*(2010), (2012)]. In the beginning, most of tribological studies have been made using imidazolium-based cation having BF₄ and PF₆ anions. The hydrophilic nature of these ionic liquids is of serious concern for their use in tribological applications, as these ILs are prone to interact with moisture to produce HX, which further facilitates the tribo-corrosive events [Minami *et al.*(2008)]. The presence of halogen, sulphur and phosphorus in ionic liquids has to be avoided because of stringent regulation for environment as well as engine protection. Furthermore, high cost of halogen precursors particularly fluorine containing anion obstruct their penetration to the industrial applications.

1.3.9. Ceramic Nanoparticles

With the rapid development of nanoscience and nanotechnology, nanoparticles have attracted much attention due to their unique properties and promising applications in electronics [Astruc *et al.*(2010)], photonics [Mirin *et al.*(2010)], magnetism [Tuysuz *et al.*(2012)] and tribology [Huang *et al.*(2013)]. Several types of ceramic nanoparticles such as CaO, CuO, ZnO, ZrO₂, TiO₂, CeO₂, lanthanum borate etc. have been successfully used as antiwear and extreme pressure lubrication additives [Battez *et al.*(2008), Gusain *et al.*(2013), Zhang *et al.*(2011), Hu *et al.*(2000a), Battez *et al.*(2010), Bakumin *et al.*(2005)]. The main advantages of these

nanoparticles over traditional additives are their limited tribochemical reactions since these are relatively insensitive to temperature [Battez *et al.*(2010)]. Different explanations were proposed for the lubrication mechanism of nanoparticles, including the ball bearing effect [Rapport *et al.*(2002), Tao *et al.*(1996)], protective film [Zhou *et al.*(1999)], mending effect [Liu *et al.*(2004)] and polishing effect [Tao *et al.*(1996)]. The replacement of organic molecules by tiny nanoparticles of solid materials is not straight forward. Unfortunately the common bare inorganic nanoparticles are inherently unstable due to their high surface energy and therefore tend to agglomerate which eventually leads to their precipitation due to gravity. To overcome these issues associated with nanoparticles many researchers have prepared surface-modified hybrid nanoparticles which do not agglomerate, forming relatively much stable dispersions in base oil and found pronounced application in tribological industries [Bakumin *et al.*(2005)]. Capping nanoparticles with the polar organic molecules, is a convenient way to stabilize them since the polar group of a capping agent interacts chemically with the surface of nanoparticles and its non-polar long alkyl chain enhances the solubility of nanoparticles in the base oil, thus, improving the tribological properties. In the light of current literature [Stachowiak *et al.*(2004), Martin *et al.*(2008)] introducing nanoparticles in lubricants is a complicated task because size, shape, nanostructure, surface functionalization, and concentration of nanoparticles have emerged as the most critical parameters influencing the tribological properties of nanoparticle-based lubrication systems. Most of the nanoparticles exhibit their pronounced tribological behaviour at relatively high concentration (>1% w/v) in base lube. These are the main drawbacks of the ceramic nanoparticles in liquid lubrication.

1.3.10. Carbon Based Nanomaterials

1.3.10.1. Graphite

Back in 1960s, solid lubricant additives began to be used as antiwear and extreme pressure agents in gear oil. Graphite and molybdenum disulfide micron particles that have layered structures were the firstly employed as solid lubricant additives. Efficient friction and wear reducing properties of these substances were ascribed to low shear strength as a result of their intrinsic crystal structure. However,

introduction of a solid lubricant additive in lubricant oil caused another problem that is the dispersion stability. Solid particles generally are not stable in liquid media, especially the large particles. The aggregation and flocculation of the solid lubricant particles cause them to separate from the lubricant by sedimentation.

Nano and submicron size particles began to be used as solid lubricant additives in the 1980s. These particles have the superior dispersibility in a lubricant base media. This greatly improves feasibility of solid particles in lubricant application and reduces the possible abrasion that the solid lubricant additives may cause to the substrate surface. Layered structural materials such as graphite, molybdenum disulfide (MoS_2), tungsten disulphide (WS_2) and hexagonal boron nitride (*h*-BN) have been extensively used as a solid lubricant additive. The bonding between molecules within each layer is strongly covalent, while each two layers are bonded together by weak van der Waals forces. Hence, low shear stress is expected and an easy-shear mechanism results when these additives are applied between sliding surfaces. Due to such structure, these materials show good tribological performance. The graphite powder is one of the mostly used solid lubricant additives in high or low temperature conditions. The tribological behaviour of graphite nanosheets as an additive in paraffin oil was investigated by Huang *et al.*(2006) with a four-ball and a pin-on-disk tribotester. The layered structure is responsible for improvement of tribological performance and 1% was found to be an optimum concentration. Graphite as a macro-scale solid lubricant has been widely studied and has been used in industry for more than 40 years [Buckley *et al.*(1975), Ruan (1994)]. Additionally, previous tribological studies using graphite flakes have indicated formation of graphite scrolls at the tribological interface [Spreadborough (1962)]. These scrolls are favourable for decreasing the surface energy [Shioyama *et al.*(2003), Li *et al.*(2005)] and reducing friction in the sliding interfaces. It is well known that bulk graphite (a source of graphene) works the best in humid environments but fails to provide low friction and wear in inert, dry or vacuum environments [Bryant *et al.*(1964)]. The reason for this behavior is the intercalation of water molecules between the graphite sheets which allows easy shearing of graphite and provides low friction.

1.3.10.2. Graphene

Graphene is an extended honeycomb network of sp^2 -hybridized carbon atoms and the first example of a close-packed two dimensional (2D) crystalline material isolated in nature exhibiting extraordinary physical, chemical and mechanical properties. Since its successful preparation by mechanical cleavage from graphite in 2004 [Novoselov *et al.*(2004)], this paradigm 2D nanomaterial has rapidly risen to be one of the hottest stars in materials science due to its many exciting and unusual characteristics [Geim *et al.*(2007), (2009)]. Theoretically single sheet of graphene exhibits very high surface area i.e. $2630 \text{ m}^2.\text{g}^{-1}$. The ability to conduct heat and electricity are driven by π -electron structure. The graphene is believed to be the strongest material yet discovered. The strength of sp^2 C-C bond gives graphene some exceptional mechanical properties possibly better than any other material. The mechanical properties of graphene including intrinsic breaking strength of free standing monolayer graphene was measured by nano-indentation using AFM and it was reported that the defect free graphene has Young's modulus of 1.0 TPa and fracture strength of 130 GPa [Wei *et al.*(2009)]. From a tribological point of view, such extreme mechanical strength is highly desirable for wear protection.

Graphene being two-dimensional material offers unique friction and wear properties that are not typically seen in conventional materials. Besides its well established thermal, electrical, optical and mechanical properties, graphene can serve as a solid or colloidal liquid lubricant. Graphene as lubricant additive is gaining large interest because of (a) remarkable mechanical strength to improve the load bearing capacity, (b) high specific surface area for ease of chemical functionalization and dispersion, (c) excellent thermal conductivity to dissipate the heat from the contact area, and (d) weak van der Waals interaction between their lamella to reduce the friction under the tribostress. Its high chemical inertness, extreme strength and easy shear capability on its densely packed and atomically smooth surface are the major favourable attributes for its impressive tribological behavior. Since it is ultrathin even

with multilayers, it can be applied to nanoscale or microscale systems such as micro electro mechanical systems (MEMS) and nano electro mechanical systems (NEMS) with oscillating, rotating and sliding contacts to reduce friction and wear. The extreme mechanical strength of graphene suppresses the material wear. Lee *et al.*(2010) tested the mechanical properties of graphene and confirmed it to be one of the strongest materials ever measured. Secondly, graphene has been shown to be impermeable to liquids and gases [Bunch *et al.*(2008)], such as water or oxygen, thus slowing down the corrosive and oxidative processes that usually cause more damage to rubbing surfaces. All the properties mentioned above make graphene very attractive for demanding tribological applications to achieve low friction and low wear regimes.

The tribotests as a function of increasing load have shown that the lifetime of the graphene protective layer is shorter under higher loads. The lifetime in dry nitrogen decreases to a few hundred cycles for 5N load (or 0.56GPa) while under low load condition (i.e.1N) the graphene protection is more durable. The graphene protective layer at 1N load (Hertz contact pressure of 0.33GPa) was shown to last without replenishment as long as 6000 cycles before the flakes of graphene started to be pushed outside of the wear track, with complete removal of the graphene layer at around 14,000 cycles. Kim *et al.*(2011) have also investigated the micro-scale tribological behavior of multilayer graphene using atomic force microscopy technique and found lower friction values but graphene detached when sliding was performed under an applied load of 5 μ N for 100 cycles. Berman *et al.*(2014) have studied the macro-scale tribological properties of graphene dispersed in ethanol. The results indicate that graphene reduced the friction coefficient greatly but was instantly removed from the sliding surface under an applied load of 5N. Therefore, an intermittent supply of graphene was needed to ensure its presence throughout the whole test period. The graphene based lubricant additives are unable to sustain the load at extreme conditions under boundary lubrication regime which limits their potential application in the field of tribology.

1.4. Statement of Problem

The addition of AW/EP additives to base oil may reduce friction and wear, control energy losses, improve mechanical efficiency and increase longevity of machines. Metal dialkyldithiophosphates, particularly those of zinc dialkyldithiophosphates (ZDDP) are one of the most established commercial multifunctional additives since 1940s and exhibit antiwear, friction-reducing, antioxidant and extreme pressure lubrication properties. Increasing awareness about ecological system has raised serious concern about the use of ZDDP based additives, since it consists of zinc, sulphur and phosphorus which are hazardous for human health and aquatic life, and poisonous for the catalytic convertor in the engine system. On thermal decomposition, ZDDP deposits and leads to poisoning of catalytic converter, thus shortening the life of engine tool. In addition to this, antiwear additives containing heterocyclic compounds and ionic liquids also have huge amount of sulfur and/or halogen and phosphorous. Thus, high level of the halogen and sulphated ash, phosphorous and sulfur contents (SAPS) limit their exhaustive application in the automotive industries. At present several norms (API CJ-4, ILSAC GF-5, ACEA C) are available which strictly limit the SAPS (Sulfated Ash, Phosphorous and Sulfur) contents of additives. Hence, there is an emergent need to design the environmentally-friendly halogen-free low/zero SAPS lubricant additives which provide efficient lubrication to the engineering parts without compromising/damaging the interacting surfaces. In this context, we have to develop different categories of AW/FM additive to overcome the lacunae as discussed in the literature review.

1.5. Aims and Objectives:

A careful literature survey reveals that the need of hour is to develop some different categories of antiwear additives having low SAPS contents to meet the high lubrication performance of modern machines. To achieve this, many researchers have made an attempt to fully and/or partially replace the most fascinating ZDDP in lubricating oils by using heterocyclic compounds, organoborate, ionic liquids, ceramic nanoparticles and graphene based nanomaterials as antiwear additives. These materials have shown potential application in reducing friction and wear similar to ZDDP to some extent but have some limitations too. A lot of research has been made on the tribological properties of N-containing heterocycles and organoborate ester

alone but no one has studied the synergistic behavior between these two under lubricating conditions. In addition to this, a comparative tribological behavior of N-containing Schiff bases with their metal complexes didn't find any place in literature. There are several reports available on the use of bare and/or surface modified ceramic nanoparticles in this context but none of them deals with effect of varying particle size of the nanoparticles. In the recent era, invention of graphene has made revolution worldwide through their diversified applications in various fields. In this scenario, graphene based nanomaterials reflect their potential application in tribology but at only low load conditions.

To implement the conceived idea, the present work was undertaken where synergistic formulation of Schiff bases with organoborate ester, Copper (II) benzoylhydrazones, Stearic acid modified- $\text{CaCu}_{2.9}\text{Zn}_{0.1}\text{Ti}_4\text{O}_{12}$ nanoparticles (SCCZTO) and TiO_2 -reinforced-B-N-codoped-MRG nanomaterials were prepared and their tribological properties were evaluated.

Main objectives of the present investigation are-

- To synthesize S, P-free Schiff bases derived from 4-aminoantipyrine with substituted aldehydes with a view to investigate their synergistic interaction with organoborate in paraffin base lube as antiwear additives.
- To synthesize substituted benzoylhydrazones ligands and their copper (II) complexes, elucidate their structure by various analytical and spectroscopic techniques and evaluate the efficiency of the synthesized additives as antiwear additives.
- To synthesize and characterize three different particle size Stearic acid modified $\text{CaCu}_{2.9}\text{Zn}_{0.1}\text{Ti}_4\text{O}_{12}$ nanoparticles with a view to investigate effect of particle size on antiwear properties of base oil.
- To synthesize and characterize B,N-codoped-MRG and TiO_2 -reinforced-B,N-codoped-MRG nanomaterials in order to study the effect of B,N-codoping and TiO_2 reinforcement on tribological properties of base oil.

- To explore the action mechanism and tribochemistry of blends of these additives using Energy Dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS) techniques.
- To analyze the surface morphology of lubricated wear track using Scanning Electron Microscopy (SEM) and contact mode Atomic Force Microscopy (AFM) techniques.
- To perform quantum chemical calculations based on density functional theory for correlation of the experimentally observed data with structure of the additives.