1.1. Tribology

The term tribology was coined by Dr. H. Peter Jost in the year 1966 in England. It is derived from the Greek word, “tribos”, meaning “rubbing” and “*logus*” means “the study of” therefore, Tribology is the study of science and engineering of interacting surfaces in relative motion [Bhushan (2001a)]. It generally deals with lubrication, control of friction and prevention of wear of the rubbing surfaces under load. In modern industry, tribology has significant importance since it is responsible for reliability, performance and durability of moving machine components in all machinery domains. To understand the subject and its application to machine elements, in depth knowledge in numerous areas such as chemistry of lubricants, physics of fluid flow, surface topography, contact mechanics, material science and mechanical engineering is required which makes it multidisciplinary. Actually, adequate application in this domain can lead to massive savings estimated as 50 times the research cost. 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 the force that resists relative motion of one body over another under the applied load. It results into energy loss of the system; high friction causes high energy loss and vice versa. The friction in our daily life can be experienced 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 of tribology are Amontons (1699), Coulomb (1785), Towers (1884), Reynolds [(1986), (1988)], Block (1937), Bowden and Tabor [(1954), (1964a,b)].

Amontons proposed the well-known laws of friction:

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

$$F_f \propto F_N \quad 1.1$$

$$F_f = \mu . F_N \quad 1.2$$

Where μ stands for coefficient of friction; Ff is frictional force and FN is applied normal load. The coefficient of friction is unit less parameter.

- **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 causes removal and deformation of material from the rubbing surfaces under the applied normal load. It may lead to material loss to an extent that sometimes replacement of the affected part is required [Bhushan (2001b)]. It is controlled by the influence of environment, properties of material like surface roughness, operating conditions, mechanical strength, hardness and shape of interacting areas. Wear can occur due to mechanical failure of highly stressed interfacial zone or influenced by environmental factors. Various types of wear are observed.

1.1.2.1. Adhesive wear

Bonding or cold weld formation occurs between the opposing asperities on interacting surfaces. Adhesive wear is the first stage of wear and does not lead directly to any loss of material from the counter bodies. The welded section may be work hardened, strengthened and shearing may not occur on asperity junction. The high load applied on the contacting asperities deforms them and adhere, forming micro-joints.

1.1.2.2. Abrasive wear

Abrasive wear is normally related with material removal when a hard sharp particle contacts with comparatively less hard (soft) material**.** Grinding of material is a good example where abrasive grains remove material from the softer surface by cutting action. Abrasive action thus, depends on relative hardness of sliding materials resulting into formation of an abrasive groove on the weaker surface and grooved volume is removed during sliding. It may be classified as two-body or three-body wear depending upon the role of worn out or dust particles in affecting phenomenon of wear [Dorinson (1985)].

1.1.2.3. Corrosive or Chemical Wear

This type of wear loses material by chemical reaction with lubricant /environment. The chemical reactivity on the metal surface combined with rubbing action that scraps off metal results in chemical wear. A lubricated system contains various chemical agents such as carbon dioxide, oxygen, water, naturally occurring sulphur compound, oxoacids of S and N, acidic oil oxidation products and antiwear /extreme pressure additives containing high SAPS. All of these aforesaid agents have a tendency to chemically attack the fresh metal surface formed by rubbing action.

1.1.2.4. Surface Fatigue Wear

Rolling and sliding conditions produce surface fatigue under high stress. It is characterized by pitting or spalling of the surfaces. 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.

1.1.3. Lubrication

The word "lubrication" stands for the introduction of foreign substance i.e. lubricant between two or more moving surfaces which prevents direct metal-metal contact and reduces the friction and wear. The lubrication is also required to achieve some other purposes such as dissipation of heat from the contact surfaces, inhibition of corrosion, subtraction of wear particles from the contact zone etc. [Dorinson (1985) and Jones (1983)]. Poor lubrication is responsible for energy as well as material losses. The lubrication plays important role in manufacturing processes and machine components. Besides this, in human body e.g. artificial joints, hip replacements etc. [Grupp *et al*.(2010) and Davim *et al.*(2010)], the lubrication is equally important. The revolution in technology that has brought changes in machine designs, recommended use of low-weight metal tools instead of heavy-weight metal and put strict regulation towards protection of environment by reducing the emissions etc. There are the challenges for proper design and development of energy efficient lubrication.

Viscosity of lubricant, applied normal load and speed are important parameters that control different lubrication regimes. These regimes can be understood on the basis of

Stribeck curve which depends on the thickness of lubricant film between the sliding surfaces. The film thickness is mainly determined by bearing parameter which is given by [(speed x viscosity)/load]. The changes in coefficient of friction vs. bearing parameter are shown in the Figure 1.1, Stribeck curve [Husban (1955) and Wang *et al.*(2006)]. On the basis of lambda ratio which is the ratio of minimum film thickness and composite roughness, lubrication regimes may be divided into three regimes such as boundary, mixed and hydrodynamic.

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

where, h = Minimum film thickness

σ^*= Composite roughness

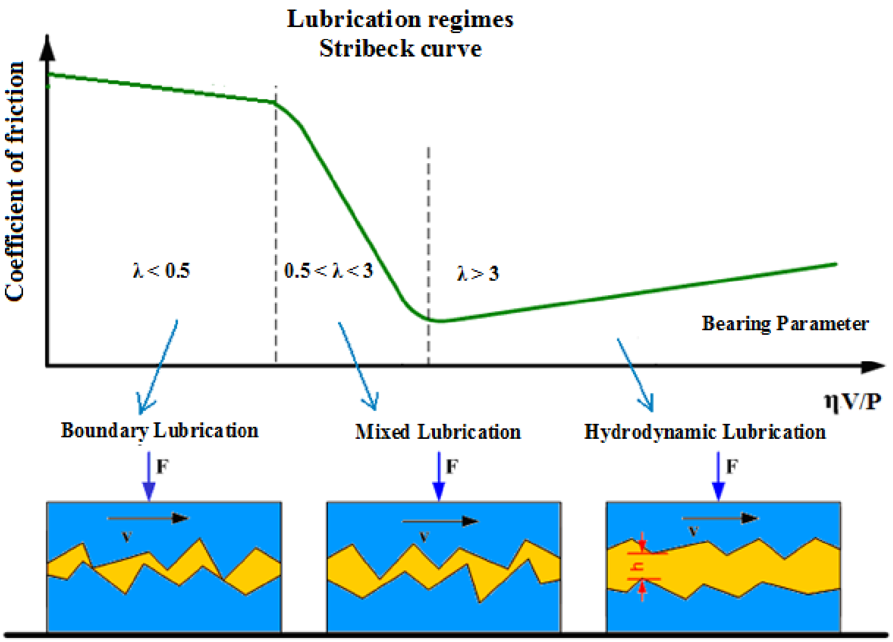


Figure 1.1. Stribeck curve: Dependence of the friction coefficient on viscosity, speed and load for a lubricated sliding system.

1.1.3.1. Hydrodynamic Lubrication

In hydrodynamic lubrication, lubricant thick film is preventing any direct asperity-asperity contact and whole load is carried by the lubricant film. Hence, in this regime, low friction and negligible wear are found. This thick film of lubricant prevents contacts of load carrying surfaces to each other, so that there is apparently no contact between the tribo-surfaces [Myshinn *et al.*(1997)]. In hydrodynamic lubrication the value of lambda is greater than 3.0.

1.1.3.2. Boundary Lubrication

The term boundary lubrication was coined by Hardy *et al*.(1922) to describe friction and wear reduction between sliding surfaces. Boundary lubrication is an outcome of the combination of low viscosity, low velocity and high load. The fluid film thickness is too much thin, almost negligible under boundary lubrication regime therefore; considerable contacts occur between the interacting surfaces and the whole load is supported by asperity-asperity contact. The value of lambda ratio is less than 0.5 in case of boundary lubrication. The regime is unfavourable since it provides high coefficient of friction causing massive loss of energy along with wear (debris of material) from the sliding surface [Myshinn *et al.*(1997)].

1.1.3.3. Mixed Lubrication

This lubrication regime is an intermediate between hydrodynamic lubrication and boundary lubrication. The lubricant film is capable to separate two contact surfaces at only some points while some asperities are in contact to each other. Due to the contact of asperities of tribo-surfaces, friction is relatively less than boundary lubrication and much more than hydrodynamic lubrication [Myshinn *et al.*(1997)].The lambda value for this lubrication regime lies in between 0.5-3.0.

1.2. Lubricants

Any substance which reduces wear and friction when incorporated between two moving surfaces, is called lubricant. The main role of a lubricant is to dissipate heat and thus to increase mechanical efficiency. Besides this, it inhibits the entry of dirt and moisture between the moving parts from environment. A lubricant, in general, should possess low volatility, excellent thermal and oxidative stability, good fluidity at low temperature, non-corrosiveness and high viscosity index [Kuratomi *et al*.(2009)]. On the basis of physical and chemical properties, the lubricants may be classified as follows:

1.2.1. Liquid Lubricants

The good liquid lubricant should have low viscosity and high viscosity index, in general, but it must be viscous enough to maintain a lubricant film under operating conditions. The liquid lubricants can bear wide range of temperatures, dissipate heat from asperities contact points and also work as cleaning agents. The liquid lubricants are divided into different categories as follows-

1.2.1.1. Vegetable oil

Vegetable-based oils are triglycerides of higher fatty acids or natural esters which are extracted from plants. Their cold temperature properties, esterification and low oxidation stability are their major disadvantages compared to petroleum-based oil. Vegetable oils are not toxic to the environment, biodegradable and have good lubricity, high viscosity index and high flash and fire points. Vegetable oils/fats have a property called “oiliness” due to which these are adsorbed on metallic surfaces. Consequently, friction coefficient is reduced and load carrying capacity is enhanced. Some important vegetables oils used as lubricants are castor oil, olive oil, coconut oil, rapeseed oil, palm oil, cotton seed oil etc.

1.2.1.2. Animal oils and fats

Animal oils are also used as lubricants such as tallow oil, lard oil, neat foot oil, whale oil, sperms oil, seal oil etc. These oils are unable to bear high temperature due to their decomposition.

1.2.1.3. Mineral oils

Mineral oils have replaced vegetable and animal oils as lubricants because these are inexpensive, easily available, reusable and highly stable under severe conditions. Paraffin oil is colorless, odourless, transparent mineral oil composed of alkanes and cycloalkanes.

1.2.1.4. Synthetic lubricants

Synthetic oils are oily liquids which are not found naturally and are not derived from refining process of crude oil. There are some important examples of synthetic oils: polyalphaolefins (PAOs), polybutenes, alkylated aromatics, aliphatic diesters, polyesters, polyols and polyalkyleneglycols, silicones, fluorocarbons etc. These oils have high viscosity index (120-170), low volatility and good oxidation stability. These oils are beneficial to mineral oils due to reduced maintenance, better reliability, safer operation, improved energy efficiency and applicability in wider operating temperature range. These oils are designed in such a way to avoid presence of sulphur, nitrogen and other elements which encourage sludge formation. Synthetic oils are pure having uniform structure and they may be designed to work in applications in which refined oils cannot work. Due to uniform structure these oils help to resist thinning in heat and thickening in cold over a system's operating temperature range. Silicones are generally used for low temperature lubricating applications. Fluorocarbons are heat resistant, chemical resistant and are not easily oxidised at high temperature.

1.2.2. Semi-solid Lubricants

Semi-solid lubricants consist of a soap dispersed in liquid lubricating oil. Greases and Vaseline are the most common examples of semi-solid lubricants. Greases are typically used in those areas where continuous supply of oil cannot be retained. Poor heat dissipation is the major drawback of greases. Besides this, if once contaminants like dust, dirt and wear debris enter into grease, it is very difficult to separate them out.

1.2.3. Solid Lubricants/dry lubricants

These lubricants are basically solid materials/solid thin films which reduce friction and wear by separating two rubbing surfaces under boundary conditions. These are used either in dry condition or in water/oil. At very high temperature solid lubricants can be used. The most common solid lubricants such as graphite, MoS_2, WS_2, ZnO, ceramic coatings are being used as antiwear additives. In general, solid lubricants must have high mechanical strength, low shear strength, high thermal and chemical stability and lamellar structure.

1.2.4. Gaseous Lubricants

Gaseous lubricants like air, oxygen, nitrogen, helium etc. are used in aerodynamic and aerostatic lubrication under wide range of temperature. When the temperature increases the viscosity of gaseous lubricants also increases. This is main advantage of gaseous lubricants over liquid lubricants. However, the storage of gaseous lubricants is the major challenge.

1.3. Lubricant Additives

Lubricant additives are the compounds/materials incorporated in to the lubricant (base oil) in small amount to modify its different properties [Ludema (1996)]. Various types of lubricants and oil additives have been reported to improve the life of the machine components. Lubricant additives have been classified into two categories on the basis of their chemical performance: chemically-inert and chemically-active. Chemically-inert additives are viscosity modifiers, foam inhibitors, and pour point depressants, modify the physical properties of the base oil while the chemically-active additives such as antiwear, extreme pressure and corrosion inhibitors improve the tribological properties of base oil. On the basis of chemical compositions, AW/AF/EP lubricant additives are further divided into the following types: 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. Details of these compounds are given below:

1.3.1. Sulfur Compounds

These types of compounds were first used during the industrial revolution to enhance the performance of machines. The main functions of sulfur-containing additives are to improve the antiwear, extreme pressure and antifrictional properties of lubricants. Sulfur containing EP/AW/AF additives namely sulfurized hydrocarbons, sulfurized fatty oils, sulfurized synthetic esters of short chain alcohol, animal or vegetable fatty acids, sulfurized ester of glycol, thioglycollic acid ester, sulfurized terpenes, alkyl or benzyl monosulfide and disulphide are being used [Shao *et al.*(2005), Otto *et al.*(1993) and Cao *et al*.(2000)]. The mechanism of the sulfur containing compounds as EP/AW additives was proposed by Davey *et al*.(1957). According to the proposed mechanism, sulfur compound gets decomposed (monosulfide or disulfide) and physically/chemically adsorbed on the metal (iron) surface forming an iron sulfide film which prevents direct metal-metal contact thus reducing friction and wear. Therefore, monosulfide forms the iron sulfide film after adsorption while the disulfide also forms the iron sulfide film through iron mercaptide. Forbes *et al*.(1973) found that, there was no evidence that pure iron sulfides were the load-carrying layers and these layers were to be mixtures of iron-sulfur, carbon-oxygen and their oxides. Dacre *et al.*(1982) told that antiwear property depends on the physisorption of mercaptide. Hiley *et al*.(1981) using polysulfide, stated that the antiwear and antiseizure properties increase with increasing sulfide component.

The polar interaction and chemical reactivity between the surfactant and iron sulfide film play a major role. It has been observed that the EP efficiency of sulfur containing additives depends on both, formation of the sulfide film and strong chemisorption of surfactant [Spikes *et al.*(1973)]. The reaction between worn surfaces and lubricant with appropriate additives leads to the formation of effective tribochemical films. Both iron sulfide and ferric oxide generated on the worn surface, are effective in EP lubrication, Figure 1.12 [Godfrey (1962)]. Nakamaya *et al*.(1981) suggested that before conducting all tribological tests optimisation of sulfur concentration is necessary for better results. Rowson *et al*.(1981) have found that at 30^{o}C sulfur as an additive is detrimental to the pitting performance but at 100^{o}C, it is beneficial. Najman *et al*.(2003) using XPS and XANES spectroscopy have observed that the composition of thin film in the presence of organosulfurs depends on the applied load. They have given chemistry of both thermo-oxidative and tribochemial films made from the organosulfur additives. They got sulfate in the non-contact areas, tribofilms of iron disulfide and sulfate are formed under operating conditions.

The variety of organic sulfur compounds such as xanthates [Agrawal *et al*.(1980), (1981)], dithiocarbamates [Mamman *et al*.(1981), (1983), (1984)], isothioamides [Kuliyev *et al*.(1983), (1988)], isothiobiurets [Trofimov *et al*.(1999), (1988)], phenylacetothioamides [Kuliyev *et al*.(1983)], thioamides [Kuliyev *et al*.(1989a)] thioacetamides [Kuliyev *et al*.(1989b)], dialkanoylacetamides [Croudace *et al*.(1990)], alkano-amidosulfides [Bhattacharya *et al*.(1995)], etc. have been reported as AW/EP additives.

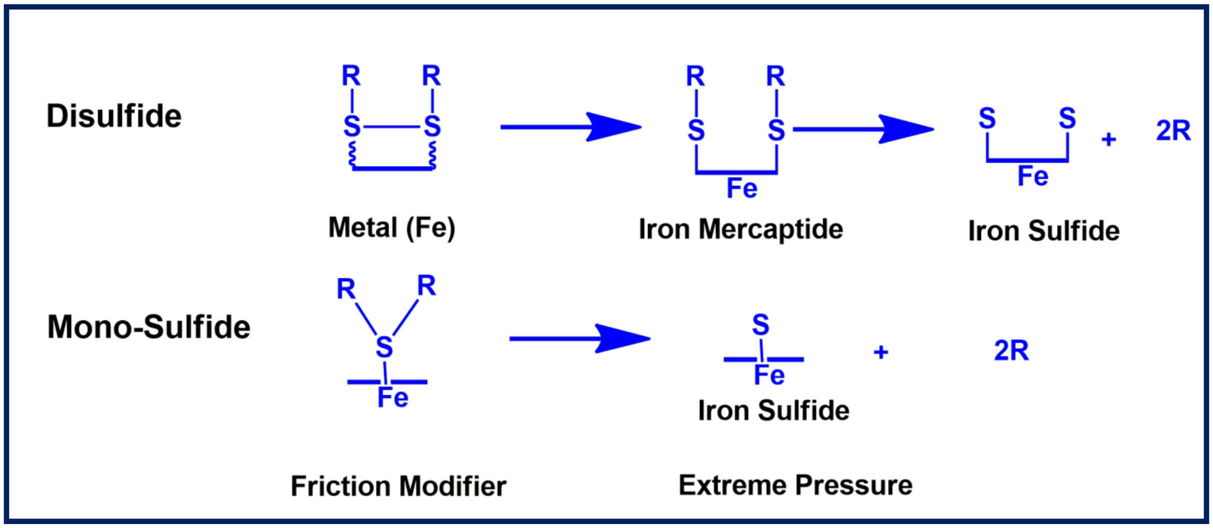
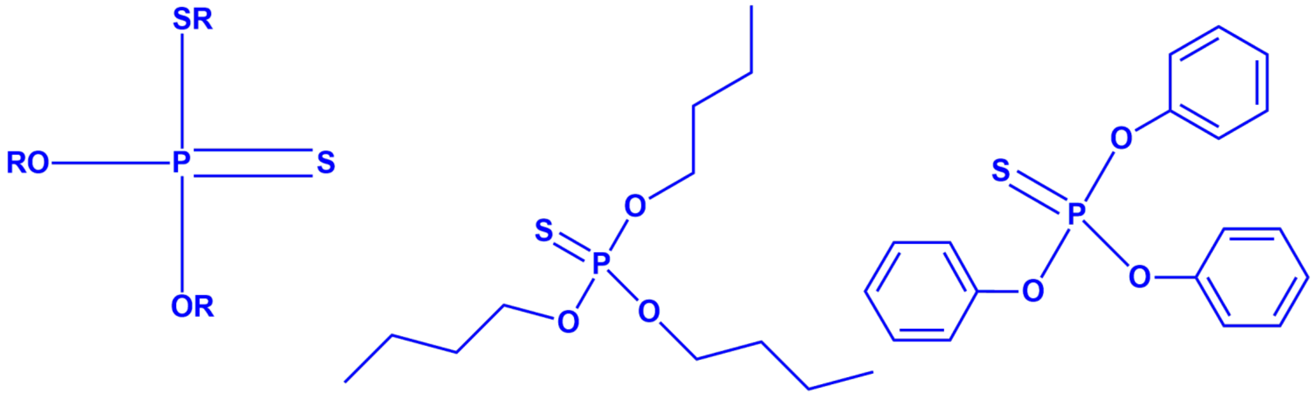


Figure 1.2. Mechanisms of formation of iron sulphide tribofilms from sulfur compounds adsorbed at iron surface. Adapted from [Godfrey (1962)]

1.3.2. Phosphorus Compounds

A number of phosphates [Najman *et al*.(2002) and Rossi *et al*.(2006)] and dithiophosphates [Najman *et al*.(2004a,b) and Sharma *et al*.(2003)] have been investigated for possible application in tribology, Figure 1.3. Zinke *et al.*(1997) studied the antiwear behavior of phosphorous and sulfur containing compounds by replacing sulfur with oxygen atoms and varying the length and branching of alkyl or aryl groups. They recognized that an increased thermal stability of phosphorus-containing compounds maintained good performance for wide range of temperature but some thermal instability is necessary to allow the decomposition of compound to react and form protective tribochemical films. Sarin *et al.*(1993) compared the antiwear, extreme pressure and antioxidative properties of a series of *O,O'*-dialkylphosphorodithionic disulfides $(RO)_2P(S)S\text{-}SP(S)(RO)_2$ and zinc dialkyldithiophosphate. They found that *O,O'*-dialkylphosphorodithionic disulfide show antiwear properties comparable to commercial zinc dialkyldithiophosphates [Heuberger *et al.*(2008)]. The antiwear performance of other dithiophosphate disulfide compounds was also studied. Disulfide groups have capability to provide better EP properties as compared to normal dithiophosphates. Heuberger *et al.*(2008) have explored the reactivity of alkylated phosphorothionates, such as triphenylphosphorothionate (TPPT) with steel surfaces.



Ashless dithiophosphate Tributyl thiophosphate (TBT) Triphenylphosphorothionate (TPPT)

Figure 1.3. General structure of phosphorous based additives

They found that the cleavage of P=S double bonds occurs at high contact pressure and under the frictional heat and sulfur reacts with iron forming iron sulphide [Zeng *et al*.(2004)]. Filippo Mangolini *et al.*(2009) explained that the thermo-oxidative behaviour of phosphorous containing antiwear additives at high temperature may contribute to understand the mechanism of thermal film and tribofilm formation on metal surfaces. They have explained that the thermo-oxidative reaction of TPPT in lubricant oil solution starts with the decomposition of the P=S bond, leading to the formation of triphenyl phosphate. Further, a group of researchers have studied the 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*-dialkylphosphorodithioate, alkylamine salt of dialkyldithiophosphoric acid, dialkyl hydrogenphosphate [Bansal *et al*.(2002)].It was observed that at temperatures lower than 373K physisorption and at temperature higher than 373K chemisorption takes place. This could be led by P=S bond scission to make trialkylphosphite, which then, in turn, undergoes P–O bond scission to produce alkoxy groups.

1.3.3. Nitrogen Compounds

From last several decades, N, S and O heterocyclic compounds are being used as antiwear and friction modifiers [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) and He *et al*.(2002)]. Heterocyclic compounds (Figure 1.4) have a tendency to get adsorbed on steel surfaces forming a tribochemical film. Ren *et al*.(1993) observed that the antiwear properties increase with increasing the number of nitrogen atoms. The benzotriazole and its derivatives are the most effective antiwear additives since N has ability to coordinate with Fe atoms. XPS examination of these N containing heterocyclic compounds has shown the same spectra for surfaces rubbed in solution and dipped in solution without rubbing.

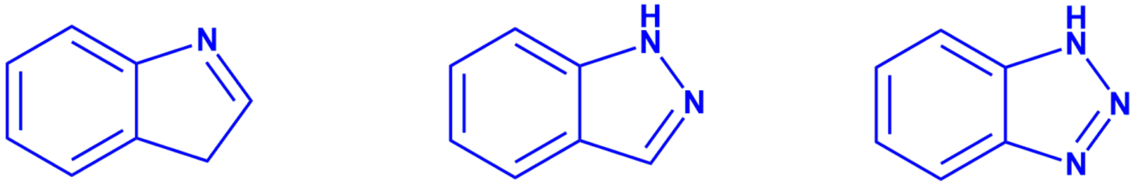


Figure 1.4. Molecular structures of N-heterocyclic compounds. Adapted from [Mtsumoto *et al*.(2003)]

Therefore, these N-compounds do not show chemically changed under operating conditions. Triazine-dialkyldithiocarbamate, Figure 1.5 and other derivatives of heterocyclic compounds have been used as multifunctional additives in both mineral and vegetable base oils [Ren *et al.*(1993), (1994) and Huang *et al.*(2004a,b,c)]. Small concentrations of triazinederivatives of dithiocarbamates added in mineral oils decrease wear of interacting surface [Huang *et al.*(2004a)] while the same additives increase wear in vegetable (rapeseed) oils [Xu *et al*.(2000) and Zhan *et al*.(2004)].

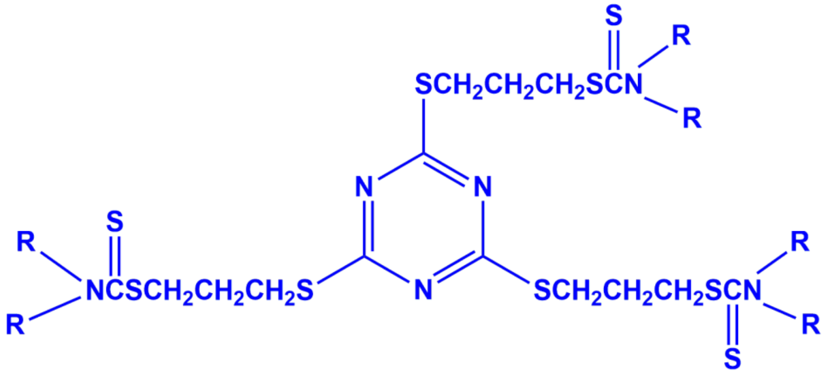


Figure 1.5. Chemical structure of triazine-dialkyldithiocarbamate

Organic compounds have a tendency to get adsorbed on metal surfaces through their lone pair or by π electrons of double-bond in aromatic moieties. Electron transfer occurs from polar (donor) groups to empty d-orbital of the metal surfaces. In the case of nitrogen containing heterocyclic compounds, saturated or unsaturated covalent bonds can be formed in the process of such chemisorption, thus, enhancing antiwear and anticorrosive properties [Zeng *et al.*(2007b)]. Nitrogen-carbon heterocyclic compounds are being used in lubricant industries as both metal passivators and effective corrosion inhibitors [Wu *et al.*(2009a)]. The chelating tendency of these compounds to form insoluble diffusion barriers on oxidized surfaces of metals, prevents metal reaction and dissolution. Benzotriazole, benzthiazole, benzimidazole, tetrazole, pyridazole, other nitrogen containing heterocycles and their derivatives have a tendency to prevent corrosion of copper, nickel, iron and other metals [Babic *et al*.(2005), Wu *et al*.(2009b), and Waynick *et al*.(2001)]. Schiff bases are frequently used because they improve antioxidant [Tang *et al*.(2007) and Chen *et al*.(2003)], antiwear [Agarwal *et al*.(1992), McHuge *et al*.(1965) and Ishchuk *et al.*(1994)], anticorrosion properties [Ju *et al*.(2008) and Asan *et al*.(2006)] and high thermal stabilities [Mohamed *et al*.(2003)]. It is required to develop low SAPS, environment friendly multifunctional lubricating oil additives.

1.3.4. Dialkyldithiocarbamate Complexes of Metals (MDTCs)

Dialkyldithiocarbamate complexes of several metals are being used as multifunctional lubricant additives. The metal and metalloids complexes of dithiocarbamates, for example [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) and Grossiord *et al*.(1998a)] have been investigated. Molybdenum dialkyldithiocarbamates (MoDTC) additives are known for their antioxidant, friction modifier and extreme pressure properties. The formation of low friction tribofilms from MoDTC-containing lubricants was the main issue of numerous studies [Grossiord *et al*.(1998b) and Morina *et al*.(2006a,b)]. It was observed that on the sliding surface MoDTCs decompose forming MoS_2 nanocrystals [Grossiord *et al*.(1998a)]. It was investigated by Barros *et al.*(2005) that under operating conditions presence of ZnDTP additives on worn surfaces get decompose and forming MoS_2. The proposed mechanism of MoS_2 formation in the presence of ZnDTP is as follows, Figure 1.6:

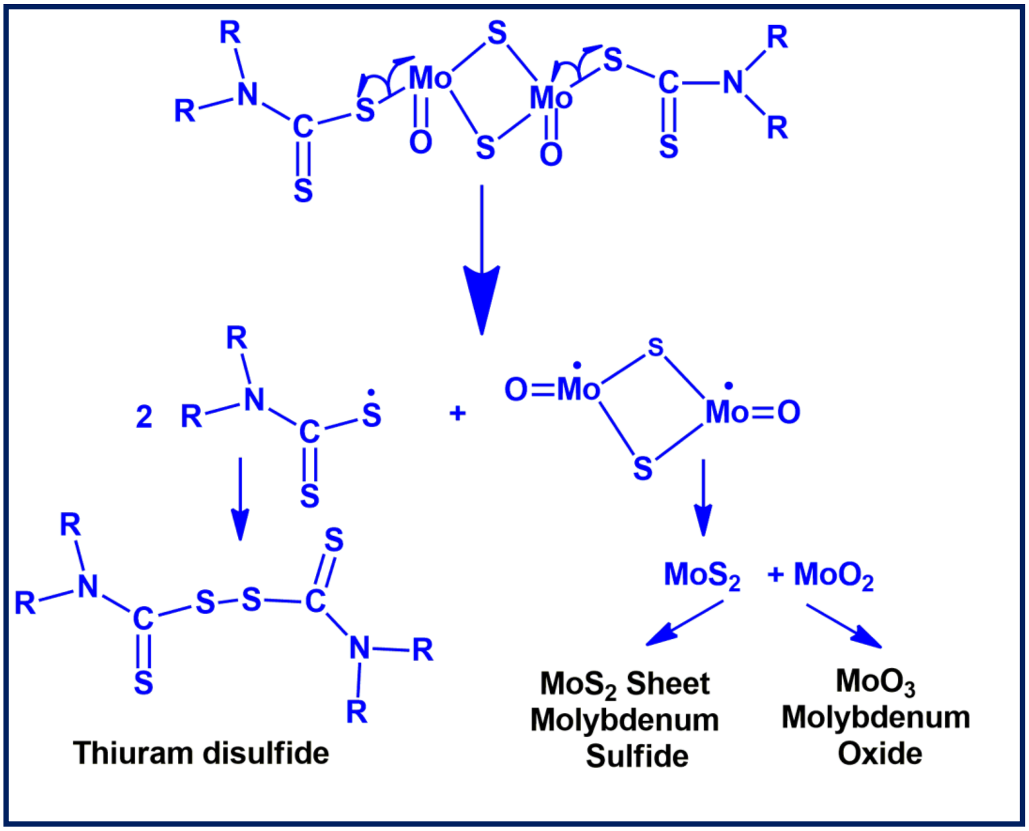


Figure 1.6. Chemical processes leading to MoS_2 formation from MoDTC. Adapted from Barros *et al*.(2005)

They advocate that the initial step towards MoS_2 formation is via electron transfer from the Mo–S bond in MoDTC to make three free radicals, one corresponding to MoO_2S_2 radical and the other two R_2NCS_2 radical. In the third step MoO_2S_2 radical decomposed into MoS_2 and MoO_2, which may further oxidise in the presence of O_2 form molybdenum, and the recombination of R_2NCS_2 radical forming thiuram disulfides. How much amount of MoS_2 formed on the rubbing surfaces, depends on the ZnDTP concentration present in the lubricant [Morina *et al.*(2007)]. These MoS_2 moieties assemble and form a lamellar sheet, which spreads over the asperity tips and enhances the reduction of friction. These lamellar sheets are made up of strong covalent bond between atomic species but there is only a very weak van der Waals interaction between lattice layers. These weak van der Waals forces between sheets are easily overcome by shearing of the molecule. These have a tendency to enhance the friction reducing properties of lubricants.

1.3.5. Dialkyldithiophosphate Complexes of Metals (MDDPs)

Dialkyldithiophosphate complexes of metals, MDDPs have been used in lubricating oil due to their multifunctional properties such as 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), and Rowe *et al*.(1967a,b)] are being used as multifunctional lubricant additives. Among all MDDPs, zinc dialkyldithiophosphates (ZDDPs) are the most widely used multifunctional additives [Born *et al*.(1992), Martin *et al*.(1984), Sheasby *et al*.(1992), Wu *et al*.(1997), George *et al*.(1979), Spedding *et al.*(1982) and Watkins (1982)].

Zinc dialkyldithiophosphates (ZDDP) are the well-known EP/AW additives for engine oil [Lin *et al*.(2004), Hu *et al*.(2003) and Hartley *et al*.(2002)]. Figure 1.7 shows the chemical structure of substituted dialkyldithiophosphates. A lot of literature survey reveals the action mechanism of ZDDP, including thermal decomposition [David (2002), Moerina *et al*.(2006), Willermet *et al*.(1995), Spikes (2004), Fuller *et al*.(1998) and Rowe *et al*.(1967b)], hydrolytic [Spedding (1982)], and oxidative [Mitchell (1984)] mechanism. Dorinson (1979) and Rounds (1981) proposed a theory that sulfur and phosphorus in ZDDP react with a rubbing surface, forming a tribochemical film. Many discussions have focused on the "frictional polymer theory", derived from the thermal decomposition investigated by Feng *et al.*(1960). The boundary lubrication film is formed on a steel surface through the formation of frictional polymer. It was also discussed by Brazier *et al*.(1967). Then, Coy *et al*.(1975) and Bird *et al.*(1980) favoured the polymer formation but they did not explain its chemical structure. Afterwards, Barcroft *et al*.(1982) brought the "double function theory" into the aforesaid frictional polymer theory on the basis of thermal decomposition mechanism by means of a "hot wire method" using three different types of ZDDPs. Their work exposed that as temperature rises the thermal decomposition takes place and ZDDP progressively forms the polymer film on both steel surface and also on surfaces of other contacting materials [Martin *et al*.(1996)]. This work also proved that the composition of developed polymer film is temperature dependent. Moreover, under severe lubrication conditions, it further decomposes due to frictional heat and forms iron sulfide and iron phosphate films [Martin (1999)]. Therefore, the "frictional polymer theory" is one of the most capable mechanisms of the ZDDP action. The major role of this polymer film is to avoid wear and then decompose over wide range of temperature to form the iron sulfide or iron phosphate, which help in preventing seizure. It was found that antiseizure or antiwear behaviour of ZDDP depends on structure and chain length of alkyl groups. In general, ZDDP reduces the wear due to tribofilm formation (50-100 nm thick) on rubbing surfaces [Barnes *et al.(*2001), Sheasby *et al*.(1991) and Minfray *et al*.(2008)] under boundary or mixed lubrication conditions. Surface analysis of worn surfaces by the X-ray Photoelectron Spectroscopy (XPS) demonstrates that the tribofilms are composed of a combination of zinc and iron short chain (ortho or pyro) phosphate glass with iron sulfides precipitates [Barros *et al*.(2003) and Minfray *et al*.(2004)].

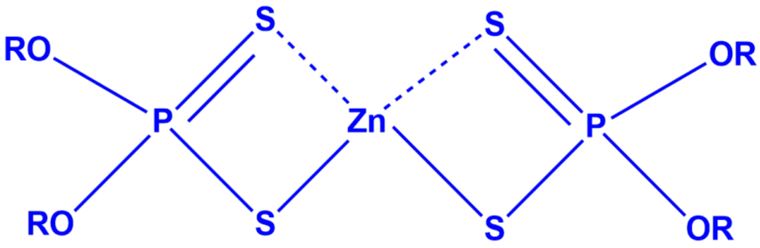


Figure 1.7. Chemical structure of dialkyldithiophosphate

As discussed above, the most commonly used additives ZDDPs with high SAPS (sulphated ash, phosphorous and sulfur) content form ash which consists of tiny metallic particles. Since, these have large amounts of sulfur, phosphorus and zinc which damage the environment directly as well as poison the exhaust catalysts and decrease the life of the emission system, international norms are available which limit the concentration of phosphorus and sulfur in engine oils, therefore the use of ZDDPs is controlled [Lin *et al*.(2004) and Morina *et al*.(2006b)].

1.3.6. Chlorine containing Compounds

These compounds are known for their antiwear and extreme pressure properties [Furey *et al*.(1973) and Gong *et al*.(1990)]. Kotvis *et al.*(1991) and Crumer *et al.*(1994) because they interact with iron surface forming iron chloride *in situ* under operating condition. The major drawback of chlorine containing additives is that they damage the environment and also affect the health. Therefore, chlorine-containing additives are not better option for modern lubricants.

1.3.7. Boron Compounds

Boron compounds are well known for their tribological behaviour. From the last decade research on boron containing additives has considerably increased. Particularly, boron compounds have been widely studied as boundary lubricating oil additives, surface coatings and solid lubricants [Kimura *et al*.(1999), Li *et al*.(2010), Klepper *et al*.(2010) and Wu *et al*.(2006)]. Organoboron compounds are capable of acting as friction modifiers, antioxidants, corrosion inhibitors and effective antiwear additives [Hu *et al*.(2000a), Liu *et al*.(1994), Herdan (2000), Zhang *et al.*(1999a) and Shen *et al*.(2000)]. Boron compounds have a tendency to form glassy structures in a similar manner to that of ZDDP but with different temperatures [Feng *et al*.(1963)]. It is well known that crystalline or amorphous boron, boron nitride and metal boride are very hard in nature.

Borates are being used as lubricant additives because these show wear resistance and friction-reducing properties [Adams (1977), (1978), Baldwin (1977), Dong *et al*.(1994) and Kreuz *et al*.(1967)]. The low toxicity and pleasant odour make them special for replacement of sulfur and phosphorus-containing additives [Kreuz *et al*.(1967)]. There are numerous kinds of borate additives which have been studied for their tribological properties. Potassium borates have been reported for their extreme pressure properties [Adams (1977), (1978)]. The micellar calcium borates have been reported to possess capability to interact with other common additives [Grossiord *et al.*(2000), Martin *et al*.(2000), Varlot *et al*.(1999) and Normand *et al*.(1998)]. Aforesaid additives form a thin amorphous film of borate glass under boundary lubrication condition. This tribofilm prevents direct metal-metal contact and reduces wear and friction due to its unique rheological properties. The major problem of inorganic borates is their low solubility in the base oil. Kreuz *et al.*(1967) have observed that the tribenzylborate ester in both, mineral and ester oils improved the load carrying and extreme pressure behaviour. Borate esters have capability to form a non-sacrificial film [Feng *et al*.(1963)]. It was observed that the S-containing additives form iron sulphides FeS_x but boron did not attack directly on iron surface. It was observed that the tribofilm was consisting ferrous oxide, boric acid and an organic phase. The borate esters are not stable in air and rapidly hydrolyze to make boric acid. Some reports are available stating higher stability of nitrogen containing borate esters [Yao (1997) and Zheng *et al*.(1998)]. These additives also produce tribofilm containing boron nitride and improve the antiwear performances at a higher load. Excellent antiwear, friction reducing and load-carrying properties of ferrous octoxyborates may be due to the formation of iron borides (FeB) in the tribofilms [Hu et al.(2000b)]. Finally, Erdemir *et al.*(1991a,b) reported the lubricating effect of self-formed boric acid on rubbing surfaces containing boron (boron, boron oxide). The organic borates are good candidates for engine and gear box lubrication, since they are soluble in base oils. However, their mechanism of action for their tribological properties is not clear. Some authors describe the tribological properties of borate glass for their particular rheological properties. On the other hand, some reports claim that the friction-reducing properties are observed due to the formation of boric acid. Besides this, abrasive nature of boric acid is also known. Choudhary *et al*.(2002) have analysed the tribofilm and found that the film is very hard, amorphous, 100-200 nm thick, and it consists of boric and ferrous oxide [Spikes (2008)]. Papay *et al*.(1998) have studied both wear and friction properties of different triborate esters. It was observed that all the tested additives possess a tendency to reduce wear and friction but the compounds with longer chains performed better. It was also observed that hydrolytic stability of borate esters improved with increasing the alkyl chain on the nitrogen atom of the additive. The hydrolysis of borate esters is shown in Figure 1.8.

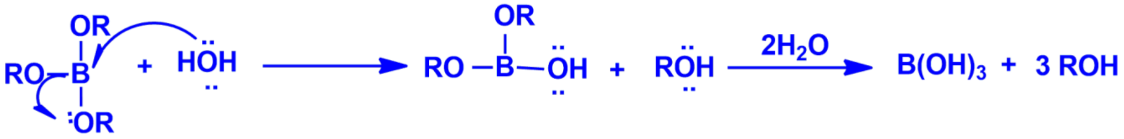


Figure 1.8. Hydrolysis of borate esters, adapted from Kreuz *et al*.(1967)

A lot of work has been done to control the hydrolysis of alkylborates: (i) Use of bulky groups like phenols, which create hindrance and prevent hydrolytic attack at the B—O bond, (ii) Use of amines which may be coordinated to boron atoms and control hydrolysis [Kreuz *et al*.(1967)]. Borate esters with mercaptobenzothiazole and dithiocarbamate have been studied for their antiwear properties. Boron and sulfur containing compounds especially borated dithiocarbamates show superior antiwear behaviour [Zhang *et al.*(1999a,c)]. Kapadia(2007) have compared the tribofilm properties of ZDDP and boron based additives in rolling-sliding contact at 100 °C by using optical interferometry and they observed that boron compounds form a tribofilm with the thickness of (~180 nm) similar to ZDDP. The levels of diffusion of boron on the worn surface have been detected using SIMS. In the moist atmosphere, oxide of boron (B_2O_3) reacts with moisture to form boric acid (H_3BO_3) which works as a solid lubricant.

Lubrication performance of boric acid is directly related to its triclinic crystal and lamellar structure. Boron, hydrogen and oxygen are closely packed and bonded to each other by covalent bond, there are weak Vander Waals interactions between the layers, Figure 1.9. These weak interactions support sliding of one layer against the other that promotes lubricity [Lovell *et al.*(2006)].

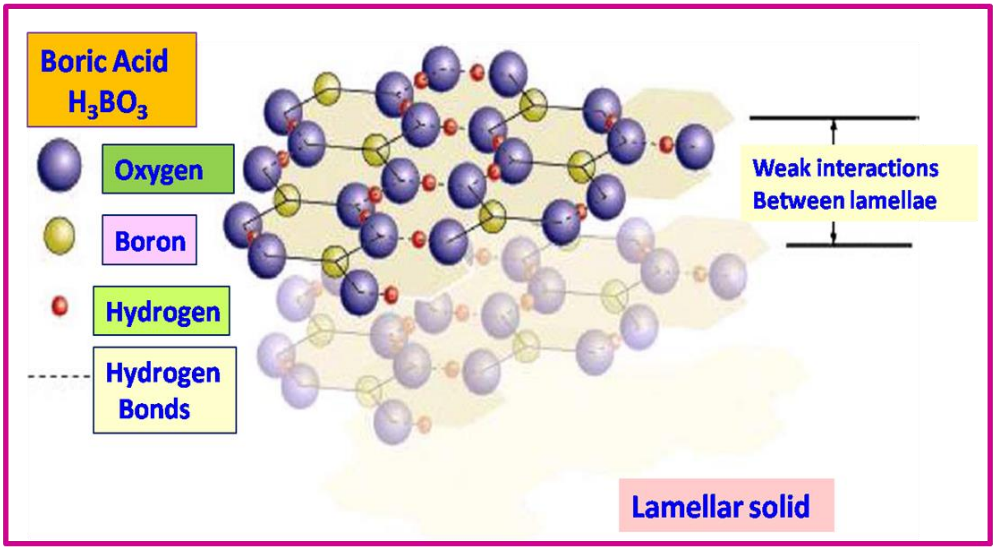


Figure 1.9. Lamellar structure of boric acid. Adapted from Lovell *et al.* (2006)

Philipp on and his co-workers (2011) have investigated the tribochemical reactions of borate esters on steel surfaces. The nature of the formed tribofilm due to decomposition of such additives has been studied. The investigations of trimethylborate (TMB) under gas phase lubrication, friction tests have been conducted on a new tribometer. X-ray photoelectron (XPS) spectroscopy (XPS) as well as Auger electron spectroscopy has been used to analyse tribofilm. It has been confirmed that reactions between iron oxide on steel surfaces and decomposition products of TMB follow the hard and soft acid base (HSAB) principle. Under operating condition due to friction, mechanical degradation of TMB takes place through the C–O bond forming CH_3^+ and BO_3^{3-} ions, can be seen in Figure 1.10. According to HSAB principle the BO_3^{3-} is ‘‘borderline’’ base, reacts with iron oxides, Fe^{2+} or Fe^{3+} which are “borderline” hard acids. The iron oxide present at the beginning of operating condition was mainly made up of $Fe_3O_{4,}$ (FeII and Fe III). When friction test was carried out borderline base (BO_3^{3-}) may partially react with hard iron oxides. Boron compounds have capability to form stable tribofilms on iron surfaces [Philippon *et al*.(2011) and Varlot *et al*.(1999)].

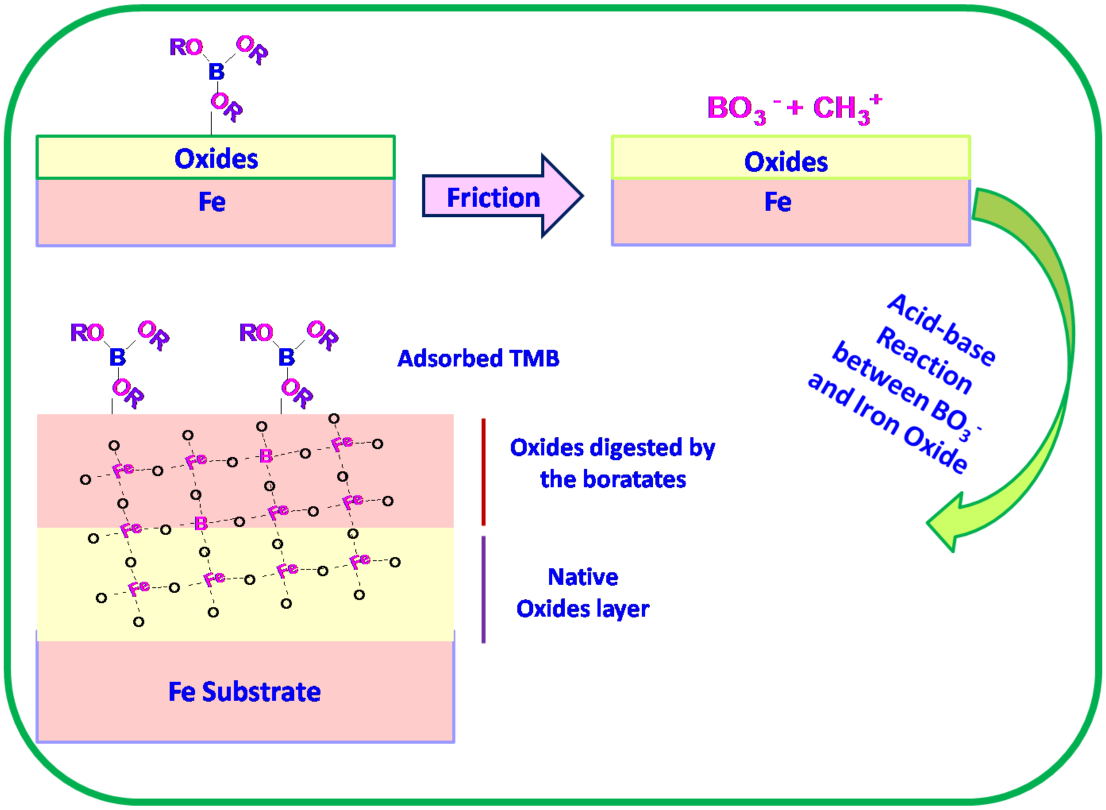


Figure 1.10. A schematic representation of the tribochemical reactions between borate esters and stainless steel surfaces, adapted from Philippon *et al*.(2011)

1.3.8. Ionic liquids

The ionic liquids as lubricants were first studied by the Ye *et al.*(2001). They investigated dialkylimidazolium tetrafluoroborate ionic liquids as lubricants on various tribo-surfaces such as steel/steel, steel/aluminium, steel/copper, steel/SiO_2, Si_3N_4/SiO_2, steel/Si(100), steel/sialon and Si_3N_4/sialon and observed high friction reducing, antiwear and load carrying capability. A lot of research has been done thereafter which shows better lubrication properties of ionic liquids over conventional lubricants additives [Zhou *et al.*(2009), Somers *et al.*(2013), Chen *et al.*(2003) and Liu *et al.*(2002)]. The lubricating properties of ILs depend upon polarity, conductivity, thermal and chemical stability. These ionic liquids react with the interacting surfaces and form tribochemical thin film which prevents direct metal-metal contact and reduces the friction and wear. The tribological behaviour is controlled by their molecular structure containing cation and anion [Atkin *et al*.(2009) and Perkin *et al*.(2010), (2012)]. In the beginning, imidazolium-based cation having BF_4 and PF_6 anions have been investigated for their tribological behaviour. Due to hydrophilic nature, these ionic liquids react with moisture to produce HX, which enhances the tribo-corrosive wear [Minami *et al*.(2008)]. The use of halogen, sulfur and phosphorus containing ionic liquids has to be limited because they spoil the environment as well as the engine.

1.3.9. Ceramic nanoparticles

From several decades, the nanoscience and nanotechnology have been developed. Nanoparticles have unique properties and have numerous applications in electronics [Astruc *et al*.(2010)], photonics [Mirin *et al*.(2010)], magnetism [Tuysuz *et al*.(2012)] and tribology [Huang *et al*.(2013)]. A lot of ceramic nanoparticles have been successfully used as antiwear, antifriction and extreme pressure additives such as CaO, CuO, ZnO, ZrO_2, TiO_2, CeO_2, lanthanum borate [Battez *et al*.(2008), Gusain *et al*.(2013), Zhang *et al*.(2011), Hu *et al*.(2000a), Battez *et al*.(2010) and Bakumin *et al*.(2005)] etc. These nanoparticles have advantage over traditional additives due to high temperature sustainability [Battez *et al*.(2010)]. Different explanations have been proposed for how these nanoparticles work, such as ball bearing effect [Rapport *et al*.(2002) and Tao *et al*.(1996)], protective film

[Zhou *et al*.(1999)], mending effect [Liu *et al*.(2004)] and polishing effect [Tao *et al*.(1996)]. The common problem of these bare inorganic nanoparticles is agglomeration due to their high surface energy. Therefore, these have a tendency to get precipitated due to gravity. To overcome these problems many researchers have used stabilizer or surfactant to prevent agglomeration, forming relatively much stable dispersions in base oil and enhancing tribological properties [Bakumin *et al*.(2005)].

1.4. Statement of Problem

The incorporation of AW/EP additives to base oil reduces friction and wear, controls energy losses, improves mechanical efficiency and increases life of machines. Metal dialkyldithiophosphates, particularly zinc dialkyldithiophosphates (ZDDPs) are one of the well-known commercial multifunctional additives. ZDDPs show antiwear, friction-reducing, antioxidant and extreme pressure lubrication properties. High sulphated ash, phosphorous and sulfur (SAPS) containing ZDDPs spoil the environment as well as the machines. These additives damage the catalytic convertor in the engine and are also hazardous for human health and aquatic life. Organic and inorganic compounds containing high amount of sulfur and/or halogen and phosphorous damage the system. Thus, the use of high level of the halogen and sulphated ash, phosphorous and sulfur contents (SAPS) in additives is limited due to their negative impacts. At present several norms are available which strictly limit the SAPS (Sulfated Ash, Phosphorous and Sulfur) contents in the additives, like API CJ-4, ILSAC GF-5, and ACEAC1. Now GF-5 has been replaced by GF-6A and GF-6B. Therefore, it is necessary to develop some environment-friendly halogen-free low/zero SAPS lubricant additives which perform better in lubrication industry without compromising/damaging the interacting surfaces. From this perspective, different categories of AW/FM additives are to be developed to overcome the aforesaid problems.

1.5. Aims and Objectives

The objective of the present investigation is to develop antiwear additives having low or zero SAPS contents but with high lubrication performance which may fully and/or partially replace the commercial ZDDP in lubricating oils. These may be heterocyclic compounds, organoborates, ionic liquids, ceramic nanoparticles and graphene based nanomaterials. A lot of research has been done on the tribological properties of N-containing heterocycles and organoborate esters, separately and their synergistic behavior under lubricating conditions can be studied. Besides this, several reports are available on the use of bare and/or surface modified ceramic nanoparticles as antiwear additive. Doping in different concentrations can be done in ceramic nanoparticles to increase their efficiency. The particle size of nanoparticles may be varied so as to get better results.

Main objectives of the present investigation are-

- To synthesize S and P - free Schiff base derived from condensation of 4-aminotriazole with indole-3-carboxylaldehyde and investigate synergistic action of Schiff base with organoborate as efficient antiwear lubricant additive
- To synthesize, characterize and evaluate tribological properties of SDS stabilized Magnesium-Doped-Zinc Oxide ($Zn_{0.88}Mg_{0.12}O$) nanoparticles

- To study tribological properties of sulfur and phosphorous-free quinolinium salts, β-lactum cephalosporin and fluoroquinolones antibiotics
- To investigate the action mechanism and tribochemistry of these admixtures using Energy Dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS) techniques
- To analyze the surface morphology of worn surfaces using Scanning Electron Microscopy (SEM) and contact mode Atomic Force Microscopy (AFM) techniques
- To perform quantum chemical calculations based on density functional theory and correlate the experimentally observed data with structure of the additives