

1.1 Tribology

The famous Jost report (1966) first introduced the term tribology, which is the union of two Greek words, tribos and logos. Tribos means rubbing, and logos is logic; thus, tribology may be described as the science of rubbing. Broadly, tribology may be defined as the “the science and technology of contacting surfaces in relative motion and of related subject and practices” [Bhushan et al. (2001a)]. It is fundamentally about materials, surfaces, lubrication, frictional properties and prevention of wear. In modern industry, it has significant importance since it is responsible for reliability, performance and durability of moving machine components. Such components include mechanical components, transportation systems, biomedical devices, living bodies, manufacturing technologies, electrical contacts and others. It is a multidisciplinary science, which addresses surface phenomena, the chemistry of lubricants, material science, physics of fluid flow, and contact mechanics, surface topography and mechanical engineering. Friction, wear, and lubrication are considered as the main components of tribology [Zhou *et al.* (2015)].

1.1.1 Friction

Friction is the force that opposes the relative motion of one object over another under the applied load. It results in energy loss of the system; higher the friction more is energy loss. The friction can be experienced 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. Friction may be classified as dry friction, fluid friction and lubricated friction. The pioneer researchers in the field of tribology

are Amontons (1699), Coulomb (1785), Towers (1884), Reynolds [(1986), (1988)], Block (1937), Bowden and Tabor [(1954), (1964 a, b)].

Amontons (1699) formulated the law of friction. He stated that

1. The friction force is directly proportional to the normal load.
2. The frictional force is independent of the apparent contact area.

The mathematical formula to calculate the frictional force can be shown by:

$$\mu = F/N \qquad 1.1$$

Where μ is the coefficient of friction (COF); F is the frictional force, and N is applied normal load.

Coulomb's law: Kinetic friction is independent of the sliding velocity.

The laws of friction have been proved experimentally under varying conditions. A deviation from the first law is shown by very hard material like a 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 load. It may lead to material loss to the extent that sometimes replacement of the affected part is required [Bhushan (2001b)]. It is controlled by the

influence of the 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 the highly stressed interfacial zone or influence of environmental factors. Various types of wear are observed.

1.1.2.1. Adhesive wear

Cold welded junctions are formed between the asperities of the proximal surfaces. Adhesive wear does not directly lead to loss of material from the interacting surfaces as it is just the initiation of wear. The welded section may be work-hardened and strengthened. Consequently, shearing may not occur on the asperity junction. The high load applied on the contacting asperities deforms them forming micro-joints.

1.1.2.2. Abrasive wear

Abrasive wear is generally related to 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 forming 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 et al. (1985)].

1.1.2.3. Chemical Wear

In chemical wear, chemical reaction with lubricant /environment is the source of loss of material; the material scraps off due to the chemical reactivity of the metal surface and rubbing action. A lubricated system consists of various chemical agents

like 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. The mentioned agents tend to 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. This kind of stress, when repeatedly applied on the surface, resulting in a detachment of wear particle, is termed as a micro-fracture event.

1.1.3. Lubrication

The word "lubrication" stands for the introduction of a foreign substance. The purpose of using lubrication is to prevent direct metal-metal contact, minimize the wear and dissipation of heat between contact surfaces. The wear and heat are correlated with friction. If somehow, the coefficient of friction is reduced, these are overpowered. In addition to lowering frictional heat and wear the other purposes of lubrication are reduction of oxidation, corrosion inhibition, removal 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 a vital role in manufacturing processes and machine components. A lower-viscosity (shear strength) material is interposed between the moving surfaces to reduce wear and frictional heat. The revolution in technology has brought changes in machine designs, recommended use of low-weight metal tools instead of heavy-weight metal and put strict regulation

towards the protection of the environment by reducing the emissions etc. There are challenges for proper design and development of energy efficient lubrication [Kuratomi *et al.* (2009)].

Stribeck (1902) expressed the variation of the friction coefficient (μ) for a sliding bearing. Stribeck has dealt with a hypothetical fluid-lubricated bearing and has given a curve where COF has been plotted as a function of the product of the absolute viscosity (η) and the rotational speed in revolutions per unit second (N) divided by the pressure (P). Based on lambda ratio or lubricant film parameter λ , which is equal to h / σ (mean film thickness / composite standard deviation of the surface heights of the two surfaces). Lubrication regimes could be identified as $\lambda \geq 3$ hydrodynamic lubrication, $\lambda = 0.5$ to 3 mixed lubrication and $\lambda < 0.5$ boundary lubrication.

$$\text{Lambda ratio, } \lambda = \frac{h}{\sigma^*} \quad 1.2$$

where h = Minimum film thickness

σ^* = Composite roughness

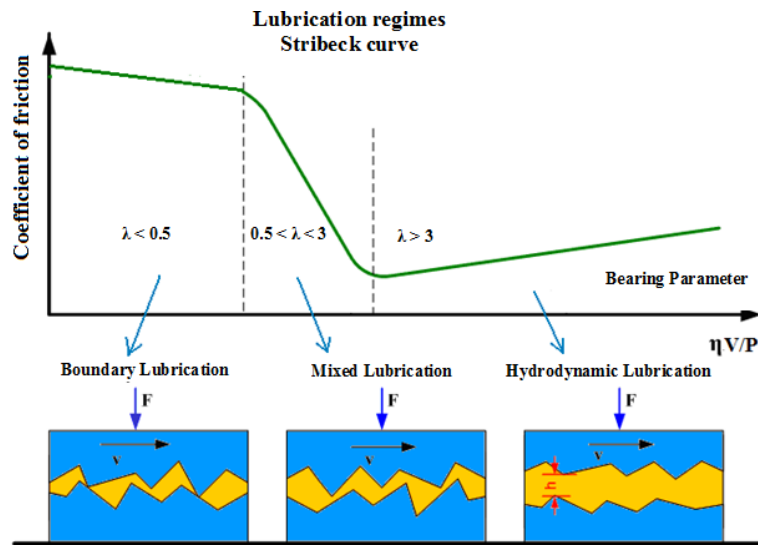


Fig. 1.1. Stribeck curve: Dependence of the friction coefficient on viscosity, speed and load for a lubricated sliding system.

1.1.3.1. Hydrodynamic Lubrication

In the hydrodynamic lubrication (HL) or thick film lubrication, a relatively viscous fluid is added to prevent asperity-asperity contact and achieve low friction coefficients. Thus, the moving surfaces are not in touch because of the adhesive and opaque oil film existing between them. The film thickness is classically around 10 to 100 times thicker than the height of the asperity of the surfaces that move. Hence, in this region, friction is the least and wear almost negligible. The contact between the load-carrying surfaces is broken by the film of lubricant having adequate thickness so that the adjacent surfaces are far apart. For hydrodynamic lubrication, the viscosity of the fluid and the speed of surfaces in motion are important as shown by the relationship: $\eta V/P$. where η , V and P stand for viscosity, speed and load.

1.1.3.2. Mixed Lubrication

In the mixed lubrication, more than one lubrication mechanisms are operative concurrently. It may occur in lubrication systems like journal bearing lubrication where conformal contact exists. In this lubricant film, hydrodynamic lubrication, as well as asperity contacts, are present. Therefore, 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.

1.1.3.3. Boundary Lubrication

The boundary lubrication was first introduced by Hardy and Doubleday (1922) to define wear and friction reduction between sliding surfaces. Boundary lubrication is an outcome of the combination of low viscosity, low velocity and high load. When the solid surfaces are in proximity, the surface interactions are quite strong, and a thin lubricated film is adsorbed on the surfaces either by physical or chemical means. The adsorbed film isolates the contact surfaces in relative motion, reducing friction and preventing surface destruction. The value of lambda ratio is less than 0.5 for thin-film or boundary lubrication. The regime is unfavourable since it provides a high coefficient of friction, causing massive loss of energy along with wear (debris of material) from the sliding surface [Myshinn *et al.* (1997)].

1.2. Lubricants

Lubricant is the substance, which minimizes friction and wear when blended between surfaces in motion. Apart from lubrication, the other functions of lubricants are dissipation of heat and wear debris, carrying additives into the contact, transmission of power, prevention of entry of dust and dirt, protection and sealing of

the surface. By reducing friction and wear, the life expectancy of a mechanical system is extended, energy loss is reduced, and emissions are controlled. 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)]., The lubricants may be classified according to their physical and chemical properties as given below-

1.1.1. Liquid Lubricants

Different types of oils are generally used as liquid lubricants. These oils reduce friction and wear by forming a thin layer of fluid film between the sliding surfaces. The low viscosity and high viscosity index make the oil excellent liquid lubricant. The liquid lubricants can bear varying temperatures, dissipate heat from asperities contact points and also work as cleaning agents. The liquid lubricants are divided into different categories as follows-

1.1.1.1. Vegetable oil

Vegetable oils are fatty acid triglycerides and are extracted from plants. Many vegetable oils such as castor oil, olive oil, coconut oil, rapeseed oil, palm oil, cottonseed oil etc. are used for lubrication. These oils possess numerous properties, which are essential for a lubricant such as high oiliness, less volatility, high viscosity index, high flash and fire points. Their feasibility for esterification, low toxicity, high biodegradability and low oxidation stability are favourable for frequent applications. Owing to the presence of triglycerides structure and polar fatty acids, these are referred to as oiliness carriers. Their interaction with the solid surfaces reduces

friction coefficient and enhances load carrying capacity, thus, making them compatible for boundary lubrication.

1.1.1.2. 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.

1.1.1.3. Mineral oils

Mineral oils are preferred over vegetable and animal oils as lubricants because these are inexpensive, readily available, reusable and highly stable under severe conditions. Paraffin oil is colourless, odourless, transparent mineral oil composed of alkanes and cycloalkanes.

1.1.1.4. Synthetic lubricants

Synthetic oils are oily liquids, which are not found naturally and are not derived from the refining of crude oil. The important synthetic oils are; polyalphaolefins (PAOs), polybutenes, alkylated aromatics, aliphatic diesters, polyesters, polyols and polyalkylene glycols, silicones, fluorocarbons etc. These oils have a high viscosity index (120-170), low volatility and excellent oxidation stability. These oils show a negligible change in their viscosity with change in temperature because of uniform structure. These oils are beneficial to mineral oils due to reduced maintenance, better reliability, safer operation, improved energy efficiency and applicability in the broader temperature range. These oils are designed in such a way to avoid the presence of sulphur, nitrogen and other elements, which encourage sludge formation. 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 a 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 tough to separate them.

1.2.3. Solid Lubricants/Dry lubricants

These lubricants are solid thin films or solid materials which reduce friction and wear by separating the adjacent surfaces. These are used either in dry condition or in water/ oil. At very high-temperature solid lubricants can be used. The often-used solid lubricants such as graphite, MoS₂, WS₂, ZnO, ceramic coatings are recognized as antiwear additives. In general, solid lubricants must have high mechanical strength, low shear strength, high thermal and chemical stability and lamellar structure. Graphite is a hexagonal layered lattice solid. The sp² hybridized carbon atoms are bonded covalently in graphite planes. In contrast, the planes are bonded through the weak van der Waals cohesive forces, causing interplanar mechanical weakness. Thus, the lubricity of graphite lies in the fact that under a shearing force, the planes slide over one another easily by intracrystalline slip. This kind of shear is termed as “deck of-cards” shear. The transition metal dichalcogenides, molybdenum disulfide (MoS₂)

and tungsten disulfide (WS_2) possess anisotropic crystal structures where strong covalent bonding is held between Mo/W and S within a plane. Still, weak van der Waals forces exist between the planes. So the planes slide easily between lamellar crystal sheets. Thus, these types of materials are used as solid lubricating films [Sun et al. (2017)]. Similarly, in hexagonal boron nitride (h-BN), hexagonal sheets consisting of strong covalent bonds between B and N, and weak van der Waals forces between sheets provide easy shearing resulting in low friction. [Shah et al. (2013)].

1.2.4. Gaseous Lubricants

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

1.2. Lubricant Additives:

Lubricant additives are materials like organic, inorganic, nanoparticle, nanocomposite dissolved or suspended into either a liquid base (mineral oil, synthetic oil), a semi-fluid, or a grease [Soul et al. (1983)]. Different kinds of additives are chosen to improve the quality of the base oil to deliver an anticipated physical, chemical or mechanical property. The properties of base oil are enhanced upon the addition of antioxidants, corrosion inhibitors, anti-foam agents and demulsifying agents. There are two types of Lubricant additives based on their chemical performance: chemically-inert and chemically-active. Chemically inert additives improve the physical properties of the lubricant base oil. Chemically active additives tend to

interact with metals to form protective films and enhance the tribological properties. Based on chemical compositions, lubricant additives are further divided into the following types: Conventional organic compound with heteroatoms (sulphur, phosphorus, nitrogen and boron etc.), ionic liquids (ILs) and nanomaterials (ceramic nanoparticles and carbon-based nanomaterials). Details of these compounds are given below:

1.2.1. Conventional organic compounds with hetero atoms

The adsorption of organic compounds occurs on the metal surfaces via the negatively charged centres, p electrons in double bonds, aromatic systems or lone pair of electrons on heteroatoms. The adsorbed additives play a significant role in improving the antiwear properties.

1.2.1.1. Sulfur compounds

Sulfur is a non-metallic element and is one of the most reactive elements of the periodic table. Sulfur alone or its compounds with other metals in different chemical compositions are widely used in lubrication. Sulfur as an additive at 30 °C has been found detrimental to the pitting performance, but at 100°C, it is beneficial [Rowson *et al.* (1981)]. Pure sulfur in the form of S₈ ring blended with liquid paraffin has produced good results. The vital role of sulfur-containing additives is to enhance antiwear, extreme pressure and antifrictional properties under severe conditions. The variety of organic sulfur compounds such as sulphurized olefins, fats, esters and terpenes, dithiocarbamates [Mamman *et al.* (1981), (1983), (1984)], xanthates [Agrawal *et al.* (1980), (1981)], thiocarbonates, isothiobiurets [Trofimov *et al.* (1999), (1988)], thioamides [Kuliyev *et al.* (1989a)], isothioamides [Kuliyev *et al.* (1983),

(1988)] thioacetamides [Kuliyev *et al.* (1989b)], phenylacetothioamides [Kuliyev *et al.* (1983)], dialkanoylacetamides [Croudace *et al.* (1990)], alkan-amidosulfides [Bhattacharya *et al.* (1995)], di-isobutyl polysulfide [Hua *et al.* (2007)], thioglycolic acid ester [Hua *et al.* (2007)], aromatic sulfur compounds viz aromatic disulfide, mercapto benzo-thiazole etc. [Forbes *et al.* (1973)], have been primarily used as AW/EP additives in lubrication. The EP behavior could be related with the ease of breaking of the C—S bond, but the good antiwear performance occurs by the disulfides with cleavage of S—S bonds. The authors suggested that antiwear efficiency was controlled by the mercaptide protective film formation, both iron sulphide and ferric oxide produced on the rubbing surface are effective in EP lubrication. According to the mechanism proposed by [Davey *et al.* (1957)], 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 sulphide film after adsorption while the disulfide also forms the iron sulfide film through iron mercaptide.

Tribological studies of mercapto benzoxazole containing N-C-S bond were conducted [Zhang *et al.* (1999)] and it was found that the rubbed surface comprised of iron sulphide, FeS or FeS₂ and FeSO₄. XPS analysis showed that the film adsorbed physiochemically through the lone pair electron of nitrogen and reaction of sulfur with the mating surfaces. It is interesting to note that the presence of an oxygen atom on to sulfur in a monosulfide weakens the carbon-sulfur bond, on the other hand, if two oxygen atoms are there the C-S bond is strengthened. Accordingly, the tribological behavior of oxygenated monosulfides can be described. Similarly,

oxygenated disulphides (thiosulfinates) performed better than disulphides [Allum *et al.* (1965, 1967)]. The main elements of the additive films were carbon and oxygen, with iron-sulfur and iron oxide compounds at the lubricated surface [Spikes *et al.* (2008)]. The mixed oxide/sulfide film was found to have a much better load capacity than a pure sulfide film under the prescribed conditions of load and sliding. On the basis of XPS and XANES spectroscopy it has been observed that the composition of the thin film in the presence of organosulfur compounds depends on the applied load [Najman *et al.* (2003)]. The chemistry of both thermo-oxidative and tribochemical films made from the organosulfur additives has been given. A tribofilm of iron disulfide and sulfate is formed under operating conditions.

1.2.1.2. Phosphorus Compounds

Several phosphorus compounds have been examined for possible applications in tribology. These contain mainly phosphates and dithiophosphates. The first step is adsorption of the phosphate group on the surface, which decomposes at a higher temperature forming alkyl-acid phosphates. Then alkyl-acid phosphates react with the surface to form salts, which are high melting solids. These salts protect the surface from friction /wear and enhance lubrication. Many ashless dialkyldithiophosphates have been investigated for tribological activity. These dialkyldithiophosphates form thermal films at higher temperatures around 150 °C by breaking off the P=S double bonds at high contact pressure and under the frictional heat. The films are composed of a mixture of iron (II) polyphosphate and iron (II) sulfate [Martin (1999)]. The ashless additive performed much better than zinc diakyl dithiophosphates(ZDDP) due to the formation of a thicker film of around 400nm thickness that contained iron (II)

polyphosphates of shorter chain length as compared to ZDDPs [Rossi *et al.* (2006), Najman *et al.* (2004), D. Johnson *et al.* (2016)].

The triarylphosphorothionates received much attention towards antiwear properties. In this type of compounds, the doubly bound oxygen is replaced with a sulphur atom. The parent in the series, triphenyl phosphorothionate, has been studied by [Heuberger *et al.* (2008)]. Thermal oxidation of a solution of triphenylphosphorothionate produced triphenyl phosphate without any oil insoluble products. However, in the presence of iron or steel, the reaction became metal-catalyzed, and a multi-layered solid film on iron/iron oxide was also formed along with triphenyl phosphate. The best performance was obtained in the case where minimum worn-out iron oxide particles were found trapped within the phosphate tribofilm [Mangolini *et al.*(2009), Najman *et al.*(2002)].

The antiwear performance of other dithiophosphatedisulfide compounds was also studied [Bansal *et al.* (2002)]. Disulfide groups can provide better EP properties as compared to normal dithiophosphates. Further, a group of researchers [Rossi *et al.* (2006), Najman *et al.* (2002), Choi *et al.* (1997)] have studied the thermal and oxidation stability of organo-phosphorous. Physisorption was found to occur at temperatures lower than 373K while beyond that, chemisorption took place. Initially, P=S bond scission results in the formation of trialkylphosphite, followed by P-O bond scission to produce alkoxy groups.

1.2.1.3. Nitrogen Compounds

In the internal combustion engine, lubricating oil containing an amine salt was used for reducing friction [Lundgren *et al.* (2015)]. It was observed that Amide performed

much better than amine. [Haung et al. (2006)]. The N-containing heterocyclic compounds show excellent antioxidation, anticorrosion, anti-wear properties along with high thermal stability and are used as potential ashless lubricant additives [Huang et al. (2006)]. It was observed that the N-containing heterocyclic compounds have a tendency to get adsorbed on steel surfaces forming a tribochemical film and behave as extreme pressure and antiwear agents [Ren et al. (1993)]. Several N-containing heterocyclic compounds like benzotriazole [Jia et al. (2011)], imidazoline [Xiong et al. (2016)], pyridine [Hea et al. (2002)], triazine [Yang et al. (2013), He et al. (2014)] and benzimidazole have been reported, therefore, as lubricant additives. The benzotriazole derivatives, oxazoline and imidazoline derivatives are the excellent ashless multifunctional lubricating additives [Hea et al. (2002)]. These additives also tend to prevent corrosion of copper, nickel, iron and other metals [Babic *et al.* (2005), Wu *et al.* (2009b), and Waynick *et al.* (2001)]. The antiwear efficiency enhances with the rise in the number of N atoms in the cyclic ring. Benzotriazole, due to the strong electron-withdrawing ability of the $-N=N-$ group can quickly release a proton forming the strongest negative ion which improves the antiwear properties.

Triazine-dialkyldithiocarbamate and other derivatives of heterocyclic compounds have been used as multifunctional additives in both mineral and vegetable base oils. Small concentrations of triazine derivatives of dithiocarbamates added to mineral oils decrease wear of interacting surface while the same additives increase wear in vegetable (rapeseed) oils [Xu *et al.* (2000), Zhan *et al.* (2004)].

1.2.1.4. Boron Compounds

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, but the layers are bonded through weak van der Waals forces. The weak interactions support the lidding of one layer against the other that promotes lubricity. Finally, It has been claimed that in the presence of boron, boric acid formed in situ on the rubbing surface provided lubrication [Erdemir *et al.* (1991a, b)].

Borates are being used as lubricant additives because of wear resistance and friction-reducing properties. The borates, including sodium metaborate, titanium borate, zinc borate, aluminium borate, ultrafine powder strontium borate, magnesium borate, lanthanum borate, and cerium borate [Shah *et al.* (2013)] have been used as additives. Potassium borates [Adams (1977), (1978)] have been reported for their extreme pressure properties. The calcium borate [Martin *et al.* (2000)] micelles have been reported to possess the capability to interact with other conventional additives. 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)]. Under boundary lubrication conditions, the borate additives form a thin glassy tribofilm of amorphous nature [Feng *et al.* (1963)]. The antiwear properties of borates are ascribed to rheological properties of the tribofilm. There is some drawback of inorganic borates such as making homogeneous solutions in base oils is difficult, which causes poor access of the particles on to the surface. In addition to this, the particles are also not adequately adhered to the surface. Surface modification of metal borates has been shown to enhance the solubility in base oils

and hence, the tribological properties. Stabilization of metal borates in base oils can be proficient by using a particular type of surfactants which contain lengthy hydrocarbon chains, functional groups, and soluble polymeric species.

The organic borates are good candidates for engine and gearbox lubrication since they are soluble in base oils. It was observed that the S-containing additives form iron sulphides FeS_x but boron is not chemically active to interact with the iron surface. Some reports claim that the antifriction properties are attributed to the formation of boric acid. Besides this, the abrasive nature of boric acid is also known. Choudhary and Pande (2002) have analyzed the tribofilm and found that the film is very hard, amorphous, 100-200 nm thick, and it consists of boric acid and ferrous oxide. Philipp and his co-workers (2011) have investigated the tribochemical reactions of trimethyl borate under gas phase lubrication produces methyl and borate ions. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxides are digested by borates. 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. Kreuz *et al.* (1967) have studied the load-carrying ability and extreme pressure properties of the tribenzylborate ester in both, mineral and ester oils and found that borate films containing both inorganic and organic species. It was also observed that the borate esters yield boric acid and alcohol on hydrolysis. Bulky groups like phenols have been used which create hindrance and prevent the hydrolytic attack at the B—O bond. Besides this, amines coordinated to boron atoms have been used to control hydrolysis [Kreuz *et al.* (1967)].

Some reports are available stating higher stability of nitrogen-containing borate esters [Yao (1997) and Zheng *et al.* (1998)]. These additives produce tribofilm containing boron nitride. Boron nitride is itself a very efficient lubricant with lamellar structure, which improves the antiwear performance at a higher load. The increase in the alkyl chain length on the nitrogen results in enhanced hydrolytic stability of borate esters. Borate esters with mercapto benzothiazole and dithiocarbamate have been studied for their antiwear properties. Boron and sulphur-containing compounds, especially borated dithiocarbamates, show superior antiwear behaviour [Zhang *et al.* (1999 a,c)].

1.2.2. Ionic liquids

Ionic liquids (ILs) are molten salts, usually below 100 °C. They consist of bulky, asymmetric cations and anions together. Charges on their ions are usually diffused owing to the huge size of the moiety and the nature of chemical groups of ions. The melting point and the viscosity of ILs are directly related to their molecular structures, the alkyl chain length and the nature of cations and anions. ILs have some useful properties including low volatility, non-flammability, thermal stability and miscibility with organic compounds which make them appropriate as potential lubricants. The tribological behaviour is controlled by their molecular structure containing cation and anion [Atkin *et al.* (2009), Perkin *et al.* (2010), (2012)]. Ye *et al.* (2001) were the first to introduce the ILs like dialkylimidazolium tetrafluoroborate (BF₄) and hexafluorophosphate (PF₆) as lubricants. Alkyl imidazolium tetrafluoroborates have been used for various tribo-surfaces such as steel/steel, steel/aluminium, steel/copper, steel/SiO₂, Si₃N₄/SiO₂, steel/Si(100), steel/sialon (Si–Al–O–N) ceramics and Si₃N₄/sialon (Si–Al–O–N) ceramics. These PF₆ and BF₄ anions are mostly

hydrophilic and react with water to produce undesirable corrosive compounds, which increase the tribo-corrosive wear. The greater alkyl chain length of the imidazolium cation improves the wear performance. The formation of protective metal fluoride tribofilm is a key to the potential performance of ILs. The tribofilm is formed due to the reaction of the fluorine of the anion with the metal surface. Minami *et al.* (2009) have studied some ammonium and imidazolium ILs and found significantly higher friction-reducing, antiwear and load-carrying ability than conventional synthetic oil. A lot of research continued after that showing much better lubrication performance over conventional lubricants additives [Zhou *et al.* (2009), Somers *et al.* (2012), Chen *et al.* (2003) and Liu *et al.* (2002)]. These ionic liquids react with the interacting surfaces and form tribochemical thin film, which is instrumental in reducing friction and wear by preventing metal-metal contact. The halogen, sulphur and phosphorus-based ionic liquids spoil the environment as well as the engine. Therefore, these have found limited applications. Besides anion, nature of cation is also important for the tribological properties of ILs. Ammonium, pyrrolidinium and phosphonium-based ILs have been found to be more effective in reducing friction and wear than the imidazolium-based. ILs are more expensive compared to mineral and synthetic and base oils, such as polyethylene glycol (PEG), polyalphaolefins (PAO), propylene glycol dioleate (PGDO) and glycerol. Therefore, their application as an additive to the base lubricants is recommended except for low-pressure environments or micro-electro-mechanical machines where these are applied as neat lubricants. As a lubricant additive, a very low concentration of ionic liquid is needed for substantial reduction of friction and wear. Ionic liquids have been used as additives in base oils including hydrocarbons, polyethylene glycol (PEG), polyalphaolefins (PAO), propylene glycol

dioleate (PGDO) and glycerol. ILs being polar are relatively less soluble in mineral oils and PAO. For preparing oil-soluble ILs, the constituting cation and anion have to be oil-soluble. The primary requirement for oil-solubility is the presence of bulkier alkyl groups. Besides [sulfosuccinate]⁻, [adipate]²⁻, [carboxylate]⁻, phosphinate⁻, and [phosphite]⁻ anions, the organophosphates [diethyl phosphate]⁻, [dibutyl phosphate]⁻, [diphenyl phosphate]⁻, and [2-ethylhexyl phosphate] have been used to synthesize oil-soluble ILs [Zhou et al. (2014), (2017)]. In the presence of ILs, FeF₂, FeF₃, FePO₄, FeS, BN and B₂O₃ are usually formed as tribochemical products on the worn steel surface, which are considered to be advantageous for reducing friction and wear [Philippon *et al.* (2011), Varlot *et al.* (1999), Sanes et al. (2009)].

1.2.3. Nanoparticles

The emergence of nanotechnology has provided the synthesis of nanomaterials, which are applied to different fields, namely; optics [Mirin *et al.* (2010)], optoelectronics, photocatalysis, biomedical, electrical and sensor devices [Astruc *et al.* (2010)]. The nanoparticles find use in tribology owing to their excellent thermal, mechanical and chemical properties. Several nanoparticles like metals [Chou *et al.* (2010), Kumara *et al.* (2018), Viesca *et al.* (2011), Ma *et al.* (2009)], metal compounds; oxide [Zhou *et al.* (2013), Ingole *et al.* (2013), Luan *et al.* (2012), Battez *et al.* (2008), Shen *et al.* (2016)] sulfides [Kang *et al.* (2008), Xie *et al.* (2016)], carbonate, borate [Hu *et al.* (2000a)], halide [Zhou *et al.* (2001)], carbon materials [Zhang *et al.* (2015)], organic material and rare-earth compounds [Li *et al.* (2014)] etc. have been successfully used as antiwear, antifriction and extreme pressure additives. Traditional lubricants are relatively more sensitive to temperature and show various

tribochemical reactions [Battez et al. (2010)]. Nanoparticles show advantages over traditional ones, such as higher temperature sustainability, faster interactions, restricted tribochemical reactions and capability to form films on the surfaces.

Some factors affect the stability of nanoparticles, like the particle size, shape and volume fractions of the nanoparticles and the properties of the base-lubricants (density, viscosity, pH and polarity). Smaller nanoparticles are not always stable because smaller nanoparticles have a high surface energy that will enhance the van der Waals attractive forces on the surfaces of the nanoparticles. These forces make the nanoparticles' surface attractive to other nanoparticles, thereby causing the agglomeration of nanoparticles. The main problem associated with the stability of the nanoparticles is agglomeration due to their high surface energy and van der Waals forces. Considerable efforts have been made to improve the stability of nanoparticles with physical treatments, use of surfactants and surface modification. 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.

Different mechanisms have been put forth for the lubrication efficiency of nanoparticles; rolling, self-repairing or restoration, polishing and tribofilm formation. Overall, it is considered to be a combined effect of all these mechanisms. Rolling mechanism [Rapport *et al.* (2002), Tao *et al.* (1996)] signifies rolling motion of the nanoparticles like a ball bearing between the proximal surfaces. The nanoparticles get

settled on the rubbing surface and fill the tiny furrows on the surface. Thus, restoration of the surfaces by nanoparticles is known as mending behavior. Polishing mechanism [Tao *et al.* (1996)] describes smoothening of the abraded surface by nanoparticles. Lastly, the nanoparticles result in the formation of protective tribofilm on the interacting surfaces preventing the metal-metal contact [Liu *et al.* (2004)].

1.2.4. Carbon-based nanomaterials

Carbon-based materials are known to possess high conductivity, thermal and chemical stability [Wang *et al.* (2016)]. Comprehensive literature is available on carbon-based nanomaterials including activated carbon, carbon nanotubes [Yu *et al.* (2015)], mesoporous carbon, graphene [Gusain *et al.* (2016)], fullerenes [Lee *et al.* (2007)], carbon spheres, carbon nano-onions [Joly-Pottuz *et al.* (2008)] as lubrication additives for reducing friction and wear. Graphene, a one-atom-thick single-layered structure derived from graphite, has drawn attention because of its distinctive properties, including lubricating characteristics [Fujii *et al.* (2014)]. The tribological applications of graphene are based on high mechanical strength, chemical stability and easy shear capability. Adherence of graphene to a steel surface is promoted by dangling bonds of carbon. Its adhesion to the surface acts as a barrier between metal-metal contact and is capable of reducing friction [Righi *et al.* (2016)]. Graphene being ultrathin even with multilayers, its importance is realized in micro-electro-mechanical systems (MEMS) and nanoelectromechanical systems (NEMS) with oscillating, rotating and sliding contacts for reducing friction and wear.

One - dimensional single and multi-walled carbon nanotubes [SWNT, MWNT] consist of graphene layer embedded on one another. These have found numerous

industrial applications. Their shape, high length-to-diameter ratio and great flexibility have made them useful solid lubricants or lubricant nano additives for improvement of the tribological activity [Ali et al. (2019)].

Applications of carbon spheres are well recognized in various fields like the supercapacitor [Liu et al. (2015)], electrode materials [Liu et al. (2014)], catalysis [Liu et al. (2015)], fuel cell [Pei et al. (2016)], hydrogen storage [Liu et al. (2015)], picolitre container, electromagnetic devices [Lv et al. (2016)]. Carbon microspheres have found usage as oil additives owing to excellent mechanical and chemical stability. These are capable of bearing high pressures of around 8 GPa [Pesika et al. (2011)]. The presence of amorphous carbon has been found in these spheres due to the low degree of graphitization. Under tribological test conditions in boundary and mixed lubrication regimes, their spherical morphology and chemical composition are retained as such. Therefore, the mechanism of lubrication is considered to be rolling motion. The efficiency of ultrasmooth submicron carbon spheres as a lubricant additive has been studied by [Mistry et al. (2015)]. The remarkable enhancement in tribological activity of carbon sphere-oil hybrid lubricant has been explained by considering carbon spheres as a third body material which fill the minute gaps between surfaces asperities. The filling of gaps increases the area of actual contact. As a result, the contact pressure is reduced. It has been found that hard carbon/ Fe microspheres act as a high-performance lubricant [Mistry et al. (2015), Cheng et al. (2016)]. CS-MoS₂ have been used an oil additive to minimize friction loss [Alazemi et al. (2016a)]. Carbon spheres have been reported to enhance the tribological properties of polyether ether ketone (PEEK) [Zhang et al. (2009)].

1.3. Statement of Problem

The blends of AW/EP additives with lubricating oil minimize the wear and friction, enhance mechanical efficacy, increase the life of machines and reduce energy consumption altogether. The prominent commercial multifunctional additives, zinc dialkyldithiophosphate (ZDDPs) exhibit excellent antiwear, friction-reducing, antioxidant and extreme pressure lubrication properties. ZDDPs contain high sulphated ash, phosphorous and sulphur (SAPS) which are harmful to the climate as well as the machines. These additives damage the catalytic converter in the engine and are hazardous for human health and aquatic life. The use of high SAPS additives in which the level of the sulphated ash, phosphorous, halogen and sulphur is very high, is limited due to their negative impacts. Nowadays, several norms are existing which strictly limit the SAPS (Sulphated Ash, Phosphorous and Sulphur) contents in the additives, like API CJ-4, ILSAC GF-5, and ACEAC1. The GF-5 has been recently replaced by GF-6A and GF-6B. Therefore, it is necessary to develop some environment-friendly low/zero SAPS lubricant additives, which perform better in the lubrication industry without compromising/damaging the interacting surfaces. From this perspective, different categories of AW/FM additives, including nano additives, are to be developed to overcome the problems mentioned above.

1.5. Aims and Objectives:

The objective of the present study is to develop low or zero SAPS antiwear additives with high lubrication efficiency, which may entirely or partially replace the commercial additives like ZDDP in lubricating oils. Tribological properties of low SAPS Schiff bases and their metal complexes have been extensively studied, but the

mechanism of triboactivity was not well understood. Other than this, different types of nanomaterials have been studied as friction and wear modifiers owing to their fast tribo action. Literature reports are available on the use of bare and surface-modified nanoparticles as antiwear additives. Doping by different elements in varying concentrations can be done in nanoparticles to increase their efficiency. Furthermore, carbon spheres being inexpensive and non-toxic, have been recognized as potential wear and friction modifiers. Since the shape of carbon spheres is contorted under high loads affecting their rolling mechanism, efforts may be put in for their reinforcement by nanoparticles.

Main objectives of the present investigation are-

- ❖ To synthesize, characterize and examine tribological properties of sulfur and phosphorus-free Schiff bases derived from the condensation of *o*-tolidine with salicylaldehyde, naphthaldehyde and 2-hydroxy naphthaldehyde
- ❖ To identify the active site of Schiff bases involved in the tribological activity
- ❖ To correlate the observed tribological activity of Schiff bases with Molecular Dynamics Simulations
- ❖ To synthesize, characterize and evaluate the tribological properties of nanomaterials
 - (i) sodium lauryl sulfate (SDS) and ionic liquid stabilized calcium-doped-ceria (Ca-CeO₂) nanoparticles
 - (ii) carbon spheres and their composite with copper nanoparticles
 - (iii) carbon spheres and their composite with silver nanoparticles (Ag@C) and Ionic liquid modified Ag@C

- ❖ To investigate the action mechanism and tribochemistry of these nanomaterials 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