CONTENTS

Friction and wear are considered as inevitable events to the engineering interfaces and lead to energy wastage, material loss thereby reducing the life of machines. The efficient lubricant system can reduce such undesirable events. Lubricants play an important role towards reduction in friction and wear between sliding surfaces by interposing a thin film. The lubrication is also required to achieve some other purposes such as dissipation of heat from the contact surfaces, inhibition of corrosion, removal of wear particles from the contact zone etc. Poor lubrication is responsible for energy as well as material losses. Over the years, various categories of lubricant additives have been employed for various purposes. To protect the engineering components from wear and tear, antiwear, antifriction and extreme pressure additives have been used in lubricant. This category of lubricant additive contains huge amount of sulfur, phosphorous, halogens and metal contents. Among these lubricant additives, zinc dialkyldithiophosphates (ZDDP) are being frequently used as excellent multifunctional lubricant additives in lubricant industries. Sustainable and environment friendly lubricants and additives are gaining attention for industrial applications. Over the last two decades there has been a growing interest to replace the ZDDP-based lubricant additives because of their toxicity to aquatic wild life, adverse effects to human-health and poisoning of automotive exhaust.

The need of hour therefore is to develop some sulfur, phosphorous and metal-free lubricant additives which are sustainable to environment, human-health and machine components. To achieve these objectives, the present work was undertaken where a variety of antiwear additives; β-lactum antibiotics, fluroquinolones, quinoline based ionic compounds, synergistic interaction of Schiff base with commercial borate ester and SDS-stabilized Mg-doped-ZnO nanoparticles have been synthesized, characterized and their tribological properties have been evaluated. The thesis has been divided into following heads: Introduction, Experimental details, Results & Discussions, Summary and References.

Chapter 1 elaborates the study about the basics of tribology in terms of friction, wear and lubrication, need of lubrication, different mechanisms of lubrication and types of lubricant additives. Special attention has been given to low SAPS additives. This chapter also contains detailed overview of literature survey regarding antiwear and antifriction lubricant additives. The in-depth knowledge gained from literature survey enabled us to frame the scope and objectives of the present investigation which have been highlighted at the end of this chapter.

Chapter 2 describes the experimental details including materials used, testing methodologies and the instrumentation which have been used to characterize the additives as well as lubricated surfaces. Quantum chemical calculations were performed using density functional theory (DFT) method to correlate the experimentally obtained results of antiwear additives with the theoretical ones.

Chapter 3 includes antiwear performance of β-lactum cephalosporin antibiotics such as cefixime, cephalexin and cefadroxil. Antiwear behavior of β-lactum antibiotics has been studied using Four Ball lubricant tester in paraffin oil. The results have been compared with high sulphated ash, phosphorous and sulfur (SAPS) containing conventional zinc dibutyldithiophosphate (ZDDP). The tests have been performed using optimized concentration of the additives (1% w/v) at various loads from 294, 392, 490, 588, 686 to 784N for 30 min. test duration and for various test durations from 15, 30, 45, 60, 75 and 90 min. at 392N load. Various tribological parameters such as mean wear scar diameter (MWD), friction coefficient (μ), mean wear volume (MWV), running-in, steady-state and overall wear rates show that all the studied antibiotics act as efficient antiwear additives. Among all the investigated antibiotics, cefixime shows excellent antiwear properties along with very high load bearing capacity. These metal, halogen and phosphorous free formulations provide excellent tribological and environment friendly compatibilities when used as additive in paraffin oil. Formation of *in situ* protective tribofilm is evident by the results of surface characterization techniques (SEM/EDX, AFM & XPS).

On the basis of variation of mean wear scar diameter and friction coefficient with time, the order of antiwear efficiency is given below:

Cefixime > Cefadroxil > ZDDP > Cephalexin > Paraffin oil

Theoretically calculated values for various molecular orbital indices including the energy of frontier molecular orbitals (E_{HOMO} and E_{LUMO}), energy gap (ΔE), ΔE_1 and ΔE_2 have been used as the criteria to investigate the interactions between lubricant additives and metal surface. The theoretical calculations have been found to be in accordance with the experimental observations.

Chapter 4 displays the tribological application of fluoroquinolones like ofloxacin, ciprofloxacin and norfloxacin studied on four ball lubricant tester in base oil. All tribological tests have been performed at optimized concentration of the additives (0.25%

w/v) at various test conditions. All the investigated additives show excellent antiwear properties and possess high load bearing capacity. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) have been used to study the surface topography of worn surface. The AFM and SEM micrographs of the wear scar in the presence of additives show a drastic decrease in surface roughness. Energy-dispersive X-ray (EDX) analysis of the worn surface in presence and absence of additives exhibits the presence of nitrogen, oxygen and fluorine on the worn surface, indicating adsorption of the additive on the rubbing surface forming a tribofilm. These *in situ* formed tribofilms are responsible for reducing wear and friction at steel-steel interface. Quantum chemical calculations based on density functional theory (DFT) have been performed and these correlated well with the experimental results.

Chapter 5 shows quinolinium derivatives as potential candidates for their antiwear behavior. The N-substituted quinolinium halides, $[DIP\text{-}Q]^{+}Br^{-}$ [DIP-Q=1-(3-(1,3-dioxoisoindolin-2-yl)propyl)quinolon-1-ium], $[DIE\text{-}Q]^{+}Br^{-}$ [DIE-Q=1-(3-(1,3-dioxoisoindolin-2-yl)ethyl)quinolon-1-ium], $[P\text{-}Q]^{+}I^{-}$ [P-Q=propylquinolon-1-ium] and $[M\text{-}Q]^{+}I^{-}$ [M-Q=methylquinolon-1-ium] have been prepared and characterized by ^{1}H and ^{13}C NMR spectroscopic techniques. Tribological performance of these quinoline based quaternary salts as antiwear additives in paraffin oil has been assessed on four-ball test rig. The observed results have been compared with those of zinc dibutyldithiophosphate (ZDDP), a high SAPS additive. The tribo-testing of these additives has been performed using 1% w/v additives concentration at different loads and time. Potentiality of these compounds as antiwear additives is evident from their observed tribological data. All the quinolinium derivatives proved to be better antiwear additives than ZDDP. Among the tested synthesized compounds, $[DIP\text{-}Q]^+Br^-$ exhibits the best tribological behavior followed by $[DIE\text{-}Q]^+Br^-$, $[P\text{-}Q]^+I^-$ and then $[M\text{-}Q]^+I^-$. The surface topography of worn surface studied by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) shows that surface roughness is reduced to a greater extent in case of quinolinium derivatives than that lubricated with ZDDP or base oil alone. Energy Dispersive X-Ray (EDX) and X-ray Photoelectron Spectroscopy (XPS) analysis of worn surfaces in presence of quinolinium additives shows that tribofilm is composed of $FeBr_3$, Fe_3O_4 and organic compounds containing carbonyl and imine bonds. Theoretical investigations using quantum chemical calculations are indicative of significant chemical interactions of these quinolinium additives with metal surface which are strongly supported by the observed experimental data.

Chapter 6 emphasizes the synergistic interaction of Schiff base derived from 4-aminotriazole and indole-3-carboxylaldehyde with commercial organoborate towards tribological performance. The tribological behavior of Schiff base has been evaluated in absence and presence of borate ester (Vanlube 289) in paraffin oil using four-ball tester. This metal, sulfur and phosphorous free formulation provides excellent tribological and environment friendly compatibilities when used as additive in paraffin oil. The pronounced tribological performance of the blend is due to their synergistic action via formation of donor-acceptor complex between nitrogen-boron which facilitates the formation of durable tribofilm preventing direct metal-metal contact. The surface topography of worn surfaces has been studied by Scanning Electron Microscopy (SEM) and contact mode Atomic Force

Microscopy (AFM) which show the drastic decrease in surface roughness in presence of synergistic mixture. The EDX analysis of worn surface lubricated with synergistic formulation exhibits nitrogen, carbon, boron and oxygen indicating the adsorption of additive on the metal surface to form *in situ* protective tribofilm which prevents direct metal-metal contact and thus reduces friction and wear. The quantum chemical calculations (QCC) studies shows that there is more significant interaction of Schiff base additive with the metal surface than those of its individual components and the data correlate very well with the obtained tribological results.

Chapter 7 gives insight on the synthesis, characterization and tribological application of SDS-stabilized Mg-doped-ZnO nanoparticles. Pure zinc oxide (ZnO) and magnesium-doped zinc oxide (ZMO) nanoparticles (NPs) having composition $Zn_{0.88}Mg_{0.12}O$ have been prepared by auto-combustion method. As synthesized ZMO nanoparticles were calcined for 2h at 800 and 1000 ^{o}C to yield ZMO nanoparticles of different size, abbreviated as ZMO-1 and ZMO-2, respectively. These nanoparticles have been characterized by powder X-ray diffraction (XRD), Energy-dispersive X-ray (EDX) and Transmission electron microscopy (TEM) techniques. The average size of these nanoparticles is found to be 30, 27, 39 and 44 nm, respectively for ZnO, ZMO, ZMO-1 and ZMO-2. A stable dispersion of ZMOs (ZMO, ZMO-1 & ZMO-2) nanoparticles in the paraffin oil has been achieved with an appropriate percentage of surfactant sodium dodecylsulphate (SDS), abbreviated as SZMOs (SZMO, SZMO-1 & SZMO-2). The effect of particle size of these nanoparticles on the tribological behavior of paraffin oil has been investigated at an optimized additive concentration (0.25% w/v with 0.10% SDS) using different ASTM D4172 and D5183 standards. These tribological tests revealed that the SZMOs nanoparticles act as excellent antiwear agents, friction modifiers and enhanced the load bearing ability. Being the smaller particle size, SZMO nanoparticles (27nm) exhibited better tribological behavior than SZMO-1 (39 nm) and SZMO-2 (44 nm). The pronounced tribological behavior of these nanoparticles is according with the decreasing particle size. The morphology of worn surfaces lubricated with nanoparticles and without SZMOs has been examined by Scanning Electron Microscopy (SEM) and contact mode Atomic Force Microscopy (AFM) analyses. Energy-dispersive X-ray (EDX) analysis of the surface lubricated with SZMO nanoparticles show the presence of zinc, magnesium, iron, carbon and oxygen on the steel surface which confirmed the adsorption of the additive on the interacting/rubbing surface. These elements form tribochemical film on the interacting surfaces and act as nanobearing to prevent the metal-metal contact thereby reducing wear and friction.

The results of tribological studies revealed that all the additives used in the present investigation significantly enhanced the antiwear and load carrying properties of paraffin base oil. Tribochemistry of the additives can be explained on the basis of strong affinity of the additives to interact with metal surfaces to form *in situ* protective tribofilm either in the form of adsorbed materials, decomposed product, nanobearings, and tribosintered nanoparticles. The observed tribological behavior exhibits excellent correlation with the various quantum chemical calculation parameters. Being free from sulfur and phosphorous, these additives have potential to be developed as environment friendly antiwear lubricant additives and may be used in place of high SAPS containing additives.