PREFACE

In mechanical systems, friction and wear are imminent for the surfaces in relative motion leading to huge energy and material losses. Consequently, the efficacy and life span of such systems are substantially reduced. Selection of a suitable lubricant may prove fruitful to overcome losses due to friction and wear. In addition to this, lubricants are multifunctional; act as cooling agents (dissipating heat), corrosion inhibitors (preventing corrosion), cleaning agents (removing wear particles from the contact zone), sealing agents (preventing entry of dirt and moisture) etc. Over the years, a variety of lubricant additives have been employed for diverse purposes to lubricants. The antiwear and antifriction additives have been used in a lubricant to protect the engineering components from wear and tear. Among these lubricant additives, zinc dialkyldithiophosphates (ZDDP) have been frequently used. Their use is restricted nowadays due to the huge amount of sulfated ash, phosphorous and sulfur contents (SAPS), which cause toxicity to aquatic life, adverse effects to human health and the poisoning of the automotive exhaust. Consequent upon several strict environmental legislations, greener lubricant additives are being continuously sought. Thus, the need of the hour is to replace such lubricant additives.

In view of the above; the present work was undertaken to develop sulfur, phosphorous-free antiwear additives which are cost-effective, environment friendly and capable to reduce both friction and wear. During the current investigation, different categories of antiwear additives; Schiff bases, Ionic Liquid and sodium dodecyl sulfate(SDS) stabilized-Ca-doped CeO_2 nanoparticles (IL-CCO and SCCO), carbon-based Cu@C and ionic liquid stabilized, IL-Ag@C materials have been prepared, 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 introduction deals with the basics of tribology in terms of friction, wear and lubrication. In addition to this, a concise review of ongoing and past researchon lubricant additives has also been described in this section. The scope and objectives of the present investigation have been highlighted at the end of this chapter.

Chapter 2 illustrates the experimental details including used materials, testing techniques and the instrumentations which have been used to characterize the additives as well as lubricated surfaces. Molecular dynamics simulations were performed to correlate the experimentally obtained results of antiwear additives with the theoretical ones.

The results and discussion of the experimental data have been spread over four chapters from 3 to 6. **Chapter 3** presents synthesis of a series of Schiff bases derived from *o*-tolidine through its condensation with salicylaldehyde (OH-BT), naphthaldehyde(H-NT) and 2-hydroxynaphthaldehyde (OH-NT).The synthesized Schiff bases have been characterized by FT-IR and ^{1}H NMR spectroscopic techniques. The triboactivity of these compounds has been studied in paraffin oil (PO) using four-ball tester (FBT) at an optimized concentration of 0.25% w/v under ASTM D4172 and D5183 test conditions. Based on tribological data, mean wear scar diameter (MWD), mean wear volume (MWV), coefficient of friction (COF), load-carrying ability and wear rate, OH-BT shows better efficiency than other additives.

Morphology and composition of wear scar have been studied by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray analysis (EDX) and relate very well with the observed tribological data. The EDX analysis of the wear scar lubricated with synthesized additives provides evidence for the presence of nitrogen and oxygen. The reaction of the most active compound OH-BT was carried out with thioglycolic acid to ascertain the active involvement of the imine group towards tribological behavior, Reduced antiwear performance of the reaction product (OH-BTS) may be directly associated with the absence of the imine group (-CH=N-). Molecular dynamics (MD) simulations have been used to study the mechanism of adsorption of the studied Schiff bases in paraffin oil on the iron slab. The order of adsorption energies of the Schiff base additive molecules has been found to agree well with the experimentally observed data.

Chapter 4 contains the calcium-doped cerium oxide (CCO) nanoparticles synthesized by sol-gel method. Their surface has been modified by surfactants, sodium dodecyl sulfate and 1-decyl-3-methyl imidazolium bis (trifluoromethyl sulfonyl) imide to yield SCCO and IL-CCO, respectively. Powder X-ray Diffraction (p-XRD) patterns of nanoparticles and surface-modified nanoparticles are indicative of the cubic phase of ceria. Fourier Transform Infrared Spectral (FTIR) studies confirm the surface modification of nanoparticles, particularly with ionic liquid. Morphology of the as-prepared nanoparticles investigated by FE-SEM, TEM/HR-TEM reveals that there is a decrease in the size of nanoparticles from CCO followed by SCCO and then IL-CCO. Wrapping of nanoparticles by ionic liquid is apparent in the SEM and TEM images. Worn surface analysis by SEM/EDX, and AFM corroborated the tribological performance. The order of the activity could be correlated with the size of the nanoparticles. Moreover, lubricating properties of ionic liquid have been found to be instrumental for the elevated activity of IL-CCO. The presence of heteroatoms of ionic liquid, nitrogen, oxygen, fluorine, sulfur along with calcium and cerium of nanoparticles in EDX analysis of the wear scar surface lubricated with IL-CCO confirms the vital role of ionic liquid towards the tribological activity.

Chapter 5 addresses the synthesis of copper nanoparticles, carbon spheres and their composite, Cu@C. The analytical techniques; powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy/high- resolution transmission electron microscopy (TEM/HR-TEM), Raman and X-ray photoelectron spectroscopy (XPS) have been employed for their characterization. Comparative activity of the base oil and the blends has been adjudicated considering the experimental data for mean wear scar diameter (MWD), coefficient of friction (COF), load-carrying capacity and wear rates collected from the above standard tests. The admixture-containing nanohybrid, Cu@C appears to show the best activity. The relative activity of different admixtures is verified by atomic force microscopy (AFM) and scanning electron microscopy (SEM) with EDX results of the wear pathway. The EDX spectrum of Cu@C shows the existence of copper together with carbon on the wear scar surface confirming their contribution in the formation of *in situ* tribofilm.

Chapter 6 illustrates the synthesis of carbon spheres and their composite Ag@C by the hydrothermal method. The composite Ag@C was stabilized by the ionic liquid, 1-decyl 3-methyl imidazolium boron tetrafluoride (DMIM BF_4) to yield (IL-Ag@C). These have been successfully characterized by various states of the art techniques like Raman, FT-IR powder XRD, SEM with EDX, HRTEM and XPS. Triboactivity of the carbon spheres and the composites were assessed in base lube, polyethylene glycol (PEG-200) at 0.5% w/v concentration on a four-ball tester under ASTM D4172 and ASTM D5183 conditions. Based on tribological data, namely coefficient of friction (COF), mean wear scar diameter (MWD), load-carrying capacity and loss of frictional power, IL-Ag@C shows better efficiency than other additives. Morphological studies of the wear scar were performed by SEM and AFM (Atomic Force Microscopy) techniques. The EDX analysis of the wear scar surface lubricated with IL-Ag@C showed iron also in addition to the constituent elements of the composite. Thus, active participation of the adsorbed additive towards tribofilm formation is validated. The XPS studies of the same surface, further confirm the presence of boron nitride, boron carbide along with iron oxide. These boron compounds have, indeed, enriched the tribofilm for improved triboactivity.