

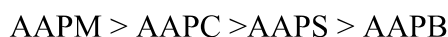
The efficiency of a mechanical device is strongly reduced due to friction and wear between moving surfaces. Friction and wear are therefore, always undesirable in such applications as these adversely affect the functionality of the mechanical device and limit its life-span. Lubricants play an important role towards reduction in friction and wear between sliding surfaces by interposing a thin film. 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 along with lubricants. Among these lubricant additives, zinc dialkyldithiophosphates (ZDDP) are being frequently used as excellent multifunctional lubricant additives in lubricant industries.

For the last two decades there has been a growing trend towards greener lubricant additives driven by several environmental legislations. As environmental legislations become more stringent, it becomes important and urgent to find a substitute that is more environmentally friendly. This is of utmost need therefore, to replace the ZDDP-based lubricant additives because of high amount of Sulfated Ash, Phosphorous and Sulfur (SAPS) contents which cause toxicity to aquatic wildlife, adverse effects to human-health and poisoning of automotive exhaust.

In view of the above, development of sulfur, phosphorous-free antiwear additives which are cost-effective, environment friendly in nature and capable to reduce both friction and wear, has drawn attention for tribological applications. The present work was undertaken with a view to develop such additives. During the present investigation, different categories of antiwear additives; Schiff bases and their synergistic formulation with organoborate ester, Copper (II) benzoylhydrazones, Stearic acid modified- $\text{CaCu}_{2.9}\text{Zn}_{0.1}\text{Ti}_4\text{O}_{12}$ nanoparticles (SCCZTO) and TiO_2 -reinforced-B-N-codoped-MRG nanomaterials 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.

A series of SAPS-free Schiff bases derived from condensation of 4-aminoantipyrine with benzaldehyde, salicylaldehyde, *p*-methoxybenzaldehyde and *p*-chlorobenzaldehyde have been synthesized and characterized. The tribological

behavior of Schiff bases has been evaluated in absence and presence of borate ester (Vanlube 289) in paraffin oil using four-ball tester. These metal, sulfur and phosphorous free formulations provide excellent tribological and environment friendly compatibilities when used as additives in paraffin oil. Being ashless, these antiwear lubricant additives have potential to find applications in various automotive industries in improving machine efficiency. The pronounced tribological performance of these blends 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. Among all of the constituents of tribofilm (BN, B₂O₃ and Fe₂O₃/Fe₃O₄) on worn surface, boron nitride is mainly responsible for their synergistic behavior which has been confirmed with the help of XPS and EDX studies. The role played by boron nitride may be because of its layered structure. The SEM and AFM studies suggest that the surfaces generated through these blends are much smoother in comparison to ZDDP/BE/base oil. Among the studied Schiff base additives, the best antiwear and load carrying properties are exhibited by AAPM which are very well supported by the theoretical studies using density functional method. Among all the AAPs-Schiff bases the following order of tribological behaviour has emerged-



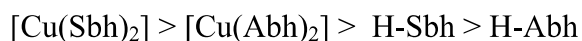
Methoxy and chloro derivatives were better adsorbed on the surface and their decomposition at higher load and/or temperature would have resulted into formation of additional triboactive metal oxide/chloride causing increase in tribological efficiency.

On the basis of MWD, COF and load carrying ability the overall tribological behaviour of different additive formulations may be arranged in the following order-



Thereafter, the synthesis, characterization and tribological investigations of a series of N-substituted benzoylhydrazones derived from condensation of substituted aromatic carbonyl compounds with benzhydrazide and their copper (II) complexes were performed in paraffin oil using four-ball lubricant tester. The Schiff base copper

(II) complexes exhibit excellent antiwear and load carrying ability which is even much better than those of ZDDP/Schiff bases at 1% w/v concentration. The pronounced tribological performance of the complexes is due to their large surface coverage which in turn, facilitates the formation of durable tribofilm preventing direct metal-metal contact. Among all of the constituents of tribofilm (decomposed nitrogen, CuO, Cu₂O and Fe₂O₃/Fe₃O₄) on worn surface, CuO and Cu₂O are mainly responsible for their excellent tribological behavior which has been confirmed with the help of XPS analysis. The SEM and AFM studies suggest that the surface generated in presence of complexes is much smoother in comparison to ZDDP/Schiff bases/base oil under various test conditions. Out of the studied Schiff bases, H-Sbh exhibits better antiwear and load carrying properties than H-Abh. Similarly, [Cu(Sbh)₂] proves to be superior antiwear additive over [Cu(Abh)₂]. Theoretically calculated values for various molecular orbital indices including the energy of frontier molecular orbitals (E_{HOMO} and E_{LUMO}), energy gap (ΔE), ΔE₁, ΔE₂ and dipole moment have been used as the criteria to investigate the interactions between lubricant additives and metal surface. These interaction parameters based on density functional theory support very well the experimentally observed tribological behavior. The antiwear properties of studied Schiff bases and their copper (II) complexes were observed to follow the order given below-



In order to investigate the effect of particle size on the tribological behavior of paraffin oil, the CaCu_{2.9}Zn_{0.1}Ti₄O₁₂ nanoparticles (CCZTO) and stearic acid (SA) modified SCCZTO nanoparticles of varying size 60, 80 and 90 nm have been synthesized and characterized. The stearic acid capped nanoparticles remain dispersed without agglomeration in paraffin oil. Tribological tests revealed that these blends effectively enhanced the antiwear properties of base oil in order of decreasing particle size. The overall, running-in and steady-state wear rates in presence of SCCZTOs nanoparticles except -12h have been found to be lower than those of ZDDP. The load bearing ability of the SCCZTOs nanoparticles was found to be far better than ZDDP and paraffin oil alone. On the basis of observed tribological results, the order of antiwear efficiency is given below:



Surface analysis by SEM and AFM also supports the observed tribological behavior of SCCZTOs nanoparticles. The EDX analysis of wear track shows presence of C, Ca, Cu, Zn, Ti, O and Fe elements in the tribofilm whereas XPS spectra revealed chemical form of these elements as -C(O)O-, C-C/C-H moieties; CaO; CuO, Cu₂O; TiO₂ and Fe₂O₃. EDX and XPS analysis support the mechanism of wear through nano bearing as well as process of tribosinterisation.

Further, with a view to study cumulative effect of nano bearing and layered materials with and without synergy, few layered thick reduced graphene oxide (MRG), B-MRG, N-MRG, B,N-co-doped-reduced graphene oxide (B-N-MRG) and TiO₂-reinforced-B-N-MRG (TiO₂-B-N-MRG) nanomaterials have been successfully synthesized by microwave assisted method. These nanomaterials have been characterized by various states of the art techniques like Raman, powder XRD, SEM with EDX, HRTEM and XPS. As novel lubricant additives, the as-prepared B-N-MRG and TiO₂-B-N-MRG nanomaterials possess appreciable dispersion stability in paraffin oil. Friction and wear characteristics of these nanomaterials were evaluated using four-ball lubricant tester at optimized concentration (0.15% w/v). The observed tribological results show that B/N/B-N doped MRG and TiO₂-reinforced MRG exhibit tremendous reduction in MWD (from 0.733 to 0.366 mm) and COF (from 0.0756 to 0.0564) values but significant enhancement in load carrying ability (from 1078 to 1470N). In addition to this, studied additives exceptionally reduced the steady-state wear rate in the range of 64-98%. SEM and AFM studies revealed that there is some pad-like deposition on the sliding surfaces lubricated with B-N-MRG and TiO₂-B-N-MRG which may be the consequence of *in situ* formed tribofilm preventing metal-metal contact. The XPS analysis of tribofilm formed on the surface lubricated with TiO₂-B-N-MRG confirmed the presence of graphitic carbon, boron nitride and tribosintered TiO₂ nanoparticles. On the basis of various antiwear and COF tests the following order of tribological behaviour of graphene based nanomaterials has emerged-

TiO₂-B-N-MRG > B-N-MRG > N-MRG > B-MRG > MRG > Paraffin oil

Above results suggest that the synthesized B-N-MRG and TiO₂-B-N-MRG nanomaterials are the potential candidates to be developed as low SAPS antiwear

lubricant additives under boundary lubricating conditions. Despite its low thickness, MRGs have improved anti-frictional properties and imparted relatively high wear resistance that makes them attractive materials for various applications in tribology.

The results of tribological studies revealed that all the additives used in the present study 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, nano bearings, and tribosintered nanoparticles or layered structures such as boron nitride and MRG. The observed tribological behavior in case of Schiff bases and copper (II) complexes 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.