# SUMMARY

Friction and wear are innately detrimental to the machine components. Rubbing of the proximal surfaces develops calamitous effects in due course. A lubricant imposed between the rubbing surfaces restrains the peril of friction and wear. For promoting lubrication, antiwear and antifriction additives are blended with the base lubricant. Various types of additives are available in the literature for their wear and friction-reducing properties, such as organic compounds containing heteroatoms, metal complexes, and nanomaterials. Zinc dialkyl dithiophosphates (ZDDP) are the most versatile additives. Still, their frequent use has been restricted due to their tendency to retard the efficiency of exhaust emission catalytic converters. Several standard norms are available in the literature, where restrictions have been imposed on the limits of sulfur, phosphorus, and sulfated ash contents (SAPS) in the additives to attain a clean environment. Organic compounds with heteroatoms are easily dispersed in typical base oils providing outstanding results. From an environmental perspective, the heterocyclic organic compounds containing nitrogen, and oxygen, are highly recommended for the purpose owing to their facilitated adsorption on the metal surface through lone pairs of electrons and ring electrons of the associated aromatic ring systems. The nature of substituents at the aromatic ring may further modulate electron density at the heteroatoms to facilitate adsorption. An increase in heteroatoms provided all of them are structurally capable of accessing the metal surface, results in enhanced adsorption. Heterocyclic systems with fused benzene rings have been widely tested for their applicability as tribologically active additives. However, fused heterocyclic systems with an increased number of heteroatoms have seldom been studied. The present investigation focuses on the synthesis and characterization of fused heterocyclic ring systems, tetrahydropyrazolopyridines (THPP-R), and substituted pyranopyrazoles (PPz-R), [where R stands for hydrogen, methyl, and methoxy] and evaluation of their tribological activity.

Nanomaterials, mainly inorganic nanoparticles, nanosheets, and composites, are well-acknowledged in the field of tribology because their fast action at the interface increases the efficiency and high chemical stability reduces emissions. The nanoparticles of certain metals, metal oxides, metal sulfides, metal halides, etc., are well known to show tribological activity through several mechanisms, like tribosinterization rolling, polishing, and the formation of tribofilm or a combination of these mechanisms. Two-dimensional nanomaterials such as graphene, molybdenum disulfide, tungsten disulfide graphitic carbon nitride, and hexagonal boron nitride have a large surface area and are known to show lubricating properties due to weak van der Waals forces between adjacent layers. In the present work, therefore, use has been made of nanoparticles and nanosheets and their composites to develop nano additives with high tribological efficiency. The blends of synthesized additives were prepared in paraffin oil, and the tribological activity of these nano lubricants exhibited enhancement in the lubricity of paraffin oil. Thus, paraffin oil-based nano lubricants containing polyaniline intercalated vanadium pentoxide nanosheets, PANI-$V_2O_5.nH_2O$ (PVO), and the composite of graphitic carbon nitride (g-$C_3N_4$) nanosheets with lanthanum orthovanadate nanoparticles in the monoclinic phase (m-$LaVO_4$), g-$C_3N_4$/m-$LaVO_4$ have been explored for enhancement of lubricity. The thesis has been divided into the following heads: Introduction, Experimental details, Results & Discussions, Summary, and References.

The additives containing a fused heterocyclic ring system, tetrahydropyrazolopyridines (THPP-H, THPP-Me, and THPP-OMe), were synthesized and characterized by NMR spectroscopy ($^1$H and $^{13}$C). The studied additives having zero SAPs contents show very high tribological activity at all the tested concentrations. The maximum activity is observed at a very low concentration, 0.25% w/v. Based on antiwear and load ramp tests at 0.25% w/v concentration, the activity of various additives could be established as -

ZDDP < THPP-H < THPP-Me < THPP-OMe

Morphological investigations (using SEM and AFM techniques) of the wear scar surface authenticate the relative tribological activity. The DFT calculations verify the experimentally found order of tribological activity. The EDX analysis of the wear scar surface shows the presence of heteroatoms, nitrogen, and oxygen, confirming the adsorption of different additives on the steel surface. The XPS spectra of the wear scar surface confirm that tribochemical film comprises decomposed products of the additive along with iron oxides.

A multicomponent synthetic pathway was adopted to synthesize another fused ring heterocyclic system, substituted pyranopyrazoles. Spectroscopic analysis by FT-IR and NMR ($^{1}H$ and $^{13}C$) revealed the successful preparation of H-, methyl-, and methoxy- group substituted pyranopyrazole molecules. All three pyranopyrazoles exhibited their maximum tribological activities at 0.25%w/v concentration. The ASTM D4172 tribological tests and wear rates showed that the activities of these pyranopyrazole derivatives followed the ascending order,

ZDDP < PPz-H < PPz-Me < PPz-OMe

The wear scar surface analysis by SEM and AFM revealed features following the order of the tribological activity. The presence of heteroatoms nitrogen and oxygen along with carbon on the steel surface validated the adsorption of the additives on the wear surface. DFT calculations show that PPz-OMe is relatively easy to polarize and interacts more strongly with the wear surface. The adsorption energies from the MD studies followed the same trend as those from the DFT calculations. The additive PPz-OMe has the most negative adsorption energy and thus interacts most strongly with the adsorbent surface. The mechanism of interaction between the additive molecules with the wear surface was understood through RDF analysis enabled by MD simulation results. The RDF plots show that nitrogen and oxygen in the pyran and pyrazole rings of PPz-OMe are almost equally associated with Fe atoms. In contrast, the additive PPz-Me interacts with the adsorbent mainly through the two nitrogen atoms of the pyrazole ring and the methyl carbon attached to the benzene ring (present at the *p*- position of the pyran ring). Thus, the optimum interaction of heteroatoms of the additive molecule with the wear surface is necessary for obtaining the best possible tribological activities.

In addition to the above, mixing borate ester with PPz-OMe enhanced the tribological activity compared with that observed for pure additive. XPS studies of the surface after the ASTM D4172 test showed the formation of boron nitride. It seems the latter is responsible for the synergistic increase in tribological activity

Further, an attempt was successfully made to improve the tribological properties of $V_2O_5$ nanosheets by grafting conductive polyaniline chains using *in situ* oxidative polymerization on $V_2O_5$, yielding the nanocomposite PANI-$V_2O_5.nH_2O$. Morphological studies of the composite by FE-SEM, TEM, and HR-TEM discern PANI intercalated into lamellar $V_2O_5$. The additives were characterized by XRD and spectroscopic techniques, FT-IR and XPS. The observed data indicate the absence of covalent interaction between PANI and $V_2O_5$ in the PVO. However, the interaction is through non-covalent forces like hydrogen bonding between organic and inorganic components, NH (PANI)......O-V ($V_2O_5$), and van der Waals forces. The intercalation of PANI between $V_2O_5$ nanosheets is evidenced by the considerably enhanced interlayer spacing between the $V_2O_5$ nanosheets. The tribological tests divulged the outstanding improvement in antiwear/antifriction efficiency and load-carrying capacity in the case of PVO. The improvement in tribological properties is attributed to synergistic interactions between $V_2O_5$ nanosheets and PANI. The feasibility of lubricating behavior of $V_2O_5$ nanosheets is apparently due to weak van der Waals forces existing between them, intercalation of PANI reinforced the structure, restricted agglomerating tendencies, and piling up the nanosheets using hydrogen bonding and van der Waals forces.

Furthermore, the graphitic carbon nitride, g-$C_3N_4$, was prepared by heating melamine, followed by ultrasonication. A solution combustion method has been used to prepare m-$LaVO_4$ nanoparticles using glycine as fuel. The preparation of the nanocomposite (g-$C_3N_4$/m-$LaVO_4$) was achieved by ultrasonication. FE-SEM, TEM, and HR-TEM were used to study the morphology of the additives. XRD, EDX, and FT-IR were used to characterize the additives. The m-$LaVO_4$ nanoparticles and g-$C_3N_4$ nanosheets are bonded together by weak physical interactions. The dispersions of the additives were found to be appreciably stable, as studied by UV/visible spectroscopy. The tribological parameters, MWD, COF, and load-carrying capacity of the synthesized additives were obtained from ASTM D4172 and ASTM D5183 tests at 0.05%w/v concentration. Undoubtedly, the nanoparticles and nanosheets show high tribological activity, but the composite shows an enormous increase in activity due to strong synergistic interactions. The SEM and AFM studies of the wear scar surface authenticate the observed activity. XPS studies reveal that the tribofilm is composed of adsorbed organic moieties of g-$C_3N_4$, $V_2O_5$, $La_2O_3$, and tribochemically oxidized $Fe_2O_3$. Thus, the nanocomposite establishes itself as a potential wear and friction modifier for lubricating systems.

Overall, all the investigated additives upgraded notably the wear/friction reducing and load-carrying properties of the base lube, paraffin oil. The nature of *in situ* formed protective tribofilm has provided the mechanism of tribological activity. The potentiality of these additives as highly tribologically active environmentally benign additives appears to be quite convincing. They may prove as substitutes for high SAPS-containing additives being free from sulfur and phosphorus.