Schiff bases being biologically active material are commonly used as antitumor, antibacterial, antifungal and anticancer drugs. These are also used as antiwear additives [Anacona *et al*.(1999) and Samanta *et al*.(2007)]. On the other hand, boron containing compounds have been used as effective antiwear additives, antioxidants, friction modifiers and corrosion inhibitors [Baldwin (1977), Herdan (2000), Wang *et al*.(2009) and Zhang *et al*.(2005)]. It is well known that boron based compounds have excellent tribological properties under high pressures and elevated temperatures in the lubricated contacts [Wang *et al*.(2013), Yang *et al*.(2011), Yan *et al*.(2011) and Reeves *et al*.(2013)]. Tribochemical processes that take place at the interfaces lubricated with boron-based additives lead to formation of surface layers containing B_2O_3 and BN [Mosey *et al*.(2005), Liu *et al*.(2002) and Ye *et al*.(2002)]. These layers protect surfaces from a direct surface-to-surface contact and reduce both friction and wear. A step towards development of sustainable additive, synergistic interaction of boron based additive with Schiff base has been undertaken in this chapter.

Herein, the present study reports synthesis of sulfur, phosphorous and halogen free Schiff base and its characterization with the help of FT-IR and ^{1}H NMR spectroscopic techniques. The friction and wear reducing properties of synergistic mixture of Schiff base with commercial borate ester in paraffin oil would be compared with Schiff base and its individual components. Quantum chemical calculations of studied Schiff base and its starting materials have been also performed using Gaussian^{03} program to correlate their experimentally obtained tribological behavior with the theoretical one.

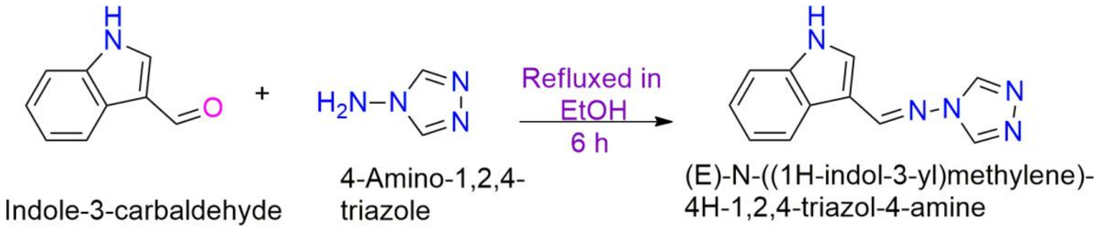
6.1. Materials and methods

6.1.1. Chemicals

The starting materials indole-3-carboxylaldehyde (97%, Sigma Aldrich) and 4-aminotriazole (98%, Sigma Aldrich) were used to synthesize the Schiff base. All other chemicals and solvents used in this work were of AR grade and used without further purification.

6.1.2. Synthesis of Schiff base lubricant additive

The Schiff base (E)-N-((1H-indol-3-yl)methylene)-4H-1,2,4-triazol-4-amine was synthesized by reacting anhydrous ethanolic solution (50ml) of indole-3-carboxylaldehyde (0.04mol) with ethanolic solution (50ml) of 4-aminotriazole (0.04mol). The reaction mixture was refluxed for 6h (Scheme 6.1). The completion of the reaction was monitored by TLC. After cooling at room temperature, the obtained light brown colored precipitate was filtered on Büchner funnel, washed several times with ethanol, recrystallized from methanol and then dried *in vacuo*.



Scheme 6.1. Synthesis of Schiff base derived from indole-3-carbaldehyde with 4-amino-1,2,4-triazole

6.1.3. Characterization of Schiff base lubricant additive

Yield (89%). **M.p.**90^{o}C. **IR (ν cm^{-1}, KBr):** 3387cm^{-1} (N-H strech), 3049cm^{-1} (Ar. C-H stretch), 2907cm^{-1} (Aliphatic C-H stretch), 1545cm^{-1} (C=C), 1612cm^{-1} (C=N), 1336 cm^{-1} (C-N stretch). **^{1}H NMR (DMSO-d$_6$, 300 MHz)** δ 7.20-7.30 (m, 2H, Ar-H), 7.51-7.54 (d, 1H, Ar-H), 8.02 (s, 1H, =CH-NH), 8.18-8.20 (d, 1H, Ar-H), 9.06-9.09 (d, 3H, =CH-), 11.98 (s, 1H, -NH), Figure 6.1.

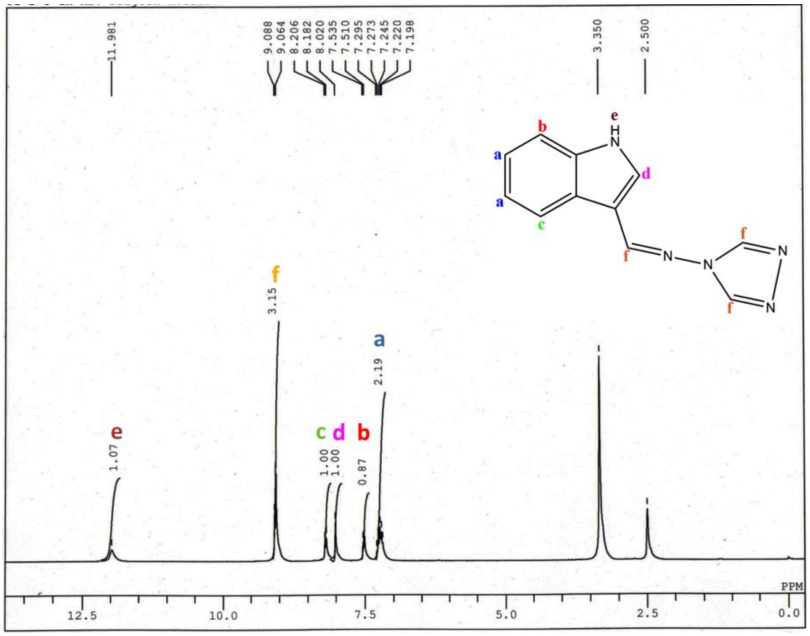


Figure 6.1. ^{1}H NMR spectra of the synthesized Schiff base additive

6.1.4. Tribological Characterization

6.1.4.1. Sample Preparation

Paraffin oil blends of Schiff base having concentrations 0.00, 0.25, 0.5, 0.75 and 1.0 % (w/v) with 1.00, 0.75, 0.50, 0.25 and 0 % (w/v) of borate ester respectively, were made by stirring for 1-2h on magnetic stirrer. The entire antiwear and load carrying tests were carried out at an optimized concentration i.e., 1.0% w/v Schiff base, 1% w/v synergistic formulation (0.5% Schiff base+0.5% BE) and compared with those of 1.0% w/v Schiff base, commercial borate ester (BE), 4-aminotriazole and indole-3-carboxylaldehyde in paraffin oil.

6.2. Results and discussion

6.2.1. Antiwear studies

The potentiality of the synthesized Schiff base and its synergistic formulation as antiwear additive in paraffin oil was investigated using four-ball tribometer. Figure 6.2 exhibits the effect of additive concentration on the mean wear scar diameter (MWD). In presence of additives, the value of MWD gets significantly reduced. As the additive concentration in base oil increases, the MWD value successively reduces up to the lowest at 1% w/v. Thus, the optimum additive concentration is observed as 1% w/v. The variation of MWD of steel balls lubricated with mixture of Schiff base to the commercial borate ester in base oil has been studied for different combinations by keeping total additive concentration as 1% w/v at 392N load for 60 min test duration, Figure 6.3. The extent of reduction in MWD values is found to be maximum in case of surface lubricated with 0.5% w/v of each Schiff base and borate ester. The value of MWD has been found to be high in case of surface lubricated with 1% w/v of 4-aminotriazole/indole-3-carboxylaldehyde but in presence of borate ester or Schiff base additive, the value of MWD was slightly reduced. By adding small amount i.e., 0.25% w/v of Schiff base additive to borate ester, significant decrease in the MWD value is observed. To show the synergy between Schiff base and BE, bar diagram has been made, Figure 6.4. The diagram evidently exhibits synergy between Schiff base and BE as MWD shows appreciable decrease in its value when 0.5% of each are taken instead of 1% alone of the individuals. Thus, entire tribological tests have been conducted at an optimized concentration of synergistic formulation of Schiff base along with borate ester (0.5+0.5% w/v) and compared with those of 1% w/v of the individual additives. Similarly, Figure 6.4 reveals that as the MWD decreases the values of COF also decrease for the different combinations of additives.

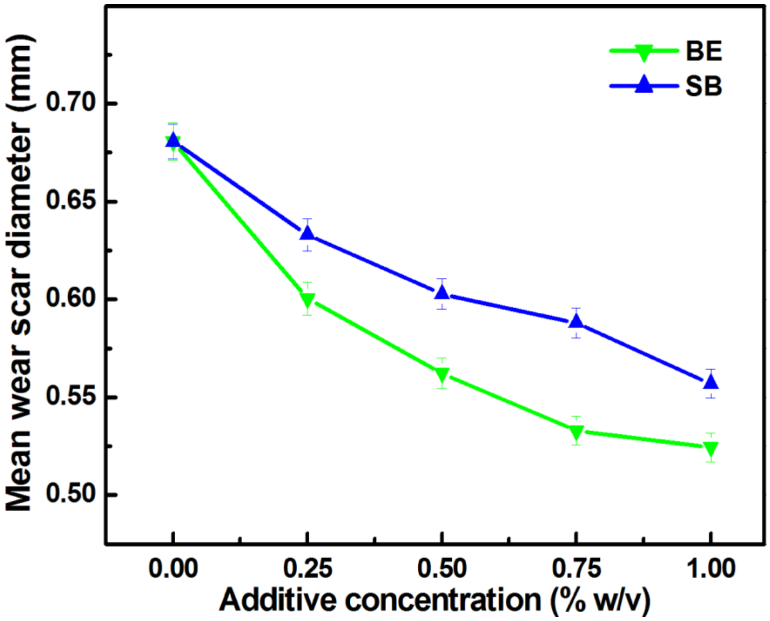


Figure 6.2. Variation of mean wear scar diameter for paraffin oil as a function of increasing different additive concentrations at 392 N applied load for 60 min test duration

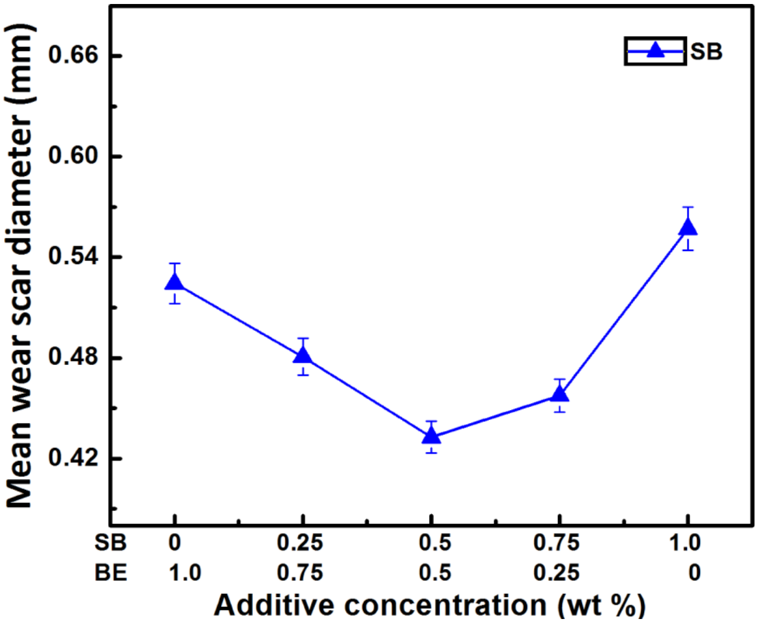


Figure 6.3. Effect of change in concentration of different additive formulations on mean wear scar diameter in paraffin oil at 392N applied load for 60 min duration

Figure 6.5 shows the variation in MWD as a function of time at 392N applied load in paraffin oil with and without studied additives at optimized additive concentration (1%

w/v). In case of paraffin oil, the MWD increases with time but in case of tested additives the MWD increases up to 30 min, after that it is stabilized. There are numerous factors which may enhance the lubrication efficiency of the additive such as conjugation, planarity of the molecule, number of donor groups [Wan *et al*.(1997)]. As the number of hetero atoms, aromatic rings and donor groups increases, the tendency of additive molecule to get adsorbed on sliding surface to form *in situ* protective tribochemical film on steel-steel interface also increases [Jaiswal *et al.(*2014)].

Figure 6.6 shows the variation of mean wear volume (MWV) with respect to time. The MWV at different time duration was calculated using eq. 2.3. The comparison of running-in and steady-state wear rates of different additives has been mentioned in Figures 6.7 and 6.8. The values of running-in and steady state wear rates are found to be lowest in case of synergistic formulations. The steady-state wear rate is a measure of machine life and it is found to be lower than that of running-in wear rate.

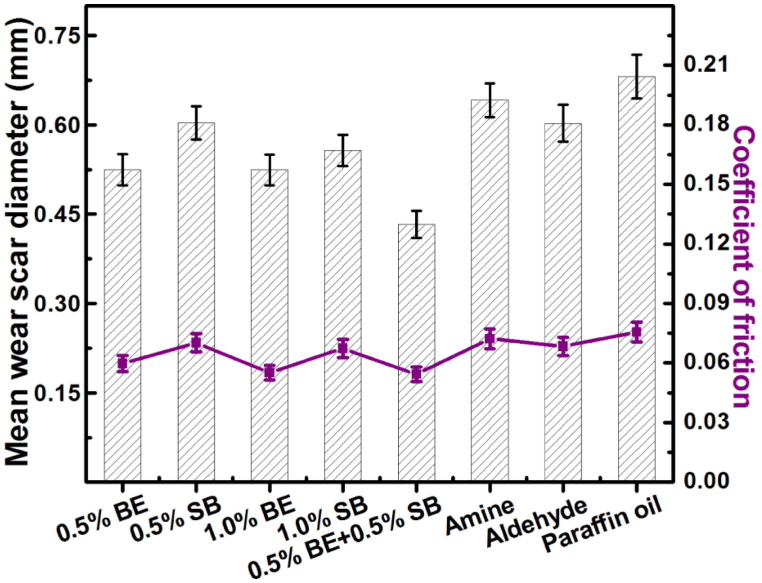


Figure 6.4. Variation of mean wear scar diameter and average coefficient of friction values in absence and presence of different additives concentrations with borate ester in paraffin oil at 392N applied load and 60 min duration

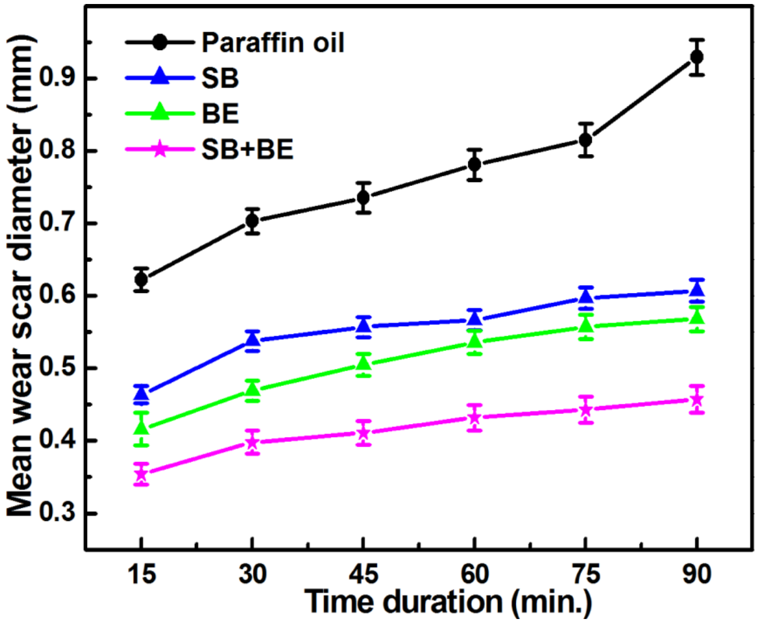


Figure 6.5. Variation of mean wear scar diameter with time in paraffin oil containing of 1% w/v of Schiff base, borate ester and synergistic formulation at 392N applied load

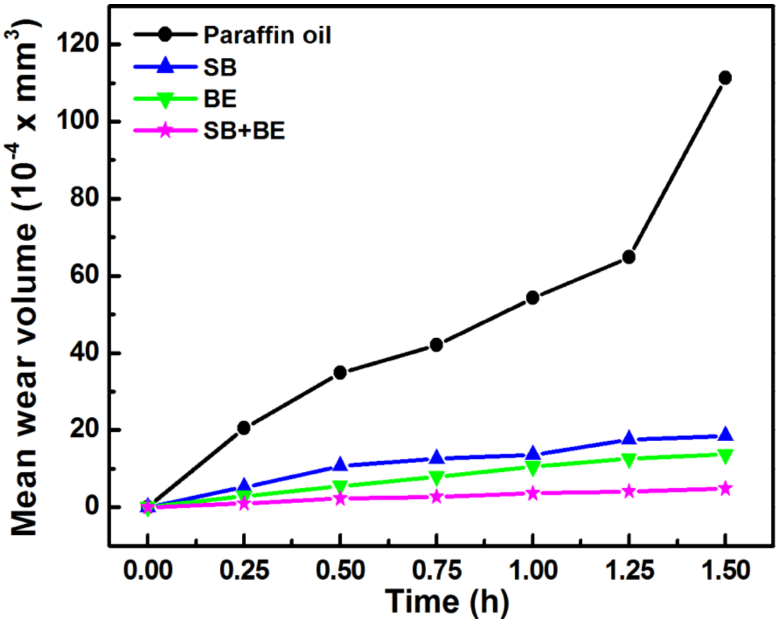


Figure 6.6. Variation of mean wear volume with time in paraffin oil containing 1% w/v of Schiff base, borate ester and synergistic formulation at 392N applied load

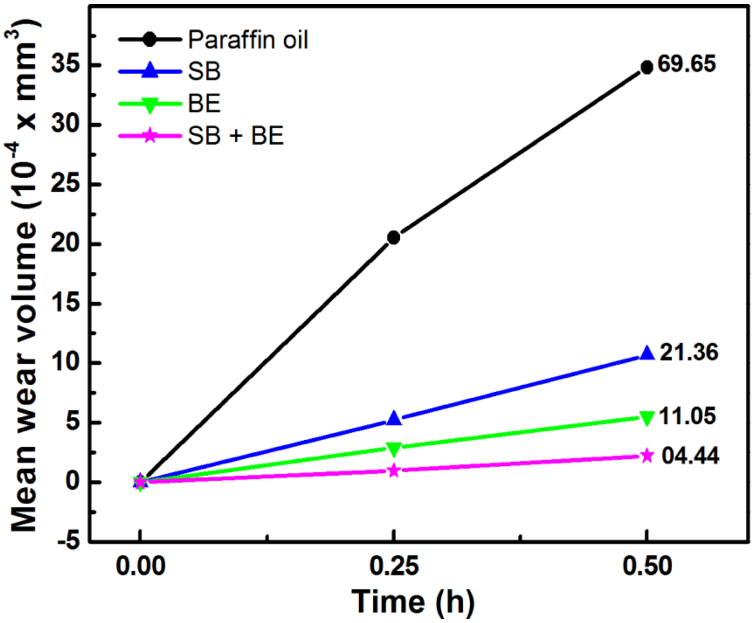


Figure 6.7. Determination of running-in wear rate for paraffin oil in the presence and absence of Schiff base, borate ester and synergistic formulation (1%w/v) at 392 N applied load

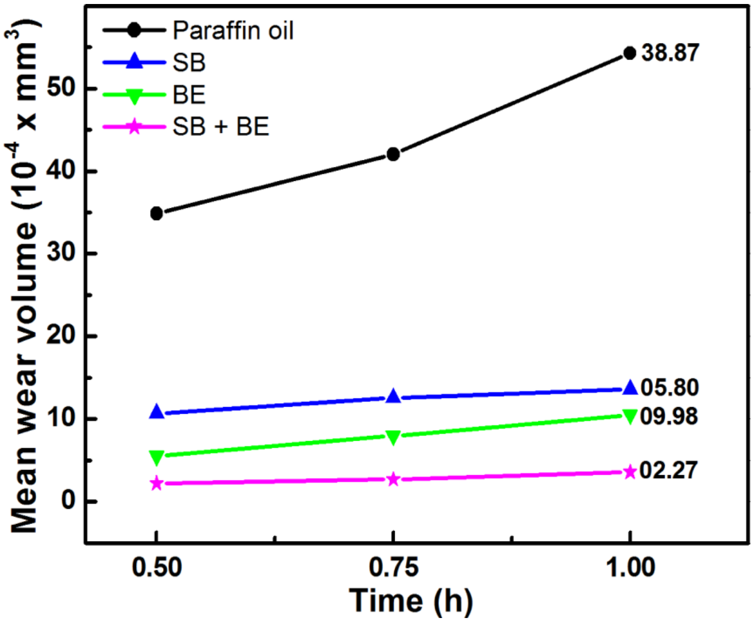


Figure 6.8. Determination of steady-state wear rate for paraffin oil in the presence and absence of Schiff base, borate ester and synergistic formulation (1%w/v) at 392 N applied load

6.2.2. Load bearing capacity test

In order to investigate the effect of applied load, the tests have been carried out at different loads 294, 392, 490, 588 and 686 N for 30 min test duration for paraffin oil in presence and absence of additives (1% w/v) and obtained results are shown in Figure 6.9. MWD was found to be very large at each tested load in absence of additives. At initial load (294N), MWD is very large in the absence of additives but in presence of Schiff base it is comparatively reduced. It further reduces in presence of synergistic formulation containing Schiff base and borate ester. MWD increases with increase in load in every case but the maximum increment was found in paraffin oil alone. However, there is large reduction in the MWD value in case of surface supplemented with synergistic mixture. The formation of tribochemical film on the steel-steel interface is facilitated due to the adsorption of additive, which resists direct metal-metal contact. Thus, the *in situ* formed tribochemical film is further capable of carrying higher load. Beyond 490N load, the thin film fails to sustain the load in case of paraffin oil alone and with borate ester whereas in case of Schiff base and its synergistic mixture the tribofilm successfully bears the load up to 686N.

6.2.3. Surface characterization

The morphology of the worn surface was examined by scanning electron microscopy (SEM). The SEM images of the wear track lubricated with or without additives (1% w/v) for 60 min duration at 392N load are exhibited in Figure 6.10. The SEM-micrographs for the surface lubricated with base oil and its admixture revealed that the surface has large wear scar diameter having deeper grooves in case of paraffin oil while it is much smoother in presence of Schiff base. However, the extent of surface smoothening in case of surface supplemented with mixture of Schiff base and borate ester has been found to be significantly improved.

The surface roughness of the worn surfaces on the steel balls after 60 minute test at 392N load for paraffin alone, Schiff base, borate ester and mixture of Schiff base and borate ester have been studied using contact mode AFM. The values of area roughness (S_q) in the above cases have been found to be 409, 259, 127 and 54nm respectively, Figure 6.11. The S_q values clearly show the role of additive in smoothening of surfaces as highest surface roughness is obtained for the surface lubricated with paraffin oil whereas comparatively the lowest value of surface roughness is found in case of synergistic mixture of Schiff base and borate ester. The EDX analysis has been performed to investigate the elemental compositions of the *in situ* formed tribofilm on the worn surface lubricated with synergistic mixture at 392N load for 60 min test time and mentioned in Figure 6.12. The presence of boron and nitrogen on the worn surface confirms the involvement of these elements in the formation of protective tribofilm.

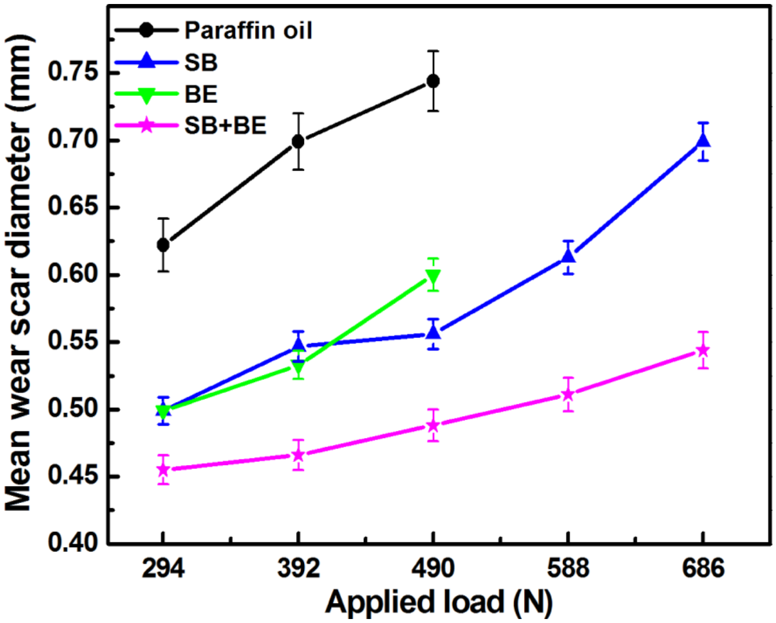


Figure 6.9. Variation of mean wear scar diameter with applied load in paraffin oil containing 1% w/v of Schiff base, borate ester and synergistic formulation for 30 min. test duration

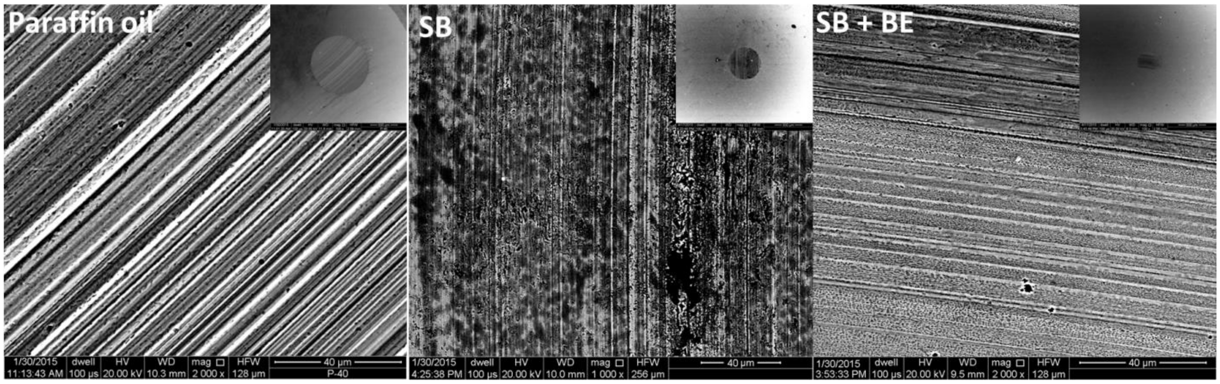


Figure 6.10. SEM micrographs of the worn steel surface lubricated with paraffin oil in presence and absence of different additives (1% w/v) for 60 min. test duration at 392N applied load: (a) Paraffin oil, (b) SB and (c) SB+BE

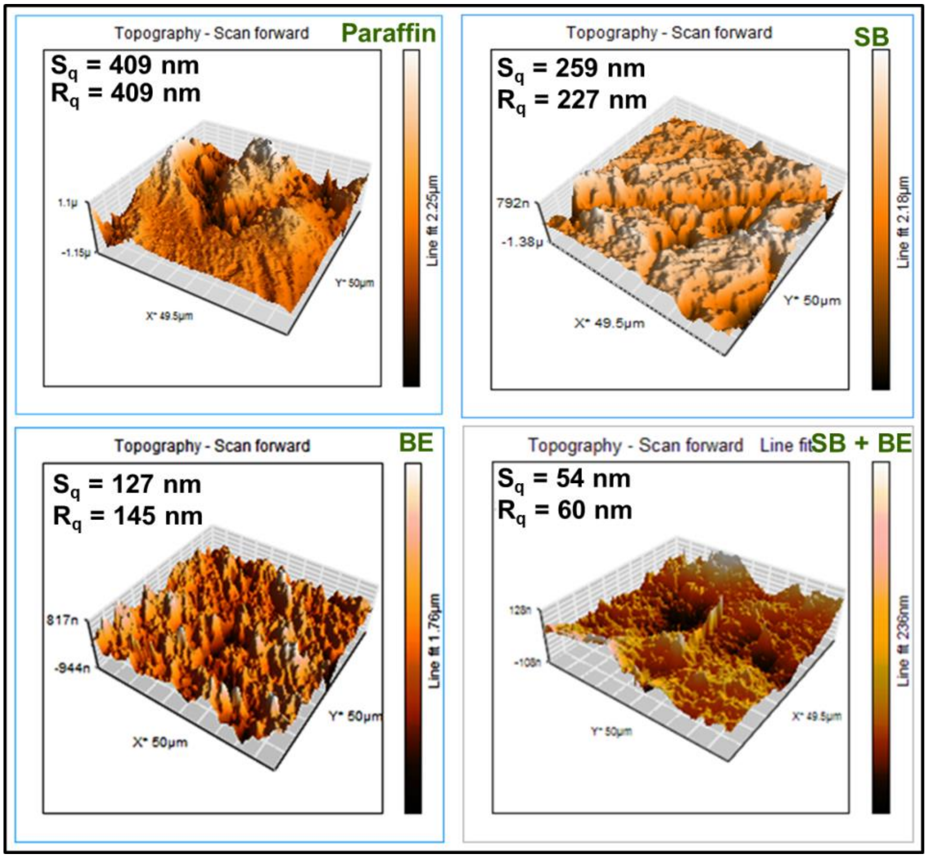
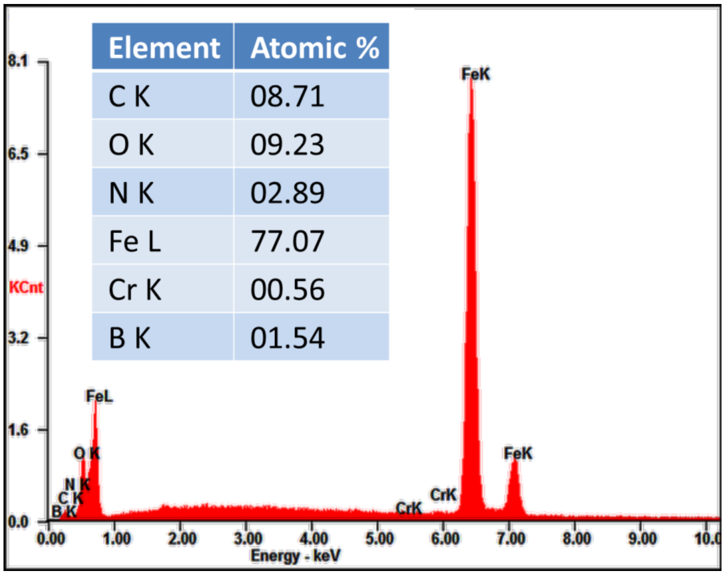


Figure 6.11. *3D*-AFM images of the worn steel surface lubricated with paraffin oil in presence and absence of different additives (1% w/v) for 60 min. test duration at 392N applied load: (a) Paraffin oil, (b) SB, (c) BE and(d) SB+BE



Element	Atomic %
C K	08.71
O K	09.23
N K	02.89
Fe L	77.07
Cr K	00.56
B K	01.54

Figure 6.12. EDX-spectra of the worn steel surface lubricated with synergistic mixture (SB+BE) for 60 min. test duration at 392N applied load

6.2.4. Theoretical studies

The Quantum chemical calculations have been performed to investigate the interactions of additive with the metal surface. A comparison between frontier molecular orbitals of the additive molecules has been done to establish a relationship between them, Table 6.1. In general, there is donation of electron density from the active centers of the additive molecules to the empty d-orbitals of metal atom [Jaiswal *et al.*(2014b) and Wang *et al.*(2007a)]. To be a good lubricant additive, it should have higher value of E_{HOMO}, lower value of E_{LUMO} and also the lower value of energy difference (ΔE) between HOMO and LUMO [Wang *et al.*(2007) and Rastogi *et al.*(2014)]. The highest value of E_{HOMO} and the lowest values of E_{LUMO} and ΔE observed in case of Schiff base prove its considerable interaction with metal surface and thus reducing friction and wear. The energies of frontier molecular orbitals of the studied additives and energy gap in between them are mentioned in Figure 6.13. Therefore, theoretical results correlate extremely well with the observed tribological behavior of the studied additives.

Table 6.1. Quantum chemical parameters for studied antiwear additives calculated with B3LYP/DGTZVP basis set

Additives	**E_{HOMO} (Hartree)**	**E_{LUMO} (Hartree)**	**ΔE (Hartree)**	**ΔE_{Fe-A} (Hartree)**
Fe_5[*Huang et al*.(2003)]	-0.18651	-0.06420	0.12231	
4-Aminitriazole	-0.27503	-0.06101	0. 21402	0.21083
Indole-3-Carbldehyde	-0.23112	-0.04558	0.18554	0.16692
Schiff base	-0.22558	-0.09770	0.15581	0.16138

$\Delta E = E_{LUMO}$ of additive - E_{HOMO} of additive

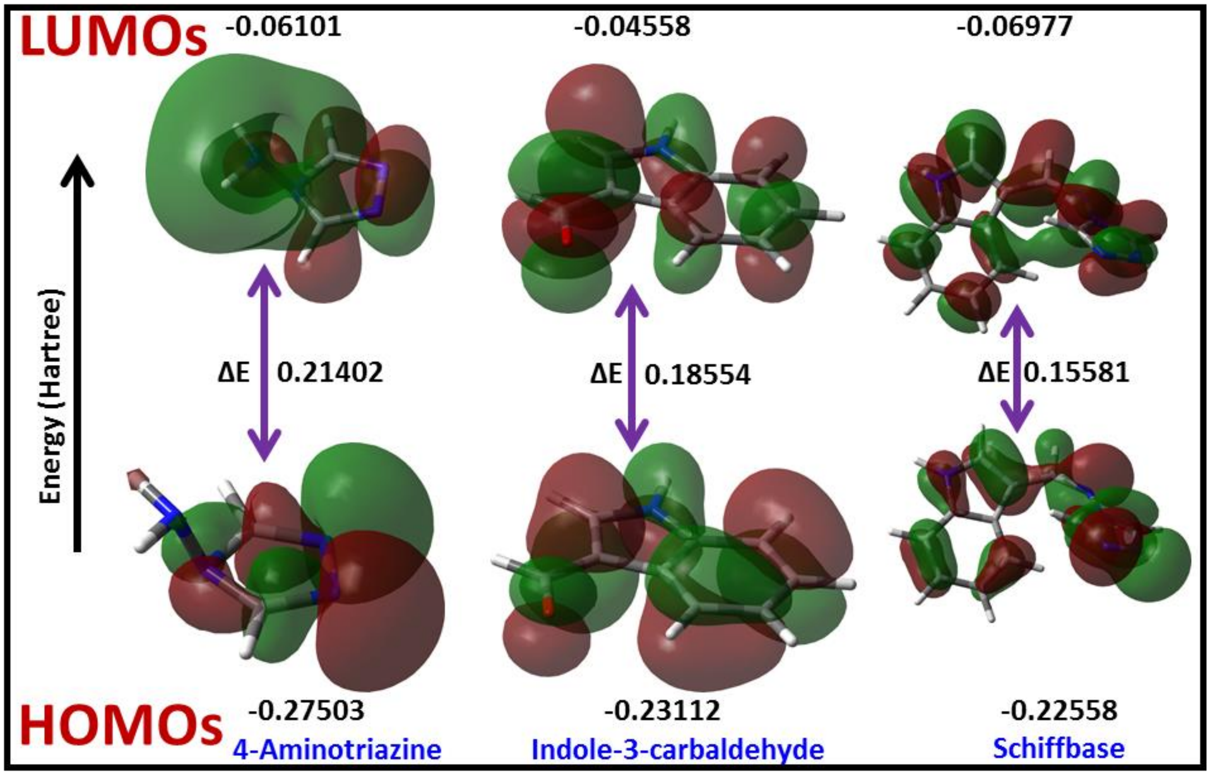


Figure 6.13. Graphical representation of energy gaps (Hartree) between HOMO and LUMO density distributions for the studied additives

6.3. Conclusions

The studied Schiff base/borate ester improved the load carrying, antiwear and friction reducing properties of the paraffin oil. Their synergistic mixture, of course, has further improved these properties to a significant extent. The excellent behavior shown by synergistic formulation can be explained by the formation of durable tribofilm preventing direct metal-metal contact. The SEM and AFM studies suggest that the surface generated in presence of Schiff base and borate ester together, is much smoother in comparison to Schiff base/base oil under various test conditions. Theoretically calculated values for various molecular orbital indices including the energy of frontier molecular orbitals (E_{HOMO} and E_{LUMO}) and energy gap (ΔE) have been used as a criterion to describe the interactions between lubricant additives and metal surface. These interaction parameters based on density functional theory support very well the experimentally observed tribological behavior.