

As discussed earlier, an appropriate additive should be added to a lubricant in order to increase the mechanical efficiency of a machine [Kotvis *et al.*(1993), Mosey *et al.*(2003)]. The efficiency of an additive depends on its ability to form a sufficiently hard and adherent protective film on the sliding surfaces. This ability is related to their action mechanism through physical adsorption and/or chemisorption. The performance of an additive depends upon: (i) the polarity of its functional groups, (ii) a composition of chemically active elements, (iii) the reactivity of the decomposition products and (iv) the chemical activity of the metal surfaces [Mosey *et al.*(2003), (2004), Willermet *et al.*(1992)]. The molecular structures of these antiwear additives usually contain triboactive elements such as boron [Yan *et al.*(2014a,b), Li *et al.*(2014)], nitrogen [Li *et al.*(2000), Zhan *et al.*(2004)], sulfur [Biresaw *et al.*(2012), Zhang *et al.*(1999a-d)], phosphorous [Mangolini *et al.*(2012), Wu *et al.*(2014)], halogens [Gao *et al.*(2004)] and metals [Kim *et al.*(2010), Rastogi *et al.*(2002a,b), Mangolini *et al.*(2009)]. Besides their antiwear properties, these additives are also being used in lubricating oils as multifunctional additives like extreme pressure [Kim *et al.*(2010), Rastogi *et al.*(2002), (2012), Mangolini *et al.*(2009)], friction modifier [Zhan *et al.*(2004)], antioxidants [Singh *et al.*(2013)] and corrosion inhibitors [Gusain *et al.*(2014), Cai *et al.*(2011)].

These days as per international standards, the SAPS contents in the antiwear additives are not allowed beyond the specified limits [Rokosz *et al.*(2001), Hartley *et al.*(2002), David (2002)]. Over the last decade, concerted efforts have been made by both researchers and industries towards developing new additives to replace the ZDDP without compromising friction and wear performances. In order to find good alternative of ZDDP from the environment and engine point of view, we have reported the sulfur and phosphorous-free Schiff bases and their synergistic formulation with borate ester in previous chapter. Being the biologically active material, Schiff bases and their copper complexes are frequently used as antitumor, antibacterial, antifungal and anticancer drugs [Samanta *et al.*(2007), Anacona *et al.*(1999)]. Schiff base copper complexes have good thermal stability with decomposition temperature above 200°C [Gao *et al.*(2012), Alagesen *et al.*(2014)]. Therefore, it seems worthwhile to design and develop low SAPS copper complexes

which are environment friendly but possess comparable tribological behavior to that of conventional high SAPS containing ZDDP.

In the present chapter, we report synthesis 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 in paraffin oil using four-ball lubricant tester. The tribological characteristics of *in situ* formed tribofilm are largely dependent on the chemistry of additive molecules of the lubricant. It is anticipated that the lubricant formulation of Schiff base copper complexes in paraffin oil may provide good antiwear properties by virtue of forming protective *in situ* tribochemical film at steel-steel interface. The characterization of tribochemical film formed on the interacting metallic surfaces and their surface topography has been done with the help of Scanning Electron Microscopy (SEM), contact mode Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). In addition to this, structure-activity relationship of the Schiff bases and their copper complexes with the iron surface using quantum chemical calculations has been done in order to correlate their experimentally obtained tribological behavior with the theoretical one. The influence of additive structures and their concentration in the lube base oil have been discussed in detail to understand the role of Schiff base copper complexes for improved tribological properties.

4.1. Experimental Section

4.1.1. Chemicals

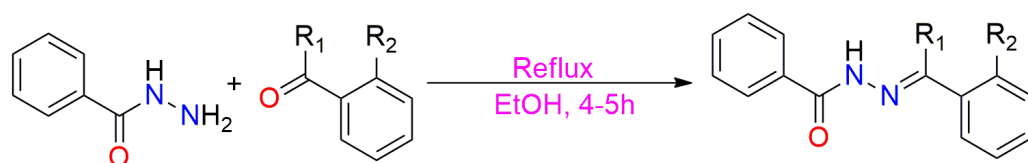
The starting materials benzhydrazide (98%, Sigma Aldrich), salicylaldehyde (98%, Sigma Aldrich), acetophenone (98%, Sigma Aldrich), hydrazine hydrate (80%, Merck) and copper acetate (98%, Merck) were used to synthesize the Schiff base ligands and their copper complexes. All other chemicals and solvents used in this work were of AR grade and used without further purification.

4.1.2. Synthesis of lubricant additives

4.1.2.1. Synthesis of Schiff base ligands [HL]

The Schiff base ligands, salicylaldehyde benzoylhydrazone (H-Sbh) and acetophenone benzoylhydrazone (H-Abh) were synthesized by the reported methods

[Alagesen *et al.*(2014), Singh *et al.*(2008)]. An anhydrous ethanolic solution (50 ml) of corresponding carbonyl compound (0.02 mol) was added drop wise to a round bottom flask containing ethanolic solution (50 ml) of benzhydrazide (0.02 mol). The reaction mixture was refluxed for 4-5 h (Scheme 4.1). The progress of the reaction was monitored by TLC. After cooling at room temperature, the obtained coloured precipitate was filtered on Büchner funnel, washed several times with ethanol, recrystallized with methanol and then dried *in vacuo*.



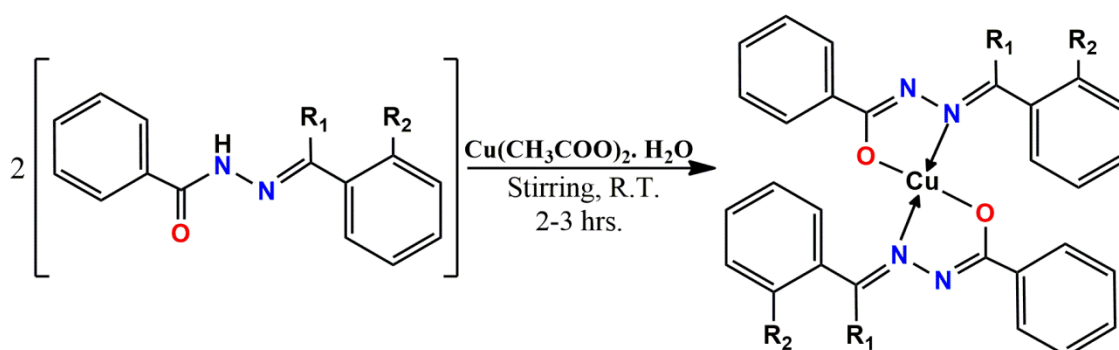
Where, $R_1 = \text{H}$, $R_2 = -\text{OH}$: H-Sbh

$R_1 = -\text{CH}_3$, $R_2 = \text{H}$: H-Abh

Scheme 4.1. Synthesis of Schiff base ligands derived from benzhydrazide with substituted carbonyl compounds

4.1.2.2. Synthesis of copper (II) complexes [CuL_2]

Copper (II) complexes of H-Sbh and H-Abh ligands were synthesized by reacting 50 ml methanolic solution of the $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (10 mmol) with salicylaldehyde benzoylhydrazone (H-Sbh) (20mmol)/acetophenone benzoylhydrazone (H-Abh) (20 mmol) solution in hot methanol (25ml) in 1:2 (M:L) molar ratio in a round bottom flask (Scheme 4.2). On stirring the reaction mixture at room temperature, Cu (II) complexes were precipitated immediately. The complexes were filtered in a G-4 glass crucible, washed several times with methanol followed by diethyl ether and dried *in vacuo*.



Where, $R_1 = \text{H}$, $R_2 = -\text{OH}$: $[\text{Cu}(\text{Sbh})_2]$

$R_1 = -\text{CH}_3$, $R_2 = \text{H}$: $[\text{Cu}(\text{Abh})_2]$

Scheme 4.2. Synthesis of Schiff bases derived from benzhydrazide with substituted carbonyl compounds

4.1.3. Characterization of lubricant additives

Salicylaldehyde benzoyl hydrazone (H-Sbh)

Cream color, Yield 86%. M.p. 156 °C. *Anal.* Calc. for $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$ (240.26): C, 69.98; H, 5.04; N, 11.66. Found: C, 69.76; H, 5.06; N, 11.59%. IR ($\nu \text{ cm}^{-1}$, KBr): $\nu(\text{OH})$ 3418b; $\nu(\text{NH})$ 3271s; $\nu(\text{C}=\text{O})$ 1674s; $\nu(\text{C}=\text{N})$ 1621s; $\nu(\text{N}-\text{N})$ 1000w. ^1H NMR (DMSO- d_6 ; δ ppm): 12.10 (1H, OH); 11.28 (1H, NH); 8.63 (1H, HC=N); 7.94-6.91 (9H, aromatic ring protons). ^{13}C NMR (DMSO- D_6 ; δ ppm) 162.82 (C=O); 157.454 (C-OH); 148.32 (HC=N); 132.78-116.41 (aromatic carbons).

Acetophenone benzoyl hydrazone (H-Abh)

White color, Yield 85%. M.p. 146 °C. *Anal.* Calc. for $\text{C}_{15}\text{H}_{14}\text{ON}_2$ (238.29): C, 75.60; H, 5.93; N, 11.76. Found: C, 75.41; H, 5.92; N, 11.69%. IR ($\nu \text{ cm}^{-1}$, KBr): $\nu(\text{NH})$ 3183m; $\nu(\text{C}=\text{O})$ 1656s; $\nu(\text{C}=\text{N})$ 1611s; $\nu(\text{N}-\text{N})$ 972w. ^1H NMR (DMSO- d_6 ; δ ppm): 10.79 (1H, NH); 7.87-7.42 (10H, aromatic protons); 3.36 (3H, $-\text{CH}_3$). ^{13}C NMR (DMSO- d_6 ; δ ppm): 163.86 (C=O); 155.52 (C=N); 138.09-126.36 (aromatic protons); 14.48 ($-\text{CH}_3$).

Salicylaldehyde benzoylhydrazone copper (II) complex; $[\text{Cu}(\text{Sbh})_2]$

Green color, Yield 70%. M.p. >250 °C. *Anal.* Calc. for $\text{C}_{28}\text{H}_{22}\text{N}_4\text{O}_4\text{Cu}$ (542.05): Cu, 11.72; C, 62.04; H, 4.10; N, 10.34. Found: Cu, 11.65; C, 61.90; H, 4.12; N, 10.27%. IR ($\nu \text{ cm}^{-1}$, KBr): $\nu(\text{OH})$ 3421b; $\nu(\text{C}=\text{N})$ 1599s; $\nu(\text{C}-\text{O})$ 1342s; $\nu(\text{N}-\text{N})$ 1041w. UV-Vis (DMSO, nm): 641. ESI-MS: $[\text{M} + \text{H}]^+$, m/z, 542.10 (7%); $[\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2 + \text{H}]^+ = 241.09$ (8%); $[\text{C}_6\text{H}_6 + \text{H}]^+ = 79.01$ (100%); $[\text{C}_6\text{H}_6 + \text{Na}]^+ = 101.00$ (87%).

Acetophenone benzoylhydrazone copper (II) complex; $[\text{Cu}(\text{Abh})_2]$

Dark brown color, yield (73%). M.p. 160-165°C. *Anal.* Calc. for $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_2\text{Cu}$ (538.11): Cu, 11.81; C, 66.95; H, 4.88; N, 10.41. Found: Cu, 11.42; C, 67.34; H, 4.32; N, 10.18%. IR ($\nu \text{ cm}^{-1}$, KBr): $\nu(\text{C}=\text{N})$ 1593s; $\nu(\text{C}-\text{O})$ 1369s; $\nu(\text{N}-\text{N})$ 1001w. UV-Vis (DMSO, nm): 645. ESI-MS: $[\text{M} + \text{H}]^+$, m/z, 538.14 (42%); $[\text{C}_6\text{H}_6 + \text{Na}]^+ = 101.00$ (100%) $[\text{C}_{15}\text{H}_{14}\text{ON}_2 + \text{H}]^+ = 239.11$ (74%); $[\text{C}_{15}\text{H}_{14}\text{ON}_2 + \text{Na}]^+ = 261.10$ (52%).

4.1.4. Tribological Characterization

4.1.4.1. Sample Preparation

Paraffin oil blends of Schiff bases having concentrations 0.00, 0.5, 1.0, 1.5 and 2.0 % (w/v) were made by stirring at 40-50 °C for 2h and thereafter sonicating for 1h at room temperature. The entire antiwear and load carrying tests were carried out at an optimized concentration i.e., 1.0% w/v of Schiff bases and their copper (II) complexes and compared with those of 1.0% w/v zinc dibutyldithiophosphate (ZDDP) in paraffin oil.

4.1.4.2. Corrosion test

The corrosion properties of these additives were studied by copper strip corrosion test according to ASTM D130-12 standard. A freshly polished and cleaned bright finished copper strip was immersed in a vial containing 30 ml of formulated base lube (1% w/v). The temperature of vial was raised to 100 °C using an oil bath. After 3h, copper strip was taken out and washed thoroughly to remove residual lubricant. The colour of the copper strips after the tests was compared with the standard colour chart. To see the effect of lubricant, surfaces of treated copper strips were further investigated using contact mode AFM and SEM microscopy. Besides copper strip corrosion test, corrosivity of studied additives towards steel surface has also been investigated under the similar experimental conditions.

4.2. Results and discussion

4.2.1. Additive Optimization

The potentiality of the synthesized Schiff bases acetophenone benzoylhydrazone (H-Abh), salicylaldehyde benzoylhydrazone (H-Sbh) and their copper complexes [Cu(Abh)₂], [Cu(Sbh)₂] as antiwear additives in paraffin oil was evaluated using four-ball tester. Since the antiwear efficiency of a particular compound generally depends on its chemical structure and concentration in the base lube, it is important to optimize additive concentration before conducting the tribological tests. The mean wear scar diameter (MWD) is an indication of extent of wear in sliding contacts. The additive concentration has been optimized by varying it from 0.5, 1.0, 1.5 and 2.0% (w/v) and measuring the corresponding MWD values at

392N applied load for 60 min test duration. Figure 4.1 exhibits the optimization results showing variation of MWD with change in concentration of the additives.

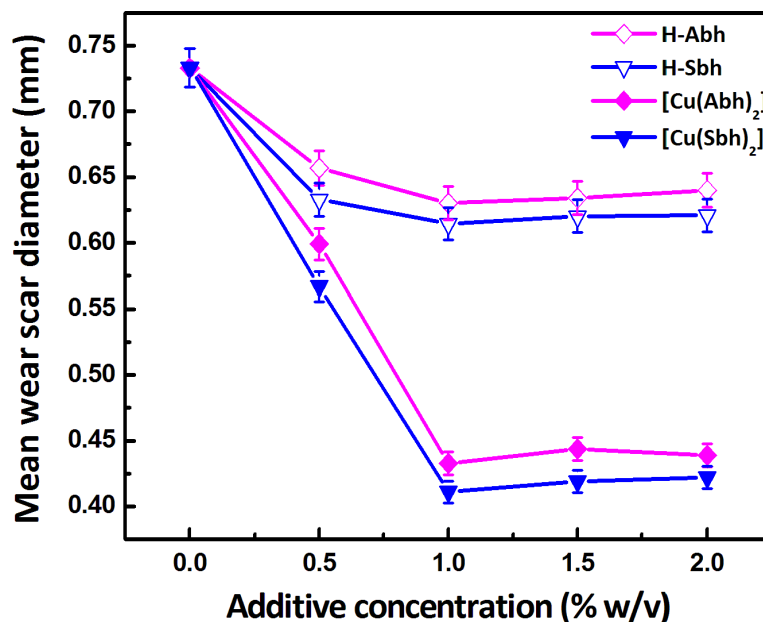


Figure 4.1. Variation of mean wear scar diameter for the paraffin oil as a function of increasing different additive concentrations at 392N applied load and 60 min duration

It is evident from Figure 4.1 that the value of mean wear scar diameter is very high in case of surface lubricated with paraffin oil alone but in presence of the additives, in general, at all the concentrations, it is significantly reduced. At the lowest concentration (0.5% w/v) of Schiff bases, appreciable decrease in the MWD value was observed. However, in case of the corresponding copper complexes, the decrease in MWD observed is of very high order. On further increasing the concentration up to 1.0 % w/v, the value of MWD slightly decreases in case of Schiff bases whereas tremendous reduction in MWD value was observed in case of complexes. Thereafter, further increase in concentration up to 1.5 and 2.0 %, the value of MWD slightly increases or remains almost constant in every case. It has been observed that the MWD values for all the additives are found to be the lowest at 1.0 % w/v concentration. Therefore, entire tribological tests have been carried out at 1% w/v which is the optimized concentration of the additives. At all concentrations, Schiff bases and their respective copper complexes significantly reduce the MWD value. However, in case of copper complexes much pronounced reduction in MWD value has been observed than the corresponding Schiff bases. Further, the lowest values of

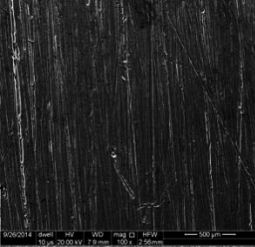
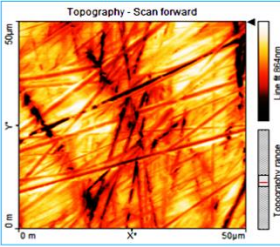
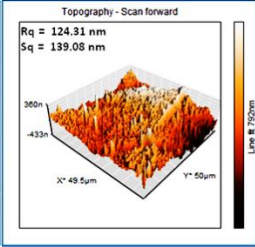
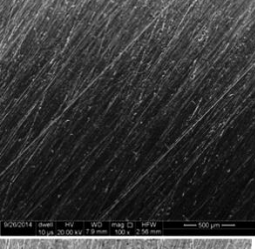
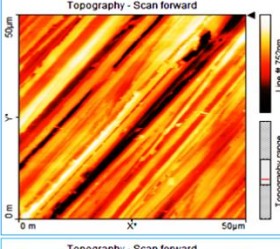
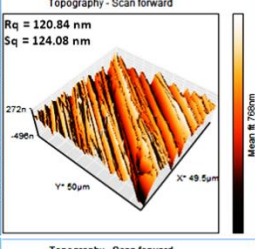
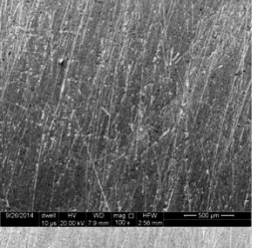
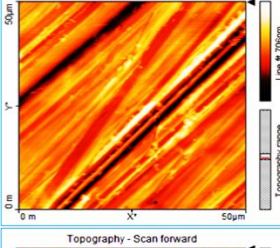
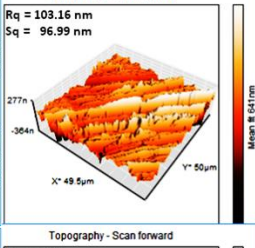
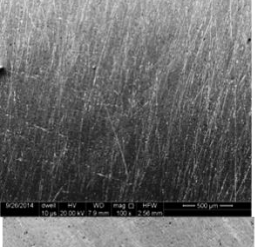
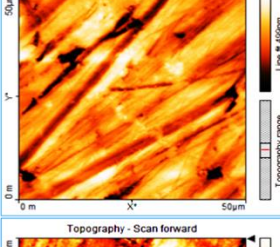
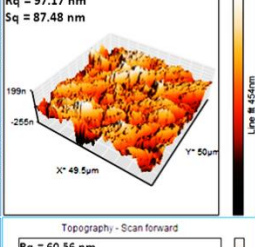
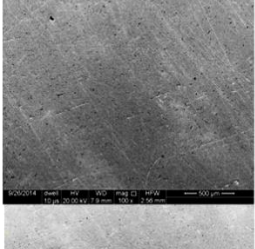
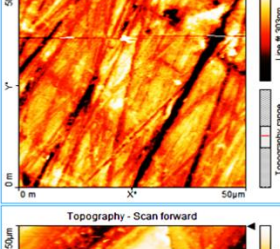
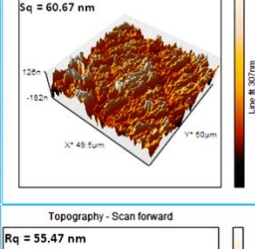
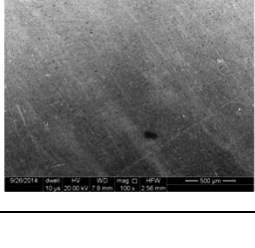
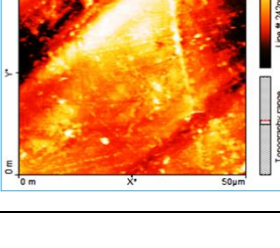
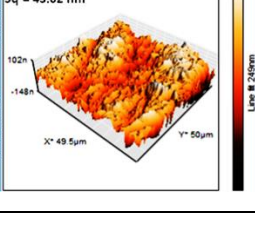
MWD are observed for the [Cu(Sbh)₂] followed by [Cu(Abh)₂], H-Sbh and then H-Abh respectively at all of the tested concentrations.

Herein, the concentration dependency of the wear reducing behavior of the additives can be explained on the basis of their affinity towards interactions with metal surface along with surface coverage. The additives with greater number of donor atoms and having larger surface area are prone to reduce wear even at comparatively lower concentrations by forming protective tribochemical films on steel-steel interfaces.

4.2.2. Copper strip corrosion test

The copper strip corrosion tests have been performed to evaluate the corrosion characteristics of the synthesized Schiff bases and their copper complexes in paraffin oil. A freshly polished bright copper strip was immersed in a vial containing 1 % w/v of each additive in the paraffin oil at 100 °C for 3h. The comparison of colour of the strips with the standard colour chart shows non-corrosive nature of paraffin oil and all the blends. To study the surface morphology of the copper strips before and after the tests, SEM and AFM images were taken after washing the strips with distilled water and then with acetone. Table 4.1 shows different images and grades of the copper strips before the test and after exposure to paraffin oil alone and 1% w/v blends of all additives. The surface features of copper strips in absence and presence of Schiff bases and copper complexes were found to remain almost unaffected showing no degradation of the copper surface. The noncorrosive behavior of the studied additives was expected since these do not contain elements like sulfur, phosphorous or halogen which facilitate corrosion. From the 3D-AFM images, it is evident that the surface roughness decreases appreciably in presence of all additives. This is due to coverage of surface by the additives to a great extent. It can be mentioned here that the surface roughness was found to be the least in case of [Cu(Sbh)₂] followed by [Cu(Abh)₂], H-Sbh and then H-Abh. SEM analysis also leads to the same observation. Considering the noncorrosive properties, these Schiff bases and their copper (II) complexes can be recommended as promising additives for the lubricant applications.

Table 4.1. Surface morphology of copper specimen and their grade after the copper strip corrosion test of studied additives at 100 °C for 3hrs

Lubricant	SEM	AFM	Corrosion Grade
Polished copper strip		 	-
Paraffin oil		 	1b
H-Abh		 	1a
H-Sbh		 	1a
[Cu(Abh) ₂]		 	1a
[Cu(Sbh) ₂]		 	1a

4.2.3. Antiwear Performance

The lubrication properties of the acetophenonebenzylhydrazone (H-Abh), salicyldehydebenzylhydrazone (H-Sbh) Schiff base ligands and their copper (II) complexes $[\text{Cu}(\text{Abh})_2]$, $[\text{Cu}(\text{Sbh})_2]$ as antiwear additives in paraffin base lube were explored for the steel-steel contact. Figure 4.2 shows the variation in mean wear scar diameter in paraffin oil with and without studied additives and ZDDP at optimized concentration (1% w/v) at 392N applied load for 60 min test duration. Addition of additives to the base oil, in general, significantly reduces the value of wear scar diameter and enhances therefore, the wear resistance behavior. It is evident from the figure that the largest value of MWD (0.733mm) was observed in case of pure paraffin oil whereas its smallest value is observed in presence of the additive $[\text{Cu}(\text{Sbh})_2]$, 0.419 mm. From the Figure 4.2, it is evident that the Schiff base additives efficiently enhance the antiwear behavior of base oil by lowering the value of mean wear scar diameter but this reduction in MWD has been found to be lower than that of ZDDP. The maximum reduction in MWD value was found in case of surface lubricated with copper complexes which is much better than that of high SAPS containing ZDDP. The presence of H-Abh, H-Sbh, ZDDP, $[\text{Cu}(\text{Abh})_2]$ and $[\text{Cu}(\text{Sbh})_2]$ additives in paraffin oil significantly reduced the MWD values by 14, 16, 24, 41 and 44% respectively, compared to paraffin oil alone. Thus the order of antiwear behavior of studied additives is as follows:



The observed antiwear behavior of studied Schiff bases and their respective copper complexes can be explained on the basis of their chemical structures. The chemical structure, IUPAC name and abbreviated form of the additives have been summarized in Table 4.2. There are several factors which may affect the lubrication efficiency of the additives such as number of hetero atoms like nitrogen, sulfur, halogen, phosphorous etc., number of aromatic rings, number of donor groups and planarity of the molecule. As the number of heteroatoms, aromatic rings and donor groups increases, their film forming tendency also increases via the process of adsorption on sliding surface [Li *et al.*(2000)]. The antiwear action of studied Schiff

bases may be ascribed to their adsorption through a number of active centres like N, O, phenyl and methyl/hydroxyl group. Superior antiwear behavior of H-Sbh over H-Abh is due to the presence of additional donor site i.e. -OH group in H-Sbh through which it may coordinate with iron of the steel surface to form donor-acceptor complex. By virtue of this, it might increase the surface coverage in order to form protective tribochemical film on steel-steel interface. The similar order of tribological behavior has been observed in case of corresponding copper complexes. However, extent of wear reduction in case of a complex has been found to be much larger than the constituent Schiff base alone. This pronounced tribological behavior of copper complexes can be explained on the basis of their square planar structure, greater surface coverage [Abdel-Gaber *et al.*(2009)] and formation of donor-acceptor complex. Owing to ionisable free -OH group in salicyldehydrobenzoylhydrazone copper (II) complex, it exhibits better tribological behavior than acetophenonebenzoylhydrazone copper (II) facilitating the interaction between -OH and iron of the steel surface.

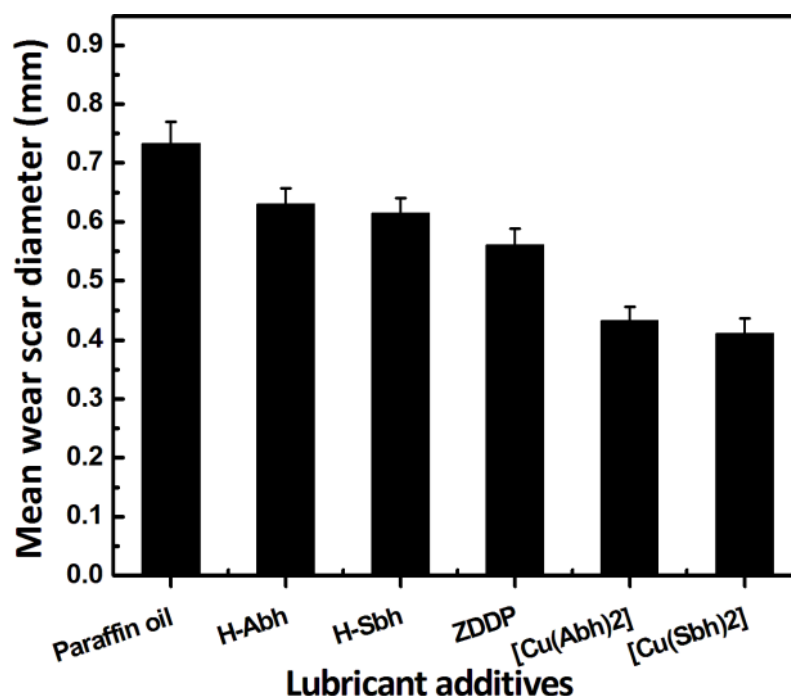
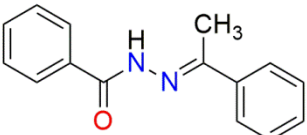
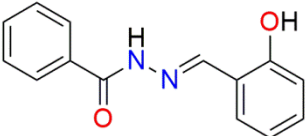
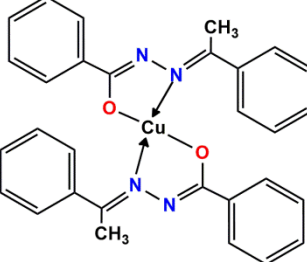
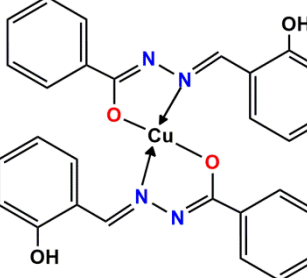


Figure 4.2. Variation of mean wear scar diameter for paraffin oil with and without different antiwear additives (1% w/v) at 392N applied load for 60 min test duration

Table 4.2. Molecular structure of investigated Schiff bases and their copper complexes as antiwear lubricant additives

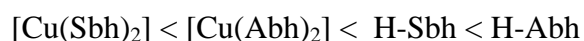
Additives	Common name	Abbreviation
	Acetophenonebenzoylhydrazone	H-Abh
	Salicylaldehydebenzoylhydrazone	H-Sbh
	Acetophenonebenzoylhydrazone copper(II)	[Cu(Abh) ₂]
	Salicylaldehydebenzoylhydrazone copper(II)	[Cu(Sbh) ₂]

In order to investigate the effect of sliding time on the mean wear scar diameter, the antiwear tests have been also carried out at 392N applied load for different time durations, 15, 30, 45, 60, 75 and 90 min for paraffin oil in presence and absence of 1% w/v concentration of antiwear additives. The variation of MWD with respect to time durations at 392N load is represented in Figure 4.3. It is evident from the Figure 4.3 that the MWD in case of paraffin oil for all the test durations is found to be much larger than in the presence of additives. Thus the tested Schiff bases and their copper complexes act as antiwear additives. However, the antiwear efficiency of Schiff bases in base lube has been found to be poorer than those of corresponding copper complexes and conventional high SAPS containing ZDDP. It is interesting to note that the copper complexes have magnificently improved the antiwear behavior of base lube by lowering the value of MWD to a greater extent which is even much better than that of ZDDP.

The tribological activity of different additives is well differentiated at each time exposure starting from 15 min to 90 min of test duration and throughout follows almost the same trend as observed above. From 15-30 min of time duration, the increase in MWD in case of complexes and paraffin oil is marginal whereas for ZDDP and Schiff base additives, it is comparatively larger. After that further increase in test duration up to 45 min, there is abrupt increase in MWD for ZDDP and paraffin oil, on the other hand, its value increases quite smoothly for Schiff bases and their copper complexes. It is noticeable that beyond 30 min up to 90 min of test duration, slope of these curves has drastically reduced in presence of these additives as compared to ZDDP and paraffin alone. For the last 15 min of test run ZDDP shows abrupt increase in MWD value.

The inherent polarity of these Schiff bases and their respective complexes is believed to provide their strong adsorption on the contact interfaces. Consequently, the thin film formed effectively separates the contact interfaces and thereby MWD is reduced. As the time increases, the additive molecules get decomposed during sliding under operating conditions and react with metal surface to form tribochemical film. According to Cavdar *et al.*(1991) formation of tribofilm is strongly time dependent; therefore, some time exposure is required to form a durable tribofilm on sliding surfaces. Owing to this, much lower increment in the MWD value has been observed in case of complexes just after the 15 min of test run whereas it takes about 30-45 min in case of Schiff bases. Thereafter, subsequent lesser increase in the value of MWD provides evidence in favour of existence of tribochemical film on the steel-steel interface.

To estimate wear more accurately it is important to investigate the variation of mean wear volume with respect to time instead of variation of mean wear scar diameter. According to equation 2.4, MWV contains MWD to the fourth power, therefore, little change in the dimension of MWD causes huge changes in the MWV. Mean wear volume in absence and presence of different additives at 392N load for paraffin oil was plotted as a function of time and a linear regression model was fitted on the points including origin to find out overall wear rate, Figure 4.4. Overall wear rate was found to be very high in base lube without additives whereas with additives it was tremendously reduced to about 10 folds. Among all the studied additives the following order has emerged for overall wear rate:-



This again is in conformity with the conclusion drawn earlier that owing to formation of stronger, adherent tribochemical film, copper complexes efficiently smoothen the surface irregularities thus reducing wear to a great extent.

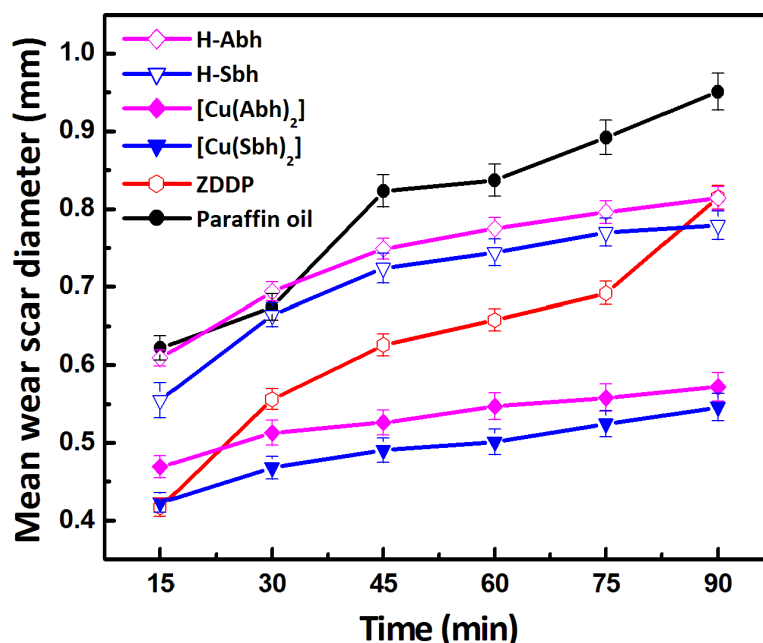


Figure 4.3. Variation of mean wear scar diameter with time for paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), Schiff bases and their copper complexes at 392N applied load

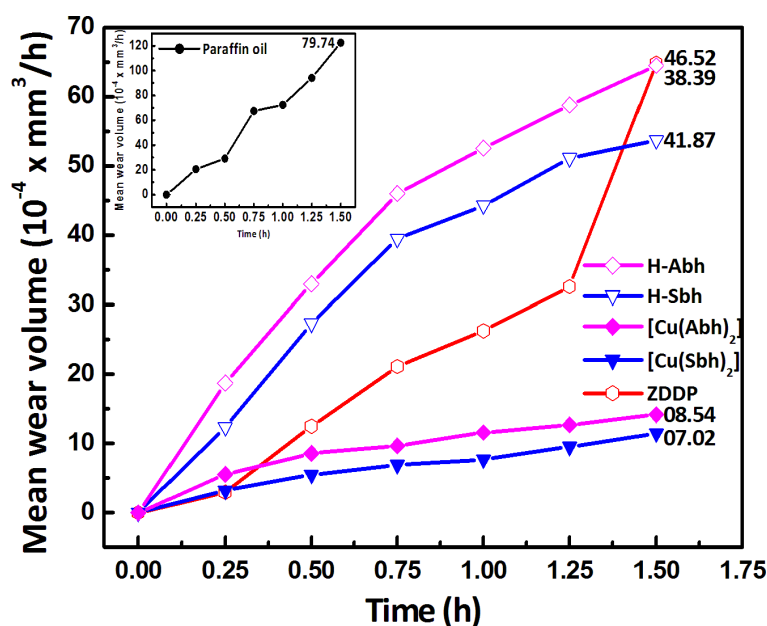


Figure 4.4. Determination of overall wear rate by varying mean wear volume with time (h) for paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), Schiff bases and their copper complexes at 392N applied load

The running-in wear rate is always higher than the steady-state wear rate as running-in process initiates the adjustment of the surfaces moving under controlled conditions. The comparison of running-in, steady-state and overall wear rate of different additives has been mentioned in Table 4.3, which shows that the values of overall, running-in and steady state wear rates have been found to be much lower in case of complexes than ZDDP, Schiff bases or paraffin oil alone. Among all of the tested additives, Schiff base H-Sbh and its copper complex [Cu(Sbh)₂] most significantly reduce the running-in, steady state and overall wear rates of base lube. In spite of large difference in the value of running-in wear rate between Schiff bases and ZDDP, it is interesting to note that the comparable values of their steady-state and overall wear rates have been found which suggest early stabilization to achieve steady state zone. Since the life of engineering components is assessed on the basis of steady-state wear rate, for a better antiwear additive it is important to achieve steady-state as early as possible and it must be stable for longer duration.

Table 4.3. Wear rates of paraffin oil in absence and presence of Schiff bases and their copper complexes as antiwear additives at 392N applied load for 90 min test duration

S.N.	Additives	Wear Rate (10^{-4} x mm ³ /h)		
		Running-in	Steady-state	Overall
1.	Paraffin oil	84.48	53.52	79.31
2.	ZDDP	29.41	22.78	38.39
3.	H-Abh	60.86	25.56	46.52
4.	H-Sbh	53.33	23.35	41.87
5.	[Cu(Abh) ₂]	12.79	06.04	08.54
6.	[Cu(Sbh) ₂]	09.19	05.19	07.02

4.2.4. Effect of load

In order to investigate the effect of applied load on the mean wear scar diameter, the tests have been carried out at different loads 294, 392, 490, 588, 686 and 784N for 30 min test duration for paraffin oil in presence and absence of different additives. The variation of MWD as a function of applied load at 30 min test duration is displayed in Figure 4.5. At initial load (294N), MWD is very large in the absence of additives but in presence of Schiff bases it is fairly reduced. It reduces further in presence of ZDDP and reaches the minimum value for the admixtures of copper complexes. With increase in load at 392N, MWD increases substantially in every case but this increase is maximum in absence of additives. However, there is slight increase in the MWD value in case of surface lubricated with complexes. This may be due to the fact that the thin film of lubricant and additive adsorbed on the steel-steel interfaces resists much increase in MWD on increasing applied load. At 490N load, both the base oil and ZDDP show abrupt increase in MWD; however, this increase is very small in presence of the Schiff base additives and their copper complexes. 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 whereas in case of ZDDP and Schiff bases, the tribofilm fails to bear the load beyond 588N. On further increase in the applied load up to 784N, blends of copper complexes in base lube could successfully bear the load. The ligand H-Sbh and its copper complex $[Cu(Sbh)_2]$ in base oil show tremendous load bearing ability with relatively much smaller wear scar diameter as compared to H-Abh and the complex thereof. Thus, it can be inferred from Figure 4.5 that the copper complexes played an important role in remarkably improving the load carrying ability of the base lube. Overall order of efficiency of additives at every load was found to be the same as stated earlier.

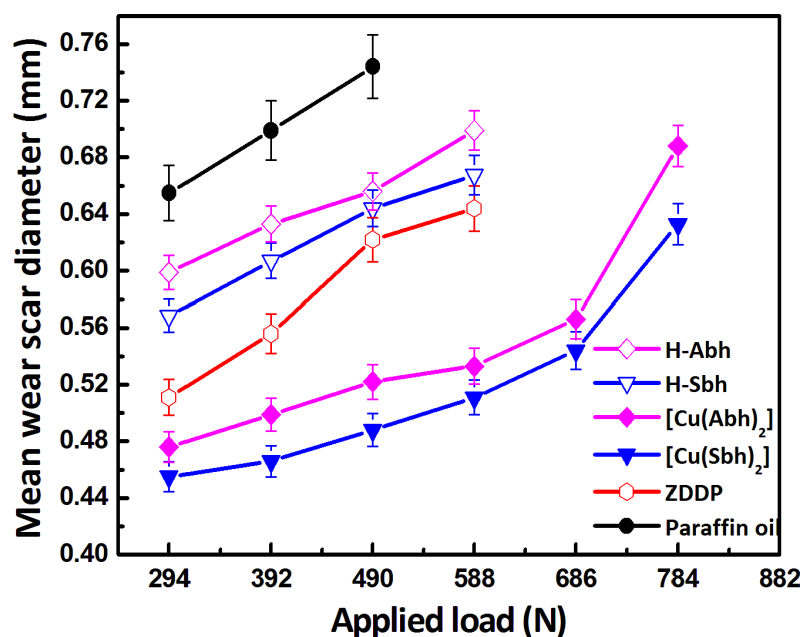


Figure 4.5. Variation of mean wear scar diameter with applied load for paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), Schiff bases and their copper complexes for 30 min test duration

4.2.5. Surface Characterization

4.2.5.1. Surface morphology

The surface morphology of wear scar generated on sliding surfaces has been studied by scanning electron microscopy (SEM) and contact mode atomic force microscopy (AFM). Figure 4.6 shows SEM images of the worn surface of steel balls in the presence and absence of ZDDP, Schiff bases and their copper complexes at 392N applied load for 90 min duration. The worn surfaces in the presence of additives are smoother in comparison to the surface lubricated with paraffin alone. In case of steel surface lubricated with base oil (Figure 4.6a), huge surface destruction with much deeper grooves and cracks is observed in absence of any tribochemical film due to adhesive wear. On the other hand, the surface supplemented with its admixture containing H-Sbh (Figure 4.6b) and H-Abh (Figure 4.6c) shows less deeper grooves along the sliding direction. In presence of ZDDP better smoothing of the surface is observed (Figure 4.6d) than the Schiff bases. There is tremendous increase in smoothness of the surface when copper complexes (Figures 4.6e & f) are used which may be due to the formation of strong and adherent tribochemical film on the sliding contacts. The smoothing of worn surfaces has been found to be maximum in case of [Cu(Sbh)₂] additive as evident from Figure 4.6e, showing extra finished surface with no grooves along the wear track. The extent of smoothing is found to be

comparatively lesser in case of $[\text{Cu}(\text{Abh})_2]$, Figure 4.6f; where some grooves are visible along the sliding direction. Besides this, the clear boundary of wear scar is also seen in case of surface lubricated with complexes which is shown in inset. The observed smoothness of micrographs in the presence of different additives follows the same order as discussed above on the basis of their tribological behavior.

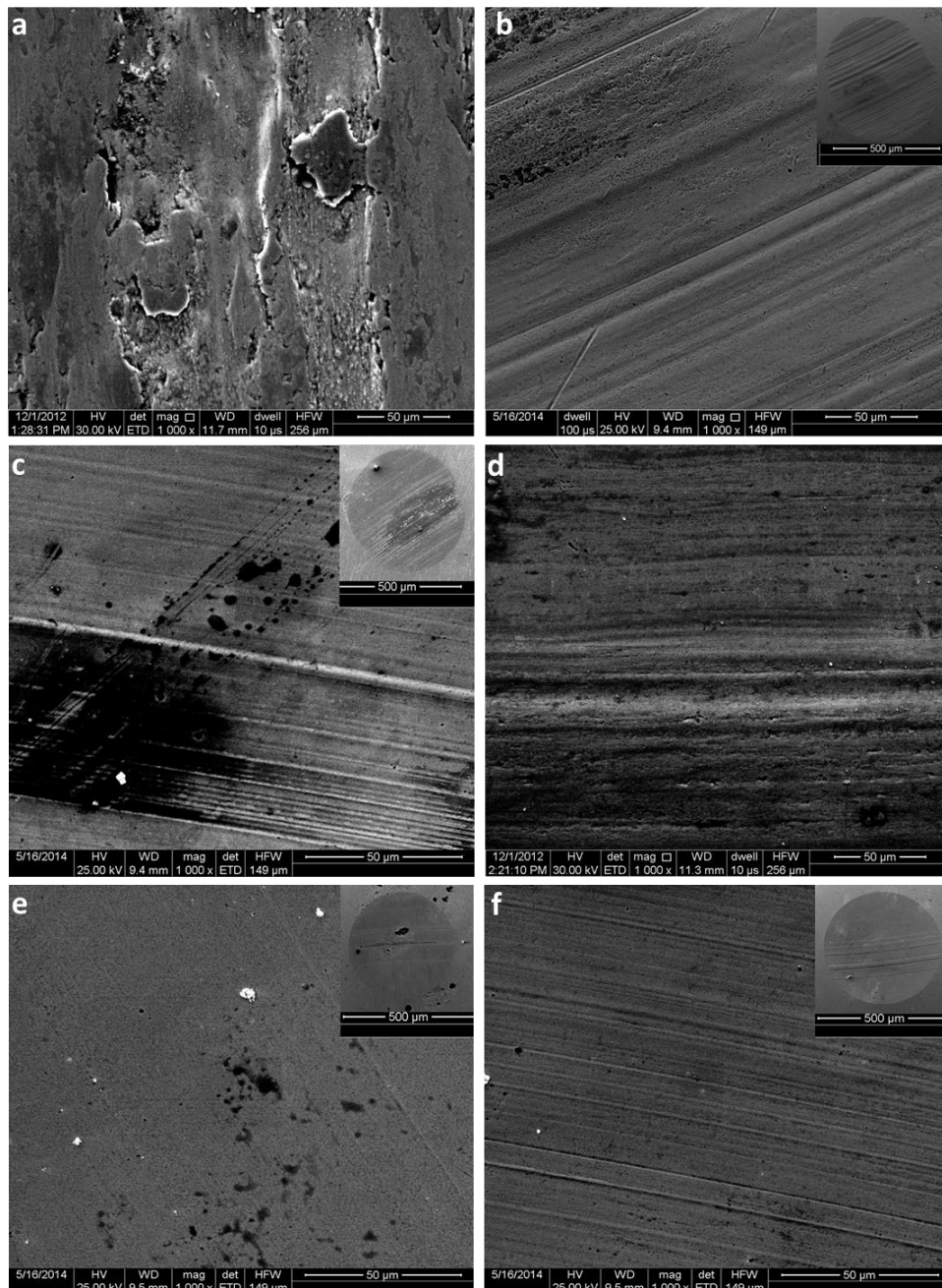


Figure 4.6. SEM micrographs at different magnifications of the worn steel surface lubricated with different additives (1% w/v) in paraffin oil for 90 min test duration at 392 N applied load: (a) Paraffin oil, (b) H-Sbh, (c) H-Abh, (d) ZDDP, (e) $[\text{Cu}(\text{Sbh})_2]$ and (f) $[\text{Cu}(\text{Abh})_2]$

To examine and compare the morphology of worn surfaces lubricated with copper complexes and ZDDP at relatively higher load, the SEM-images have also been taken at 588N load for 30 min test duration, Figure 4.7. It is evident from the figure that there is much more surface destruction due to adhesion in case of ZDDP (Figure 4.7a), on the other hand, relatively much smoother surface has been obtained with copper complexes (Figures 4.7b,c). From Figure 4.7b, it can be clearly seen that well finished surface has been generated with $[\text{Cu}(\text{Sbh})_2]$ while ploughing effects due to scuffing are visible on the wear track lubricated with $[\text{Cu}(\text{Abh})_2]$. Thus, the suitability of these compounds at higher load is fully supported by these SEM-images.

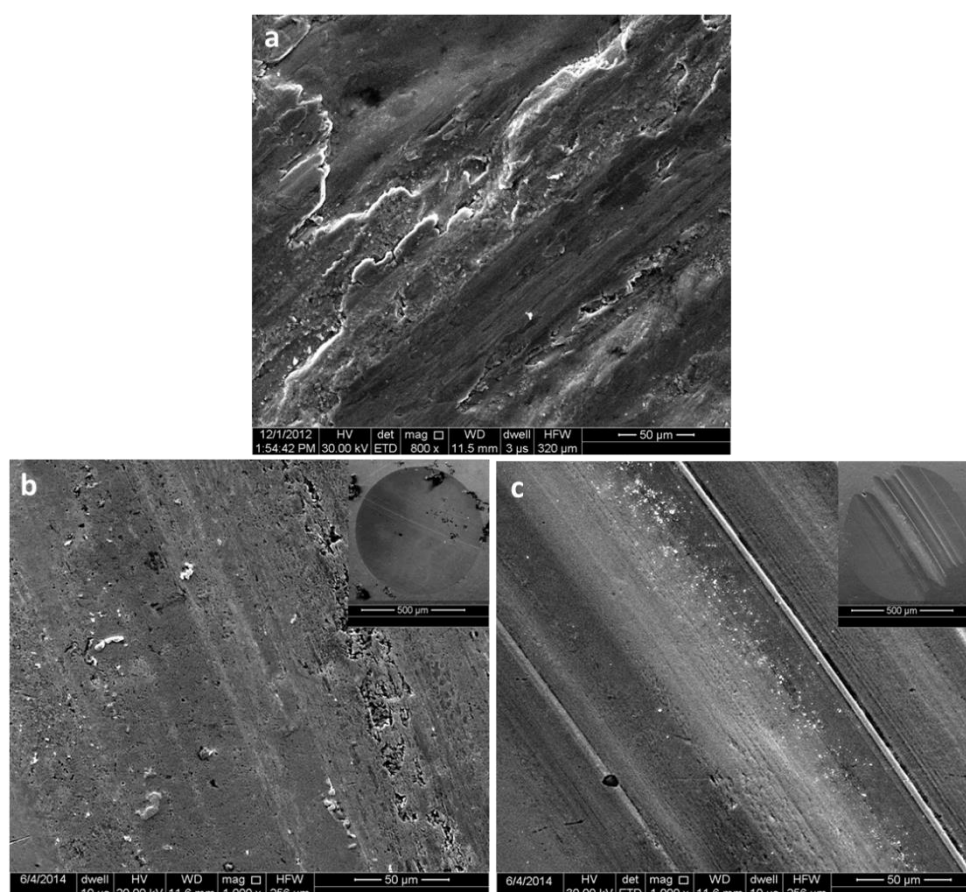


Figure 4.7. SEM micrographs of the worn steel surface lubricated with (a) ZDDP, (b) $[\text{Cu}(\text{Sbh})_2]$ and (c) $[\text{Cu}(\text{Abh})_2]$ (1% w/v) in paraffin oil for 30 min test duration at 588N applied load

The surface irregularities of the worn steel surfaces lubricated with base lube and admixture of additives observed after antiwear and load carrying tests in paraffin oil were examined by contact mode AFM at 392N load for 90 min test duration. The 2D and 3D-AFM images of the wear scar are shown in Figure 4.8(a-f). On comparing the obtained data, it has been found that the values of area as well as line roughness are extremely large in case of paraffin oil (2630nm) whereas these have surprisingly reduced in presence of additives (53-118nm). The comparison of roughness parameters like root mean square area roughness (S_q), peak-valley height (S_y) and root mean square line roughness (R_q) of different additives has been made in Figure 4.9. The smallest values of R_q , S_q and S_y are observed in case of $[Cu(Sbh)_2]$ additive, 59, 66 and 421 nm, respectively while their largest values are observed for paraffin oil i.e. 491, 409 and 2630 nm, respectively. From Figure 4.9, it is apparent that the copper complexes of Schiff base additives/ZDDP in base lube exhibit drastic reduction in area and line roughness as well as average asperity-valley height than the base oil or base oil supplemented with Schiff bases alone. Besides this, from the 3D-AFM images it can be clearly seen that there are much smoother surfaces with less intense asperities in case of copper complexes which is supposed to be due to presence of durable tribofilm formed under lubricating conditions resulting into very low running-in wear rate and early stabilization of steady-state wear rate.

In order to investigate the applicability of these additives towards effective lubrication under extreme conditions i.e., high load and high temperatures, the AFM-images have also been taken at 588N applied load for 30 min test duration (Figure 4.10). It is apparent from the figure that the value of surface roughness has increased at this load for each additive. The observed trend of the additives towards the reduction of surface roughness under extreme conditions is the same as that in case of 392N load for 90 min duration. Thus, the AFM-images fully support the observed results of tribological tests.

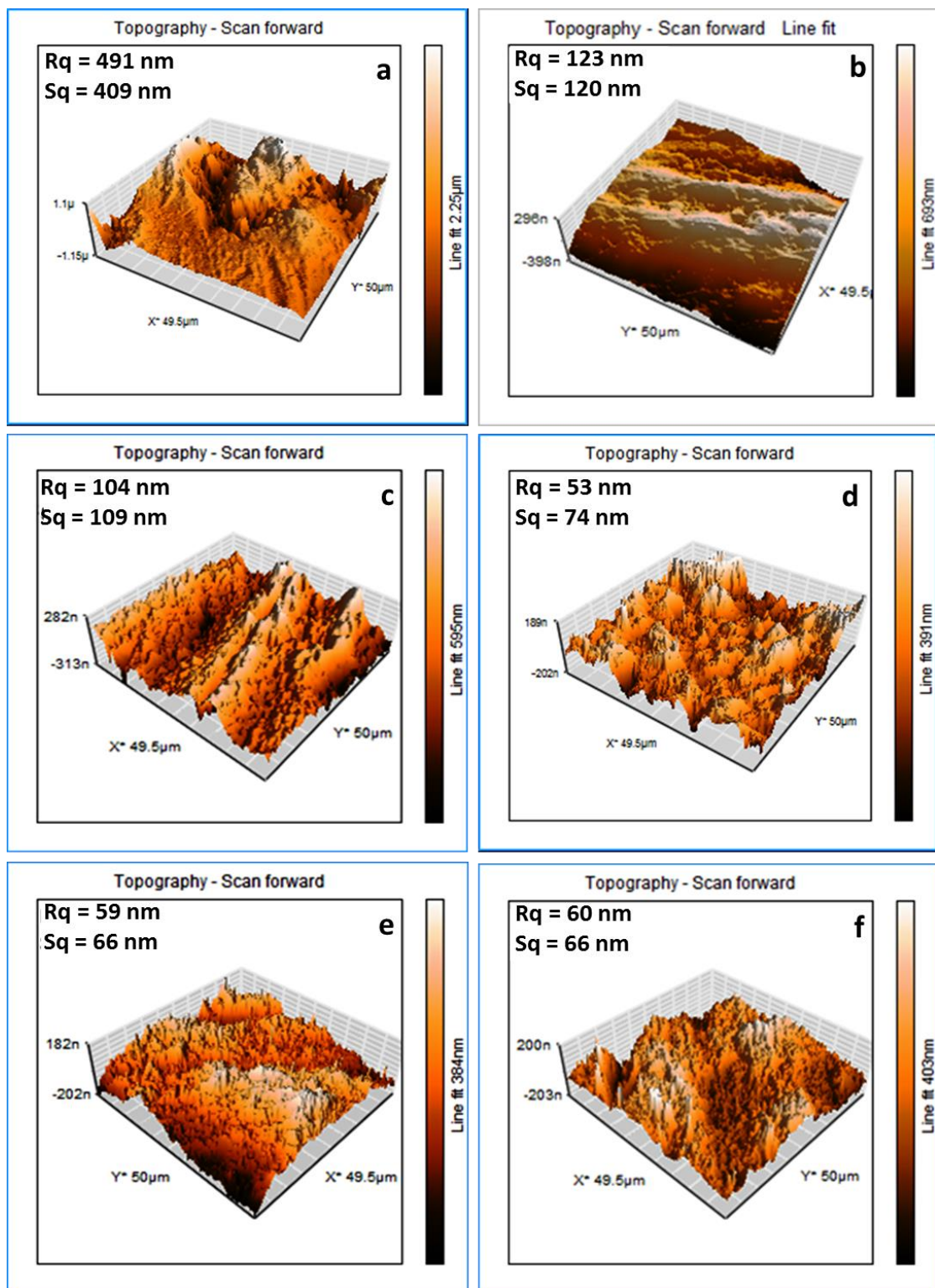


Figure 4.8. 2D and 3D-AFM images of the worn steel surface lubricated with different additives (1% w/v) in paraffin oil for 90 min test duration at 392N applied load: (a) Paraffin oil, (b) H-Abh, (c) H-Sbh, (d) ZDDP, (e) [Cu(Abh)₂] and (f) [Cu(Sbh)₂]

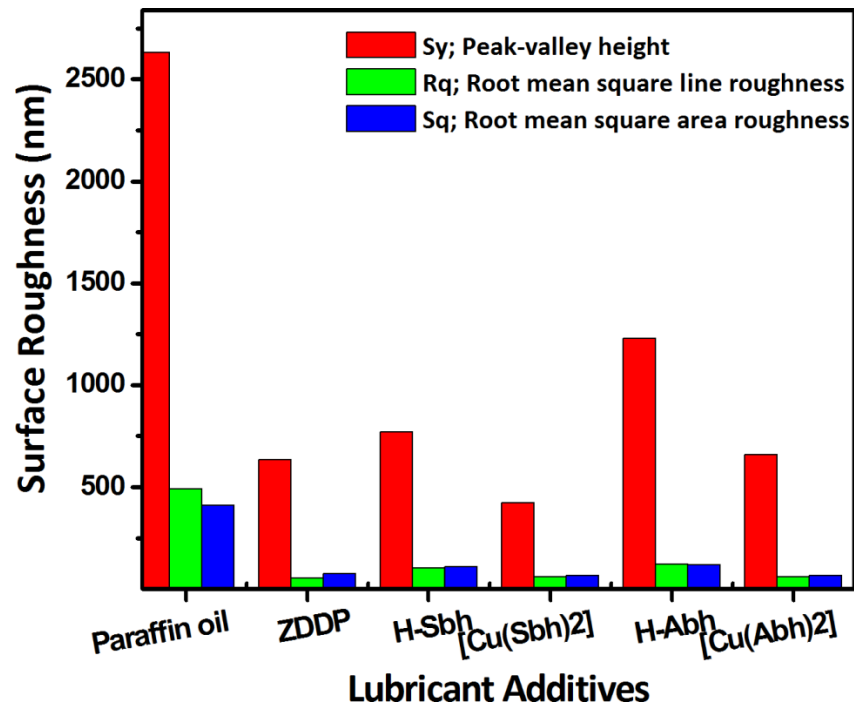


Figure 4.9. Surface Roughness parameters obtained from digital processing software of Nanosurf basic Scan 2 for different additives at 392N load for 90 min test duration

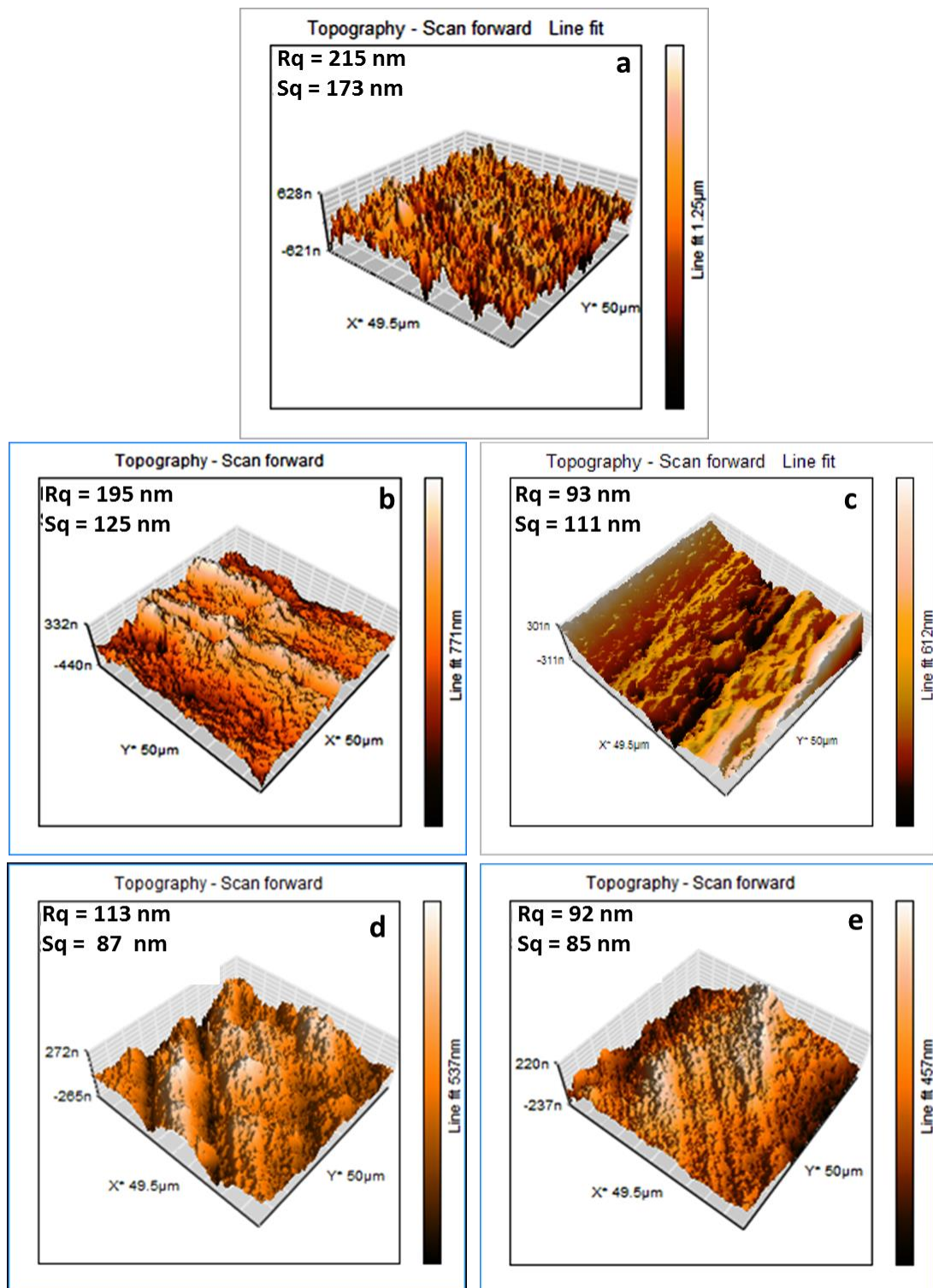


Figure 4.10. 3D-AFM images of the worn steel surface lubricated with different additives (1% w/v) in paraffin oil for 30 min test duration at 588N applied load: (a) H-Abh, (b) H-Sbh, (c) ZDDP, (d) [Cu(Abh)₂] and (e) [Cu(Sbh)₂]

4.2.5.2. Tribochemistry

The Energy dispersive X-ray analysis has been performed to determine the elemental composition of the worn surfaces lubricated with and without ZDDP in paraffin oil at 392N load for 90 min test duration. The observed data are summarized in Table 4.4. It is apparent from the table that wear track lubricated with paraffin oil alone does not show presence of any hetero atom except oxygen which may be due to the oxide formation. However, the lubricity of ZDDP is due to tribofilm containing hetero-atoms zinc, phosphorous, sulfur and nitrogen on the worn surface. In order to investigate the detailed tribochemistry behind the excellent wear reducing behavior of Schiff base copper complexes over the other additives, the X-ray Photoelectron Spectroscopy (XPS) analysis has been performed. The XPS spectra of C 1s, N 1s, O 1s, Cu 2p and Fe 2p of worn surface lubricated with [Cu(Sbh)₂] at 392N load for 90 min test duration are shown in Figure 4.11.

Table 4.4. EDX analysis data of the worn steel surface lubricated with paraffin oil in presence and absence of ZDDP (1% w/v) for 90 min test duration at 392N applied load

Lubricants	Atomic %					
	C	O	Fe	Zn	S	P
Paraffin oil	16.74	21.14	62.12	-	-	-
ZDDP	13.64	15.42	62.46	05.02	01.42	02.04

The spectrum of C 1s on the worn surface exhibits peaks at 285.9 and 287.3 eV corresponding to C-C/C-H and -C-O- moieties respectively, which suggest that the decomposed products of copper complex were adsorbed on the steel surface [Wang *et al.*(2006)]. The appearance of peak around 399.9 eV in the spectrum of N 1s strongly supports the role of nitrogen in the complex tribofilms as it corresponds to nitrogen in the form of -N=C/-N-C- moieties [Wu *et al.*(2009)]. There are two peaks around 529.8 and 531.8 eV in the spectrum of O 1s. The spectrum of Cu 2p on worn surface illustrates the existence of two peaks at 933.8 and 953.2 eV due to Cu 2p_{3/2} and Cu 2p_{1/2} respectively [Chen *et al.*(2011)]. The Cu 2p_{3/2} signal contains both the CuO (933.0 eV) and Cu₂O (934.0eV) oxides whereas Cu 2p_{1/2} shows only Cu₂O (953.2 eV). Besides this, a satellite peak of Cu(II) at 943.8 eV also appeared. The presence of CuO is expected, as copper is present as Cu(II) in the complex while formation of Cu₂O is probably due to the partial reduction of Cu(II) because of its interaction with surface or the other constituents [Battez *et al.*(2010)]. Oxidation of iron to Fe₂O₃ and/Fe₃O₄ during rubbing process has been confirmed by combining the binding energies of Fe 2p at 711.2eV with O 1s at 529.8 eV [Zhou *et al.*(2001), Li *et al.*(2010)]. Thus, the major constituents of complex tribofilm for the surface

lubricated with $[\text{Cu}(\text{Sbh})_2]$ under the boundary conditions are C-C/C-H, -C-O-, -N=C/-N-C-, CuO, Cu_2O , Fe_2O_3 and Fe_3O_4 which make it excellent antiwear lubricant additive.

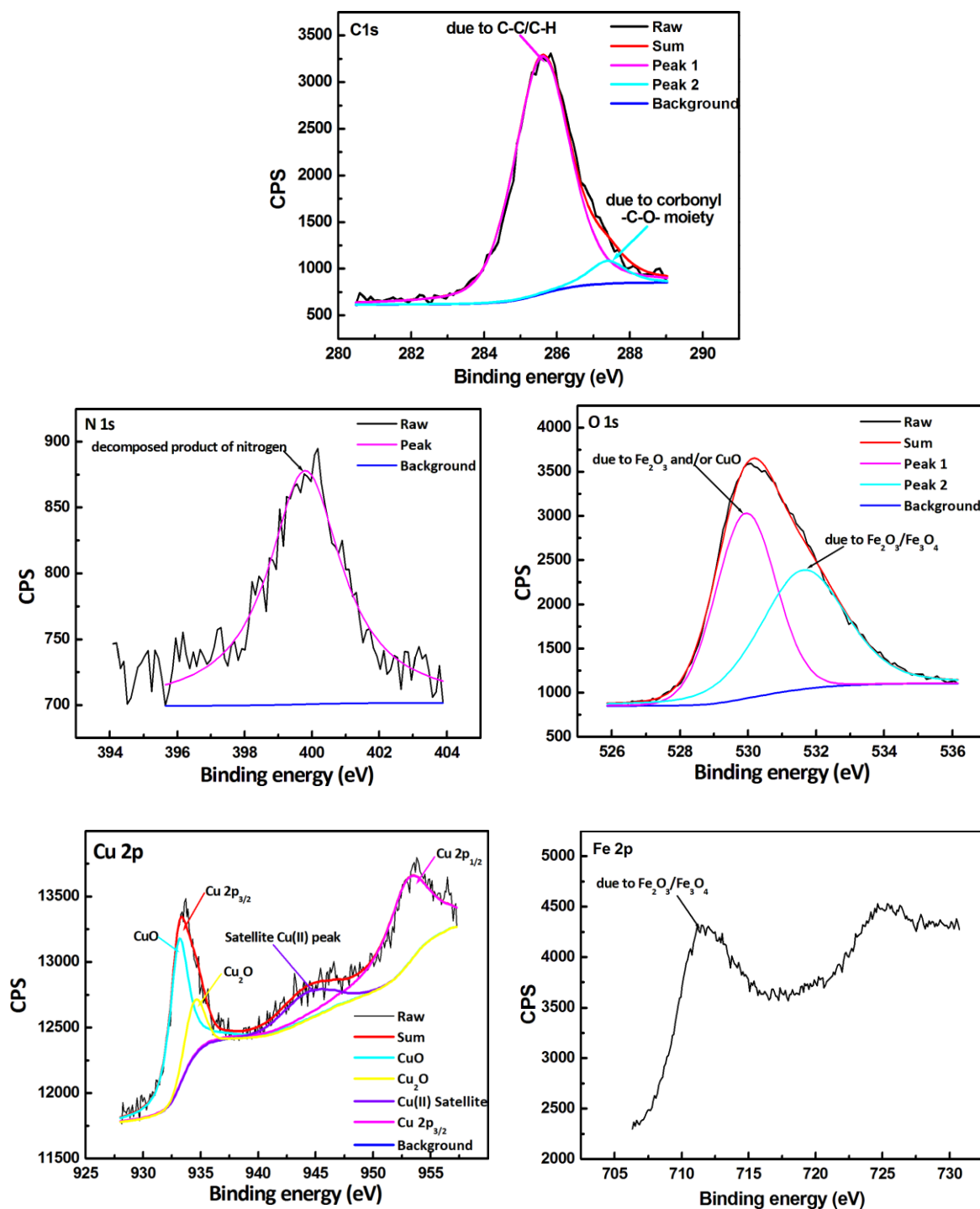


Figure 4.11. XPS spectra of tribochemical film formed on worn steel surface lubricated with $[\text{Cu}(\text{Sbh})_2]$ (1% w/v) at 392N applied load for 90 min test duration in liquid paraffin: (a). C 1s, (b). N 1s, (c). O 1s, (d). Cu 2p and (e). Fe 2p

4.2.6. Proposed mechanism

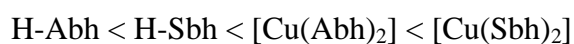
The above surface analysis and tribochemical investigation of worn surfaces under different test conditions demonstrate that the N-containing Schiff bases act as ligands and their copper complexes provide greater surface area for the initiation of adsorption. During the sliding condition, *in situ* tribochemical reactions occurred between the lubricant and the steel surfaces leading to formation of iron-additive complexes. As suggested by Cavdar *et al.*(1991) i.e. formation of tribofilm is time dependent and it will take time to form stable tribochemical film on the surface of tribopairs. High temperatures and longer sliding durations favour the complexation process. As a consequence of the complex formation, wear of the surfaces due to shearing of asperities does not lead to the formation of debris particles. During running-in period, the sliding surfaces become very conformal and the contact pressure is strongly reduced. An important consequence of many tribochemical reactions is the increase in local temperature during contact at asperities which could accelerate chemical reactions dramatically [Furlong *et al.*(2014)]. This behavior shows that the processes occurring during the running-in time are strongly temperature dependent and that a certain energy barrier has to be overcome to induce wear-resistance properties. Thus, in addition to the mechanical energy imparted to the molecules during shearing, additional thermal energy is required. There is rise in temperature during strong rubbing due to asperity-asperity interaction. Consequent upon the rise in temperature, the additive can react with steel surfaces. The kinetics of wear and complex formation are strongly related to each other. However, the reduction in contact pressure inhibits the rise in temperature; therefore the tribochemical reaction is ceased. It is interesting to note that small changes in the chemical structure of the additives which influence the rate of tribofilm formation may lead to strongly varying tribological results. Owing to the presence of additional -OH group in [Cu(Sbh)₂] additive makes it superior antiwear additive over [Cu(Abh)₂] by facilitating the complex formation between -OH and iron ions generated from surface oxidation during the tribological test. Initially, the additive molecules may physically and/chemically adsorb on the metal surface via the hetero atoms present in it. Later on, as the temperature increases (due to increase in load or due to increase in frictional heat), the adsorbed film may decompose to form complex protective tribofilm [-C-O-, C-C/C-H, -N=C/ -N-C-, CuO, Cu₂O, Fe₂O₃ and Fe₃O₄ in case of Cu(Sbh)₂ complex] during sliding conditions on the metal surface. Under the

rubbing process, as the time and/load increases, additives bring about chemical reactions among themselves or with the metal surface to form tribochemical film. This effective molecular adsorption on the sliding pairs and tribochemically generated protective films on the metallic surface separate the asperities and thus minimizing wear. Herein, it can be supposed that the CuO and Cu₂O produced due to tribochemical reaction play a major role in the lubrication process.

4.2.7. Quantum chemical calculation studies

Quantum chemical calculations based on density functional theory (DFT) were performed to investigate the presence of different substituents on the Schiff base additives H-Abh, H-Sbh and their respective copper complexes [Cu(Abh)₂] and [Cu(Sbh)₂]. An attempt has been made to establish the relationship between the molecular structures of these compounds and the experimentally observed lubrication behavior. The calculated quantum chemical parameters like dipole moment (μ), E_{HOMO} , E_{LUMO} , ΔE , ΔE_1 and ΔE_2 of the additive molecules are presented in Table 4.5. The interaction mechanism between lubricants or lubricant additives and metal surface include adsorption phenomenon. The antiwear behavior of an additive is explained on the basis of formation of a physically and/or chemically adsorbed film on the metal surface [Karelson *et al.*(1996)]. The extent of adsorption of lubricants on metallic surface depends on the dipole moment, functional groups, electron density on donor atoms and electrostatic attraction between the polar head of the additive molecules and the metal surface. Adsorption of additive on the metal surface is not only a precursor of surface chemical reaction but also provides important contribution to tribological performance of lubricants. It is well known that organic/or inorganic compounds which act as additives are polar molecules having heteroatoms such as sulfur, nitrogen, oxygen, and π -electron clouds through which these are adsorbed well on the metal surface [Zhang *et al.*(1999a-d)]. It has been found that as the dipole moments of additive molecules increase, their tribological efficiencies also increase. Figure 4.12 shows that studied Schiff bases and their respective copper complexes have different HOMO and LUMO distributions. HOMO density distributions are mainly localized around the hydrazine moiety and substituted carbonyl components including phenyl ring, -OH and -CH₃ groups. However, the LUMO density distributions are significantly distributed throughout the respective molecules. According to the frontier molecular orbital (FMO) theory, increasing values of E_{HOMO} indicate that there is high tendency of the additive molecules to donate electrons to the

appropriate acceptor molecules having empty molecular orbitals. On the other hand, decreasing energy of E_{LUMO} indicates the ability of a molecule to accept the electrons. Therefore, lower the value of E_{LUMO} , it is more probable that the molecule will accept electrons [Jayadas *et al.*(2006)]. The difference between E_{LUMO} and E_{HOMO} i.e., the energy gap (ΔE), is the important stability index that has been found to have excellent correlation with antiwear efficiencies in a tribological reaction. The larger value of ΔE implies high stability or inertness of a moiety in a reaction. The ΔE has also been associated with the hardness and softness of the involved additives. The small energy gap (ΔE) between interacting HOMO and LUMO orbitals of the molecule is indicative of its soft nature i.e. it can be easily polarized whereas large energy gap corresponds to its hard behavior [Wang *et al.*(2007)]. Therefore, it can be stated that antiwear efficiency of the additives would increase when the values of ΔE decrease. On the basis of E_{HOMO} , E_{LUMO} and ΔE values for the studied Schiff bases and their copper complexes, the order of efficiency is given below:-



The above order is consistent with the experimentally found tribological data.

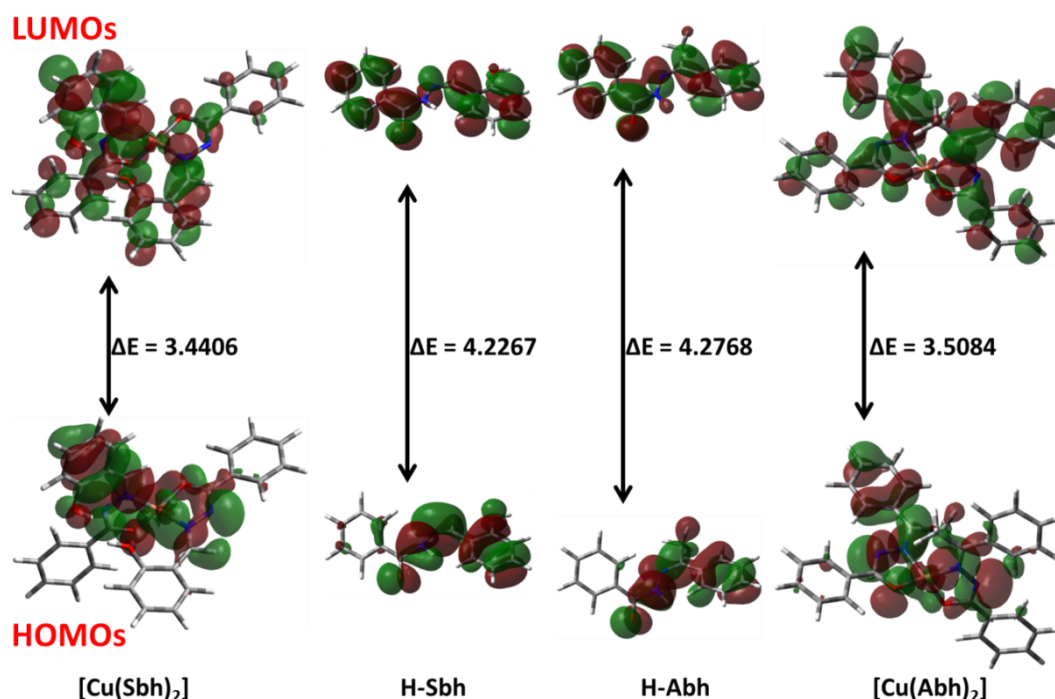


Figure 4.12. Graphical representation of energy gaps (eV) between HOMO and LUMO density distributions for the studied Schiff base ligands and their respective copper complexes

Table 4.5. Calculated quantum chemical parameters of antiwear lubricant additives calculated with B3LYP/LanL2DZ basis set

Additives	Dipole moment (D)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	ΔE_1 (eV)	ΔE_2 (eV)	Mulliken charge		Wear rate ($10^{-4} \times \text{mm}^3/\text{h}$)
							N_1/N_2	O_1/O_2	
Fe ₅		-5.0752	-1.7469	3.3282					
H-Abh	3.5370	-6.1484	-1.8716	4.2768	4.4015	3.2036	-0.034/0.103	-0.272	46.52
[Cu(Abh) ₂]	4.5554	-5.6284	-2.1200	3.5084	3.8815	2.9552	-0.150/-0.322	-0.458	08.54
H-Sbh	3.7502	-6.0670	-1.8392	4.2267	4.3201	3.2359	-0.064/0.090	-0.285/-0.222	41.87
[Cu(Sbh) ₂]	5.7523	-5.6401	-2.1995	3.4406	3.8932	2.8757	-0.207/-0.254	-0.449/-0.502	07.02

$\Delta E_1 = E_{\text{LUMO}}$ of iron - E_{HOMO} of additive

$\Delta E_2 = E_{\text{LUMO}}$ of additive - E_{HOMO} of iron

In order to construct a cumulative effect of an additive molecule, it is important to focus on parameters which directly influence the electronic interaction of the additive molecules with the metal surface. Further, the full geometry optimized structures with Mulliken charges of the studied Schiff bases and their copper complexes are shown in Figure 4.13. According to classical chemical theory, all the chemical interactions are by nature either electrostatic (polar) or orbital (covalent) [Huang *et al.*(2003)]. Electrical charges in the molecules are obviously the driving force of electrostatic interactions. The additive may form a stable adsorption film on the metal surface via electrostatic interactions which may prevent direct asperity-asperity contacts at steel-steel interface [Jaiswal *et al.*(2014)]. It can be stated that stronger the electrostatic and covalent interactions, better is the ability of additives to minimize friction and wear [Eddy *et al.*(2011)]. Thus, the more polar molecules are prone to interact appreciably with metal surface. The atoms which possess high negative net charges are the most probable sites for electrostatic interactions. The structure of the studied compounds shows that phenyl ring, nitrogen and oxygen atoms in the additive molecules are the probable sites for electrostatic interactions. The data presented in Table 4.5 reveal that the value of Mulliken charges (-ve) were found to be maximum in case of complexes than their respective ligands. Schiff base H-Sbh exhibits greater negative charges on O₁/O₂ and N₁/N₂ atoms than H-Abh whereas the amount of negative charges on these atoms were further increased and reached to maximum value in case of [Cu(Sbh)₂] complex. Thus, the critical examination of these values of negative charges supports the observed behavior of additive-metal interactions.

The tribological behavior of an additive molecule depends on its film forming tendency which further depends on several kinds of additive-metal interactions. A literature survey reveals that the adsorption of heterocyclic compounds on the metal surface can occur through donor-accepter interaction between the active centres of the

heterocyclic compound and the vacant d-orbitals of metal atom [Karelson *et al.*(1996), Wang *et al.*(2007)]. Therefore, for the investigation of antiwear properties it is important to correlate molecular orbital energies of the additive molecules to those with the energy of metal. To be a good lubricant additive, it is important to correlate mutual FMO energies of additive and iron. Huang *et al.*(2007) have reported the energy of frontier molecular orbitals of iron by considering iron as five-atom clusters. The interaction between additives and iron can be discussed on the basis of ΔE_1 ($\Delta E_1 = E_{\text{LUMO}}$ of iron - E_{HOMO} of additive) and ΔE_2 ($\Delta E_2 = E_{\text{LUMO}}$ of additive - E_{HOMO} of iron) as mentioned in Table 4.5. From these values it is evident that the additive molecules are electron donors while iron acts as an electron acceptor and there is nucleophilic interaction between iron and additive molecules [Huang *et al.*(2003)]. The results show that the difference between E_{HOMO} of H-Sbh and E_{LUMO} of iron (ΔE_1) is found to be lower than that of H-Abh. In their corresponding copper complexes the same order of ΔE_1 prevails. This further suggests that the maximum interaction will take place between $[\text{Cu}(\text{Sbh})_2]$ and iron. For a good antiwear additive, besides donation of electron from HOMO of the additive molecules to the LUMO of the vacant d-orbitals of the iron atom, interaction between the HOMO of iron and LUMO of the additive molecules (Reterodonation/Backbonding) is equally important. A greater transfer of electron density from additive molecules to the vacant d-orbital of iron atom accumulates the electron density on the iron. Consequently, it develops better tendency to donate back electron to the vacant orbital of the additive. This favours the extent of back donation (Synergistic bonding). It is evident from Table 4.5 that the values of interaction parameters ΔE_1 (E_{LUMO} of iron - E_{HOMO} of additive) are always higher than ΔE_2 (E_{LUMO} of additives - E_{HOMO} of iron) for all the additives. The order of antiwear efficiency of the additives emerged on the basis of values of ΔE , ΔE_1 and ΔE_2 is found to be exactly the same as that of their antiwear lubrication behavior evaluated experimentally with four ball lubricant tester.

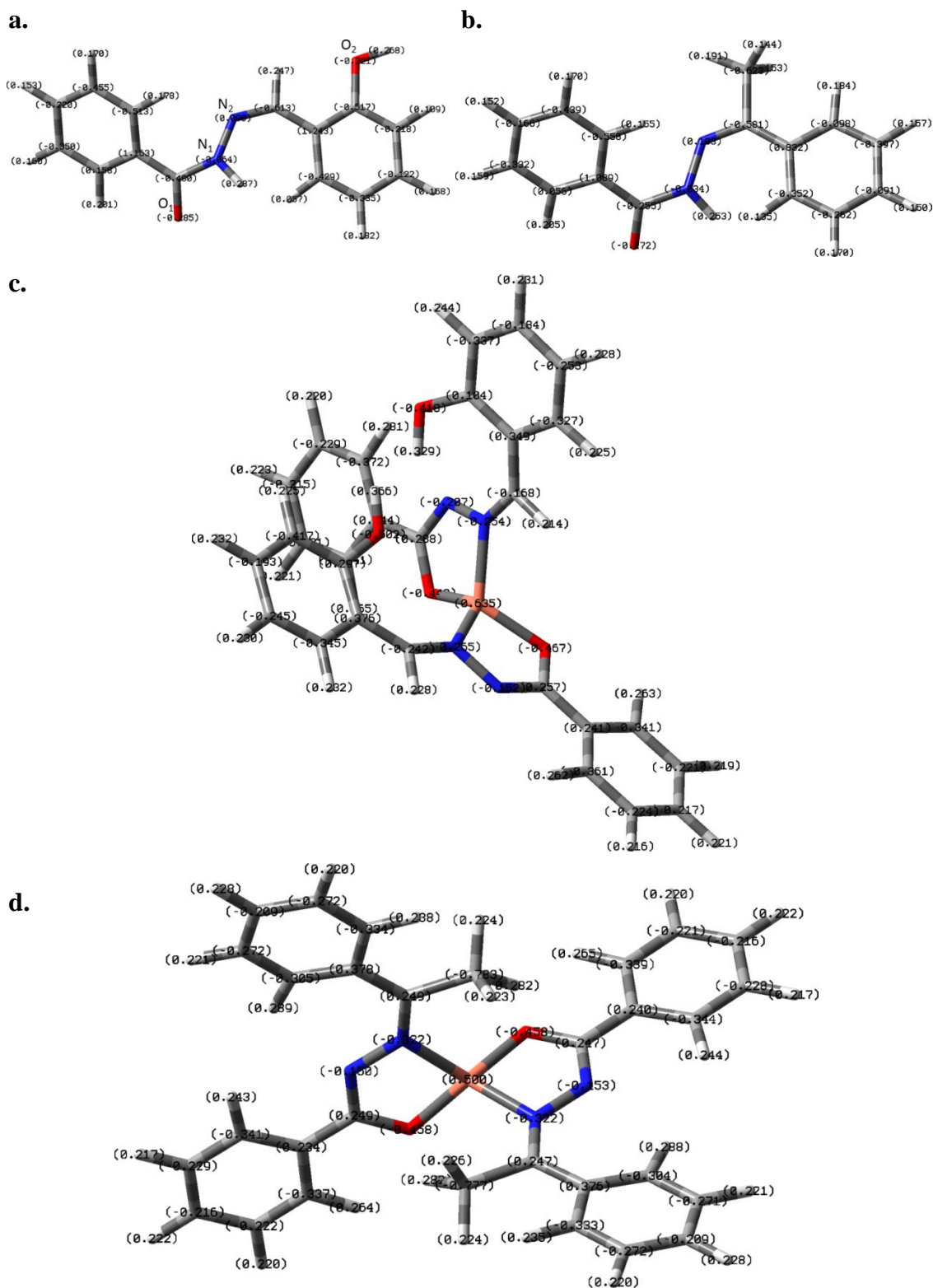


Figure 4.13. Optimized structures with Mulliken charge of Schiff bases and their copper complexes; (a) H-Sbh, (b) H-Abh, (c) $[\text{Cu}(\text{Sbh})_2]$ and (d) $[\text{Cu}(\text{Abh})_2]$

4.3. Conclusions

The non-corrosive behavior of the Schiff bases and respective copper complexes was confirmed by copper strip test. Alloy steel AISI 52100 also remained unaffected in presence of the tested blends. Anticorrosive behavior of these additives was attributed to non-existence of corrosion prone elements such as halogen, phosphorus and sulfur in these additives. All the studied Schiff base additives remarkably improved the antiwear properties of the paraffin base lube. However, their antiwear efficiency is slightly poorer than that of ZDDP. The Schiff base copper (II) complexes exhibit excellent antiwear and load carrying ability even much better than that 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), ΔE_1 , ΔE_2 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.