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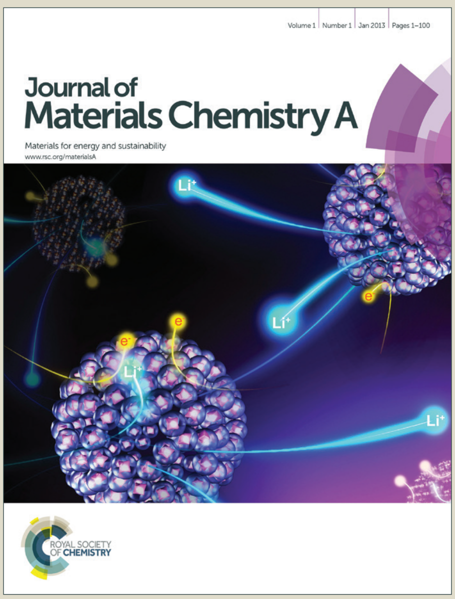

Tribological studies of some SAPS-free Schiff bases derived from 4-aminoantipyrine and aromatic aldehydes and their synergistic interaction with borate ester

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Abstract

Tribological performance of sulfur, phosphorous and metal-free Schiff bases of 4-aminoantipyrine with benzaldehyde(AAPB), salicylaldehyde(AAPS), *p*-chlorobenzaldehyde(AAPC) and *p*-methoxybenzaldehyde(AAPM) and their synergistic formulations with borate ester(BE) in paraffin oil has been evaluated using four-ball tester at optimized concentration of Schiff bases (1%w/v) and their synergistic formulations with BE (0.5%w/v for each) by varying load for 30 min duration and varying test durations at 392N load. Synergistic formulations effectively enhance antiwear properties of oil and possess high load carrying capacity in comparison to the conventional zinc dibutyldithiophosphate (ZDDP)/BE/Schiff bases alone. The best efficiency is shown by AAPM, followed by AAPC, AAPS and then AAPB. The same order is observed in their corresponding synergistic formulations. AFM and SEM micrographs of wear scar lubricated with synergistic formulations show drastic decrease in surface roughness in comparison to borate ester/ZDDP alone. EDX analysis of worn surface in presence of AAPM+BE exhibits nitrogen, boron and oxygen indicating adsorption of additive on surface. XPS of tribofilm shows B_2O_3, BN, Fe_2O_3, Fe_3O_4 and adsorbed carbon in the form of -C-C- and -C(O)O- moiety. Quantum chemical calculations(DFT) for interactions of Schiff bases with surface show good agreement with experimental results.

Keywords: Steel, Antiwear lubricant additives, Synergistic formulations with borate ester, Surface characterization: AFM, SEM/EDX, XPS, Tribochemistry and Theoretical calculations.

1. Introduction

A wide variety of lubricant formulations have been used to reduce interfacial friction and enhance wear-resistance of the moving surfaces. Sulfur,[1-3] phosphorous,[4-7] halogen,[8] nitrogen,[9-13] boron[14-16] containing additives and metal complexes[17-27] are being used in lubricating oils as multifunctional additives like antiwear, extreme pressure, antioxidant and corrosion inhibition. The lubricant is believed to perform these functions by forming a stable interfacial tribochemical film between two proximate surfaces, thereby reducing wear and friction and increasing the life of contacting surfaces.[28-32] The extent to which a lubricant composition enhances antiwear and antifriction properties of base oil, depends on a number of factors like structure of the additives and their concentration, interface chemistry, sliding speed, applied load, contact temperature and finally tribochemical characteristics of the lubricating film formed at the surface.[33] A literature survey reveals that the tribological applications of zinc, molybdenum and lanthanum complexes of dithiohydrazodicarbonamides,[17,18] dialkyldithiophosphates,[19,20] dithiocarbamates,[21,22] tricresylphosphates[23] are extensively recognized. Among the variety of additives, zinc dialkydithiophosphates (ZDDP) are arguably the most successful multifunctional lubricant additives ever invented.[23-27] However, the excessive use of additives containing phosphorous, sulfur, halogen and metals has been limited due to the several negative impacts they have caused to the environment as well as to the engines.[34] The phosphorous and sulfur contents adversely affect the catalytic efficiency of exhaust emission catalytic converters.[35] In addition to environmental pollution, the health hazards include eye irritation, allergic contact dermatitis and mutagenicity.[36,37] Now a days there are several norms to strictly limit the SAPS (Sulfated Ash, Phosphorous and Sulfur) contents of additives.[38,39] Therefore, concerted efforts have been made in this direction to develop new antiwear additives to replace ZDDP and reduce the SAPS content of additives without compromising the performance of the base oil.

Modern lubricant formulation, in addition to its high level performance needs to be environment friendly also. Recently, Schiff base derivatives and borate esters have attracted much more attention.[40-42] Schiff bases being biologically active materials, are frequently used as antitumor, antibacterial, antifungal and anticancer drugs. On the other hand, boron containing compounds have also been used as effective antiwear additives, antioxidants, friction modifiers and corrosion inhibitors.[14-16,43] Their tribological behavior is comparable to that of ZDDP, because like ZDDP, these compounds also form glassy film on the metal surface. Thus boron containing compounds appear to be an attractive alternative to the conventional additives, showing almost similar antiwear performance as that of ZDDP but without adding sulfur and phosphorous to the base oil. This has been explored well in our earlier work on thiosemicarbazones and their synergistic mixtures with borate esters as efficient low/zero SAPS antiwear additives in paraffinic base oil.[40-42]

In continuation to that, the present communication reports synthesis of a series of SAPS-free Schiff bases derived from condensation of 4-aminoantipyrine with benzaldehyde, salicylaldehyde, *p*-methoxybenzaldehyde and *p*-chlorobenzaldehyde. The base 4-aminoantipyrine (4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one) has been chosen as it is free from S, P, metal and contains phenyl ring and pyrazolone moiety having a number of triboactive centers like N, O and methyl groups which assist in lubrication through adsorption. 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 are expected to provide excellent tribological and environment friendly compatibilities when used as additive in paraffin oil. Being ashless, these antiwear lubricant additives have potential to find applications in various automotive industries as sludge formation is reduced to improve machine efficiency. A comparison of the observed tribological behavior of Schiff bases and their synergistic formulations with that of ZDDP shows that these formulations offer an environment friendly alternative to the conventional high SAPS containing antiwear lubricant additives ZDDP. The characterization of tribochemical film formed on the interacting metallic surfaces and their surface topography have been studied with the help of X-ray Photoelectron Spectroscopy (XPS), Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscopy (SEM) and contact mode Atomic Force Microscopy (AFM). Quantum chemical calculations of studied Schiff bases have been also performed using Gaussian 03 program to correlate their experimentally obtained tribological behavior with the theoretical one.

2. Experimental Section

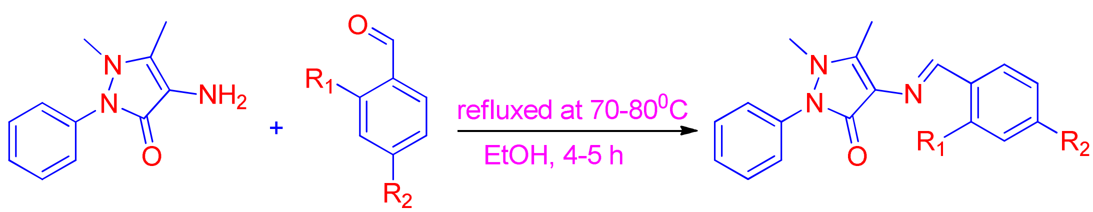
2.1 Chemicals

The starting materials 4-aminoantipyrine (99%, Merck), benzaldehyde (98%, Merck), salicylaldehyde (99%, Merck), 4-chlorobenzaldehyde (99%, Merck) and 4-methoxybenzaldehyde (99%, Merck) were used without further purification. All of the solvents used throughout the experiments were of analytical grade and were used without further purification.

The lubricating base oil, neutral liquid paraffin oil (Qualigens Fine Chemicals, Mumbai, India) having specific gravity 0.82 at 25°C, kinematic viscosity at 40°C and 100°C , 30 and 5.5 c*S*t respectively, viscosity index 122, cloud point -2°C, pour point -8°C, flash point 180°C and fire point 200°C, was used without further purification. Commercial borate ester was obtained as a gift under the trade name of Vanlube 289 which contains borate ester as main component. This is a yellow liquid (color ASTM D1500 L1.5) with boron content 1.00%, density 0.99 mg/mm^3 at 15.6°C and viscosity 458.00 cSt and 22.30 cSt at 40°C and 100°C respectively.

2.2 Synthesis and characterization of Schiff base lubricant additives

The Schiff bases have been synthesized by the earlier reported methods.[44,45] An anhydrous ethanolic solution (30 ml) of 4-amino-1,5-dimethyl-2-phenylpyrazol-3-one (0.3 mol) was drop wise added to a round bottom flask containing ethanolic solution (30 ml) of substituted benzaldehyde (0.3 mol) equipped with magnetic stirrer and condenser. The reaction mixture was refluxed for 4-5 h (Scheme 1). The progress of the reaction was monitored by TLC. After cooling, the obtained yellow color precipitate was filtered, washed several times with ethanol and recrystallized with ethanol, and then dried in *vacuo*. The purity of compounds has been confirmed by TLC using *n*-hexane and ethyl acetate (6:4).



Where, R_1 = H, R_2 = H : AAPB
R_1 = OH, R_2 = H : AAPS
R_1 = H, R_2 = Cl : AAPC
R_1 = H, R_2 = OCH_3 : AAPM

Scheme 1. Synthesis of Schiff bases of 4-aminoantipyrine with different substituted aldehydes

The ^1H NMR and ^{13}C NMR spectra of these Schiff base additives have been mentioned in supplementary information **[S1].**

2.4 Tribological Characterization

2.4.1 Sample Preparation

Paraffin oil blends of Schiff bases 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 1-2 h on magnetic stirrer. The entire antiwear and load carrying tests were carried out at an optimized concentration i.e., 1.0% w/v Schiff bases, 1% w/v synergistic formulations (0.5% Schiff base+0.5% BE) and compared with those of 1.0 % w/v zinc dibutyldithiophosphate (ZDDP) and commercial borate ester (BE) in paraffin oil.

2.4.2 Specimen

The balls of 12.7 mm diameter made up of AISI 52100 alloy steel having hardness 59-61 HRc were used for the tests. Before and after each test, balls were cleaned with *n*-hexane and thoroughly air-dried.

2.4.3 Antiwear Testing

The friction and wear properties of these compounds and their synergistic formulations as antiwear additives in base oil were evaluated using Four-Ball Lubricant Tester (Stanhope-Seta, London Street, Chertsey, UK) at 1475 rpm (equivalent to a sliding speed of 567 mm/sec) using different loads for different time durations according to ASTM D4172. The wear scar diameter on the lower three balls was measured after running for 15, 30, 45, 60, 75 and 90 min respectively at 392N load and at various loads 294, 392, 490, 588 and 686N for 30 min test duration. In order to get more reliable values, each tribological test was repeated thrice. An optical microscope was used to measure the wear scar diameter of three stationary balls, then a mean value was calculated and cited here as mean wear scar diameter (MWD). The details of experimentation and various tribological parameters have been mentioned in supplementary information **[S2].**

2.5 Surface Characterization

Scanning electron microscope (SEM) images of the worn surface areas of the steel balls were taken using a ZEISS SUPRA 40 electron microscope. The elemental compositions of tribofilm formed on the worn surface of the steel balls were determined by using energy dispersive X-ray spectroscopy (EDX). Contact mode Atomic Force Microscope (Model No. BT 02218, Nanosurf easyscan 2 Basic AFM, Switzerland) was used to investigate roughness of the worn surfaces with Si_3N_4 cantilever (Nanosensor, CONTR type) having spring constant of ~0.1Nm^{-1} and tip radii more than 10 nm. The X-Ray Photoelectron Spectroscopy (AMICUS, Kratos Analytical, Shimadzu, U.K.) was used for analyzing the chemical composition of tribofilm formed on the worn surface. After testing the synergistic formulation of Schiff base with borate ester (0.5+0.5 wt%) under load of 392 N for 90 min duration, one of the three lower balls was ultrasonically cleaned in hexane for about 5 min and allowed to dry in the atmosphere. The XPS of wear scar on this ball was recorded. The radiation source Mg Kα line with pass energy of 29.35 eV and the binding energy of C1s (284.6 eV) was used as a reference.

2.6 Computational details

Density Functional Theory (DFT) is found to be a suitable method for theoretical calculations of electron densities at various centers of a molecule. All the calculations were performed using B3LYP[46] that uses Becke's three-parameter functional (B3) and includes a mixture of Hartree-Fock with DFT exchange terms associated with the gradient corrected exchange-correlation functional of Lee, Yang and Parr (LYP)[47]. It has comparatively lesser convergence problems than those found in pure DFT methods. Thus, B3LYP has been used in this paper to carry out quantum calculations. Full geometry optimizations of all additives were carried out with the standard B3LYP/6-31G++(d,p) basis set[48] using Gaussian 03, D.01.[49]

2. Results and discussion

The potentiality of the synthesized Schiff base compounds and their synergistic formulations as antiwear additives in paraffin oil were evaluated using four-ball tester. Since the antiwear efficiency of a particular compound depends on its concentration in base lube, it is important to optimize additive concentration before conducting the tribological tests. The mean wear scar diameter is an indication of extent of wear when sliding contact occurs. Fig. 1a shows the variations of mean wear scar diameter (MWD) of steel balls lubricated with the different combinations of synthesized Schiff bases and commercial borate ester in paraffin oil by keeping total additive concentration as 1% w/v at 392N load for 60 min test duration. It is evident from Fig. 1 that all of the additives when mixed in paraffin oil in different concentrations reduce wear scar diameter on steel surface. The value of mean wear scar diameter has been found to be high in case of surface lubricated with borate ester/Schiff base additives alone at 1% w/v. By adding small amount (0.25% w/v) of Schiff base additive to borate ester, significant decrease in the MWD value is observed. There is maximum decrease in MWD when Schiff base and BE both are 0.5 % w/v. On further increasing the concentration of Schiff base up to 0.75% w/v and keeping BE 0.25%, the value of MWD increases abruptly. The increase in concentration of Schiff base to 1% w/v (absence of BE) further raises the MWD. Thus, the best wear resistance behavior is shown when Schiff bases and borate ester both are present at 0.5% w/v concentration of each. Out of all the tested Schiff bases, the minimum MWD value is obtained in case of synergistic formulation containing AAPM. To show synergy between Schiff bases and BE, bar diagram has been constructed, Fig. 1b, taking together BE and AAPM as the best antiwear Schiff base additive. The diagram evidently exhibits synergy between AAPM 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 with an optimized concentration of synergistic formulation of Schiff bases along with borate ester (0.5+0.5% w/v) and compared with those of 1% w/v of the individual additives.

Herein, the concentration dependence of the wear reducing ability of the additives can be explained on the basis of their affinity towards additive-additive interactions along with interactions of the additives with metal surface. More active additives are prone to reduce wear even at comparatively lower concentrations by forming protective tribochemical films on sliding interfaces.

3.1 Antiwear behavior

A series of friction and wear tests have been conducted to evaluate the tribological properties of synthesized Schiff bases and their mixtures with commercial borate ester in paraffin oil. Fig. 2 illustrates the variation of mean wear scar diameter with time duration 15, 30, 45, 60, 75 and 90 min at 392N applied load in absence and presence of 1% concentration of Schiff base additives/borate ester/ZDDP and mixtures of Schiff bases with borate ester having 0.5% of each. From Fig. 2, it is evident that MWD in paraffin oil decreases, in general, in presence of Schiff bases than in their absence. Thus the tested Schiff bases act as antiwear additives. However, the antiwear efficiency of Schiff bases alone in base lube has been found to be poorer than those of conventional high SAPS containing ZDDP and commercial BE. It is interesting to note that the mixtures of the synthesized additives with BE significantly improved the antiwear behavior of base lube showing a lowering in the value of MWD to a greater extent.

The antiwear behavior of paraffin oil as a function of time in presence of different additives can be discussed on the basis of Fig. 2. After 15 min of time duration there is slight increase in MWD but after 30 min there is abrupt increase in MWD. A substantial increase in MWD is observed after 60 min of time duration which progressively continues up to 90 min time duration. Almost similar nature of curves is observed in presence of admixtures of paraffin oil with Schiff bases/BE/ZDDP/mixtures of Schiff bases with BE. As apparent from the figure beyond 30 min time duration, slope of these curves has drastically reduced in presence of these additives as compared to paraffin oil alone.

Furthermore, the MWD of *p*-methoxyphenyl, *p*-chlorophenyl, *o*-hydroxyphenyl and phenyl Schiff base derivatives is reduced by 36, 29, 23 and 19%, respectively, compared to paraffin base lube. However, there is appreciable enhancement in reduction of MWD to 51, 49, 48 and 47% respectively for their corresponding mixtures with commercial borate ester. Thus, there is significant improvement in antiwear efficiency in synergistic mixtures as compared to Schiff bases alone. The overall antiwear behavior of different additives on the basis of MWD values may be arranged in the following order:

Schiff bases+BE > ZDDP > BE > Schiff bases > Paraffin oil

The observed antiwear behavior with respect to time can be discussed on the basis of tribofilm formation. Initially, there is no tribofilm on the interacting surfaces. As the time increases the additive molecules get uniformly adsorbed over the matting surfaces during sliding under operating conditions and may react with metal surface to form tribochemical film. The formation of tribofilm is time dependent; therefore, some time exposure is required to form a durable tribofilm on sliding surfaces.[50] During first 15 min test, the tribofilm formation on the interacting surfaces could not get initiated, consequently large values of MWD are observed in every case. Later on, increase in MWD value becomes lesser in case of Schiff base additives after 30 min of test run, however, in case of corresponding synergistic mixtures it is after 15 min only i.e. earlier than the Schiff base. A subsequent lesser increase in the value of MWD thereafter, suggests the existence of some tribofilm on the surface.

The antiwear action of Schiff bases may be ascribed to their adsorption through a number of active centers like N, O, phenyl and methyl group. To understand the effect of substituents on additives towards their adsorption on contact surfaces, different derivatives of Schiff bases like *p*-methoxyphenyl, *p*-chlorophenyl and *o*-hydroxyphenyl have been tested. On the basis of +I and +R effects, these groups may be arranged in the following order:

$$OCH_3 > -OH > -Cl$$

Accordingly increase in the electron density on the ring is expected to occur in the above order. Consequently adsorption of the additive and hence its antiwear action should also follow the above order. However, the antiwear behavior of *p*-chlorophenyl derivative has been found to be superior over *o*-hydroxyphenyl derivative. This may be due to the -I and +R nature of -Cl group which results in increase in electron density on chloro group instead of the ring causing more adsorption through chloro group.

The similar order of tribological behavior has been observed in case of corresponding synergistic formulation of Schiff bases with borate ester. However, extent of wear reduction in case of a synergistic formulation has been found to be much larger than the initial Schiff base alone. This can be explained on the basis of formation of donor-acceptor complex where N-containing additives donate their lone pair of electrons to electron deficient boron atom of commercial borate ester. Thus during sliding conditions, the donor-acceptor complex further facilitates their adsorption on steel-steel interface by increasing surface coverage in order to form tribochemical film showing pronounced synergistic action. These synergistic formulations in paraffin show excellent wear reducing behavior even much better than that of ZDDP and BE alone.

Fig. 3 illustrates the variation of friction coefficient with time in absence and presence of 1% BE/ZDDP/Schiff base additives and their mixtures with BE in paraffin oil at 392N applied load. It can be seen that the blends of different Schiff base additives with BE show lower friction coefficient values than in case of ZDDP or BE. In every case, friction coefficient increases progressively from 15 to 30 min duration due to static friction caused by direct asperity-asperity contact. From 30 to 45 min run usually friction coefficient decreases in most of the cases, on the other hand, between 45-60 min run some irregular trend is observed. This irregular trend can be explained on the basis of formation and breakdown of tribofilm occurring almost simultaneously in the beginning. As the test time increases tribofilm formed on the sliding surfaces prevents metal-metal contacts and lowers frictional force. The time required for the formation of persistent tribofilm may be different for different additive compositions. Further, friction coefficient increases abruptly after 75 min run in every case. This may be due to the wear assisted surface damage and generation of wear debris produced with time under operating conditions at the interface.[51]

The friction coefficient data support the order of efficiency for different additives and their mixtures with BE as discussed before, accordingly the highest coefficient of friction for every run is observed for base lube and the lowest for the synergistic mixtures of AAPM with

BE. Thus, both antiwear and friction reducing properties of blends of Schiff base additives with BE in base lube are considerably better than those of the reference and commercial additives ZDDP and BE respectively. Variation in these properties in case of different Schiff bases can be correlated well with the composition of tribofilm formed on the surface due to different substituents present around the additive skeleton.

To estimate wear more realistically it is important to examine the variation of mean wear volume with time instead of variation of mean wear scar diameter with time.[52] 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, Fig. 4. Overall wear rate was found to be very high in absence of additives. Among all the AAPs-Schiff bases the following order has emerged for overall wear rate:-

AAPM > AAPC >AAPS > AAPB

The same order of overall wear rate has been observed for their corresponding mixtures with BE. This again is in conformity with the conclusion drawn earlier that owing to formation of stronger, adherent tribochemical film, synergistic formulations efficiently smoothen the surface irregularities thus reducing wear to a great extent.

The running-in wear rate is always higher than the steady-state wear rate as it involves morphological modifications of the surfaces (Fig. S1 and S2). The comparison of running-in, steady-state and overall wear rate of different additives and their synergistic formulations with BE has been displayed in Fig. 5, which clearly reflects that the addition of AAPs-Schiff bases to the base lube significantly reduces the running-in, steady-state and overall wear rate of base lube. However, this reduction in wear rates was found to be poorer than the surface lubricated with BE and ZDDP. Among all of the studied Schiff bases, AAPM most significantly reduces the running-in and overall wear rates of base lube. It is noteworthy that the value of its steady-state wear rate has been found to be much lower than ZDDP and BE alone.

The steady-state wear rate in the presence of the studied synergistic formulations, in general, reduces drastically. Since the life of engineering components is estimated 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.[58] It is interesting to note that the steady-state wear rate has been found to be the lowest in case of synergistic mixture of AAPM+BE, however, its value for AAPM alone was also found to be comparable with those of the other studied synergistic formulations.

3.2 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 and 686N for 30 min test duration for paraffin oil in presence and absence of synthesized Schiff base additives and their mixtures with borate ester (1% w/v). Fig. 6 illustrates the plots of MWD as a function of applied load at 30 min test duration.

At initial load (294N), MWD is very large in the absence of additives but in presence of Schiff base additives it is fairly reduced. It reduces further in presence of ZDDP and borate ester and attains the minimum value for the mixtures of Schiff base additives with BE. At 392N load, MWD increases considerably in every case but this increase attains the minimum value in presence of synergistic mixtures. This may be due to the fact that the thin film of lubricant and additive adsorbed on the interacting surfaces resists much increase in MWD on increasing applied load. At 490N load the base oil, borate ester and ZDDP show abrupt increase in MWD; however, this increase is very small in presence of the Schiff base additives and their mixtures with BE. Thus, the tribochemical film formed *in situ* is further capable of carrying higher load. Beyond 490N load the tribofilm fails to sustain the load in case of paraffin oil alone and in presence of borate ester while in case of ZDDP/AAPs, the film fails beyond 588N load. On further increase in the applied load up to 686N, blends of AAPs with BE could successfully bear the load without surface destruction. Among all the synthesized additives, *p*-methoxyphenyl derivative and its blend with BE in base lube show tremendous load bearing ability with relatively much smaller wear scar diameter. Moreover, it can be inferred from Fig. 6 that the synergistic formulations of Schiff base additives played an important role in remarkably improving the load carrying ability of the base lube.

A correlation between friction coefficient and applied load at 1% concentration of BE/ZDDP/Schiff bases and blends of Schiff base additives with BE (0.5% of each) for 30 min test run is presented in Fig. 7. The increase in friction coefficient with load is much higher in case of paraffin oil in absence of additives whereas in presence of additives it progressively increases with load. The efficiency of Schiff base additives towards their antifriction behavior lies in the same order as obtained from MWD vs. load plots.

3.3 Surface characterization

3.3.1 Surface Morphology

The surface morphology of wear scar has been studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Fig. 8 shows the SEM images of the worn surface of steel balls in the presence and absence of 1% ZDDP, AAPM and mixture of AAPM with borate ester (0.5% of each) at 392N applied load for 90 min duration. The worn surfaces in the presence of additives are smoother in comparison to surface lubricated with paraffin alone. 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.

In case of steel surface lubricated with base oil (Fig. 8a) huge surface destruction with much deeper grooves is observed due to the adhesive wear, on the other hand, the surface lubricated with its admixture having AAPM (Fig. 8b) shows less deeper grooves along the sliding direction. In presence of ZDDP better smoothening of the surface is observed (Fig. 8c). There is tremendous increase in smoothness of the surface when synergistic formulation of AAPM with BE (Fig. 8d) is used which may be due to the formation of strong and adherent tribochemical film on the sliding contacts. At higher load (588N for 30 min duration) also, the extent of smoothening of contacting surfaces has been found to be in the same order as discussed above.

The surface irregularities of the worn steel surfaces observed after antiwear and load carrying tests in paraffin oil were examined by contact mode Atomic Force Microscopy in the presence and absence of synergistic formulations, ZDDP and borate ester at 392N load for 90 min test duration. The roughness parameters, root mean square (S_q) and peak-valley height (S_y) obtained through the software Nanosurf basic Scan2 are mentioned in Fig. 9. From Fig. 9 it is apparent that the synergistic admixtures of Schiff base additives with borate ester in base lube exhibit drastic reduction in area roughness and average asperity height of the lubricated surfaces than the base oil or base oil with borate ester/ZDDP alone. This pronounced reduction of surface roughness in case of synergistic formulations is supposed to be due to very low running-in wear rate and early stabilization of steady-state wear rate which is caused by the interaction between the N-atoms of Schiff bases (Lewis base) and the boron of borate ester (Lewis acid) resulting into formation of a durable tribofilm under lubricating conditions. This behavior can be exemplified by the values of area roughness 409 nm (Sq) for the paraffin oil, 19 nm (S_q) for the blend of AAPM with borate ester and 74 nm (Sq) for the conventional additive ZDDP. The similar observations are also evident from their *3D*-AFM and corresponding line profile graphs (Fig. S3).

In order to investigate the suitability of these additives and their blends with BE towards smoothening of surfaces 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 **(**Fig. S4**)**. The observed trend of the additives towards the reduction of surface roughness under extreme conditions is the same as above in case of 392N load for 90 min duration.

3.3.2 Tribochemistry of synergistic lubricant formulation

The Energy dispersive X-ray analysis has been performed to determine the elemental compositions of the worn surfaces lubricated with and without ZDDP, AAPM and AAPM+BE in paraffin oil at 392N load for 90 min test duration. The observed data are summarized in Table 1a. 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. On the other hand, in case of surface lubricated with ZDDP, presence of hetero-atoms zinc, phosphorous, sulfur and nitrogen is evident. The elemental compositions of wear scar surface lubricated with mixture of AAPM with borate ester show the presence of boron, nitrogen, iron and oxygen on the wear track whereas all of these elements except boron were found in case of surface lubricated with AAPM alone. Herein, the presence of boron on worn surface lubricated with the AAPM+BE, reflects strong additive-additive interaction resulting into formation of donor-acceptor complex through which their adsorption is facilitated. This brings about its tribochemical reaction with metal surface to form stable protective layers reducing friction and wear. The increase in the atomic concentration of the boron and nitrogen on increasing applied load (588N: 30min) suggests that the formation of tribofilm is more favourable at higher load. It is evident from Table 1b, that the atomic concentration of different elements increases appreciably with increase in load in case of Schiff base AAPM+BE while its reverse is observed in case of ZDDP. This contrast may be due to the strengthening of tribofilm in the former case while its rupture in the latter one.

The XPS analysis of the worn surface is subjected to ascertain the chemical compositions of the tribofilm formed during sliding conditions and to study the mechanism of the observed synergistic behavior of *p*-methoxyphenyl derivative with borate ester in paraffin oil. The XPS spectra of C 1s, B 1s, N 1s, O 1s and Fe 2p of worn surface lubricated with AAPM+BE at 392N load for 90 min test duration are shown in Fig. S5.

The spectrum of C 1s on the worn surface exhibits peaks at 285.9 and 287.3 eV corresponding to -C(O)O- and C-C/C-H moieties respectively, which suggest that the decomposed products of borate ester were adsorbed on the steel surface.[52] Formation of BN on the worn surface has been confirmed by combining the binding energies of the prominent signal of B 1s appearing at about 189.7 eV with the binding energy of N 1s at about 398.7 eV.[53,54] Appearance of an additional weak peak around 194.0 eV in the spectrum of B 1s indicates presence of some amount of boron in the form of B_2O_3.[55] Furthermore, combining the binding energies of O 1s with B1s, the peak at 532.9 eV also confirms the presence of B_2O_3 on the worn surfaces.[55,56] It is interesting to note that for FeB or Fe_2B, peaks are not observed in the spectrum showing that boron does not react with metal surface. Oxidation of iron to Fe_2O_3 and/ Fe_3O_4

during rubbing process has been confirmed by combining the binding energies of Fe 2p at 711.5eV with O 1s at 530.8 eV.[57]

3.4 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 a ligands (Lewis base) and may initially interact with electron deficient boron of the borate ester (Lewis acid) in order to form adduct.[58] These adducts get easily adsorbed on the metal surface through their active centers (especially B, N,–CH=N- moiety and phenyl group) due to its greater surface coverage area than their individual ones. 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. As suggested by Cavdar *et al.*[50] i.e. formation of tribofilm is time dependent and it will take time to form stable tribochemical film on the surface of tribo-pairs. As the temperature increases (due to increase in load or due to increase in frictional heat), these adducts may decompose to form boron nitride film during sliding conditions on the metal surface. EDX analysis also confirmed that the formation of tribofilm is more favorable at relatively higher temperature i.e. extreme conditions. Herein, it can be supposed that the boron nitride produced due to tribochemical reaction plays a major role in the lubrication process and its lubricity is related to its layered structure. In general, for the formation of boron nitride, much higher temperature will be needed but during rubbing process it seems to be easily formed.[58,59] The occurrence of boron nitride on the metallic surface has been also confirmed from the XPS spectra. Besides this, the adsorbed nitrogen, boron oxide and iron oxide were also responsible for improving tribological behavior of base oil to the some extent.

3.5 Quantum chemical calculation

Quantum chemical calculations based on density functional theory (DFT) were performed for the Schiff base additives AAPM, AAPC, AAPS and AAPB. An attempt has been made to establish the relationship between the molecular structures of these compounds with the experimentally observed wear-rates. The full geometry optimized structures of the studied Schiff bases AAPM, AAPC, AAPS and AAPB are shown in Fig. 10. The calculated quantum chemical parameters like total energy, E_{HOMO}, E_{LUMO} and orbital energy gap (ΔE) between HOMO and LUMO of the additive molecules are presented in Table 2. The interaction mechanism between lubricants or lubricant additives and metal surface usually include adsorption phenomenon. The strength of adsorption of lubricants on metallic surface depends on the electrostatic attraction of the polar head of the additive molecules with the metal surface. Adsorption of molecular additive on the metal surface is not only a precursor of surface chemical reaction but also provides important contribution to tribological performance of lubricants. According to the frontier molecular orbital (FMO) theory, the energy of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) are the important indices for predicting the reactivity of any chemical species. 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.[60,61] The larger value of ΔE implies high stability or inertness of a moiety in a reaction.[62] 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. Therefore, it can be stated that antiwear efficiency of the additives would increase when the values of ΔE decreases. On the basis of ΔE values for the studied Schiff bases, the order of efficiency is given below:-

$$AAPB < AAPS < AAPC < AAPM$$

The above order is consistent with the experimentally found wear-rates.

4. Conclusions

All the studied Schiff base additives exhibit better antiwear behavior than the paraffin oil. However, their activity is slightly poorer than that of ZDDP or borate ester. The blends of these Schiff bases with BE exhibit excellent antiwear and load carrying ability even much better than that of ZDDP/BE at 1% w/v total concentration. 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, B_2O_3 and Fe_2O_3/Fe_3O_4) 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 methods.

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Table's Caption

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

Table 1b. EDX analysis data of the worn steel surface lubricated with different additives (1% w/v) for 30 min test duration at 588N applied load

Table 2. Calculated quantum chemical parameters of Schiff base antiwear lubricant additives calculated with B3LYP/6-31G++(dp) basis set

Figure's Caption

Figure 1a. 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 1b. Variation of mean wear scar diameter in absence and presence of different concentrations of AAPM with borate ester in paraffin oil at 392N applied load and 60 min duration

Figure 2. Variation of mean wear scar diameter with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations at 392N applied load

Figure 3. Variation of friction coefficient with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations at 392N applied load

Figure 4. Determination of overall wear rate by varying mean wear volume with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations at 392N applied load

Figure 5. Wear-rates for paraffin oil in the presence and absence of different additives and their synergistic formulations (1%w/v) at 392 N applied load for 90 min test duration

Figure 6. Variation of mean wear scar diameter with applied load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations for 30 min test duration

Figure 7. Variation of friction coefficient with applied load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations for 30 min test duration

Figure 8. SEM micrographs of the worn steel surface lubricated with paraffin oil in presence and absence of different additives (1% w/v) for 90 min test duration at 392N applied load: (a) Paraffin oil, (b) AAPM, (c) ZDDP and (d) AAPM+BE

Figure 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 10. Optimized structures of Schiff bases calculated with B3LYP/6-31G++(dp) basis set: **(a)** AAPB, **(b)** AAPS, **(c)** AAPC and **(d)** AAPM

Tables

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

Lubricants	Atomic %							
	C	O	B	N	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
AAPM	06.57	11.66	-	04.53	76.62	-	-	-
AAPM+BE	08.71	09.23	01.84	02.89	77.26	-	-	-

Table 1b. EDX analysis data of the worn steel surface lubricated with different additives (1% w/v) for 30 min test duration at 588N applied load

Lubricants	Atomic %							
	C	O	B	N	Fe	Zn	S	P
ZDDP	17.89	19.57	-	-	61.60	00.49	00.14	00.30
AAPM	06.04	07.08	-	07.36	79.30	-	-	-
AAPM+BE	06.11	06.70	02.81	06.81	77.84	-	-	-

Table 2. Calculated quantum chemical parameters of Schiff base antiwear lubricant additives calculated with B3LYP/6-31G++(dp) basis set

Additives	Total Energy (a.u.)	E_{HOMO} (Hartree-fock)	E_{LUMO} (Hartree-fock)	ΔE (Hartree-fock)	Wear rate (10^{-4} x mm^3/h)
Fe_5[58]		-0.18651	-0.06420	0.12231	
AAPM	-1050.14	-0.18772	-0.05623	0.13149	11.73
AAPC	-1395.21	-0.20064	-0.06803	0.13261	18.77
AAPS	-1010.83	-0.19474	-0.05929	0.13545	28.37
AAPB	-0935.61	-0.19859	-0.06310	0.13549	30.79

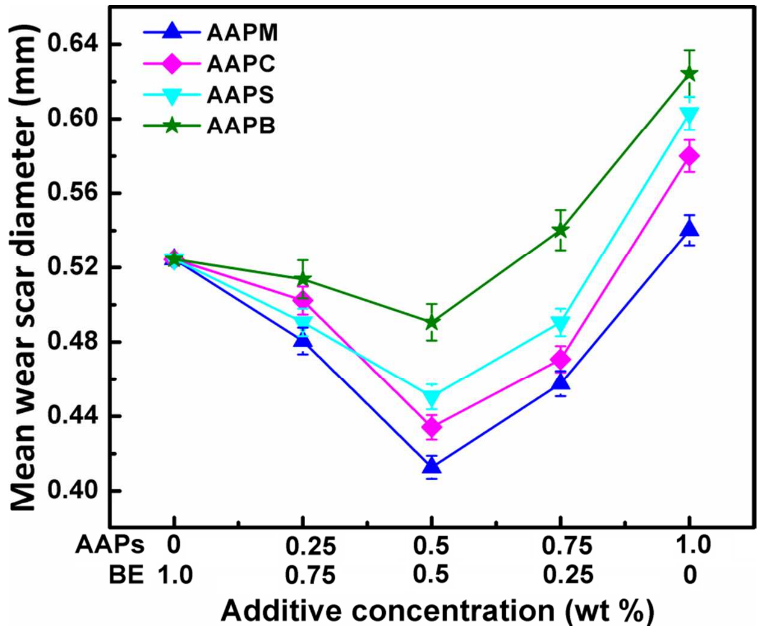


Figure 1a. Effect of change in concentration of different additive formulations on mean wear scar diameter in paraffin oil at 392N applied load for 60 min duration

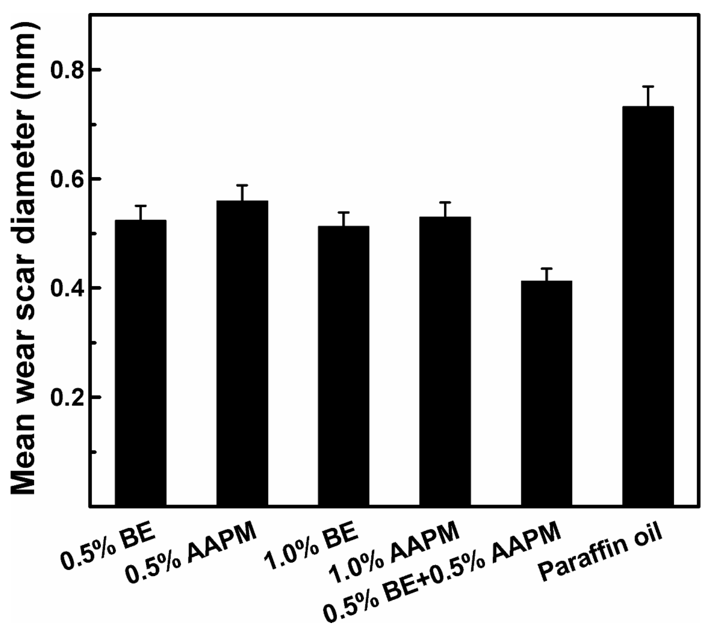


Figure 1b. Variation of mean wear scar diameter in absence and presence of different concentrations of AAPM with borate ester in paraffin oil at 392N applied load and 60 min duration

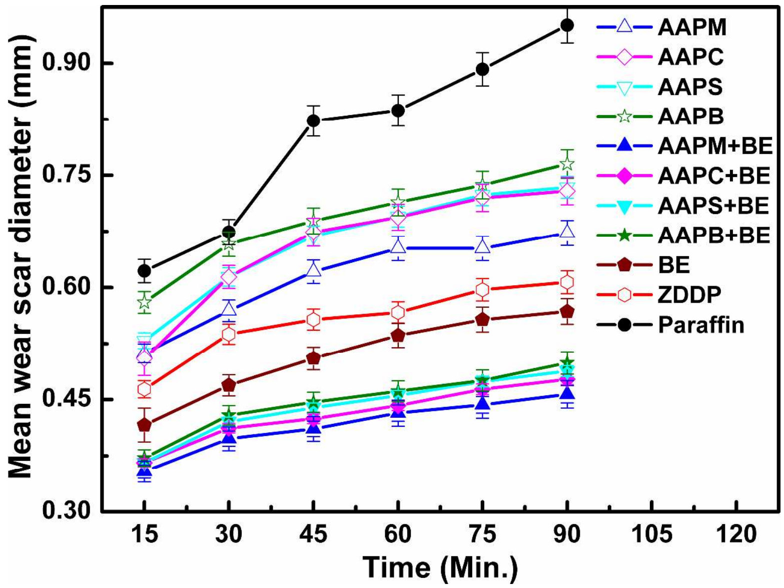


Figure 2. Variation of mean wear scar diameter with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations at 392N applied load

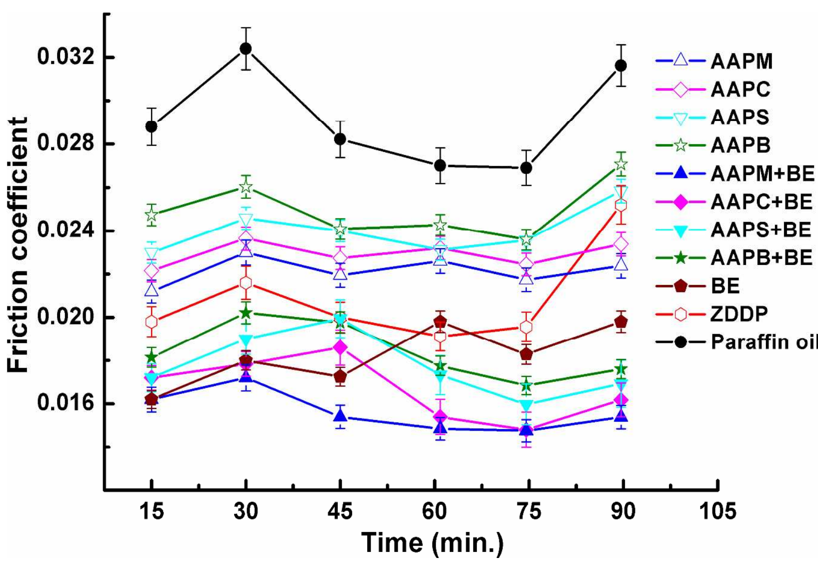
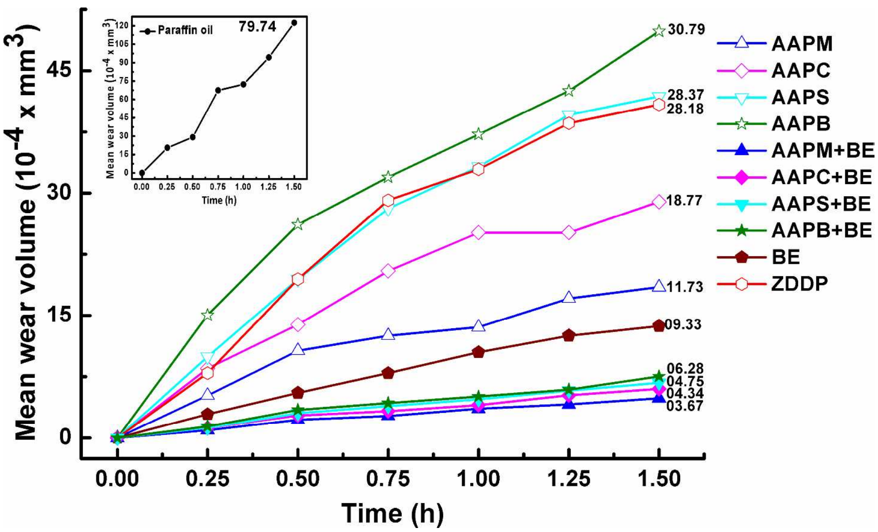


Figure 3. Variation of friction coefficient with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations at 392N applied load



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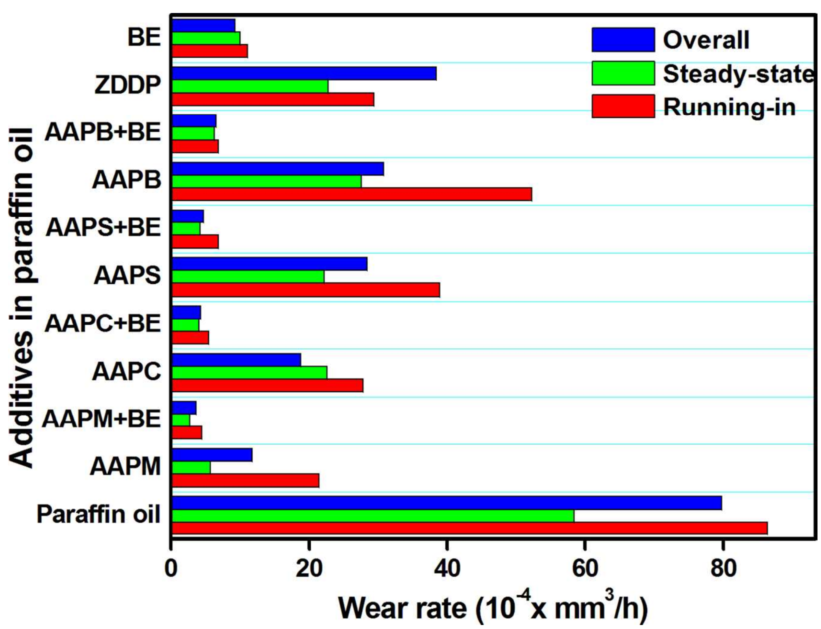


Figure 5. Wear-rates for paraffin oil in the presence and absence of different additives and their synergistic formulations (1%w/v) at 392 N applied load for 90 min test duration

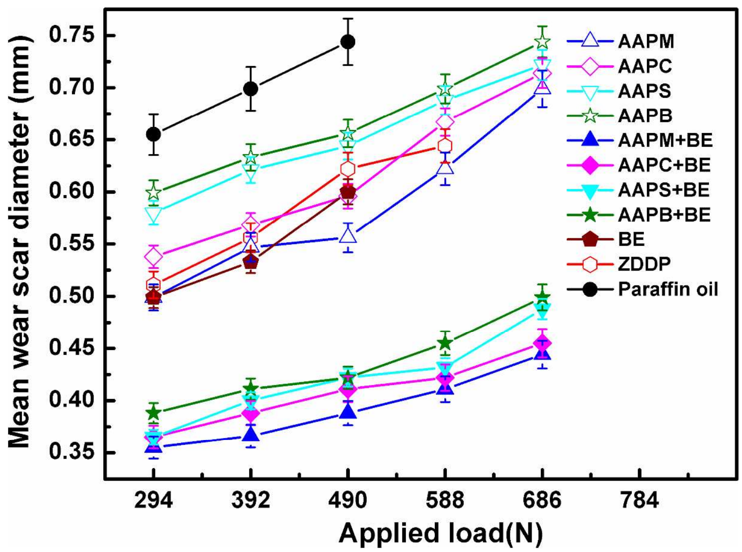


Figure 6. Variation of mean wear scar diameter with applied load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations for 30 min test duration

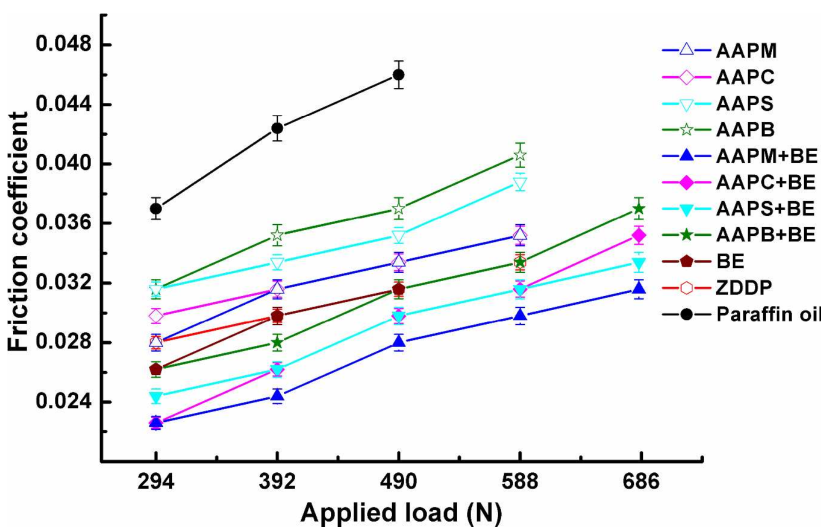


Figure 7. Variation of friction coefficient with applied load in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations for 30 min test duration

Figure 8a.

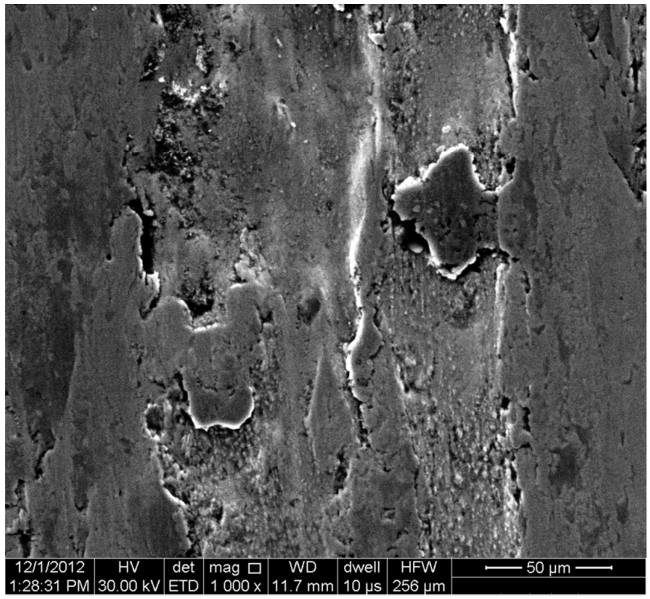


Figure 8b.

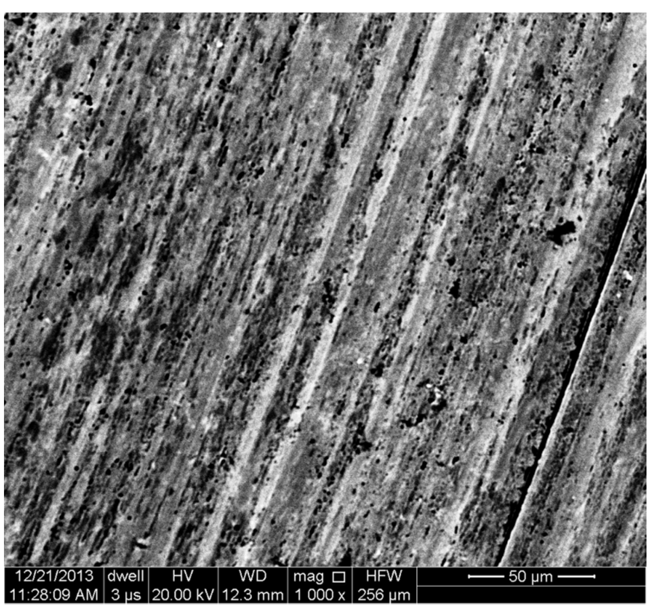


Figure 8c.

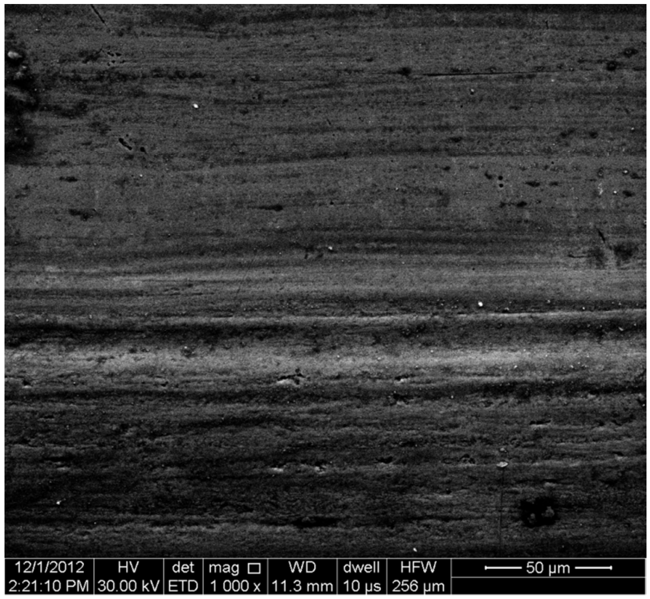
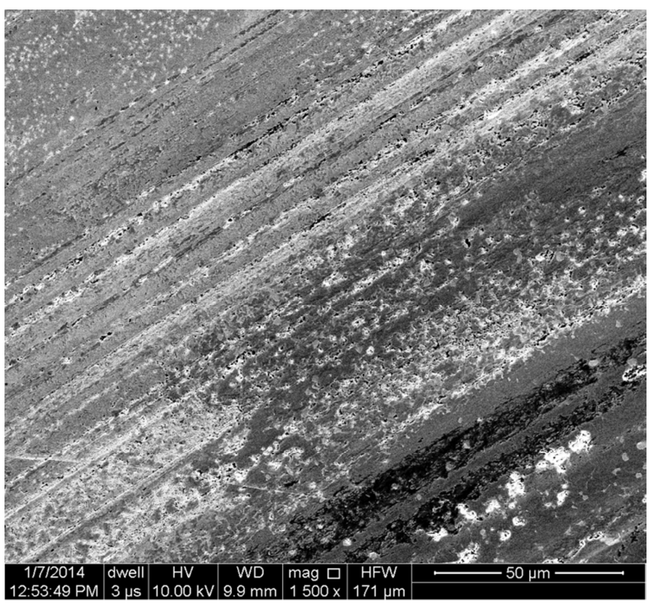


Figure 8d.



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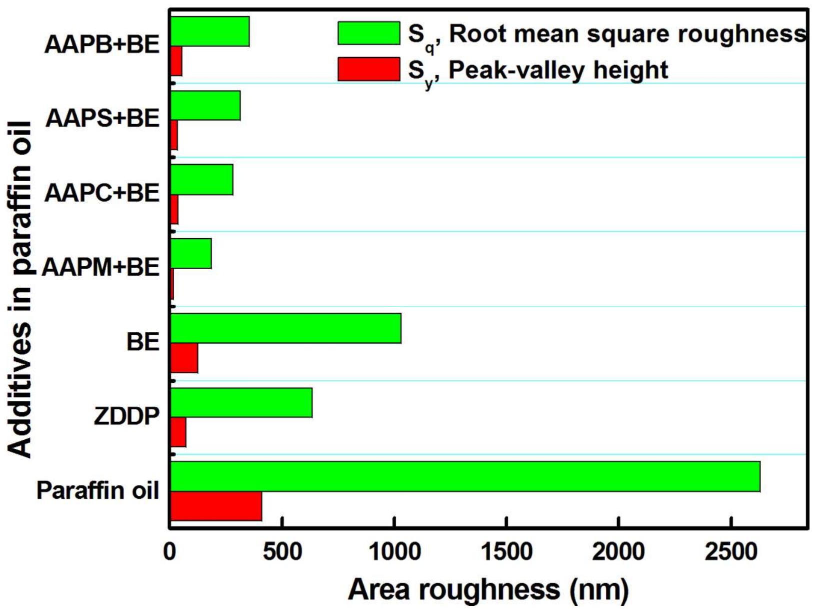


Figure 9. Surface Roughness parameters obtained from digital processing software of Nanosurf-basic Scan 2 for different additives at 392N load for 90 min test duration

Figure 10a.

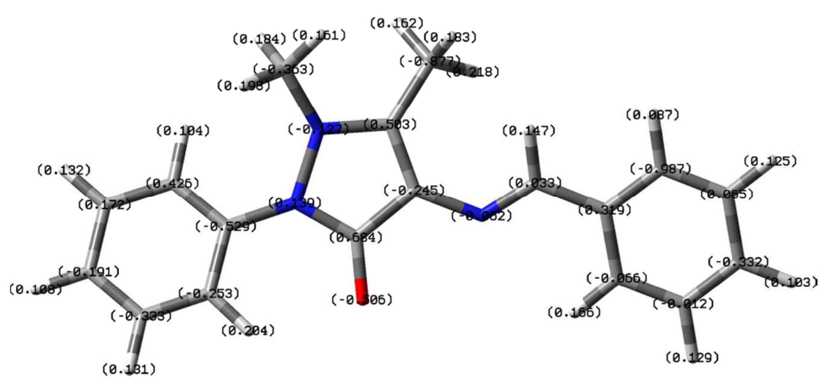


Figure 10b.

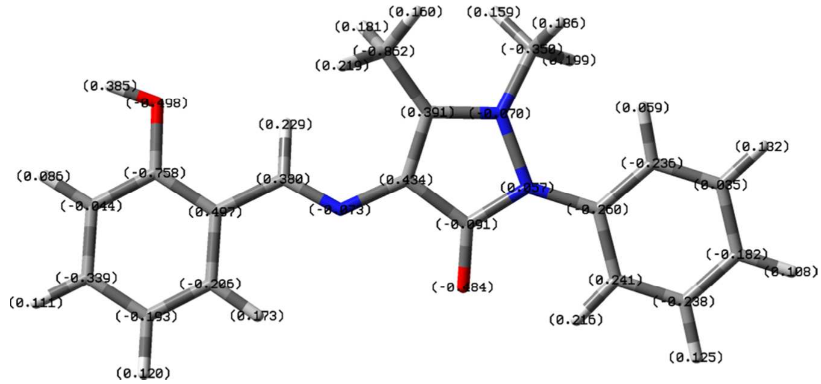


Figure 10c.

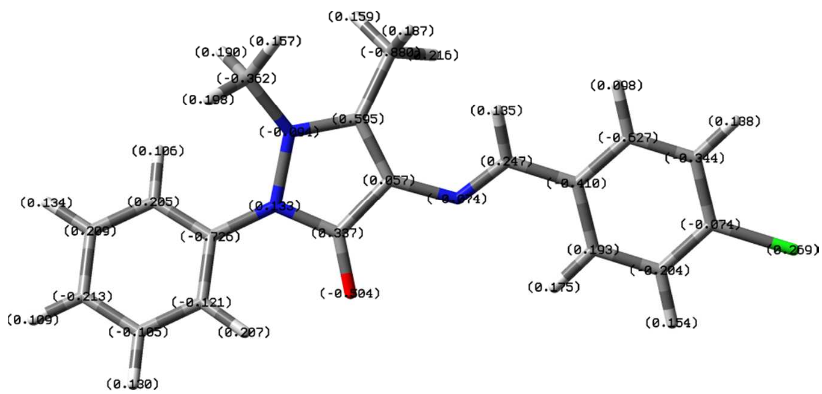
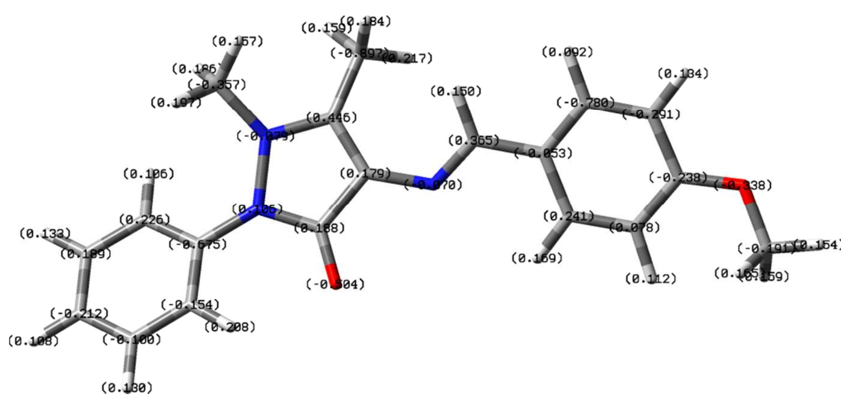


Figure 10d.



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