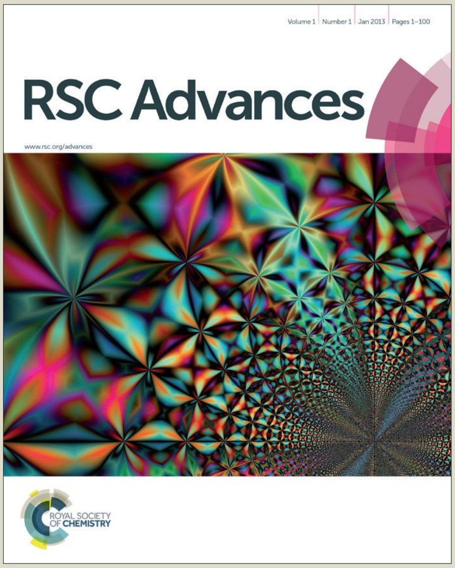
RSC Advances

This article can be cited before page numbers have been issued, to do this please use: R. K. Singh, A. Kukrety, O. P. Sharma, G. D. Thakre, N. Atrey and S. S. Ray, *RSC Adv.*, 2015, DOI: 10.1039/C5RA13507A.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

View Article Online
DOI: 10.1039/C5RA13507A

Capacity of Thiourea Schiff Base Ester as Multifunctional Additive: Synthesis, Characterization and Performance Evaluation in Polyol

Raj K. Singh,[a,*] Aruna Kukrety,[a] Om P. Sharma,[a] Gananath D. Thakre,[b] Neeraj Atray,[c] Siddharth S. Ray[a]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

A novel thiourea schiff base ester *TSBE* was synthesized following two step reaction. At first, thiourea and salicylaldehyde were reacted in ethanol to obtain thioura schiff base *TSB*. In the second step, esterification of *TSB* was done with lauroyl chloride catalyzed by 4-(dimethylamino)pyridine (DMAP) in N,N-dimethylacetamide (DMAc) solvent to obtain final product *TSBE*. The synthesized compounds were characterized using the CHN analysis, FT-IR and NMR. The antioxidant property of this additive was assessed via the universal oxidation test (IP-306) and rotary bomb oxidation test (ASTM D2272) while antifriction and antiwear properties was evaluated in terms of average friction coefficient and average wear scar diameter respectively by doing the four ball test (ASTM D4172). Study revealed that *TSBE* had good antioxidant property. Test carried out by four ball test machine indicated that the additive *TSBE* could reduce the friction to 45.6 % while wear to ~20 % when compared with the pure polyol base oil.

Zinc dialkyldithiophosphates (ZDDP) is considered to be the most important and commercially successful antioxidant, antiwear and anticorrosive multifunctional additive (MFA) since its discovery in 1940.[1] It is uncomparable in term of wide usage. Its effectiveness made it the most preferred additive for the formulated lubricants too for decades until now when the environmental concerns and stringent laws goes against the use of those compounds which have elements like Zn, P and S.[2] Apart from the environmental toxicity, few other shortcoming are also associated with ZDDP that are forcing the technologists to discover new MFA e.g. the catalytic converter poisoning and the particulate emissions due to its ash content.[3] Similarly, MFAs like over based metal sulfonate and mannich adducts have similar environmental problems.[4,5] So it would be beneficial if we could replace some of the toxic elements from the additive structure without sacrificing the performance.

Some efforts have been made to develop the MFAs having only S but devoid of P and heavy metals. Most of these meaningful efforts are restricted to sulfurized vegetable oils, heterocyclic compounds and derivatives of natural compounds having inherent disulfide groups e.g. sulfurized soybean, sunflower, cottonseed, high erucic rapeseed, canola, limnanthes (meadowfoam) and prime lard oils have been used as additives for metalworking and industrial oils.[6] A heterocyclic derivative of S-[2-(acetamido) benzothiazol-1-yl]N,N-dibutyl dithiocarbamate was synthesized and its performance as an multifunctional additive in liquid paraffin was evaluated. The novel additive shows excellent antiwear property and friction reduction property similar to ZDDP, and exhibits better load-carrying capacity than ZDDP. It has good anticorrosive property and high thermal stability too.[7] Two non-phosphorus and ashless multifunctional additives 1,3,4-thiadiazole-2-thione derivatives, 5-dodecyldithio-3-phenly1,3,4-thiadiazole-2-thione and 5-cetyldithio-3-phenyl-1,3,4-thiadiazole-2-thione were synthesized and evaluated in rapeseed oil. The results indicated that the additives possessed good thermal stabilities, corrosion inhibiting abilities and excellent load-carrying capacities. Both of them had good anti-wear and friction-reducing property.[8] A novel borate ester derivative containing benzothiazol-2-yl and disulfide group was synthesized and evaluated as multifunctional additive in rapeseed oil. Results showed that it possesses comprehensive tribological properties in load-carrying, friction-reducing, antiwear, corrosion-inhibiting, and antioxidation, so probably had a chance to replace ZDDP partially.[9] A novel ashless and non-phosphorus oil-soluble compound, 2,4,6-trioctylthio-1,3,5-triazine was synthesized and its performance as additive in a liquid paraffin was evaluated using both; a four-ball wear tester and a four-ball EP wear test machine. The results showed that it behaved extremely better as anti-wear and friction-reducing additive.[10] Three novel phosphorus-free triazine derivatives, ZOO, ZOS and ZDION were synthesized and evaluated as multifunctional additives in rapeseed oil. The results suggested that all the synthesized compounds had good thermal stability, corrosion inhibiting ability and excellent tribological behaviour.[11] Two ashless and non-phosphorus hydroxyl-containing dithiocarbamate-triazine compounds, 2,4,6-tri[N,N-di-n-butyldithiocarmate(2'-hydroxyl)-propionylthio]-1,3,5-s-triazine and 2,4,6-tri[N,N-di-i-octyldithiocarmate-(2'-hydroxyl)-propionylthio]-1,3,5-s-triazine were prepared and their tribological behaviors as additives in rapeseed oil (RSO) were evaluated using a four-ball tester. The results indicated that the additives possessed high thermal stabilities, good load-carrying capacities, good anti-wear and friction reducing property.[12] The tribological behaviors of laurylamino-methylthio-1,3,5-triazine-2,4-dithiol and diisooctylamino-methylthio-1,3,5-triazine-2,4-dithiol as additives in raped seed oil and diester were evaluated using four-ball friction and wear tester. The results suggested that these synthesized compounds had excellent tribological behaviours.[13]

Disulfides are also known to have load-carrying capacity e.g. the tribological performance of binary additive blends with

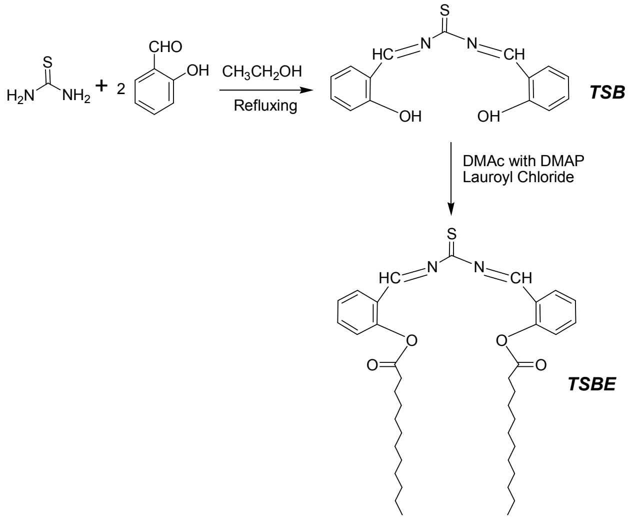
DOI: 10.1039/C5RA13507A

dibenzyl disulphide and some chlorinated and brominated compounds was tribologically investigated.[14] Recently cystine (Cys), an essential amino acid obtained from natural sources has been used for synthesizing novel environmentally adapted lubricant phosphorus and metal free additives. The carboxyl groups in Cys_2 were converted to corresponding esters by reaction with long-chain alcohols. The resultant diesters having the disulfide group were soluble in poly-alpha-olefin (PAO) and ester type synthetic oils. The Cys-derived additives exhibited comparable antiwear properties to the conventional additive zinc dalkyldithiophosphate (ZDDP).[15]

In view of developing a new phosphorus and metal free multifunctional additive, in the present work a novel thiourea schiff base ester was synthesized and characterized. Its antioxidant, antiwear and antifriction properties as an additive in polyol base oil were evaluated and its tribological mechanism was investigated by energy-dispersive X-ray spectroscopy.

Synthesis of *TSB and TSBE*

The synthesis of the *TSBE* additive was done using two step reactions route as shown in the Scheme 1. The white color of thiourea changed to yellow in the thiourea schiff base (*TSB*) which produced the direct evidence of the successful imine bond formation as shown in the Fig. 1. This intermediate along with the synthesized *TSBE* was also characterized using various analytical techniques like CHN analysis, FT-IR and NMR. The observed results of elemental analysis performed on the Perkin Elmer Series II CHNS/O 2400 analyzer are given in Table 1 which were found to be in good agreement with the calculated values for the given molecular structures in Scheme 1.



Scheme 1: Reaction scheme for synthesizing *TSB* and *TSBE*.

Fig. 1: Thiourea schiff base (*TSB*) with salicylaldehyde.

Table 1: The elemental analysis data of synthesized *TSB* and *TSBE* [a].

Sample	% Content			
	C	*H*	*N*	*S*
TSB	62.96 (63.36)	4.48 (4.25)	9.24 (9.85)	10.84 (11.28)
TSBE	73.11 (72.18)	8.25 (8.70)	4.86 (4.32)	4.24 (4.94)

[a]Values in parentheses are calculated.

FT-IR spectroscopy

The FT-IR characterization of *TSB* and *TSBE* was also done in support of their successful synthesis. In the FT-IR of the *TSB* as shown in the Fig. 2a, the appearance of the broad O-H stretching peak at ~3300-3400 cm^{-1}, aromatic C=C stretching at ~1600 cm^{-1} and C=N stretching peaks at around 1659 cm^{-1} indicates the imine coupling of thiourea with salicylaldehyde. The other characteristics peak of the thiourea frame work persists in the spectrum as C=S stretching peak at 1091 cm^{-1} as well as at 755 cm^{-1} and C-N stretching peak at 2058 cm^{-1} while the intense peak at ~3100 cm^{-1} disappeared which is a characteristic feature of $–NH_2$ groups (N-H stretching) of the thiourea.

In the FT-IR spectra of *TSBE* (Fig. 2b), the appearance of C=N stretching peaks at around 1645 cm^{-1} along with the C=C stretching of phenolic ring at 1565 and 1627 cm^{-1} confirms the schiff bond existence. Further appearance of characteristic C=O stretching (ester) band at 1726.6 cm^{-1} determines the successful esterification. The appearance of prominent peaks at around 2924.9 and 2853.4 cm^{-1} attributed to the asymmetric and symmetric C-H (CH_2) stretching band of the fatty lauryl chain along with the appearance of the undesired OH stretching signal at 3186.3 cm^{-1} which belongs to the residual unesterified phenolic OH. The bands appear at 1460 cm^{-1}, 1401.3 cm^{-1} & 1259 cm^{-1} could be easily assigned to asymmetric C-H bending, symmetric C-H bending & C-O stretching (phenol) respectively. The bands at around 1152.2 cm^{-1}, 1108.5 cm^{-1} and 755.7 cm^{-1} attribute to C-N stretch (aliphatic amines), C-O stretching (ester), and CH_2 rocking respectively.

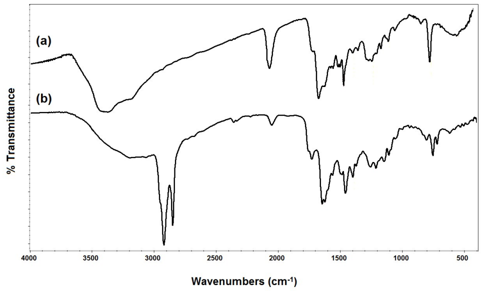


Fig. 2: FT-IR spectra of a) Thiourea schiff base, *TBS;* b) Thiourea schiff base ester, *TSBE*.

View Article Online
DOI: 10.1039/C5RA13507A

NMR spectroscopy

In addition to FT-IR analysis, NMR also presents strong evidence in favor of successful synthesis of *TSBE*. Fig. 3 shows the ^{13}C NMR of the additive *TSBE* in CDCl$_3$ at 25 °C. The appearance of the signal of >C=O at 172.5 ppm is strong evidence of the esterification. The existence of C=N downfield signal at 158 ppm is a strong evidence of imine coupling of thiourea with salicylaldehyde. Lauryl fatty chain carbons are observed in the range 0-40 ppm where signal at 15 ppm corresponds to the terminal methyl group proton and other signal between 20 to 40 ppm attributes to the other methylene proton of long alkyl chain. The aromatic carbons are observed between 120-140 ppm.

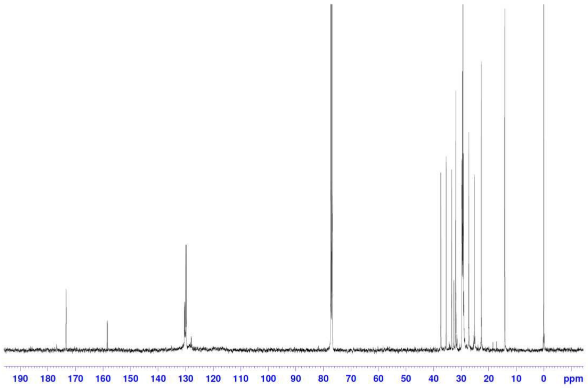


Fig. 3: ^{13}C NMR of the additive *TSBE* in CDCl$_3$ at 25 °C.

Thermogravimetry

In order to determine the thermal stability of the synthesized compounds and working temperature range of the *TSBE*, TG curves were recorded. Fig. 4 shows the TG profiles of the thiourea (*TU*), intermediated schiff base (*TSB*) and thiourea schiff base lauroyl ester (*TSBE*). It is clear from the graph that the esterification enhances the thermal stability of the thiourea schiff base. *TSB* starts to degrade at around 100 °C while the degradation temperature for *TSBE* is near to 160 °C. So the compound *TSBE* show the sufficient thermal stability to be used as lubricant additive.

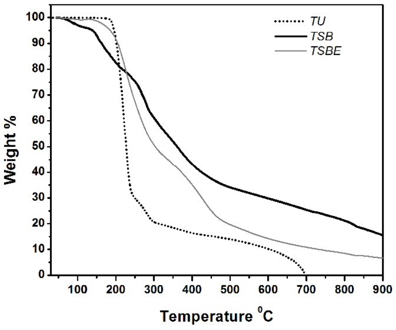


Fig. 4: TG curves of the thiourea (*TU*), intermediated thiourea schiff base (*TSB*) and thiourea schiff base ester (*TSBE*).

Antioxidant property

The coupling of thiourea with salicylaldehyde will not only introduce the aromatic ring to the thiourea framework but also create imine bond which may increase the metal chelating abilities and so may impart the antioxidant property to the thiourea molecule. Esterification in second step will make this thiourea schiff base soluble in the base oils. So the antioxidant performance of the synthesized additive *TSBE* was determined by RBOT test following ASTM2272.[16] The reference lube base taken for this study was polyol (pentaerythritol tetraoleate). The tests with polyol were performed at varied temperatures for the optimization. 150 °C was found to be most appropriate because at higher temperature oxidation time was too short while at low temperature it was long. The dosage of the *TSBE* in the blend was varied between 500-3000 ppm. It can be inferred from results of RBOT that *TSBE* at 3000 ppm concentration enhances the RBOT time of reference oil from 6 min 43 sec up to 7 min 24 sec. This is about 23.6 % increase. The response of additive is not very encouraging at low concentration as it don't enhances the RBOT time at 500 ppm (5 min 49 sec) while RBOT time increases slightly only up to the value of 6 min 55 sec at 1500 ppm concentration. So 3000 ppm is the optimum concentration of the additive *TSBE*.

The antioxidant performance of the synthesized additive *TSBE* in polyol base fluid was also determined by IP-306 oxidation test.[17] The antioxidant property may be quantized in terms of the increase in the volatile acidity, soluble acidity, total sludge and total oxidation products. It may be observed from Table 2 that *TSBE* shows antioxidant activity to a good extent. This property increases as the concentration increases from 1000 ppm to 3000 ppm. Specifically, *TSBE* at 3000 ppm showed the best performances for which the volatile acidity, soluble acidity, total sludge and total oxidation products is 0.03366 ± 0.01587 mg KOH/g, 13.5762 ± 0.15867 mg KOH/g, 0.02584 % and 4.39267 ± 0.04579 %, while these values for polyol base oil are 0.23562 ± 0.01587 mg KOH/g, 15.9885 ± 0.07934 mg KOH/g, 0.08064 % and 5.25386 ± 0.02550 % respectively. Higher concentration is not favorable as indicated by the results at 4000 ppm.

Table 2: Effect on universal oxidation test (IP 306) characteristics by varying additive concentration in base oil.

Samples	**Total Acid Number (mg KOH/g)**		**Total Sludge (S %)**	**Total Oxidation Products (TOP %)**
	Volatile Acidity	**Soluble Acidity**		
Blank –Polyol	0.23562 ± 0.01587	15.9885 ± 0.07934	0.08064	5.25386 ± 0.02550
1000 ppm *TSBE*	0.19074 ± 0.01587	14.5299 ± 0.07934	0.01264	4.73586 ± 0.02034
2000 ppm *TSBE*	0.06732 ± 0	13.6884 ± 0.15867	0.08088	4.49448 ± 0.05091
3000 ppm *TSBE*	0.03366 ± 0.01587	13.5762 ± 0.15867	0.02584	4.39267 ± 0.04579
4000 ppm *TSBE*	0.05610 ± 0.01587	15.9324 ± 0.15867	0.06180	5.1918 ± 0.04582

Antifriction & anti-wear property

The surface-complex film forming tendency of the sulfur compounds and organic schiff compounds is well known.[1,18-21] Duo hindered the metal-metal contact leading to the antifriction & anti-wear properties. As our designed additives have imine bonds along with the inherent sulfur end and polar ester groups that may also provide it the film forming tendency, we have tested the *TSBE* for lubricity property too using four ball test machine following standard test ASTM D4172[22] keeping the standard parameters described in the experimental. Antifriction property was evaluated

View Article Online
DOI: 10.1039/C5RA13507A

in terms of average friction coefficient by testing samples prepared by blending *TSBE* in polyol base in different concentrations. Results shown in the Table 3 reveal that the *TSBE* has the excellent antifriction property as it remarkably reduce the average friction coefficient of polyol from 0.19259 ± 0.0173 to 0.10481 ± 0.0128 when its 2500 ppm concentration was used (Fig. 5). This is a 45.6 % decrease.

Table 3: Average friction coefficients at different concentrations of *TSBE* in polyol.

Samples	Average Friction Coefficient	Std. Dev. σ
Blank –Polyol	0.19259	0.0173
500 ppm *TSBE*	0.16426	0.0130
1000 ppm *TSBE*	0.17661	0.0153
1500 ppm *TSBE*	0.18249	0.0190
2000 ppm *TSBE*	0.16772	0.0166
2500 ppm *TSBE*	0.10481	0.0128
3000 ppm *TSBE*	0.17111	0.0145

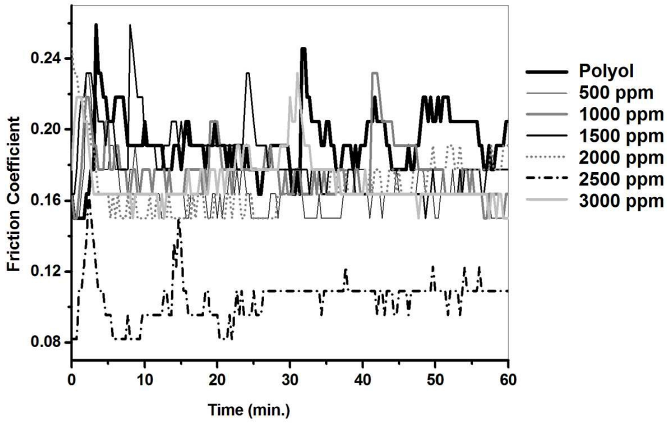


Fig. 5: Friction coefficient vs. time graph for the different concentrations of *TSBE* in polyol.

The anti-wear potential is also estimated in terms of the AWSD (averag wear scar diameter). The additive is found to have the moderate antiwear property as the value of AWSD for the base oil i.e. 473.33 ± 20.88 µm reduces to a value of 379.16 ± 21.54 µm at 500 ppm and 450 ± 25.43 µm at 1000 ppm concentration of *TSBE* respectively. The higher additive concentration does not favor the anti-wear performance and maximum reduction is observed at 500 ppm which is the optimum concentration. The antifriction and antiwear property of the *TSBE* can be attributed to the formation of surface film of the additives on the rubbing metallic surface so the image of the ball worn surface is also observed using SEM and EDX to give the evidence in favor of film formation. Figure 6a & 6b shows the SEM micrographs of the worn out test specimens lubricated with polyol base oil and 500 ppm *TSBE* respectively. The rubbed surface lubricated by 500 ppm had comparatively smaller wear scar diameter than poly oil base indicating that the synthesized additive had a boundary lubrication function avoided direct contact of the frictional pairs. The EDX analysis of surface lubricated with polyol shows that carbon, iron, chromium, and oxygen are prominent on the surface owing to the steel (Fig. 6c). However, strong evidence is observed for contribution from the additive in film formation on the surface lubricated by 500 ppm *TSBE* as sulfur is also observed in the EDX analysis on the surface revealing some interaction of the metal surface with the additive (Fig. 6d).

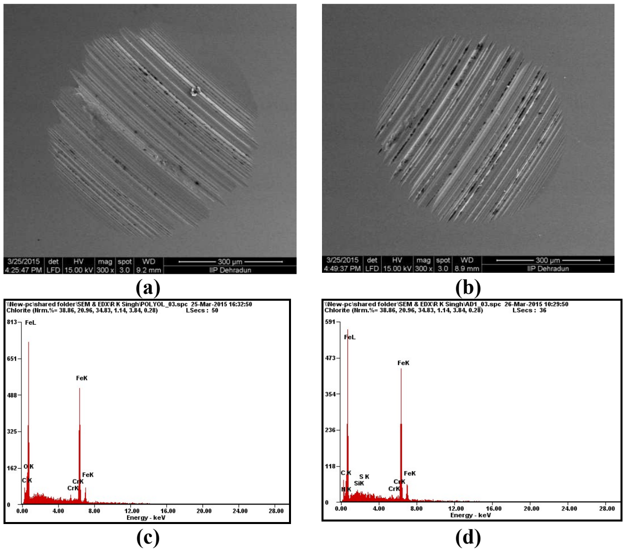


Fig. 6: SEM micrographs of the worn out ball test specimens lubricated with (a) polyol base (b) 500 ppm *TSBE*; EDX results for the worn out ball test specimens lubricated with (c) polyol base (d) 500 ppm *TSBE*.

Conclusions

The synthesis of the *TSBE* additive was done using a two step reaction. At first the thiourea schiff base (*TSB*) was synthesized by the reaction of salicylaldehyde with thiourea and then its esterification was done with lauroyl chloride. *TSBE* was also characterized using the various analytical techniques like CHN analysis, FT-IR and NMR. *TSBE* was evaluated as MFA in polyol. According to oxidation test results carried out as per ASTM 2272, *TSBE* at 3000 ppm concentration enhances the RBOT time of reference oil from 6 min 43 sec up to 7 min 24 sec. This is about 23.6 % increase. *TSBE* shows antioxidant activity as revealed by IP306 test too. This property increases as the concentration increases from 1000 ppm to 3000 ppm. Specifically, *TSBE* at 3000 ppm showed the best performances. It is found that *TSBE* can remarkably reduce the average friction coefficient of polyol when its 2500 ppm concentration was used. The average friction coefficient value for the polyol decreases 45.6 % by adding 2500 ppm *TSBE*. The antiwear potential is estimated in terms of the AWSD (average wear scar diameter) using four ball test machine following standard test conditions (ASTM D4172). Maximum reduction of AWSD is observed at 500 ppm i.e. ~20 %. The sulfur is also observed in the EDX analysis on the surface lubricated by *TSBE* revealing some interaction of the metal surface with the additive

Experimental

Materials

Thiourea, salicylaldehyde, lauroyl chloride and 4-(dimethylampino)pyridine (DMAP) was purchased from Sigma-Aldrich. N, N-Dimethyl-acetamide (DMAC) was purchased from Merck Millipore. Reference polyol base fluid (pentaerythritoltetraoleate) was purchased from Mohini Organics

View Article Online
DOI: 10.1039/C5RA13507A

Pvt. Ltd. India. All other chemicals were of the highest available grade and were used without further purification.

Synthesis of thiourea schiff base (*TSB*)

The intermediate compound (*TSB*) was synthesized by reacting 1.44 g (18.92 mmol) thiourea and 4.62 g salicylaldehyde (37.83 mmol) in 60 mL ethanol taken into a 250 mL three-necked round-bottomed flask equipped with a magnetic stirrer, thermometer and condenser. The mixture was heated at 90 °C for about 24 h. After reaction completion, the ethanol was removed under reduced pressure by rotatory evaporator. The yellowish product obtained was dried at 60 °C overnight. The yield obtained of the final crushed product was 2.22 g.

Synthesis of thiourea schiff base ester (*TSBE*)

1.42 g (4.99 mmol) *TSB*, 2.18 g (9.98 mmol) lauroyl chloride was taken in a 250 mL round bottom flask equipped with a stirrer, thermometer, and condenser. 1.22 g 4-(dimethylampino)pyridine was added as a catalyst and 90 mL N, N-dimethylacetamide added as a solvent. The mixture was heated to 150 °C for about 24 h. The reaction content was poured in to cold water to precipitate the product and filtered. Washing was done 2-3 times with saturated aqueous sodium bicarbonate solution. The brown semisolid product was vacuum dried at 100 °C. The obtained yield of the *TSBE* was 3.24 g.

Characterizations

The synthesized intermediate *TSB* and product *TSBE* were characterized by using many analytical techniques**.** CHNS analysis was performed on the Perkin Elmer Series II CHNS/O 2400 analyzer. Fourier transform infrared (FTIR) spectra were recorded using a Thermo-Nicolet 8700 Research spectrophotometer by KBr pellet method with a 4 cm^{-1} resolution. NMR spectra were also recorded for the synthesized compound on a Bruker Avance 500 spectrometer in the proton noise-decoupling mode with a standard 5-mm probe. Perkin Elmer EXSTAR TG/DTA 6300 was used for recording thermogravimetry curves using aluminum pans. The experiments were carried out under continuous nitrogen flow of 200 mL min^{-1}. The temperature ramp was set at 10 °C min^{-1}. The mass loss was recorded from 30 to 1000 °C.

Rotating bomb oxidation test (RBOT)

Rotating bomb oxidation tests were conducted on a RBOT apparatus manufactured by Stan-hope Seta, U.K. following the ASTM D2272.[16] The temperature was kept 150 ºC. Samples were measured near to 50.0 ± 0.5 g and 5.0 ml of reagent water added to the sample. The copper catalyst was measured and cleaned with 220 grit silicone carbide sand paper and was used immediately. The wire was converted into spring-coil shape having an outside diameter of 44–48 mm, weight of 55.6 ± 0.3 g and height of 40–42 mm. The bomb was assembled and slowly purged twice with oxygen. The bomb was charged with 87.0 ± 0.5 w (620 kPa) of oxygen then tested for leakage by immersing in water. The test was considered completed after the pressure dropped more than 175 kPa from the original pressure. All tests were run in duplicate and the average time was reported.

Universal oxidation test (IP 306)

Another type of oxidation test IP 306 also known as universal oxidation test was carried out to evaluate the potentianl of synthesized compounds as antioxidant additive.[17] Differnent concentrations (1000, 2000, 3000 and 4000 ppm) of *TSBE* were doped in polyol base oil to prepare the different samples. 25 g of the each sample was taken in oxidation tube and connected with the absorption tube with a connecting plastic tube. The 25 mL water was added in each absorption tube. Experiment was run at 120 °C for 48 hours and at 1 litre/hour oxygent flow. After the test the oil sample was recovered using 150 mL heptane. the choroform was added for some samples which were difficult to remove from oxidation tubes. The samples were kept in dark for 48 hours. The samples were then filtered by vaccum filteration using the filteration crucible and the solution was maked up to 500 mL by adding heptane. Titration of 10 mL aliquotes was done in duplicate with 0.1 M alcoholic KOH solution using phenolphthalein as an indicator and calculate soluble acidity as per the given formula:

$$\text{S.A} = \frac{A\times 56.1\times M}{10}$$

A is the volume of KOH used to neutralised n-heptane/oil solution. M is the molarity of KOH solution used. S. A. is soluble acidity.

The water from asborption tube was used to calculate the volatile acidity. 5 mL water was titrated against 0.1 M KOH solution. Volatile acidity was calculated according to the formula:

$$\text{V.A.} = \frac{A\times 56.1\times M}{5}$$

Where, A is the volume of KOH used to neutralised n-heptane/oil solution. M is the molarity of KOH solution used. V. A. is volatile acidity.

Ther sludge formed was measured after filtration of oil/heptane solution through crucibles.

$$\text{Total sludge (S \%)} = a\times 4$$

Where, a is the weight of sludge.

For analysing the additive effect on oxidative characteristics of additives in base oil, TOP (total oxidation product) was calculated according to formula:

$$\text{Total oxidation products (TOP \%)} = \text{Total sludge} + \frac{180\times(S.A+V.A)}{561}$$

Four ball test (ASTM 4172A)

The performance of *TSBE* as antifriction and antiwear additive in polyol base oil in different concentration was evaluated using ASTM D4172A[22] standard test method on a four-ball rolling contact fatigue tribotester (Ducom India) where the four balls remains in contact in the tetrahedral geometry in which top ball is fixed into the spindle rotating at a predefined speed while bottom three balls kept in a ball pot filled with blended sample making the three point contacts with top ball. The 12.7 mm test ball specimens are made up of AISI standard steel no. E-52100 and have Rockwell C 64−66 hardness. Tests were performed at a rotating speed of 1200 rpm; load, 198 N; temperature, 75 °C and time, 60 min. The antifriction and anti-wear characteristics were estimated in terms of average friction coefficient and average wear scar diameter (AWSD). The morphology of specimen balls was examined by FEI Quanta 200F SEM (FEI, Hillsboro, OR, U.S.A.) equipped with EDX analysis. The parameters used are as follows; chamber Pressure: 10 Pa; High voltage: 20.00 kV; Tilt: 0.00; Takeoff: 35.00; AMPT: 102.4; Resolution: 133.44. The powdered samples were analysed without coating and carbon cement as adhesive.

We kindly acknowledge Director, CSIR-IIP for his kind

View Article Online
DOI: 10.1039/C5RA13507A

permission to publish these results. Analytical science division of the Institute is kindly acknowledged for providing support in analysis of samples.

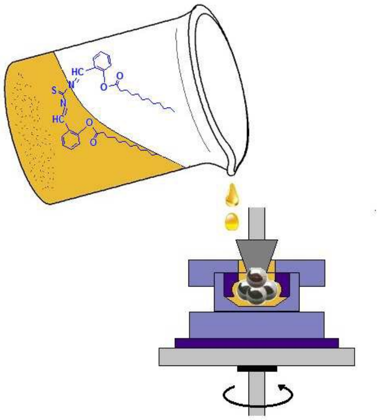
Notes and references

[a] *Chemical Sciences Division, CSIR-Indian Institute of Petroleum, Dehradun-248 005, India; Tel: +91-135-2525708 (O); Fax: +91-135-2660202; Email: rksingh@iip.res.in*
[b] *Tribology Division, CSIR-Indian Institute of Petroleum, Dehradun-248 005, India*
[c] *Bio Fuels Division, CSIR-Indian Institute of Petroleum, Dehradun-248 005, India*

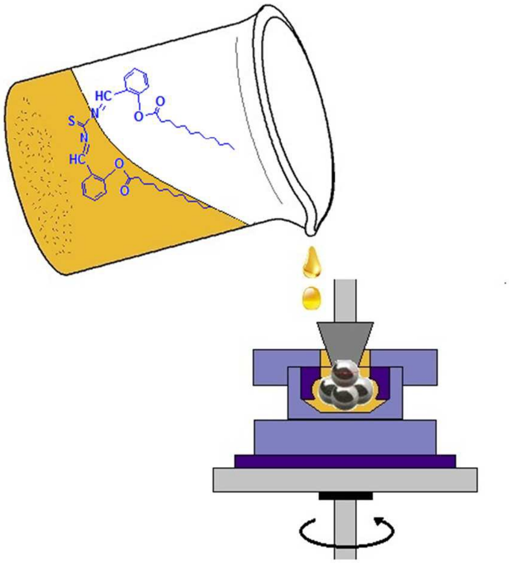
1. H. Spikes, *Tribol. Lett.* 2004, **17**, 469–489.
2. L.R. Rudnick, *lubricant additives: chemistry and applications*, Taylor & Francis Group, Boca Raton, 2009.
3. C.I. Betton, Lubricants and their environmental impact. In: M. Roy, R.M. Mortier, M.F. Fox and S.T. Orszulik, (eds.) *Chemistry and technology of lubricants*, Springer, Heidelberg, USA, 3rd Ed., 2010, pp. 435–457.
4. M. Najman, M. Kasrai, G.M. Bancroft and R. Davidson, *Tribol. Int.* 2006, **39**, 342–355.
5. E. J. Seddon, C.L. Friend and J.P. Roski, Detergents and dispersants. In: M. Roy, R.M. Mortier, M.F. Fox and S.T. Orszulik, (eds.) *Chemistry and technology of lubricants*, Springer, Heidelberg, USA, 3rd Ed., 2010, pp. 213–236.
6. K.P. Kammann Jr. and A.I. Phillips, *J. Am. Oil Chem. Soc.* 1985, **62**, 917–923.
7. W. Huang, J. Dong, G. Wu and C. Zhang, *Tribol. Int.* 2004, **37**, 71–76.
8. F. Zhu, W. Fan, A. Wang and Y. Zhu, *Wear* 2009, **266**, 233–238.
9. J. Li, X. Xu, Y. Wang and T. Ren, *Tribol. Int.* 2010, **43**, 1048–1053.
10. X. Zeng, H. Shao, W. Rao, Z. He and T. Ren, *Wear* 2005, ***258***, 800–805.
11. X. Zeng, H. Wu, H. Yi and T. Ren, Wear 2007, **262**, 718–726.
12. X. Zeng, J. Li, X. Wu, T. Ren and W. Liu, *Tribol. Int.* 2007, **40**, 560–566.
13. R. Qiao, J. Li, H. Wu, T. Ren, Y. Zhao and C. Ma, *Appl. Surf. Sci.* 2011, **257**, 3843–3849.
14. S. Płaza, G. Celichowski and L. Margielewski, *Tribol. Int.* 1999, **32**, 315–325.
15. I. Minami, S. Mori, Y. Isogai, S. Hiyoshi, T. Inayama and S. Nakayama, *Tribol. T.* 2010, **53**, 713.
16. ASTM D 2272-11, Standard test method for oxidation stability of steam turbine oils by rotating pressure vessel. In: Annual Book of ASTM Standards, ASTM International: West Conshohocken, PA, 2011.
17. IP 306, Institute of Petroleum testing methods for petroleum, fuel products: High Temperature Universal Oxidation Test Method, Part I. Institute of Petroleum, UK, 2004.
18. R.K. Singh, A. Kukrety, A.K. Chatterjee, G.D. Thakre, G.M. Bahuguna, S. Saran, D.K. Adhikari and N. Atray, *Ind. Eng. Chem. Res.* 2014, **53**, 18370–18379.
19. R.K. Singh, S. Pandey, R.C. Saxena, G.D. Thakre, N. Atray and S.S. Ray, *J. Ind. Eng. Chem.* 2015, **26**,149–156.
20. R.K. Singh, A. kukrey, G.D Thakre, N. Atrey and S.S. Ray, *RSC Adv.* 2015, **5**, 37649-37656.
21. R.K. Singh, S. Pandey, R.C. Saxena, G.D. Thakre, N. Atray and S.S. Ray, *New J. Chem.* 2015, **39**, 5354 – 5359.
22. ASTM D4172-94, Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method). In Annual Book of ASTM Standards, ASTM International: West Conshohocken, PA, 2010.

Capacity of Thiourea Schiff Base Ester as Multifunctional Additive: Synthesis, Characterization and Performance Evaluation in Polyol

R. K. Singh, A. Kukrety, O.P. Sharma, G.D. Thakre, N. Atray, S.S. Ray



View Article Online
DOI: 10.1039/C5RA13507A



Novel thiourea schiff base ester evaluated by four ball test as multifunctional additive in polyol base oil showing the excellent antifriction activity and moderate anti-wear property.