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Derivatizing L-histidine to develop novel additive for polyol based biolube

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Abstract

Two novel histidine schiff base esters *HSE-A* and *HSE-B* were synthesized following two step reaction. The synthesized compounds were characterized using the CHN analysis, FT-IR and NMR. The antioxidant and anticorrosion property of these additives were assessed via the universal oxidation test (IP-306) and standard accelerated corrosion testing procedure, which reveals that both the additives have good antioxidant and anticorrosion properties. Lubricity test carried out by four ball test machine indicated that both the additives could reduce the wear when compared with the pure polyol base oil. Overall additive *HSE-A* is more effective than additive *HSE-B* as antioxidant/antiwear/anticorrosion biolubricant additive.

Introduction

A lubricant typically contains 90% base oil and 10% additives. A lubricant is supposed to lubricate two moving metallic surfaces in contact in a condition which is very favorable for oxidation, corrosion, wear and tear.¹ The conditions become worst in case of high temperature, the presence of oxygen and moisture, etc. So, lube base oils must be selected judiciously having inherent properties enabling a lubricant to combat such factors during operation. Mostly used group I, II, III (mineral oils) and group IV (synthetic polyalphaolefins) base oils have such characteristics quite well but the new emerging vegetable oil based base oils are very prone to thermal and oxidative degradation and have poor cold flow properties and high cost.^{2,3} So, the addition of powerful antioxidant, anticorrosion and lubricity additive in lube base oils is essential to make a complete lubricant formulation at par with the requirement of the specific application. Increased maintenance cost and drastic reduction in the fuel efficiency may be observed with the lubricants devoid of such components. A dozen of additives are generally in use such as antioxidants, detergents, anti-wear, metal deactivators, corrosion inhibitors, rust inhibitors, friction modifiers, extreme pressure, anti-foaming agents, viscosity index improvers and emulsifiers etc.⁴ Additives which are capable of imparting or enhancing more than one type of the properties are known as the multifunctional additives (MFA's). Zinc dialkyldithiophosphate (ZDDP) is an important MFA used virtually in all motor oil and is dominant since its discovery in the 1940s. It is used mainly as anti-wear agent but it is also possesses the anti-corrosive and anti-oxidative character. The major shortcoming associated with the ZnDDP is its toxicity towards living organisms and the environmental hazards. It is not readily biodegradable too and poisonous to the catalytic converter.^{5,6} Although the additives are not a major constituent

of a lubricant but their toxicity cannot be ignored in order to make a lubricant ecofriendly. The biodegradability of the formulation is also affected greatly by them.⁷ So to develop new ecofriendly multifunctional additives is a matter of great concern now days. Also it is supposed to be developing these additives from the renewable materials due to the depleting natural petroleum resources.

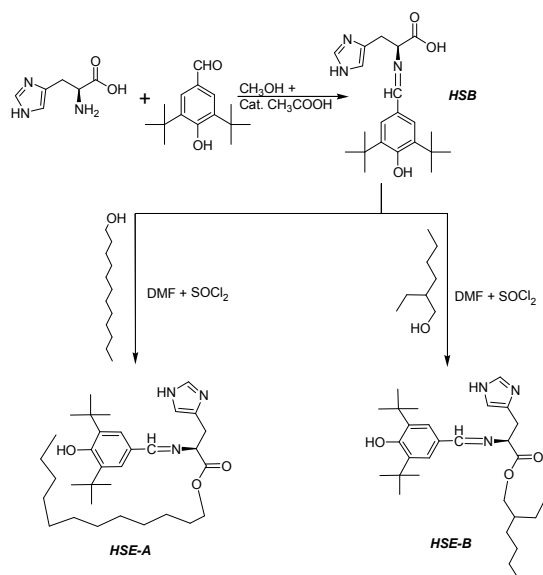
Many type of renewable resources have been tried to derive the environmental friendly lubricant additives e.g. in carbohydrates, cellulose as such has been tested to be utilized as antioxidant for vegetable oil.⁸ In cellulose ethers, methylcellulose and ethylcellulose have been used as thickener for castor oil based lubricating greases.^{9,10} Another cellulose ether, carboxymethylcellulose has been used as a viscosity modifier and water retention agent in drilling mud.¹¹ Some other natural polysaccharides as chitin and chitosan have been utilize for preparing environmentally acceptable thickeners for castor oil based grease formulations by simple acylation or isocyanate-functionalization with 1, 6-hexamethylene diisocyanate.^{12,13} The environmentally friendly friction-reducing, anti-wear, and extreme pressure additives were also prepared utilizing the cashew nutshell liquid and soybean lecithin.^{14,15}

Other important natural feedstock's which could be utilized in the lubricant additive area are amino acids as *dl*-valine was found to a good ecofriendly detergent/dispersant additives for vegetable-oil based lubricants when evaluated by blotters spot.¹⁶ Cysteine and histidine, were examined as corrosion inhibitor in hydrocarbon media by standard copper corrosion test.¹⁷ Studies has been reported on L-tryptophan to be used as corrosion inhibitor for low carbon steel in hydrochloric acid solution.¹⁸ In spite of having the amine and carboxylic groups which could be derivatized for including the important functionalities required for providing the useful additive properties, they are underutilized although few literature reports are available. An environmentally adapted antiwear additive for poly-alpha-olefin and synthetic esters has been synthesized from cystine through acylation reaction which improves its solubility in base oil. It is found to show the performance equivalent to the ZnDDP.¹⁹ Some ionic liquid were also synthesized utilizing the aspartic and glutamic acid. They were evaluated to be efficient antiwear and friction-reducing additives for mineral base oils.²⁰ N-protected aspartic acid tetraalkylammonium and tetraalkylphosphonium salts were tribo tested as antiwear and antifiction additive.²¹ The antioxidant property of the L-histidine is well known fact and it has been shown to scavenge both the hydroxyl radical

and singlet oxygen in many studies but for the pharmaceutical applications.²² In order to utilize this character in lubricant area, the present manuscript describes the synthesis of two new histidine schiff base esters in two step; first imine derivatization using the 3,5-di-*t*-butyl-4-hydroxybenzaldehyde followed by the esterification using the lauryl alcohol and 2-ethylhexanol respectively in the second step. The compounds were characterized using CHN analysis, FT-IR and NMR. The utility of these synthesized compounds as antioxidant, anticorrosion and antiwear additive was evaluated by standard test in the polyol reference biolubricant base oil.

Results and discussion

The two ecofriendly additives *HSE-A* and *HSE-B* were synthesized in two steps as outlined in Scheme 1. At first, the intermediate histidine schiff base (*HSB*) was synthesized through the imine coupling of histidine with 3,5-di-*t*-butyl-4-hydroxybenzaldehyde in 1:1 molar ratio. In second step, esterification of this intermediate schiff base was done with lauryl alcohol and 2-ethyl hexanol to obtain *HSE-A* & *HSE-B* respectively.



Scheme 1: Reaction scheme for synthesizing *HSB* and *HSB-A* & *B*.

The first evidence in the support of the successful synthesis of these compounds was obtained by means of elemental analysis (Table 1). However the yellow colour of the *HSB* is also a strong indication of its formation. The observed results were in good agreement with the calculated values for the given molecular structures in Scheme 1.

Table 1: The elemental analysis data of synthesized *HSB*, *HSE-A* and *HSE-B*^a.

Sample	% Content		
	C	H	N
<i>HSB</i>	67.63 (67.90)	7.17 (7.87)	10.92 (11.31)
<i>HSE-A</i>	72.84 (73.43)	9.17 (9.90)	7.93 (7.78)
<i>HSE-B</i>	71.54 (72.01)	9.16 (9.38)	9.15 (8.69)

^aValues in parentheses are calculated.

To characterize the successful imine bond and then ester bond formation in the synthesized compounds, FT-IR spectroscopy was used. Figure 1a and 1b shows the IR spectra of *HSB* & *HSE-A* respectively. The *HSB* spectrum shows the strong band at 3432.51 cm⁻¹ which indicates the N-H stretching of secondary amine while band at 3000.36 cm⁻¹ corresponds to the aromatic C-H stretching. Distinct bands at 2956.14 cm⁻¹ and 2872.64 cm⁻¹ attribute to the asymmetrical and symmetrical C-H stretching of CH₃ groups (tertiary butyl) introduced with the hindered phenolic moiety in the molecular structure. The inherent histidine CH₂ group's produces asymmetric and symmetric C-H stretching band at 2913.29 cm⁻¹ & 2734.14 cm⁻¹. The most prominent evidence of imine bond formation between histidine amine group with 3,5-di-*t*-butyl-4-hydroxybenzaldehyde is the appearance of a new band at 1667.50 cm⁻¹ characteristic of C=N stretching. The presence of prominent C=C stretching bands at 1632.47 cm⁻¹ (histidine imidazole ring) & 1594.54 cm⁻¹ (hindered phenolic ring) further confirms the schiff base formation. The band at 1570.59 cm⁻¹ represents the C=O stretching vibrations of carboxylate ion. The band appears at 1452.66 cm⁻¹, 1428.88 cm⁻¹, 1296.06 cm⁻¹ & 1261.87 cm⁻¹ could be easily assigned to asymmetric C-H bending, symmetric C-H bending, C-O stretching (phenol) & C-N stretching (imidazole) respectively. Further the bands at around 1194.65 cm⁻¹, 1100.46 cm⁻¹, 967.7 cm⁻¹, 890.52 cm⁻¹ and 795.5 cm⁻¹ attribute to C-N stretch (aliphatic amines), C-O stretching (acid), C-H bending (alkenes), N-H wagging and CH₂ rocking respectively (Figure 1a).

Similarly in the FT-IR spectra of *HSE-A* (Figure 1b), the appearance of characteristic C=O stretching (ester) band at 1743.33 cm⁻¹ along with sharp C=N stretching peaks at around 1666.83 cm⁻¹ determines the successful esterification. All other characteristic peaks indicating the intact hindered phenolic groups can easily observed as aromatic, asymmetric and symmetric C-H stretching band appears between 3001.25-2854.61 cm⁻¹ respectively. *HSE-B* also shows similar FT-IR spectrum as *HSE-A*.

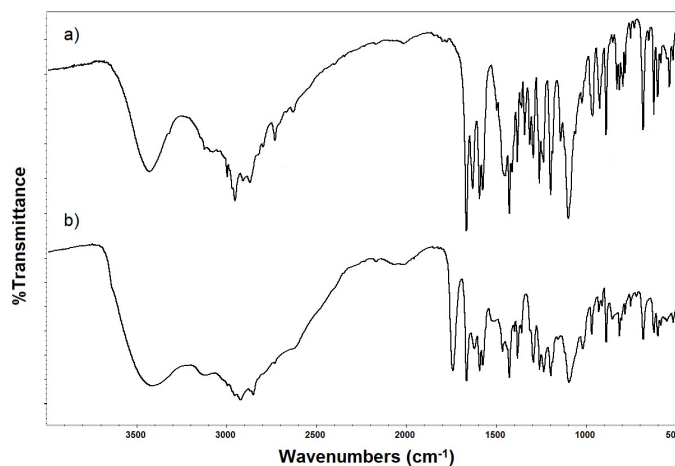


Fig. 1: FT-IR spectra of a) histidine schiff base, *HSB*; b) histidine schiff base ester, *HSE-A*.

Apart from the FT-IR analysis for characterization of the synthesized additives, the NMR was also recorded to further

present the strong evidence in favor of the successful synthesis of the additives *HSE-A* and *HSE-B*. Figure 2 shows the ^{13}C NMR of the additive *HSE-B* in CDCl_3 at 25 °C. The signals corresponding to the 2-ethylhexyl chain carbons and CH_3 of the tertiary butyl groups of the phenolic moiety are clearly observed between 10-40 ppm. The aromatic carbons and histidine imidazole ring carbons are observed between 115-160 ppm. The presence of the signal of C20 ($>\text{C}=\text{O}$) at 191.9 ppm along with the C11 signal at 66 ppm is strong evidence of the esterification while the appearance of C19 downfield signal at 160 ppm is a strong evidence of imine coupling of 3,5-di-*t*-butyl-4-hydroxybenzaldehyde. ^1H NMR of the *HSE-B* in CDCl_3 at 25 °C also shows all the characteristic proton signals (ESI Fig. S1). Similarly the ^{13}C NMR of the additive *HSE-A* shows all the characteristic signals (ESI Fig. S2). The GC/MS of the synthesized additives were also recorded on HP 5890 Series II mass spectrometer with EI source and quadrupole detector. GC reveals the quite high purity of the compounds (ESI Fig. S3) and mass spectrum shows all the peaks attributing to important fragments of the additives. (ESI Fig. S4; Table S1)

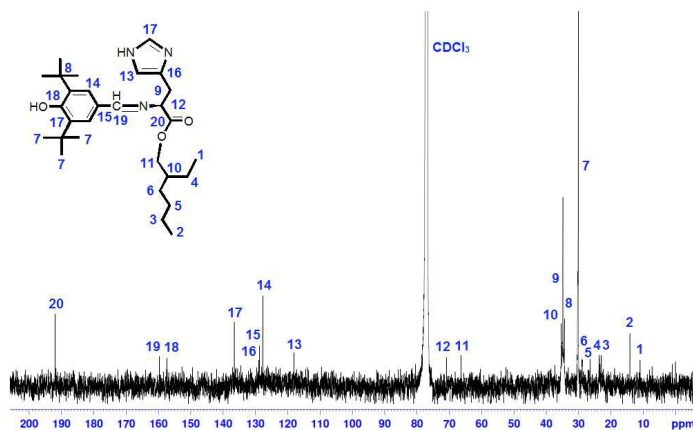


Fig. 2: ^{13}C NMR of additive *HSE-B* in CDCl_3 .

In order to see the workable temperature range of the synthesized additives, TG profiles were also recorded for *HSB*, *HSE-A* & *HSE-B* as shown in Figure 3. Although it is apparent that both the additives have lower thermal stability in comparison to *HSB*. *HSB* started to degrade at around 200 °C while the degradation temperature for *HSE-A* & *HSE-B* is 160 °C & 155 °C respectively. The esterification makes the histidine schiff base thermally unstable and this tendency is more in ethylhexyl chain than the lauryl chain due to steric effects.

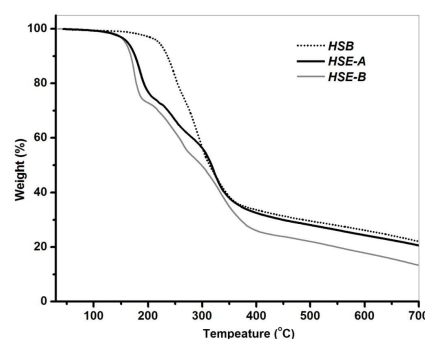


Fig. 3: TG curves of histidine schiff base and histidine schiff base esters.

Now for the performance evaluation of the compounds as antioxidant, antiwear and anticorrosion additives, the blends were prepared in the polyol with different concentrations. Polyol has been taken as the biolubricant reference base fluid.

Antioxidant performance

The hindered phenolic compounds are well established antioxidants for lubricant and fuels⁴ and the inherent antioxidant property of histidine is realized earlier too specially for the pharmaceutical applications.²² So in this work, we have tried to exploit the antioxidant activity of histidine in conjugation with the introduced hindered phenolic group in its framework through imine coupling with 3,5-di tertiary butyl 4-hydroxybenzaldehyde. This derivatization is also supposed to increase its metal chelating abilities. Esterification in second step will make this histidine schiff base soluble in the lubricant base oil. So the antioxidant activity of the synthesized additives *HSE-A* & *B* in polyol base oil was studied by IP-306 oxidation test (Figure 4)²³ and antioxidant character of the synthesized additives is quantized in terms of volatile acidity, soluble acidity, total sludge (S%) and total oxidation products (TOP%). The results are tabulated in Table 2 reveals that both the additives have the antioxidant property with the concentration effect up to the optimum concentration value. The optimum concentration of *HSE-A* and *HSE-B* is 2000 & 3000 ppm respectively. The values of volatile acidity, soluble acidity, total sludge (S%) and total oxidation products (TOP%) for polyol base oil are quite high as 3.8709, 0.4619, 29.5532 and 30.9434 respectively. 2000 ppm *HSE-A* reduces these value to 0.7106, 0.3296, 0.0692 and 0.4030 while 3000 ppm *HSE-B* reduces these values to 0.6807, 0.4628, 0.0628 and 0.4297 respectively. The higher activity in case of *HSE-A* could be explained on the basis of its higher thermal stability and little bit higher solubility in comparison to the *HSE-B*.

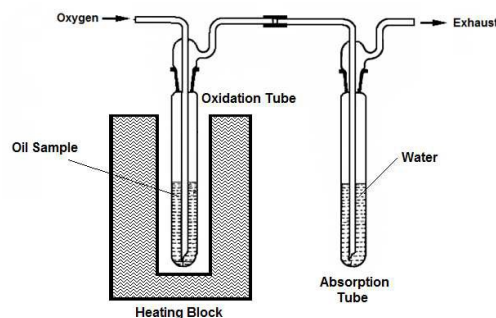


Fig. 4: Arrangement of universal oxidation test (IP 306).

Table 2: Effect of additives on oxidative characteristics of polyol in universal oxidation test (IP 306).

Samples	Total Acid Number (mg KOH/g)		Total Sludge (S%)	Total Oxidation Products (TOP%)
	Volatile Acidity	Soluble Acidity		
Polyol base oil	3.8709	0.4619	29.5532	30.9434
1000 ppm <i>HSE-A</i>	4.6002	0.4432	0.0712	1.6894
2000 ppm <i>HSE-A</i>	0.7106	0.3296	0.0692	0.4030
3000 ppm <i>HSE-A</i>	2.5806	0.6395	0.0780	1.1112
1000 ppm <i>HSE-B</i>	6.9564	0.6339	26.4760	28.9114
2000 ppm <i>HSE-B</i>	1.8289	0.5021	0.0652	0.8131
3000 ppm <i>HSE-B</i>	0.6807	0.4628	0.0628	0.4297

Anti-wear property

Organic schiff compounds are reported to have some anti-wear property as they forms a surface-complex film leading to the hindered metal-metal contact.²⁴ In the present work also the synthesized additive *HSE-A* & *HSE-B* has the imine bond along with the polar ester groups. Considering this fact, both the additives were tested for antiwear property in terms of wear scar diameter using four ball test machine at standard test (ASTM D4172) conditions.²⁵ The value of WSD for the base oil i.e. 896 μm reduces to a value of 824 μm and 820 μm at 1000 ppm concentration of *HSE-A* & *HSE-B* respectively (Figure 5). When 2000 and 3000 ppm additives concentration was used the WSD increases to a value near 850 μm . So the optimum concentration is 1000 ppm for both the additives with similar antiwear characteristics.

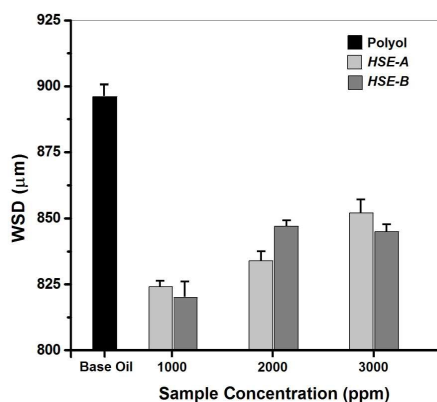


Fig. 5: Reduction in WSD with increasing concentration of histidine schiff base esters *HSE-A* and *HSE-B* in polyol base.

Anticorrosion test

Schiff bases are reported to have the anticorrosion properties as they react with the metal surface to form a surface-complex film.²⁴ Some studies have been done on the anticorrosion activity study of the schiff bases in the aqueous hydrochloric acid medium.²⁶⁻²⁸ In view of this fact, the synthesized additives *HSE-A* & *HSE-B* blends with polyol base oil were tested using the standard corrosion test and the anticorrosion tendency was measured in terms of weight loss, corrosion rate, penetration rate and acidity. A result shown in Table 3 reveals that both the compounds are active but the *HSE-A* is more effective as

anticorrosion additives. The optimum concentration of the *HSE-A* to be used as anticorrosion additive is 2000 ppm while for *HSE-B*, it is 3000 ppm. At 2000 ppm *HSE-A* concentration the values for the weight loss, corrosion rate, penetration rate and acid value difference (before and after test) decrease to 0.9 mg, 0.93 mdd, 0.12 mpy and 0.77 mg/g KOH from the original values of 12.6 mg, 13.02 mdd, 1.67 mpy and 2.04 mg/g KOH for the polyol base. At 3000 ppm concentration of *HSE-B* the values of weight loss, corrosion rate, penetration rate and acid value difference comes out be 1.4 mg, 1.45 mdd, 0.19 mpy and 0.92 mg/g KOH respectively. The reason for the higher activity of *HSE-A* at low concentration could be its higher thermal stability and little bit higher dispensability in polyol base oil. Up to the optimum concentration, the anticorrosion effect increases with the increasing concentration.

Table 3: Corrosion behavior of carbon steel in base oil and various blends of additive vis a vis acid values.

Samples	Weight Loss (mg)	Corrosion Rate, mdd	Penetration rate, mpy	Acid value mg/g KOH		
				Before	After	Diff.
Polyol base oil	12.6	13.02	1.67	3.37	5.41	2.04
1000 ppm <i>HSE-A</i>	1.6	1.65	0.21	2.93	5.22	1.29
2000 ppm <i>HSE-A</i>	0.9	0.93	0.12	4.07	4.84	0.77
3000 ppm <i>HSE-A</i>	1.0	1.03	0.13	3.65	4.84	1.19
1000 ppm <i>HSE-B</i>	4.0	4.13	0.53	3.93	7.26	3.33
2000 ppm <i>HSE-B</i>	2.1	2.17	0.35	4.21	5.36	1.15
3000 ppm <i>HSE-B</i>	1.4	1.45	0.19	4.21	5.13	0.92

Conclusions

In this study, two histidine schiff base esters *HSE-A* and *HSE-B* were synthesized and evaluated an antioxidant, anti-wear and anticorrosion additive in polyol biolube reference base fluid. The synthesized additive *HSE-A* when added in 2000 ppm concentration and *HSE-B* in 3000 ppm concentration showed significant enhancement of oxidative stability and anticorrosion performance. So the *HSE-A* is comparatively more effective as antioxidant and anticorrosion additive and at low concentration than *HSE-B*. The reduction in wear is almost same for both the additives *HSE-A* and *HSE-B* with a maximum reduction on the order of $\sim 8.5\%$. The optimum concentration for anti-wear property is 1000 ppm. So both the additive could be considered as mild antiwear additive.

Experimental

Materials

L-histidine, ethanol, lauroyl alcohol, 2-ethyl hexanol, dimethylformamide (DMF), acetic acid and toluene were purchased from E-Merck, Darmstadt, Germany. Sodium bicarbonate and 3,5-di-*t*-butyl-4-hydroxybenzaldehyde was purchased from Sigma Aldrich. Thionyl chloride (SOCl_2) was obtained from Across Organics, India. All other chemicals were of the highest available grade and were used without further purification.

Synthesis of histidine schiff base (*HSB*)

2.33 g (0.015 mol) histidine was taken in 100 mL round bottom flask equipped with a reflux condenser and added the 15 mL

ethanol and 10 mL toluene with heating at 50 °C and stirring for 30 min. 3.55 g (0.015 mol) 3,5-di-*t*-butyl-4-hydroxybenzaldehyde dissolved in 10 mL ethanol was then added drop wise in next 15 min. 4-5 drops of glacial acetic acid was also added as a catalyst for increasing imine condensation. Then continuous refluxing was done for next 12 hours maintaining temperature at 110 °C. The reaction solvent was removed by rotatory evaporator and unreacted 3,5-di-*t*-butyl-4-hydroxybenzaldehyde was soxhlet extracted with ethanol/ether for 2-3 days. The final product was vacuum dried at 60 °C. Yield; 5.12 g.

Synthesis of histidine schiff base ester (*HSE-A & B*)

A 100 mL round bottom flask having 10 mL toluene and 4 mL dimethylformamide was taken and added 3.80 g (0.01 mol) *HSB* and 1.87 g (0.01 mol) lauryl alcohol with stirred for 30 min. Then the RB was kept in ice and slowly added the 1.0 mL SOCl_2 with stirring. The temperature was increased slowly to 90 °C in next 30 min and stirred for next 10 h. The content is made concentrated by solvent evaporation under reduced pressure by rotatory evaporator. The left reaction content was poured in to cold water and product was precipitated and filtered. Washing was done 2-3 times with saturated aqueous sodium bicarbonate solution. The brown semisolid product was vacuum dried at 80 °C. The obtained yield of the *HSE-A* was 5.14 g. Similar reaction condition was used for synthesizing *HSE-B* utilizing 1.35 g (0.01 mol) 2-ethyl hexanol. Yield obtained for *HSE-B* was 4.73 g.

Techniques used

The synthesized intermediate *HSB* and products *HSE-A & B* were characterized by elementary analysis, infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR) and thermo gravimetric analysis (TGA). Perkin Elmer Series II CHNS/O 2400 analyzer was used for elemental analysis. Fourier transform infrared spectra (FTIR) was recorded using a Thermo-Nicolet 8700 research spectrophotometer by KBr pellet method with a 4 cm^{-1} resolution. ^{13}C NMR was obtained by a Bruker Avance 500 spectrometer in the proton noise-decoupling mode with a standard 5-mm probe. The thermal stability curves of intermediate and products was measured on a Perkin Elmer EXSTAR TGA/DTA 6300, over a temperature range from 30 to 700 °C under inert N_2 atmosphere, at a rate of increase of 10 °C/min.

Antioxidant activity

Universal oxidation test IP 306²³ was performed using the standard apparatus manufactured by Sarbi engineering, India. Polyol was used as a base oils and different samples were prepared by doping this polyol base oil with synthesized additives in different concentrations. The vessels having the samples are immersed in an aluminum block heater maintained at 120 °C and dry oxygen was passed for 48 hrs. Oxygen flow was maintained at 1 ± 0.1 litre per hour. The volatile acids driven off by the flowing oxygen are absorbed in water kept in the secondary vessels. Volatile and oil soluble acidities, and the sludge produced in the oil are determined at the completion of the test. Weight loss and carbon residue formed was measured as per standard procedure. Tests were run in duplicate.

Antiwear property

The Antiwear property of the synthesized additives *HSE-A* and *B* in polyol base was evaluated in terms of wear scar diameter (WSD) using a four ball test machine (Ducom, India) as per ASTM D4172 standard test method.²⁵ Tests were performed

with 12.7 mm steel balls at rotating speed of 1200 rpm; 198 N load; 75 °C temperature for 60 min.

Anticorrosion test

The anticorrosion activity of both the synthesized additives was evaluated using the standard corrosion testing procedure.^{29,30} At first the carbon steel metal was cut into small pieces of size 15 mm × 10 mm × 2 mm (area 0.6 sq. inches) by machining and milling. After machining and milling these metal pieces were hand polished using carborundum emery paper grade number C 201 AH extra fine. Afterwards, these metal pieces were degreased using xylene-isopropanol mixture (1:1). These coupons were weighed up to an accuracy of 0.1 mg before exposing in base oil and various blends of additive in the base oil. These degreased and preweighed metal specimens were suspended using teflon thread separately in base oil and various blends of additive in the base oil contained in stopped measuring cylinders. These static immersion studies were carried out for a period of 25 days (600 hrs.) at 110 °C maintained in an air oven. The test metal specimens were evaluated after 25 days for qualitative and quantitative estimation of corrosion. After the test duration the metals were derusted using derusting solution (36% HCl containing 5% Sb_2O_3 + 4% SnCl_2) and finally weighed up to an accuracy of ± 0.1 mg. The weight loss of each test metal was recorded and the corrosion rate was calculated according to the equation 1.

$$\text{Corrosion Rate} = \frac{\text{Wt. Loss} \times 15.5}{(\text{Area})(\text{Time})} = \text{mg}/(\text{sq.dm})(\text{day}) \text{ or } \text{mdd} \quad (1)$$

By taking density of carbon steel (7.8 g/cm^3) into account penetration rate was also calculated according to the equation 2.

$$\text{Penetration Rate} = \frac{\text{Wt. Loss} \times 22.3}{(\text{Area})(\text{Time})(\text{Metal Density})} = \text{mils}/\text{year or } \text{mpy} \quad (2)$$

*weight loss was obtained after derusting metal samples using 36% HCl containing 5% Sb_2O_3 + 4% SnCl_2 .

Where wt. loss is taken in mg; area in sq. inches of metal surface exposed; time in days exposed; density in g/cm^3 ; Total acid number (TAN), a measure of the extent of fuel oxidation as well as corrosion was also evaluated before and after corrosion test as per ASTM standard test method (D664-11a).³¹

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Notes and references

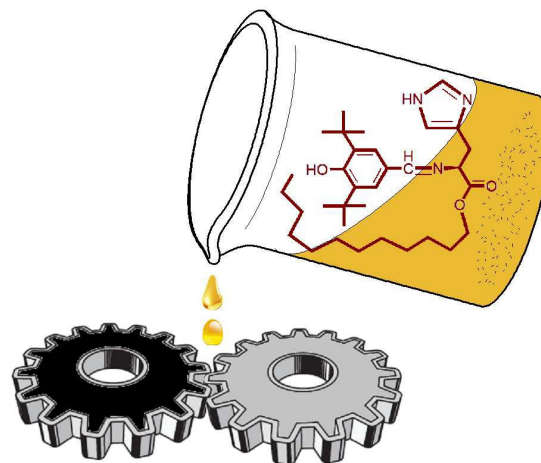
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