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Development of new ecofriendly detergent/dispersant/antioxidant/antiwear additives from L-histidine for biolubricant applications

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Two novel over based Ca salts of histidine schiff base esters *Ca-HDS-L* and *Ca-HDS-M* were synthesized following three step reaction. The histidine schiff base (*HDS*) was synthesized first by imine coupling of histidine with salicylaldehyde. Then its phenolic group was esterified using lauroyl chloride and myristoyl chloride to obtain the *HDS-L* and *HDS-M* respectively. Finally in the third step, their respective over based salts *Ca-HDS-L* and *Ca-HDS-M* were synthesized by reaction with $\text{Ca}(\text{OH})_2$. All the synthesized compounds were characterized using the FT-IR, NMR, CHN and TG analysis. Panel coker federal test (FTM 3462), blotter spot test (ASTM D7899), universal oxidation test (IP-306) and four ball test (ASTM 4172A) were used for the evaluation of detergent, dispersant, antioxidant and antiwear activity respectively of the synthesized additives in polyol base oil. Both the additives are active but overall *Ca-HDS-L* is more effective as detergent and dispersant while *Ca-HDS-M* is more effective as antioxidant and antiwear multifunctional biolubricant additive.

Despite the limitations related with environmental concerns and exhaust emission catalytic converters poisoning, zinc dialkyldithiophosphates (ZDDP) remains an important and popular antiwear, antioxidant and anticorrosion multifunctional additive (MFA) since its discovery in 1940s especially for the automobile lubricant formulations.^{1,2} Similarly, over based metal sulfonate and mannich adducts are still in use as antioxidant, detergent and dispersant multifunctional additives.^{3,4} Sulfonate and mannich bases have similar environmental problems. Although they works well in the emerging biolubricant base oils too⁵ but to formulate a complete ecofriendly biolube, the use of such additives is highly undesirable because it leads to toxicity to water bodies and land soils by decomposing and generating S- and P-containing toxic compounds.⁶ It is a challenge before us to replace such MFA's with the environmental friendly, biodegradable additives with comparable performance having no such toxic elements. Some efforts have been made to screen out the ecofriendly substitutes but most of them are restricted to additives having single property.^{7,8}

Further, it is desirable to develop these innovative MFA's from the sustainable raw materials. Some recent efforts have been made to use sustainable materials to develop additives but mostly with single additive character e.g. natural garlic oil (NGO) has been evaluated as high-performance, environmentally friendly, extreme pressure additive for

lubricating oils.⁹ Cellulose fatty esters have been evaluated as the lubricity additive for biolubricant base oils.^{10,11} Boron-containing soybean lecithin has been tribologically tested as environmentally friendly lubricant additive in synthetic base fluids.¹² Potential of dextrose, sucrose and cellulose dodeceny succinate esters have been investigated as lubricity additive.¹³ Acylated and Isocyanate-functionalized chitin and chitosan have been reported to be used as thickener agents for preparing vegetable oils based grease.^{14,15}

Mixed esters of pentaerythritol monooleate with gallic acid and 3,5-di-tert-butyl-4-hydroxybenzoic acid have been evaluated for antioxidant and detergent dispersant along with lubricity properties using the rotary bomb oxidation test, blotter spot test, and four ball test.¹⁶ Homopolymers of sunflower oil and soybean oil have been evaluated as a pour point depressant and viscosity index improver or modifier for lube oil.¹⁷ Condensation product di(alkylphenyl)phosphorodithioic acid derived from cashew nutshell liquid, with various amines have been evaluated as anti-oxidant, antiwear, friction-modifying, and extreme-pressure additives in lubricant compositions.¹⁸

Amino acids are abundant, natural, renewable and biodegradable resource but still underutilized as lubricant additive feedstock. Few reports describe the use of aminoacids e.g. novel environmentally adapted lubricant additives were synthesized from cystine (Cys_2) by its carboxyl group's derivatization to corresponding esters by reaction with long-chain alcohols. The Cys_2 -derived additives exhibited comparable antiwear properties to the conventional additive ZDDP in synthetic hydrocarbons such as poly-alpha-olefin.¹⁹ Some ionic liquid derived from aspartic and glutamic acid was evaluated to be efficient antiwear and friction-reducing additives in mineral base oils.^{20,21} Amino acids as such were also used sometimes e.g. *dl*-valine was found to a good ecofriendly detergent/dispersant additives for vegetable-oil based lubricants when evaluated by blotters spot.⁷ So there exists ample scope to use them as for developing multifunctional lubricating oil additives.

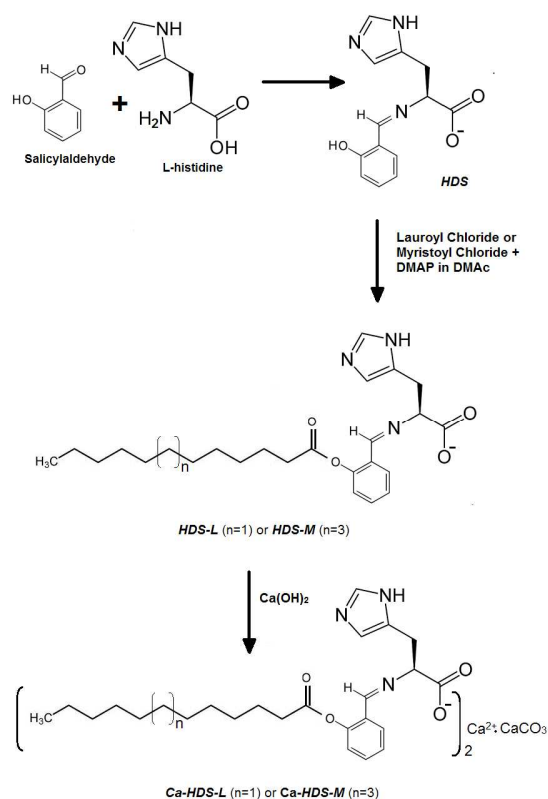
L-histidine has attracted our attention as it shows the anticorrosion activity when tested in hydrocarbon media and also the antioxidant property well realized in pharmaceutical applications.^{22,23} So in this paper, we have developed new multifunctional additive having antioxidant, detergent, dispersant and antiwear properties from L-histidine. Novel histidine based salts (abbreviated as *Ca-HDS-L* and *Ca-HDS-*

M) were synthesized and characterized. Their antioxidant, detergent, dispersant and antiwear additive performances were evaluated in polyol base oil.

Synthesis of *Ca-HDS-L* and *Ca-HDS-M*

The synthesis of the *Ca-HDS-L* and *Ca-HDS-M* additives was done using three step reactions route as shown in the Scheme 1. The L-histidine white colour changes to yellow in the histidine schiff base (*HDS*). This gives the direct evidence of the successful imine bond formation as shown in the Fig. 1. This along with all other synthesized compounds were also characterized using the various analytical techniques like CHN analysis, FT-IR and NMR. The observed results of elemental analysis given in Table 1 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 *Ca-HDS-L* and *Ca-HDS-M*.



Fig. 1: Histidine schiff base (*HDS*) with salicylaldehyde.

Table 1: The elemental analysis data of synthesized *HDS*, *HDS-L* and *HDS-M*^a.

Sample	% Content		
	C	H	N
<i>HDS</i>	59.17 (60.22)	4.96 (5.05)	16.42 (16.21)
<i>HDS-L</i>	68.25 (68.00)	8.17 (7.99)	9.12 (9.52)
<i>HDS-M</i>	69.14 (69.05)	8.78 (8.37)	9.15 (8.95)

^aValues in parentheses are calculated.

FT-IR spectroscopy

The successful synthesis of the compounds was also supported by FT-IR as shown in Fig. 2. The *HDS* spectrum shows the strong band at 3397.92 cm⁻¹ which indicates the N-H stretching of secondary amine while band at 3015.01 cm⁻¹ corresponds to the aromatic C-H stretching. The inherent histidine CH₂ group's produces asymmetric C-H stretching band at 2868.59 cm⁻¹. The most prominent evidence of imine bond formation between histidine amine group with salicylaldehyde is the appearance of a strong band at 1632.80 cm⁻¹ characteristic of C=N stretching. Although it consists the other overlapping peak as histidine imidazole ring C=C stretching band. Also the appeared peak at 1589.36 cm⁻¹ pertaining to C=C stretching of phenolic ring further confirms the schiff bond formation. This may also consist the overlapping peak of C=O stretching vibrations of histidine carboxylate group.

The band appeared at 1457.45 cm⁻¹, 1413.13 cm⁻¹, 1271.66 cm⁻¹ & 1248.64 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 1145.9 cm⁻¹, 1112.26 cm⁻¹, 925.43 cm⁻¹ and 754.57 cm⁻¹ attribute to C-N stretch (aliphatic amines), C-O stretching (acid), N-H wagging and CH₂ rocking respectively (Fig. 2a). In the FT-IR spectra of *HDS-M* (Fig. 2b), the appearance of characteristic C=O stretching (ester) band at 1728.25 cm⁻¹ along with persistent sharp C=N stretching peaks at around 1640.18 cm⁻¹ determines the successful esterification. Further the appearance of prominent peaks at around 2920.65 and 2850.43 cm⁻¹ attributed to the asymmetric and symmetric C-H (CH₂) stretching band of the fatty myristyl chain. Similar IR spectrum was observed for the *HDS-L*. The FT-IR spectra of the Ca salts of histidine schiff base esters *Ca-HDS-L* and *Ca-HDS-M* were also recorded showing all the characteristics peaks as in the *HDS-L* and *HDS-M* along with the appearance of the undesired OH stretching signal at 3643.77 cm⁻¹ which belongs to the residual Ca(OH)₂ used during the third step of over basing (Fig. 2c).

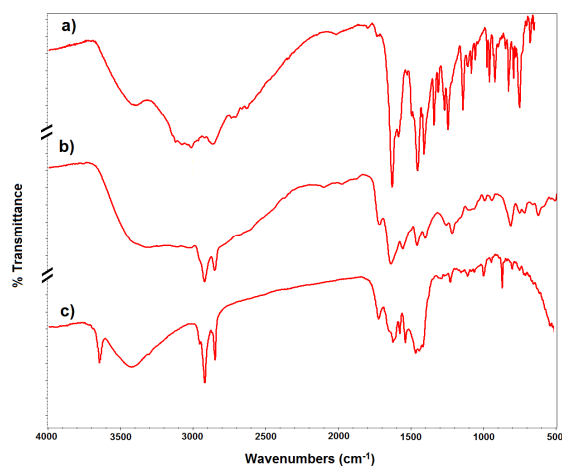


Fig. 2: FT-IR spectra of a) histidine schiff base, *HDS*; b) histidine schiff base ester, *HSD-M*; c) calcium salt of histidine schiff base ester, *Ca-HSD-M*.

NMR spectroscopy

In addition with FT-IR analysis, NMR also presents strong evidence in favour of successful synthesis of *HDS-L* and *HDS-M*. Fig. 3 shows the ^{13}C NMR of the additive *HDS-L* in d^6 -DMSO at 25 °C. Lauroyl fatty chain carbons (C1-C9) are observed in the range 0-40 ppm where signal at 15 ppm corresponds to the terminal methyl group carbon and other signal between 20 to 40 ppm attributes to the other methylene carbons of long alkyl chain. The histidine imidazole ring carbons (C11-C13) are observed between 105-120 ppm. The aromatic carbons (C16-C20) are observed between 130-140 ppm. The existence of C15 downfield signal at 158 ppm is a strong evidence of imine coupling of histidine. The appearance of the signal of C21 ($>\text{C}=\text{O}$) at 172.5 ppm along with the C22 signal at 175 ppm is strong evidence of the esterification. *HDS-M* also shows all the characteristics NMR signals too (ESI Fig. S1).

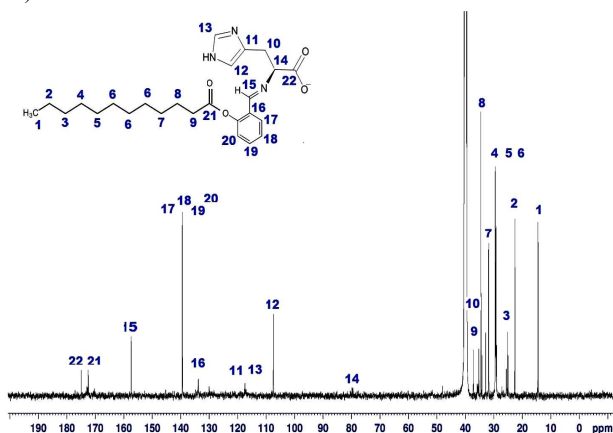


Fig. 3: ^{13}C NMR of *HDS-L* in d^6 -DMSO.

Thermogravimetry

TG curves were recorded for determining the thermal stability of the synthesized additives. Fig. 4 shows the TG profiles of

the *HDS*, *HDS-L*, *HDS-M*, *Ca-HDS-L* and *Ca-HDS-M*. It is clear from the graph that the esterification lowers the thermal stability of the histidine schiff base. *HDS* starts to degrade around 270 °C while the degradation temperature for *HDS-L* and *HDS-M* is near to 200 °C. Finally the Ca salts formation provides them the stability as the degradation temperature for *Ca-HDS-L* and *Ca-HDS-M* found to be 379.75 °C and 372.67 °C respectively. So both compound *Ca-HDS-L* and *Ca-HDS-M* show the good thermal stability to be used as lubricant additives.

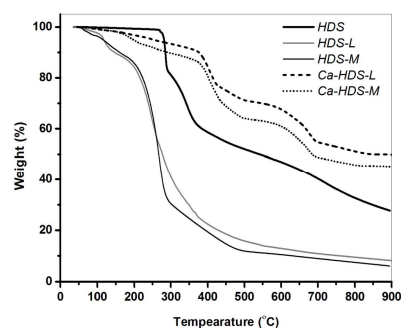


Fig. 4: TG curves of histidine schiff base, histidine schiff base esters and their Ca salts.

Detergency test

After the characterization of the synthesized additives and determining their working temperature range, the samples with different concentrations as 1000, 2000 and 3000 ppm were prepared by dispersing the additives *Ca-HDS-L* and *Ca-HDS-M* in the poly base oil by sonication with heating. The first additive property tested was the detergency, since the both molecules have the hydrophilic polar end (carboxylate) and the lipophilic fatty chain. The panel coker federal test method (FTM 3462) performance test determines the tendency of oil to form solid deposits on metal panel surface at elevated temperatures and thereby evaluates the detergency. The “coking value” determined by the panel coker apparatus is indicative of the high temperature detergency. Lower the coking value means higher the detergency. It is evident that the polyol have quite high value of coking value i.e. 0.043 g (σ ; 0.0017). The test results indicate that both the additives *Ca-HDS-L* and *Ca-HDS-M* show the antioxidant behaviour even on higher temperature. The behaviour increases as the concentration increases. The additive *Ca-HDS-L* decreases the coking value at 1000, 2000 and 3000 ppm to a value of 0.041 g (σ ; 0.0010), 0.039 g (σ ; 0.0017) and 0.035 g (σ ; 0.0016) respectively. Similar trend were observed with the *Ca-HDS-M* but less effective than *Ca-HDS-L* (Fig. 5). The reason may be the slightly higher thermal stability of the *Ca-HDS-L*. Comparison was also made with the commercially available detergent i.e. calcium alkyl salicylate (TBN no. ≥ 150). Its detergency observed with the panel coker test is high (coking value 0.027 g (σ ; 0.0015)) than both the synthesized additives may be due to its higher TBN number. In spite this low activity than commercial additive, the work is significant breakthrough in the direction of developing the environmentally benign additives from the sustainable resource.

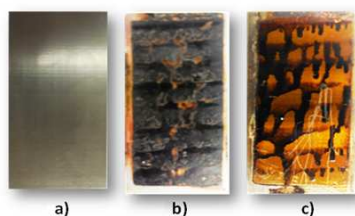


Fig. 5: Panel coker test specimens, a) specimen before test; b) specimen after test with polyol; c) specimen after test with 3000 ppm *Ca-HDS-L* in polyol.

Dispersancy test

Both the additives *Ca-HDS-L* and *Ca-HDS-M* were evaluated for their dispersant capabilities as per modified ASTM D7899 method which is popularly known as blotter spot test.²⁴ Although the dispersing capability of the additives can be evaluated in terms of the several parameters as size of centre black spot, colour of centre spot, size of diffusion zone, colour of diffusion zone (black, gray), density (translucent or opaque) but we have measured the size of the spot only in this study (Fig. 6) as described by the N.S. Ahmed.²⁵ The results indicate that both the additives have the dispersing property. The dispersion is found to be increasing with the increasing *Ca-HDS-L* concentration from 1000–2000 ppm (spot size increased from 0.50 cm to 0.65 cm). *Ca-HDS-L* (spot size 0.65 cm) is dispersing soot in base oil little bit better than *Ca-HDS-M* (spot size 0.60 cm) at 2000 ppm with respect to polyol blank (spot size 0.45 cm). At 3000 ppm concentration the dispersion is found to be decreased as compared to 2000 ppm. So the optimum concentration is the 2000 ppm.

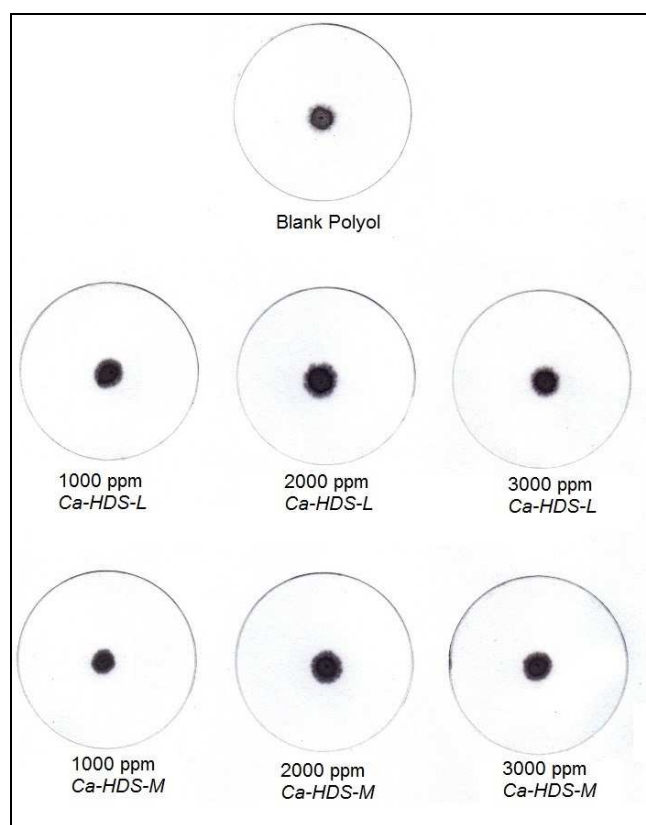


Fig. 6: Blotter spot test of additives *Ca-HDS-L* and *Ca-HDS-M*

Antioxidant performance

Then antioxidant property was also evaluated as L-histidine is reported in the literature to have the antioxidant character although for the pharmaceutical applications.²⁶ The histidine schiff base moiety may provide metal chelating abilities to the additives too. The overbasing in the third step of the additive synthesis also gives it the acid neutralization capabilities. Total base number (TBN) determined by ASTM standard D974³⁰ is 57.5 mg KOH/g and 61.32 mg KOH/g for *Ca-HDS-L* and *Ca-HDS-M* respectively. These entire factors are supposed to make the *Ca-HDS-L* and *Ca-HDS-M* a good antioxidants and this was realized too through the experiments carried out on the universal oxidation test apparatus following IP-306 (Fig. 7).²⁴ The antioxidant potential of the additives was estimated in terms of volatile acidity, soluble acidity, total sludge (S%) and total oxidation products (TOP%). The results tabulated in the Table 2 reveal that both the additives show the antioxidant properties at higher concentration than 1000 ppm. At 1000 ppm the volatile acidity is higher than the blank polyol. Otherwise, property increases with the increasing concentration of both the additives from 2000 ppm to 3000 ppm in terms of all determined parameters. *Ca-HDS-M* shows slightly better results than *Ca-HDS-L* at 3000 ppm concentration. The values of volatile acidity, soluble acidity, total sludge (S%) and total oxidation products (TOP%) for polyol base oil are quite high as 4.095, 2.019, 32.454 and 34.416 respectively. 3000 ppm *Ca-HDS-M* reduces these value to 2.165, 1.458, 0.021 and 1.183 while 3000 ppm *Ca-HDS-L* reduces these values to 3.478, 1.402, 0.013 and 1.579 respectively. The higher activity in case of *Ca-HDS-M* could

be explained on the basis of its little bit higher solubility in comparison to the *Ca-HDS-L* due to longer fatty chain and also the TBN value.

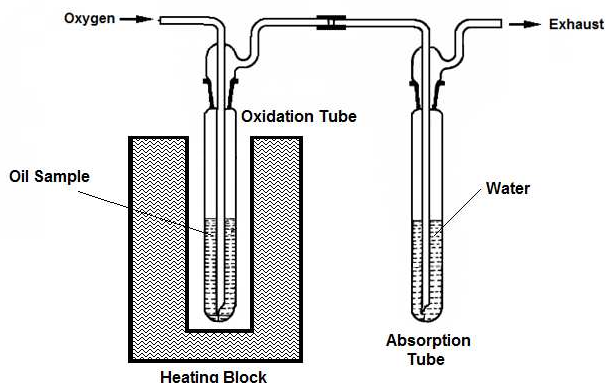


Fig. 7: Arrangement of universal oxidation test (IP 306)

Table 2: Additive effect on oxidative characteristics at various concentrations of additives in base oil in universal oxidation test (IP 306).

Samples	Total Acid Number (mg KOH/g)		Total Sludge (S %)	Total Oxidation Products (TOP %)
	Volatile Acidity	Soluble Acidity		
Blank -Polyol	4.095	2.019	32.454	34.416
1000 ppm <i>Ca-HDS-L</i>	7.854	1.598	0.497	3.530
2000 ppm <i>Ca-HDS-L</i>	2.468	1.514	0.022	1.300
3000 ppm <i>Ca-HDS-L</i>	3.478	1.402	0.013	1.579
1000 ppm <i>Ca-HDS-M</i>	6.874	0.476	0.065	2.423
2000 ppm <i>Ca-HDS-M</i>	2.244	1.514	0.076	1.282
3000 ppm <i>Ca-HDS-M</i>	2.165	1.458	0.021	1.183

Anti-wear property

It is well reported fact that duo the surface-complex film forming tendency, organic schiff compounds hindered the metal-metal contact leading to the anti-wear property.²⁷ As our designed additives have an imine bond along with the polar end and imidazole ring which may provide the film forming tendency, so we have tested the *Ca-HDS-L* and *Ca-HDS-M* as antiwear additive too. The antiwear potential is estimated in terms of the WSD (wear scar diameter) using four ball test machine following standard test conditions (ASTM D4172).²⁴ Both the additives are found to have the antiwear property as the value of WSD for the base oil i.e. 896 μm reduces to a value of 690 μm and 614 μm at 1000 ppm concentration of *Ca-HDS-L* and *Ca-HDS-M* respectively (Table 3). The *Ca-HDS-M* is comparatively more effective may be due to the little bit higher solubility. At higher additives concentration also, the WSD is lower than the blank but higher than what we observed for 1000 ppm concentration. So the optimum concentration is the 1000 ppm (Fig. 8).

Table 3: Four ball test results.

Compounds	Concentration (ppm)	WSD (μm)	Std. Dev. σ
Blank	-	896	13.8684
<i>Ca-HDS-L</i>	1000	690	6.0277
<i>Ca-HDS-L</i>	2000	736	7.5498
<i>Ca-HDS-L</i>	3000	744	8.5049
<i>Ca-HDS-M</i>	1000	614	9.0737

<i>Ca-HDS-M</i>	2000	680	14.1067
<i>Ca-HDS-M</i>	3000	727	15.7162

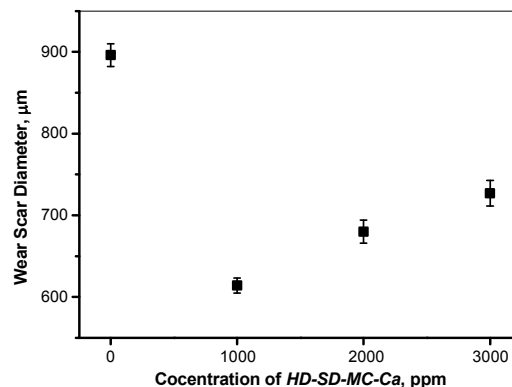


Fig. 8: Reduction in WSD with increasing concentration of *Ca-HDS-M* in polyol base.

Also the feedstock of both the additives being a natural amino acid and the considering the results of ASTM D5864²⁴ they may be considered as environmental friendly to a significant extent.

Conclusions

Two new histidine based additives *Ca-HDS-L* and *Ca-HDS-M* were synthesized and evaluated as detergent, dispersant, antioxidant and anti-wear additive in polyol taken as biolube reference base fluid. Both the additives were found to have the tested activities but *Ca-HDS-L* is comparatively more effective as detergent and dispersant additive while *Ca-HDS-M* is more effective as antioxidant and antiwear. 1000 ppm concentration of *Ca-HDS-M* reduces the wear of the polyol base oil to 31.47 %.

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Notes and references

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Experimental

Materials

L-histidine, N, N'-dimethylacetamide and calcium hydroxide was purchased from Merck Millipore. Salicyldehyde, lauroyl chloride, myristoyl chloride, 4-(dimethylamino)pyridine and methanol was purchased from Sigma-Aldrich.

Synthesis of histidine schiff base (HDS)

3.1 g (~20 mmol) L-histidine and 2.5 g (~20 mmol) salicylaldehyde was taken in 250 mL round bottomed flask equipped with a water condenser. Methanol was used as solvent. The mixture was refluxed with stirring for 18 hours. The yellow coloured compound was obtained by filtration and then drying in oven. Yield obtained was 5.2 g.

Synthesis of histidine schiff base esters (*HDS-L* and *HDS-M*)

2.6 g (~10 mmol) of the synthesized *HDS* was reacted with 4.37 g (~10 mmol) lauroyl chloride in round bottomed flask using 1.22 g (~10 mmol) 4-(dimethylamino)pyridine (DMAP) as HCl scavenger and N, N'-dimethyl-acetamide (DMAc) as solvent. The stirring was carried out at 130 °C for around 15 hours. The content was poured in the cold water and the precipitate was filtered and washed several times with methanol and water. The dark brown compound (*HDS-L*) was obtained after drying in vacuum oven overnight at 60 °C. Yield obtained of *HDS-L* was 3.98 g. Similarly the *HDS-M* was synthesized by the same reaction protocols using 4.92 g (~20 mmol) myristoyl chloride. Yield obtained of *HDS-M* was 4.32 g.

Synthesis of Ca salt of histidine schiff base esters (*Ca-HDS-L* and *Ca-HDS-M*)

Excess amount (twice the equimolar concentration) of calcium hydroxide was taken and moisten with few drops of water and then added the chloroform. The solution was sonicated for 30 min for proper dispersing. *HDS-L* or *HDS-M* was added slowly to this solution and vigorous stirring was done for next 8-10 hours with CO₂ purging in to it. The precipitate was washed several time with water to remove the excess calcium hydroxide. The compound was dried in vacuum oven overnight for obtaining *Ca-HDS-L* and *Ca-HDS-M*.

Techniques used

The synthesized additives were also characterized using CHN analyzer, FT-IR, NMR and TG. Fourier transform infrared spectra were recorded on Thermo-Nicolet 8700 Research spectrophotometer with a 4 cm⁻¹ resolution using potassium bromide window. NMR measurements were carried out on a Bruker Avance 500 spectrometer in the proton noise-decoupling mode with a standard 5-mm probe. Thermo gravimetric analyses (TG) of samples were carried out using Perkin Elmer EXSTAR TG/DTA 6300 using aluminum pans. Analysis was carried out in the temperature range of 30 to 900 °C under nitrogen flow (200 mL min⁻¹) with heating rate of 10 °C/min.

Panel coker federal test (FTM 3462)

The panel coker federal test method (FTM 3462) performance test²⁴ was used to determine the detergency property of the synthesized additives in the polyol lube base oil in terms of the coking value. The "coking value" i.e. solid deposits on metal panel surface at elevated temperatures determined by the panel coker apparatus is indicative of the detergency. A panel coker test apparatus from Tribotech Technologies Pvt. Ltd., New Delhi was used. The tarred, polished steel test panel is placed in the coking splashed apparatus in a position such that the polished surface thereof comes in the contact with oil thrown on it by means of the splashier immersed in the sample. The test sample was prepared and placed in coker bath. The test panel is heated to the temperature of 300±10 °C and the oil was heated to the temperature of 120±10 °C and maintained at this temperature while the splashier is operated for a period of 30 min., after which the panel is removed, cooled, washed with petroleum ether, dried

and weighted. The difference in weight before and after the test was taken as the "coking value".

Blotter spot test (ASTM D7899)

Blotter spot test was performed following the modified ASTM D7899²⁴ for analyzing the dispersing efficiency of the synthesized additives. At first, a reference blank stock was prepared by dispersing the 5.0 g lamp black in the 1000 mL base oil (polyol ester) taken in a beaker. Now the three different samples were prepared by adding the 1000, 2000 and 3000 ppm concentration of the additives in this stock solution. Samples were homogenized by using sonicator and used for the blotter spot test in which a sheet of whatman filter paper was clamped in an aluminium frame having circular holes of equal area. Boundaries and centre of these circles were marked with pencil. Oil sample were drawn with the help of capillary tube and one drop of sample was placed on the centre of each circle. The oil spreaded on the filter paper as it was kept for 10-12 hours. The dispersancy of samples is evaluated in terms of the size of the black carbon spot.

Universal oxidation test (IP-306)

The potential of synthesized compounds as antioxidant additive was analyzed by universal oxidation test performed as per IP 306.²⁴ Samples with different concentrations as 1000, 2000 and 3000 ppm were prepared in polyol base oil. 25 g of the each sample was taken in oxidation tube and connected with the absorption tube with a connecting plastic tube. The absorption tube was also filled with the 25 mL water. Apparatus was run at 120 °C for 48 hours. Flow of the oxygen was maintained at the rate of 1 litre/hour. After the test the oil sample was recovered using 150 mL heptane. For some samples which were difficult to remove, the chloroform was added. The samples were kept in dark for 48 hours. The samples were then filtered by vacuum filtration using the filtration crucible and the solution was made up to 500 mL by adding heptane. Titration of 10 mL aliquotes was done with 0.1 M alcoholic KOH solution using phenolphthalein as an indicator and calculate soluble acidity as per the given formula:

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

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 absorption 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:

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

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.

The 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 anti-wear performance evaluation of synthesized additives as blends with polyol base oil was carried out on the four-ball rolling contact fatigue tribotester (Ducom India) as per ASTM D4172A standard test method.²⁴ The anti-wear characteristics were estimated in terms of average wear scar diameter (WSD) of the four balls 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. Each of the additive blends is tested thrice and the average results were reported.

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