Journal of Industrial and Engineering Chemistry 26 (2015) 149–156

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Study of cystine schiff base esters as new environmentally benign multifunctional biolubricant additives

Raj K. Singh [a,*], Shubham Pandey [a], Rakesh C. Saxena [a], Gananath D. Thakre [b], Neeraj Atray [c], Siddharth S. Ray [a]

[a] Chemical Science Division, CSIR-Indian Institute of Petroleum, Dehradun 248 005, India
[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

ARTICLE INFO

Article history:
Received 9 September 2014
Received in revised form 20 November 2014
Accepted 25 November 2014
Available online 3 December 2014

Keywords:
Cystine schiff base ester
Antioxidant
Antifriction
Antiwear
Anticorrosion

ABSTRACT

Two additives *CySBE-A* and *B* were prepared via a two step synthesis. First, the cystine schiff base (*CySB*) was synthesized utilizing 3,5-di-*t*-butyl-4-hydroxybenzaldehyde. In the second step, its esterification with lauroyl alcohol and 2-ethyl hexanol results the final products *CySBE-A* and *B* respectively. Both additives were evaluated as multifunctional additive in polyol base oil for antioxidant, antifriction, antiwear and anticorrosion property. Universal oxidation test (IP-306) was used for evaluating antioxidant property. Antifriction and antiwear properties in terms of average friction coefficient and wear scar diameter (WSD) were evaluated using four ball test. The *CySBE-A* was found to be effective than *CySBE-B*.

Introduction

Lubricants are used mainly to reduce the friction and wear between two moving metallic surfaces in contact. They also facilitate other functions like heat dissipation, corrosion control, cleanliness, providing seal at moving contact etc. In order to perform these functions, a lubricating formulation must have specific chemical and physical characteristics. The lubricant base oils obtained either from the conventional petroleum resources or synthetics do not have all these characteristics so different additives are used to achieve the desired application specific characteristics [1]. Now due to depletion of petroleum reserves, increasing crude oil prices and legislation regarding environment protection, emphasis has been shifted to the biodegradable and environmentally friendly lubricant compositions obtained from the bio-based materials [2,3]. Lube base oil from vegetable oil has immerged as an alternative in the last two decades [4]. For a completely biodegradable lube formulation, additives should also be biodegradable along with base oil [5]. Although additives are present in low levels but their toxicity affects the biodegradability of the whole lubricant blend. Zinc dialkyldithiophosphates (ZDDP) works well in biolubricants base oil too as antiwear, antifriction, antioxidant and anticorrosion additive but it is non-biodegradable, toxic to the humans and other living organisms. The catalytic converters poisoning is also caused by the generated sulfated ash, phosphorous and sulfur [6,7]. Most of the other commercial multifunctional additives like sulfonate and mannich bases have the similar problems. So it is the need of hour to develop new environmentally benign additives from renewable resources.

Previously some efforts have been made to utilize the natural resources to develop the environmental friendly additives to avoid the environmental nondegradability. For example, an ashless antioxidant, antiwear, friction-modifying and extreme-pressure additive for lubricant was synthesized by utilizing the di-(alkylphenyl)phosphorodithioic acid derived from cashew nutshell liquid [8]. The homopolymer of sunflower oil (SFO) and soybean oil (SBO) was used as pour point depressant (PPD) and viscosity index improver (VII) or modifier (VM) for lube oil.[5] An environmentally friendly friction-reducing, anti-wear, and extreme pressure additive for synthetic base fluids was synthesized by the reaction of boric acid with soybean lecithin obtained from soybean seeds [9]. Natural garlic oil (NGO) showed great promise to be used as a high-performance, environmentally friendly, extreme pressure additive for lubricating oils [10]. Mixed esters of pentaerythritol

* Corresponding author. Tel.: +91 135 2525708; fax: +91 135 2660202.
E-mail address: rksing@iip.res.in (R.K. Singh).

http://dx.doi.org/10.1016/j.jiec.2014.11.027
1226-086X/

monooleate with gallic acid and 3,5-di-tert-butyl-4-hydroxybenzoic acid have been evaluated as ecofriendly, biodegradable and environmentally benign multifunctional lubricant additives [11]. Cellulose as such has been used as antioxidant additive for the vegetable oil [12]. Carboxymethylcellulose is used as an ingredient of drilling mud as a viscosity modifier and water retention agent [13]. Cellulose fatty esters are also evaluated to be used as the lurbricity additives [14].

Many environmentally acceptable thickeners from renewable sources for grease formulations have been reported in the literature, e.g. methylcellulose and ethylcellulose for castor oil based lubricating greases [15,16]; acylated derivatives of chitin and chitosan for vegetable oils based oleogel [17]; isocyanate-functionalized chitin and chitosan with 1,6-hexamethylene diisocyanate for castor oil based grease [18]; sorbitan monostearate for castor oil based grease [19].

Amino acids, the essential components of living organisms are another important, inherently safe, nontoxic natural resource. They are underutilized with respect to the utilization in the lubricant additive area in spite of having the important functional groups. Only few reports are available, e.g. acylated cystine has been used as environmentally adapted antiwear additive for poly-alpha-olefin and synthetic esters. Esterification improves the solubility in the base oils too [20]. Aspartic acid and glutamic acid derived ionic liquids were also found to be efficient antiwear and friction-reducing additives for mineral base oils [21]. Tetraalkylammonium and tetraalkylphosphonium salts of N-protected aspartic acid were evaluated by a ball-on-flat type tribo-test under reciprocating motion as antiwear and antifiction additive for ionic liquid [22]. DL-Valine has been studied as ecofriendly detergent/dispersant additives for vegetable-oil based lubricants by blotters spot and it is categorized as good [23]. Cysteine and histidine, in hydrocarbon media has been examined as corrosion inhibitor for copper by a standard corrosion test [24].

It is widely known fact that disulfides improve the tribological properties. Cystine has the disulfide moiety which is supposed to help in surface film formation. In order to utilize this fact, in the present manuscript, two new cystine schiff base ester were synthesized in two step; first imine derivatization using the 3,5-di-*t*-butyl-4-hydroxybenzaldehyde followed by the esterification with the lauryl alcohol and 2-ethylhexanol respectively in the second step. The compound was characterized using FT-IR, NMR, CHN and TG. The applicability of this derivative as green multifunctional lubricating oil additive was explored by testing the antioxidant, antifriction, antiwear and anticorrosion properties in polyol which was taken as reference base fluid.

Experimental

Materials

L-Cystine and 3,5-di-*t*-butyl-4-hydroxybenzaldehyde were purchased from Sigma Aldrich. lauryl alcohol was procured from CDH Laboratory Reagents, India. 2-Ethylhexanol, sodium bicarbonate, toluene, acetic acid and ethanol were obtained from E-Merck, Darmstadt, Germany. Thionyl chloride was obtained from Across Organics, India. Reference polyol base fluid (pentaerythritol tetra oleate) was purchased from Mohini Organics Pvt. Ltd. India. All other chemicals were of the highest available grade and were used without further purification.

Synthesis of cystine schiff base (CySB)

The intermediate compound (*CySB*) was synthesized by reacting 3.7 g (0.015 mol) L-cystine with 7.1 g (0.030 mol) 3,5-di-*t*-butyl-4-hydroxybenzaldehyde in a 250 mL round bottom flask containing 100–150 mL ethanol as a solvent. 8–10 drops of glacial acetic acid was used as a catalyst for increasing imine condensation. Light yellowish sparkling crystals of *CySB* were obtained after regular stirring for 16 h at 80–90 °C. The solvent was removed by rotatory evaporator and un-reacted aldehyde was soxhlet extracted with ethanol/ether for 2–3 days. The final product was vacuum dried at 60 °C. Yield; 10.50 g.

Synthesis of cystine schiff base esters (CySBE-A and B)

6.73 g (0.01 mol) *CySB* and 3.73 g (0.02 mol) lauryl alcohol was taken in a 250 mL round-bottomed flask with 100 mL toluene and stirred for 30 min. Then this round-bottomed flask was kept in ice and slowly added 6.5 mL $SOCl_2$ with stirring at 0 °C. Now solution was stirred for next 18 h at around 90–100 °C. After reaction completion, the toluene was removed under reduced pressure by rotatory evaporator. 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 80 °C. The obtained yield of the *CySBE-A* was 9.44 g. Similar reaction condition was used for synthesizing *CySBE-B* utilizing 2.7 g (0.02 mol) 2-ethyl hexanol. Yield obtained for *CySBE-B* was 8.32 g.

Characterization

The synthesized intermediate *CySB* and both the products (*CySBE-A* and *CySBE-B*) were characterized by using many techniques. Fourier transform infrared (FTIR) spectra were recorded using a Thermo-Nicolet 8700 Research spectrophotometer by KBr pellet method with a 4 cm^{-1} resolution. ^{1}H and ^{13}C NMR were also recorded for all the synthesized additives 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. CHNS analysis was performed on the Perkin Elmer Series II CHNS/O 2400 analyzer.

Antioxidant performance analysis

High temperature oxidation tests were conducted on a Universal Oxidation Apparatus (Fig. 2) manufactured by Sarbi Engineering, India using the standard method IP 306 [25] with using oxygen instead of air. Polyol base oils were doped with synthesized additives with different concentrations and experiments were run at 150 °C for 12 h. Samples were measured near to 25.0 g and placed. 25 mL neutral distilled water was taken in absorption tube. Flow of oxygen was adjusted to 1 ± 0.1 L per h. The test was complete after the 12 h. All samples and absorbent water were analyzed for acidity. Weight loss in the samples and carbon residue formed was also measured as per standard procedure. Tests were run in duplicate.

Tribological test

The antiwear and antifriction properties in terms of wear scar diameter (WSD) and average friction coefficient of the synthesized additives *CySBE-A* and *CySBE-B* were measured on a four-ball test machine, Ducom, India according to the ASTM D4172 A standard test method [26]. All tests were carried out using 12.7 mm steel ball under the load rotated against three stationary steel balls clamped in the holder (Fig. S1). During these experiments, the four balls were covered with lube samples (additive *CySBE-A* or *CySBE-B* in polyol base oil in different