Tribology International 42 (2009) 353–358

Contents lists available at ScienceDirect

Tribology International

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

Friction and wear behavior of thioether hydroxy vegetable oil

Brajendra K. Sharma [a,b,*], A. Adhvaryu [a,b], Sevim Z. Erhan [b,**]

[a] Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, USA
[b] USDA/NCAUR/ARS, Food and Industrial Oil Research, 1815 N. University Street, Peoria IL 61604, USA[1]

ARTICLE INFO

Article history:
Received 20 June 2007
Received in revised form
1 July 2008
Accepted 10 July 2008
Available online 21 August 2008

Keywords:
Antiwear additive
Ball-on-disk
Epoxidized vegetable oil
Four-ball
Lubricant additive
Sulfur

ABSTRACT

This work describes the tribochemical evaluation of vegetable oil based antiwear additive obtained through chemical modification. The Sulfur was incorporated using a chemical reaction of epoxidized vegetable oil and common thiols, resulting in formation of a hydroxy thioether derivative of vegetable oils. The synthesis retains the vegetable oil structure, eliminates poly-unsaturation in the molecule, and adds polar functional groups that significantly improve adsorption on metal surfaces. These additives are obtained by chemical modification of oils originated from natural resources. The tribochemical behavior of sulfur incorporated vegetable oil was studied by measuring friction coefficient using ball-on-disk configuration and wear scar diameter using four-ball configuration. Comparative tests with commercial antiwear additives demonstrate the effectiveness of these derivatives. The derivatives were found useful as agriculturally based antiwear additives for lubricant applications.

1. Introduction

Antiwear/antifriction lubricants typically comprise a base oil that has been blended with any number of additives that enhance the ability of the base oil to withstand the mechanical stresses of interacting working surfaces under boundary lubrication conditions. Most of the lubricants and many of the additives currently in daily use originate from petroleum base stocks that are toxic to environment, making it increasingly difficult for safe and easy disposal. There has been an increasing demand for "green" lubricants [1] and lubricant additives in recent years due to concerns about loss of mineral oil-based lubricants to the environment and increasingly strict government regulations controlling their use. A renewable resource, vegetable oil is good alternative to mineral oil because of its environmentally friendly, non toxic and readily biodegradable nature [2,3]. The triacylglycerol structure of vegetable oil is amphiphilic in character that makes it an excellent candidate as lubricants and functional fluids [4,5]. It makes them very attractive for industrial applications that have potential for environmental contact through accidental leakage, dripping or generates large quantities of after-use waste materials requiring costly disposal [6,7]. In addition double bonds present in triacylglycerol structure offer sites for additional functionalization, for further improving technical properties such as thermo-oxidative, low temperature stability and lubricity. Vegetable oil in its natural form has limited use as industrial fluids due to poor thermo-oxidation stability [8,9], low temperature behavior [10,11], and other tribochemical degrading processes [12,13] that occur under severe conditions of temperature, pressure, shear stress, metal surface and environment. To meet the increasing demands for stability during various tribochemical processes, the oil structure has to withstand extremes of temperature variations, shear degradation and maintain excellent boundary lubricating properties through strong physical and chemical adsorption with the metal. Triacylglycerol molecules orient themselves with the polar end at the solid surface making a close packed monomolecular [14] or multimolecular layer [15] resulting in a surface film believed to inhibit metal-to-metal contact and progression of pits and asperities on the metal surface. Strength of the fluid film and extent of adsorption on the metal surface dictate the efficiency of lubricants performance and it has also been observed that friction coefficient and wear rate are dependent on the adsorption energy of the lubricant [16].

The antiwear properties of commercial additives are derived from a variety of elements capable of reacting with the metal surface and establish a stable protective film. Phosphorus, sulfur, nitrogen and zinc constitute the active element in most mineral oil based

* Corresponding author at: Food and Industrial Oil Unit, National Center for Agricultural Utilization Research, United States Department of Agriculture, Agricultural Research Service, 1815 N. University St., Peoria, IL 61604, USA. Tel.: +1 309 681 6532; fax: +1 309 681 6340.
** Corresponding author.
E-mail addresses: Brajendra.Sharma@ars.usda.gov (B.K. Sharma), Sevim.Erhan@ars.usda.gov (S.Z. Erhan).

[1] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

0301-679X/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.triboint.2008.07.004

commercial antiwear additives. However due to environmental and toxicological considerations, phosphorus may phase out with time due to catalyst deactivation fitted in auto gas exhaust [17]. Biodegradable additives are indispensable for environmentally friendly lubricants. According to German 'Blue Angel' criteria, environmentally friendly lubricants must not contain carcinogens/mutagens, chlorine, nitrites, or metal (except potassium and calcium). Such lubricants can only contain up to 7% of potential biodegradable additives (biodegradability not less than 20% by OECD 302B method), and 2% low toxicity and non-biodegradable additives [18].

Organic sulfur compounds have been used widely in lubricating compositions for their extreme-pressure (EP) as well as their antiwear/antifriction properties [19–23]. Extensive work has been done and is reflected by the volume of literature published in characterizing and relating the structure of the organic sulfur compounds to their EP and antiwear performance [19–22]. Reports are also available where a reaction layer is formed on the metal surface containing FeS and FeS_2 [24]. Elrod et al. described formulation of aqueous drilling fluid [25] consisting of essentially the reaction product of a fatty vegetable oil with 4,4′-thioldiphenol. Baldwin et al. [26] disclosed a metal working lubricant comprising a mineral or synthetic oil, and optionally a vegetable oil, and a sulfur-containing carboxylic acid (R-S-R′CO_2H) such as n-dodecythioacetic acid and n-butylthioacetic acid. The attempts to sulfurize vegetable oils as replacements for sulfurized sperm whale oil have resulted in products that displayed a high level of intermolecular crosslinking, and were thus characterized by unacceptable viscosities [27–29]. Previously, we have reported the synthesis of hydroxy thioether derivatives of vegetable oil using epoxidized soybean oil and common organic thiols [30]. This process retains the vegetable oil structure and its associated benefits (high flash point, viscosity index, lubricity and eco-friendly) while it allows for removal of poly-unsaturation in the fatty acid chain with addition of polar functional groups that significantly improves surface adsorption on metal and also contributes to the formation of a protective film through chemical reaction during the tribochemical process. The work reported in this paper discusses the tribochemical evaluation of these thioether hydroxy derivatives of vegetable oil using ball-on-disk and four-ball test methods.

2. Experimental procedure

2.1. Synthesis of polyhydroxy thio-ether derivative of soybean oil

Epoxidized soybean oil (ESBO) was obtained with a purity level of 98% from Elf Atochem (Philadelphia, PA), and was used without any further purification. Perchloric acid ($HClO_4$, 70%, ACS Reagent), methylene chloride, sodium bicarbonate, anhydrous magnesium sulfate from Fisher Scientific (Springfield, NJ) and 1-butane thiol from Aldrich Chemicals (Milwaukee, WI) was used as obtained.

Butyl thioether of hydroxy vegetable oil (BTHV) was synthesized by reacting 1-butanethiol with epoxidized soybean oil dissolved in methylene chloride using perchloric acid as catalyst under dry nitrogen atmosphere. Similarly, 1-decanethiol, cyclohexyl mercaptan, and 1-octadecanethiol were used to prepare the decyl thio-ether of hydroxy vegetable oil (DTHV), the cyclohexyl thio-ether of hydroxy vegetable oil (CTHV), and the octadecyl thio-ether of hydroxy vegetable oil (OTHV) respectively. The detailed description of synthesis and structural characterization using NMR and FTIR has been reported elsewhere [30]. Based on the NMR and FTIR analysis, the tentative structures of BTHV, DTHV, CTHV, and OTHV are shown in Fig. 1.

All the additive concentrations are expressed in weight percentage.

2.2. PDSC method

The experiments were done using a computer controlled DSC 2910 thermal analyzer from TA Instruments (New Castle, DE). Typically 2.0 mg sample, resulting in a less than 1 mm film thickness, was taken in a hermetically sealed type aluminum pan with a pinhole lid and oxidized in presence of air. Dry air (Gateway Airgas, St. Louis, MO) was pressurized in the module at a constant pressure of 1379 KPa (200 psi) and 10 °C/min heating rate was used during the length of the experiment. The oxidation onset temperature (OT) was calculated from the exotherm in each case. The OT is the temperature at which a rapid increase in the rate of oxidation is observed and is obtained by extrapolating the tangent drawn on the steepest slope of reaction exotherm. A higher OT would suggest a higher oxidation stability of the sample. All samples were run in triplicate and the average OT was reported with standard deviation < 1.0.

2.3. Four-ball configuration

The experiment is designed to study the anti-wear properties of additives under sliding contact by four-ball test geometry using a Falex apparatus (Model Multi-Specimen, Falex® Corporation, Sugar Grove, IL). The test zone is a top ball rotating in the cavity of three identical balls in contact and clamped in a cup below, containing the test fluid. The resistance to the motion of the ball is measured by a load cell connected to the stationary cup on the load platform,

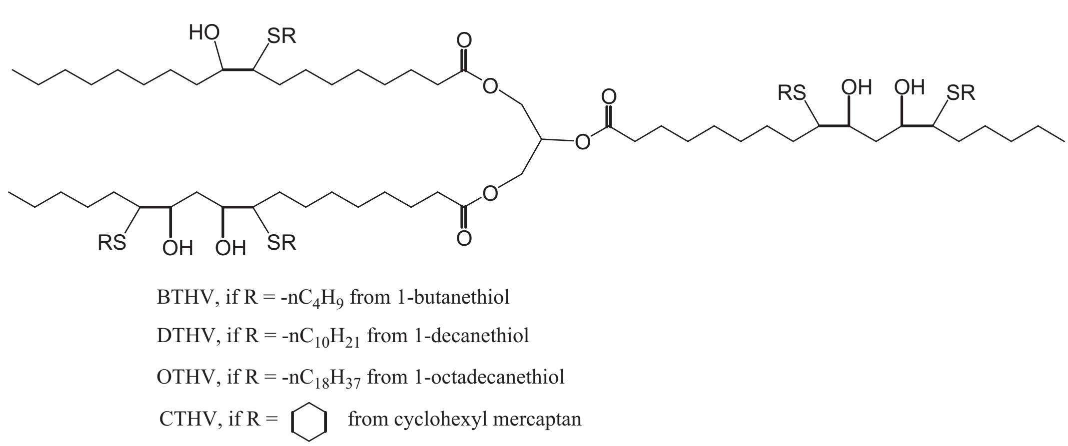

Fig. 1. Average chemical structures of butyl thioether of hydroxy vegetable oil (BTHV), decyl thio-ether of hydroxy vegetable oil (DTHV), cyclohexyl thio-ether of hydroxy vegetable oil (CTHV), and octadecyl thio-ether of hydroxy vegetable oil (OTHV).