# Biobased Grease with Improved Oxidation Performance for Industrial Application

Brajendra K. Sharma,[†,‡] Atanu Adhvaryu,[†,‡] Joseph M. Perez,[†] and Sevim Z. Erhan*,[‡]

Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, and Food and Industrial Oil Research, NCAUR/Agricultural Research Service, U.S. Department of Agriculture, 1815 North University Street, Peoria, Illinois 61604

Vegetable oils have significant potential as a base fluid and a substitute for mineral oil for grease formulation. This paper describes the preparation of biobased grease with high oxidative stability and a composition useful for industrial, agriculture/farming equipment, and forestry applications. The process utilizes more oxidatively stable epoxy vegetable oils as the base fluid, metal−soap thickener, and several specialty chemicals identified to address specific applications. Performance characteristics of greases used for industrial and automotive applications are largely dependent on the hardness and the oxidative stability of grease. Grease hardness was determined using standard test methods, and their oxidative stabilities were determined using pressurized differential scanning calorimetry and rotary bomb oxidation tests. Wear data were generated using standard test methods in a four-ball test geometry. Results indicate that grease developed with this method can deliver at par or better performance properties (effective lubrication, wear protection, corrosion resistance, friction reduction, heat removal, etc.) than existing mineral oil-based greases currently used in similar trades. Therefore, developed greases can be a good substitute for mineral oil-based greases in industrial, agriculture, forestry, and marine applications.

**KEYWORDS: Vegetable oils; epoxidized vegetable oil; lithium grease; oxidative stability**

## INTRODUCTION

The search for environmentally friendly materials that have the potential to replace mineral oil in various industrial applications is considered a priority research in the fuel and energy sector. This emphasis is largely due to the rapid depletion of world fossil fuel reserves and increasing concern for environmental pollution from excessive mineral oil use and disposal. The U.S. Government Federal Executive Order 13010 (which set a goal that 25% of all government purchases be biobased) has been encouraging companies to make use of renewable, biodegradable basestocks, rather than petroleum basestocks, in many applications (*1*). Achieving the U.S. Federal Government's goal of tripling the use of biobased products and bioenergy by 2010 could create $15−20 billion in new income for farmers and rural America and reduce fossil fuel emissions by an amount up to 100 million metric tons of carbon (*2*). Renewable resources like vegetable oils and their derivatives are being considered as potential replacements for mineral oil base stocks in certain lubricant applications, where immediate contact with the environment is anticipated. The nontoxic and readily biodegradable characteristics of vegetable oil-based lubricants pose less danger to soil, water, flora, and fauna in case of accidental spillage or during disposal (*3*).

Liquid lubricants possess certain shortcomings and have difficulty coping with an exponential rise in performance requirements in automotive and industrial sectors. Technology is constantly being challenged to develop multifunctional lubricants to operate at higher temperatures and pressures and with a variety of contact surfaces, to minimize friction and increase system efficiency. This has triggered a steady rise in the development and application of greases in elastohydrodynamic regimes. The thickness and stability of lubricant films are largely dependent on the unique chemistry and composition delivered by greases.

Grease is a preferred form of lubrication in certain applications because it gives low friction, is easily confined, and has a long lubricating life at low cost. Oxidative stability and consistency of the grease matrix control a wide variety of performance properties in grease lubrication. These properties include the ability to flow under force and subsequently lubricate hard-to-reach points; lower friction coefficients through adhesion on surface (*4*), effective over a wide temperature range; be water stable; seal out contaminants as a physical barrier; decrease dripping and spattering; decrease frequency of relubrication (act

Biobased Grease with Improved Oxidation Performance

*J. Agric. Food Chem.,* Vol. 54, No. 20, 2006 **7595**

as a sink for lubricating oils), etc. It is important to note at this point that grease structure and composition undergo significant modification by shearing and oxidation while working. The usefulness of grease in a particular application is controlled to a large extent by the ability of the grease to resist changes in temperature, pressure, operating environment, and shearing force. Studies on composition (*5*), oxidative stability, viscosity changes with temperature, friction, and wear characteristics of vegetable oil-based grease formulations (*6, 7*) are reported in the literature.

Lubricating greases are colloidal dispersions of a thickener in a lubricating fluid and are generally formed by heating the two components together until the thickener swells and absorbs the oil. They owe their consistency to a gel-forming network where the thickening agent is dispersed in the lubricating base fluid. Greases may include various chemical additives for specific property enhancement (*8*). A typical grease composition contains 60−95% base fluid (mineral, synthetic, or vegetable oil), 5−25% thickener (fatty acid soaps of alkali or alkaline metals), and 0−10% additives (antioxidants, corrosion inhibitors, antiwear/extreme pressure, antifoam, tackiness agents, etc.) (*9*). Thickeners can be nonsoap also, such as modified clays (*10*) and substituted ureas (*11*). The base fluid imparts lubricating properties to the grease while the thickener, essentially the gelling agent, holds the matrix together. Therefore, it is important to understand the structure and composition of base fluid and thickener since in combination they can affect most of the physical and chemical properties of grease.

Development of vegetable oil-based greases has been an area of active research for several decades (*12, 13, 10*). As a result of active research, environmentally friendly lubricants and greases are already in the market (*14*). Biodegradability and toxicity of lubricating greases and the methods used to evaluate such products have been extensively documented (*15*). These products are very desirable in total loss lubricants like railroads, since their release does not cause any harm to the environment when it comes in contact with soil and water. However, vegetable oil-based greases have poor thermo-oxidative stability and thus cannot be used at high temperatures. It has been shown that epoxidized soybean oil (ESO) has better thermo-oxidative stability as compared to soybean oil (SBO) and is thus a potential candidate for high-temperature lubrication (*16*).

The present study utilizes epoxidized vegetable oil (EVO) as the base fluid along with metal−soap thickener and several specialty additives to develop biobased greases with high oxidative stability. No prior reported work was found on the use of EVOs as base fluids in lithium stearate greases. The study discusses the oxidative and wear characteristics of such biobased greases.

## MATERIALS AND METHODS

**Materials.** ESO (7% epoxy oxygen) used as the base fluid was obtained from Elf Atochem North America Inc. (Bloomington, MN). The oil was used as received commercially without any further purification and processing. The fatty acid composition was determined by gas chromatographic method AACC 58-18 (*17*). Lithium hydroxide monohydrate (LiOH·H$_2$O, 98%) and stearic acid (95%) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without any further purification. Five commercial greases (COM-ML, COM-AP, COM-DG, COS-1, and COS-2) were used for comparison in the study. COM-ML is mineral oil-based, COM-AP and COM-DG are synthetic oil-based, and COS-1 and COS-2 are SBO-based greases. COM-ML, COM-AP, and COM-DG contain molybdenum disulfide for protection against heavy shock loads, while COS-1 and COS-2 have graphite for better lubrication and wear properties. All of these greases are used for heavy duty applications.

**Table 1.** Composition of Epoxy Vegetable Oil-Based Grease

| greases | metal soap[a]: oil[b] | antioxidant APDD (wt %) | friction reducers/ EP-antiwear additives (wt %) |
|---|---|---|---|
| EGR1 | 1:5 | 3.33 | ADSO (3.33%) |
| EGR2 | 1:8 | 2.67 | STD (1.78%) |
| EGR3 | 1:7 | 3.45 | ADSO (3.45%) |
| EGR4 | 1:7 | 1.38 + MDDC (2.76%) | MOLY (2.76%) |

[a] Lithium stearate. [b] Ratio of lithium soap and epoxy vegetable oil on mass basis (the oil content varies from 75 to 85 wt %).

**Additives.** A commercial antioxidant additive package containing alkylated phenol, dithiophosphoric acid ester, and diphenylamine (APDD) obtained from Lubrizol was used in the preparation of the greases. Other antiwear and load-carrying additives including substituted 1,3,4-thiadiazole (STD), methylene-bis-dibutyldithiocarbamate (MDDC), molybdenum dibutyldithiocarbamate (MOLY), and a synergistic mixture of antimony dithiocarbamate/sulfurized olefin (ADSO) were obtained from Vanderbilt Co., Inc. (Norwalk, CT).

**Preparation of Greases.** The greases were prepared via saponification of a fatty acid (stearic acid) with a metal hydroxide, LiOH. A mixture of LiOH·H$_2$O, fatty acid (molar ratio, 1:0.75), ESO (in equivalent weight ratio of the lithium−fatty acid mixture), and additive (0−6 wt %) was mechanically stirred using a mixer blade (diameter, 65 mm; and height, 60 mm) attached to Stir-Pak high speed, low torque mixer head (Cole Parmer Instrument Co., Chicago) at a speed of 460 rpm. The mixture was heated to a temperature of 190 °C using a heating rate of 100 °C/h in an open kettle (3 L wide mouth glass reactor). The temperature was maintained at 190 °C for 2 h to ensure complete reaction of the thickener. The mixture appeared to boil as saponification started, with reaction byproducts (water) being released. The soap thickener began to body-up as the reaction continued simultaneously with dehydration. The reaction progress was tracked using Fourier transform infrared to identify the point at which saponification and dehydration were completed. Saponification goes to completion relatively quickly once initiated. Complete disappearance of the peak at 1710 cm$^{-1}$ for COOH stretching and emergence of an additional doublet peak at 1580/1560 cm$^{-1}$ for COO$^-$ asymmetric stretching confirmed the completion of saponification step. The mixture was then quench cooled using an additional amount of ESO (80% of the total reaction mixture) and antioxidant. The mixture was then reheated to maintain the temperature at 150 °C with mixing for 60−90 min. After thorough mixing, the temperature of the mixture was cooled using the remaining ESO base fluid and maintained at 110 °C. The stirring was continued until the addition of oil and selected additive package (0−10 wt % of the total reaction mixture) were complete. The mixture was gradually cooled down to room temperature (with slow stirring) to obtain the grease. Four ESO greases (EGR1, EGR2, EGR3, and EGR4) were prepared with various additive concentrations and combinations (**Table 1**).

**Grease Milling.** Each grease was milled using three-roll mill equipment. The grease was passed through the rollers three times until it was thoroughly homogeneous. The final product had a smooth pastelike texture. A similar procedure was used to prepare all of the ESO-based greases with the additive combinations as shown in **Table 1**.

**Penetration Test for Grease.** This test was done using a microprocessor-based digital penetrometer from Koehler Instrument Co. (Bohemia, NY). The ASTM D-217 method (*18*) was followed in which a stainless steel tip brass cone (45° cone and weight of 102.5 g) initially touching the grease surface was allowed to drop and penetrate freely for 5 s through the grease medium. The penetration value (10$^{-4}$ m) was digitally displayed after each test. The test was repeated three times, and the average value was taken. The NLGI grade corresponding to the cone penetration value was subsequently used in the Results and Discussion.

**Oxidation Stability.** The oxidation stability of the greases was evaluated using two methods, pressurized differential scanning calo-

rimetry (PDSC) and the rotating bomb oxidation test (ASTM Test Method D942) (*18*).

*PDSC.* All of the experiments were done using a PC-controlled DSC 2910 thermal analyzer from Thermal Analysis (TA) Instruments (New Castle, DE). Approximately a 2.0 mg sample was taken in an open aluminum pan and weighed using a microbalance. The module was temperature calibrated using the melting point of indium metal (156.6 °C) at 10 °C/min heating rate. The pan containing the grease sample and the reference pan (empty) were then heated at 10 °C/min in the pressure cell under a constant air pressure of 200 psi (1379 kPa). The onset temperature (OT) was calculated from the exothermic plot in each case. The OT is defined as the temperature when rapid increase in the rate of oxidation is observed in the test sample. The higher the OT is, the higher is the level of oxidative stability for the grease matrix (*19, 20*). The OT is the temperature obtained from the intersection of a tangent drawn on the steepest slope of the exothermic plot and the baseline.

*RBOT.* Rotary bomb oxidation tests of the grease formulations were carried out as per ASTM D942 (*18*) test for 100 h. This method determines resistance of lubricating greases to oxidation when stored statically in an oxygen atmosphere in a sealed system at an elevated temperature under conditions of the test. In RBOT, the bomb containing the grease sample is charged with oxygen to 110 psi pressure and then oxidized by placing it in an oil bath maintained at 99 °C. The bomb is rotated, and the pressure is recorded with time for 100 h. The degree of oxidation after 100 h is determined by the corresponding decrease in oxygen pressure. The pressure drop shows the amount of oxygen consumed in the grease oxidation reaction. A large pressure drop corresponds to a higher rate of oxidation of grease in the bomb.

**Four-Ball Wear Test.** This test was designed to study the antiwear properties of greases under sliding point contact using the four-ball test geometry (model Multi-Specimen, Falex Corp., Sugar Grove, IL). The test zone was a rotating top ball in contact with three identical balls clamped in a cup containing the grease. The appropriate load was applied from below, and the top ball was rotated at a set speed (1200 rpm) for a preset length of time. Prior to the test, the balls (52100 steel, 12.7 mm diameter, 64−66 Rc hardness and extreme polish) were thoroughly cleaned with methylene chloride and hexane before each experiment. The sample chamber was fitted with a thermocouple to record any change in temperature during the test period. Grease was added to the test cup to cover the stationary balls. The instrument was equipped with a PC that allowed automatic acquisition and display of data (torque, normal load, sliding speed, and chamber temperature of test grease) in real time at any selected rate.

The test sequence was similar to ASTM D 2266 method and allowed the speed to attain a set rpm of 1200 before a normal load of 392 N was applied at a 75 °C temperature for 60 min. Duplicate tests were done with new sets of balls. Scar diameters on balls were measured with a digital optical microscope. Two measurements, perpendicular to each other, were recorded for each scar on a ball, and the average of six measurements for three balls was taken in each case. The scar diameter is reported in millimeters. The standard deviation of six measurements was less than 0.04 in all of the experiments.

## RESULTS AND DISCUSSION

**Optimization of Various Components of Grease.** The preparation of lubricating grease is a complicated trial-and-error process in which the optimization of the reactants and the reaction protocol are critical to achieve the desired grease consistency. For low and high temperature applications, regulating the base oil quantity and fatty acid composition can help control grease hardness. A variety of performance characteristics of grease depend on its consistency (NLGI hardness) including dropping point, pumpability, viscosity, adhesion, and rheological behavior. In order to prepare vegetable oil-based grease possessing good thermo-oxidative stability with desired hardness, a logical approach is to optimize the amount of various components (metal, fatty acid, and base oil) in the final formulation.

The soap fibers derived from short chain fatty acids are not well-developed and sufficiently elaborate to hold and stabilize the base oil within its mesh structure. The fatty acid chain length to be used in soap preparation has been optimized in a previous study (*21*). It was observed that longer fatty acid chain lengths in the metal soap make stronger interlocking fibers. Starting with $C_{12}$ fatty acids, there is a significant increase in grease hardness up to $C_{16}$, with an optimum reaching at $C_{18}$ chain length, yielding NLGI 2 grease. Harder grease offers more resistance to oxidative breakdown due to a more compact soap network that binds the base oil well within its fiber structure. The chemistry of the fatty acid soap structure is responsible for certain performance characteristics of grease including rust/corrosion inhibition, friction, and wear resistance (*22*). It has been found that $C_{16}$ to $C_{18}$ fatty acids are optimally preferred in the metal−soap (thickener), to achieve a stable grease matrix. The current study used stearic acid ($C_{18}$ chain length) for soap preparation.

The ratio of metal to fatty acid in the soap structure has a significant effect on the thermo-oxidative stability of grease. Results from a previous study (*21*) indicated that the optimum lithium hydroxide to stearic acid equivalent ratio of 1:0.75 in the soap composition with SBO in the final formulation resulted in stable NLGI 2 grease with good oxidative stability as compared to one with a 1:1 equivalent ratio.

As the SBO percentage in grease increases from 65 to 80%, the NLGI grease hardness decreases from 4 to 2 (*21*). A further increase in the SBO content resulted in NLGI 1 or lower grade grease (softer grease). The metal−soap thickener in grease is capable of holding a specific amount of base fluid within its fiber network. Any increase in oil content beyond a critical amount in a given composition may result in oil separation from the grease matrix during prolonged high temperature applications or extended storage. This phenomenon also results in dripping, poor dropping point, bleeding at room temperature, increase in evaporation, and susceptibility to water washout. In the present study, lithium stearate was prepared in situ as a thickener along with 78 wt % EVO to obtain grease with NLGI 1 hardness, while 84 wt % of EVO provided grease with NLGI 0. A higher oil percentage in soap resulted in increased oxidative stability and lubricity of greases (*19*).

**Preparation Process.** Preformed grease thickeners are typically 50−75% more costly than the manufacture of soap thickeners from metal hydroxide and fatty acids but are used because they are easier to use. The process used in this study presents a greater challenge than one using a preformed soap thickener. Although complex and difficult, this process uses soap thickener, EVOs as base fluid, antioxidants, and extreme pressure/antiwear additives and was found suitable for the preparation of greases for moderate to high temperature applications.

**Oxidative Stability of Greases Using PDSC and RBOT.** The physical properties of the ESO are compared with SBO in **Table 2**. It should be noted that the ESO has a low iodine value and high viscosity as compared with regular SBO. The vegetable base oils are relatively prone to oxidation when compared to mineral base oils, due to the presence of polyunsaturation in the fatty acid chain of the triacylglycerol molecule. In epoxy vegetable oils, these double bonds are replaced by the epoxy rings, which results in low iodine values for ESO as compared to SBO (**Table 2**). The reduction in double bonds of ESO provides more oxidative stability to its structure. Therefore, in the present study, a more stable epoxy vegetable oil was used to improve the oxidative stability of biobased greases. The

Biobased Grease with Improved Oxidation Performance

*J. Agric. Food Chem.,* Vol. 54, No. 20, 2006 **7597**

**Table 2.** Physical Properties of SBO and ESO

| properties | SBO | ESO |
|---|---|---|
| appearance | light yellow | colorless |
| kinematic viscosity[a] at 40 °C, cSt | 32.93 | 170.85 |
| kinematic viscosity[a] at 100 °C, cSt | 8.08 | 20.41 |
| acid value (mg KOH/g) (AOCS, Ca 5a-40)[b] | 0.16 | 0.09 |
| peroxide value (mequiv/kg) (AOCS, Cd 8-53)[b] | 9.76 | 0.0 |
| iodine value (mg $I_2$/g) (AOCS, Cd 1-25)[b] | 144.8 | 9.11 |
| biodegradability[c] | 70 | 55 |
| fatty acid composition by GC (AACC, 58-18)[d] in % | | |
| $C_{16:0}$ | 6.0 | |
| $C_{18:0}$ | 5.5 | |
| $C_{18:1}$ | 22.0 | |
| $C_{18:2}$ | 66.0 | |
| $C_{18:3}$ | 0.5 | |

*[a]* ASTM D-445. *Annual Book of ASTM Standards*; ASTM: West Conshohocken, PA, 2000; Vol. 05.01. *[b]* AOCS. *Official Methods and Recommended Practices of the AOCS*, 5th ed.; AOCS: Champaign, IL, 1998. *[c]* Reported from: Shogren, et al. *J. Polym. Environ.* **2004**, *12* (3), 173. *[d]* *Approved Methods of the American Association of Cereal Chemists*, 10th ed.; American Association of Cereal Chemists: St. Paul, MN, 2000; Vol. II.

**Table 3.** Physical Properties of Epoxy Vegetable Oil-Based Grease

| greases | NLGI hardness[a] | OT (°C)[b] | RBOT (psi)[c] | wear scars (mm)[d] |
|---|---|---|---|---|
| EGR1 | 1 | 262 | 16.9 | 0.853 |
| EGR2 | 0 | 256 | 19.8 | 0.933 |
| EGR3 | 1 | 276 | 17.0 | 0.814 |
| EGR4 | 1 | 214 | 30.7 | 0.541 |
| COM-AP | 2 | 259 | 15.4 | 0.45 |
| COM-ML | 2 | 233 | 14.1 | 0.65 |
| COM-DG | 2 | 242 | 12.1 | 0.45 |
| COS1 | 1 | 175 | | 0.64 |
| COS2 | 1 | 208 | | 0.72 |

*[a]* ASTM D 217 method. *[b]* OT, obtained using PDSC, is the average value of three independent experiments with a standard deviation <1.0. *[c]* RBOT pressure drop (psi) after 100 h of oxidation as per ASTM D 942; the average value is of two experiments with standard deviation <2. *[d]* Wear scar from four-ball experiment as per ASTM D 2266; the value is the average of six readings with standard deviation <0.04.

oxidative stability of these biobased greases was studied by PDSC, which is a rapid way of measuring oxidation characteristics of vegetable oil-based greases. **Figure 1** shows PDSC exothermic plots of epoxy vegetable oil-based grease, commercial mineral oil-based grease, and commercial SBO-based greases. The OTs of the various epoxy vegetable oil-based greases were compared with three commercial mineral oil-based greases, COM-AP, COM-ML, and COM-DG, and two commercial SBO-based greases, COS1 and COS2, in **Table 3**. The OT obtained using PDSC exotherms corresponds to the temperature at which the antioxidants no longer control the rate of oxidation. As a result, oxidation rapidly accelerates to a maximum. The epoxy vegetable oil-based greases with the exception of EGR4 have similar or better oxidative stabilities than commercial greases. The highest OT obtained for commercial mineral oil-based greases is 259 °C for COM-AP. Two of the epoxy vegetable oil-based greases, EGR1 and EGR3, have higher OTs than COM-AP, while EGR2 has nearly the same
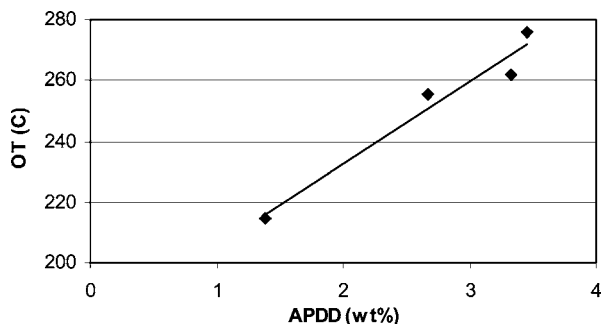
OT as COM-AP. All four epoxy vegetable oil-based greases have higher OTs as compared to commercially available vegetable oil-based greases COS1 and COS2. This higher oxidative stability of EVO-based greases as compared to SBO-based greases is due to the higher oxidative stability of epoxy oils used in preparation of these greases. The oxidative stability of EGR samples increased linearly with increasing antioxidant APDD concentration (**Figure 2**). Therefore, a desired oxidative stability of grease can be obtained by adjusting the amount of antioxidant. The presence of additive MDDC does not improve the oxidative stability of EGR4 grease.

The rotary bomb oxidation test is another method of choice to determine the oxidative stability of greases closely simulating end use conditions. This method determines resistance of lubricating greases to oxidation when stored statically in an oxygen atmosphere in a sealed system at an elevated temperature under conditions of test. **Figure 3** shows pressure drops of epoxy vegetable oil-based grease, commercial mineral oil-based grease, and commercial SBO-based grease using RBOT. The RBOT pressure drops for various greases are reported in **Table 3**. The average pressure drops for the commercial mineral oil-based greases are slightly lower than EGR1, EGR2, and EGR3. EGR4
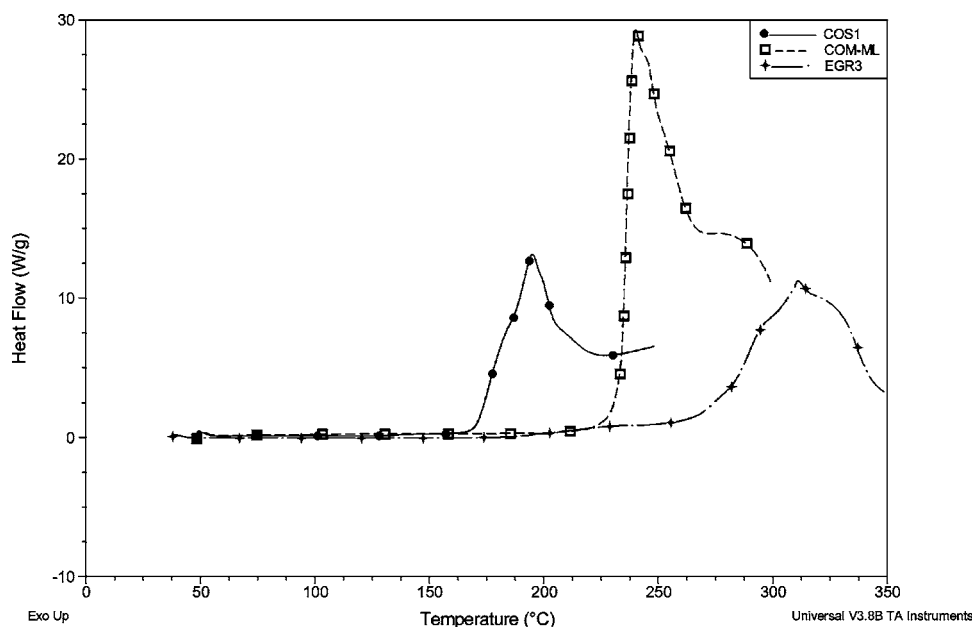


**Figure 1.** Typical PDSC exotherm of greases EGR3 (epoxy vegetable oil-based), COM-ML (mineral oil-based), and COS1 (SBO-based) using temperature ramping method (at 10 °C/min in presence of air at 200 psi pressure).

**7598** *J. Agric. Food Chem.,* Vol. 54, No. 20, 2006

Sharma et al.



**Figure 2.** Variation of PDSC OT of epoxy vegetable oil-based greases with wt % of antioxidant additive APDD.
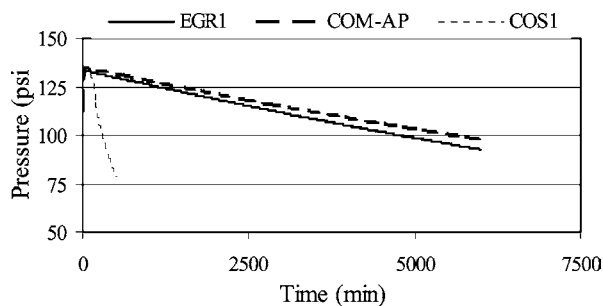


**Figure 3.** Pressure drop of greases EGR1 (epoxy vegetable oil-based), COM-AP (mineral oil-based), and COS1 (SBO-based) using Rotary bomb oxidation test.
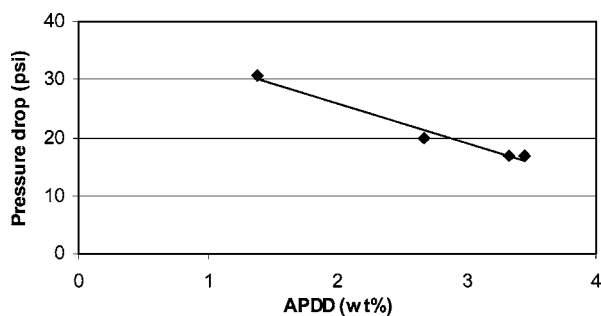


**Figure 4.** Concentration effect of antioxidant additive APDD on oxidative stability of epoxy vegetable oil-based greases determined by RBOT pressure drop.

was found to have a lower oxidative stability (RBOT pressure drop, 30 psi) as compared to commercial mineral oil-based greases, similar to that found in PDSC results. **Figure 4** shows the effect of increasing antioxidant additive concentration on RBOT pressure drop. The RBOT pressure drop decreases linearly with increasing additive concentration. The poor oxidative stability of EGR4 may be explained due to its lower additive concentration.

Grease additives (*23*) are specialized compounds that improve the existing physical and chemical performance properties of grease. These compounds are required in small quantities, are evenly dispersed in the grease matrix, and undergo physical and/ or chemical interaction with the moving mechanical metal part during use (*24*). Influence of the same additive in liquid lubricants and greases can be different, mainly because greases are sensitive products due to their gel structure that can be affected by the additive molecules. The total amount of different additives in a grease formulation can reach 10% of the total grease weight. The optimum additives combination must satisfy a broad spectrum of system requirements including oxidative stability, load carrying capacity, wear, and corrosion protection.

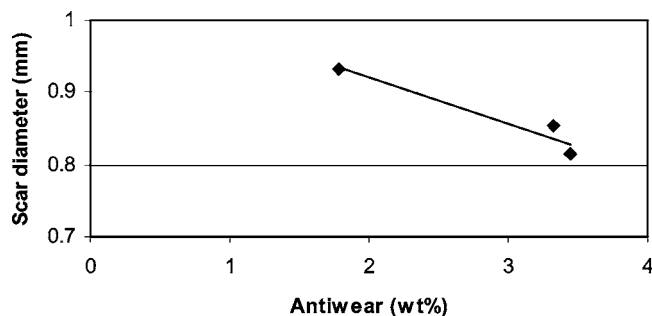The presence of antiwear additive ADSO in EGR1 and EGR3

has a slight synergistic effect on antioxidant efficiency of additive APDD present in these greases, leading to a higher oxidative stability of these greases. The antiwear additive ADSO is a dual action antioxidant additive, which serves both as a "free radical scavenger" and a "hydroperoxide decomposer". This additive is sparingly soluble in the grease matrix and appears as a finely dispersed material after milling and homogenization. Using PDSC OT method and RBOT, additive concentrations were optimized in the final grease formulation. The optimum additive level of 3.5 wt % of APDD in the EGR grease composition was achieved with a maximum observed OT of oxidation (276 °C) as shown in **Figure 2**. One of the problems of vegetable oil-based greases, i.e., poor oxidative stability, can easily be solved by using EGR greases having high oxidative stability.

**Friction-Wear Behavior of Greases Using Four-Ball Method.** Important performance properties such as adhesion, rheology, and lubrication are largely dependent on the grease hardness and its ability to maintain a stable lubricating film at the metal contact zone. The tightly adsorbed grease layer on metal is highly effective in lowering metal-to-metal friction (*25*). Therefore, the application of grease is particularly useful in open lubrication systems where the lubricant is in direct contact with the environment. Under boundary lubrication regime, active components from the additive help form stable chemical films on the metal surface. The active component of the additive does not generally have a chemical interaction with the Li soap or base oil. They are primarily dispersed in the oil in the grease matrix. The presence of additive in grease indicates a lowering of scar diameter using the four-ball test. A test method similar to ASTM D 2266 was designed for the evaluation of wear characteristics of EVO-based greases and commercial mineral oil- and vegetable oil-based greases. The scar diameter quantifies the extent of wear resulting from the use of grease samples under specified conditions.

It is observed from **Table 3** that scar diameter for COM greases is in the range of 0.45−0.65 mm, while the commercial NLGI 1 SBO-based greases are in the range of 0.64−0.72 mm. The scar diameter obtained for EGR4 is in the range of COM greases and is relatively less as compared to commercial SBO-based greases. This shows that one of the EGR greases prepared in this study has similar wear characteristics as commercial mineral oil-based greases but better than commercial vegetable oil-based greases. The other three EGR greases have slightly higher wear scar values as compared to the commercial greases.

On comparing these four EGR greases, it was found that their composition is almost the same with the same lithium stearates and same antioxidants, except for the presence of MOLY in EGR4. Although the antiwear additive concentration is less in EGR4 as compared to EGR1 and EGR3, it has a smaller wear scar diameter. This shows that MOLY provides a better antiwear characteristic to the grease EGR4. Either it is a more effective antiwear additive as compared to ADSO and STD in these grease formulations or there is some antagonistic effect due to competition between the sulfur and the higher phosphorus content of EGR1 and EGR3. The low scar diameter in EGR4 is due to the ability of the additive molecules to effectively form stable surface coatings. In most cases, scar diameter up to 0.5 mm is an acceptable limit for most industrial antiwear applications. The EGR4 grease in its current form is at par with other commercial mineral oil- and vegetable oil-based greases.

The additive concentration does have an effect on antiwear properties of greases as shown in **Figure 5**. In this figure, the data are shown only for EGR1, EGR2, and EGR3, although

Biobased Grease with Improved Oxidation Performance

*J. Agric. Food Chem.*, Vol. 54, No. 20, 2006 **7599**



**Figure 5.** Effect of antiwear additives on the four-ball wear scar diameters obtained using epoxy vegetable oil-based greases.

the additive in EGR2 is different from that in EGR1 and EGR3. The effectiveness of additive STD in EGR2 appeared similar to that of ADSO in EGR1 and EGR3. The antiwear additive MOLY is highly effective, and its concentration dependence does not match that of other antiwear additives and is thus not included in the graph. In general, higher additive concentration results in a lower wear scar diameter of the corresponding grease (**Figure 5**). With a further increase in the concentration of antiwear additive ADSO in EGR1 and EGR3 or STD in EGR2, it is possible to bring the wear scar diameter down to 0.5 mm or less. This is because the polar vegetable oils and additives compete for the metal surfaces and a higher proportion of additive will increase its rate of diffusion to the metal surface.

Development of vegetable oil-based grease comparable to or exceeding mineral oil-based products presents a major challenge in terms of cost and low oxidative stability. This study demonstrated that the use of the right composition of lithium hydroxide, fatty acid, antioxidants, antiwear additives, and a choice of an oxidatively stable base oil (epoxy vegetable oil) provided greases with good consistencies and excellent oxidative stabilities. Greases developed with this method deliver at par or better performance properties such as excellent oxidative stability, effective lubrication, wear protection, and friction reduction as compared to most commercially available mineral oil- and vegetable oil-based greases. The biobased nature of epoxy-based greases combined with easy preparation and high oxidation stability potentially make these highly suitable alternatives to existing mineral oil-based greases in industrial applications. This is a big advantage in commercialization of vegetable oil-based greases.

## LITERATURE CITED

(1) Patin, L. J.; James, D. K. Biodegradable and fire resistant hydraulic fluids: Now you can have both. *Lubricants World* **2002**, *November*, 26−29.

(2) 'Bioenergy' conference aims to help power US energy independence. *Soya Oilseed Ind. News* **2003**, *Oct 30*.

(3) Stempfel, E. M. Practical experience with highly biodegradable lubricants, especially hydraulic oils and lubricating greases. *NLGI* **1998**, *62* (1), 8−23.

(4) Odi-Owei, S. Tribological properties of some vegetable oils and fats. *Lubr. Eng.* **1989**, *11*, 685−690.

(5) Teresa, R. M.; Nuria, F. Determination of oil and grease by solid phase extraction and infrared spectroscopy. *Anal. Chim. Acta* **1999**, *395* (1−2), 77−84.

(6) Kernizan, C. F.; Pierman, D. A. Tribological comparison of base greases and their fully blended counterparts. *NLGI* **1998**, *62* (2), 12−28.

(7) Hurley, S.; Cann, P. M. Grease composition and film thickness in rolling contacts. *NLGI* **1999**, *63* (4), 12−22.

(8) Couronne, I.; Vergne, P.; Ponsonnet, L.; Truong-Dinh, N.; Girodin, D. Influence of grease composition on its structure and its rheological behaviour. In *Thinning Films and Tribological Interfaces*; Dowson, D., Ed.; Elsevier Science: Netherlands, 2000; pp 425−432.

(9) Stempfel, E. M.; Schmid, L. A. Biodegradable lubricating greases. *NLGI* **1991**, *55* (8), 25−33.

(10) Grives, P. R. The manufacture of Biodegradable nontoxic lubricating greases. *NLGI Spokesman* **2000**, *63* (11), 25−29.

(11) Willrich, H.; Erkel, H.-J. Polyurea greases−High-performance lubricants for various applications. *Tribol. Schmierungstech.* **2004**, *51* (2), 41−44.

(12) Dresel, W. H. Biologically degradable lubricating greases based on industrial crops. *Ind. Crops Prod.* **1994**, *2* (4), 281−288.

(13) Hissa, R.; Monterio, J. C. Manufacture and evaluation of Li-greases made from alternate base oils. *NLGI* **1983**, *3*, 426−432.

(14) Sullivan, T. Soy grease on track for sales boom. *Lube Rep.* **2003**, *July 22*.

(15) Grives, P. R. Readily biodegradable and low toxicity railroad track lubricants. Proc. Locomotive Maintenance Officer Association, 54th Annual Meeting, 9/1992, Chicago, IL.

(16) Adhvaryu, A.; Erhan, S. Z. Epoxidized soybean oil as a potential source of high-temperature lubricants. *Ind. Crops Prod.* **2002**, *15*, 247−254.

(17) *Approved Methods of the American Association of Cereal Chemists*, 10th ed.; American Association of Cereal Chemists: St. Paul, MN, 2000; Vol. II.

(18) *Annual Book of American Society for Testing and Materials, Section V, Petroleum Products, Lubricants, and Fossil Fuels*; ASTM: West Conshohocken, PA, 2000; Vol. 05.01.

(19) Sharma, B. K.; Adhvaryu, A.; Perez, J. M.; Erhan, S. Z. Soybean oil based greases: Influence of composition on thermo-oxidative and tribochemical behavior. *J. Agric. Food Chem.* **2005**, *53* (8), 2961−2968.

(20) Adhvaryu, A.; Erhan, S. Z.; Perez, J. M. Oxidation kinetic studies of oils derived from unmodified and genetically modified vegetables using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochim. Acta* **2000**, *364*, 87−97.

(21) Adhvaryu, A.; Erhan, S. Z.; Perez, J. M. Preparation of soybean oil based greases: Effect of composition and structure on physical properties. *J. Agric. Food Chem.* **2004**, *52* (21), 6456−6459.

(22) Honary, L. A. T. Field test results of soybean based greases developed by UNI-ABIL research program. *NLGI* **2000**, *64* (7), 22−28.

(23) Silverstein, R. S.; Rudnick, L. R. Additives for greases. In *Lubricant Additives: Chemistry and Applications*; Rudnick, L. R., Ed.; Marcel Dekker: New York, 2003.

(24) Hunter, M. E.; Baker, R. F. The effect of rust inhibitors on grease properties. *NLGI* **2000**, *63* (12), 14−21.

(25) Hurley, S.; Cann, P. M. Infrared spectroscopic characterization of grease lubricant films on metal surfaces. *NLGI* **2000**, *64* (7), 13−21.