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Preparation of Soybean Oil-Based Greases: Effect of Composition and Structure on Physical Properties

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Vegetable oils have significant potential as a base fluid and a substitute for mineral oil in grease formulation. Preparation of soybean oil-based lithium greases using a variety of fatty acids in the soap structure is discussed in this paper. Soy greases with lithium−fatty acid soap having $C_{12}-C_{18}$ chain lengths and different metal to fatty acid ratios were synthesized. Grease hardness was determined using a standard test method, and their oxidative stabilities were measured using pressurized differential scanning calorimetry. Results indicate that lithium soap composition, fatty acid types, and base oil content significantly affect grease hardness and oxidative stability. Lithium soaps prepared with short-chain fatty acids resulted in softer grease. Oxidative stability and other performance properties will deteriorate if oil is released from the grease matrix due to overloading of soap with base oil. Performance characteristics are largely dependent on the hardness and oxidative stability of grease used as industrial and automotive lubricant. Therefore, this paper discusses the preparation methods, optimization of soap components, and antioxidant additive for making soy-based grease.

KEYWORDS: Vegetable oils; Li-grease; NLGI hardness; oxidative stability

INTRODUCTION

The search for environmentally friendly materials that have the potential to substitute for mineral oil in various industrial applications is currently being considered a top priority 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 its disposal. Renewable resources such as seed 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 the case of accidental spillage or during disposal (*1*).

Liquid lubricants possess certain shortcomings and are not able to cope 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.

Development of vegetable oil-based greases has been an area of active research for several decades (*2*, *3*). Lubricating greases are semisolid colloidal dispersions of a thickening agent in a liquid lubricant matrix. 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 (*4*). 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, anti-wear/extreme pressure, antifoam, tackiness agents, etc.) (*5*). The base fluid imparts lubricating properties to the grease, whereas the thickener, essentially the gelling agent, holds the matrix together. This is a two-stage process. First, the absorption and adhesion of base oil in the soap structure results, and, second, the soap structure swells when the remaining oil is added to the reaction mixture. Therefore, it is important to understand the structure and composition of the base fluid and thickener because in combination they can affect most of the physical and chemical properties of greases.

The semisolid nature of lubricating grease has several advantages over lubricating oils. Oxidative stability and consistency of the grease matrix control a wide variety of performance properties in grease lubrication: the ability to flow

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under force and subsequently lubricate hard-to-reach points; lowered friction coefficients through adhesion on the surface (*6*); effectiveness over a wide temperature range; water stability; acting as a physical barrier to seal out contaminants; decrease in dripping and spattering; decrease in frequency of relubrication (acts as sink for lubricating oils), etc. It is important to note that grease structure and composition undergo significant modification while working by shearing and oxidation. The usefulness of grease in a particular application is controlled to a large extent by the ability of the grease to sustain changes in temperature, pressure, operating environment, and shearing force.

Studies are also available on the composition (*7*), oxidative stability, viscosity changes with temperature, and friction and wear characteristics of vegetable oils used in grease formulation (*8*, *9*). However, a detailed investigation is still required to understand the nature and structure of the metal/fatty acid composition on the physiochemical characteristics of formulated grease. This study presents the preparation of lithium-based greases with soybean oil as the base fluid. Variation in the lithium to fatty acid ratio and fatty acid structure in the soap composition resulted in significant changes in grease hardness and oxidative stability. An effort was made to optimize the lithium to fatty acid ratio and base oil amount to prepare NLGI (National Lubricating Grease Institute) no. 2 grease following the reaction protocol as described below.

MATERIALS AND METHODS

Materials. Soybean oil used as the base fluid was obtained from Pioneer Hi Bred International Inc., Des Moines, IA. The oil was alkali refined with the following fatty acid composition determined by gas chromatographic analysis (AACC 58-18) (*10*): $C_{16:0} = 6\%$; $C_{18:0} = 5.5\%$; $C_{18:1} = 22.0\%$; $C_{18:2} = 66.0\%$; $C_{18:3} = 0.5\%$. It should be noted that the soy oil used for this study has low linolenic content (0.5%) compared with regular soy oil (linolenic content ≈ 8%). Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, 98%) and lauric (98%), myristic (99.5%), palmitic (90%), stearic (95%), oleic (90%), and linoleic acids (90%) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without any further purification.

Additive. A commercial additive package containing a synergistic mixture of antimony dithiocarbamate and sulfurized olefin used in the grease preparation was obtained from Vanderbilt Co., Inc. (Norwalk, CT).

Synthesis of Grease. A mixture of $LiOH{\cdot}H_2O$, fatty acid (taken in 1:0.75 to 1:1 equivalent ratio with the lithium hydroxide), soybean oil (in equivalent weight ratio of the lithium−fatty acid mixture), and additive (0−6 wt %) was mechanically stirred while heating to a temperature of 90 °C in a 3 L wide-mouth glass reactor. Then the temperature was steadily raised to 150 °C, when an additional amount of soybean oil was added (60−80 wt % of the total mixture) to the reaction mixture. The temperature was increased and maintained at 190 ± 2 °C for a total of 3 h. After the stipulated time, the final mixture was allowed to gradually cool to room temperature (with slow stirring) to obtain the grease.

Grease Milling. All of the greases were milled locally using three-roll mill equipment. The grease was passed through the rollers three times until it was thoroughly homogeneous and the particle size reached 2−3 μm. The final product had a smooth pastelike texture. A similar procedure was used to prepare other greases with various compositions of fatty acid, metal/fatty acid ratio, and additive concentration.

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 (*11*) was followed in which a stainless steel tip brass cone (45° cone and weight = 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 (in 10^{-4} m) was digitally displayed after each test. The test was repeated three times and the average value taken. The NLGI grade (**Table 1**) corresponding to the cone penetration value was subsequently used under Results and Discussion.

Table 1. NLGI Grease Classification

grade	ASTM penetration (10^{-4} m) (ASTM D 217)
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

Table 2. Composition and Physical Properties of Soybean Oil-Based Grease

fatty acid	metal[a]/ fatty acid	metal soap/oil[b]	NLGI hardness[c]	T_o[d] (PDSC, °C)	antioxidant[e] (wt %)
lauric (C_{12})	1:1	1:3	00	117.84	
myristic (C_{14})	1:1	1:3	0	118.52	
palmitic (C_{16})	1:1	1:3	2	118.82	
stearic (C_{18})	1:1	1:3	2–3	120.39	
linoleic (C_{18})	1:1	1:3	1	124.34	
oleic (C_{18})	1:1	1:2	4	108.78	
oleic (C_{18})	1:1	1:3	2–3	109.12	
oleic (C_{18})	1:1	1:4	2	109.56	
stearic (C_{18})	1:1	1:3	2	146.51	2
stearic (C_{18})	1:0.75	1:3	2	170.11	2

[a] Lithium hydroxide monohydrate (in equivalent ratio with fatty acids). [b] Ratio of lithium soap and soybean oil (oil content varies from 66 to 80 wt %). [c] ASTM D-217 method (NLGI no. obtained from grease penetration range, **Table 1**). [d] PDSC data reported are the average value of three independent experiments (2.0 mg of sample, 10 °C/min heating rate under 3450 kPa static air pressure); the repeatability of the data is ±0.05. [e] Synergistic mixture of antimony dithiocarbamate and sulfurized olefin.

Pressurized Differential Scanning Calorimetry (PDSC). All of the experiments were done using a PC-controlled DSC 2910 thermal analyzer from Thermal Analysis (TA) Instruments (New Castle, DE). Approximately 2.0 mg of 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 a 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 constant air pressure (3450 kPa). The onset (T_o) temperature was calculated from the exothermic plot in each case (**Table 2**). T_o is defined as the temperature when a rapid increase in the rate of oxidation is observed in the test sample. Higher T_o corresponds to higher level of oxidative stability for the grease matrix compared to grease with lower T_o (*12*). This temperature was obtained by extrapolating the tangent drawn on the steepest slope of the exothermic plot.

RESULTS AND DISCUSSION

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 to 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. The base oil and the composition of the thickening agent, therefore, play important roles in grease consistency. The effect of oil concentration on grease hardness is presented in **Figure 1**, where the weight ratio of soybean oil

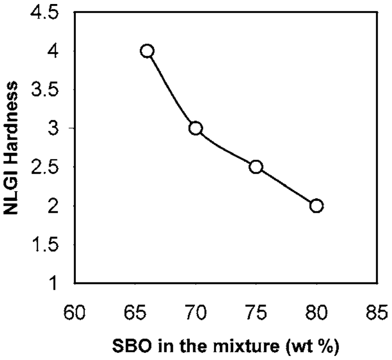

Figure 1. Variation of grease NLGI hardness with wt % soybean oil in the reaction mixture using 1:1 equivalent ratio of lithium to fatty acid in the thickener system.

to lithium soap is varied from 65:35 to 80:20. The metal soap thickener in grease is capable of holding a certain amount of base fluid within its fiber network. The metal soap thickener is sometimes thought of as a "three-dimensional fibrous network" or "sponge" that holds the oil in place, where the base fluid imparts lubricating properties to the grease, whereas the thickener, essentially the gelling agent, holds the matrix together. This is a two-stage process. First, the absorption and adhesion of base oil in the soap structure results, and, second, the soap structure swells when the remaining oil is added to the reaction mixture. 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 results in dripping, poor dropping point, bleeding at room temperature, increase in evaporation, and susceptibility to water washout. Using a 1:1 equivalent ratio of lithium hydroxide to oleic acid, a maximum of 80 wt % soybean oil (the remaining 20 wt % being lithium soap) could be used to obtain grease with NLGI no. 2 hardness (**Table 2**). Further increases in the oil content resulted in NLGI no. 1 or lower grease (softer grease). However, the oxidative stability for the above system determined by PDSC onset temperature method showed no significant change (from 108.78 to 109.56 °C) when the base oil content was increased from 65 to 80 wt %. It may be inferred that as long as the base oil is stabilized within the thickener structure, oxidative degradation is not an issue. Oxidation becomes more predominant when the base oil is released from the soap structure due to softer grease consistency or degradation of thickener fiber structure. In general, 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. Therefore, the oxidative stability of biobased greases should not be compared on the same scale as mineral oil-based products primarily containing hydrocarbon structures. Applications of such biobased greases are generally dictated by the severity of temperature for a given application.

Grease hardness depends mainly on the metal soap thickener microstructure. 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. Longer fatty acid chain length (C_n; n = number of carbon atoms) in the metal soap makes stronger interlocking fibers, resulting in a harder grease matrix. Starting with C_{12} fatty acids, there is a significant increase in grease hardness up to C_{16}, with an optimum reached at C_{18} chain length, yielding NLGI no. 2 grease (using a 1:1 equivalent ratio of lithium to fatty acid and 75 wt % of soybean oil in the grease mixture) (**Table 2**; **Figure 2**).

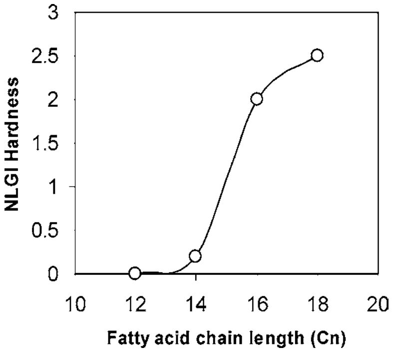

Figure 2. Lithium soap fatty acid chain length effect on soy-grease NLGI hardness (1:1 equivalent ratio of lithium to fatty acid in the thickener; 1:3 wt % ratio of soap to base oil).

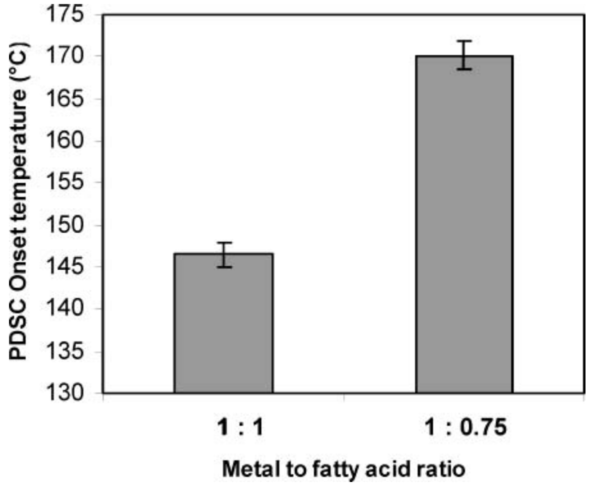

Figure 3. Effect of lithium hydroxide to fatty acid ratio on the oxidative stability of soy-grease (1:3 wt % ratio of soap to base oil, NLGI no. 2 and antioxidant level of 2 wt %).

Thermal and oxidative stabilities of greases are not significantly affected by the fatty acid chain length used in the lithium soap (**Table 2**). The lithium soaps derived from various fatty acid moieties show similar and low thermal/oxidative stabilities for $C_{12}-C_{16}$ with a minor increase in C_{18} chain length. The data suggest breakdown of the grease structure with softer consistency. Harder grease offers more resistance to such breakdown due to a more compact soap network, which also binds the base oil well within its fiber structure. These results indicate that $C_{16}-C_{18}$ fatty acids in lithium thickener are optimally preferred to achieve stable grease matrices with NLGI no. 2 hardness.

The ratio of metal to fatty acid in the soap structure has a significant effect on the thermo-oxidative stability of grease. Results indicated the optimum lithium hydroxide to stearic acid equivalent ratio to be 1:0.75 in the soap composition, and a 75−80 wt % base oil in the final formulation resulted in stable NLGI no. 2 grease. The effect of the lithium hydroxide to fatty acid ratio in the soap composition on PDSC onset temperature is presented in **Figure 3**. 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 chemistry of the fatty acid soap structure is responsible for certain performance characteristics of grease including rust/corrosion inhibition, friction, and wear resistance (*13*). Polar components in grease are surface active and therefore have a

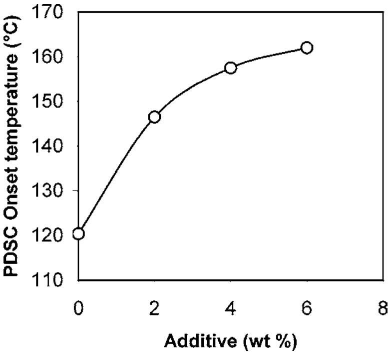

Figure 4. Optimization of antioxidant additive (synergistic mixture of antimony dithiocarbamate and sulfurized olefin) concentration in soy-grease composition using PDSC method (2.0 mg of sample, 10 °C/min heating rate under 3450 kPa static air pressure).

strong affinity for metal surfaces, whereas the hydrocarbon tail is directed away, resulting in the prevention of oxygen and water (rust and corrosion agents) and dust particles from coming in direct contact with metal surfaces. Also, the tightly adsorbed grease layer on metal is highly effective in lowering metal-to-metal friction (*14*). Therefore, the application of grease is particularly useful in open lubrication systems where the lubricant is in direct contact with the environment.

Grease additives are specialized compounds that improve the existing physical and chemical performance properties of a grease. These compounds are required in small quantities, are evenly dispersed in the grease matrix, and undergo physical and/or chemical interaction with the base fluid or the moving mechanical metal part during use (*15*). The influence of the same additive in fuels and greases can be different, mainly because greases are sensitive products due to their gel structure, which can be affected by the additive molecules. The total amount of different additives in a grease formulation can reach 10% of the total weight. The optimum additives combination must satisfy a broad spectrum of system requirements including oxidation stability, load-carrying capacity, wear, and corrosion protection.

We studied a synergistic combination of antimony dithiocarbamate and sulfurized olefin as a dual action antioxidant additive, which served both as a “free radical scavenger” and as a “hydroperoxide decomposer”. This additive is sparingly soluble in the grease matrix and appears as a finely dispersed material after milling and homogenization. Using the PDSC onset temperature method, additive concentrations were optimized in the final grease formulation. The optimum additive level of 6 wt % in the following grease composition (lithium hydroxide to stearic acid equivalent weight ratio of 1:1 and 80 wt % base oil) was achieved with maximum observed onset temperature of oxidation (T_o = 165.2 °C at 3450 kPa constant air pressure) (**Figure 4**). Any further addition of additive resulted in no significant improvement in grease oxidation.

In conclusion, the development of vegetable oil-based grease comparable to or exceeding mineral oil-based products presents a major challenge. The primary drawback is due to the low oxidative stability resulting from the highly unsaturated nature of vegetable oils and poor low-temperature properties. This study investigated the effect of fatty acid structure and composition of lithium hydroxide, fatty acid, and base oil (soybean oil) on grease thickness and oxidative stability. The lithium to fatty acid ratio and the nature of the fatty acid and base oil content can be carefully regulated and optimized to prepare grease with the desired hardness and stability. We observed that the length of the fatty acid chain in the lithium−soap structure affects grease hardness, which will subsequently influence important physical performance properties such as viscosity, boundary lubrication, and rheological behavior. Metal soaps prepared with short-chain fatty acids resulted in softer grease. Grease consistency increased with long-chain fatty acids used for the synthesis of lithium soap thickener. As long as the base oil is confined within the soap fiber network, NLGI no. 2 grease with good oxidative stability can be achieved. Oxidative stability and other performance properties fail if the base oil is released from the grease matrix due to overloading of soap with base oil. A higher metal to fatty acid ratio can result in greases with better oxidative stability. Further work on metal−soap structure and their effect on friction, wear, and rheological behavior of grease is in progress and will be reported shortly.

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